

Division of Polymer Chemistry (POLY)

Graphical Abstracts



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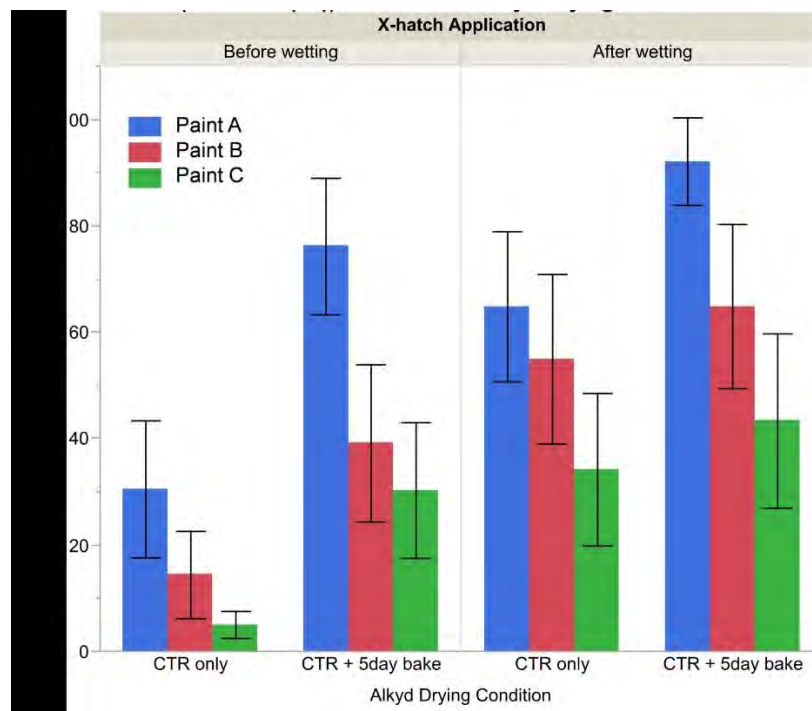
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POLY 1: Design of experiments based approach to investigate the adhesion of latex paints over alkyd surfaces

Partha S. Majumdar¹, PSMajumdar@dow.com, Jeff Sweeney², Christopher Kozak¹, Scott A. Carpenter¹, Sonya Eberly¹, William Howell¹, Louis C. Fioravanti¹, Alan M. Piwowar³. (1) Dow Coating Materials, Dow Chemical, Collegetown, Pennsylvania, United States (2) Dow Chemical, Midland, Michigan, United States (3) Dow Chemical, Collegetown, Pennsylvania, United States

Adhesion of latex paints over substrates previously coated with alkyd paints is a property of interest as the paint industry is transitioning towards waterborne systems. A thorough understanding of the variables associated with the test method for assessing the adhesion of latex paints over alkyd surfaces is required to improve data reproducibility and thereby improve differentiation among latex paints. This study focused on the effects of environmental and application conditions on adhesion following ASTM D3359 method. A set of six variables were identified as potential root causes such as alkyd substrate curing time, latex paint drying conditions, and latex paint thickness. D-optimal design of experiments was conducted for estimating Taylor-Series Expansion models involving main effect and two factor interaction terms. Data were collected, analyzed, and predictive models were developed to estimate the trends in the adhesion responses associated with the variables. Finally, optimized levels of each of the significant factors were identified to improve differentiation among latex paints. Analytical characterization techniques such as atomic force microscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry were also used to further understand the changes in the alkyd surfaces due to changes in the environmental conditions.



POLY 2: Measurement and control of migrating species on waterborne coatings surfaces

James Bohling, *jbohling@dow.com*, Joy Gallagher, Ashley Gong, Kelly David, Beth Cooper. The Dow Chemical Company, Lansdale, Pennsylvania, United States

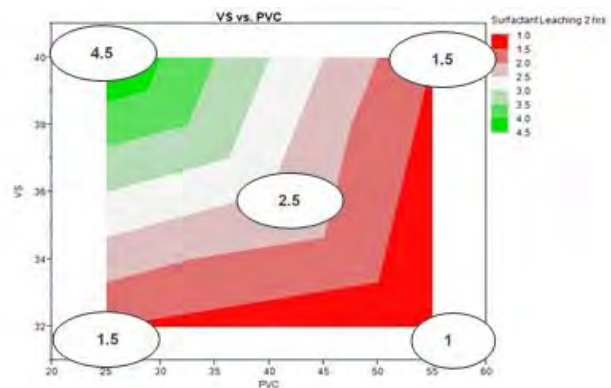
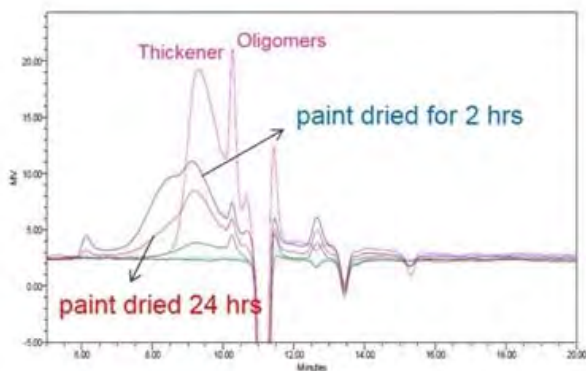
In the United States, there are approximately 700 million gallons of house paint sold each year. Since the 1940s, the amount of Volatile Organic Compounds (VOC) in architectural paints has declined dramatically. The first step change occurred in the 1950s, with the advent of the first waterborne polymers which enabled architectural paints with only 400 g/L VOC compared to typical solvent borne paints with over 700g/L VOC. Today, it is not uncommon to see architectural paints with less than 5 g/L VOC content.

The demand for water-based, “near 0” VOC architectural paints with low odor has been driven by both environmental groups and health conscious consumers, with the expectation that all other performance properties would remain unchanged.

Traditionally, volatile coalescents were added to waterborne coatings to improve a number of properties including film formation. As paint companies began to reduce volatile coalescent levels in their formulations, polymer suppliers responded by adjusting polymer Tg and/or incorporating ambient cure chemistry, surfactants and other (often water soluble) additives to retain (and hopefully improve) film formation performance.

Unfortunately, due to higher exudation of water soluble materials in these films, these changes have created new performance challenges, such as, leaching of surfactants and color rub off.

A number of analytical tools including NMR, SEM, TOF-SIMS and LC techniques have been applied to understand these issues. Data generated from these investigations and possible mechanisms will be discussed.



POLY 3: Mussel inspired coatings based on tannic acid and polyamines

Iskender Yilgor¹, iyilgor@ku.edu.tr, Emel Yilgor², Cagla Kosak¹. (1) Koc University, Istanbul, Turkey (2) Koc University Chem Dept, Sariyer Istanbul, Turkey

Mussels attach to solid surfaces in the sea through their adhesive (foot) proteins which are rich in 3,4-dihydroxy-L-phenylalanine (DOPA). The catechol unit in DOPA, which oxidizes to quinones is extremely reactive to both amines and thiols by Schiff base or Michael addition reactions, was found to be responsible for the adhesion capability of mussels [1]. In the past few years, researchers have been trying to mimic mussel foot proteins to fabricate multifunctional polydopamine based coatings [2]. Inspired by the mussel foot proteins, we prepared coatings using tannic acid (TA) and various polyamines (PA) instead of DOPA. TA, which is a polyphenol, is highly reactive towards amine or thiol groups. In this study, thin TA/PEA films and coatings on glass slides were produced. Effect of PA structure and TA/PA ratio on the properties of the coatings were investigated. Depending on the TA/PA composition it was possible to get extremely rigid to highly elastomeric materials. Films obtained were characterized by ATR-IR spectroscopy, DSC, SEM, AFM, tensile tests and advancing and receding water contact angle measurements.



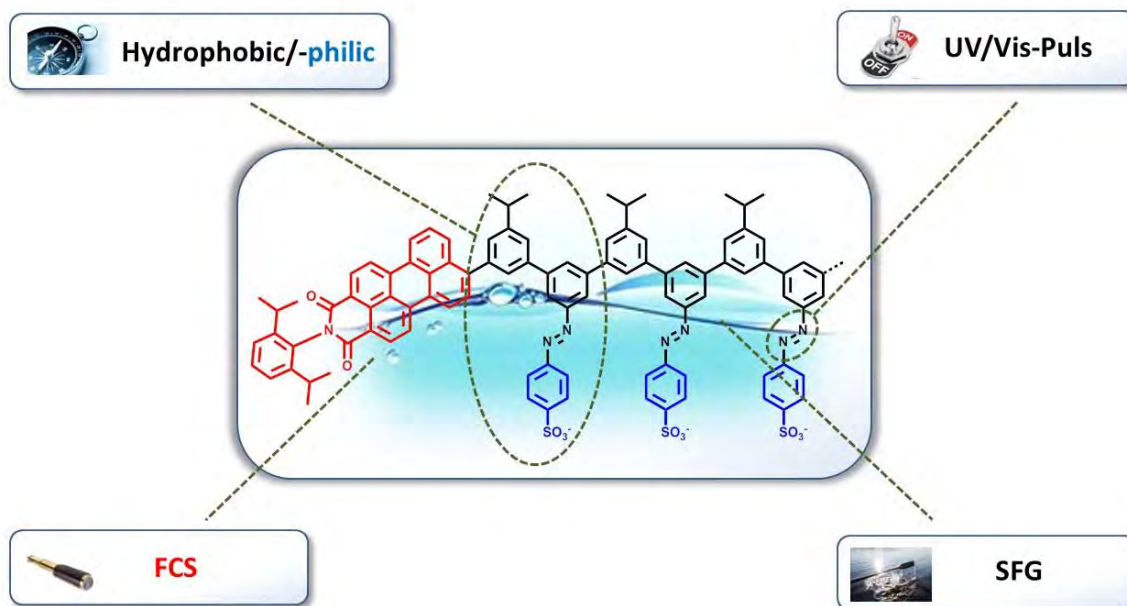
POLY 4: Polymer walking on water

Christoph Sonnenschein, sonnenschein@mpip-mainz.mpg.de. Chemistry, Max Planck Institute of Polymer Research, Mainz, Germany

Making use of a poly-*meta*-phenylene derivative we studied if a polymer can walk/swim on an air-water interface. As shown in Figure 1 the building blocks were a hydrophobic hydrocarbon backbone to which polar azobenzene units were attached and a PMI (perylene diimide) was used as endcapping material.

The amphiphilicity of the polymer was necessary to induce a specific orientation on the surface. The crucial features were the azobenzene units which offer the possibility of an external control of a motion within the polymer. The idea then is that the *cis-trans* isomerization should act like a paddle rowing a boat and therefore leading to a motion of the whole polymer. Different polymers were synthesized and their surface behavior was analyzed by Langmuir trough and static sum frequency generation spectroscopy (SFG). In the next step the interactions between water and the molecular paddles were analyzed by transient SFG. For certain time delays after UV excitation, the change in the SFG signal was detected for both – the water molecules and the methyl groups of the polymer.

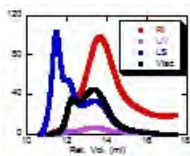
In the last step a PMI was attached to enable monitoring of the polymer motion through fluorescence correlation spectroscopy (FCS). Here the comparison of the diffusion coefficients of the Brownian motion and the UV-light induced motion are utilized to prove that the polymer is walking on water.



POLY 5: Macromolecular characterization of biopolymers as alternative depressants for iron ore flotation

Alina M. Alb, linocika12 @live.com. R&D, Kemira Chemicals, Atlanta, Georgia, United States

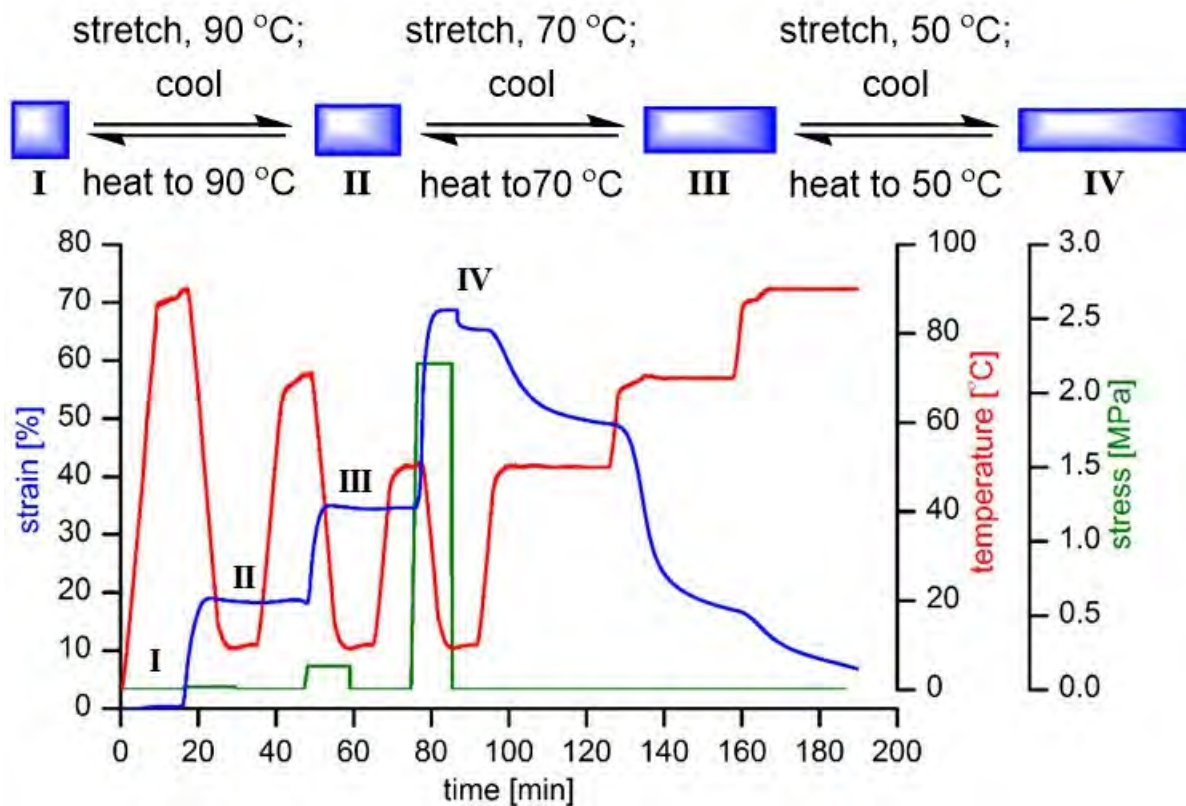
The need of modern science to achieve a sustainable future development through strategies less harmful to environment has been a major research focus. Nature has continuously provided materials for many applications. Thus, polysaccharides, in natural or chemically modified form, have become increasingly attractive to both research and industrial communities, due to their good solubility in water, high chemical reactivity and viscosity, at low cost and toxicity. An example of such biomaterials is xylan, extracted from corn fiber, used in the industrial production of iron ore pellets and other high-quality metallurgical raw materials, which requires the use of flotation to reduce impurities content. The special affinity of the iron oxide minerals for polysaccharides led to the use of xylan to facilitate their depression during reverse cationic flotation of silica. Comprehensive characterization of the materials involved in this process is a crucial requirement, especially challenging in the case of natural products, where variations due to different sources and extraction conditions may affect performance. Light scattering-based unique methodologies together with traditional methods (FTIR, SEM, TGA) were used in the characterization studies of xylan samples extracted under different conditions, with focus on quantification of sample components (protein, lignin, amylose/amylopectin) and on understanding of how critical parameters, such composition, molecular weight distribution, size, hydrophilic/hydrophobic character, and structure affect their performance as depressants. Monitoring viscosity and light scattering signatures during these modification reactions allowed correlations between polymer characteristics and variables used in extraction process (NaOH, H₂O₂) to be made by following their evolution in real time and led to process optimization. It is hoped that the knowledge gained from these studies will offer convincing arguments in proving that the modified polysaccharides represent efficient depressants.



POLY 6: Shape memory polymers from amino acid-based poly(ester urea)s

Gregory I. Peterson, gpeterson@uakron.edu, Erin P. Childers, Jiayi Yu, Hao Li, Andrey Dobrynin, Matthew Becker. University of Akron, Akron, Ohio, United States

The thermal shape memory behavior of a series of amino acid-based poly(ester urea)s has been explored. We have shown that these materials exhibit excellent shape memory performance in dual- and triple-shape thermomechanical testing using a number of amino acids and chain extender lengths. The mechanism of shape transformation and recovery is attributed to activation of chain mobility above the T_g as well as a strong hydrogen bonding network among the urea segments. Additionally, we demonstrate that the shape memory properties of these materials can be tuned precisely using a polymer blending approach, enabling quadruple-shape memory cycles.



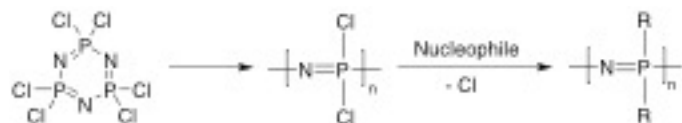
Representative example of a quadruple-shape memory cycle for a poly(ester urea) blend.

POLY 7: Platform of possibilities: Polyphosphazenes' structure-property correlations and applications

Zhongjing Li, zul19@psu.edu, Harry Allcock. Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States

Featuring backbones of alternating nitrogen and phosphorus atoms, polyphosphazenes are special polymers as platforms of possibilities fundamentally and practically. They are generally prepared by macromolecular substitutions on poly(dichlorophosphazene) to replace all chlorines on phosphorus with various nucleophiles. A rich library of polyphosphazenes have been synthesized with adjustable properties when different nucleophiles are employed to introduce different side groups. Polyphosphazenes can be applied in various fields such as high performance elastomers, fire resistant materials, optical materials, polymer electrolytes, biomaterials, microfibers, and superhydrophobic coatings.

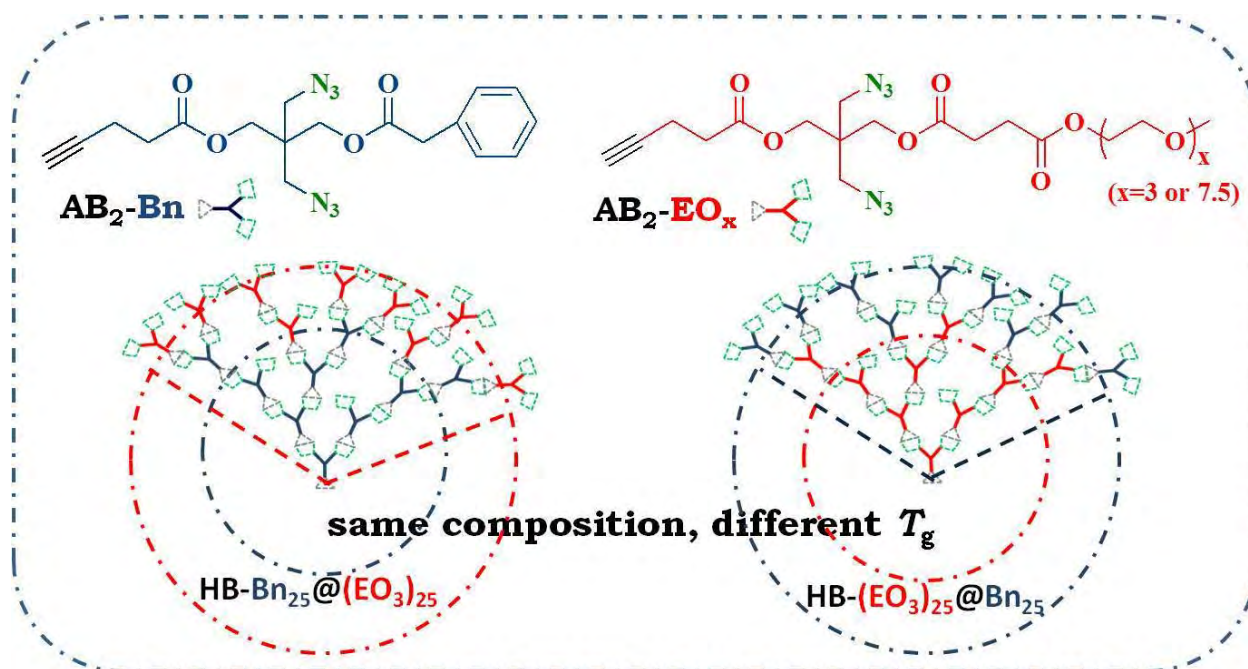
Incorporating two different types of side groups on a single polyphosphazene chain is a feasible way to tailor engineering properties at molecular level. Combinations of the two side groups can be functional and auxiliary side groups, hydrophobic and hydrophilic side groups, or flexible etheric and rigid bulky side groups. Variation of the ratios between the two side groups are used to tune polymer hydrophobicity, degradability, crystallinity, T_g , mechanical properties, and gas permeability and selectivity. For example, the color density and microcrystallinity of a polymeric dye can be adjusted by varying the ratios between the light absorbing dye and the auxiliary side group, the degradability of a bioerodible polymer can be adjusted by the percentage of hydrolytic side groups, and the variation of the ratios between flexible etheric and rigid aliphatic side groups can generate polymers from adhesives to amphiphiles to thermoplastics and thermosets.



POLY 8: Effect of monomer sequence on the properties of hyperbranched copolymers

Yi Shi, Yi.Shi.27@nd.edu, Haifeng Gao. Chemistry and Biochemistry, University of Notre Dame, South Bend, Indiana, United States

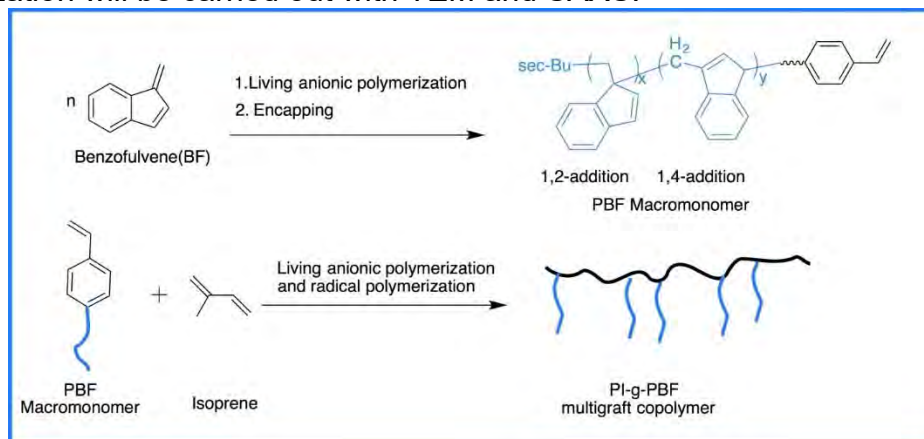
This talk presents our recent progress in the synthesis of segmented hyperbranched copolymers with systematically varied compositions, molecular weights, and segmented structures from a chain-growth CuAAC polymerization by sequential monomer addition in one pot. The AB₂ monomers with various dangling groups (benzyl, oligo-PEO_x) were applied to tune the physical properties of these hyperbranched polymers, including glass transition, solubility. These results demonstrated unique tunability of physical properties in segmented hyperbranched copolymers and may stimulate further interest to investigate the isolation properties of segmented hyperbranched polymers.



POLY 9: Synthesis and characterization of new high temperature multigraft copolymer superelastomer: Polyisoprene-graft-polybenzofulvene

Huiqun Wang³, hwang52@vols.utk.edu, **Weiyu Wang**³, **Wei Lu**², **Xinyi Lu**², **Nam-Goo Kang**³, **Jimmy W. Mays**¹. (1) Univ of Tennessee, Knoxville, Tennessee, United States (2) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (3) Chemistry, University of Tennessee, Knoxville, Tennessee, United States

Thermoplastic elastomers (TPEs) are multiphase materials consisting of an elastomeric continuous phase that provides rubber-like properties and dispersed hard domains that provide reinforcement and elastic recovery. They have been developed into a formidable array of materials since the 1960s, among which, multigraft copolymer superelastomers have attracted much interest in the last decade. This is due to their possessing superior mechanical properties, especially improved elongation at break and superior elastic recovery when compared to conventional linear triblock TPEs, which is obtained from having multiple tethering points along the rubbery backbone. Styrenic thermoplastic elastomers (S-TPEs) are one of the most commercially utilized TPEs. However, a critical issue that hinders the extensive applications of S-TPEs is the upper service temperature (UST). In this work, we use polybenzofulvene (PBF) as side chains to increase the UST of the TPE; meanwhile, incorporating the multigraft architecture in order to improve mechanical properties of S-TPEs. A class of new high temperature multigraft copolymers, polyisoprene-g-polybenzofulvene (PI-g-PBF), was synthesized by using a macromonomer approach. PBF macromonomers were randomly grafted through the polyisoprene backbone. Both macromonomers and multigraft copolymers were prepared by living radical and/or living anionic polymerization. More specifically, we investigated several living anionic synthetic methods towards PBF macromonomer and compare their performance. In the case of copolymerization, different macromonomer molecular weights and numbers of branch points per polymer chain were to gain insight into structure-properties relationships. The macromonomer chain end functionality was verified by applying MALDI-TOF MS. Thermal analyses were performed using DSC and TGA. Mechanical properties will be evaluated by DMA and tensile tests to correlate mechanical properties to molecular weight of macromonomers and number of branch points. Additionally, morphological characterization will be carried out with TEM and SAXS.

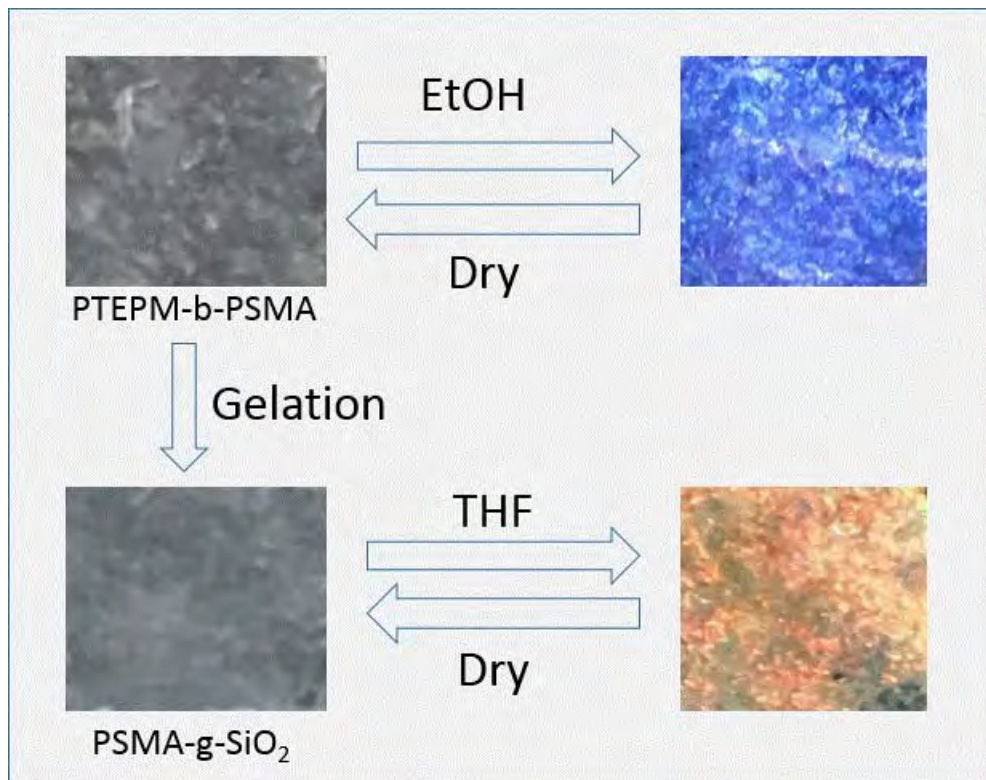


Scheme

POLY 10: Tunable photonic nanocomposite film formed by gelation of self-assembled block copolymer

Yucheng Huang, butan15@gmail.com, Yang Zheng, Julia Pribyl, Brian C. Benicewicz. chemistry and biochemistry, University of south carolina, Columbia, South Carolina, United States

Block copolymers (BCPs) can self-assemble into well-ordered microstructures by tuning the molecular weight and copolymer composition. One-dimensional photonic crystals can be formed from lamellar structure of self-assembly of block copolymers. The domain spacing of the lamellar structure needs to be high enough ($d > 150\text{nm}$) to reflect visible light. Herein we report a photonic crystal nanocomposite film formed by gelation of one domain of block copolymer, poly(3-(triethoxysilyl)propyl methacrylate)-block-poly(stearyl methacrylate) (PTEPM-b-PSMA). The PTEPM-b-PSMA film was responsive to alcohol with blue color while dry film is colorless. After gelation of the PTEPM domain to form SiO_2 , the PSMA-g- SiO_2 film showed a bright orange color in THF with long term stability.

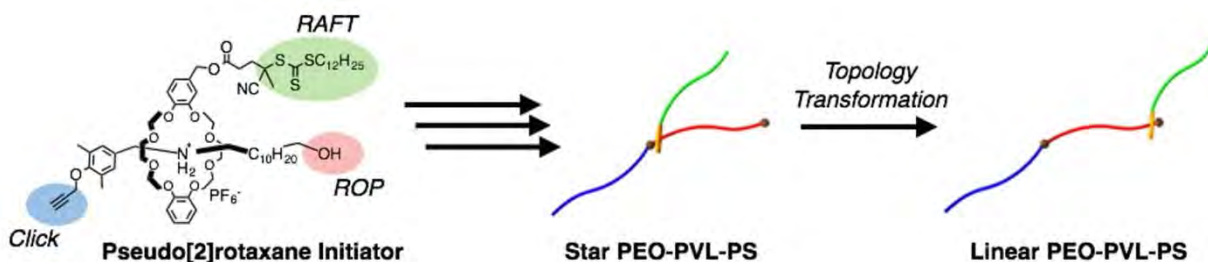


POLY 11: Topology transformation of rotaxane-linked star/linear ABC terpolymer: Synthesis and characterization

Hiroki SATO, hsato@polymer.titech.ac.jp, Daisuke Aoki, Toshikazu Takata.
Department of Chemical Science and Engineering, Tokyo Institute of Technology,
Tokyo, Japan

In recent polymer science, control of polymer topology has attracted much attention because macroscopic property and function of polymer are largely influenced by its topology. For example, Matsushita *et al.* reported that triblock copolymers with different topologies clearly form different microphase-separated structure. On the other hand, we have reported the transformation of the polymer topology facilitated by mechanically linking of polymer chain. Herein, to clarify the morphology change caused by the polymer topology change, an ABC triblock copolymer with the polymer chains connected through a rotaxane linkage at the junction point was synthesized and characterized.

A trifunctional pseudo[2]rotaxane with a *sec*-ammonium axle having both alkyne and hydroxyl moieties across the bulky group, and a crown ether wheel having a trithiocarbonate group for RAFT polymerization was prepared as a key initiator. Three polymer chains were introduced by the ring-opening polymerization from the hydroxyl group, the RAFT polymerization, and the click reaction, to afford ABC-type star polymer. The polymer topology was transformed from star to linear by the acetylation of the *sec*-ammonium moiety, leading to the dissociation of the crown ether/ammonium complex and association of the crown ether wheel with the urethane moiety at the end of the axle. These two polymers were characterized by NMR, GPC and MALDI-TOF-MS, and the properties depending on the polymer topology were studied by DSC, AFM and water contact angle measurement.



POLY 12: Visualizing randomness: Synthesis and imaging of statistical and segmented colloidal copolymers

Nick G. Pavlopoulos, *ngpavlopoulos@email.arizona.edu*, Jeffrey Pyun. University of Arizona, Tucson, Arizona, United States

In recent years, interest in ensemble properties of colloidal nanoparticles has led to the development of new systems with properties of self-assembly. These assemblies of inorganic nanomaterials, termed *colloidal polymers*, have been shown to exhibit properties (optical, electronic, magnetic, catalytic) distinct from their discrete components (*colloidal monomers*), which can be tuned as a function of extent of assembly (*degree of polymerization*). To this end, akin to traditional polymer systems, selective tuning of monomer functionality, assembly motif, and polymer architecture for colloidal polymer systems is of key interest to exploit the unique properties of new monomer units.

Recently we have demonstrated the design of new colloidal monomers, consisting of a II-VI semiconductor (SC) functional group carrying a single gold nanoparticle (AuNP) as a polymerizable unit. Through a simple, one pot reaction, dipolar cobalt shells can be grown selectively on the AuNP tips, resulting in magnetic associations and effective polymerization into linear structures. We have demonstrated the ability to tune SC pendant group, from nanorod (NR) to tetrapod (TP) structures, allowing for clear visualization of polymer composition through TEM. Further, in addition to homopolymer systems from these units, blending of NR and TP monomers with AuNP tips of identical size, followed by dipolar cobalt deposition allowed access to statistical copolymers. Intriguingly, by varying the size of AuNP tip (and thus Au/Co tip size), monomer reactivity could be tuned, with smaller particles leading to weaker dipolar interactions. This discovery allowed for the first ever analogue of reactivity ratio control for colloidal polymer systems, wherein blending of NR and TP monomers with drastically different AuNP tip sizes prior to polymerization afforded segmented copolymers. For traditional copolymer systems, reactivity ratios are typically monitored by comonomer kinetics. For the first time with these colloidal copolymers, we can tune reactivity ratios controllably, and directly correlate reactivity ratios with polymer composition that can be intuitively visualized by TEM, unlike classical polymer systems.

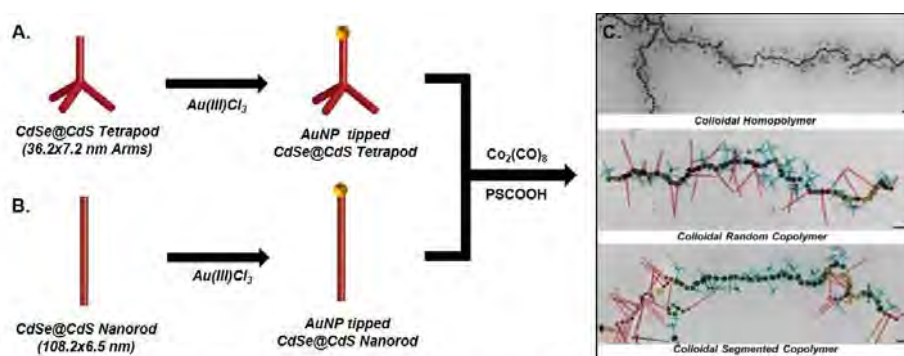
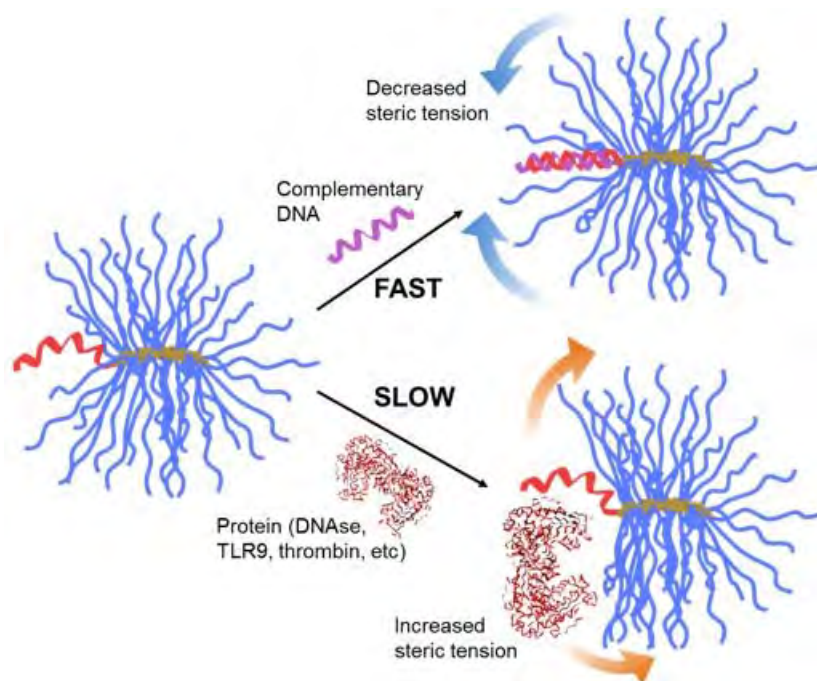


Figure 1. Total synthesis scheme for colloidal copolymers. A) Synthetic pathway to obtain tetrapod functionalized monomers. B) Synthetic pathway to prepare nanorod functionalized monomers. C) Visualized polymers via transmission electron microscope imaging, highlighting colloidal homopolymers, random copolymers (false colored for clarity), and segmented copolymers (false colored for clarity), accessed through blending of AuTP and AuNR comonomers and subsequent deposition of dipolar cobalt. Scale bars are 50 nm.

POLY 13: Antisense gene regulation with non-cationic polymer carriers

Ke Zhang, *k.zhang@neu.edu*. Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States

We demonstrate that protection of DNA can be achieved by inserting it into an intermediate-density brush polymer environment, which enables the DNA to bind selectively to a complementary DNA strand, while access by various proteins is limited. The binding of DNA with proteins such as nucleases, toll-like receptor 9, and thrombin is generally the first step to non-hybridization side effects. We demonstrate that these conjugates can effectively regulate gene expression while suppressing side effects. The brush polymer-based strategy has the potential to be applied to essentially all forms of oligonucleotides, i.e. antisense DNA, siRNA, microRNA, aptamers, ribozymes, etc., to improve their biopharmaceutical characteristics.

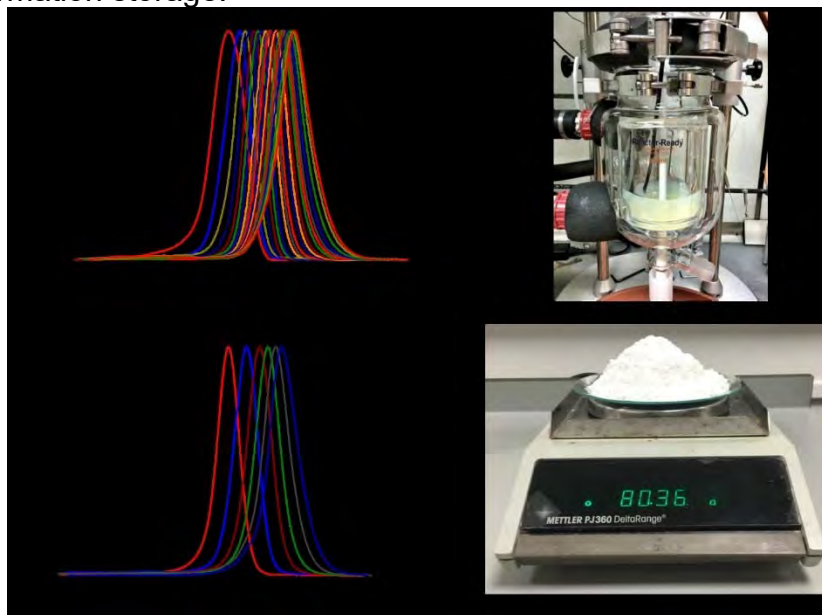


The congestion of the dense PEG side chains of the brush polymer provides the attached DNA strand with kinetic and thermodynamic advantage for binding with complementary strand vs. proteins.

POLY 14: Sulfur-free RAFT, sequence-controlled methacrylic multiblock copolymers via emulsion polymerization

David M. Haddleton³, D.M.HADDLETON@WARWICK.AC.UK, Athina Anastasaki², Nikolaos Engeli³, Vasiliki Nikolaou¹, Gabit Nurumbetov¹. (1) Chemistry, Univ Warwick, Coventry, United Kingdom (2) University of California, Santa Barbara, Coventry, United Kingdom (3) Chemistry, University of Warwick, Coventry, United Kingdom

Translating precise monomer sequence control achieved in nature over macromolecular structure, for example, DNA, to whole synthetic systems has been limited due to the lack of synthetic methodologies. RAFT and ATRP have limitations with regards being efficient in both emulsion polymerisation and for methacrylates. We report a rapid and quantitative synthesis of sequence-controlled multiblock polymers via an emulsion polymerization approach in which a vinyl-terminated macromolecule, as prepared by catalytic chain transfer polymerization, is used as a chain transfer agent. This approach is environmentally friendly, fully translatable to industry and thus represents an advance in the development of complex macromolecule synthesis, where a high level of molecular precision or monomer sequence control confers potential for molecular targeting, recognition and biocatalysis, as well as molecular information storage.

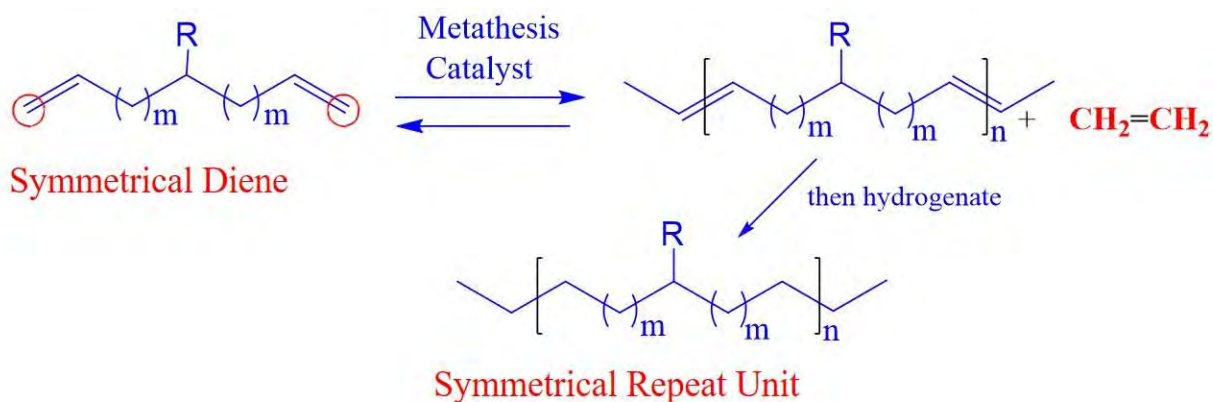


Scalable synthesis of the high-molecular-weight hexablock copolymer. The copolymer consists of BMA, BzMA, EHMA and MMA at 85 °C (in a 0.5 l reactor with monomer-starved conditions) via a segregation approach of emulsion polymerization using KPS as initiator and PMMA (~ 2,000 g mol⁻¹) as the initial CTA. a, Molecular weight distributions of heneicosablock multiblock copolymer by SEC. b, Image of the double-jacketed 0.5 l reactor used for the high-scale synthesis. c, Molecular weight distributions of heptablock copolymer by SEC. d, Total amount of material/product obtained after six successive additions.

POLY 15: Precision functional polyethylene-based polymers via acyclic Diene Metathesis (ADMET)

Kenneth B. Wagener, wagener@chem.ufl.edu, Michael H. Bell, Hong Li, Taylor W. Gaines. Dept. of Chemistry, University of Florida, Gainesville, Florida, United States

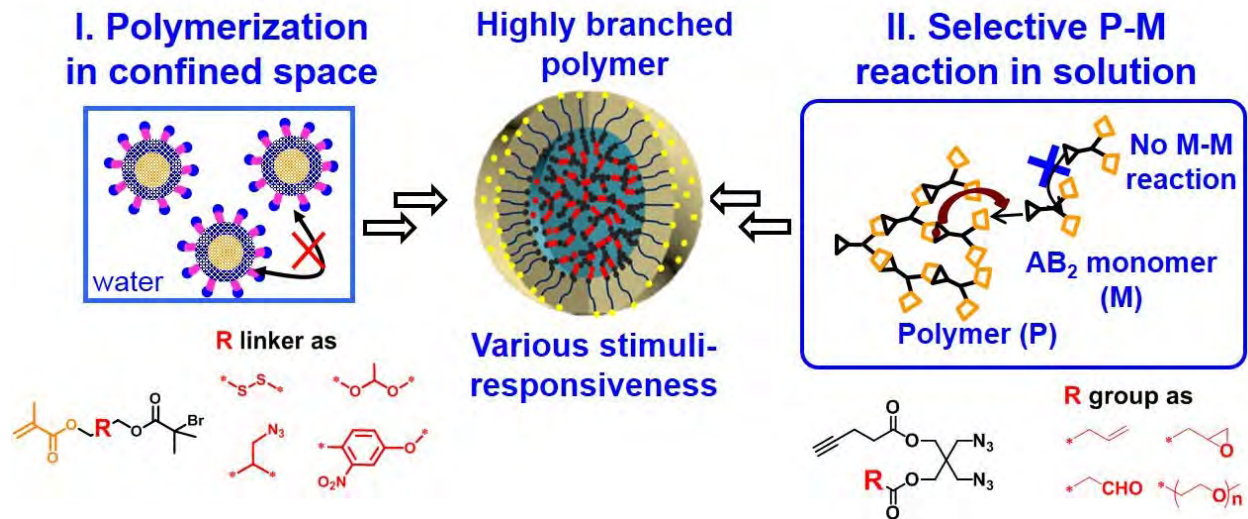
Polyethylene is the most common synthetic polymer in the world. An inherent complexity in most polyethylene-based materials is their structural complexity including irregular branching from free-radical polymerization methods and random placement of the functional groups. Acyclic diene metathesis (ADMET) chemistry provides unprecedented structural control of functionalized linear polyethylenes with a precise number of methylene groups between alkyl branching or added functional groups. These remarkable materials promise to improve both performance and structure-property correlations. Through a combination of careful monomer design and ADMET polymerization, our group has been able to study the structure property relationships of precision aliphatic polyethylene-based polymers containing added functionality or regular alkyl branching. The highlighted materials show unique thermal properties and crystalline behavior. Presented is the synthesis, characterization, and properties afforded by the precision polyethylene-based materials.



POLY 16: One-pot synthesis of responsive polymers with highly branched structures

Haifeng Gao, gaohaifeng1@gmail.com, Yi Shi, Xiaosong Cao. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States

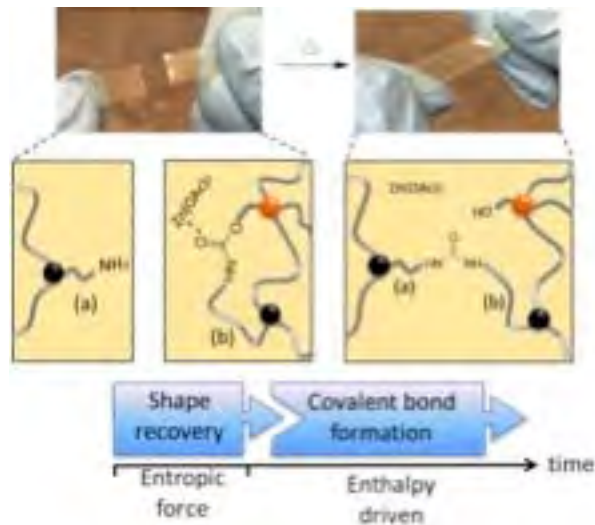
This talk presents our recent efforts on the one-pot synthesis of highly branched polymers with tunable molecular weights (10^3 - 10^6), high degree of branching ($DB = 0.5 - 1$) and low polydispersity ($M_w/M_n \sim 1.1$). The methods include 1) the polymerization in confined nanospace and 2) chain-growth CuAAC polymerization of AB_m monomers in solution. The produced nanostructured polymers can be easily functionalized with various reactive groups and functional segments showing various response to environmental stimuli.



POLY 17: Shape memory in self-healing polymers: Synchronized physico-chemical events

Ying Yang¹, Christopher C. Horna², **Marek W. Urban**¹, mareku@clemson.edu. (1) Materials Science and Eng., Clemson University, Anderson, South Carolina, United States (2) Materials Science and Eng., Clemson University, Clemson, South Carolina, United States

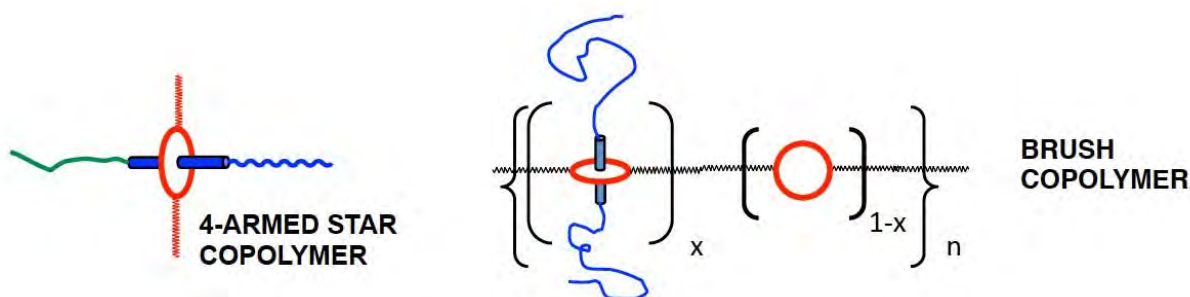
Significant advances in stimuli-responsive materials in general, and polymers in particular, have shown how reversible and irreversible chemical reactions can be utilized to repair mechanically damaged polymer networks. Although the role of shape memory effects (SME) in polymers is intuitively appreciated, quantitative aspects and the role of SME on self-healing has not been addressed. In this presentation we will address the impact of localized chemical events synchronized with nano-, micro- and higher length scale repairs in which SMEs play a key role. The proposed approach encompasses the maximum strain (ϵ_{max}), stress (σ_{SF} at ϵ_{max}), and energy storage by taking into account physical polymer architecture, molecular weight, molecular weight distribution, and viscoelastic behavior, thus allowing quantitative assessments of the SME and its role on chemical processes responsible for covalent rebonding during self-healing.



POLY 18: Host-guest chemistry to control polymeric architecture and conformation

Harry W. Gibson, *hwgibson@vt.edu*, Terry Price, Hanlie Wessels, Zachary Bear.
Chemistry, Virginia Tech, Blacksburg, Virginia, United States

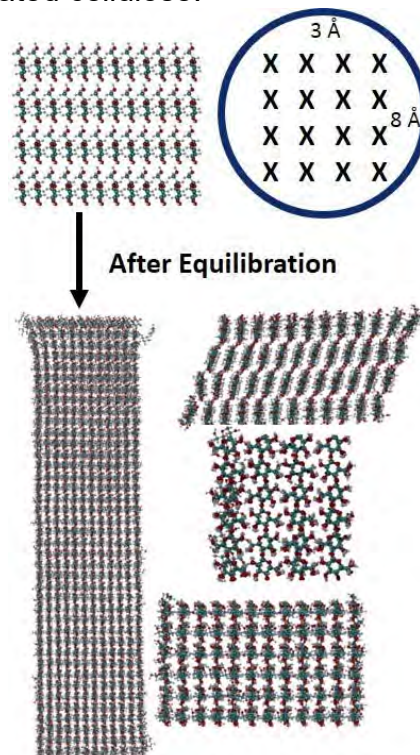
We report the use of pseudorotaxane and rotaxane self-assembly to alter and control the structures and properties of macromolecules. In order to produce block, graft, brush and star polymers from host- and guest-functionalized components efficiently, high association constants ($K_a > 10^4 \text{ M}^{-1}$) are required. Pyridino cryptands afford association constants in the range of 10^4 to 10^6 M^{-1} with paraquats. Here we will report template-based methods for formation of the precursor crown ethers and the cryptands in high yields. In functionalized derivatives these powerful hosts enable new avenues to create new types of polymeric structures and control conformational aspects of polymers. These studies will be discussed along with characterization of the resultant novel materials.



POLY 19: Molecular dynamics simulation of cellulose nanofibrils used to modify polymer gels

Yelena Sliozberg^{1,2}, yelena.r.sliozberg.ctr@mail.mil, Shawn Coleman², Hong Dong², James Snyder², Abby West², Tanya Chantawansri². (1) SURVICE Engineering, Aberdeen Proving Ground, Maryland, United States (2) U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States

Chemically and physically cross-linked polymer networks and gels represent an important class of soft materials, whose mechanical properties can be adapted for multiple applications in diverse areas such as the military, industry, and biomedicine. However, conventional polymer gels are soft, weak, and brittle. Nano-inclusions can be utilized to modify structural and mechanical properties of polymer gels. Cellulose nanofibrils have been used as reinforcement nanofillers for polymer nanocomposites. Cellulose nanofibrils have high aspect ratios that enable formation of a percolated network at a low concentration in polymer matrices. Supplementary to experimental efforts, modeling approach provides a powerful means to investigate a broad range of parameters, which is challenging to explore experimentally. Toughening mechanisms of nanocomposite films were investigated through coarse-grained simulations, where the results demonstrated that a favorable polymer-nanofibril interface together with percolation of the nanofibrils, both facilitated through hydrogen bonding interactions, contributed to the toughness improvement in these nanocomposites. Additionally, we will use all-atom molecular dynamics to gain insight into the effect of initial chain orientation in bacteria generated cellulose.

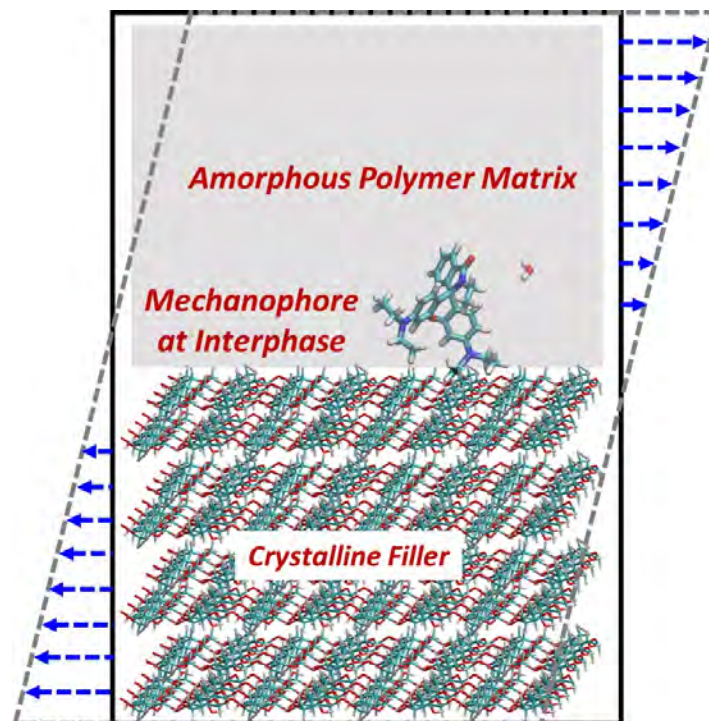


Model system is composed of one terminal complex triplet, where three chain arrangements will be considered in a TC subunit: regular, staggered, or circle

POLY 20: Mechanophore activation at the crosslinked epoxy-nanocellulose interface: Insight from density functional theory and molecular dynamics simulations

Ketan S. Khare^{1,2}, ketan.khare@nist.gov, **Frederick R. Phelan**¹. (1) MSED, National Institute of Standards and Technology, Gaithersburg, Maryland, United States (2) Physics, Georgetown University, Washington, District of Columbia, United States

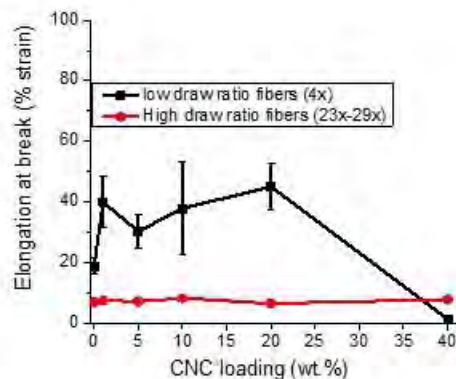
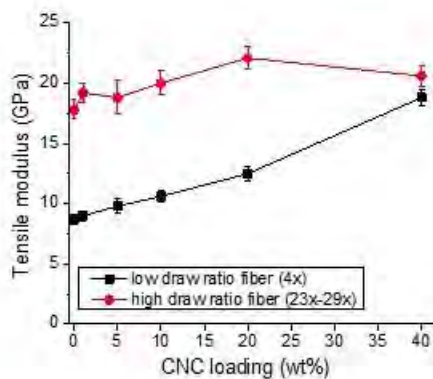
The objective of the Sustainable Composites Project at NIST is to develop tools for measuring the fundamental structure-processing and structure-property relations associated with sustainable polymer composites. One area of study is mechanically activated leuco dyes (mechanophores), which have been recently proposed and are being tested as damage sensors in polymeric materials. The use of such dyes is particularly promising as a means to understand the polymer composite interphase, where load transfer between the matrix and the filler is difficult to measure directly. Here, we use a multi-faceted modeling approach to understand the activation of these dyes in at the interface of cross-linked epoxy-nanocellulose composites. Density functional theory (DFT) calculations are used to quantify the forces and the energetics involved in the mechanical activation of mechanophores. This information is then used to parameterize a bond-breaking potential to be used in molecular dynamics simulations of atomistic models of interphases in cross-linked epoxy based composites. This approach allows us to study the necessary conditions for the activation of the mechanophores at the matrix-filler interface.



POLY 21: Ductile polyacrylonitrile fibers with high cellulose nanocrystals loading

Huibin Chang^{1,2}, hbchang@gatech.edu, Jeffrey Luo^{1,2}, H. c. Liu^{1,2}, Amir Bakhtiary Davijani¹, Po-Hsiang Wang¹, George Lolov³, Ryan Dwyer¹, Satish Kumar^{1,2}. (1) Material Science Engr, Georgia Tech, Atlanta, Georgia, United States (2) Renewable Bioproducts Institute, Georgia Institute of Technology, Atlanta, Georgia, United States (3) Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

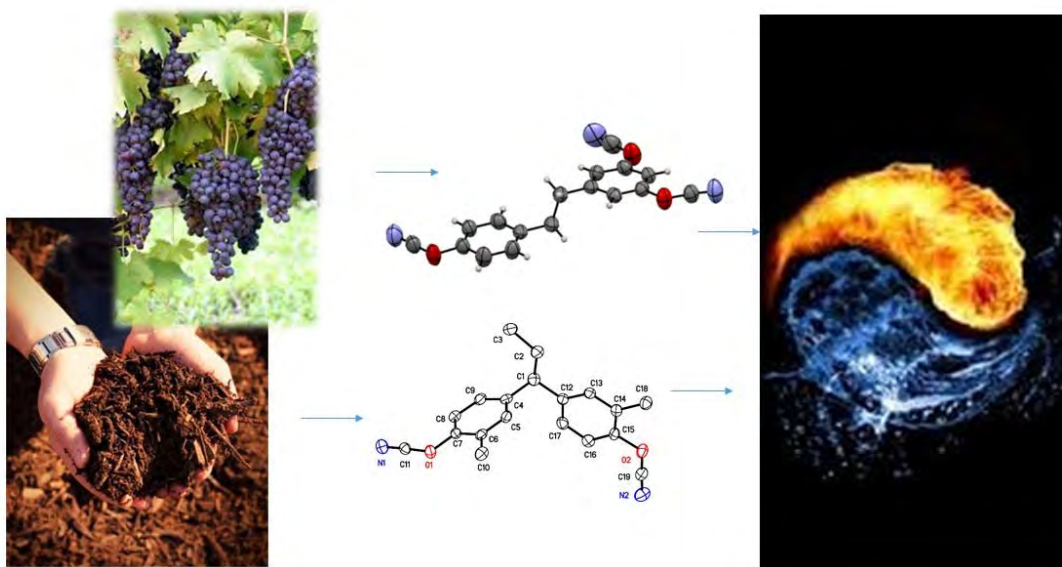
Polyacrylonitrile (PAN) fibers containing up to 40 wt% cellulose nanocrystals (CNC) with good properties were processed. Structure, mechanical property and dynamic mechanical property of these fibers were systematically investigated. The crystallinity, crystal size and crystallite orientation of PAN in PAN and PAN/CNC fibers significantly increases as the draw ratio increases from 4x to 15x. At 4x draw ratio, highly oriented CNCs help align PAN chain and this becomes more obvious as the CNC loading increases. At 4x draw ratio, work of rupture increases by a factor of 2 only for 1 wt% CNC loading and tensile modulus significantly increases from 8.7 GPa for PAN fiber to 18.8 GPa for PAN/CNC 40 wt% fibers. Though PAN/CNC 40 wt% fiber becomes very brittle at 4x draw ratio, the elongation at break is significantly improved as fiber was drawn to 29x and it is comparable to that for the control PAN fiber. This is the first study of such a high concentration of nano reinforcement in PAN (or any other polymer) processed into good property fibers. These results should prove important in reinforcing broader class of polymers with CNCs, without making them brittle, which is a common draw back with other nano reinforcements.



POLY 22: New and unexpected properties from polycyanurate networks prepared from bio-based monomers

Andrew J. Guenther², andrewguenther@gmail.com, Benjamin G. Harvey⁵, Andrew P. Chafin⁵, Matt C. Davis⁴, Jacob Zavala³, Kevin Lamison¹, Josiah Reams³, Michael D. Ford³, Kamran Ghiassi⁶, Thomas J. Groshens⁵, Joseph M. Mabry². (1) Air Force Research Laboratory, Lancaster, California, United States (2) Aerospace Systems Directorate, Air Force Research Laboratory, Lancaster, California, United States (3) ERC Inc., Lancaster, California, United States (4) Navy NAWCWD Michelson Lab, Ridgecrest, California, United States (5) Chemistry, US Navy, Ridgecrest, California, United States (6) Rocket Propulsion Division, Air Force Research Laboratory, Edwards AFB, California, United States

One of the most important yet least appreciated benefits of bio-based sources for polymeric material is the ability to access new and unexpected combinations of high-performance properties due to the straightforward availability of a wider set of structural motifs than can be derived readily from petroleum-based starting materials. In the field of polycyanurate networks, we have taken advantage of these benefits to create new resins that exhibit exceptional fire resistance (using resveratrol as a source) or unexpectedly low moisture uptake (using lignin as a source). The exceptional physical properties of these networks have been established and traced to specific chemostructural features, such as extended conjugation or steric crowding effects. Not only the monomers themselves, but also structural analogs that help to establish the chemical basis for the observed physical properties, have been created thanks to investigations of bio-based materials.



POLY 23: Styrene-free soybean oil-based thermosets and their natural fiber composites

Wendi Liu¹, *wdliu9054@163.com*, **Renhui Qiu²**. (1) College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, China (2) College of Transportation and Civil Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian, China

A styrene-free soybean oil-based thermosetting (IM-AESO) resin was formulated from acrylated epoxidized soybean oil (AESO) and methacrylated isosorbide (IM) as a comonomer. The IM was synthesized from isosorbide with methacrylate anhydride (MAA) by a solvent-free, ultrasonic-assisted method. The formulated IM-AESO blend was further modified with MAA to impart the resin (IM-MAESO) with higher degree of unsaturation through replacing the hydroxyl groups of AESO with methacrylate groups. Results indicated that both the IM-AESO and IM-MAESO resins had much lower viscosities, activation energies, and curing temperatures as well as higher polymerization rates and curing degrees than pure AESO due to the incorporation of IM as a reactive diluent. The combination of stiff IM and flexible AESO resulted in biobased networks with superior flexural strengths, flexural moduli, flexural strains, storage moduli, and glass transition temperatures. MAA modification gave rise to the crosslinking degree and hence flexural properties and dynamic mechanical properties of the resins when curing. The biobased thermosets were used as matrices for the preparation of hemp fiber- and bamboo fiber-reinforced composites to evaluate the effects of resin composition and fiber type on the performance of the composites. The composites from hemp fibers with the thermosets indicated much higher flexural strengths, flexural moduli, flexural strains, storage moduli, and glass transition temperatures than those from bamboo fibers. MAA modification for AESO significantly increased the storage modulus and glass transition temperature of the composites, but showed an insignificant effect on flexural properties of the composites.



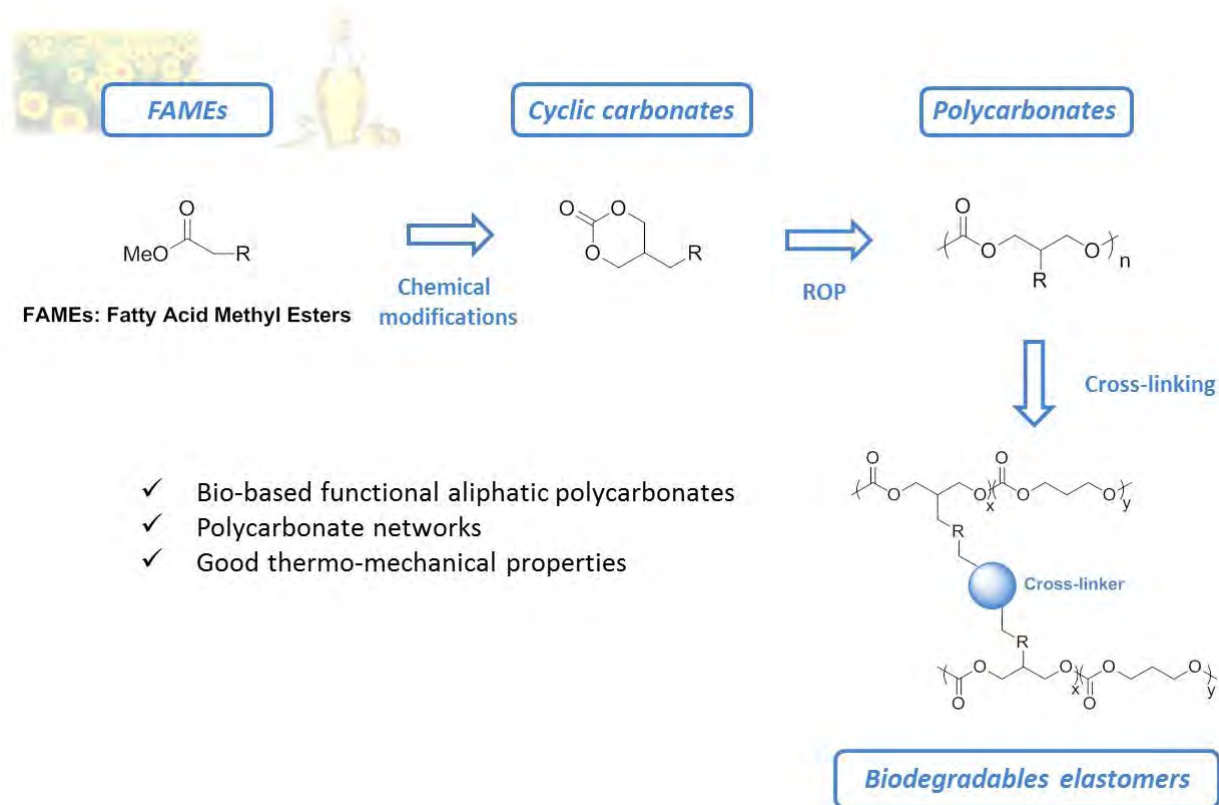
POLY 24: Synthesis and properties of new cross-linked bio-based aliphatic polycarbonates

Pierre-Luc Durand^{1,2}, pierre-luc.durand@enscbp.fr. (1) Bordeaux University, LCPO, Talence, France (2) CNRS, Bordeaux, France

Presently, most of the industrial chemicals are produced from oil resources. However, rapid depletion and price increase of fossil resources are encouraging chemists to point their research towards designing chemicals and materials from renewable feedstocks. Fatty acid derivatives (FAD) appear as a versatile platform to develop bio-based polymers. Based on FAD, a lot of work has been done so far in the field of polyurethanes, polyesters, polyamides, etc. However, not as much attention has been paid to the preparation of aliphatic polycarbonates.

Aliphatic polycarbonates are used in widespread biomedical applications, due to their high biocompatibility, biodegradability, low toxicity, and better mechanical properties as compared to similar polyesters. Ring-opening polymerization of cyclic carbonates raised lot of attentions for the formation of aliphatic polycarbonates.

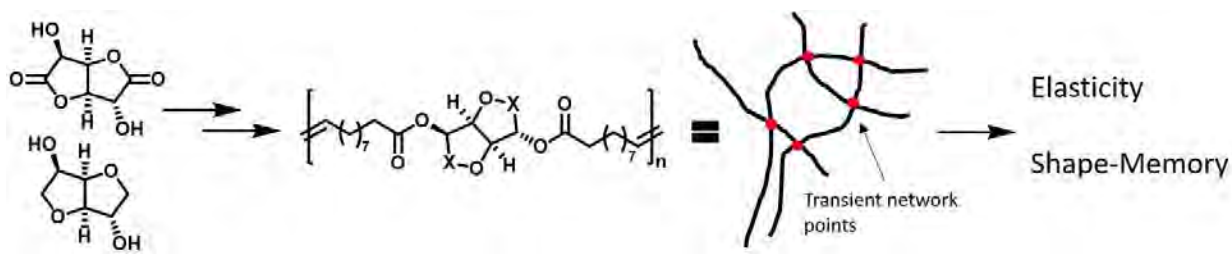
To that purpose, this presentation will discuss the synthesis of a large platform of fatty acid-based six-membered cyclic carbonates and their organo-catalyzed polymerization, leading to original functional linear aliphatic polycarbonates. Polycarbonate networks were also prepared that exhibit good thermo-mechanical properties and, in certain instances, were thermally reversible.



POLY 25: Transient networking in glucarodilactone-containing polyesters

Leon M. Lillie¹, leon.m.lillie@gmail.com, **William B. Tolman**², **Theresa M. Reineke**¹. (1) Chemistry, University of Minnesota, Saint Paul, Minnesota, United States (2) Chemistry Dept, University of Minnesota, Minneapolis, Minnesota, United States

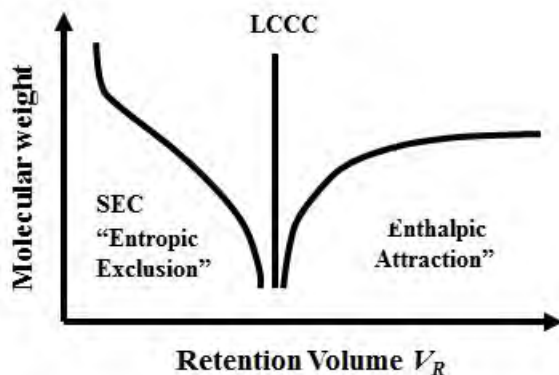
Carbohydrates have great potential as renewable building blocks for the development of sustainable materials that can compete with the mechanical performance and cost of conventional petroleum-based plastics. This work initially sought to bring enhanced degradability to polyesters through the incorporation of degradable sugar-derivative glucarodilactone (GDL) into polyester materials. This was accomplished by coupling 10-undecenoic acid to the GDL and the better known analog isosorbide, forming two α,ω -dienes that are suitable for Acyclic Diene Metathesis (ADMET) polymerization. Small structural changes between the isosorbide and GDL units allows for highly tunable mechanical performance and material degradability. The importance of GDL in the ultimate mechanical strength, elasticity, and shape memory abilities were revealed with the synthesis and characterization of a compositional matrix of GDL and isosorbide containing copolymers, along with the direct replacement of either GDL or isosorbide with 2,5-bis(hydroxymethyl)furan. Rheological characterization of these materials was used to identify transient networking within GDL-containing copolymers, and is believed to be the source of the previously reported elasticity and shape memory abilities of the GDL-containing polyesters.



POLY 26: Theoretical perspective on the separation mechanism of complex polymers by interaction chromatography

Yongmei Wang, ywang@memphis.edu. Department of Chemistry, University of Memphis, Memphis, Tennessee, United States

Interaction chromatography has found great use for the separation and characterization of complex polymeric systems. To effectively use the interaction chromatography, a good understanding of the theoretical foundation of the interaction chromatography is important. One can gain a good understanding of the separation mechanism through simple Monte Carlo simulations. Simulations allow one to look into how a polymer chain with different chemical composition and/or chain architecture interacts with the column substrates and how that translate into separation seen in experiments. In this talk I will present how we have used Monte Carlo simulations to understand the separation of complex polymers by interaction chromatography. I will focus on the adsorption of polymers in pores studied by Monte Carlo simulations and discuss the impact of chain architecture on the polymer adsorption.



POLY 27: Polymer microstructure analysis by HPLC

Dean Lee¹, *Dlee3@dow.com*, **Sam Qiu**¹, **Jeff Munro**², **Colin Li Pi Shar**², **Tianzi Huang**³, **Rongjuan Cong**³. (1) Analytical Sciences R&D, The Dow Chemical Company, Midland, Michigan, United States (2) Dow Elastomers R&D, The Dow Chemical Company, Freeport, Texas, United States (3) Plastics Characterization & Testing, The Dow Chemical Company, Freeport, Texas, United States

It is known that the arrangement of monomers on a polymer backbone causes a shift in adsorption and therefore HPLC retention time [1]. The arrangement of monomers that creates certain patterns on polymer backbones is referred to as polymer microstructure. Understanding behavior of polymers in HPLC elution will shine light on polymer microstructure, especially in complex systems.

In this presentation, the authors will present the chemical composition of fractions separated by HPLC. Both off-line fraction collection and on-line two-dimensional chromatography are used to measure composition of HPLC fractions. Off-line fraction collection gives flexibility in choosing different techniques for composition determination as the interference of HPLC eluent can be removed by evaporation. On-line two dimensional chromatography is automated and less labor intensive. The interference of HPLC eluent is removed by the second dimension SEC[2]. The measured compositions indicate that polymer with blocky structure interacts relatively more strongly with the HPLC column. By comparing the compositions at a given retention time, the blockiness of polymers can thus be evaluated.

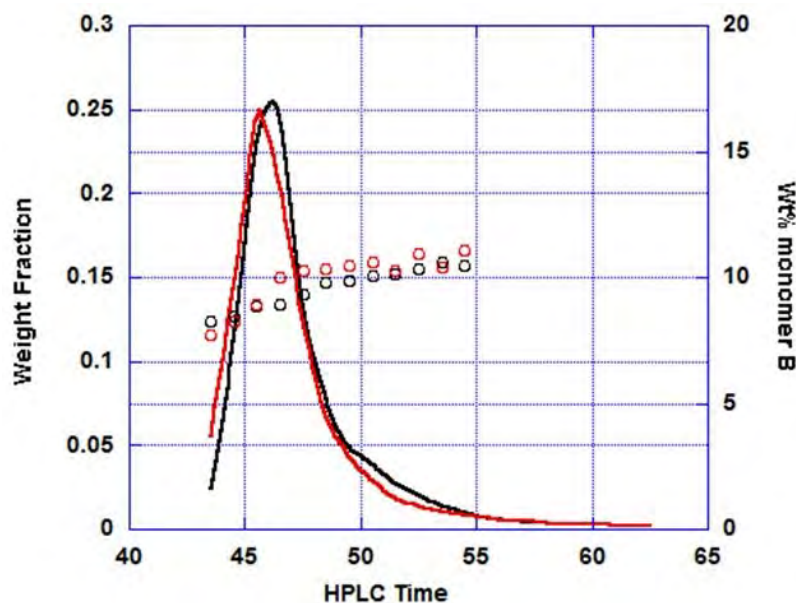


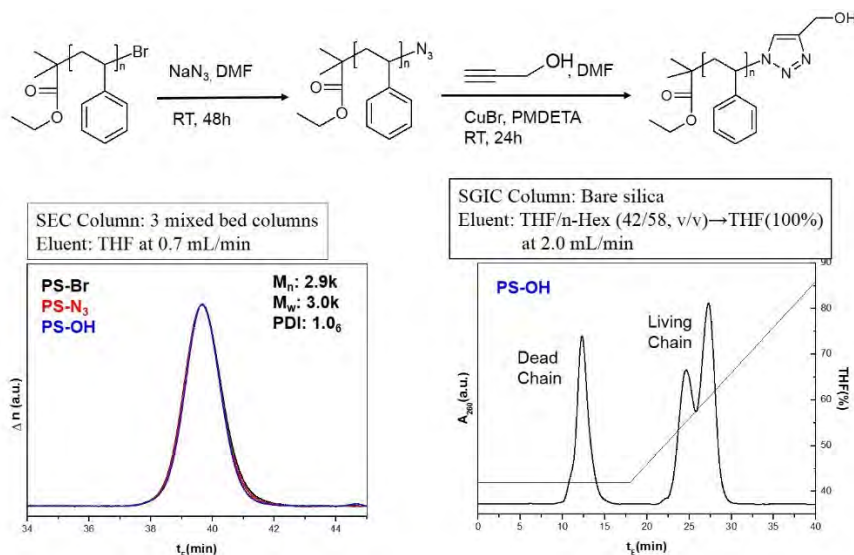
Figure. A schematic example showing HPLC chromatograms (solid lines) with chemical composition of the separated fractions (open circles).

POLY 28: Separation and characterization of living and dead chains in polystyrene synthesized by ATRP

Taihyun Chang, 30019351@acs.org. Pohang Univ Chemistry Dept, Pohang, Korea (the Republic of)

Atom transfer radical polymerization (ATRP) is a very useful method to obtain polymers with relatively narrow molecular weight distribution (MWD) and various chain-end functionalities (CEF). However, dead chains are always formed by suppressed but unavoidable termination reactions between free radicals while chains are growing in ATRP that results imperfect CEF. Thus the dead chains are inevitable by-product that affects the purity in the synthesis of block copolymers or topological polymers by ATRP. Nonetheless, the true MWD and CEF of polymers prepared by ATRP is yet to be addressed critically. Let alone the resolution limitation of size exclusion chromatography (SEC), the molecular characterization technique predominantly used for MWD analysis of synthetic polymers, their MWD is intrinsically an overlapped distribution of both living and dead chains.

In this study, living and dead chains of polystyrenes synthesized by ATRP are separated by HPLC after the chain-end substitution reaction. After the polymerization, only living chains carries a bromine end group which can be easily converted to another polar functional group such as hydroxyl group. Then, HPLC can effectively separate the polymers according to the chain end functionality. Living chains with polar chain end interact more strongly with polar stationary phase such as bare silica than dead chains. MALDI-TOF MS is used to identify the chain end in the separated fractions. Finally, dead chain fraction and true MWD of living chain by ATRP are experimentally determined and compared with the theoretical predictions.



Top: Chain end modification scheme of living chains

Bottom left: Identical SEC chromatograms of PS-Br, PS-N₃ & PS-OH

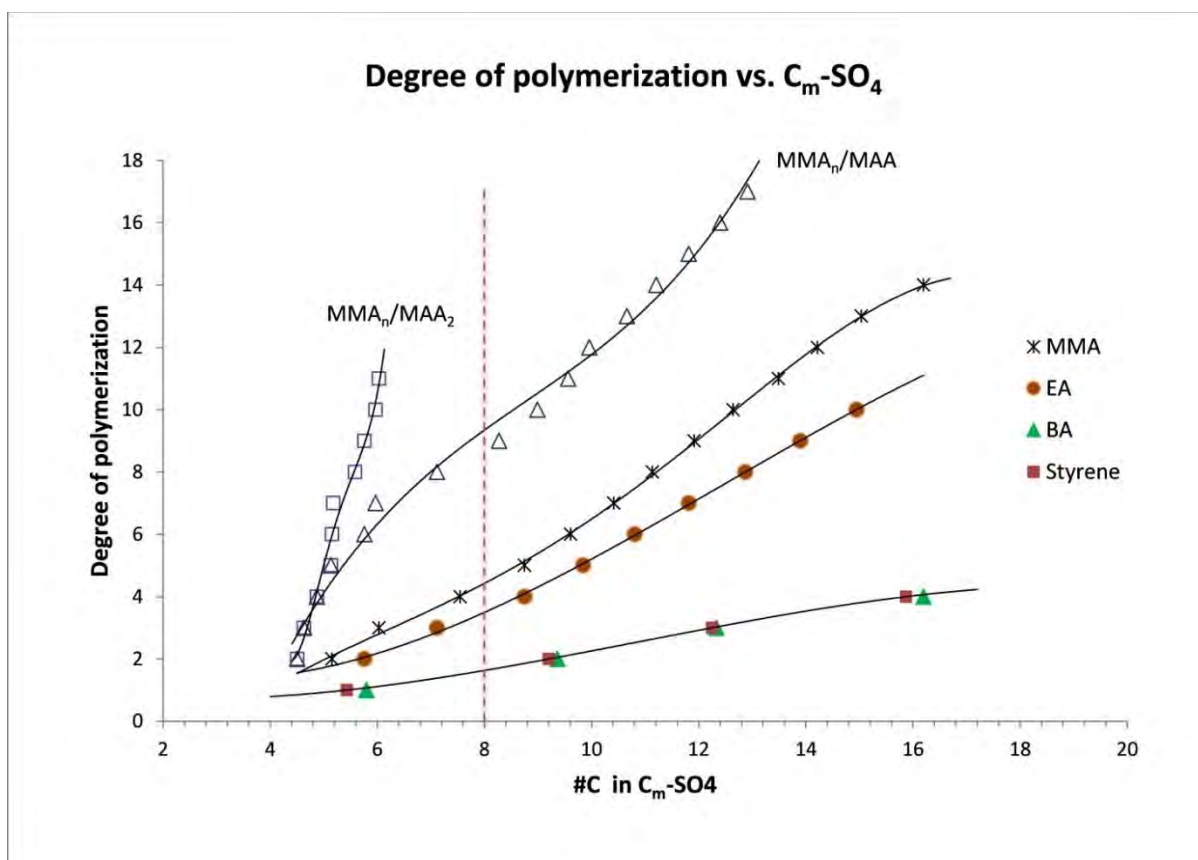
Bottom right: Solvent gradient IC chromatograms of PS-OH

POLY 29: Understanding of aqueous oligomers formed during emulsion polymerization and their interfacial behavior via LC-MS

Tianlan Zhang, tianlanzhang@dow.com, Bryan McCulloch, Wei Gao, Ralph Even.
Core R&D, The Dow Chemical Co, Collegetown, Pennsylvania, United States

Interfacial characteristics of oligomeric molecules plays an important role in emulsion polymerization. For example, surfactants and dispersions are used to stabilize latex particles during and after emulsion polymerization. Water soluble initiator radical needs to react with monomer in the aqueous phase until they reach a composition where they become surface active, either leading to particle nucleation, or adsorbed onto a pre-existing particle to carry out the intended chain propagation.

In this study, a model emulsion polymerization system was established to generate oligomers with various compositions and chain lengths. We have determined the interfacial properties of oligomeric species using liquid chromatography and linked the interfacial behavior to the oligomer composition obtained by mass spectrometry. By correlating elution times to known alkyl sulfate surfactant standards we have been able to quantify the hydrophobicity or surface activity of the water soluble oligomeric species. Serum phase chemistry was also explored in this study to understand the formation of aqueous oligomer through emulsion polymerization process.



Surface activity vs. oligomer composition

POLY 30: Copolymer structure elucidation by multidimensional techniques with focus on UPLC x ESI-TOF-MS

Jana Falkenhagen, jana.falkenhagen@bam.de. BAM, Berlin, Germany

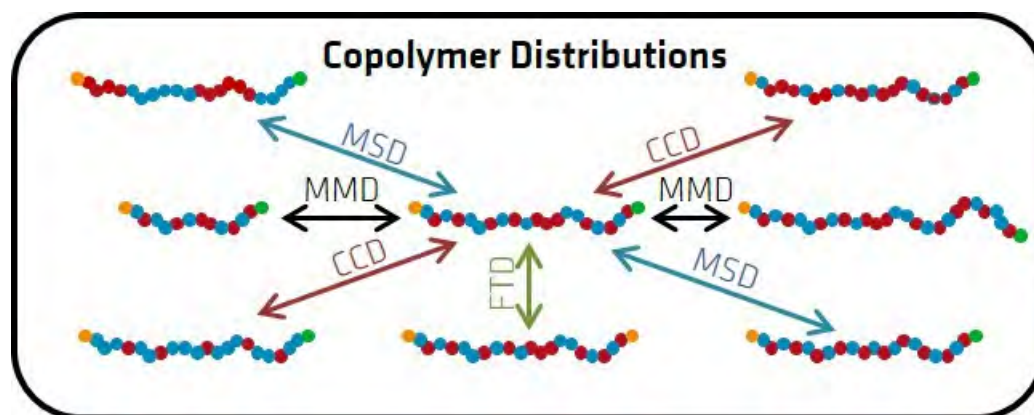
Structure elucidation of complex synthetic copolymers still represents a challenge. An one-dimensional separation technique cannot give the answer to the question: What are the molar mass distribution, the functionality distribution, the copolymer composition distribution, the topology differences within a single broad distributed polymer sample?

Since the first LC/ ESI-MS experiment of the Nobel prize winner John B. Fenn in 1984, the coupling of liquid chromatographic to mass spectrometric techniques gained a continuous rapid development.

Often the deficiencies of stand-alone methods can be bridged. LC, blind to structural information needs mass spectrometry as one of the most powerful detectors able to give detailed information on e.g. the repeat units, functionalization or copolymer composition of the chromatographic separated constituents. A separation prior to MS reduces radical the dispersity which is one of the reasons for failing of MS. Also problems with different ionization probabilities in complex mixtures can partly be overcome.

Different LC separation techniques as size exclusion chromatography (SEC), liquid adsorption chromatography (LAC), liquid chromatography at critical conditions (LCCC) and gradient elution liquid chromatography (GELC) combined with Matrix assisted Laser Desorption Ionization (MALDI) respectively Electrospray Ionization (ESI) Time of Flight (TOF) mass spectrometry are able to give information which otherwise are completely inaccessible. In some cases CID tandem mass spectrometry is applied. Fragmentation of suitable precursor ions resulted in typical fragment ion patterns. This technique enables an additional information on e.g. sequences, structural defects and topology of complex polymer mixtures.

Herein a new approach is demonstrated to provide evidence of different functionalities and short block sequences in statistical EO-PO copolymers. Furthermore silsesquioxane mixtures and Polyglycerols are investigated concerning occurring topology effects.



POLY 31: Application of different chromatographic techniques to characterize chemical and molar mass heterogeneity in graft copolymers

Ralf Leinweber, Peter Montag, Jasmin Preis, **Wolfgang Radke**, wradke@pss-polymer.com. PSS Polymer Standards Service, Mainz, Germany

Graft copolymer products can be heterogeneous in different respects. Besides the molar mass heterogeneity inherent in any polymerization product, the reaction products of grafting processes can contain homopolymers of the backbone and side chains as well. In addition, the actual formed graft copolymer might vary in composition.

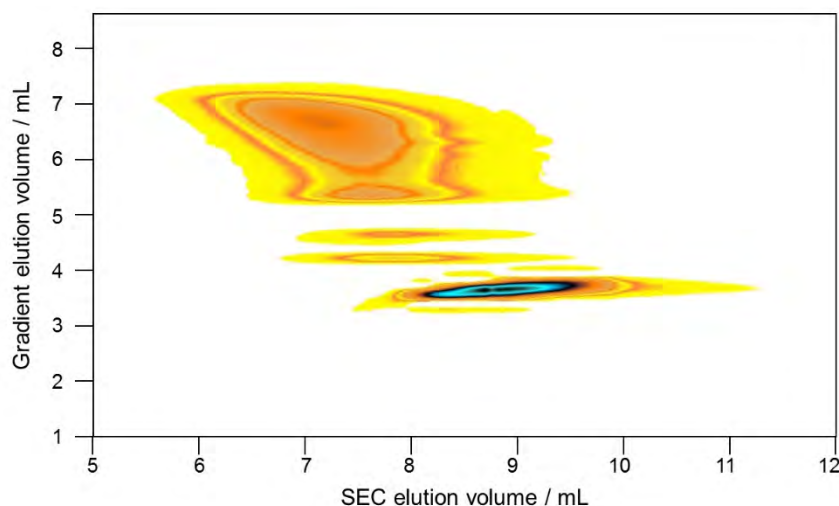
While the average composition can be obtained straight forward by spectroscopic techniques, elucidating the distribution of the different homo- and copolymers in a graft copolymer product is more complicated. Separation of the different species is required. For the present study two graft copolymer samples of identical composition were synthesized by grafting living polystyrene anions onto a broadly distributed PMMA backbone, using two slightly different reaction protocols.

While the average composition was identical for both products, their product distributions differed substantially.

To identify how the different reaction protocols influence the product distribution, the samples were analysed by conventional Gel Permeation Chromatography/ Size exclusion chromatography (GPC/SEC), GPC/SEC with viscometry and light scattering detection, GPC/SEC with UV and RI dual detection, gradient chromatography and 2-dimensional chromatography.

It could be shown that the two samples contain different amounts of residual homopolymers. In addition, the graft copolymers produced differed in grafting density and thus in chemical composition. While one product contained a heavily grafted product besides large amounts of homo PMMA, the other product was composed of graft copolymer of lower degree of grafting with nearly no residual PMMA.

The presentation will discuss which information can be expected from the different separation techniques and how these information help understanding the product distribution.

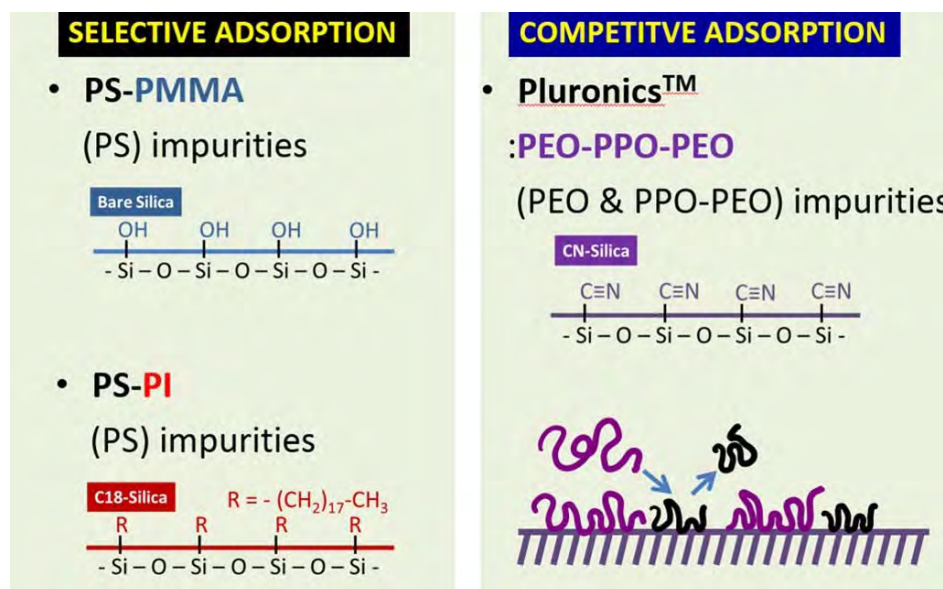


2D-chromatogram of a poly(methyl methacrylate)-graft-poly(styrene). 1st. dimension gradient chromatography, 2nd. dimension SEC.

POLY 32: Large-scale separation and purification of block copolymers via selective and competitive adsorption on silica

Chang Y. Ryu, *ryuc@rpi.edu*. Chemistry and Chemical Biology, Rensselaer Polytech Inst, Troy, New York, United States

As a new variant of polymer liquid chromatography techniques, the adsorption-based interaction chromatography can be ideally suited for the analysis of chemical heterogeneity in block copolymers, because the polymer adsorption conditions in solution are dependent on the chemical nature of polymer chains. Furthermore, the knowledge of block copolymer adsorption from the interaction chromatography can be transferred to develop a large scale purification method of block copolymers by manipulating the adsorption of homopolymers and block copolymers on to silica in solution. Here, we have demonstrated two examples of block copolymer purification in large scale. The first case utilized the selective adsorption of block copolymers on silica by tuning the solvent quality. Specifically, we have demonstrated how the polystyrene-b-poly(methyl methacrylate) (PS-PMMA) diblock copolymers synthesized by anionic polymerization can be purified using a simple silica gel gravity column to obtain homopolymer-free PS-PMMA block copolymers in a large scale. The second case was developed based on the competitive adsorption of block copolymers on silica surface in solution. Specifically, we will demonstrate how one can purify Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide), PEO-PPO-PEO, Pluronic block copolymers by taking advantages of competitive adsorption of block copolymers in solution using beakers and simple filtration systems. Finally, the impacts of the block copolymer purification on the self-assembly and properties of block copolymers will be highlighted to emphasize the utility of the large scale purification methods in the study of block copolymer materials.

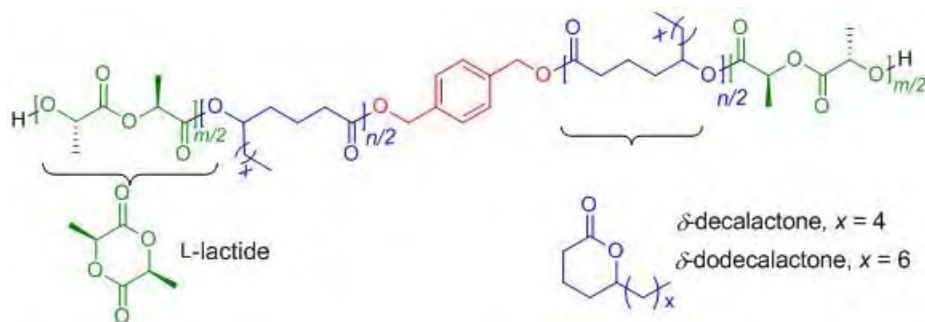


Schematic diagram to show the block copolymer purification by selective adsorption and competitive adsorption on silica surface

POLY 33: Green synthesis of renewable triblock polymers in the organic chemistry laboratory: Not your typical white solid

Jane E. Wissinger, *jwiss@umn.edu*. Chemistry, University of Minnesota, Plymouth, Minnesota, United States

This presentation will share a versatile and engaging polymer experiment designed for the organic chemistry teaching laboratory. Triblock polymers are synthesized from δ -decalactone and δ -dodecalactone, both commercially available flavors, and poly(L-lactide) in the bulk and using green solvents for isolation. The resulting thin film thermoplastics elastomers can then be studied by ^1H NMR analysis to estimate the overall M_n and quantify the mass percent of the midblock and endblock polymers present. A discovery-based variation of the experiment involves having students synthesize triblocks of different compositions and then creatively design their own methods to test their mechanical properties. Students enjoy this fun day in lab as a contrast to the typical ochem experiment resulting in a clear liquid or white solid. This modern polymer experiment highlights plastics in our society and efforts to design more sustainable materials.

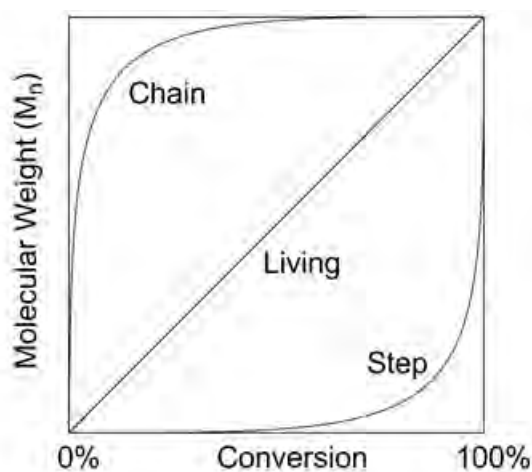


Triblock polymers in the Ochem Lab

POLY 34: Undergraduate polymer synthesis developed for lecture and laboratory experiments

Philip J. Costanzo, *phil.costanzo@gmail.com*. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

Presenting polymer synthesis to undergraduate students can be challenging due to the highly interdisciplinary nature of the material, but that same hurdle is also an ideal opportunity to engage a wide range of students. Strategies for developing lecture topics and assignments will be discussed. Additionally, a variety of different polymer synthesis laboratory experiments with topics ranging from step-growth, chain-growth, controlled radical polymerization and “click” chemistry will also be presented. [figure1]



POLY 35: Integration of polymerization kinetics in polymer, physical chemistry, and chemical engineering courses

Allan Guymon, Allan-Guymon@uiowa.edu. Univ of Iowa, Iowa City, Iowa, United States

Chemical kinetics are an integral part of chemical engineering and physical chemistry instruction in relating the importance of rate in chemical processes. Likewise, kinetics of polymerization reactions are key in understanding ultimate conversion, molecular weight evolution, and network formation. This presentation will focus on presentation of chain and step growth polymerization mechanisms and kinetics, and particularly how the kinetics influence ultimate properties and can be integrated into chemical reaction design. Specific examples detailing the impact of segregation in liquid crystalline systems to illustrate the impact of concentration of kinetics will also be discussed.

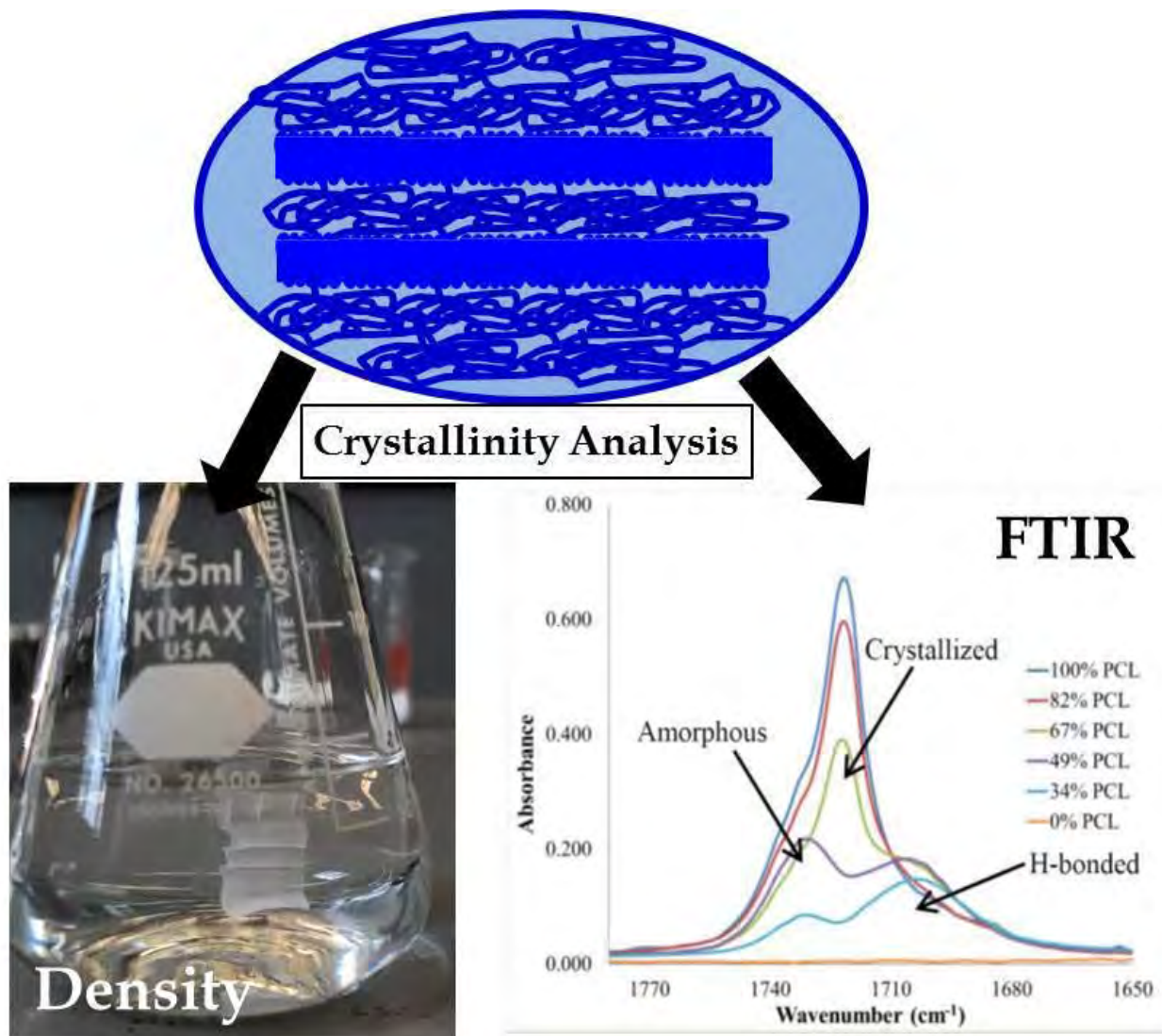
$$R_p = k_p[M] \sqrt{\frac{fk_d[I]}{k_t}}$$

The development and application of the basic chain polymerization rate expression is an excellent example to be used for chemical reaction kinetics in both chemistry and chemical engineering courses.

POLY 36: Polymer physical structure labs at Allegheny College

Ryan M. Van Horn, rvanhorn@allegheny.edu. Allegheny College, Meadville, Pennsylvania, United States

In the chemistry department at Allegheny College, we have developed introductory and upper-level physical characterization labs to introduce students to polymers and polymer science. These labs focus on phase structures of the polymer. In the introductory lab, students estimate crystallinity using bouyancy titration to find the density of various polymer materials. In the upper-level lab, students use FTIR to determine the crystalline and hydrogen-bonded content in PCL/PVPh blends using the C=O band around 1700 cm^{-1} . These rudimentary labs develop important skills for course content while exposing students to unique aspects of polymer science that are technologically relevant.



POLY 37: Studying the thermomechanical properties of copolymers to develop laboratory, theoretical, and communication skills essential to a successful research career

Stefanie A. Sydlik, *ssydlik@andrew.cmu.edu*, William Koshut, Zoe Wright, Zachary Smith. *Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States*

Graduate and undergraduate education is the key to success in all branches of science: in industry and academia alike. In particular, Carnegie Mellon University is widely recognized as a leader in polymer chemistry, and many classes are offered, as well as research experiences, to prepare students for graduate studies and careers in the field. Despite this breadth, a comprehensive class that provides the hands on laboratory, writing, and presentation skills, as well as theory in the field does not exist. Even after many classes and years of research experience, students enter graduate school or the work force still uncertain about the demands and expectations of how to learn new laboratory techniques, what is required in the writing of a paper or a grant, and what constitutes a good scientific presentation. Further, students many rely on instrumentation to produce results, without a deeper understanding of the principles applied by that instrument.

This project overcomes these deficits and equips students with the analytical and practical skills necessary to be successful in a prestigious research environment. We have designed a course centered around a laboratory experiment. Specifically, students use advanced Schlenk technique to synthesize a series of acrylate copolymers. These copolymers are designed to demonstrate the effect of copolymerization on the thermomechanical properties of the polymers, teaching the students, in effect, material design. Students analyze these polymers using techniques essential to the field, including H-NMR (including end group analysis), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), dynamic scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The laboratory techniques are accompanied by in class lectures describing the theory and mathematics behind the measurements. Further, the course is augmented with opportunities to teach technical communication skills, including creative grant writing, technical presentations, writing a compelling journal article, and making effective images and figures.

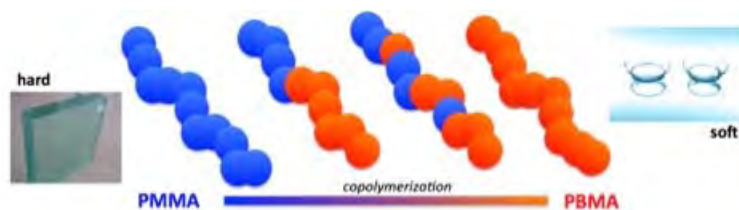
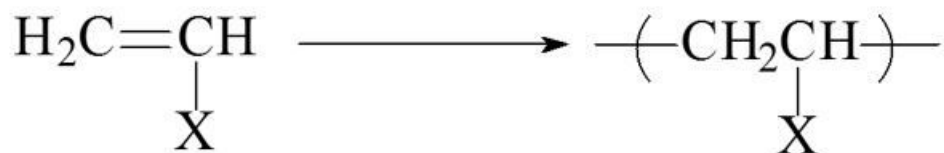


Figure 1. Schematic showing the breadth of properties that can be achieved through ATRP copolymerization proposed in this project.

POLY 38: Polymeric materials in the beginning organic chemistry course

Bob A. Howell, *bob.a.howell@cmich.edu*. Central Michigan Univ, Mount Pleasant, Michigan, United States

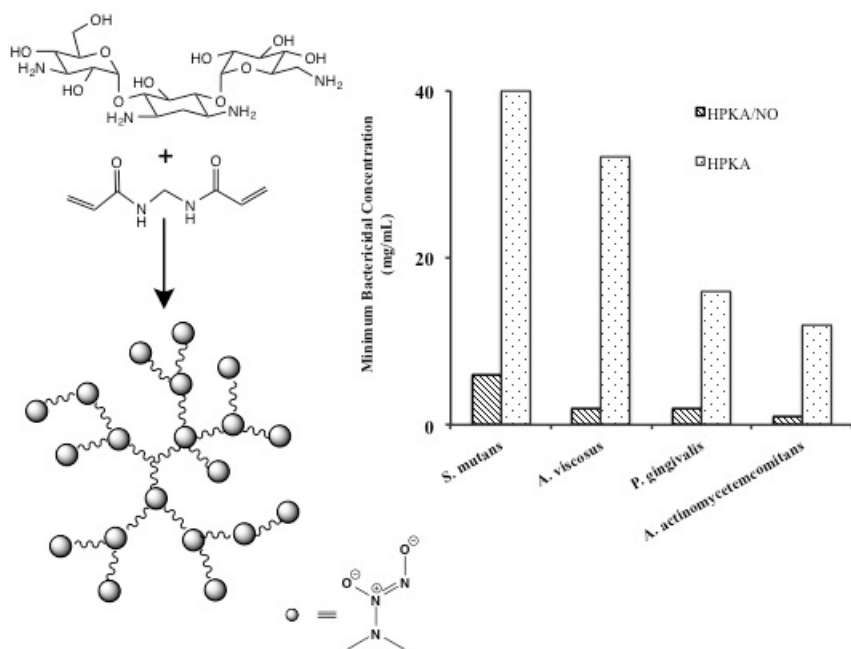
Polymeric materials are immensely important to modern society. In fact, these materials are largely responsible for the high standard of living enjoyed by citizens of the developed world. In addition, most chemistry graduates at any level (B.S., M.S., Ph.D.) work in industry in a polymer or polymer-related area. The Committee on Professional Training (CPT) of the American Chemical Society has belatedly recognized the importance of a treatment of polymeric materials as a part of B.S. training in an approved program. Such training is now a requirement for program approval. The requirement may be met in two ways. The first, and perhaps simplest, is to provide a stand-alone course in Polymer Chemistry. Alternatively, the elements of polymer chemistry may be distributed in courses across the curriculum. The beginning organic chemistry course is particularly appropriate for the inclusion of a treatment of polymeric materials. Vinyl polymerization is the most important societal/economic reaction of alkenes which are generally encountered relatively early in the first semester of the course. Discussion of these materials not only serves to introduce polymer structure and properties but to relate them to small molecule properties that the students have already encountered. Importantly, it promotes student awareness (surroundings, impact of polymeric materials on their daily lives, Wal-Mart shopping, important historical events, prominent scientists of the 20th century) and generates enthusiasm for the course. Later (second semester) when treating carboxylic acid derivatives, step-growth polymerization may be introduced. Again, there is a wealth of historical and biographical information that may be introduced to enhance student interest.



POLY 39: Nitric oxide-releasing hyperbranched polykanamycin as an oral therapeutic

Lei Yang, yanglei@unc.edu, Xingzhi Wang, Dakota J. Suchyta, Mark Schoenfisch. Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States

Nitric oxide (NO) is a known antibacterial agent due to its oxidative and nitrosative nature. Previous studies have demonstrated the efficacy of NO-releasing dendrimers and silica nanoparticles as novel oral therapeutics. For certain applications, the utility of these macromolecular scaffolds is limited due to lack of biodegradability and cytotoxicity concerns. Herein, we describe the development of NO-releasing hyperbranched aminoglycosides (i.e., kanamycin) as a biodegradable alternative to dendrimers and silica. The synthetic approach is straightforward and results in materials capable of storing $\sim 0.4 \mu\text{mol NO mg}^{-1}$ scaffold. The antibacterial action of the hyperbranched polykanamycin was evaluated against *Streptococcus mutans*, *Actinomyces viscosus*, *Porphyromonas gingivalis*, and *Aggregatibacter actinomycetemcomitans*, key pathogens associated with dental caries and periodontal diseases. Analogous to other NO-release systems, the NO donors-modified hyperbranched polykanamycin demonstrated broad-spectrum bactericidal efficacy. At antibacterial concentrations, the scaffold also proved non-toxic to human gingival fibroblasts. Work on and comparison to other NO-releasing hyperbranched aminoglycosides (e.g., gentamicin, neomycin) will also be presented.



POLY 40: New medical glue: Instant, non-toxic, injectable underwater adhesives

Kollbe Ahn^{1,2}, kollbe.ahn@gmail.com. (1) University of California, Santa Barbara, Santa Barbara, California, United States (2) ACatechol, Inc., Santa Barbara, California, United States

There is no such medical glue that adheres wet tissues instantly and reversibly. Inspired by biological wet adhesion, non-toxic instant glue has been developed by a start-up company (ACatechol, Inc) in Santa Barbara. The technologies are about non-toxic water-based injectable medical glue that works on wet tissues and medical implants in 5 seconds and is reversible. In this talk, we will discuss fundamental concepts of biological wet adhesion, and its technology-transfer story from a lab at UC Santa Barbara to a start-up company in downtown Santa Barbara (raised over one million dollar investments from angels and contracted with large consumer product distributors in medicine).



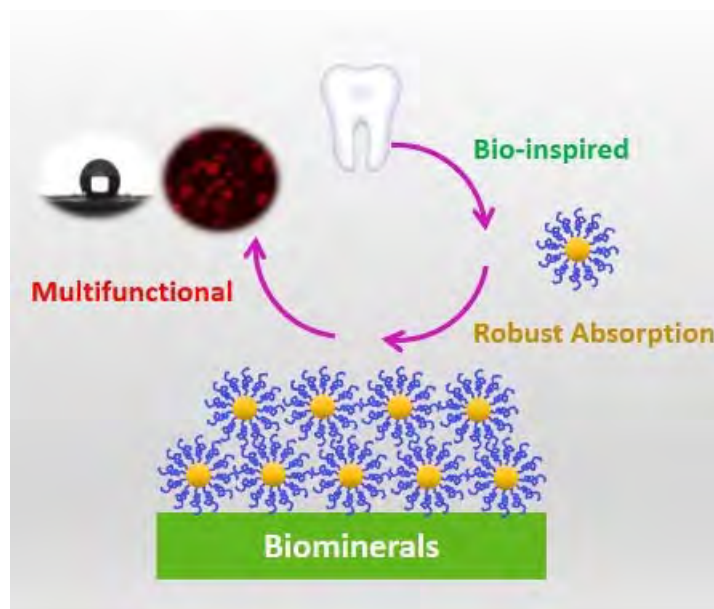
WaterGlue

Non-toxic, water-based, injectable medical adhesive, named "Water Glue", has been developed by ACatechol, Inc. (Santa Barbara, CA). The Water Glue adheres wet tissues and wet implants under physiological condition instantly and is reversible.

POLY 41: Universal multifunctional coating of biominerals based on salivary acquired pellicle inspired dendrimer

Yang Xiao, 317190026@qq.com, Li Jianshu. Sichuan University, Chengdu, China

Manipulation of the surface properties of biominerals is very important for their biomedical applications. However, the straightforward preparation of a multifunctional and stable coating on biominerals remains a challenge. Here, a rapid and universal method for multifunctional coatings was developed based on a salivary acquired pellicle (SAP) inspired dendrimer. The dendrimer has a highly branched structure and an external surface modified with DDDEEK peptide sequence. It mimics the adsorption function of statherin, which is one of the main components of salivary acquired pellicle, to endow the coating with a universal capability for adhesion on biominerals. The coating can be formed by a simple dip-coating method on various biominerals within 10 min, and is stable for more than one month. It also provides a universal platform of secondary modifications for different applications.



POLY 42: Impact of particle modulus on vascular-targeted drug delivery *in vitro* and *in vivo*

Margaret Fish³, mrgrtfish@gmail.com, Catherine Fromen³, Timothy F. Scott², Reheman Adili⁴, Michael Holinstat⁴, Omolola Eniola-Adefeso¹. (1) 3074 H. H. Dow, University of Michigan, Ann Arbor, Michigan, United States (2) 3074 H.H. Dow Building, University of Michigan, Ann Arbor, Michigan, United States (3) Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States (4) Pharmacology, University of Michigan, Ann Arbor, Michigan, United States

Vascular-targeted drug carriers (VTCs) are designed to preferentially localize to the site of disease, thereby decreasing systemic side effects while also increasing therapeutic delivery to the disease site. The ability of VTCs to localize and bind to a targeted, diseased endothelium determines their overall clinical efficacy. Size and shape are known physical parameters that prescribe VTC vascular wall localization and adhesion. Here, we present the first investigation into the role of particle deformability in adhesion to the vascular wall under physiological blood flow conditions. Hydrogel particles are fabricated via photopolymerization of polyethylene glycol (PEG) diacrylate. Modulus is controlled by varying the amount of PEG in the particle matrix and targeting functionality is covalently linked. Our results indicate that microparticle modulus enhances particle adhesion in a shear-dependent manner. At low shear, deformable particles show favorable adhesion, while at high shear, rigid particles show superior adhesion. Mechanistically, particle collisions with leukocytes drive these trends. For both VTC sizes examined, more deformable particles adhere better than rigid counterparts to inflamed endothelium *in vivo* in mouse mesentery vessels with low shear blood flow. Overall, this work demonstrates the importance of VTC modulus as a design parameter for enhanced VTC interaction with vascular walls, and thus, contributes important knowledge for development of successful clinical theranostics with applications for many diseases.

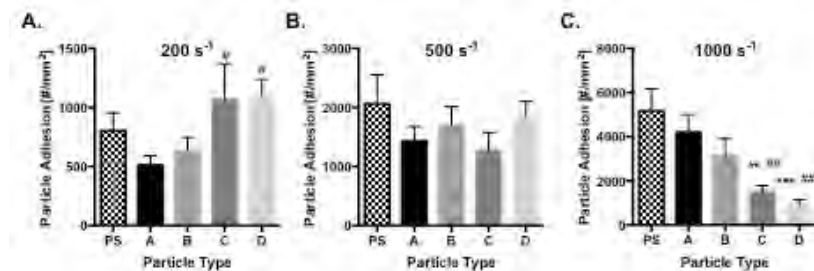


Fig 1. 2 μm particle adhesion to inflamed HUVEC monolayer as a function of particle modulus. Hydrogel particle adhesion at (A) 200 s^{-1} , (B) 500 s^{-1} , and (C) 1,000 s^{-1} by modulus after 5 mins of laminar blood flow over an IL-1 β activated HUVEC monolayer.

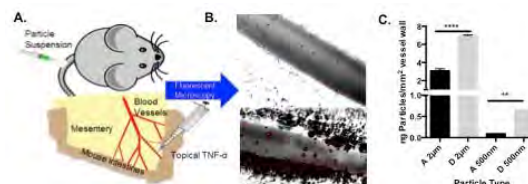
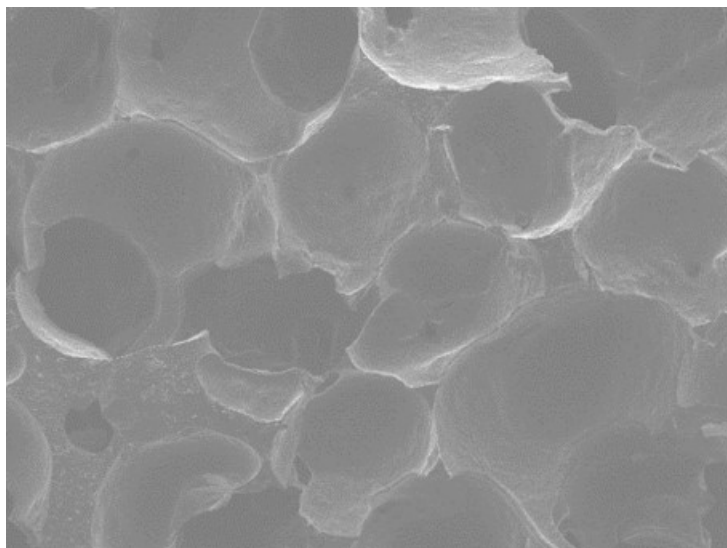


Fig 2. Particle adhesion to inflamed mesentery as a function of modulus and size. (A) Mouse surgical technique. (B) Fluorescent images of particle adhesion, corresponding to A-2 μm and D-2 μm (top to bottom). (C) Quantified adherent density of hydrogel particle conditions.

POLY 43: Kaolin-Polyurethane foam composites for multifunctional wound dressing applications

Jeffrey Lundin, jeff_lundin@hotmail.com, Grant C. Daniels, Christopher L. McGann, Benjamin Streifel, Spencer L. Giles, James H. Wynne. Chemistry Division, Naval Research Laboratory, Washington, District of Columbia, United States

Kaolin-polyurethane foam composites were developed and characterized for potential application as a durable, long-lasting hemostatic wound dressing material. A series of polyurethane foams with increasing kaolin loading were formulated via a facile, one-pot, and solvent free synthesis. Incorporation of kaolin, up to 25 wt% loading, did not affect the polymerization of the foams. Absence of the isocyanate absorption band in ATR-IR and gel fractions greater than 90% for all foams indicated complete polymerization. DSC and TGA analyses demonstrated that kaolin did not affect T_g and degradation onset temperature; additionally, thermal analysis also served to confirm loading concentrations. EDS and XRD provided evidence of thorough dispersion of kaolin at all loading levels. Kaolin significantly reduced polyurethane foam mechanical properties, specifically tensile strength and ultimate elongation. Wound dressing specific analyses comprised ciprofloxacin drug-release and whole blood clotting assay. These materials are able to potentially serve as multi-functional wound dressings.



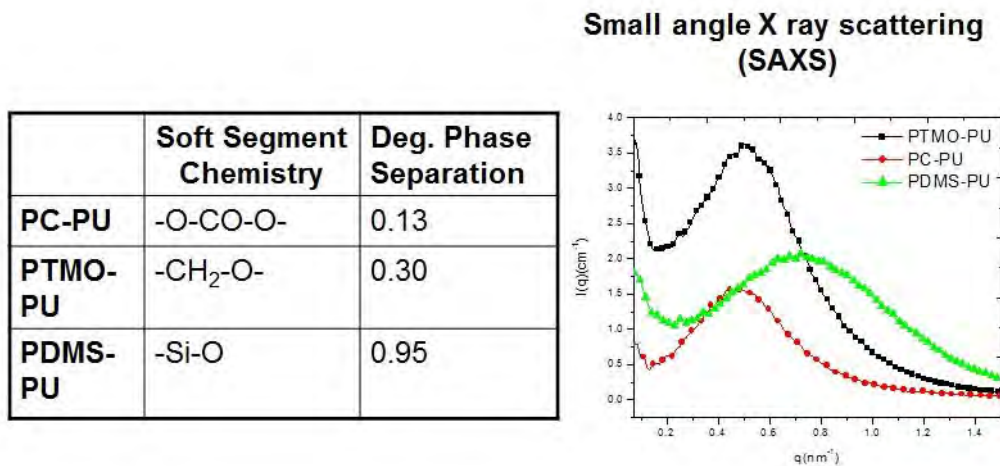
POLY 44: Evolution of morphology in polyurethane biomaterials: Effect of time and storage on material properties

Emily Chen, *chene05@sjm.com*, *Sarath Eam*, *Ajay Padsalgikar*. *St Jude Medical, St Michael, Minnesota, United States*

Thermoplastic polyurethanes (TPUs) are separated into ordered, urethane rich hard segments and amorphous, polyol dominated soft segments. This phase separation occurs as the TPUs cool down from the molten stage. The difference in the thermodynamic solubility parameters between the hard and the soft segment drives the rate and the degree of phase separation.

Different polyols or soft segment chemistries as well as the storage conditions can change the rate of phase separation and as a result can significantly affect the measured physical properties. In this study, we examine the extent of phase separation over time and the formation of allophanate linkages in polyurethane biomaterials. The differences in the soft segments are examined by using different amounts of siloxane in the polyol, a polycarbonate based polyol, and a polyether based polyol. A special focus is on Optim™, a siloxane-based polyurethane used for implanted cardiac leads. Optim™ uses a large amount of siloxane in the soft segment and is notable in that the polarity difference between the hard and soft segment is especially large, so phase separation and allophanate formation is especially evident. This high degree of phase separation contributes to Optim's biostability.

We present SAXS data demonstrating the effect of siloxane content on microstructure, and track hard segment organization over time as a function of the siloxane content of the polyurethane. We measure hard segment organization over time via modulated DSC, and we track the effect on mechanical properties via DMA. We also track allophanate formation over time as a function of siloxane content, and examine the effect of allophanate formation on molecular weight and rheology.

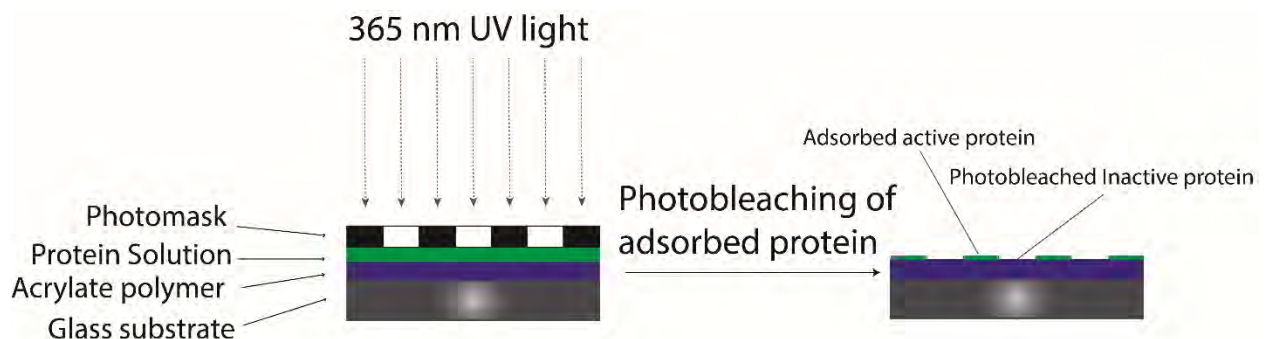


Caption: Degree of phase separation and SAXS data for polyurethane biomaterials with different soft segment chemistries.

POLY 45: Tuning surface properties of acrylate polymers to direct neurite growth

Braden Leigh¹, *braden-leigh@uiowa.edu*, **Kristy Truong**², **Reid Bartholomew**², **Marlan R. Hanser**², **Allan Guymon**¹. (1) *Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa, United States* (2) *University of Iowa, Iowa City, Iowa, United States*

Cochlear implant (CI) devices restore hearing to patients suffering from sensorineural hearing loss through direct electrical stimulation of the spiral ganglion neurons (SGNs), the inner ear neurons. However, CIs suffer from limited tonal resolution due, in large part, to spatial separation between stimulating electrode arrays and primary neural receptors or SGNs. One strategy to overcome this spatial separation is to direct the regrowth of proximate axons toward the stimulating elements. In this work, a combination of physical and chemical micropatterns, formed on acrylate polymers, are used to direct the growth of primary SGNs. Utilizing the inherent temporal and spatial control of photopolymerization, physical microgrooves are fabricated using a photomask in a single step process. The spatial control of the photon-induced reaction forms ridges under transparent bands and depressions under reflective regions. Biochemical patterns are generated by adsorbing laminin, a cell adhesion protein, to acrylate polymer surfaces followed by irradiation through a photomask with UV light to deactivate protein in exposed areas and generate parallel biochemical patterns. SGN neurites show increased alignment to both biochemical and physical patterns when evaluated individually and compared to unpatterned controls. To further evaluate the ability of biochemical and physical features to be used in overcoming conflicting cellular cues, competing patterns were tested. Physical microgroove channels were first fabricated followed by a perpendicular laminin protein pattern. The strength of the physical cues was varied by independently changing both the amplitude and the band spacing of the microgrooves, with higher amplitudes and shorter band spacing strengthening the cue. SGN neurites aligned to laminin patterns with lower amplitude and thus weaker physical cues. Alignment of SGNs shifted towards the physical pattern with higher amplitude patterns representing stronger cues. These results demonstrate the ability of photopolymerized microfeatures to modulate alignment of inner ear neurites even in the presence of conflicting physical and biochemical cues and help lay the groundwork for next generation cochlear implants and neural prosthetic devices.



Schematic of the photopatterning of active laminin.

POLY 46: Evolution of polymer science at IBM: From microelectronics to Watson Health

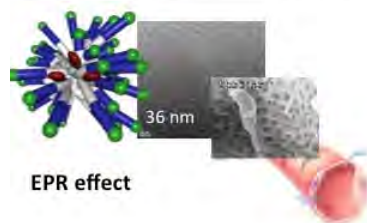
J Hedrick, hedrick@us.ibm.com. IBM Research, San Jose, California, United States

IBM Research has traditionally supported its core technologies including the Microelectronic and Storage Divisions with innovations ranging from lithography to high performance insulators to storage materials. As many of these technologies have been divested in IBM's continued re-invention, efforts have evolved to support emerging grow areas including, for example, cognitive computation, cloud and Watson Health.

Our current work focuses on developing new technologies in support of Watson Health, as the emerging field of nanomedicine offers tremendous promise for improving human health, curing disease, or repairing damaged tissues by applying the tools of nanotechnology to create and control materials with molecular-level medical effects. The targeting and controlled release of therapeutic agents as well as macromolecular therapeutics to specific organs and specific cells in the body is one of the major challenges in developing more effective therapies. Central to this goal are the many materials challenges associated with the encapsulation, transport and release of such agents at a specific time and place in the exceedingly complicated and dynamic environment of living organisms. We think that designed novel polymers with controlled functionalities, molecular weights, polydispersities, molecular architectures and topologies will play essential roles in the development of the field, particularly in the high-value areas of drug encapsulation, transport and delivery, as well as alternative antimicrobial agents. Nature's ability to assemble macromolecules into highly cooperative and functional assemblies provides an inspiration for our efforts to devise synthetic design criteria to interrogate and exploit the relationship between molecular structure, non-covalent interactions and processing conditions to create new functional macromolecular assemblies.

Delivery Technology

Leverage polymer chemistry expertise to encapsulate, deliver and release therapeutics: efficacious delivery and synergistic delivery to mitigate tumor and tumor stem cells to prevent metastasis.

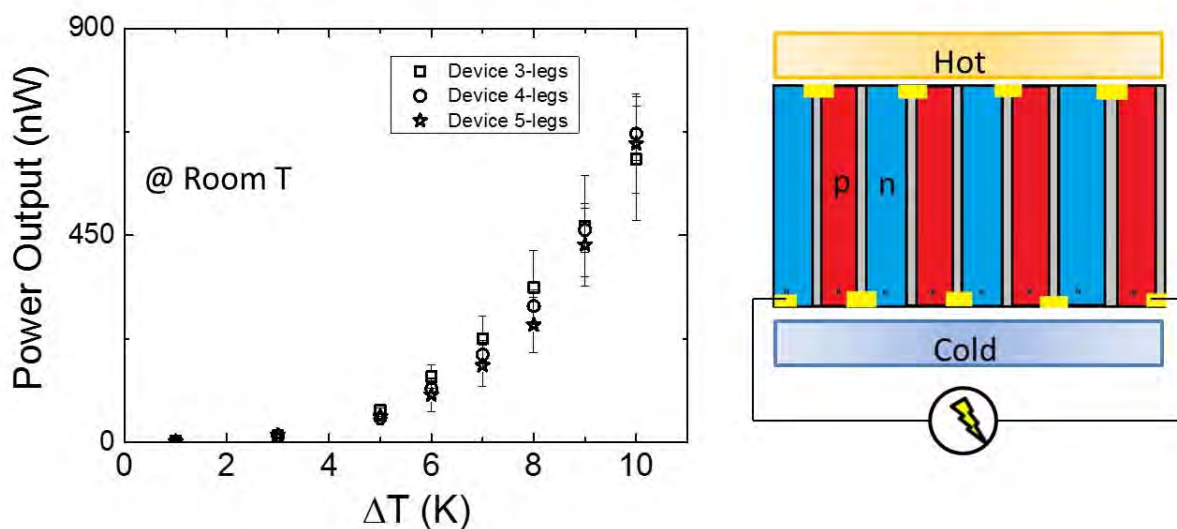


POLY 47: High performance polymer and polymer/inorganic thermoelectric materials

Georges Hadziioannou, *hadzii@me.com*. LCPO, University of Bordeaux, Bordeaux, France

Conducting polymers (CPs) have recently gained the attention of the scientific community due to their prospective use in thermoelectric applications. Particularly, it has been proven that an important parameter for tuning the thermoelectric properties and the charge transport behavior of CPs is the shape of the density of states (DoS) near the band edge, where a steeper band edge initiates a transition from a Fermi glass to a semi-metal leading to higher thermoelectric efficiencies. In the present study, we discuss the correlation between material structure, electronic structure and transport/thermoelectric properties for a series of poly(3,4-ethylenedioxythiophene) samples of constant carrier concentration, for which hopping transport was demonstrated to be the dominant charge transport mechanism. Additionally, a metal-to-insulator transition was observed for these systems at low temperatures, which was dependent to the increasing thin film crystallinity. Finally, the CPs were combined with inorganic components, in thin film configuration, creating hybrid thermoelectric materials to further enhance the thermoelectric efficiency. The thermoelectric properties of these hybrid materials were tuned via the electronic interfacial properties resulting to high performance hybrid thermoelectric generators operating at room temperature conditions.

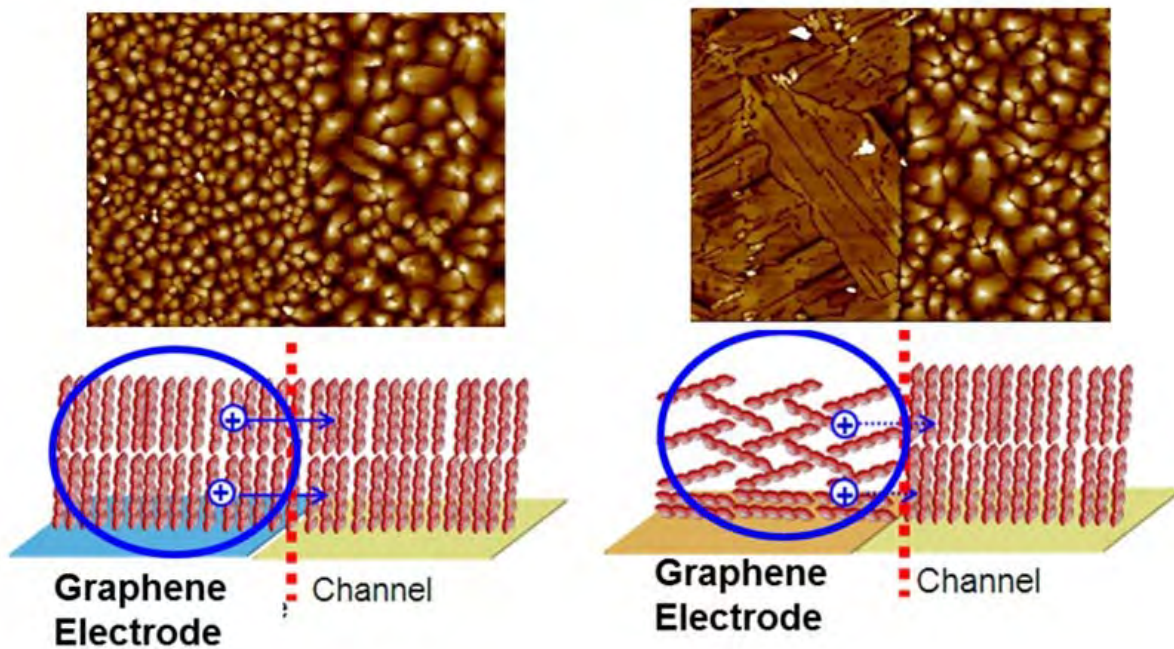
Hybrid thermoelectric generator



POLY 48: Surface-directed molecular assembly of organic semiconductors for organic electronics

Kilwon Cho, *kwcho@postech.edu*. Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of)

Microstructure in organic semiconductor thin films has been regarded as the key factor determining the performance of the organic electronics. In the case of organic field effect transistors (OFETs) and organic photovoltaics (OPVs), the control of the surface characteristics of underlying substrates can govern the mesoscale and/or nanoscale ordering of the semiconductor assembled on them. Here, we present various approaches for controlling the growth of organic semiconductors on gate dielectrics and electrodes to achieve high performance OFETs and OPVs.



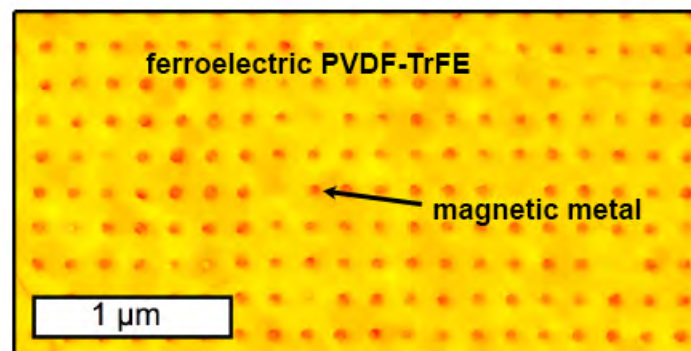
AFM images and schematic representations of the possible molecular orientations of pentacene depending on surface characteristics of graphene

POLY 49: Multifunctional layers and memory devices based on ferroelectric polymers

Alain M. Jonas, *alain.jonas@uclouvain.be*. Institute of Condensed Matter and Nanoscience, University of Louvain, Louvain-la-Neuve, Belgium

Ferroelectric polymers have been known for decades, with poly(vinylidene fluoride) and its random copolymers with trifluoroethylene (PVDF-TrFE) being prominent examples; they are used for applications in sensing, actuation, and data storage. Compared to inorganic ferroelectric materials such as perovskite oxides, the performance of ferroelectric polymers is generally lower, limiting them to niche applications. However, a distinct advantage of ferroelectric polymers is ease of processing, which may provide access to new device configurations.

Therefore, we have developed nano-patterning of PVDF-TrFE, leading to regular arrays of ferroelectric nanostructures, and shown the beneficial graphoepitaxial alignment of crystals when crystallization happens in confinement. By filling the cavities opened in these arrays by a second functional component, typically a semiconducting polymer or a magnetic metal, composite bifunctional layers are prepared. In these layers, coupling of the two materials results in the emergence of synergetic properties. For instance, modulation of the carrier density of a semiconducting polymer close to the polarized ferroelectric material results in hysteretic current-voltage loops, leading to the fabrication of memory nanodiodes and nanowire memory transistors. Electromechanical coupling between magnetic nanodots and the ferroelectric polymer leads to systems wherein the electric polarization can be flipped by a magnetic field at room temperature. We will discuss the physical principles behind these effects, including depolarization and mechanical relaxation of the ferroelectric polymer.

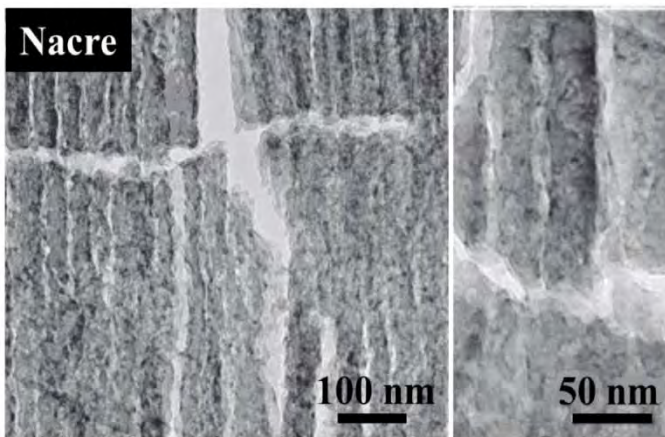


SEM image of a magnetolectric layer

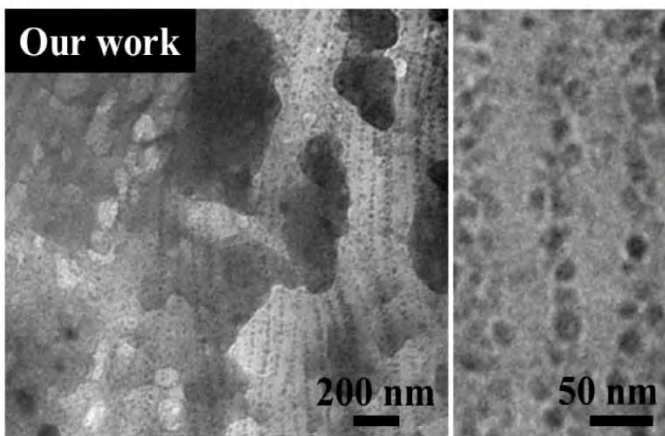
POLY 50: Multiscale nanoparticle ordering by polymer crystallization

Sanat Kumar, *sk2794@columbia.edu*. Columbia University, New York, New York, United States

Inspired by the unique material properties found in Nature (e.g., Nacre, wood, bone), there is continuing interest in hierarchically ordering nanoparticles (NPs) in a polymer matrix across multiple length scales. However, most current methods cannot achieve this ordering in a single step. Here, we use polymer melt crystallization, which yields a multiscale structure spanning lamella [(10 nm)], fibrils (μm) and spherulites (mm), to template such ordering in the commercially relevant polymer-rich limit. We show that melt-miscible spherical NPs are engulfed by polymer crystals and hence do not spatially order for crystal growth rates, v , faster than a critical value. However, for lower v the NPs simultaneously order into parallel layers with a spacing of (10-100 nm) in the interlamellar zone, and as fractal objects at the interfibrillar scale, (1-10 μm), with the relative amounts determined by v . This ordering, which doubles the elastic modulus while leaving fracture toughness unaffected even at 3 volume% NP, thus offers a novel means to design materials with tunable functionality.



95% aragonite/5% chitin



40% silica-g-PMA/PEO

POLY 51: Controlled morphology and Its impact on digital memory behavior of well-defined functional polymers in nanoscale thin films

Moonhor Ree, ree@postech.ac.kr. POSTECH, Pohang, Korea (the Republic of)

A series of well-defined functional polymers bearing charge-trapping moieties was investigated in aspects of nanoscale thin film morphology and electrical memory performance. Synchrotron grazing incidence X-ray scattering analysis found that the polymers either self-assemble or phase-separate, revealing a variety of nanostructures and orientations depending on the chemical architectures and the film process conditions. Such nanostructures and orientations were found to make significant influences on the memory device performances including memory modes. The device performances were further affected by the molecular orbital nature of electrically active groups incorporated in the brush polymer systems, tuning the memory modes and types. In addition, the individual polymer systems had a certain thickness window to reveal electrical memory performances. We have attempted to understand the observed memory performances in correlations of physicochemical nature, chemical architecture and thin film morphology and orientation.

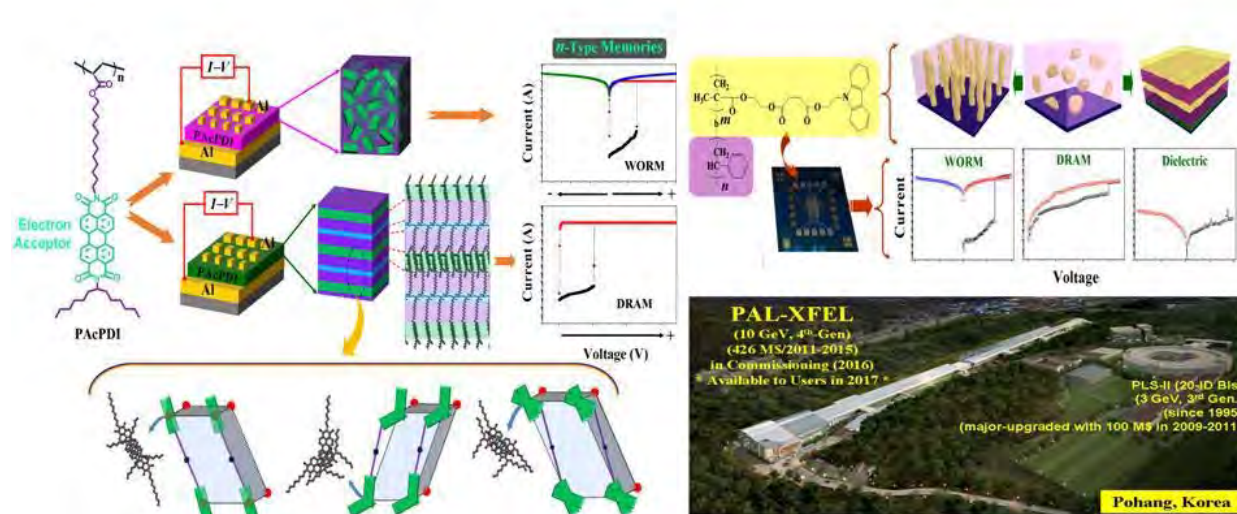
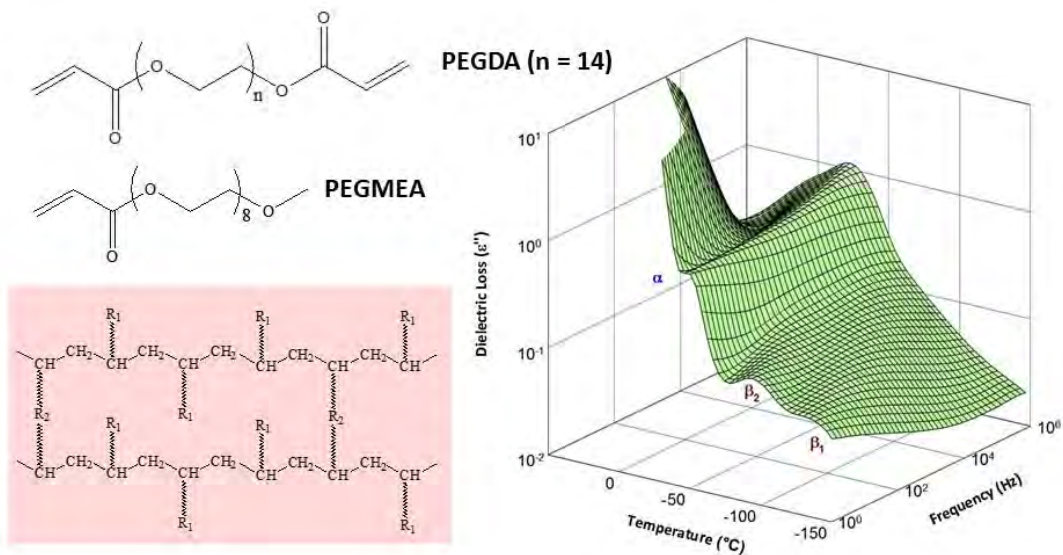


Figure 1. Self-assembled structures and orientations (which were determined by synchrotron grazing incidence X-ray scattering) and their impacts on digital memory performances.

POLY 52: Molecular relaxation studies of crystalline polymers, blends and copolymer networks

Douglass S. Kalika, kalika@engr.uky.edu. Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky, United States

Over the last 25 years, our laboratory has employed dynamic thermal analysis techniques (i.e. dynamic mechanical analysis; broadband dielectric spectroscopy) in combination with static characterization methods for the investigation of glass-rubber and sub-glass molecular relaxations in polymer systems. Variations in polymer composition, chain architecture and processing history have been used to elucidate relaxation mechanisms in semi-crystalline polymers, blends and copolymer networks. This presentation will provide an overview of these studies, with an emphasis on investigations related to the design of rubbery copolymer networks for use as gas separation membranes. Systematic modifications in network composition, crosslink density and the strategic introduction of chain pendants have been applied to tailor the chemical and physical free volume characteristics of these networks and their resulting gas separation performance. In this context, dynamic mechanical and broadband dielectric studies provide valuable insight as to inherent segmental mobility and motional constraint, relaxation environment, and their influence on small molecule transport.



Dielectric contour plot: crosslinked 50/50 PEGDA/PEGMEA rubbery network for CO₂ selective membrane

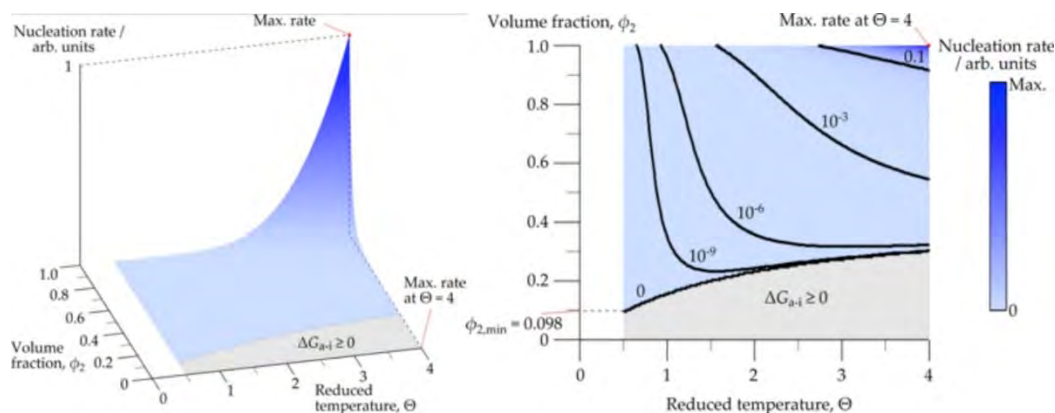
POLY 53: Big sticks and soft interactions (speaking of liquid crystals)

Christopher Viney, *cviney@ucmerced.edu*. School of Engineering, Univ of California Merced, Merced, California, United States

A common theme from several research projects, catalyzed by a stint as a visiting scientist at IBM Almaden, will first be explored. The starting point is a scale-independent Monte Carlo model for predicting the equilibrium between aligned and random phases in an assembly of rigid rods. A serendipitous encounter with a versatile system of model compounds (intrinsically rodlike, with tailorable soft interactions) will then be described. The tale continues with the discovery and characterization of liquid crystalline order in diverse biological materials, including silk, mucus, levan, and hippopotamus “sweat”. Liquid crystalline order in such materials often involves the formation of supramolecular rods by globular chains, and in at least one case takes the form of chimeric aggregates in which a small concentration of rods (DNA) imposes nematic order on a larger concentration of bound globular molecules (levan). In these different but related endeavors, the recurring theme has been the molecular characteristics and environmental factors (temperature, concentration) that stabilize liquid crystallinity.

Inevitably (and especially in the context of biological materials, which are produced slowly compared to typical industrial products), questions arise regarding the *rate* at which a liquid crystalline phase can form. The kinetics of supersaturation-driven phase transformations can be richly displayed on time-concentration-temperature-transformation (TCTT) diagrams, derived with reference to the time-temperature-transformation (TTT) diagrams used by metallurgists.

The theory of nucleation and growth can be generalized, and the transformation diagram concept can be extended, to systems in which change is driven by system variables other than temperature and concentration. The generalized model allows for simultaneous changes in multiple system variables, as well as nucleation and growth in an arbitrary number of spatial dimensions, and offers the possibility of extension to the spread of disease, or the spread of information in social systems, if the corresponding features of such systems can be identified and expressed in appropriate units.



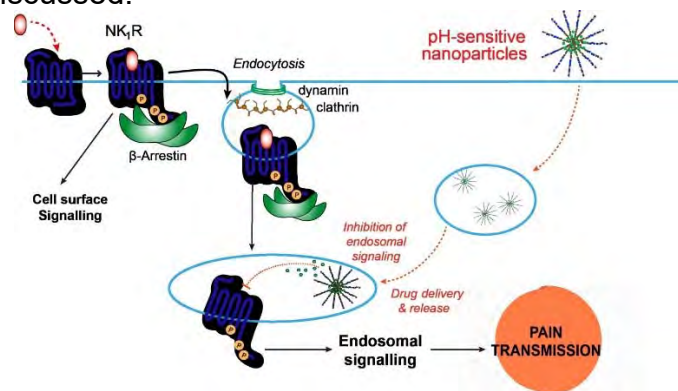
Relative rate of nematic phase growth from Flory-Warner theory; rod axial ratio = 20.

POLY 54: Adaptive nanoparticles for regulation of endosomal signalling: Targeting pain at the source

Nicholas Veldhuis², nicholas.veldhuis@monash.edu, Michael Whittaker³, Paulina Ramirez-Garcia², Quynh Ma², TinaMarie Lieu², Nghia Truong⁴, John Quinn¹, Thomas Davis⁵, Nigel W. Bunnett². (1) Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria, Australia (2) ARC Centre of Excellence in Convergent Bio-Nano Science & Technology, Monash Institute of Pharmaceutical Sciences, Melbourne, Victoria, Australia

Chronic sensory conditions that cause sustained pain and inflammation could benefit from targeted therapeutic delivery to modulate cellular processes. While chemotherapeutic nanoparticle approaches are designed to induce cell death by “endosomal escape” of a cytotoxic agent, nanoparticle delivery systems that enhance cellular drug uptake while maintaining cell viability may also be therapeutically advantageous. We have recently determined that a G Protein-Coupled Receptor known as the Neurokinin 1 Receptor (NK₁R) promotes sustained spinal neuron excitability and central pain transmission from endosomes. To develop novel analgesic agents that target endosomal pain transmission, we have designed and tested pH-responsive nanoparticles that selectively release cargo (NK₁R antagonists) into endosomes, without disrupting cellular function.

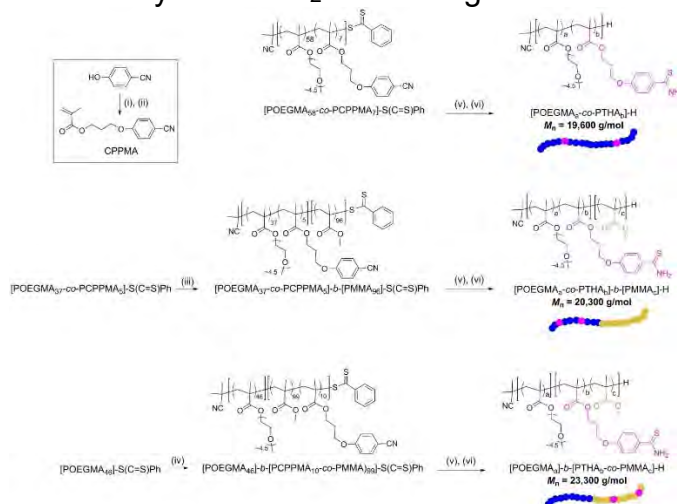
The acidic environment within the lumen of early and late endosomes (~pH 6.5-5.9) was exploited as a trigger for nanoparticle disassembly and cargo release. Inspired by the work of Gao et al.¹, a library of nanoparticles was generated comprising block copolymers synthesized via RAFT polymerisation. The particles comprised a nonfouling hydrophilic shell incorporating poly(ethylene glycol) methacrylate (PEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) units. The hydrophobic core incorporated units derived from either 2-(diethylamino)ethyl methacrylate (DEAEMA, pK_a ~7.1) or 2-(diisopropylamino)ethyl methacrylate (DiPAEMA, pK_a ~6.1). While the particles were stable at physiological pH, the reduced pH environment with endosomal uptake leads to promotes monomer protonation and a hydrophobic-hydrophilic solubility switch that facilitates nanoparticle disassembly and release of cargo in endosomes. We have also explored the potential for introduction of diethylene glycol methacrylate (DEGMA) units into the core-forming block to increase cell viability. Outcomes of cell toxicity, drug loading, intracellular uptake and trafficking, and *in vitro* and *in vivo* responses will be discussed.



POLY 55: Triggering cellular signalling processes with novel macromolecular hydrogen sulfide donors

Francesca Ercole¹, Friederike Mansfeld⁴, Maria Kavallaris⁴, Michael Whittaker³, Michelle Halls¹, Thomas Davis², **John Quinn**¹, john.f.quinn@monash.edu. (1) Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria, Australia (4) Childrens Cancer Institute of Australia, Sydney, New South Wales, Australia

The gasotransmitters (nitric oxide, carbon monoxide and hydrogen sulphide) are a family of otherwise gaseous molecules which are critical to many cell signalling processes. Among these, hydrogen sulfide (H₂S) has been implicated in a great diversity of cell signaling cascades which sit behind physiological events ranging from vasodilation to cell proliferation. Further, misregulation of H₂S signaling has been associated with a number of different pathologies. As such, the development of materials that can release H₂S in a cellular environment is of clear potential. This presentation will report the synthesis of macromolecular H₂S donors which can trigger cell signaling pathways in both the cytosol and at the cell membrane. The macromolecular donors were synthesized by first preparing copolymers having pendent oligo(ethylene glycol) and benzonitrile groups, and then transforming the benzonitrile groups into primary aryl thioamide groups via thionation with sodium hydrosulfide. The release of H₂S under simulated physiological conditions was demonstrated, with the release kinetics being impacted by both the molecular architecture of the donor and the presence or absence of a suitable trigger for H₂S release. In addition to aryl thioamides, macromolecular donors incorporating other H₂S donating moieties will also be presented. Specifically, the transformation of the thiocarbonylthio endgroup formed during RAFT polymerization into an H₂S-donating moiety will be discussed, along with the application of this chemistry to form H₂S releasing nanostructures.



Synthesis of CPPMA monomer, precursor polymers, and subsequent conversion to macromolecular H₂S donors; (i) 3-bromo-1-propanol, K₂CO₃ and DMF (ii) methacrylic anhydride, TEA and DCM (iii) MMA, 70 °C, 1,4-dioxane (iv) MMA, CPPMA, 70 °C, 1,4-dioxane (v) polymer end-group removal (vi) thionation. CPPMA = 3-(4-cyanophenoxy) propyl methacrylate; OEGMA = oligo(ethylene glycol) methyl ether methacrylate with average M_n = 300 g/mol; MMA = methyl methacrylate.

POLY 56: Toward a cure for facial acne without bacterial resistance buildup

Kenneth J. Wynne¹, kjwynne@vcu.edu, **Sithara Nair**¹, **Matthew Beckwith**¹, **Dennis Ohmar**². (1) VCU Dept of Chem Engr, Richmond, Virginia, United States (2) Microbiology and Immunology, VCU, Richmond, Virginia, United States

The pathogenic bacterium *Propionibacterium acnes* is directly associated with acne vulgaris or simply “acne”, which is one of the most common skin conditions in the world. Mild acne is cared for with over-the-counter (OTC) medications but moderate to severe acne is treated with oral antibiotics including erythromycin, clindamycin, and doxycycline. Because of widespread use the buildup of resistance against antibiotics has resulted in *P. acnes* “super-bugs”. Recently, we employed “intelligent design” to produce polymer drug X-1 with a mode of action that mimics naturally occurring antimicrobial peptides (AMPS). We showed that X-1 halted the growth of a facial acne bacterial strain at a very low concentration (6.3 micrograms per milliliter). Importantly, the effectiveness of X-1 as an antimicrobial *remained constant with no resistance buildup* over 10 challenges or “passages”. On the other hand, parallel studies with the commonly prescribed antibiotic erythromycin confirmed previously reports of resistance buildup with a *doubling* of effective dose over 10 sequential challenges. The results for X-1 have importance in opening the door to a new approach for combatting *P. acnes* “super-bugs”. Our hypothesis for the mechanism of X-1 antimicrobial effectiveness is bacterial membrane disruption. This mechanism stands in contrast to conventional antibiotics, which enter into the bacterial metabolic process. This hypothesis for X-1 effectiveness has been validated by direct observation of bacterial membrane disruption in real time and in medium by atomic force microscopy.

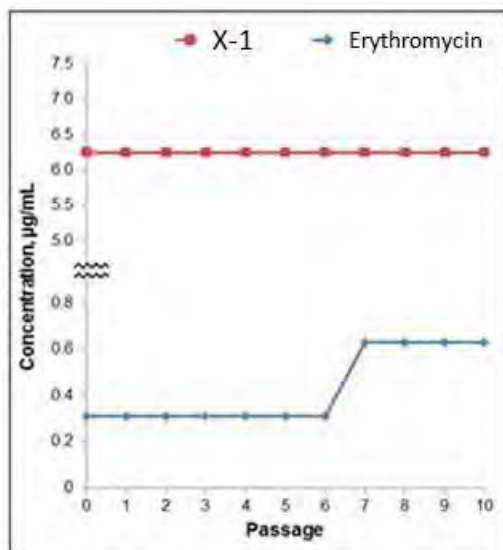
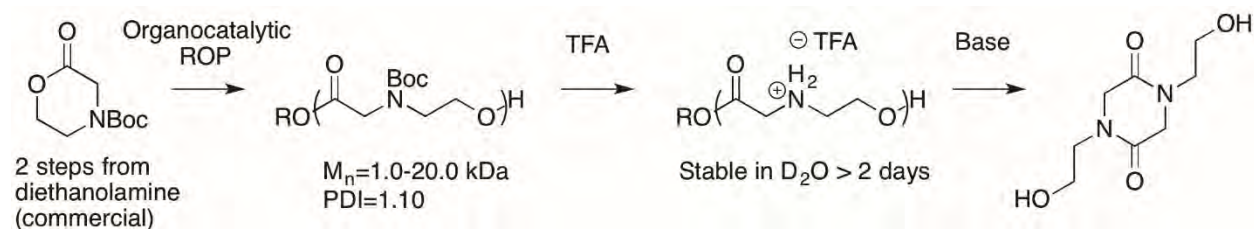


Figure 1. A comparison of resistance buildup for X-1 and erythromycin

POLY 57: Synthesis and environmentally-responsive properties of poly(α -aminoesters): Applications for the delivery of messenger RNA

Timothy Blake¹, tblake@stanford.edu, **Robert M. Waymouth**². (1) Chemistry, Stanford University, Palo Alto, California, United States (2) Dept of Chemistry, Stanford University, Stanford, California, United States

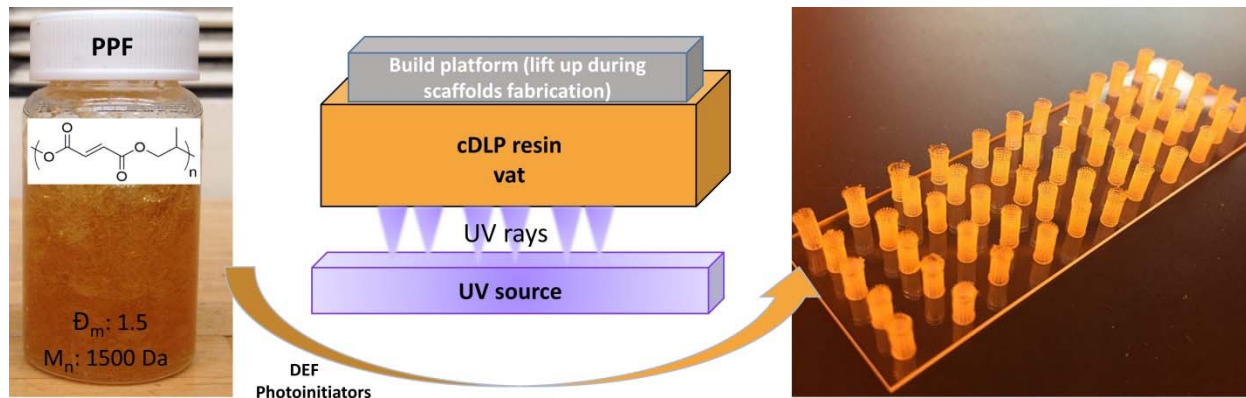
Polyesters have been employed as biodegradable materials for myriad therapeutic biomedical applications. The organocatalytic ring-opening polymerization of N-acyl morpholin-2-ones occurs readily to generate functionalized poly(α -aminoesters). Deprotection of the N-Boc protected poly(aminoesters) yields water-soluble, cationic materials. These materials are stable in neutral D₂O for over two days, however, upon exposure to alkaline or buffered conditions, these cationic poly(α -aminoesters) rapidly degrade to afford the hydroxyethyl diketopiperazine. Mechanistic investigations suggest a remarkable immolative mechanism allows for the rapid degradation of these water-soluble polymers, the rate of which is dependent on environmental pH. Poly(carbonate-co-aminoesters) that feature a segment of the rapidly degrading poly(α -aminoester) backbone were employed for the complexation, delivery and translation of mRNA both in vitro and in vivo, resulting in robust protein expression. Mechanistic studies indicate that the degradation of these cationic oligomers contributes to the efficient release and expression of mRNA inside cells.



POLY 58: Synthesis and biological evaluation of well-defined poly(propylene fumarate) oligomers and their use in 3D printed scaffolds

Yuanyuan Luo, y186@zips.uakron.edu. Polymer Science, The University of Akron, AKRON, Ohio, United States

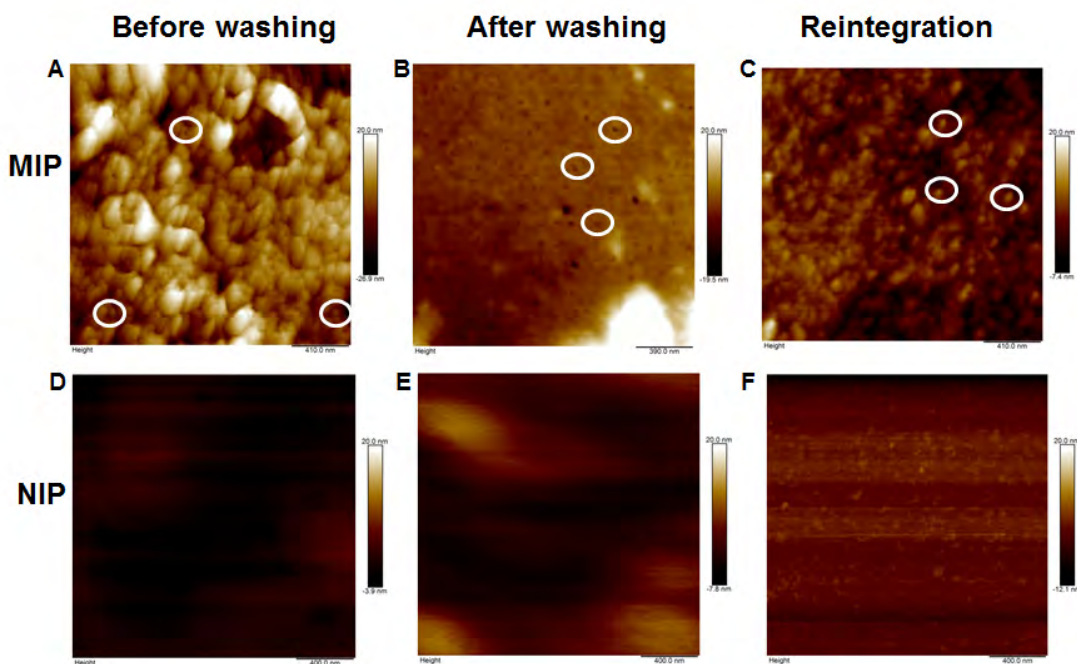
A ring opening polymerization method for synthesizing oligomeric poly(propylene fumarate) (PPF) provides a rapid, and scalable method of synthesizing PPF with well-defined molecular mass, molecular mass distribution, and viscosity properties suitable for 3D printing. These properties will also reduce the amount of solvent necessary to ensure sufficient flow of material during 3D printing. MALDI mass spectrometry precisely shows the end group fidelity, and size exclusion chromatography (SEC) demonstrates narrow mass distributions (<1.6) of a series of low molecular mass oligomers (700–3000 Da). The corresponding intrinsic viscosities range from 0.0288 ± 0.0009 dL/g to 0.0780 ± 0.0022 dL/g. The oligomers were printed into scaffolds via established photochemical methods and standardized ISO 10993-5 testing shows that the 3D printed materials are nontoxic to both L929 mouse fibroblasts and human mesenchymal stem cells.



POLY 59: Molecularly imprinted polymers for high-density lipoprotein: Characterization and functionalization

Suticha Chunta, *suticha_c@hotmail.com*, Peter Lieberzeit. *Physical Chemistry, University of Vienna, Vienna, Austria*

Herein we report molecularly imprinted polymers (MIP) of high-density lipoprotein (HDL), which are potentially useful as biomimetic recognition elements on diagnostic sensors for atherosclerosis marker analysis. Sensor layers are based on co-polymers of methacrylic acid and N-Vinyl pyrrolidone crosslinked with N,N'-(1,2-dihydroxyethylene) bisacrylamide. Atomic force microscopy (AFM) revealed that HDL-MIP before removing template (Fig.1A) showed a large number of spherical structures, whose dimensions were in the range of 41.81 ± 20.04 nm across and 1.88 ± 1.24 nm high. The HDL-MIP surface (Fig.1B) obviously revealed circular cavities that were on average 46.18 ± 15.50 nm across and 1.21 ± 0.80 nm deep. MIP after coating and reintegration with 200 mg/dL HDL (Fig.1C) displayed discrete circular particles representing re-uptake HDL on the MIP surface. In contrast to this, NIP surfaces (Fig.1D-F) completely lack those features. PeakForce quantitative nanomechanical property mapping (PF-QNM) was also used to demonstrate the different adhesion forces of blank MIP and reintegrate MIP. The adhesion force was approximately ten times higher (mean value of 26.02 nN) on the MIP with rebound HDL compared to the blank MIP (mean value of 2.59 nN). Secondly, HDL-MIP was screened on each 10 MHz dual-electrode quartz crystal microbalances (QCM). It revealed linear sensor characteristic toward HDL cholesterol (HDL-C) in the clinically relevant ranges of 2-250 mg/dL in 10 mM PBS without significant interference: low density lipoprotein yielded 5% of the HDL signal, both very low density lipoprotein and human serum albumin 0%. Therefore, both polymer surface characterization using AFM and PF-QNM and polymer functionalization using QCM strongly support successful synthesis of HDL-MIP.



POLY 60: Molecular interactions among cartilage proteoglycans

Ferenc Horkay, horkayf@helix.nih.gov, Peter J. Basser. Section on Quantitative Imaging and Tissue Sciences, National Institutes of Health, Bethesda, Maryland, United States

The load-bearing ability of cartilage is defined by its composition, hierarchical organization, and the interactions among the polymeric constituents of the extracellular matrix (ECM). Macroscopic measurements such as osmotic swelling pressure measurements and stress-strain measurements probe the tissue at large length scales and yield information on the thermodynamic and mechanical properties. The osmotic pressure contains contributions from various interactions (e.g., electrostatic interactions, hydration forces, hydrophobic interactions). Knowledge of these interactions between the major biopolymer components of the ECM is necessary to quantify their relative effects on the macroscopic behavior and function of the tissue. These macroscopic measurements, however, do not provide insight into the underlying molecular interactions that control tissue's biomechanical properties.

We developed a multiscale experimental approach to study the structure and interactions in biological tissues. Our approach covers a wide range of length scales from small angle x-ray and neutron scattering, covering the nano-scale to osmotic pressure and mechanical measurements covering the macro-scale properties. Information on the dynamics of proteoglycan assemblies is obtained from dynamic light scattering, neutron spin echo and rheological measurements. We report systematic osmotic and scattering studies made on cartilage polymers and their assemblies in near physiological salt solutions.

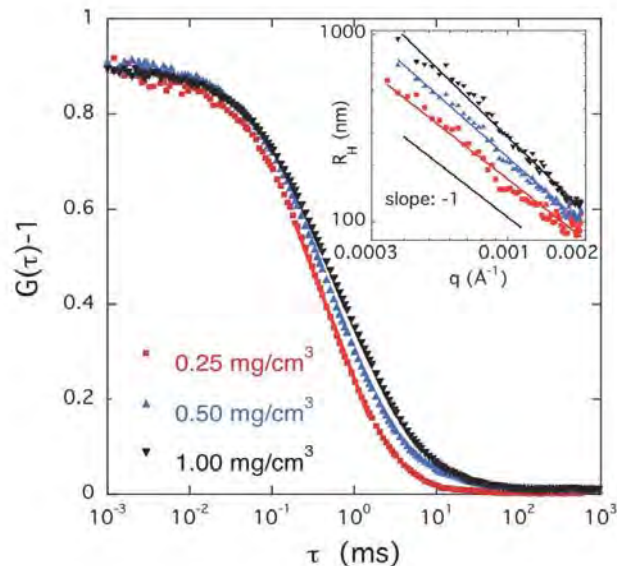
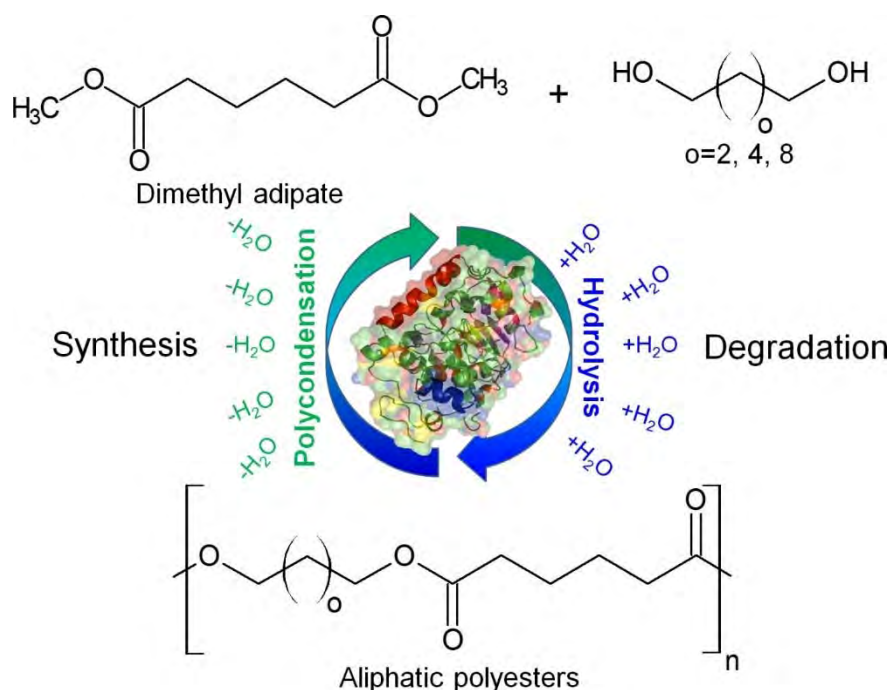


Figure 1. Dynamic light scattering correlation functions $G(t)-1$ at 90° for aggrecan solutions at three concentrations 0.25, 0.50 and 1,00 mg/cm³. Inset: hydrodynamic radius R_H as a function of wave vector q for aggrecan solutions.

POLY 61: *Thermobifida cellulositytica* cutinase as a powerful tool for the synthesis and functionalization of biobased polyesters

Alessandro Pellis³, alessandro.pellis@gmail.com, Enrique Herrero Acero¹, Valerio Ferrario⁴, Lucia Gardossi⁴, Georg M. Guebitz². (1) c/o Inst. for Environmental Biotechnology, Austrian Centre of Industrial Biotechnology, Tulln, Austria (2) Environmental Biotechnology, BOKU, Vienna, Tulln, Austria (3) Agrobiotechnology, Universitat fur Bodenkultur Wien, Tulln, Lower Austria, Austria (4) University of Trieste, Trieste, Italy

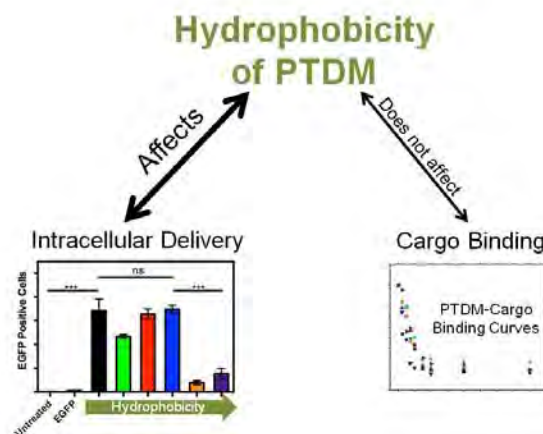
Since several years, the polymer industry is under pressure to mitigate the environmental cost of petrol-based plastics. On that respect, biotechnology contributes to the gradual replacement of petrol-based chemistry and the development of new renewable products, leading to the closure of carbon circle. Enzymes add higher value to bio-based polymers by catalyzing not only their selective functionalization but also their synthesis under mild and controlled conditions. Enzymes belonging to the cutinase class demonstrated their ability both to hydrolyze and synthesize polyesters. In this work, the promising properties of cutinase 1 from *Thermobifida cellulositytica* are described in terms of ability to catalyze the synthesis of aliphatic oligoesters in solvent-free conditions in a fully renewable context. Furthermore, cutinases catalyze also the hydrolysis of various bio-based polyesters including poly(L-lactic acid) and poly(ethylene furanoate), thus enabling the targeted introduction of chemical functionalities on the polymeric surfaces. Data on reactivity and structural features confirm the potential of this enzyme for the green processing of bio-based polyesters.



POLY 62: Modulating the hydrophobicity of cell penetrating peptide mimics for binding and intracellular delivery of protein cargo

Nicholas D. Posey¹, nposey@mail.pse.umass.edu, Leah M. Caffrey², Lisa M. Minter^{3,4}, Gregory N. Tew^{1,4}. (1) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) University of Massachusetts Amherst, Amherst, Massachusetts, United States (3) Veterinary and Animal Science, University of Massachusetts Amherst, Amherst, Massachusetts, United States (4) Molecular and Cellular Biology Program, University of Massachusetts Amherst, Amherst, Massachusetts, United States

Cell penetrating peptide mimics (CPPMs) and protein transduction domain mimics (PTDMs) have a well-established ability to enable cellular uptake of macromolecular cargos such as proteins and siRNA which has significant implications in the field of drug and biologics delivery. Synthetic PTDMs that feature both a hydrophobic and cationic block in their polymer architecture perform superiorly in terms of facilitating cellular uptake when compared to their cationic homopolymer counterparts. Modulating PTDM hydrophobicity has been shown to affect the ability to enhance cargo uptake, but the role of hydrophobicity in PTDM-binding of the desired cargo is not fully understood. Herein, block copolymer PTDMs synthesized from a palette of hydrophobic monomers were synthesized via ring-opening metathesis polymerization to probe the effect of varying hydrophobicity on the ability of the PTDM to bind enhanced green fluorescent protein (EGFP). The correlation between hydrophobicity and binding was extended further to clarify how both aspects affect cellular uptake of EGFP in Jurkat T cells. High performance liquid chromatography was used to quantify the relative hydrophobicity of the monomers in the series, while binding experiments through fluorescence quenching demonstrated that all polymers, regardless of hydrophobicity, bound EGFP similarly. Interestingly, cellular uptake of EGFP into Jurkat T cells, measured by flow cytometry, revealed that intermediately hydrophobic PTDMs facilitated optimal EGFP uptake despite similar binding observed for all PTDMs, suggesting that PTDM hydrophobicity has more influence over cellular uptake than cargo binding.



POLY 63: Novel self-assembled nanoparticle platform based on eight-arm-poly(ethylene glycol)-diosgenin prodrugs for co-delivery of anticancer drugs in cancer therapy

Chunxiao Li, *chunxiaoli@bjfu.edu.cn*, **Jiandu Lei**, *ljd2012@bjfu.edu.cn*. Beijing Forestry University, Beijing, China

In this study, a nanoparticle platform for co-delivery of anticancer drugs based on eight-arm-polyethylene glycol–diosgenin (8arm-PEG–DGN) was presented. 8arm-PEG–DGN was synthesized by introducing drug molecules (diosgenin, DGN) to hydrophilic molecules (8arm-PEG). Then, we encapsulated another anticancer drug, hydroxycamptothecin (HCPT) into the self-assembled nanoparticles by a simple nanoprecipitation method. These 8arm-PEG–DGN/HCPT nanoparticles (NPs) had a small size (~150 nm) and high drug loading. Flow cytometry and laser confocal scanning microscopy clearly showed that 8arm-PEG–DGN/HCPT NPs promoted intracellular uptake of the drugs by B16 melanoma tumor cells and Lewis lung carcinoma cells (LLC). Cytotoxicity assay showed that the IC₅₀ of 8arm-PEG–DGN/HCPT NPs were lower than that of the corresponding free drugs and mPEG–DGN/HCPT NPs. Therapeutic benefits were examined on B16F10 melanoma tumors subcutaneously growing in C57BL/6 mice. In vivo study demonstrated that 8arm-PEG–DGN/HCPT NPs exhibited the most pronounced tumor regression effect. These results suggest that the drug delivery system 8arm-PEG–DGN NPs for co-encapsulation of another anticancer agents HCPT may be a promising strategy for cancer treatment.

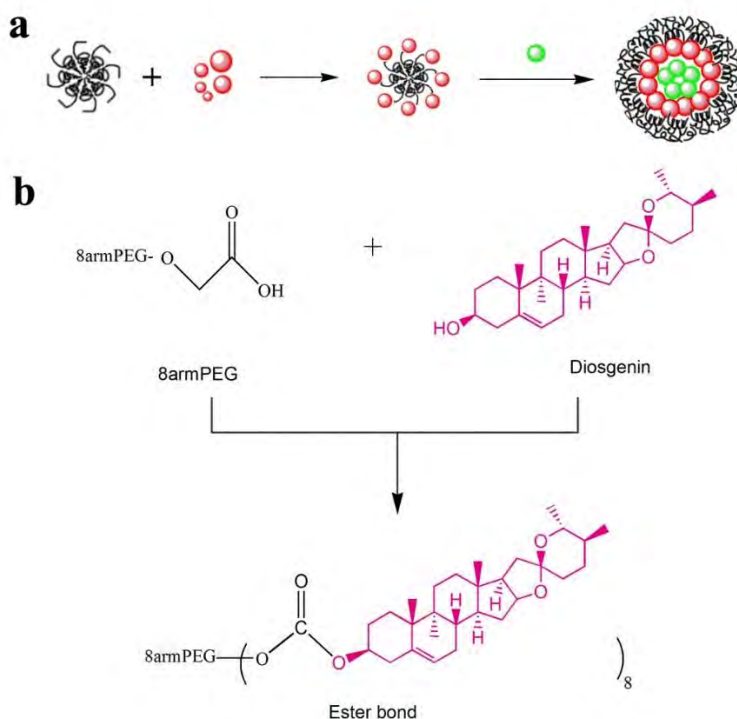
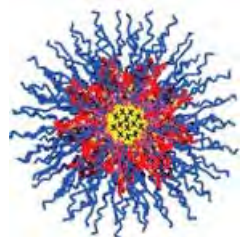


Illustration of 8arm-PEG-Diosgenin nanoparticles encapsulated HCPT for co-delivery (a). The synthesis of the amphiphilic 8arm-PEG–DGN prodrugs (b).

POLY 64: Recent developments in drug-loaded brush-arm star polymers

Matthew Golder, *goldermr@gmail.com*, Jeremiah A. Johnson. Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

The development of well-defined drug-conjugated organic nanoparticles addresses an ongoing demand for efficient methods to deliver and release small molecule pharmaceuticals. We report the highly scalable syntheses of drug-loaded brush-arm star polymer (BASP) nanoparticles via a two-step, one-pot ring-opening metathesis polymerization (ROMP) process. The nanoparticles are highly modular, allowing for tuning of both the drug loadings and the hydrolytically labile drug-polymer ester linkages. Preliminary in vitro and in vivo results provide promise for these BASPs to modulate tumor microenvironments, allowing for more efficient cancer treatment in conjunction with a chemotherapeutic agent.



POLY 65: Polymer-Based nanoparticle therapeutics

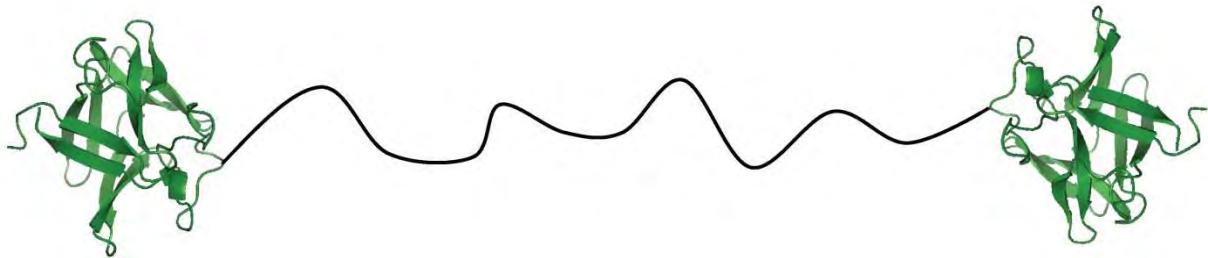
Mark E. Davis, *mdavis@cheme.caltech.edu. California Inst of Technology, Pasadena, California, United States*

We have translated three polymer-based nanoparticles into the clinic for use as cancer therapeutics. One of these nanoparticle, experimental therapeutics was the first to show functional RNA interference (RNAi) in humans. At this time, these nanoparticles have been investigated in over 10 different clinical trials. I will describe how we translated these nanoparticles from the laboratory at Caltech into clinical, experimental therapeutics. In addition to investigations of polymer-based nanoparticle therapeutics for cancer, we are now concentrating on developing polymer-based nanoparticles that cross the blood-brain-barrier. Our recent efforts will be presented.

POLY 66: Synthesis of rationally designed polymers for wound healing applications

Heather D. Maynard, maynard@chem.ucla.edu. Chemistry and Biochemistry, UCLA, Los Angeles, California, United States

Chronic wounds are a major health problem in the United States. One way to treat wounds that take more than several months to heal is by the addition of growth factors. In our group we have been focusing on one such protein, the heparin-binding protein, fibroblast growth factor 2 (FGF2) also called basic fibroblast growth factor (bFGF). FGF2 promotes various processes in wound healing including cell proliferation, migration, and vasculogenesis. We have focused our efforts on increasing the stability and efficacy of this important protein. In particular, we have designed heparin-mimicking polymers that increase the stability of the protein to stresses such as temperature and acidic pH by electrostatic interaction with the protein. We have also discovered a polymer using a small library cell-screening assay that binds to the FGF2 receptor. By preparing a block copolymer containing both the stabilizing and receptor-binding polymer segments, we were able to prepare FGF2 conjugates that are more stable and more active than the native protein. By dimerizing the protein (see Figure) with the appropriate polymeric tether length, the activity was also greater than the native protein. The design, synthesis, cell culture studies, angiogenesis investigations and in vivo results of FGF2 polymer conjugates will be discussed in this talk.

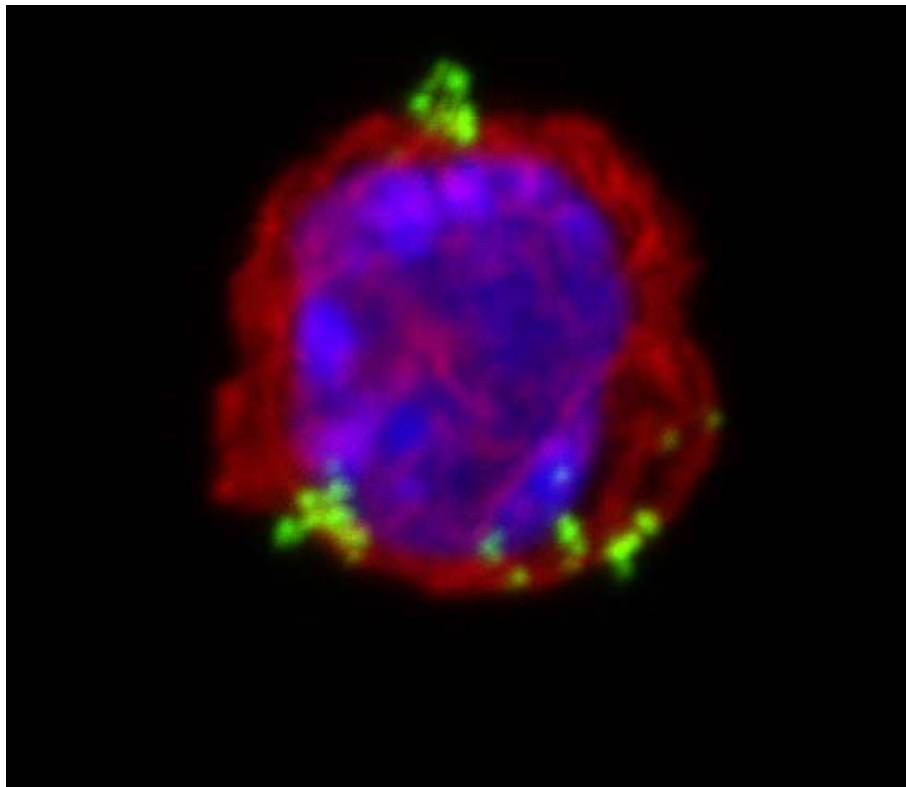


FGF2-polymer dimers are more active than the native protein.

POLY 67: Engineering cell surfaces with synthetic polymers

Harm A. Klok, harm-anton.klok@epfl.ch. STI-IMX-LP, EPFL, Lausanne, Switzerland

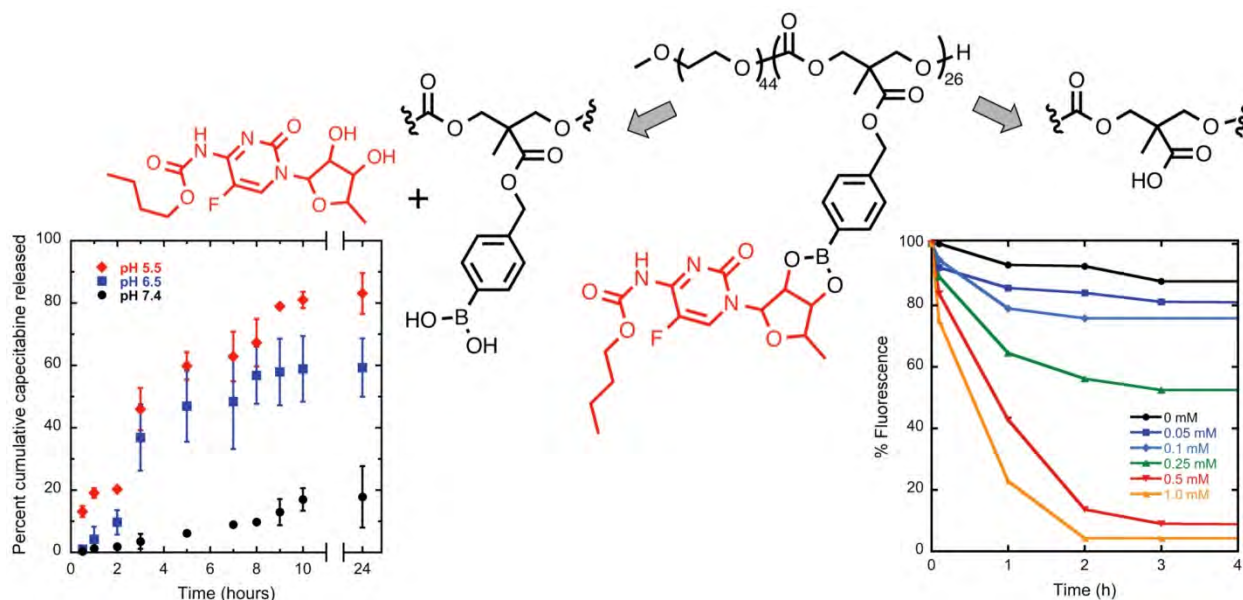
Cells provide attractive opportunities to develop innovative drug delivery systems. Red blood cells e.g. are uniquely designed to circulate in the bloodstream for extended periods of time. Immune cells, in particular lymphocytes from the adaptive immune system, are attractive as they potentially provide possibilities to home in to the disease site in a highly selective manner. Modifying the surfaces of these cells with synthetic polymers or polymer nanoparticles provides manifold opportunities to further enhance their functionality. Successful polymer cell surface engineering, obviously, requires conjugation chemistries that proceed under biological conditions and in high yields and without compromising cell viability and function. This presentation will discuss various polymer cell surface modification strategies and compare these different approaches in terms of the possibilities they offer to modify cell surfaces as well as their impact on cell viability and function. It will be shown that under appropriate conditions live cells can be surface modified with synthetic polymers while retaining their viability and functional properties.



POLY 68: Functional polycarbonates as oxidative- and pH-responsive materials

Margarita Herrera-Alonso, herrera@jhu.edu. Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States

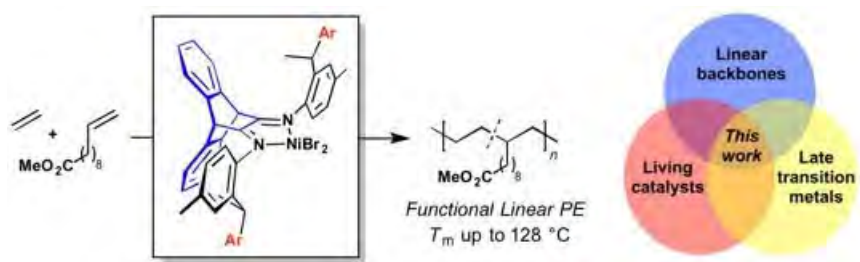
The growing need for increasingly versatile biomaterials has spurred the development of functional versions of traditionally used polymers, on occasions with unique molecular architecture. Among these are aliphatic polycarbonates, the physicochemical properties of which can be readily modified by installation of functional reactive handles, including 1,3-diols and boronic acids. Organoboron polymers are particularly interesting because of their capacity to reversibly bind to diol- and catechol- containing molecules, and reactivity toward acidic conditions or in the presence of hydrogen peroxide. We have studied the responsiveness of diol- or boronic acid-containing polymers in the context of polymer-based nanoparticle delivery systems for hydrophobic and hydrophilic solutes. Nanoparticle formation was triggered by a large and rapid change in solvent quality, yielding structures far from equilibrium with high solute loading capacity. We have examined the conditions under which pendant boronic acids can be used to allow for pH-dependent delivery of capecitabine, and to establish the conditions that would trigger nanoparticle destabilization in a oxidative environments.



POLY 69: Advances at the interface of catalyst design and polymer chemistry

Geoffrey W. Coates, gc39@cornell.edu. Cornell Univ, Ithaca, New York, United States

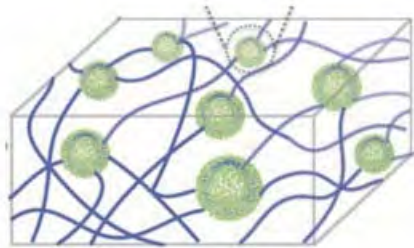
This presentation will focus on new advances in catalyst discovery and highlight new applications in polymer synthesis.



POLY 70: Biopolymeric conjugates in the design of hybrid biomaterials

Kristi L. Kiick, *kiick@udel.edu*. Dept of Materials Sci Eng, University of Delaware, Newark, Delaware, United States

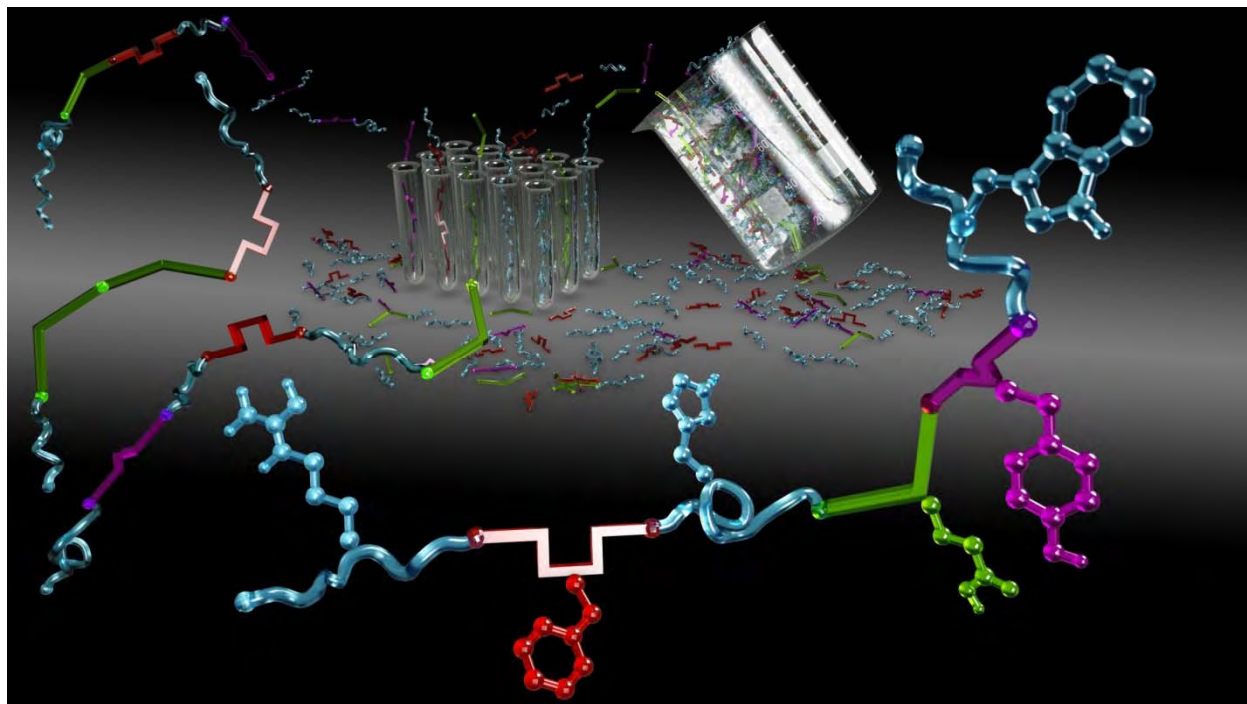
Motifs from structural proteins, such as collagen and resilin, offer important opportunities in designing biomaterials with interesting mechanical and stimuli-responsive behavior. Their conjugation to polymers, including poly(ethylene) glycol, poly(ethyleneimine), or thermally responsive poly(acrylate)-based polymers, affords biomaterials with diverse properties responsive to multiple biologically relevant triggers. Conjugates are able to form a range of structures that modulate cell behavior and influence the retention and release of cargo, offering substantial improvement in cargo activity. These materials can be designed with microstructural heterogeneity as well as into particles that may be useful in a variety of drug delivery approaches.



POLY 71: Bio-inspired materials, synthesis and function

Craig J. Hawker, hawker@mrl.ucsb.edu. Univ of California, Santa Barbara, California, United States

Marine organisms use organic building blocks in unique ways to achieve materials with exceptional properties. With inspiration from these natural systems, the design of synthetic building blocks to mimic these capabilities and extend them to common polymeric materials will be described.



Building block approach to materials design

POLY 72: Designing tunable multifunctional macromolecules: From sustainable polymers to selective drug and gene delivery vehicles

Theresa M. Reineke, *treineke@umn.edu*. Chemistry, University of Minnesota, Minneapolis, Minnesota, United States

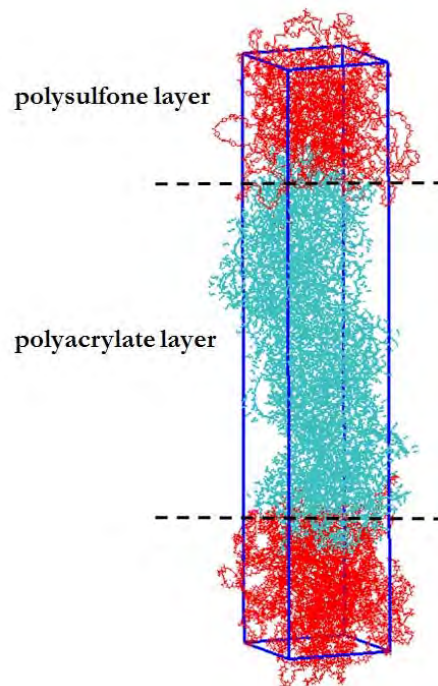
Multifunctional macromolecules have a tremendous impact on a multitude of applications. For example, the development of polymer excipients can improve the solubility and bioavailability of intractable drugs, nucleic acid delivery vehicles have promise to promote selective genome editing, and materials from sustainable monomers may lower the environmental impact of plastics. While the materials function is diverse across these fields, the polymer chemistry is similar and should be readily tunable for each specific application while remaining biologically and environmentally benign. Bio-based feedstocks such as carbohydrates and their derivatives offer great promise for tailoring materials development for a multitude of uses due to their rich functionality (high heteroatom content and stereochemistry), renewable production on an impressive scale, low toxicity, and the potential for triggered degradation. In addition, renewable feedstocks offer high glass transition temperatures, the ability to modulate solubility through chemical modification, and the utility to target delivery to selective tissue types. Indeed, the chemical, physical, mechanical, and morphological properties of polymers containing sustainable and biologically-friendly monomers can be tuned based on chemistry, sequence, and composition to yield diverse function and properties. Herein, the design and development of tailored polymers using a variety of synthetic pathways will be presented. Their application in the development of sustainable polymers, improvement of oral pharmaceutical bioavailability, and design of nucleic acid delivery vehicles for genome editing applications will be presented.

POLY 73: Dynamics of solvent molecules in polyacrylate gels supported on a polymeric substrate

Rafikul Islam, Sriramvignesh Mani, **Rajesh Khare**, rajesh.khare@ttu.edu. Chemical Engineering, Texas Tech University, Lubbock, Texas, United States

Pervaporation using polymeric membranes offers an attractive alternative to distillation for energy efficient separation of dilute alcohol-water mixtures that result from the fermentation of biomass during the biofuels production process. In recent work, we used molecular dynamics simulations to demonstrate the viability of polyacrylate gels as candidate materials for pervaporation membranes for separating dilute alcohol-water mixtures. Specifically, we showed that dynamics of water molecules is strongly coupled with polymer dynamics in swollen gels whereas ethanol molecules do not exhibit such strong coupling. In practical applications, the polymeric pervaporation membranes are supported on a solid substrate which typically consists of another polymeric material such as polysulfone or cellulose acetate. The interaction between the gel and the polymeric support will affect the dynamics of the gel atoms, which in turn, will have an effect on solvent dynamics in the swollen supported gel.

In this work, we have used molecular dynamics simulations to study water and ethanol molecule dynamics in polyacrylate gels that are supported on a polysulfone substrate. The polyacrylate gels studied in this work are poly butyl acrylate, 50-50 random copolymer of butyl acrylate and 2-hydroxy ethyl acrylate, and poly 2-hydroxyethyl acrylate. Solvent dynamics in the polysulfone supported polyacrylate gels is compared with our previous results for the solvent dynamics in the same gels but in the absence of the polysulfone support. The results are used to elucidate the mechanism of solvent molecule diffusion in supported polymeric membranes.



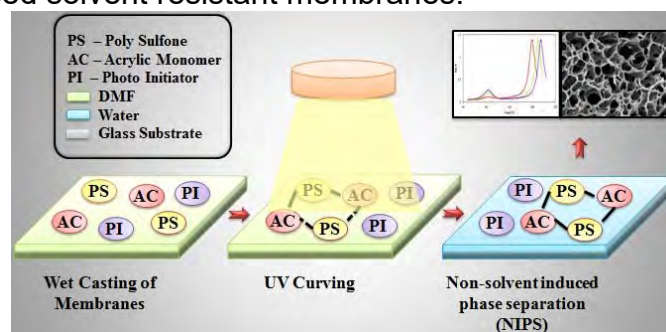
POLY 74: Promising chemical stable membranes developed through combined effect of radical polymerization and non-solvent induced phase separation of acrylic functionalized polysulfone

Mian Farrukh F. Mehmood¹, *mian.mehmood@polito.it*, Sangermano Marco¹, Paula Bosch², Mattia Giagnorio³, Alberto Tiraferri³. (1) Department of applied science and technology, Politecnico Di Torino, Torino, Piemonte, Italy (2) Instituto de Ciencia y Tecnologia de Polimeros, Madrid, Spain (3) Department of Environment, Land and Infrastructure Engineering, Politecnico Di Torino, Torino Italy, Torino, Italy

The acrylic functionalization of polysulfone (PSU) has been an attractive strategy to improve the chemical stability of polysulfone based membranes but this modification has also led to significant drop in the flux when compared with pristine polysulfone. While pristine polysulfone membranes, developed through phase separation, are not resistant to majority of organic solvents.

In order to overcome the aforementioned discrepancy; the current research was aimed to modulate the morphology and the performance of membranes in a way that a cross-linked network is developed for chemical stability and the pores morphology is retained for sufficient flux. For this purpose we incorporated two structurally different di acrylates, bisphenol A ethoxylate di acrylate (BEDA) and poly (ethylene glycol) di acrylate (PEGDA), into 15% PSU soln. in DMF. We optimized all the related parameters like percentage of acrylic functionality, total energy (UV) dose to ensure a cross linked network, wet thickness of the membranes and controlled non-solvent induced phase separation (NIPS). The thin films containing PSU, acrylic monomer and photo initiator, phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO), were casted on glass substrate, UV cured and subjected to NIPS.

The UV curing behaviour, thermo - mechanical and morphological properties of membranes were fully investigated. The performance of membranes was evaluated in terms of static contact angle, dead-end flux, qualitative solvent resistance and latex 20 nm particles rejection. The best formulation, 10 % BEDA functionalized PSU, was found to have 241 L m⁻² h⁻¹ bar⁻¹ flux, 92 % rejection of Latex 20 nm particles and resistant to DMF, THF, DMSO, acetone, toluene, and ethyl acetate after 120 hours of immersion. The developed membranes, as per best of our knowledge, exhibited performance far better than previously reported. The flux obtained is also higher than commercially available PVDF based solvent resistant membranes.



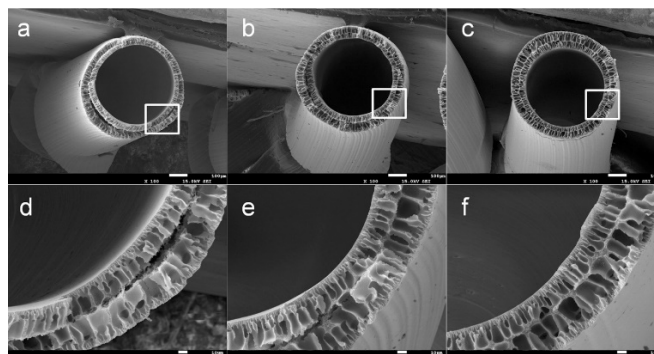
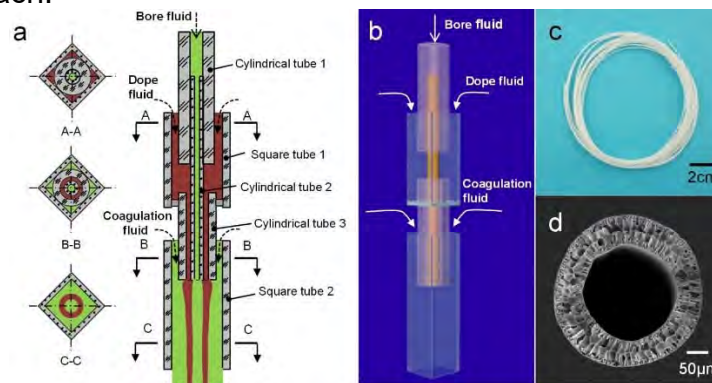
scheme of research methodology

POLY 75: Microfluidic spinning of polyethersulfone hollow fiber membranes

Ke Deng¹, shenli199-0@qq.com, Zhuang LIU¹, Feng Luo¹, Rui XIE¹, Xiao-Jie JU¹, Wei WANG¹, Liang-Yin CHU². (1) Chemical Engineering, Sichuan University, Chengdu, Sichuan, China (2) School of Chemical Engineering, Sichuan University, Chengdu, Sichuan, China

Preparation of hollow fiber membranes involves more affecting factors than that of flat sheet membranes during membrane formation process. It is important to obtain a uniform hollow fiber in a production line. Recently, microfluidic spinning has attracted much attention in fiber fabrications. Unfortunately, microfluidic spinning of polyethersulfone hollow fiber membranes is still a challenging task. Especially, the relationship between the microfluidic spinning parameters and the microstructures of prepared polyethersulfone hollow fiber membranes still needs systematically investigation. Here, we develop a novel capillary-based co-axial microfluidic device for microfluidic spinning of polyethersulfone hollow fiber membranes.

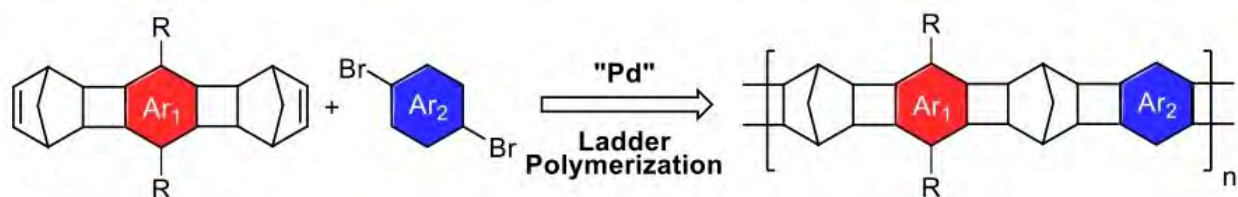
The polyethersulfone hollow fiber membranes are spun in the microfluidic device with dope solution used as the middle phase, and 20% (w/w) PEG 20000 aqueous solution used as both the bore fluid and outer coagulation bath phases. The effects of fabrication conditions including microfluidic flowrates, PES concentration in dope fluid and operation temperature on the structures of microfluidic-fabricated PES hollow fiber membranes are investigated systematically. Ternary fluid-flow diagrams are created for fabricating PES hollow fiber membranes with different PES concentrations and operation temperatures. The results in this study provide valuable guidance for fabricating hollow fiber membranes with controllable microstructures and dimensions via microfluidic approach.



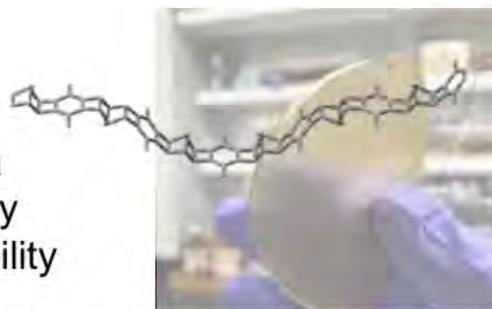
POLY 76: Efficient synthesis of functionalized shape-persistent ladder polymers for gas separation

Holden W. Lai, hwhlai@stanford.edu, Yew Chin Teo, Yan Xia. Department of Chemistry, Stanford University, Stanford, California, United States

Ladder polymer is a chain of an uninterrupted series of rings connected by sterically restrictive links. We recently developed Catalytic Arene-Norbornene Annulation (CANAL) polymerization, which produces shape-persistent ladder polymers with benzocyclobutene backbone linkages from aryl dibromides and functionalized dinorbornenes. These ladder polymers possess high molecular weight, low polydispersity, and bear a wide range of functionalities, which allow the ladder polymers to be further derivatized, grafted, and crosslinked. The ladder architecture results in high microporosity, making them attractive membrane materials for gas separation.



- High surface area
- High microporosity
- High thermal stability

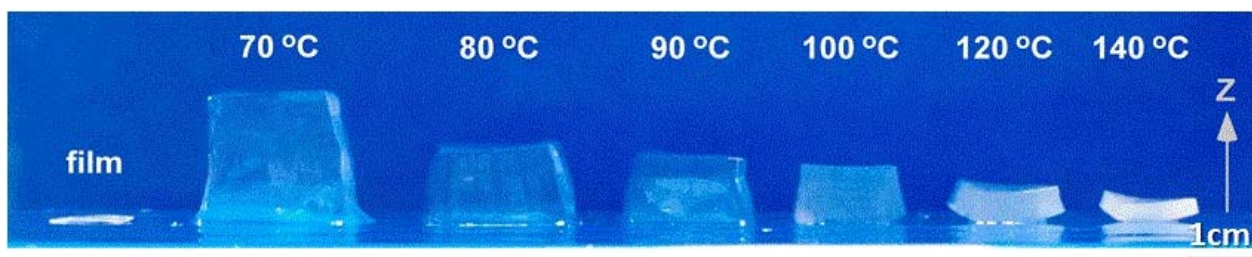


POLY 77: Super-Anisotropic swelling of hydrogels layered by domino-effects of cyanobacterial LC megamolecules

Maiko Okajima², *k-maiko@jaist.ac.jp*, **Tatsuo Kaneko**¹. (1) *Jaist Sch Materials SCI, Nomi, Japan* (2) *Japan Advanced Institute of Science and Tech, Ishikawa, Japan*

Anisotropic gels have been studied very widely in the fields of soft-biomaterials due to their possible application as biomedical, optical, and electronic materials. The anisotropy was effected by various stimuli such as self-assembly, directional diffusion, directional freezing, elongation, solvent-cast and so on. The solvent-cast method is one of the most facile methods of film preparation, inducing in-plane molecular orientation of the resulting film by solvent removal stress. If the cast film is cross-linked and re-swells in solvent, the gels should be formed. Such an in-situ hydrogelation method is useful because the dried precursor film has a resistance to decay and soon re-swells in water just before use. Thinner films should have a higher efficiency of polymer chain orientation, but are generally less self-supporting or too thin as film with a thickness of less than one micrometer cannot be used as a precursor of hydrogels in reality. Although the films that are thick enough to self-support should be better for the precursor, molecular orientation is quite difficult to produce.

Sacran is a supergiant cyanobacterial polysaccharide with an extremely high absolute molecular weight over 10^7 g/mol (molecular length: over 30 μm) and a very high rigidity parameter, r , of 3.8 to exhibit a liquid crystalline (LC) phase at an extremely low concentration of 0.3 wt%. When sacran LC aqueous solution is cast and annealed at a temperature range of 70-140 $^{\circ}\text{C}$, anisotropic hydrogels are formed by immersion in water, where the thickness change of the film by swelling is 70 fold higher than the width change. Increase in the film thickness or decrease in sacran chain length reduced the swelling anisotropies, indicating that LC chains with micrometer-scale size comparable with a thickness of self-standing film showed domino-effects to align along the substrate surface during drying. Thus uniaxially-swelling hydrogels were efficiently created.

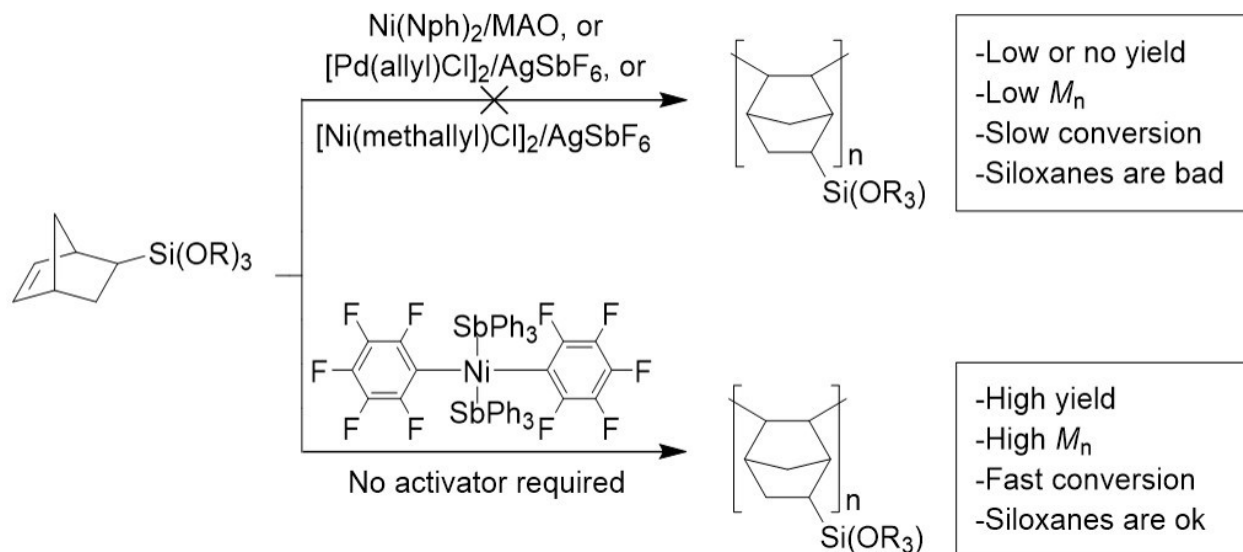


Anisotropic swelling behavior of layered hydrogels of cyanobacterial exopolysaccharides with LC properties

POLY 78: Siloxane-substituted polynorbornenes as advanced gas separation membranes

Brian K. Long, long@utk.edu, Kevin R. Gmernicki, Christopher Maroon, Morgan A. Higgins. Chemistry, University of Tennessee, Knoxville, Tennessee, United States

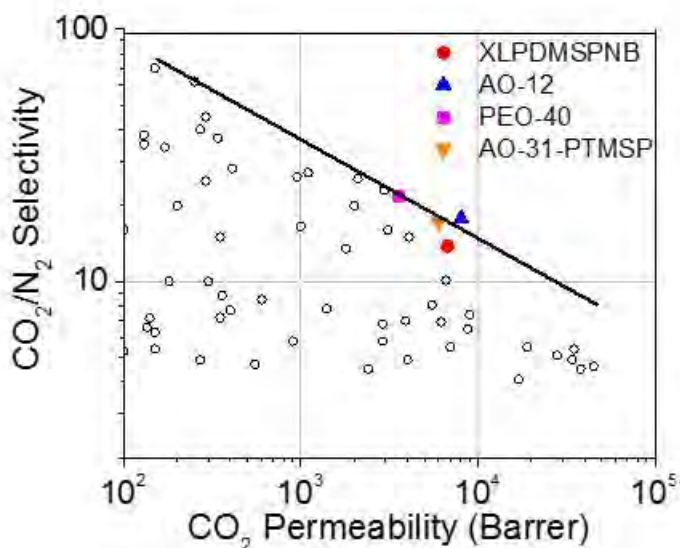
Carbon dioxide (CO₂) comprises approximately 84% of all U.S. greenhouse emissions each year. In an effort to decrease these emissions, polymeric membranes have been targeted as an efficient means to separate CO₂ from other non-greenhouse gases. Polymeric membranes operate by a passive diffusion mechanism that holds promise to mitigate CO₂ emissions while being less energy intensive than other methods such as physical adsorption or cryogenic distillation. Particular challenges that are associated with CO₂ separation are that: 1) CO₂ is only one component in a complex flue gas mixture, thereby requiring membranes with high selectivity 2) CO₂ has a remarkably similar molecular size to N₂, which is the main constituent in flue gas, prohibiting the use of traditional "size-sieving" membranes, and 3) high CO₂ permeabilities are required to handle the tremendous volumes associated with coal-fired power plant flue gas streams. To address these challenges, we will present the synthesis and characterization of a new class of vinyl-added polymers bearing siloxane-functionalized pendant groups. These polymers were previously thought to be inaccessible; however, careful catalyst choice has enabled us to access them in good yields and with molecular weights exceeding 100 kg/mol. These polymers produce large area, defect-free films that are flexible, thermally robust, and that have high CO₂ permeability as well as exceptional CO₂/N₂ ideal selectivity. These attributes make these materials attractive candidates for future CO₂/N₂ separation membranes.



POLY 79: CO₂-philic polymer membranes for high flux CO₂ separation

Tao Hong³, Pengfei Cao¹, Bingrui Li¹, Shannon M. Mahurin¹, De-en Jiang², Konstantinos Vogiatzis³, Jimmy W. Mays³, Brian K. Long³, Alexei P. Sokolov¹, **Tomonori Saito**¹, saitot@ornl.gov. (1) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Department of Chemistry, University of California, Riverside, Riverside, California, United States (3) Dept of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

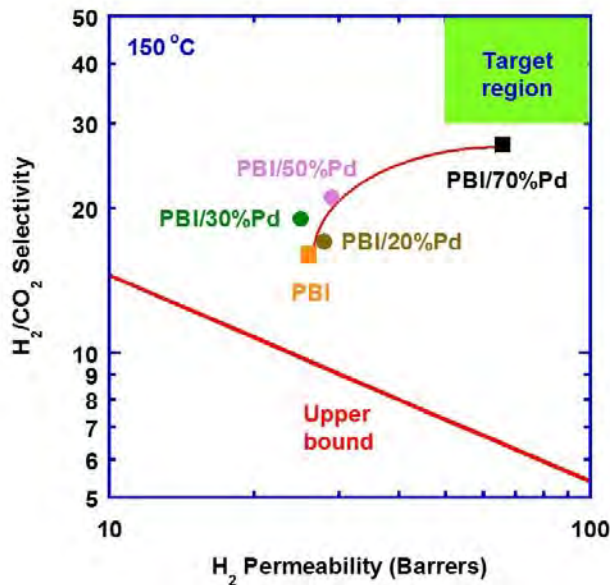
The vast majority of the world's energy is presently derived from the burning of fossil fuels, which releases vast quantities of carbon dioxide (CO₂) into the environment and results in undesirable climate change. Practical and cost efficient methods of CO₂ separation and capture would thus solve one of the most challenging problems today. This presentation summarizes our effort on the development of novel polymer membranes functionalized with CO₂-philic groups for high flux CO₂ separation. Our strategy focuses on tuning solubility selectivity in addition to diffusivity selectivity for achieving high permeability membranes combined with good selectivity. Various synthetic techniques including ROMP and post functionalization were used and the careful design permits to prepare well-defined novel high permeable polymers containing CO₂-philic groups. This study demonstrated the addition of CO₂-philic groups (e.g. amidoxime and PEO) significantly increased the solubility selectivity of CO₂ over N₂. The membrane performance is also highly dependent on the balance of gas/functional group interaction, intra/inter- molecular interaction (H-bonding etc.) of membrane, packing, and polymer dynamics. Tuning the balance of the interaction enables to achieve the CO₂ separation performance over the Robeson upper bound, e.g. CO₂ permeability 3000-8000 Barrer and CO₂/N₂ selectivity 18-20. The structure-property relationships especially on CO₂ uptake, CO₂ and N₂ permeability, CO₂/N₂ selectivity to the polymer structure will be discussed.



POLY 80: Mixed matrix materials containing Pd nanoparticles with superior membrane H₂/CO₂ separation properties

Haiqing Lin, haiqingl@buffalo.edu, Lingxiang Zhu, Deqiang Yin, Shailesh Konda, Mark Swihart. Dept. of Chemical Biological Engineering, University at Buffalo, SUNY, Buffalo, New York, United States

Polymeric membranes have been widely explored for energy-efficient and low-cost CO₂ capture and H₂ purification in the integrated gasification combined cycle (IGCC) processes. Conventional approaches are focused on designing rigid polymers with strong size sieving ability achieving high H₂/CO₂ diffusivity, such as poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (PBI). In contrast, we investigate polymer-based mixed matrix materials (MMMs) containing palladium (Pd) nanoparticles, which have strong affinity towards H₂ and thus exhibit extremely high H₂/CO₂ solubility selectivity. Uniform Pd nanoparticles (with diameters of 6-8 nm) are prepared via hot-injection approaches, which show H₂/CO₂ solubility as high as 840, compared with <0.1 for typical polymers. The m-PBI is selected as a model polymer matrix, due to their good H₂/CO₂ separation properties. The effect of Pd loading (0 – 70 wt%) and temperature on the H₂/CO₂ separation properties is thoroughly evaluated. The loading of Pd nanoparticles increases H₂ permeability and H₂/CO₂ selectivity at temperature of 50 – 200 °C. For example, addition of 70 wt% Pd in the m-PBI increases the H₂ permeability from 25 Barrers to 70 Barrers, and H₂/CO₂ selectivity from 13 to 29 at 150 °C. This presentation will also examine the morphology of the MMMs aiming to derive the structure/properties relationship. These high performance MMMs demonstrate their potential for industrial CO₂ capture and H₂ purification.

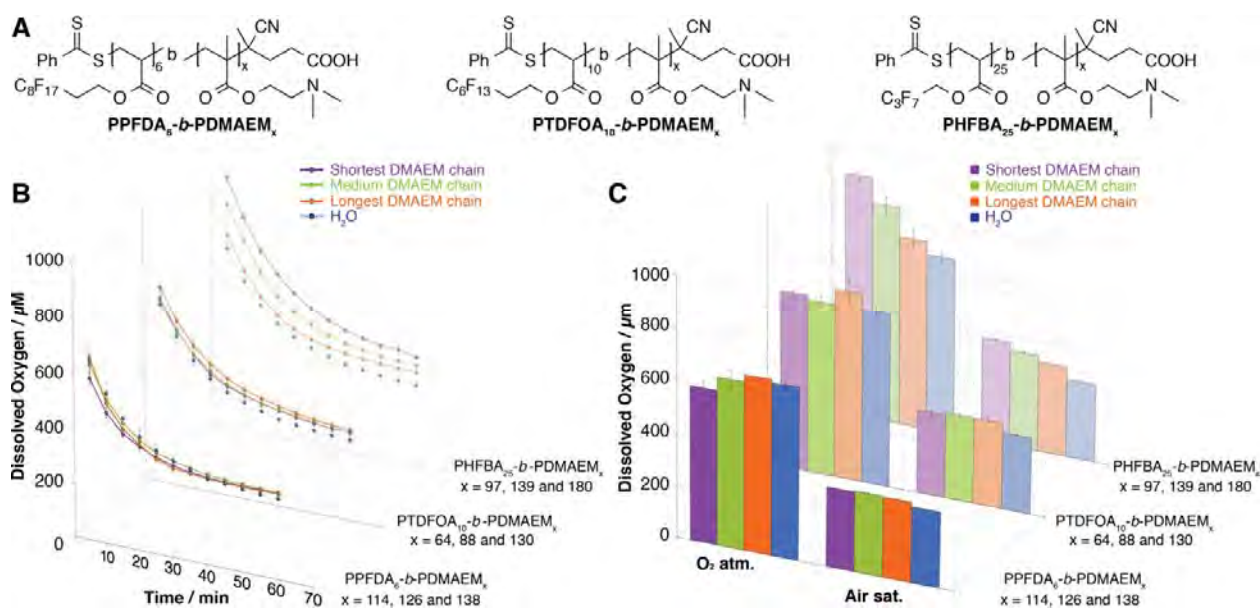


POLY 81: pH-Sensitive linear amphiphilic block copolymers for transport and controlled release of molecular oxygen

Valentin O. Rodionov, *3plus2@gmail.com*. PSE/KCC, King Abdullah University of Science and Technology, Rockville, Maryland, United States

One of the more remarkable properties of saturated fluorocarbons (SFCs) is their ability to dissolve significant amounts of gases, including oxygen, carbon dioxide, xenon and nitrogen. This enabled the use of SFCs in gas transport applications, such as liquid ventilation and selective capture of carbon dioxide from fuel gas steams. Emulsions of SFC compounds in water are also competent gas carriers that are often more practical than pure SFCs.

The mechanistic aspects of the anomalous gas solubility in SFCs and their emulsions have been explored previously, but the exact nature of the non-covalent interactions involved remains uncertain. Here we report the synthesis of a library of amphiphilic SFC block-copolymers incorporating different fluorinated monomers and the results of a systematic investigation of their capacity for oxygen transport in water. We found that the structure of the fluorinated monomer employed has a profound effect on both the oxygen-carrying capacity and the gas release kinetics of the polymer emulsions (Figure 1). An optimal fluorinated monomer and block-copolymer composition were identified. Furthermore, we could trigger the release of O₂ from the polymer dispersion by changing the pH of the solution. This is the first example of a polymer-based system for controlled release of a non-polar, non-covalently entrapped respiratory gas.

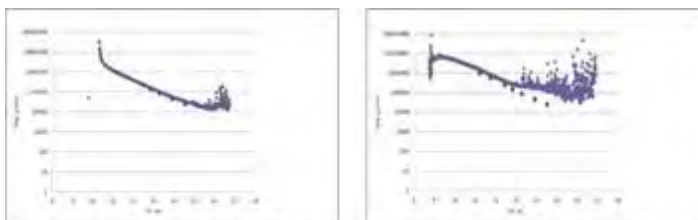


POLY 82: Gel permeation chromatography of ultralarge polymers: Challenges and limitations

David M. Meunier¹, dmmeunier@dow.com, Yongfu Li¹, Wei Gao². (1) The Dow Chemical Company, Core R&D Analytical Sciences, 1897 Building, Midland, Michigan, United States (2) The Dow Chemical Company, Core R&D Analytical Sciences, 400 Arcola Road, Collegeville, Pennsylvania, United States

Analysis of ultrahigh molecular weight, or more precisely, ultra large polymers (ULP) represents one of the most challenging applications for techniques like gel permeation chromatography (GPC) and field flow fractionation. The fundamental obstacles to successful analysis of ULPs by GPC^[1] were thoroughly described by Giddings in the 1980's. Despite this earlier work, many of these obstacles remain today, especially for polymers having a significant weight fraction (e. g., > 3 wt. %) of material exceeding ~250 nm R_g in their molecular weight distribution. For reference purposes, 250 nm R_g corresponds to the size of 17,000,000 g/mol linear polystyrene or 7,000,000 g/mol linear polyethylene dissolved in good solvents.

We have developed a protocol and strategy for finding ideal, or near ideal GPC conditions for ULPs. We have applied our approach to a number of ULP systems, including several water soluble polymer materials used in food and pharma applications. One success story, where ideal or near ideal GPC conditions have been identified, will be highlighted to illustrate the approach.^[2] When ideal, or near-ideal conditions can be identified, GPC coupled with molecular weight sensitive detection provides an accurate molecular weight distribution. A second, more challenging, example will be presented and discussed. This second example will serve to illustrate some of the key limitations toward successful separation and analysis of ULPs. Ideas for overcoming these limitations will also be presented.



Molar mass versus elution volume plots for narrow molecular weight (red points) and broad ultrahigh molecular weight (blue points) polyethylene oxide. Left plot shows ideal or near-ideal GPC behavior, while the right plot shows non-ideal GPC behavior.

POLY 83: Detailed characterization of gelatins from different sources using aqueous gel permeation chromatography with on-line triple detection and multi-angle light scattering detection

Benjamin Crawshaw¹, *benjamin.crawshaw@pfizer.com*, Dawn Herrick¹, Wei Gao², Xiaojun M. Liu¹. (1) Global R&D, Pfizer, Richmond, Virginia, United States (2) The Dow Chemical Company, Collegeville, Pennsylvania, United States

Gelatins are mixtures of water soluble proteins obtained by denaturation and partial hydrolysis of collagen, the main fibrous protein in animal bones, cartilage and skins. The use of gelatins plays an important role in pharmaceutical and consumer healthcare industries in widespread applications such as hard and soft capsules, gummies, coatings and numerous drug delivery media. The properties provided by different grades of gelatins can vary significantly based on their manufacturing processes, animal sources, collagen sources and other variables. Various molecular weight averages and the molecular weight distribution of gelatin can have significant impact on final product properties. However, limited molecular weight distribution information is available for gelatin. Gel permeation chromatography (GPC) is the most widely used technique for characterizing molecular weight distributions of macromolecular systems. The intent of this research is to develop practical analytical method(s) to determine absolute molecular weight averages, molecular weight distributions, molecular sizes, intrinsic viscosities, and other physical properties of gelatins using GPC with triple detection (GPC-TD) and with multi-angle light scattering (GPC-MALS). Several GPC methods were compared, and the best practical conditions were identified. Raw material gelatins from various sources were examined by GPC-TD and GPC-MALS, and significant differences in average molecular weights and molecular weight distributions were revealed and used to relate and predict processability and product performance of soft gelatin capsules. GPC may be used for characterizing raw materials, drug-gelatin interactions, and crosslinking of gelatin-based products.

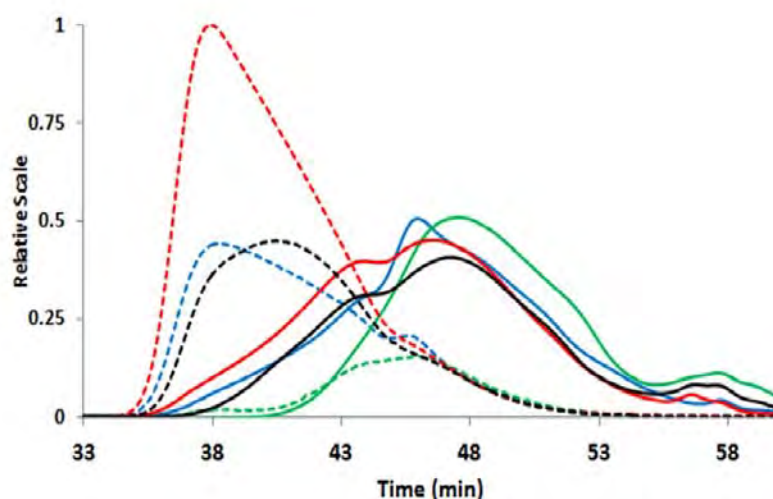


Figure 1. GPC-MALS chromatograms of four different type B gelatins. (Solid lines are differential refractive index detector responses, dotted lines are 90 degree light scattering responses)

POLY 84: Characterization of biopolymer stability by size-exclusion chromatography and asymmetric flow field-flow fractionation

Yongfu Li, ylli@dow.com, Krishna Kuppannan, Margaret Covington, Danielle Dodage, David M. Meunier. Analytical Sciences, Dow Chemical Company, Midland, Michigan, United States

Biopolymers in pharmaceutical applications need careful formulation to maintain bioactivity of the drug. Aggregation is one of the common denaturation pathways of biopolymers, and the aggregates might also cause serious undesired biological reaction. Monitoring molecular weight changes can enable development of novel additives to improve stability of biopolymers in formulations. Size-exclusion chromatography (SEC) and asymmetric flow field-flow fractionation (AF4) are widely used techniques for characterization of biopolymers and their aggregation. In this talk, SEC and AF4 method development for characterization of biopolymers, including abatacept (ORENCIA®), immunoglobulin G (IgG) and bovine serum albumin (BSA), in their native states and after heat stress will be discussed. Detailed comparison of SEC versus AF4 will be presented. The results suggest that SEC and AF4 are complementary techniques yielding similar molecular weight and aggregation level on the studied biopolymers. However, AF4 shows unique advantages in characterization of biopolymer aggregation, as it yields better separation between unimer and aggregates, and has no anomalous elution of aggregates. Also, AF4 yields more accurate characterization of aggregation level because there is less shear force imparted on the aggregates during fractionation, as compared to SEC separation. These studies demonstrate that the combination of AF4 and SEC will provide an efficient analytical tool for the characterization of biopolymers, and yield essential information for development of various additives to improve stability of biopolymers in the formulation.

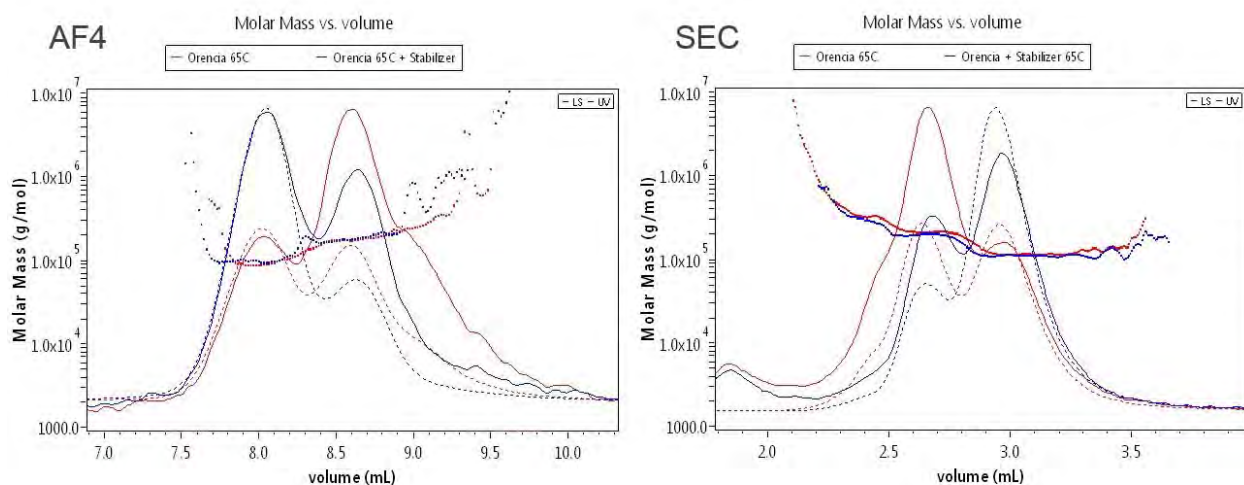


Figure 1. Comparison of AF4 versus SEC separation of ORENCIA® solution with (blue) and without (red) stabilizer after heating at 65 °C for 22 hours. Similar molecular weight and aggregation level were observed by both AF4 and SEC. ORENCIA® solution with stabilizer has much less aggregates.

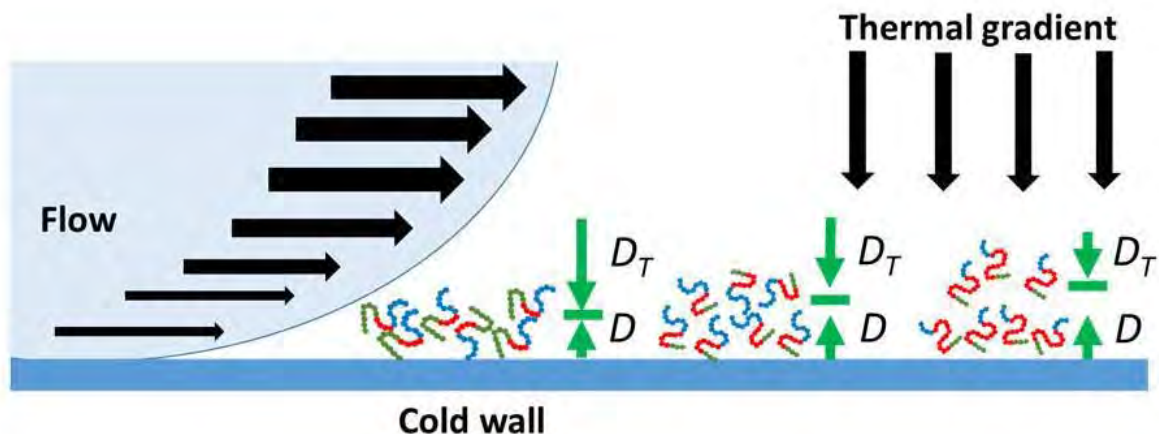
POLY 85: Composition and microstructure separations of polymers and nanoparticles using thermal field-flow fractionation

Kim R. Williams, *krwillia@mines.edu*, William C. Smith, Marley B. Pillion, Kevin Bierbaum, James Oliver, Carmen R. Bria. Colorado School of Mines, Golden, Colorado, United States

Thermal field-flow fractionation (ThFFF) has evolved from a technique for separating homopolymers by differences in molecular weight (MW) to one that can also yield much needed information about other critical distributions, e.g., composition, microstructure, and architecture. ThFFF utilizes a temperature gradient 'field' to move polymers and nanoparticles into different flow velocity streamlines of a parabolic flow. This transport usually occurs in the direction of higher to lower temperature and gives rise to the thermal diffusion coefficient D_T . The retention time t_r in ThFFF is given by the equation

$$t_r \approx (D_T \Delta T t^0) / 6D \quad (1)$$

where ΔT is the difference in temperature between a hot and cold wall, t^0 is the void time, and D is the normal diffusion coefficient. Equation 1 looks deceptively simple since all parameters are known or measurable. However, the key lies in the D_T term which has been shown to be sensitive to the polymer-solvent interface and thus polymer composition and microstructure. Furthermore, the D_T/D term gives insights into the number of polymer chain ends and hence architecture. This presentation focuses on the development of ThFFF for polymer composition and microstructure separations. Homo-, co-, and ter-polymers of polystyrene and polyacrylates are used as examples to demonstrate ThFFF's abilities for determining composition distributions and polybutadiene serves as the example for microstructure analysis. Finally, the knowledge gained from polymer systems forms the foundation for our recent development of ThFFF composition analysis for complex nanoparticles such as metal hybrids and core-shell structures.



POLY 86: Separation and quantification of colloidal particles and polymers made by emulsion polymerization using asymmetrical flow field-flow fractionation with advanced detection: Challenges and progresses

Wei Gao, weigao@dow.com, Stan Brownell, James Bohling, Pu Luo, Ashley Gong, Kinjal Joshi, Fanwen Zeng. The Dow Chemical Company, Collegetown, Pennsylvania, United States

Colloids play a very significant role in nature and in our daily life. The Dow Chemical Company produces millions of pounds of colloid-based materials for coatings, home and personal care and many other industrial applications. The analytical capability for characterization of colloidal particles and polymers made by emulsion polymerization is essential to product development, quality control, intellectual property protection, and fundamental research.

Many analytical techniques have been used for colloidal particle characterization; however, there are still many challenges to obtain necessary information with high precision and accuracy in a reasonable time frame especially for the systems with multimodal distributions. In addition, polymers made by emulsion polymerization processes can have ultra-high molecular weight, branching and/or microgel, which challenge the limits of Gel Permeation Chromatography.

In this presentation, we will use standards and industrially relevant examples to demonstrate the capability of Asymmetrical Flow Field-Flow Fractionation (AF4) with on-line multi-angle light scattering (MALS) and refractive Index detector (dRI) to determine the particle size distribution, particle concentration, particle mass, and apparent density of particle. In addition, we will also demonstrate the benefit of using AF4-MALS-dRI for characterizing ultrahigh molecular weight polymer/microgel made with emulsion polymerization process. The separation power and quantification precision and accuracy will be discussed in detail. Meanwhile, challenges in characterizing these colloidal systems will also be discussed to stimulate future developments in this arena.

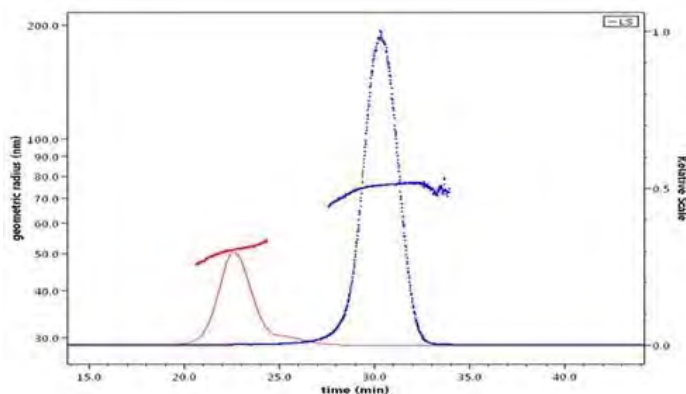
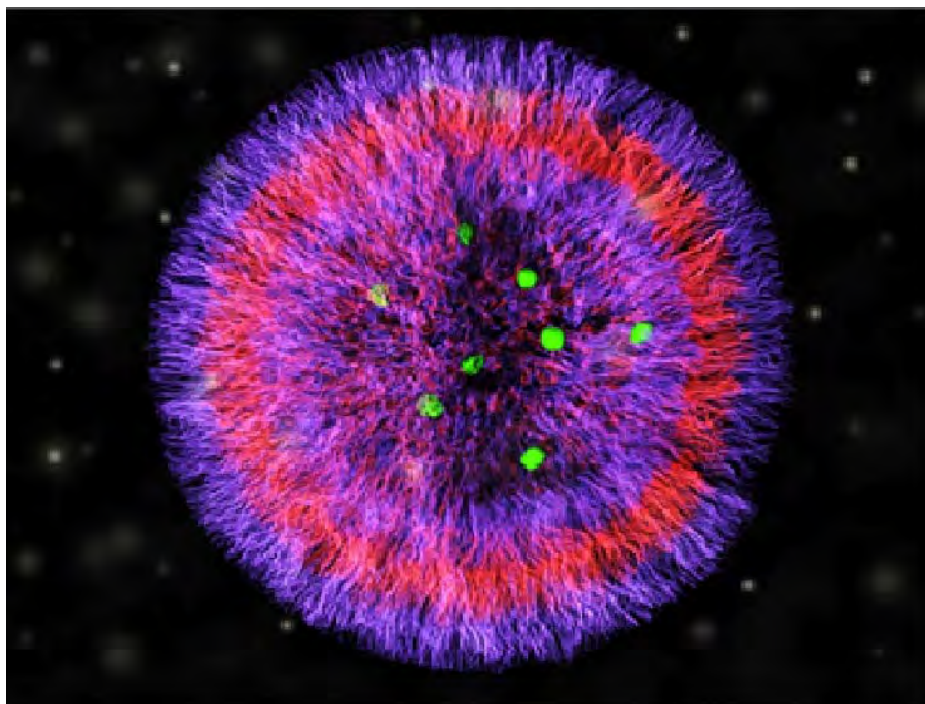


Figure. AFFF-MALS fractograms (90 degree light scattering response) of 100 nm (in red) and 150 nm (in blue) polystyrene particle size standards and the geometric radii determined from MALS using sphere model

POLY 87: Correlation between structural properties and encapsulation efficiency in polymersomes

*Hannes Gumz, Susanne Boye, Dietmar Appelhans, **Albena Lederer**, lederer@ipfdd.de. Leibniz-Institute of Polymer Research Dresden, Dresden, Germany*

The field of nanoscience is the key to develop advanced biomedical applications. In this regard, many drug delivery nanocarriers have been extensively explored. An innovative approach is the transport using polymersomes, particles which mimic the natural phospholipids based liposomes. The polymersomes are based on synthetic block-co-polymers with amphiphilic nature. The formation of the polymers into polymersome vesicles is driven by self-assembly leading to a membrane, which is stabilized by crosslinking. The vesicles possess high potential as excellent nanocarriers because of their prospective biotechnological applications as drug delivery, in vivo imaging and in cell mimicry. The incorporation of pH-responsive functionalities allows the polymersomes to open and close their membrane reversibly.¹ This property makes them promising carries for smaller or bigger drug molecules or enzymes. Though, for biotechnological applications systematic understanding of the encapsulation mechanism, the structural and interaction properties of the polymersome vesicles in the inner part, at the surface and in the internal part of the membrane is crucial. This study shows an extensive investigation of polymersome properties based on series of cargo molecules with different size and interaction parameters. Assymetrical flow field flow fractionation, light scattering techniques and advanced microscopy studies give an insight into the complexity of these carrier systems.



POLY 88: Developing polymer research lessons for the high school classroom – NSF RET at The University of Southern Mississippi

Kim Wingo¹, kimberly.wingo@usm.edu, Sarah E. Morgan². (1) The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

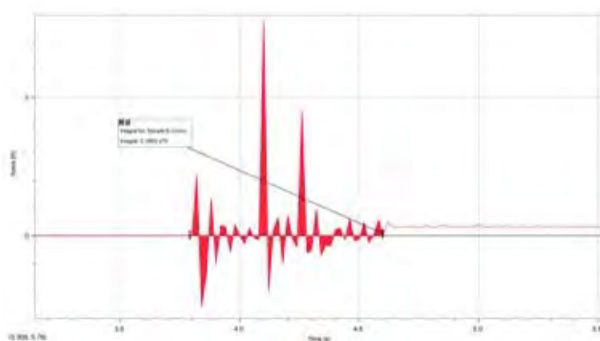
The goal of the National Science Foundation sponsored “Research Experience for Teachers Site for Sustainable Polymer Engineering Research” (RET) at The University of Southern Mississippi is to develop long-term professional relationships between faculty researchers and local teachers by providing meaningful research experiences. This is achieved through partnership with local community college instructors and high school teachers who participate in a six-week summer research experience with polymer science and engineering faculty members. During the summer teachers perform research in the area of sustainable materials, and pair with faculty to perform research in three areas: (1) improved efficiency polymer solar cells, (2) high-performance polymers and composites, and (3) environmental impact of synthetic materials in sea water. Teachers are also involved in professional development workshops to enhance their oral and written communication skills. By the end of their research experience, teachers develop classroom lessons and laboratory activities with content based on their own research findings. The lessons are designed to engage students in experiments with relevance to the world around them and that address national science standards. A few research projects that were developed into successful classroom lessons will be highlighted. During the summer, teachers present a research update and scientific poster presentation. Teachers also publish their activities and experiments in “Teach Engineering” as well as present them at the annual Mississippi Science Teachers Association meeting. This presentation will highlight successful tools used to develop lessons and improve the impact of polymer research in the classroom.



POLY 89: Cross-linking physics and polymers: Making an impact in STEM education

Mary Boleware¹, *mary.boleware@jcc.edu*, **Amit Sharma**², **Jeffrey S. Wiggins**². (1) Science, Jones County Junior College, Ellisville, Mississippi, United States (2) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States

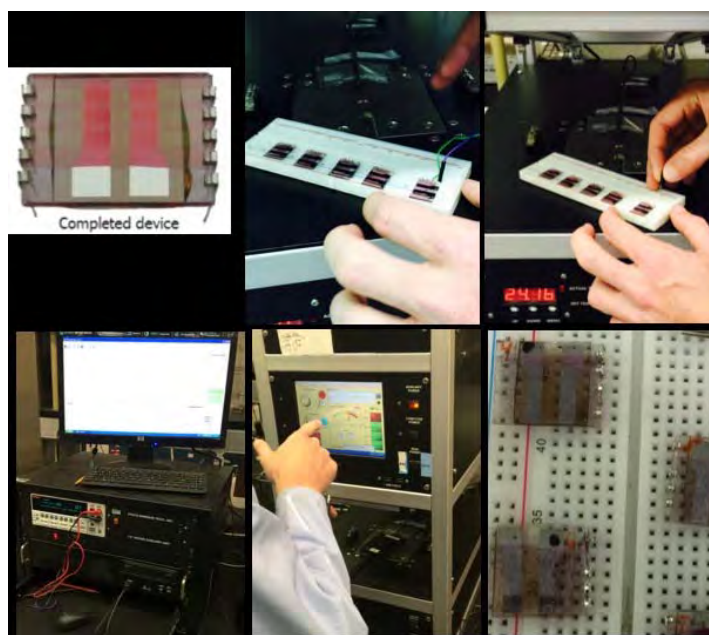
Human lives are made easier and more efficient each day by polymers used in clothing, electronic devices, sporting equipment, and so much more. Research and development of these materials is essential and an ever-growing field of study. Globally in education, increased emphasis is being placed on STEM fields for today's students. Activities are needed that allow students to bridge between STEM fields in order to stress the importance of interdisciplinary collaboration and the use of knowledge and to raise awareness of scientific career opportunities. Physics and polymers are conceptually and literally "cross-linked" in the activity described herein. Sophomore-level college physics students are introduced to polymers and the idea of chemical cross-linking to generate different varieties of polymers. Students create three pre-determined variations of polymers and use the physics of collisions to investigate the impact forces on each of these polymer mixtures. Using digital force probes and graphical analysis software, students will examine graphs like the one shown below in Figure 1 to determine which mixture provides greater protection from impact and propose possible hypotheses that explain the increased protection. Based on these hypotheses, student will design and test their own polymers. Creating such "cross-links" between STEM fields for students ensures better scientists for the future.



POLY 90: Synthesis and characterization of di(perylene bisimides) for use as an electron accepting material in polymer photovoltaic devices

James Brownlow¹, james.brownlow@hattiesburgpsd.com, Turkesa Bullock¹, Levi Moore², Mark Norman², Sarah E. Morgan². (1) CTE, Hattiesburg High School, Hattiesburg, Mississippi, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Organic photovoltaics (OPVs), in contrast to conventional silicon-based solar cells, have the potential to be mass produced at much lower costs through simple methods like spin coating and inkjet printing. However, OPVs exhibit lower efficiencies than conventional cells. Present high-efficiency OPV devices utilize fullerene derivatives as the electron accepting and transport material, which give good performance but have many drawbacks including high cost, narrow light absorption, environmental instability, and poor processability. Our summer research is to improve the performance of polymer photovoltaics through replacement of the current standard fullerene electron acceptor material (PCBM) with new electron accepting materials, di-perylene bisimides (di-PBIs). The research completed will be transformed into a lesson plan for students in the polymers and robotics classrooms. Students will be asked to consider U.S. energy demands, and also to consider how we get this energy today and how we will meet our increasing needs in future. Focusing on solar energy, students will visit a local solar panel company to see how traditional solar cells are manufactured. After contemplating the need for solar power and the limitations of traditional cells, students will make their own organic solar cells, and then they will visit the polymer labs at USM to see how the OPVs were developed and tested. As a culminating activity, students will write our state congressmen to entreat them to continue funding research into alternative energies for Mississippi — especially as it pertains to creating better OPV technologies.

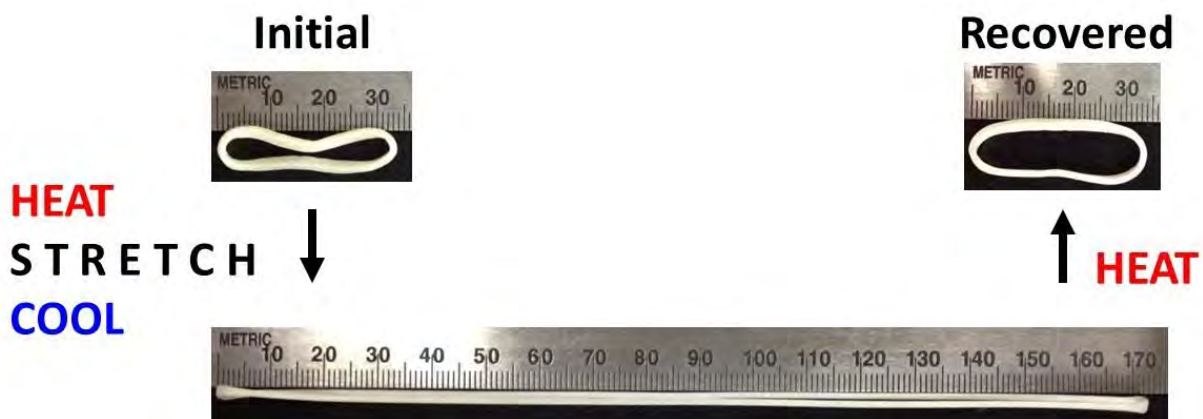


OPV cell testing on the solar simulator

POLY 91: Innovation at the intersection of research and outreach

Kevin A. Cavicchi, kac58@uakron.edu. University of Akron, Akron, Ohio, United States

The Research Experience for Teacher Program at the University of Akron brings teachers to the University for the summer where they take part in research and use this experience to develop a lesson plan for their classroom. This exercise provides an opportunity for innovation as the constraints on chemicals, equipment, and time force outside of the box thinking. This talk will present how participation in outreach have led to new approaches for the fabrication of shape memory polymers and bending actuators. In addition to leading to exciting outreach activities, the potential for these approaches to explore fundamental polymer science and engineering topics will be discussed.



POLY 92: Augmenting primary and secondary education with polymer science and engineering

Rose Cersonsky¹, rosecers@umich.edu, **Leanna Foster**¹, **Ryan J. Hall**¹, **Taeyong Ahn**¹, **Harry L. van der Laan**¹, **Timothy F. Scott**^{1,2}. (1) *Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States* (2) *Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States*

Within state and national science standards, there is a notable scarcity of polymers education in primary and secondary classrooms. To address this, we have developed a graduate student-run initiative that brings free, interactive polymers lessons to Detroit and Ann Arbor area schools. These lessons, in the form of three separate modules, are tailored to the Michigan State Science standards and have proved successful in their applicability across different grade levels. The lessons focus on introducing students to polymer science through real-world examples, experimentation, and higher-level application. We have identified two aims of our program: 1) Introducing polymers education to young students in order to build upon their current science curriculum and 2) Preparing future polymers educators (graduate students) to effectively communicate polymer science to a greater population, and have analyzed our success in these aims through performance analysis and participant surveys.

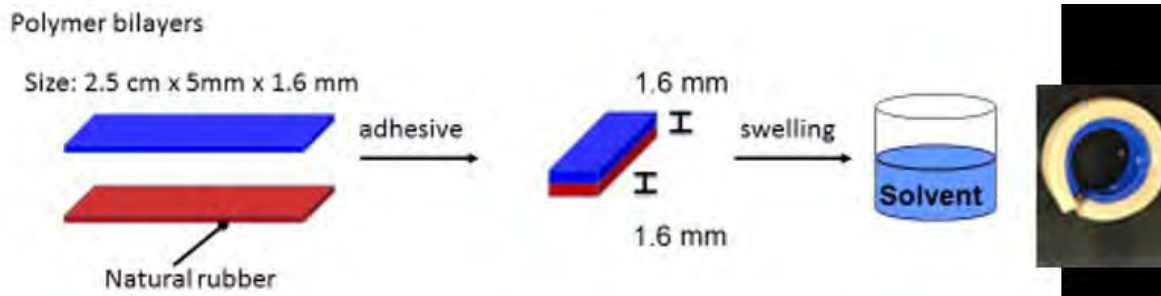


Students enjoy cross-linking white glue with borax solution in our *Recycling and Remanufacturing* module

POLY 93: Polymers inspired by biomimetic bilayers

Kevin A. Cavicchi¹, **Josh Oldham**², oldham13@gmail.com. (1) University of Akron, Akron, Ohio, United States (2) Firestone High School, Akron, Ohio, United States

Self actuating surfaces will respond to external or environmental conditions such as temperature and humidity. An example of this in nature is a pine cone, which will open and close depending on the humidity. This phenomenon occurs due to the composition of the pine cone being comprised of bilayers of different densities. Commercially viable polymer products that automatically respond to environmental conditions are being created. I will present a lesson that discusses polymers inspired by these naturally occurring biomimetic bilayers. This presentation will include activities for student engagement, exploration, and evaluation v of the scientific process.



POLY 94: Are mushrooms the new plastic? Harnessing student design thinking using ecovative materials

Mollie C. Enright, mollie_enright@beyondbenign.org, Kate Anderson. *Beyond Benign*, Wilmington, Massachusetts, United States

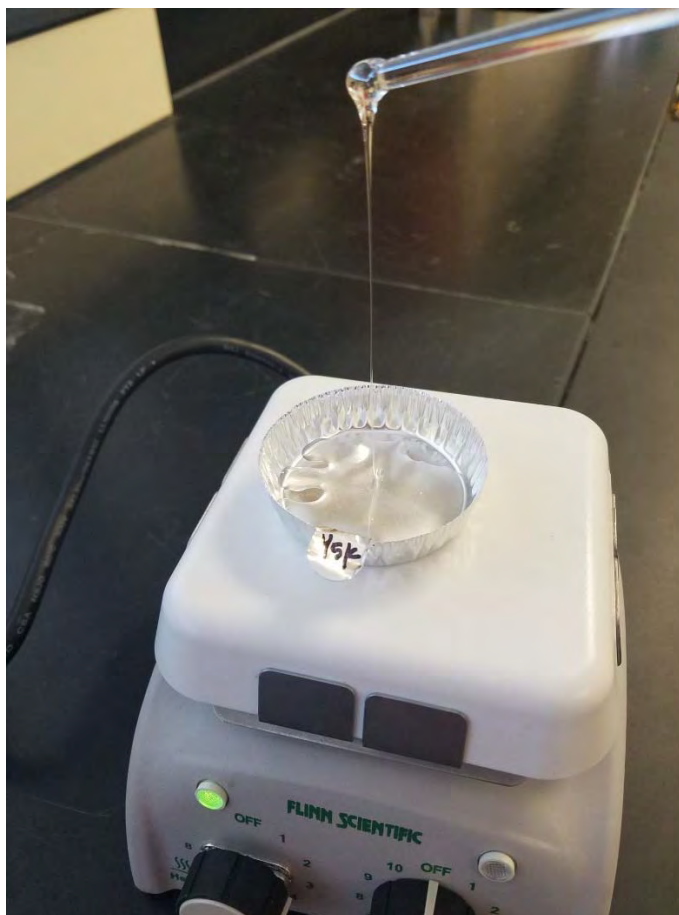
Highlighting industrial examples of sustainable design along with innovative products and processes is one way to engage students and meet the NGSS. Steelcase Inc. is an international office furniture company who is leading the way with innovative sustainable product development. Beyond Benign, Steelcase Inc., and a group of high school chemistry teachers have teamed up to bring unique case studies to life for students through curriculum modules. By asking students “What if we could grow our own packaging?” we invite them to explore Ecovative materials, a polystyrene packaging alternative grown from mycelium and agricultural waste. Students are given the power to create their own products and to design the materials tests to analyze what they’ve made. Learn how this cutting edge technology is serving as a tool to capture the imagination of the next generation of problem solvers. Teachers and students both delight in this interactive and engaging activity that brings these innovative ideas, designs and applications to life.



POLY 95: Exploring polymers in the high school classroom through medical sutures

Cassandra Knutson³, cassandra.knutson@isd624.org, Jane E. Wissinger², Cassidy Javner⁴, Debbie K. Schneiderman¹. (1) Chemistry, University of Minnesota, Magnolia, Minnesota, United States (2) Chemistry, University of Minnesota, Plymouth, Minnesota, United States (3) White Bear Lake High School, White Bear Lake, Minnesota, United States (4) Shakopee High School, Shakopee, Minnesota, United States

The topic of medical sutures (commonly known as stitches) is exploited in an experiment designed to teach high school/introductory college students about the structure and properties of polymers. Commercially available poly(ϵ -caprolactone) of different molecular masses are melted and pulled into threads, mimicking threads of medical sutures. Their tie-ability and strength are then compared to actual medical sutures through the use of simple force probes and degradation testing. The fact that medical sutures can be made of polymers that are non-absorbable and absorbable serves as a platform to discuss non-degradable and degradable plastics in society and efforts to develop more environmentally-friendly materials. This presentation will share the details of this fun and versatile four-part experiment as well as the positive feedback received from teachers and students of classrooms where it was performed.

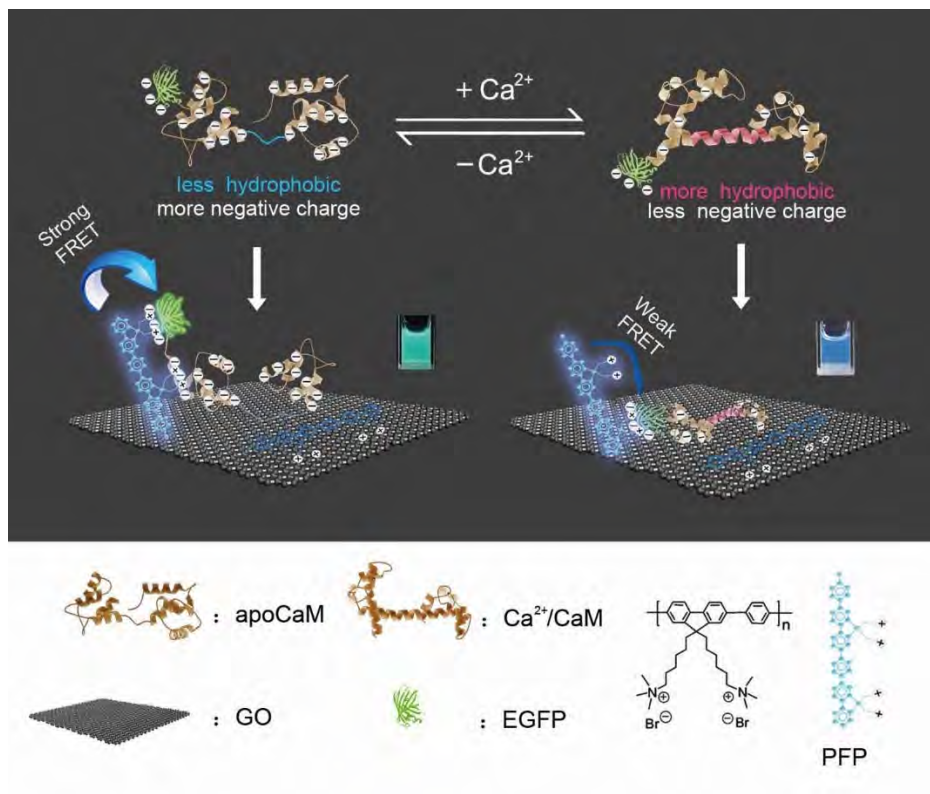


Drawing threads from poly(ϵ -caprolactone)

POLY 96: Graphene oxide-conjugated polymer hybrid materials for protein sensing

Chengfen Xing, *xingc@hebut.edu.cn*. Institute of Biophysics, Hebei University of Technology, Tianjin, China

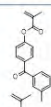
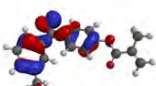
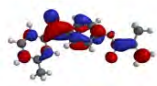
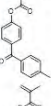
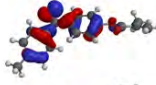
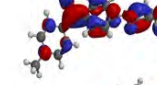
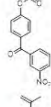
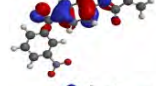
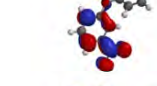
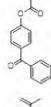

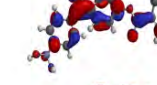
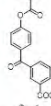
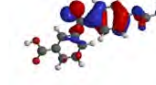
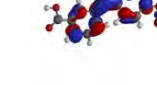
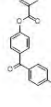
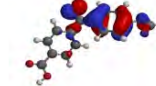
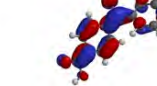
The new functional materials and efficient approaches for protein sensing is promising for understanding the molecular mechanism of signal transduction pathways and developing antagonists for therapy. In our recent study, we have designed and developed a novel and unconventional hybrid material consisting of graphene oxide (GO) and cationic conjugated polymer for detection of the conformation transition of a cellular Ca^{2+} -binding protein of 148 calmodulin (CaM) by using fluorescence resonance energy transfer (FRET) technique. This effort provides first example of how FRET technique can be used with emerging types of graphene oxide and optical functional materials in order to detect CaM and its conformation change not readily obtained otherwise. We also have developed a water-soluble poly(phenylene vinylene) derivative (PPV-NMe₃⁺)-based system to detect and inhibit the HEWL aggregation triggered by UV illumination. PPV-NMe₃⁺ will be of theoretical and practical significance for the better understanding of protein aggregation and provides an efficient strategy to prevent and treat diseases caused by proteins aggregation. This system will produce a profound influence on the future protein drug development, meaningful for the realization of the rapid commercialization of protein drug.



POLY 97: Photo-curable betaine copolymer with high resistance to thrombus and biofilm formation

Zheng Zhang, *waldenzz@gmail.com*, Daniel Wallach, Jun Li, Mathew Taylor, Angela Roussell, Victoria Wagner. Teleflex Medical, Cambridge, Massachusetts, United States

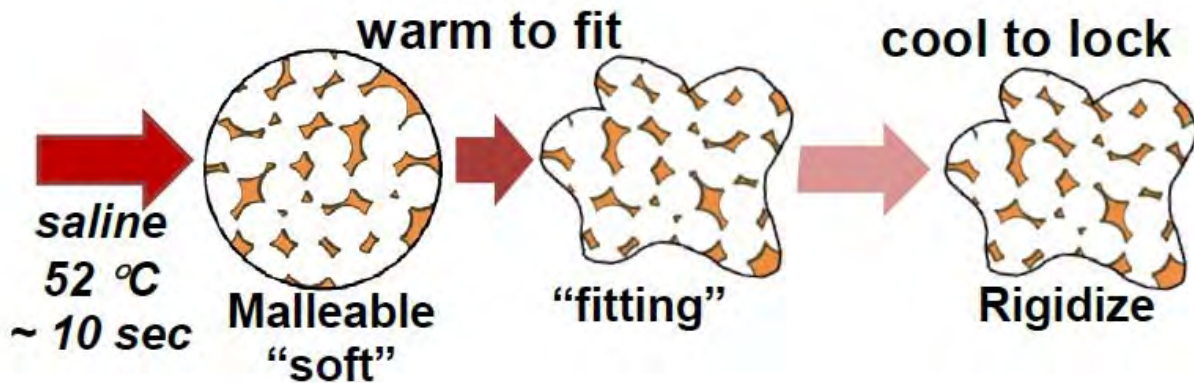
This study synthesizes a series of photo-reactive betaine copolymers, and investigates their performance as coatings to reduce medical device infection and other device-associated complications. Derivatives of benzophenone methacrylate (BPMA) containing either electron-withdrawing groups or electron-donating groups at different positions were synthesized. The photoactive derivatives were copolymerized with sulfobetaine methacrylate (SBMA) with different concentration. The copolymers were characterized and their photo-reactivity was evaluated with UV-Vis spectrometer as a function of UV dosage. As applied on polyurethane substrates and exposed under UV, the surfaces were evaluated by ATR-FTIR and XPS. The coating stability was evaluated by hydrolytical and oxidative aging tests. Copolymers containing BPMA derivatives with carboxy-, nitro-, and methyl groups, while all present higher photo-reactivity, exhibit different surface performance as applied on the surfaces. Betaine groups that provide a charged environment may contribute to the hydrogen abstracting of the BPMA moieties. The coated substrates were evaluated with radio-labelled protein adsorption assay. A coating formulation were developed that reduce 100% thrombus formation with a blood loop thrombus assay. Performance of biofilm resistance of the coating is also evaluated with a few clinical-related bacteria strains.

| Monomer | Structure | HOMO | LUMO | HOMO→LUMO (eV) |
|---------|---|---|--|----------------|
| 3'-MMB |  |  |  | 4.7 |
| 4'-MMB |  |  |  | 4.7 |
| 3-NMB |  |  |  | 4.3 |
| 4-NMB |  |  |  | 4.3 |
| 3'-CMB |  |  |  | 4.7 |
| 4'-CMB |  |  |  | 4.6 |

POLY 98: Self-fitting scaffolds based on PCL-PLLA semi-IPN Shape Memory Polymers (SMPs)

Melissa Grunlan, *mgrunlan@tamu.edu*, Lindsay L. Woodard, Vanessa M. Page, Kevin T. Kmetz. *Biomedical Engineering, Texas AM University, College Sta, Texas, United States*

We have previously described a shape memory polymer (SMP) scaffold having the capacity to conformally “self-fit” into irregular bone defects and improve healing. This scaffold was based on poly(ϵ -caprolactone-DA) (PCL-DA) whose shape may be actuated by a transition temperature have shown utility for a variety of biomedical applications. Important to their utility is the ability to modulate mechanical and degradation properties. Thus, in this work, SMPs are formed as semi-interpenetrating networks (semi-IPNs) comprised of a cross-linked PCL diacrylate (PCL-DA) network and thermoplastic poly(L-lactic acid) (PLLA). The semi-IPN uniquely allows for requisite crystallization of both PCL and PLLA. The influence of PLLA (PCL:PLLA weight % ratio) and PCL-DA molecular weight (n) on film properties are investigated. PCL-PLLA semi-IPNs are able to achieve enhanced mechanical properties and accelerated rates of degradation.



SMP scaffolds based on PCL-PLLA semi-IPNs self-fit into irregular bone defect.

POLY 99: Effects of gel mass age on critical process parameters of soft gelatin capsule encapsulation

Mallik Karamsetty, *mallik.karamsetty@pfizer.com*, Ray Lau. Pfizer Consumer Healthcare, Richmond, Virginia, United States

Typically gel mass (mixture of gelatin, plasticizer and water) is manufactured and held between 2 to 96 hours prior to encapsulation of soft gelatin capsules. This study was designed to understand the effects of aging gel mass on the critical process parameters like capsule weight and wedge temperature required to obtain optimal seals.

Gel mass was manufactured and held for four different time periods – 2, 5.5, 10.75 and 25.5 hours. Slugs (empty soft gelatin capsules) were manufactured using this gel mass. It was observed that as gel mass ages; the slug weight decreases (Figure 1). It was also observed that wedge temperature needed to obtain optimal seals is decreased with matured gel mass.

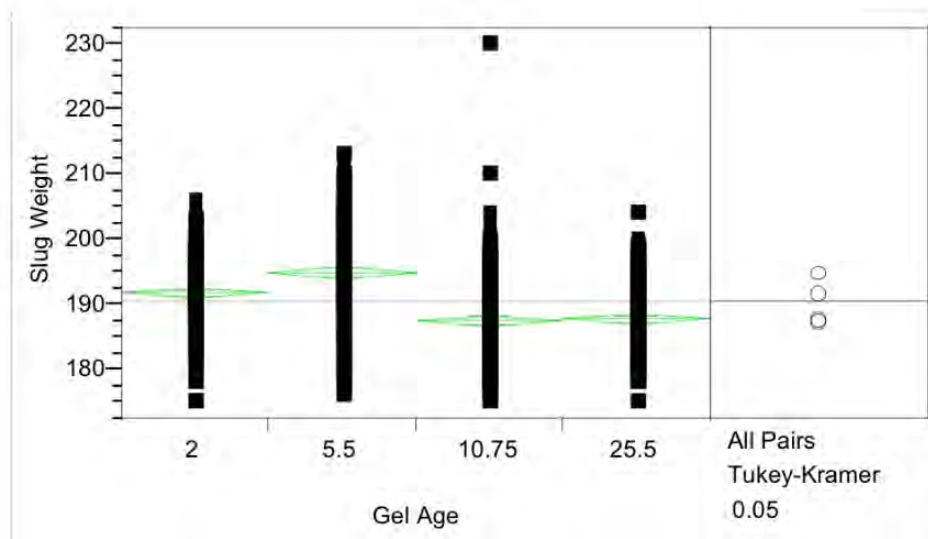
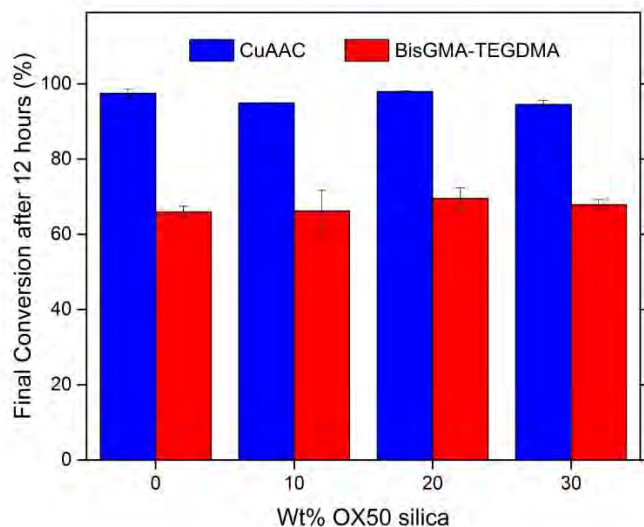


Figure 1. Effects of Gel age (in hours) on slug weight (in mg)

POLY 100: Photo-CuAAC applications in dental restorative materials

Bassil El-Zaatari¹, bassil@udel.edu, **Abhishek Shete**³, **Christopher J. Kloxin**^{2,3}. (1) *Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States* (2) *Dept of Chemical Engineering, University of Delaware, Newark, Delaware, United States* (3) *Materials Science and Engineering, University of Delaware, Newark, Delaware, India*

Tooth decay is the most prevalent chronic disease in the United States where over one hundred million dental restorations are performed annually. These dental procedures typically utilize photopolymerizable composites based on dimethacrylate chemistries, specifically bisphenol A-glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA). This chemistry has remained in use despite key limitations where the system suffers from low final double bond conversions (only up to 55 - 75%) as well as undesired side reactions which can lead to polymer shrinkage, mechanical wear, and degradation, which has been shown to promote bacterial growth, and shortens the overall lifetime of dental materials. To enhance the durability and longevity of dental composite materials, we propose the use of a photopolymerizable click reaction. Click reactions are selective, high yielding, and occur under mild reaction conditions. The photoinduced copper(I) catalyzed azide—alkyne cycloaddition (CuAAC) reaction is a potential replacement for the currently used dimethacrylate system. Towards this goal, I will demonstrate the suitability of this reaction in dental materials. The synthesis of various CuAAC composites using different loadings of silica with various functional groups has been performed and the composites show similar mechanical properties to that of the methacrylate system used in dental materials. Moreover, the current polymerization schemes are completely compatible with dental lamps, where the reaction can be initiated under blue light. Importantly, we demonstrate that the polymerization kinetics have been better understood and enhanced, and the final conversion of the reaction increased to over 95%.



POLY 101: All-organic conductive fabrics for continuous monitoring of Electrocardiogram (ECG) response

Gregory A. Sotzing, *g.sotzing@uconn.edu*. Chemistry, University of Connecticut, Storrs, Connecticut, United States

The conductive polymer, poly(3,4-ethylenedioxy)thiophene-polystyrene sulfonate (PEDOT-PSS) reacts with delustering agents such as silica in synthetic fabrics to induce a phase segregation enriching the surface to air interface with PEDOT providing sheet resistances down to 1 ohm/sq. This procedure provides a means for permanent affixation of PEDOT-PSS to the textile surface providing it stability to mechanical abrasion. PEDOT-PSS was screen printed onto a compression shirt for continuous monitoring of ECG while running on a treadmill up to a heart rate of 160 bpm. Here, we explore the effect of changing the redox potential, and the impedance of the PEDOT and the effect this has on the ECG amplitude. Impedance trends of the individual chemical components of sweat will be analyzed, and an analysis of the performance of PEDOT-PSS coated fabrics to monitoring ECG in the dry, dry with gel, wet, and underwater submersion in tap, chlorinated, and salt water will be presented. Conductive polymer coated fabrics approximately maintain the feel of the original fabrics, and could provide comfort with continuous ECG monitoring. Further, these conductive polymer coated fabrics would not induce skin irritation and may provide an alternative to ECG monitoring over prolonged periods of time and under high-sport activity.

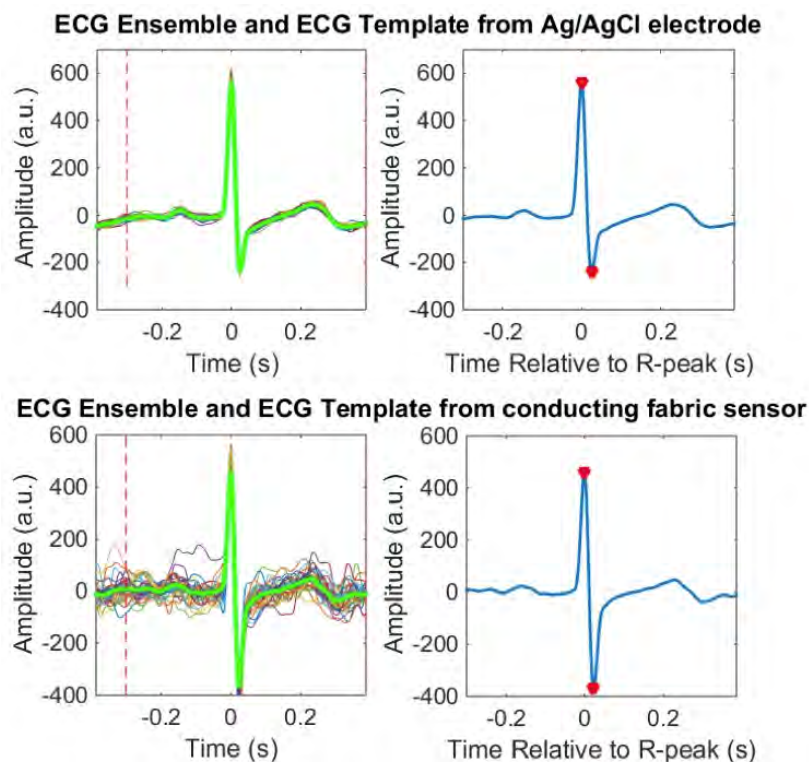


Figure: A side-by-side comparison of ECG response using a commercial Ag/AgCl electrode and a PEDOT-PSS coated 4-way spandex.

POLY 102: Polymer materials in medical devices: Addressing issues through material testing and failure analysis

Stephanie J. Benight, sbenight@gmail.com. *Polymer Science and Materials Chemistry, Exponent, Inc., Menlo Park, California, United States*

Polymer-based materials, such as plastics and adhesives, are used in a range of medical devices from implantable devices to surgical tools to wearables. In general, polymer-based materials offer advantages such as cost and weight savings, ease of processability, resistance to corrosion, and biocompatibility in some cases. However, in the context of sophisticated device architectures and various end-use conditions, polymeric materials can display unforeseen issues. To determine what may have gone wrong, a variety of methods can be employed to perform failure analysis and understand why certain polymer materials did not perform as expected. Often times, carrying out accelerated aging tests to understand how polymer materials may change over a targeted shelf life is insightful and useful in supporting FDA submissions. In this talk, some methods utilized in carrying out failure analysis involving polymeric materials will be discussed. Microscopy, materials characterization methods, and analytical chemistry techniques can be employed and are often valuable tools to understand plastics material failures, the chemical compatibility of adhesives, and to determine whether contamination is present. Some case study examples will be discussed.



POLY 103: Polymers at interfaces

Thomas P. Russell, russell@mail.pse.umass.edu. Univ of Massachusetts, Amherst, Massachusetts, United States

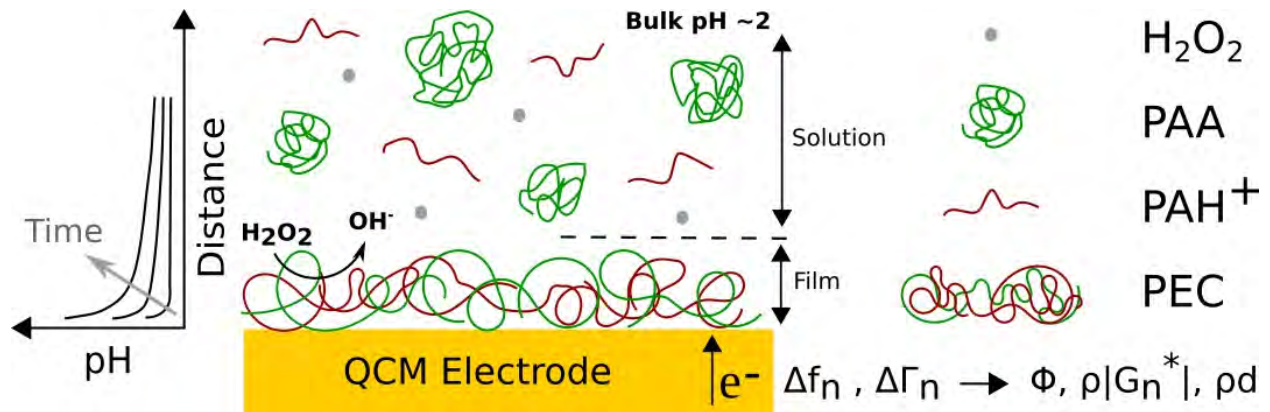
An interface defines the boundary between two disparate materials. Yet, for many applications, how long chain polymers behave at an interface is crucial. Whether or not multi-layered structures can be produced, depends on the adhesion of the polymers at the interface, i.e. the interfacial interactions and mixing at the interface. In organic electronic devices, charges must be transported across an interface between an organic polymer and an inorganic conductor. Consequently, the work function of the polymer and inorganic must be balanced which can be achieved by the surface modification of the inorganic. Similarly, with composite materials, where an organic or inorganic filler is added to a polymer, how the filler interacts with the matrix polymer, i.e. the interfacial interactions, is key in determining whether enhancements in the mechanical, optical or conductive properties are achieved. In thin films of multicomponent systems, the preferential interactions of the different polymer with a substrate or differences in the surface energies of the components are key in controlling orientation in block copolymer microdomains or propagating a morphology into the bulk of the film. While enthalpic interactions between polymers and interfaces are important for the topics mentioned above, the long-chain nature of a polymer molecule and the packing of the polymer at the interface introduces the importance of entropy which can dictate the orientation or morphologies in block copolymers. Interfaces can, also, be responsive to external stimuli. In this presentation we will discuss how interfacial interactions have been used to control and manipulate polymers and multi-component polymer systems to enhance performance.



POLY 104: Deposition, mechanics and phase behavior of polyelectrolyte complex films

Kenneth R. Shull, *k-shull@northwestern.edu*. Northwestern Univ, Evanston, Illinois, United States

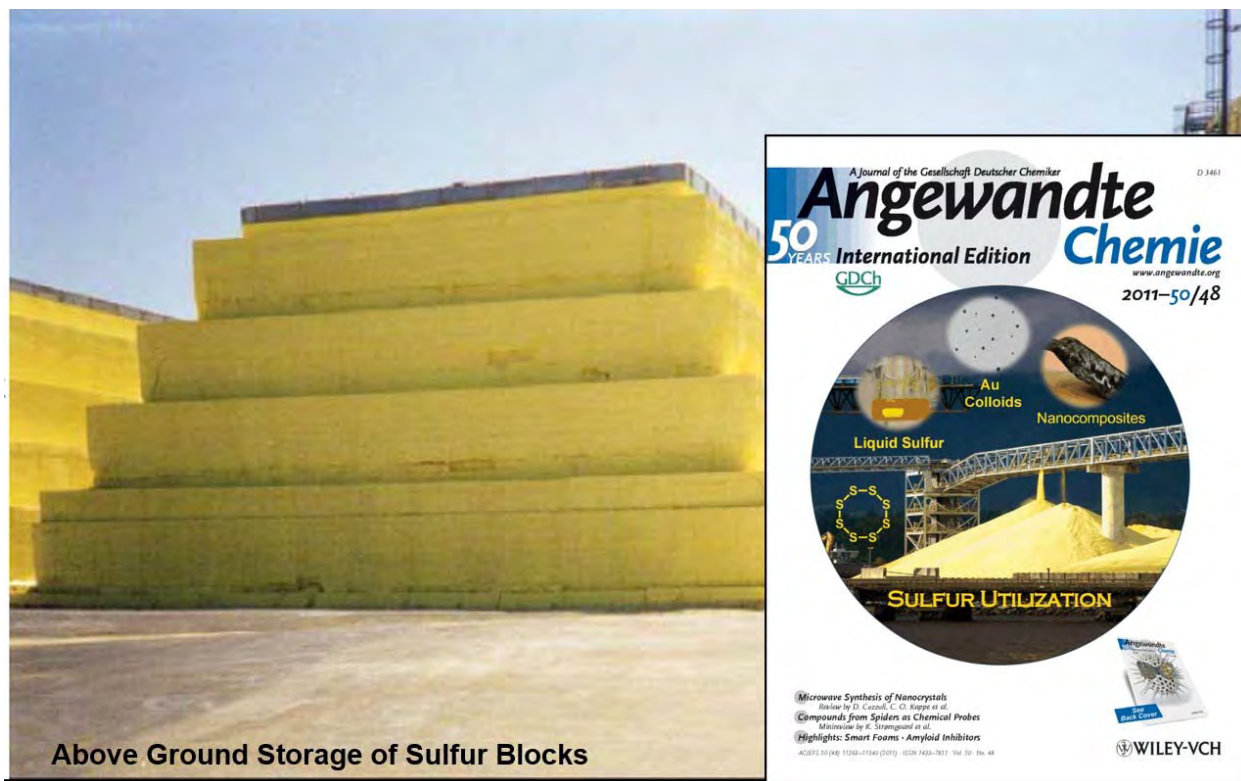
Complexes formed from oppositely charged polymers are relevant in a range of applications ranging from water purification to biomedical implants. This talk is an overview of some of our work in this area, much of which involves uses of the electrochemical quartz crystal microbalance (eQCM). When correctly applied, the quartz crystal microbalance behaves as a fixed-frequency rheometer, able to quantify the viscoelastic response of the material at 15 MHz with a precision that rivals that obtained with conventional, low frequency shear rheometry. A variety of examples involving the use of this technique to study material interfaces in the presence of charged polymers will be discussed.



POLY 105: From industrial wastes to functional materials: Hybrid materials based on sulfur

Kookheon Char, *khcharxxx@snu.ac.kr*. School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of)

With ever-increasing human population, depleting natural resources, and rapid climate change confronting humanity, the role of chemistry is becoming more crucial in addressing these issues and establishing systems for sustainable growth. Herein, recent efforts in our research center (National CRI Center for Intelligent Hybrids), utilizing both organic and inorganic material design and synthesis, to address key issues to such an end are described. We have established novel chemical methods for the direct utilization of elemental sulfur. More than seven million tons of elemental sulfur are produced in excess each year and are stockpiled in landfill-like deposits in remote areas. Sulfur and sulfur-containing materials exhibit a variety of desirable properties ranging from high electrochemical capacities to high refractive indices, which are of high interest from both industrial and academic perspectives. Useful conversion of such industrial wastes into functional materials in processible forms, through novel chemistry, for key applications such as Nexgen Li-sulfur batteries, thermal IR imaging, and high refractive optical systems will be introduced.



POLY 106: Self-organization in materials science: From quantum dot LEDs to mechanical actuators

Rudolf W. Zentel, zentel@uni-mainz.de. Chemistry, University Mainz, Mainz, Germany

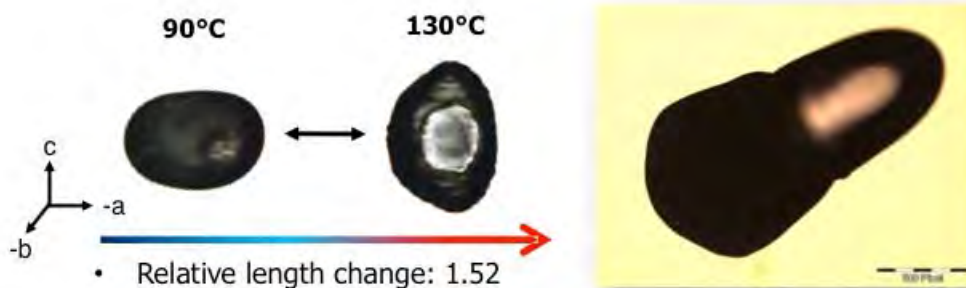
Self-organization allows the tuning of many properties in materials science. Here I will focus on two aspects. The first is the formation of a polymer corona from conducting polymers around a fluorescent quantum dot. These inorganic/organic hybrids can be used for the preparation of quantum dot LEDs and allow a homogeneous dispersion of the quantum dots in a polymer matrix. Recent studies demonstrate the superior properties of these hybrid systems.

The alternative self-organized structures are liquid crystalline elastomers (LCEs), which are used as artificial muscles. To improve the applicability of these systems two points are crucial. On one hand it would be attractive to induce complex director pattern into the sample to allow complex deformation and secondly it gets important to control the deformation at the transition quantitatively to allow a controlled gradual transition. This requires a local control of the temperature.

Here two examples will be presented. By aligning the monomeric LC-precursor in a radial magnetic field LCEs, which act like an artificial iris can be prepared. The incorporation of heating wires into the material allows it to preset a very controlled actuation.

If a multitude of small actuating samples is the goal, microfluidics is the method of choice. Here the flowing conditions in micrometer-sized channels can be used to induce an ordered director field in the liquid crystalline material. This concept could be demonstrated in previous publications. Thereby it gets possible to prepare micrometer-sized actuators with different shapes, ranging from spheres to disks to highly shape anisotropic fibers.

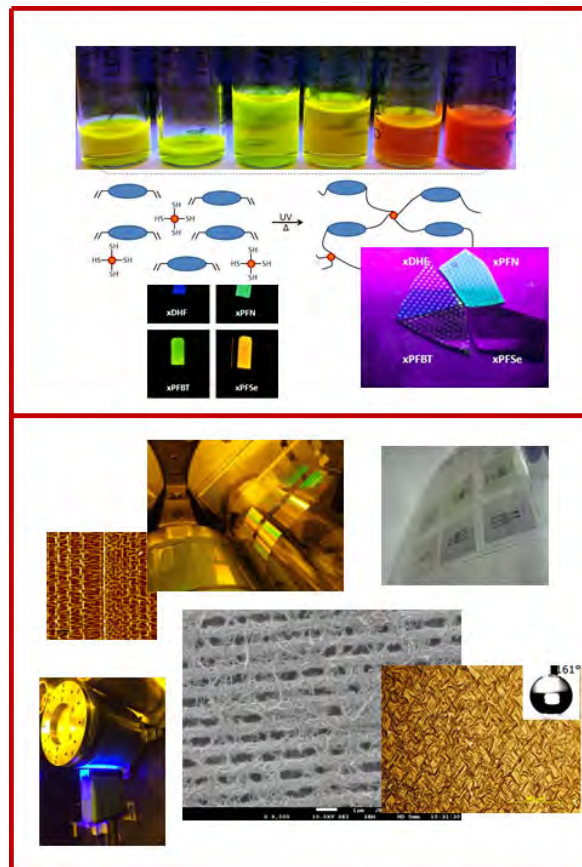
Concerning more complex actuators, we succeeded recently in the fabrication of one-piece micropumps from liquid crystalline core-shell elastomers via a microfluidic double-emulsion process. Also Janus-particles with one actuating part get accessible in this way.



POLY 107: Synthesis and fabrication of functional polymer thin films

Kenneth R. Carter, krcarter@polysci.umass.edu. A416, UMASS, Amherst, Massachusetts, United States

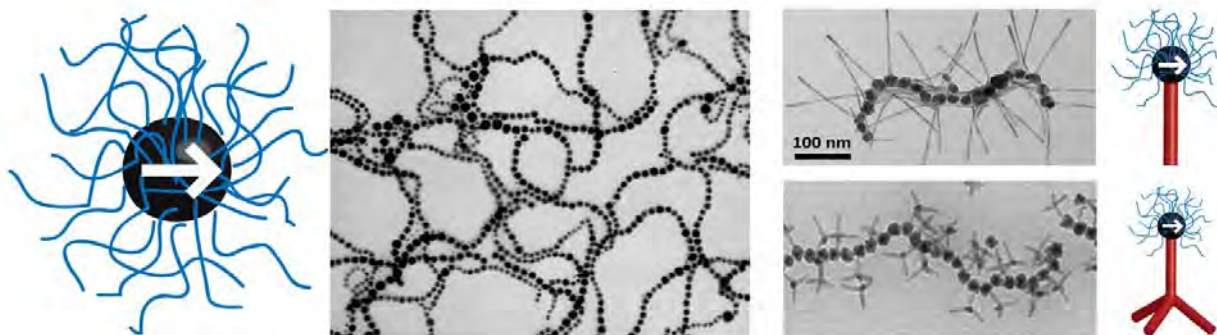
The core of our work involves gaining a detailed understanding on how to precisely control functionality and performance of materials over multiple length scales. Polymeric materials have found widespread use over the last century due to the ability to design structures with a wide variety of properties. To exploit all of this potential what is needed is a systematic way to develop materials with specified properties by controlling structure, chemistry and shape at the nanoscale – effectively placing active materials where they are needed. Through a combination of synthetic polymer chemistry and high resolution fabrication techniques, we are able to create materials that serve advanced applications by controlling both functionality and shape over a wide range of length-scales (nm – mm). Specific research project within the group include: (1) the synthesis and design of electrical and optically active polymers e.g. FETs, PLEDs, memory and photovoltaics; (2) modification of surfaces with polymers –we tailor surface functionality through coating including grafting reactions as well as the growth of dense polymer brush layers on flat and particle surfaces; and (3) imprint lithography of polymers and organics, where we work on enabling materials and processes that allow unprecedented control of size and shape and design processes that are ultimately useful in real manufacturing environments, including roll-to-roll fabrication.



POLY 108: From polymers to particles and back to polymers

Jeffrey Pyun^{2,4}, jpyun@email.arizona.edu, **Nick G. Pavlopoulos**³, **Nicola Pinna**⁵, **Kookheon Char**¹. (1) Seoul Natl Univ Sch Chem Eng, Seoul, Korea (the Republic of) (2) University of Arizona, Tucson, Arizona, United States (3) Chemistry and Biochemistry, university of Arizona, Tucson, Arizona, United States (4) School of Chemical & Biological Engineering, Seoul National University, Tucson, Arizona, United States (5) Chemistry, Humboldt University, Berlin, Germany

We will discuss our recent efforts to prepare polymer nanoparticle composite materials that polymerize to form mesoscopic polymeric materials, termed, colloidal polymers. In the past decade, we have investigated the preparation of self-organizing nanoparticles (i.e., colloidal monomers) that are capable of forming micron sized colloidal polymers via magnetic dipolar associations. We will discuss our efforts to prepare functional colloidal monomers of these materials and colloidal polymerization to prepare a new family of complex mesoscopic materials. In particular, we will discuss the novel synthetic methods required to prepare new colloidal monomers based on semiconductor nanocrystals that can be selectively functionalized with dipolar cobalt nanoparticle “tips” to enable the formation of colloidal polymers with semiconductor nanocrystal side chains. [figure 1]

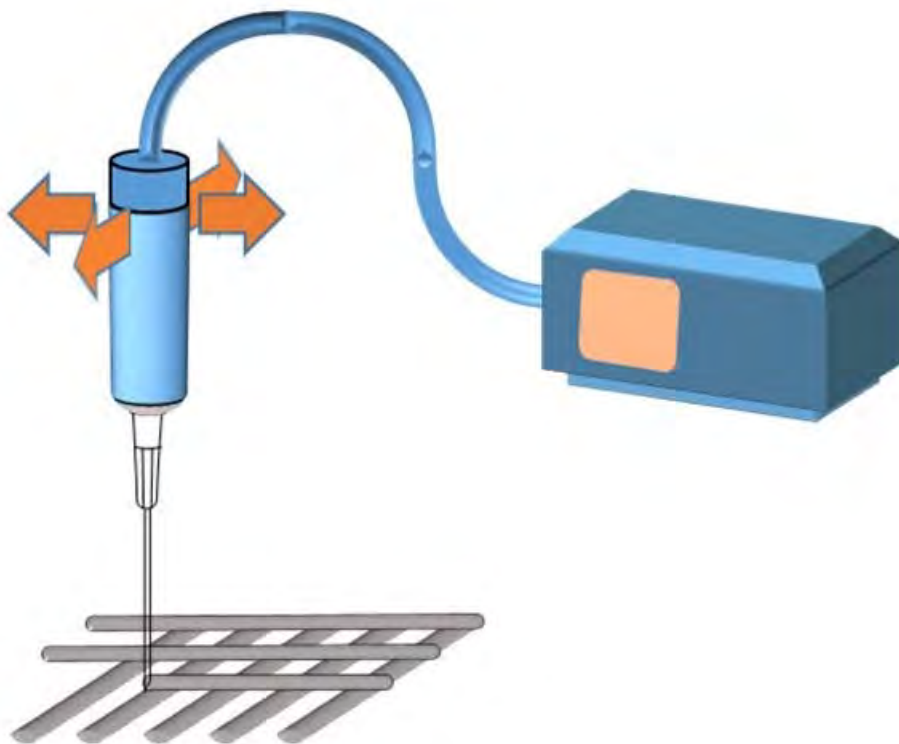


Colloidal Polymers from Nanoparticle Monomers

POLY 109: Multi-stimuli-responsive inks for 3D printing

Alshakim Nelson, alshakim@uw.edu. Chemistry, University of Washington, Seattle, Washington, United States

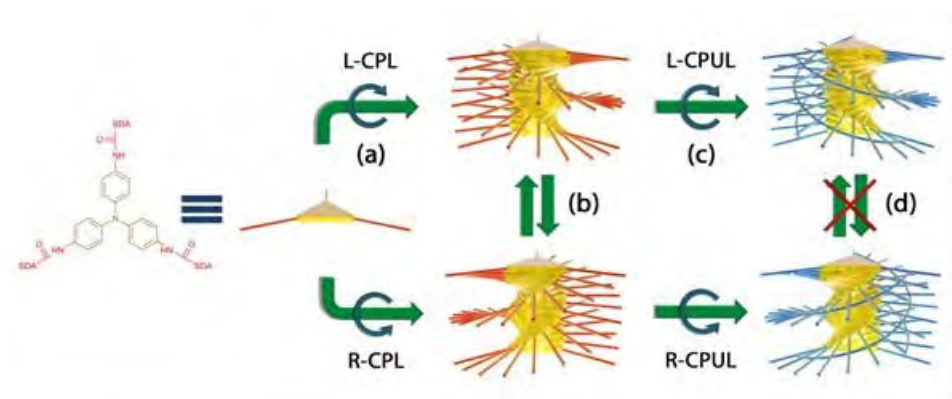
Additive manufacturing (or 3D printing) has re-emerged into the spotlight in the last 5 years driven by the rapid progress in hardware and software. Despite these advances, new materials are required to meet the demands of emerging technologies. Herein, we present a multi-stimuli-responsive hydrogel for direct-write 3D printing. These materials are reversibly stimuli-responsive to temperature and pressure, and can ultimately undergo UV-initiated cross-linking. The syntheses, characterization, and patterning of these materials will be presented.



POLY 110: Light-induced self-assembly of achiral molecules containing triphenylamine for supramolecular chirality and chiral polymers

Sang Y. Kim, kimsy@kaist.ac.kr. Dept of Chemistry, KAIST, Daejeon, Korea (the Republic of)

Evolution of supramolecular chirality from self-assembly of achiral compounds and control over its handedness is closely related to the evolution of life, and development of supramolecular materials with desired handedness has been a very challenging issue. We have demonstrated that the entire process of induction, control, and locking of supramolecular chirality can be manipulated by light. Combination of triphenylamine (TPA) and diacetylene (DA) moieties in the molecular structure allowed photoinduced self-assembly of the molecule into helical aggregates in a chlorinated solvent by visible light and covalent fixation of the aggregate via photopolymerization by UV. Simply by employing circularly polarized light (CPL) as a light source in the self-assembly process of a TPA-containing molecule, we show that self-assembled aggregates with supramolecular chirality can be generated, driven by the helical stacking of the TPA moieties. Our data suggests that the chiral bias generated by irradiation of the TPA moiety with CPL is amplified by the self-assembly process, which promotes enrichment of one enantiomer by the enantioselective helical stacking and forms aggregates with specific handedness. The handedness of the aggregates is exclusively dictated by the rotational direction of the CPL and can even be switched in a totally reversible fashion. Furthermore, by incorporating a diacetylene moiety that undergoes topochemical photopolymerization by UV (254 nm), we demonstrate that the desired handedness can be permanently locked by circularly polarized UV light (CPUL) irradiation, which knits the self-assembled structure with covalent bonds.



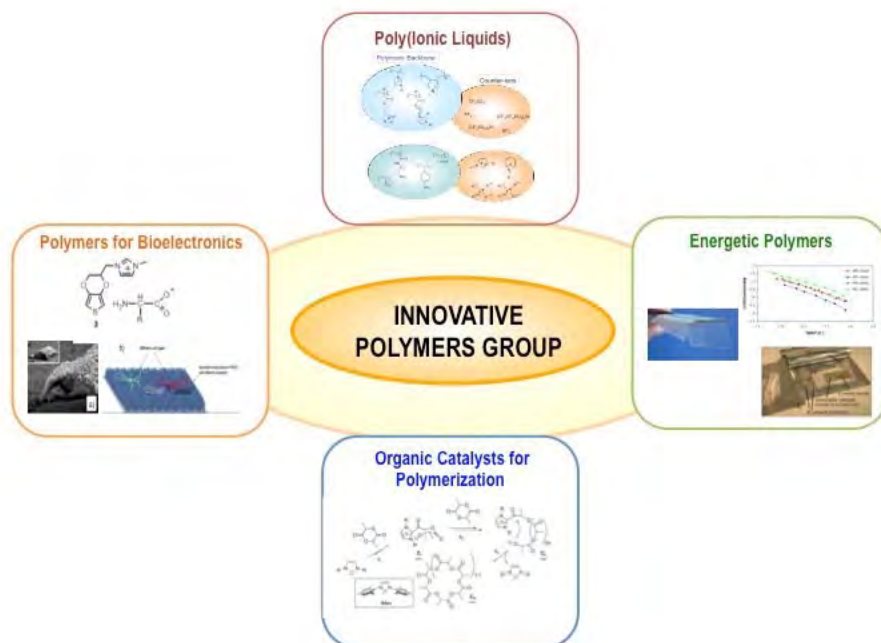
Induction, control, and locking of supramolecular chirality by circularly polarized light

POLY 111: From Almaden to Donostia: A trip from polymer brushes and self-crosslinking nanoparticles to poly(ionic liquid)s

David Mecerreyes, *david.mecerreyes@ehu.es*. POLYMAT, University of the Basque Country, Donostia-San Sebastian, Gipuzkoa, Spain

The properties and classical applications of polyelectrolytes are being outspreading in the last years by the introduction of new ionic moieties (cations and anions) into the polymeric backbone. These new ionic moieties are being developed due to the scientific and technological interest in the field of ionic liquids and for this reason, some of the new polyelectrolytes are being named polymeric ionic liquids (PILs). Examples are found in the figure including polycations and polyanions having i.e. new cations; imidazolium, pyridinium, guanidinium, pyrrolidonium and anions including tetrafluoroborates, hexafluorophosphates, triflates, amidotriflates, and carboxylates. In the last few years, those innovative polyelectrolytes have been finding a wide range of applications in different technological fields such as polymer electrolytes for batteries, electrochromic devices, biosensors, solar cells, gas membranes, anion sensitive block copolymer micelles and materials for water purification.

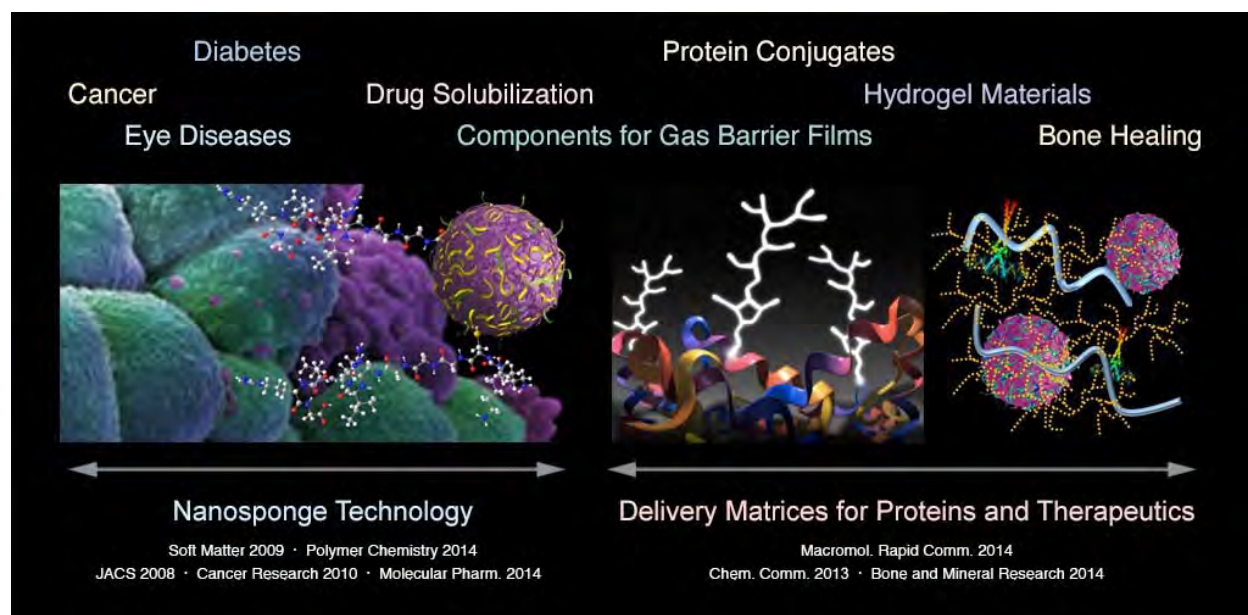
In this presentation, we will review the recent developments in the synthesis and application of new poly(ionic liquid)s by introducing the author's recent work and his perspectives for the field. The 15 years journey from Almaden times as a post-doc working with polymer brushes and self-crosslinking nanoparticles through his activities in Innovative Polymers Group at POLYMAT- University of the Basque Country will be summarized.



POLY 112: Research frontiers of the IBM Research Center as inspiration for the design of biological active materials

Eva Harth, eva.m.harth@vanderbilt.edu. Vanderbilt Univ, Nashville, Tennessee, United States

This lecture will exhibit the impact research opportunities at the IBM Almaden Research Center can have for an academic career. The work on the interface of polymer chemistry and materials science has been fundamental to design polymer based systems that are prepared from tailored building blocks to be then transformed into defined nano- or microsized structures. Controlled crosslinking reactions have been developed to produce precise nanosized materials as crucial additives in the production of low-dielectric constant materials at IBM and inspired nanoparticles from two component crosslinking reactions for applications in biomedical engineering. Furthermore, the combination of linear and semibrached building blocks has been applied in the use as dual drug delivery matrices in which light induced crosslinking and oxime chemistry one of the factors for injectable and implantable materials.



POLY 113: Variable temperature ROMP: Achieving targeted molar mass and low dispersities from low ring-strain monomers

*William J. Neary, **Justin G. Kennemur**, kennemur@chem.fsu.edu. Chemistry & Biochemistry, Florida State University, Tallahassee, Florida, United States*

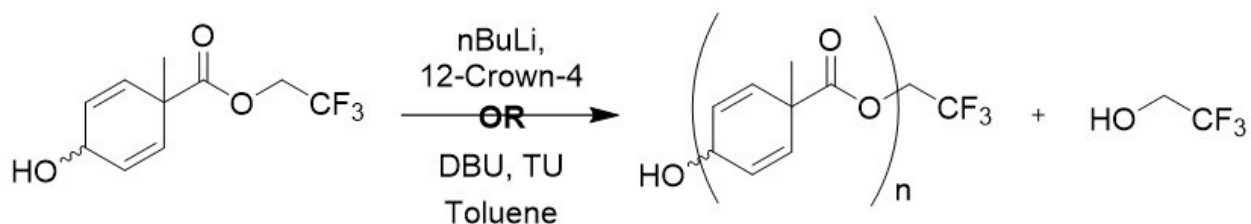
Due to equilibrium polymerization thermodynamics, low ring-strain cycloalkenes, such as cyclopentenes, require lower temperatures to achieve high conversions through ring-opening metathesis polymerization (ROMP). As a result of this requirement, many common ruthenium-based ROMP catalysts suffer a reduced performance in initiation kinetics at these lower temperatures: leading to higher dispersities and molar masses higher than theoretical. Furthermore, deleterious effects to sample dispersity from rate of cross-metathesis is also sensitive to temperature. We will discuss our findings that careful manipulation of the reaction conditions throughout a ROMP can overcome these limitations to afford both high conversion and low dispersity while retaining molar masses that are close to targeted. This universal approach is then shown to be applicable to other low ring-strain monomers.



POLY 114: Synthesis and characterization of aromatizing polyester

Wontae Joo¹, wtjoo864@gmail.com, Austin Lane², Di Liu¹, Kensuke Matsuzawa², Ryan A. Mesch¹, Wade Wang², Benjamin Cassidy¹, Andrew dick², Scott T. Phillips³, Carlton G. Willson². (1) Chemistry, The University of Texas at Austin, Austin, Texas, United States (2) Dept Chem Eng, Univ Texas Austin, Austin, Texas, United States (3) Pennsylvania State University, University Park, Pennsylvania, United States

Chemically amplified resists (CARs) have played an important role in the advancement of photolithography and indirectly, the advancement of semiconductor technology. The design of CARs is based on photogeneration of acid catalysts that mediate chain reactions. This design offers very high radiation sensitivity but it suffers from the conflict between a requirement for efficient diffusion of the acid catalyst to provide high photosensitivity and the problems of bias, image blur and line edge roughness (LER) that are the direct result of the acid diffusion. The goal of this work is to design a resist has high radiation sensitivity that does not employ a catalyst and therefore, does not suffer from the resolution and LER limitations of the CAR system. The new design exploits “unzipping” polymers that depolymerize upon irradiation such that a single radiochemical event results in breaking many covalent bonds, which provides gain, but the bond breaking is limited to a single chain which limits bias and LER. The key polymer, an aromatizing polyester was successfully prepared by two distinctively different synthetic routes. A cyclic oligomerization side reaction was confirmed by x-ray crystallography and a means to avoid the side reaction was established. A resist formulated from the new polyester blended with m-cresol novolac demonstrates high resolution, high contrast and higher sensitivity than conventional resists under electron beam exposure. The formulation successfully achieves gain without employing a catalyst and it shows promising for the future of this new design for high resolution imaging materials.



Synthesis of Aromatizing Polyester

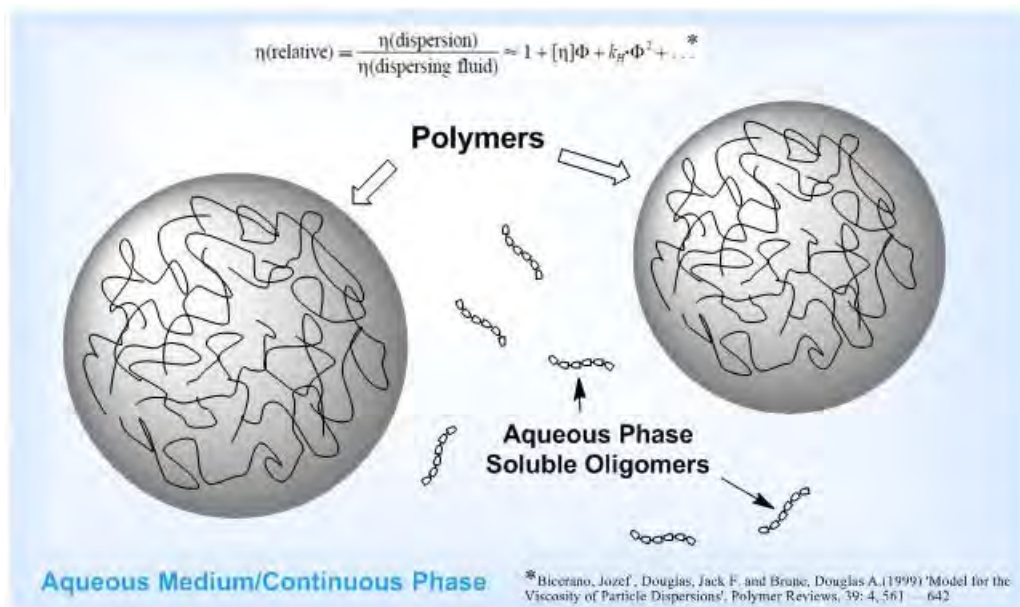
POLY 115: Synthetic approach for reducing viscosity in commercially relevant polymer latexes

Pu Luo², luopu_11@hotmail.com, James Bohling³, Kebede Beshah¹. (1) Dow Chemical Company, Spring House, Pennsylvania, United States (2) Advanced Materials, Dow Chemical Company, King of Prussia, Pennsylvania, United States (3) The Dow Chemical Company, Lansdale, Pennsylvania, United States

Emulsion polymer latexes are gaining increasing market interest in high-performance low-VOC waterborne architectural coatings. Weight fraction (solid concentration) and viscosity are among the most important parameters for commercially relevant solution and colloidal polymer systems. Although very high weight fractions are desired (minimizes the shipping and storage costs, and also broaden the formulation marketability), the polymer latex system must have sufficiently low viscosity to flow.

Molecular weight and temperature are two important factors that influence the viscosity of a solution polymer. However, molecular weight and temperature have much less impact on the viscosity of a latex. For polymer latex, the particle size and particle size distribution are much more important parameters in determining the viscosity of a latex. Additionally, factors such as ionic content can also influence the double layer surrounding latex particles which can affect both viscosity and the stability of a latex.

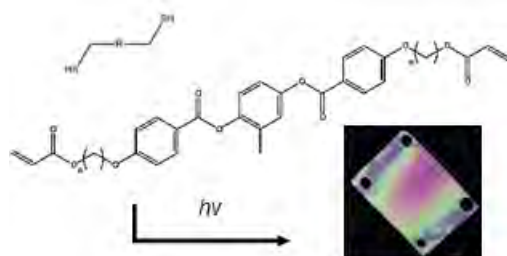
This paper will discuss the impact of variables on the viscosity and stability using a vinyl acetate latex as a model for case study. Potential routes to lowering the viscosity of the latex polymer while maintaining a high weight fraction, will be discussed. Mechanistic validation using state of the art pulsed field gradient diffusion filter NMR technology will also be discussed.



POLY 116: Facile synthesis of robust, photopolymerizable liquid crystal elastomers

Nicholas P. Godman^{1,3}, *nicholas.godman.1.ctr@us.af.mil*, **Anesia D. Auguste**², **Timothy J. White**¹. (1) *Materials and Manufacturing Directorate, Air Force Research Laboratory, Centerville, Ohio, United States* (2) *Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States* (3) *Azimuth Corporation, Beavercreek, Ohio, United States*

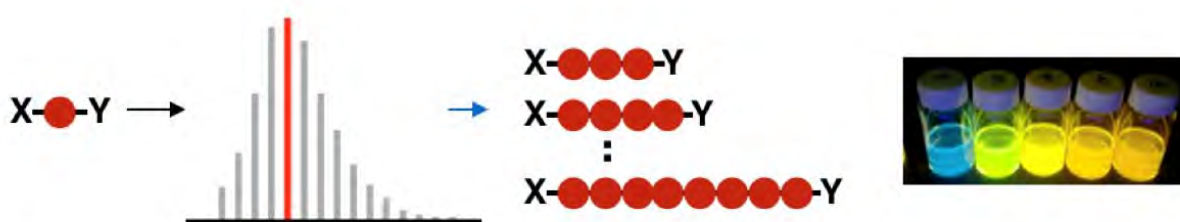
Liquid crystal elastomers (LCE) are loosely crosslinked, anisotropic polymer networks that can exhibit exceptionally large and potentially useful shape changes with applied stimuli. Recent reports have detailed the ability to locally orient the director profile within LCEs and “program” the material for a desired applications, i.e. actuators, dampeners, or sensors. Here, we will detail our efforts in making and improving upon chemistry formulations that are conducive to LCE photoalignment orientation methods. Specifically, we employ a so called “click” reaction between thiols and alkenes to prepare programmable LCEs. A major advantage of the thiol-ene reaction is the ease at which it can proceed: either via radical addition to olefins or through anionic addition to α,β -unsaturated carbonyl compounds. Herein, we explore new thiol-ene formulations targeted at generating more robust LCEs by systematically varying the chain length of the reactive mesogens and the nature of the dithiols employed. The solventless, photochemical methods employed here allows for easy film generation, and improvements to the LCEs strength, toughness, and elasticity based on the change in substituents and polymerization method used will be discussed.



POLY 117: Versatile and general strategy to precision conjugated oligomers (PDI= 1.0)

Jimmy Lawrence⁴, jimmylawrence@gmail.com, Eisuke Goto^{4,5}, Alaina McGrath³, David S. Laitar¹, Paul Clark¹, Craig J. Hawker^{2,4}. (1) The Dow Chemical Company, Midland, Michigan, United States (2) Univ of California, Santa Barbara, California, United States (3) University of California Santa Barbara, Santa Barbara, California, United States (4) Materials, University of California Santa Barbara, Santa Barbara, California, United States (5) Yamagata University, Yamagata, Japan

Due to their statistical chain growth, all synthetic polymers are polydisperse materials containing a distribution of polymer chains of unequal length. This presentation discloses a general strategy to obtain a library of near to truly monodisperse conjugated oligomers in one synthesis-purification step. Facile access to a library of discrete oligomers allow polydispersity tuning and the preparation of artificial mixtures with unique properties.

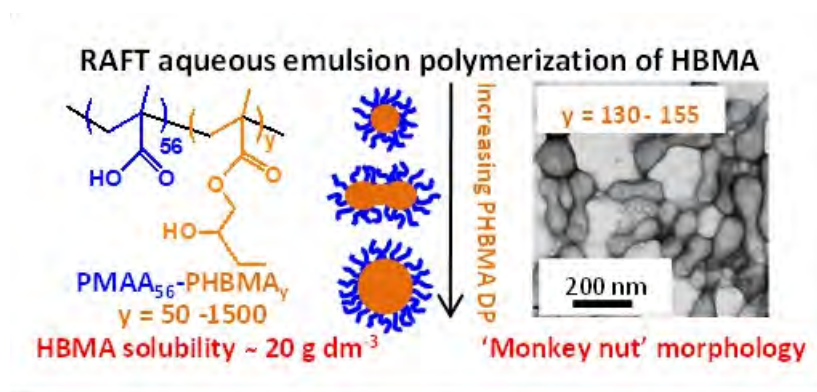


One synthesis & purification step to a library of discrete oligomers

POLY 118: Effect of monomer solubility on the evolution of copolymer morphology during polymerization-induced self-assembly in aqueous solution

Amy A. Cockram³, acockram1@sheffield.ac.uk, Thomas J. Neal³, Matthew J. Derry⁴, Oleksandr Mykhaylyk², Neal S. Williams⁵, Martin W. Murray⁵, Simon N. Emmett⁵, Steven P. Armes¹. (1) Univ of Sheffield Dept of Chem, Sheffield, United Kingdom (2) University of Sheffield, Sheffield, United Kingdom (3) Chemistry, University of Sheffield, Sheffield, United Kingdom (4) Department of Chemistry, University of Sheffield, Sheffield, United Kingdom (5) Decorative paints, AkzoNobel, Slough, United Kingdom

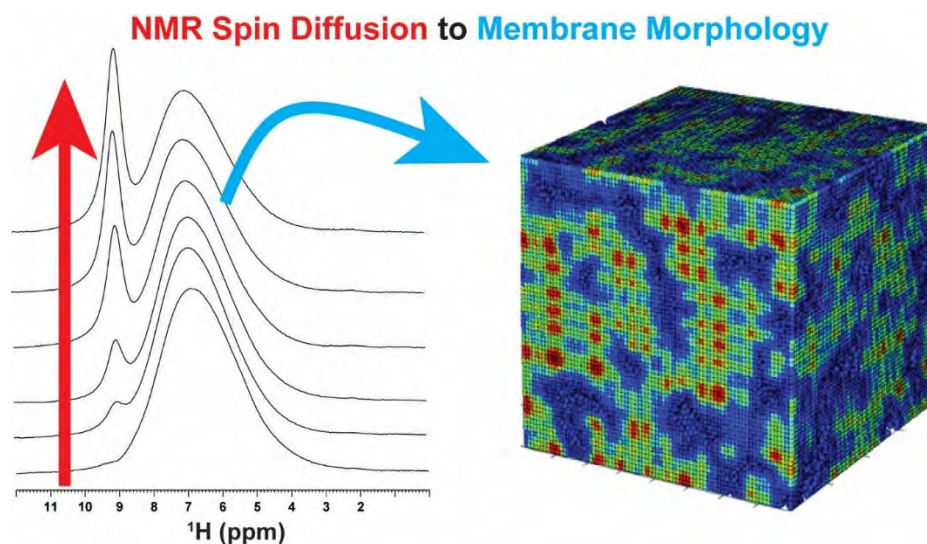
Polymerization-induced self-assembly (PISA) has become a widely-used technique for the design of diblock copolymer nano-objects in concentrated aqueous solution. Depending on the specific PISA formulation, reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerization typically provides straightforward access to either spheres, worms or vesicles. In contrast, RAFT aqueous emulsion polymerization formulations often lead to just kinetically-trapped spheres. This limitation is currently not understood and only a few empirical exceptions have been reported in the literature. In the present work, the effect of monomer solubility on copolymer morphology is explored for an aqueous polymerization-induced self-assembly (PISA) formulation. Using 2-hydroxybutyl methacrylate (20 g dm^{-3}) instead of benzyl methacrylate (0.4 g dm^{-3}) for the core-forming block allows access to an unusual 'monkey nut' copolymer morphology over a relatively narrow range of target degrees of polymerization when using a poly(methacrylic acid) RAFT agent at pH 5. These new nanoparticles have been characterized by transmission electron microscopy, dynamic light scattering, aqueous electrophoresis, shear-induced polarized light imaging (SIPLI) and small-angle X-ray scattering.



POLY 119: Impact of hydration and sulfonation on the nanoscale morphology of water in polyphenylene polymer membranes

Todd M. Alam¹, tmalam@sandia.gov, **Eric G. Sorte**¹, **Cy Fujimoto**¹, **Lauren J. Abbott**², **Amalie L. Frischknecht**². (1) Organic Materials Science, Sandia National Laboratories, Albuquerque, New Mexico, United States (2) Computational Materials & Data Science, Sandia National Laboratories, Albuquerque, New Mexico, United States

Proton exchange membranes (PEMs) continue to see active development for use in a wide range of energy storage applications including fuel cells and batteries. The performance of these polymer membranes, including mechanical stability, degradation characteristics and conductivity, are strongly influenced by the local chemical environment and the size and shape of the polymer domains. Here the characterization for a series of sulfonated Diels-Alder polyphenylene (SDAPP) polymers using solid state ¹H MAS NMR spectroscopy is described. Using ¹H-¹H double quantum (DQ) filtered NMR spin diffusion experiments the nanoscale morphologies of the hydrophilic domains created by the hydrated sulfonic acids were measured as a function of ionic exchange capacity (IEC) and level of hydration. The NMR spin diffusion magnetization recovery curves were modeled using both a simplistic 3D model of randomly dispersed hydrophilic domains and more complex models obtained directly from structures proposed for hydrated SDAPP polymers obtained from recent molecular dynamics (MD) simulations (Abbott and Frischknecht, 2016). These NMR results support the emerging description of isolated, “stringy”, poorly connected hydrophilic (sulfonic acid + water) domains at low water concentrations that evolve to larger hydrophilic domains to form percolated water/acid domains at higher hydration levels. The impact these nanoscale morphology changes have on the local water transport and proton conductivity in the membrane will be discussed.

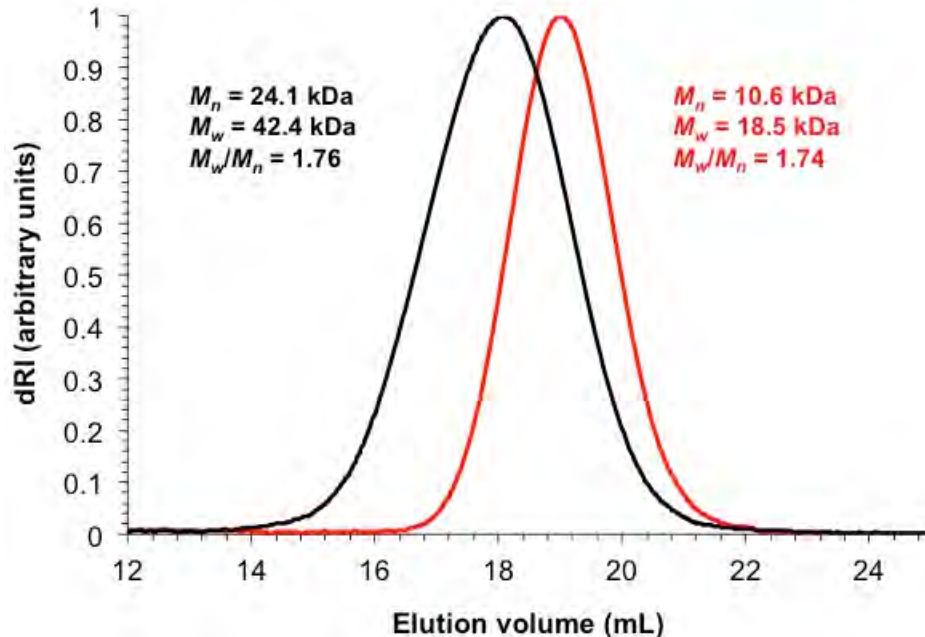


Proton (¹H) MAS NMR spectroscopy spin diffusion experiments are used to measure variations in the nanoscale morphology of the water+sulfonic acid hydrophilic domain in SDAPP proton exchange membranes (PEMs).

POLY 120: Innovations in the design and synthesis of charged polysulfones

Matthew Green, mdgreen8@asu.edu, Yi Yang. Arizona State University, Tempe, Arizona, United States

Polysulfones have been implemented in a variety of applications, including membrane technology, dielectric capacitors, flame retardant materials, and impact resistant displays. Introducing charged moieties into the polymer repeat unit introduces added functionality, develops new morphological features, improves thermomechanical performance, and expands potential applications (e.g., ion-conducting battery electrolytes). This work reviews recent developments in the preparation of polysulfones that can undergo post-polymerization modification reactions to introduce pendant cations, anions, or zwitterions. The synthesis, subsequent characterization, and processing to form thin film and hollow fiber membranes will be discussed.

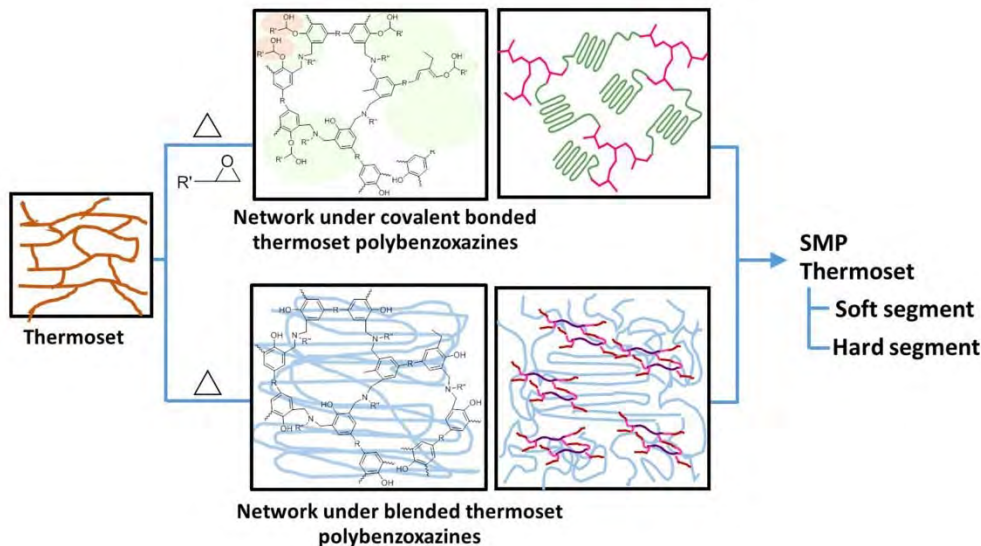


Size exclusion chromatogram of polysulfones for which a stoichiometric imbalance was used to control the molecular weight.

POLY 121: Thermoset in thermoplastic for shape memory polymer: Selective role for net point or switching segment under crosslink network

Suwabun Chirachanchai, *suwabun.c@chula.ac.th*. Polymer Science, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Bangkok, Thailand

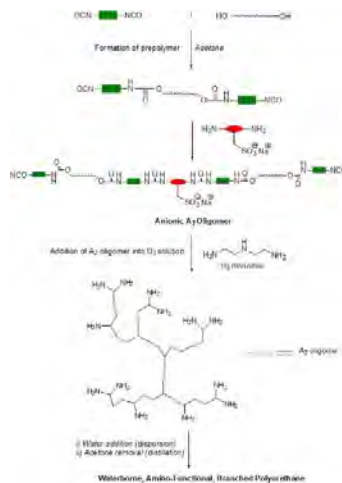
Nowadays, challenges on polymer system to express shape memory effect are (i) the combination of net point or hard segment and switching segment or soft segment, and (ii) the simple and effective triggers. The present work proposes a shape memory polymer (SMP) under the combination of thermoplastic and thermoset polymers. Polybenzoxazine (PolyBZ) is a good candidate for thermoset polymer to confirm how shape memory can be induced in thermoplastic matrix and at that time thermoset polymer plays the role either as the net point (hard segment) or switching segment (soft segment). By connecting melamine-based polybenzoxazine (Me-Bz) with poly(ϵ -caprolactone) (PCL), the rapid and reversible SMP is obtained. The systematic studies prove to us that Me-BZ provides crosslink network which functions as the hard segment. Furthermore, when silver nanoparticles (AgNPs) is added in the system, light triggered shape memory can be easily obtained. In contrast, an in-situ reactive blending between polyoxymethylene (POM) and bisphenol-A together with aniline at molten stage results in formation of oligobenzoxazine (oligoBZ) in POM matrix. At that time, the oligoBZ provides the amorphous as the soft segment to combine with the highly crystalline POM hard segment to result in the material with shape memory. The presentation, for the first time, declares how the same crosslink network of thermoset can play the role as either net point or switching segment to obtain SMP.



POLY 122: Synthesis and characterization of waterborne, silane functional, branched polyurethanes for self-crosslinking coatings in textile applications

ayse durmus¹, aysedurmus@sabanciuniv.edu, Deniz Anil¹, E. Billur Sevinis Ozbulut¹, Yusuf Z. Menceloglu^{1,3}, Serkan Una^{2,3}. (1) Faculty of Engineering and Natural Sciences, Material Science and Nanoengineering, Sabanci University, Istanbul, Choose a State or Province, Turkey (2) Nanotechnology Research and Application Center, Sabanci University, Istanbul, Turkey (3) Integrated Manufacturing Technologies Research and Application Center & Composite Technologies Center of Excellence, Sabanci University, Istanbul, Turkey

In waterborne coating and adhesive applications, self-crosslinking polymers offer unique advantages of both one-component and two-component systems such as the ease of use and enhanced mechanical properties, respectively. The present study focuses on the synthesis and characterization of silane functional, waterborne branched polyurethanes (WBPU) via the oligomeric A₂ + B₃ methodology. Firstly, amino-functional, anionic WBPU were synthesized as shown in Figure 1. For the synthesis of silane functional WBPU, amino end-groups in Figure 1 were reacted with 3-isocyanatopropyltriethoxysilane prior to the dispersion and distillation steps. Subsequently, one-component, solvent-free waterborne dispersion products were obtained upon the dispersion by addition of water and distillation for removal of acetone. The dispersion stability of final products was confirmed by dynamic light scattering (DLS), solution viscometry and pH measurements. As expected, coatings obtained from silane functional WBPU self-crosslinked by hydrolysis and condensation of ethoxysilane end-groups during the film formation and drying processes, resulting in enhanced mechanical properties and chemical resistance compared to amino- and urea-functionalized analogues. The crosslinked structure, enhanced mechanical and chemical properties of resulted coatings were confirmed by soxhlet extraction, dynamic mechanical analysis (DMA) and solvent swelling tests. The influence of the degree of branching, distance between branch points and chemical structure of silane end-groups on the dispersion properties and thermo-mechanical behaviour of polyurethane coatings were investigated systematically and will be presented with an emphasis on textile coating applications.



Synthesis of waterborne, amino-functional, branched polyurethanes

POLY 123: Producing macroporous polymers by emulsion templated polycondensation or polyaddition

Imane Barbara, *imane.barbara@u-bordeaux.fr*. Chemistry, University of Bordeaux, BORDEAUX, France

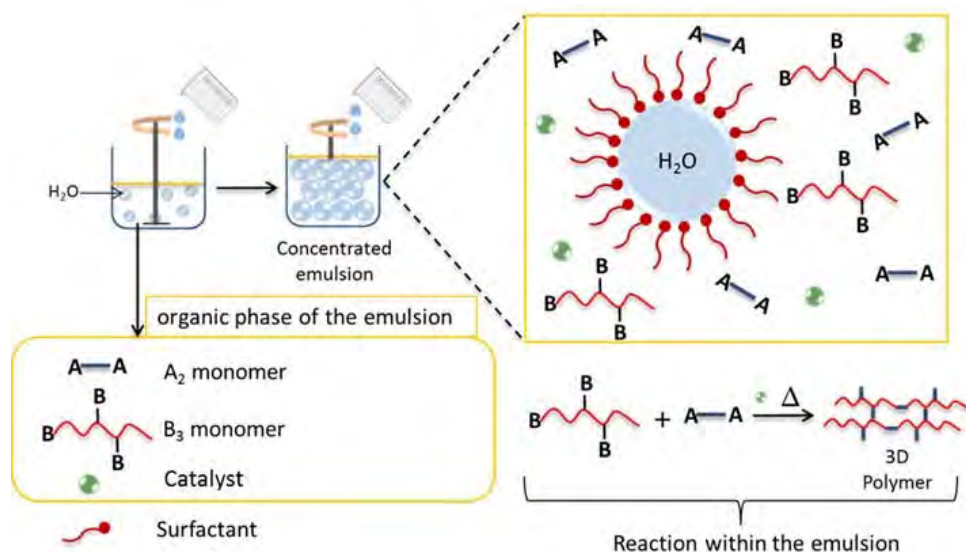
PolyHIPE (high internal phase emulsion) materials are a class of porous polymers typically obtained by emulsion templating polymerisation whereas this method is mainly limited to the radical polymerisation apart from very few exceptions.

The objective of this project is to prepare macroporous polymers by emulsion templated polycondensation or polyaddition of $A_2 + B_3/B_4$ monomers consisting of the continuous phase of water in oil HIPE. Indeed, biodegradable macroporous polyesters materials prepared by polycondensation within a HIPE would be interesting for three dimensional cell culture applications. It will also be a great interest to produce polyurethanes by emulsion templated polycondensation, these materials can be used as supports for catalysts.

However, polycondensation conditions are usually not compatible with the stability of high internal phase emulsions (HIPEs).

It is necessary to formulate stable HIPEs, use reactive monomers and water stable catalysts to achieve the polycondensation within the emulsion and produce macroporous polymers by emulsion templated polycondensation.

Monomers were first synthesized or derivatized then used as the continuous phase of a HIPE ; catalysts were used to perform the polymerization within the emulsion. After drying the monoliths obtained were analyzed using Transmission electron microscopy (TEM), pycnometry and Brunauer-Emmett-Tellet method (BET).



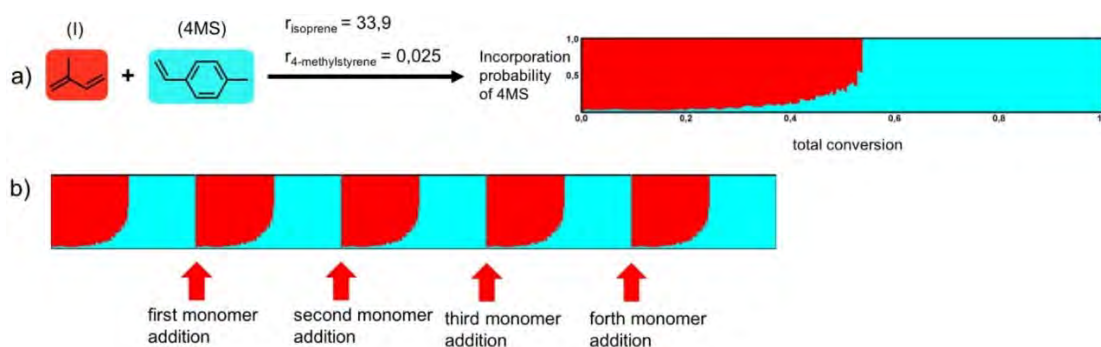
Schematic representation of emulsion templated polycondensation

POLY 124: Linear multiblock copolymers with up to ten blocks and high molecular weights: A novel in-situ block copolymer formation approach

Eduard Grune^{1,2}, edgrune@uni-mainz.de, Axel Mueller¹, Holger Frey¹. (1) Institute of Organic Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany (2) Graduate School of Excellence Materials Science in Mainz, Mainz, Germany

Complex macromolecular architectures, such as linear multiblock copolymers have become the subject of great interest, resulting in a growing number of approaches to prepare these materials. Besides the controlled radical polymerization techniques, the living anionic polymerization is still the most powerful method to prepare tailored multiblock copolymers with low dispersities and high molecular weights. The living character of the chain end enables sequential monomer addition, resulting in an unmatched level of block sequence control. At the same time the carbanion is highly sensitive to impurities and every monomer addition step increases the fraction of terminated chains.

Our approach is to minimize the amount of required additions by using a monomer mixture with appreciably different reactivity ratios. Investigations of the simultaneous copolymerization of isoprene (I) and various styrene derivatives showed that 4-methyl styrene (4MS) is a suitable comonomer with a much lower reactivity than isoprene. Due to the strong deviation of reactivity ratios ($r_I = 33.9$; $r_{4MS} = 0.025$) the simultaneous copolymerization of I/4MS results in block like gradient copolymers with only a short gradient spacer between the poly(isoprene) and poly(4-methyl styrene) block. Examinations of copolymers from I/4MS by dynamic scanning calorimetry (DSC) and transmission electron microscopy (TEM) confirmed the block copolymer like character, exhibiting specific glass transition temperatures for each polymer segment and a strong phase separation behaviour. Combining this one-step block copolymer synthesis with sequential monomer addition enables facile and rapid access to linear multiblock copolymers with adjustable length and number of blocks. Using this rapid approach, various linear alternating multiblock copolymers were synthesized from I/4MS with up to ten blocks, molecular weights up to 400 kg/mol and low dispersities (1.04-1.08). Investigations of the mechanical properties by dynamic mechanical analysis (DMA) and strain-stress experiments revealed extraordinary properties for multiblock copolymers $(I/4MS)_n$ with $n > 4$.



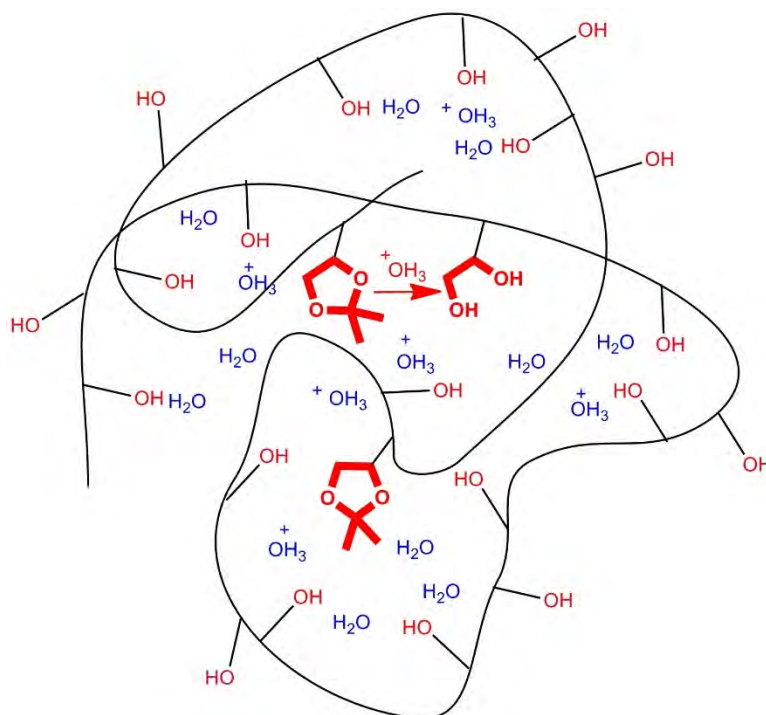
a) In-situ block copolymer formation of I/4MS b) Resulting microstructure of a decablock copolymer, red = isoprene; blue = 4-methyl styrene.

POLY 125: Multiresponsive polymers for drug delivery and sensors

Richard Hoogenboom, *richard.hoogenboom@ugent.be*. Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium

In the last decades, responsive polymeric materials are gaining significant interest for the development of smart materials. Within this context, thermoresponsive polymers that undergo a solution phase transition in aqueous solution are especially interesting. Polymers that phase-separate upon heating, so-called lower critical solution temperature (LCST) behaviour, are widespread based on entropy-driven dehydration of polymers with intermediate hydrophilicity, such as poly(*N*-isopropylacrylamide), poly(oligoethyleneglycol (meth)acrylate)s and poly(2-oxazoline)s. In recent years, the focus is moving more and more towards the development of multi-responsive polymers.

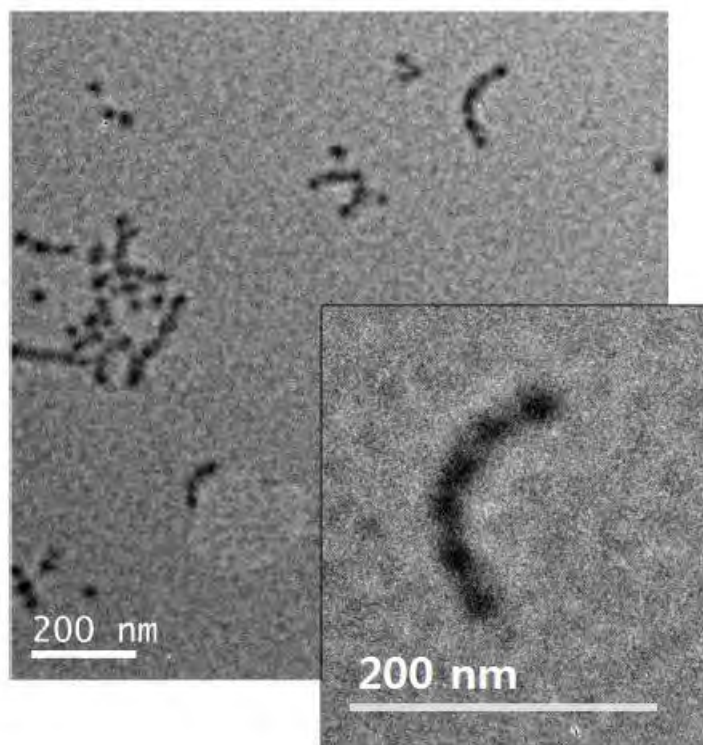
Recent progress from our group in the area of multi-responsive polymers in aqueous solution will be addressed in this contribution. First of all, we have developed pH-degradable thermoresponsive polymers for biomedical applications based on a comonomer having a cyclic acetal side chain. These polymers are soluble at low temperatures and aggregate or form micelles upon heating to 37 °C. Importantly, at pH 7.4 the polymers are stable but they readily degrade at lower pH enabling selective release of coupled or encapsulated drug molecules after endocytosis or in the direct, slightly, acidic, environment of tumors (see graphical abstract). A second topic that will be discussed are multi-responsive solution polymer sensors, that simultaneously respond to temperature and pH or temperature and salt. These latter systems are based on polymer coated gold nanoparticles and also act as logic gates.



POLY 126: In Situ nanoparticlization of conjugated polymers

Tae-Lim Choi, *tlc@snu.ac.kr*. School of Chemistry, Seoul National University, Seoul, Korea (the Republic of)

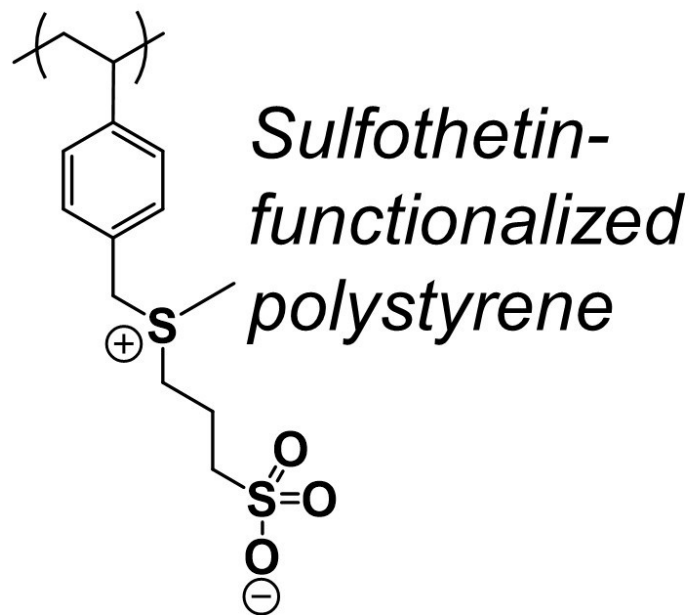
In some cases, the single polymer chain itself exhibits the nanostructures while others do so via self-assembly process. In this presentation, we will focus on the formation of nanostructures via the self-assembly approach. We will introduce a new concept of self-assembly termed “in situ nano-particlization of conjugated polymers”. This method produce supramolecules directly during the polymerization and no further post-modification is required. These polymers are characterized by UV-vis, IR, AFM, TEM, and DLS to obtain the detailed structural information. Here, we will show two reactions, ROMP of cyclooctatetraene and GRIM polymerization of various aromatic monomers and discuss how various nanostructures are formed in each cases.. Lastly, we will finish this talk by introducing very simple one-shot polymerization to achieve INCP and this greatly simplifies the process getting to nanostructures.



POLY 127: Polymeric sulfobetaines as solution responsive smart materials

Todd Emrick, tsemrick@mail.pse.umass.edu. Univ of Massachusetts, Amherst, Massachusetts, United States

This lecture will describe the synthesis of polymeric zwitterions, specifically methacrylic and styrenic polymers containing pendent sulfobetaine zwitterions, and describe their behavior in solution and when segregated to fluid-fluid interfaces. While polymer zwitterions containing sulfobetaine and carboxybetaine moieties are well-known, sulfobetaine zwitterions have only recently been integrated into polymers. We found that the salt-responsive nature of sulfobetaine-containing methacrylate and styrenic polymers translates to oil-in-water emulsion droplets that are stabilized with these polymer zwitterions. Droplets stabilized by these polymers reversibly aggregate (stack) or disperse based on salt concentration and this property offers opportunities to build droplet-based structures with smart, reversible, triggered assembly properties.



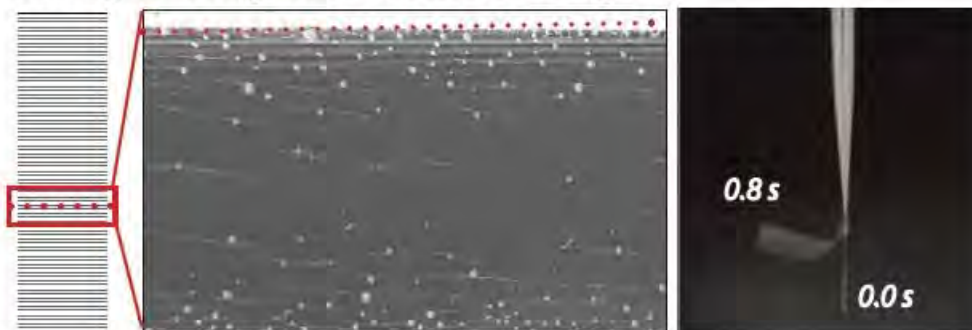
POLY 128: Humidity- and electro-responsive actuation in anisotropically aligned protein films

Tijana Zarkovic Grove, *tijana.grove@vt.edu*, Nathan Carter. Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States

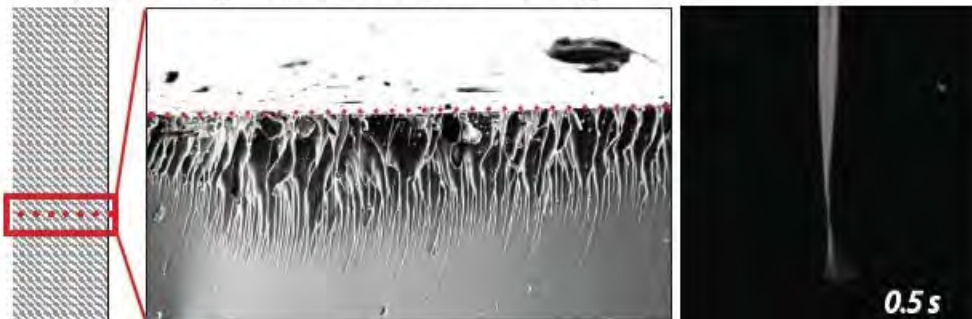
Humidity-responsive actuators are of especial interest for applications such as smart textiles, artificial muscles, and sensors. In nature, bending, folding, and curling shape deformation in response to environmental changes is enabled by the hierarchically structure of biological materials. Here we use a bottom-up strategy for the design of humidity- and electro-responsive actuators, which utilize the macro-scale, anisotropically self-assembled films of the modular Concensus Tetratricopeptide Repeat protein (CTPR).

CTPR films display discrete, tunable anisotropic nano and meso-scale morphologies, which direct the film's bending, folding, or curling in response to changes in relative humidity and electric potential. Furthermore, anisotropic architecture has the ability to generate mechanical work by reversibly deforming through rapid swelling/deswelling, a motion that is further amplified under an applied electrical potential.

Orthogonal Alignment Cause Bending



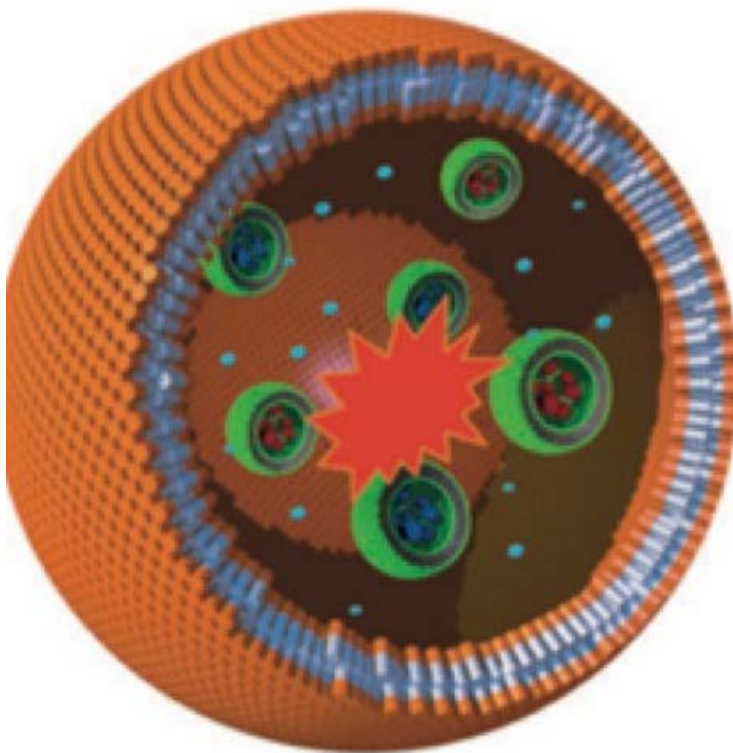
Diagonal Alignment Causes Twisting



POLY 129: Smart biomimetic polymersomes

Sebastien Lecommandoux, lecommandoux@enscbp.fr. LCPO-ENSCP, Univ. Bordeaux, Pessac, France

Polymersomes are among the most attractive systems for drug delivery applications. We report here an overview on the self-assembly in water of amphiphilic block copolymers into polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules. We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles. These copolymers that mimic the structure and function of glycoproteins represent an example of the effectiveness of a biomimetic strategy in implementing materials design. Finally our recent advances in using “biomimicry approaches” to design complex, compartmentalized materials will be proposed. Such a system constitutes a first step towards the challenge of structural cell mimicry and functionality.



POLY 130: Topological transformations via dynamic-covalent chemistry

Hao Sun, Christopher P. Kabb, Yuqiong Dai, Megan R. Hill, **Brent S. Sumerlin**, sumerlin@chem.ufl.edu. Department of Chemistry, University of Florida, Gainesville, Florida, United States

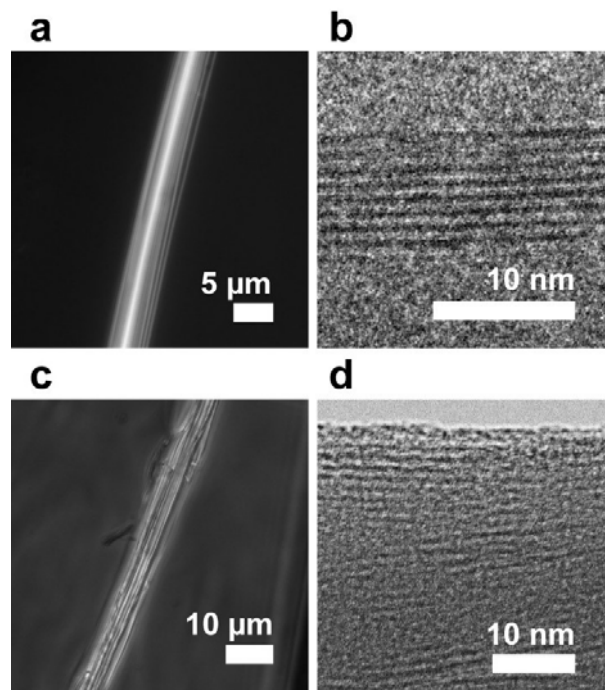
By relying on a variety of reversible covalent reactions that lead to readily cleaved bonds, we have prepared materials that combine the physical integrity of covalent materials and the structural dynamics of supramolecular complexes. Oximes, boronic esters, boronate esters, and Diels-Alder linkages have all been employed to prepare these responsive and dynamic materials, with particular attention having been dedicated to the preparation of hydrogels, elastomers, and nanoparticles. We seek to exploit the reversible nature of these bonds to prepare responsive and self-healing materials.



POLY 131: Exceptional flame resistance and gas barrier with thick-growing clay-chitosan multilayer coatings

Jaime C. Grunlan¹, *jgrunlan@tamu.edu*, Tyler Guir². (1) Texas A M Univ, College Station, Texas, United States (2) Texas A&M University, Bryan, Texas, United States

Layer-by-layer (LbL) assembly is a powerful and versatile technique to deposit functional thin films, but often requires a large number of deposition steps to achieve a film thick enough to provide a desired property. By incorporating amine salts into the aqueous cationic chitosan solution and its associated rinse, layer-by-layer clay-containing nanocomposite films can achieve much greater thickness ($> 1 \mu\text{m}$) with relatively few deposition cycles (≤ 6 bilayers). Amine salts interact with nanoclays, causing nanoplatelets to deposit in stacks rather than as individual platelets. This technique appears to be universal, exhibiting thick growth with multiple types of nanoclay, including montmorillonite and vermiculite, and a variety of amine salts (e.g., hexylamine and diethanolamine). The characteristic order found in LbL-assembled films is maintained despite the incredible thickness. Films assembled in this manner achieve oxygen transmission rates below $0.009 \text{ cc m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ with just 6 bilayers of chitosan/vermiculite deposited. These thick clay-based thin films also impart exceptional flame resistance. A two bilayer film renders a 3.2 mm polystyrene plate self-extinguishing, while an eight bilayer film ($3.9 \mu\text{m}$ thick) prevents ignition entirely. This ability to generate much thicker clay/chitosan multilayers with amine salts opens up tremendous potential for these nanocoatings in real world applications.

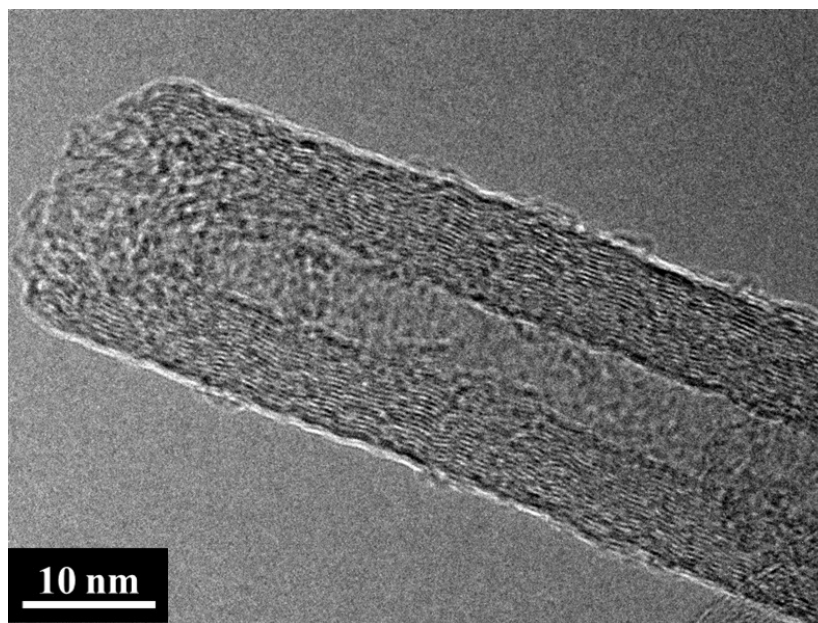


(a) Phase contrast optical micrograph and (b) outside edge TEM micrograph of the cross-section of an 8 BL CH+tris/MMT film deposited on PET. (c) Optical micrograph of the cross-section of an 8 BL CH+tris/VMT film on PET and (d) TEM micrograph of a 1 BL CH+tris/VMT film on PET.

POLY 132: Phosphorous-functionalized multi wall carbon nanotubes as flame retardants for polystyrene and poly (methyl methacrylate)

David P. Durkin², durkin@usna.edu, **Miranda J. Gallagher**³, **Benjamin P. Frank**², **Elizabeth D. Knowlton**⁴, **Paul C. Trulove**⁵, **Douglas Fox**¹, **Howard Fairbrother**². (1) American University, Washington, District of Columbia, United States (2) Johns Hopkins University, Annapolis, Maryland, United States (3) Johns Hopkins University, Baltimore, Maryland, United States (4) National Institute of Standards and Technology, Gaithersburg, Maryland, United States (5) United States Naval Academy, Annapolis, Maryland, United States

Carbon nanotubes (CNTs) are attractive flame retardants for polymers because they can be used in low concentrations and can act as a synergist with conventional additives. In the present work, we functionalize multi-wall CNTs (MWCNTs) with phosphorous, a known flame retardant, to prepare phosphorous CNTs (PCNTs). These PCNTs were incorporated into polystyrene (PS) and poly (methyl methacrylate) (PMMA) by solution blending, and the composites' thermal properties were investigated through thermal gravimetric analysis (TGA) and micro combustion calorimetry (MCC). In PS, the PCNTs were well dispersed and improved thermal stability in proportion to the phosphorus loading, effectively reducing PS flammability. In PMMA, the PCNTs were more aggregated, and they only moderately improved the polymer's thermal stability by delaying the onset of thermal degradation. Material characterization of the PCNT powders, composites, and TGA residues indicated that PCNT flame retardants primarily act in the condensed phase, encouraging char formation of the dispersed CNT network to protect the underlying polymer. Our results show how targeted functionalization of MWCNT with flame retardant heteroatoms can improve the thermal stability of synthetic polymers when properly dispersed throughout the matrix.

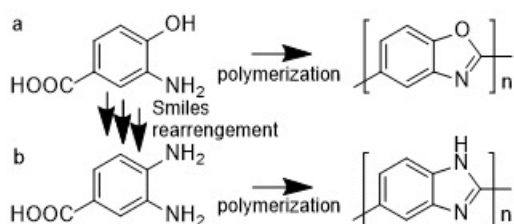


Phosphorus Functionalized Multi-Walled Carbon Nanotube

POLY 133: Ultra-high thermostability in polybenzazoles from wholly-aromatic amino acid

Tatsuo Kaneko^{1,2}, kaneko@jaist.ac.jp, Makoto Watanabe¹, Mohammad Asif Ali¹, Maninder Singh¹. (1) Jaist Sch Materials SCI, Nomi, Japan (2) JST-CREST, Tokyo, Japan

Wholly-aromatic amino acid, 3-amino-4-hydroxybenzoic acid (34AHBA), was derived from the culture media of genetically-manipulated *Streptomyces griseus*. 34AHBA is an exotic amino acid and unused in industry but has a potential as a monomer for high-performance polymers with a rigid structure. We previously prepared a thermotropic liquid crystalline polyesters by a thermal polycondensation of hydroxyl and carboxyl groups of 34AHBA and another hydroxyacid derivative. However the resulting polyesters were too brittle to extend the researches and then we here change the concept of macromolecular design derived from 34AHBA into polybenzazoles which generally exhibit super-high thermostability and mechanical performances. If all the functional groups of hydroxyl, amine, and carboxyl in 34AHBA are used, poly(2,5-benzoxazole) should be formed (Scheme 1a). At first we tried to optimize the polymerization condition of 34AHBA to produce the poly(2,5-benzoxazole)s according to the literature and got the films. However we failed to get tough film presumably due to too rigid structure. Next we converted hydroxyl group of 34AHBA into amine to get 3,4-diaminobenzoic acid (34DABA), in order to use the product as a monomer of poly(2,5-benzimidazole) and its derivatives. For this purpose, we used 2-bromoisobutyramide which was easily reacted with hydroxyl of 34AHBA to form ether bond and the resultant showed Smiles rearrangement under a certain condition. After hydrolysis, we successfully got 34AHBA (Scheme 1b). By using bio-based 34AHBA and 34DABA, we made macromolecular designs for polybenzazoles with ultra-high thermostability and good toughness.



Scheme 1 a) Poly(2,5-benzoxazole) synthesis from wholly-aromatic amino acid, 3-amino-4-hydroxybenzoic acid, derived from *Streptomyces* sp. b) Poly(2,5-benzimidazole) synthesis from the same amino acid via 3,4-diaminobenzoic acid.

POLY 134: Hyperconnected network architectures as a new route to exceptional mechanical properties

Joe Burg², joeburg@stanford.edu, Reinhold Dauskardt¹. (1) Dept of Materials Science Eng, Stanford University, Stanford, California, United States (2) Materials Science and Engineering, Stanford University, Stanford, California, United States

Hybrid materials are a particularly important class of nanomaterials as the combination of organic and inorganic species at the molecular scale leads to novel properties and functionalities. The strength and stiffness of these intrinsically porous and generally brittle materials scale with density, which is controlled by the underlying molecular structure and network connectivity. However, designing hybrid nanomaterials to maintain high levels of mechanical strength and stiffness remains a significant challenge that can ultimately limit the integration of these materials into emerging nanotechnologies ranging from microelectronics to antireflective coatings and molecular sieves. To address this challenge, we have exploited the fundamental dependence of the elastic properties on network connectivity and discovered hyperconnected network architectures, wherein a silicon atom's connectivity within the network extends beyond its chemical coordination number, resulting in exceptional mechanical properties. We show the distinction between 4-fold and 5-fold connected architectures in Fig. 1. We initially predict the remarkable performance of hyperconnected architectures by modeling a 1,3,5-benzene hyperconnected material with molecular dynamic (MD) simulations and found that the hybrid network was stiffer than fully dense silica even at a lower density. Subsequently, we calibrated the MD model via synthesis and characterization of an intrinsically porous hybrid glass processed from 1,3,5(triethoxysilyl)benzene. Importantly, we show that novel synthesis routes to optimize a material's mechanical properties are fundamentally limited by the underlying molecular architecture. A hyperconnected architecture, wherein an atom's network connectivity exceeds its coordination number, is a new nanoscale design strategy to achieve exceptional mechanical properties for nanomaterials where the elastic properties are fundamentally controlled by the underlying network connectivity.

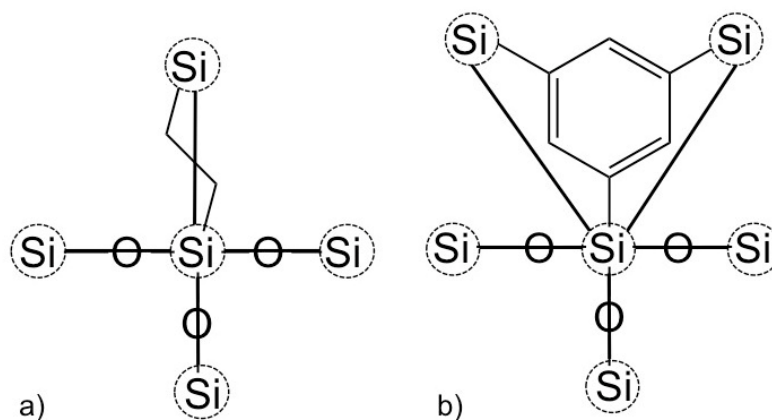
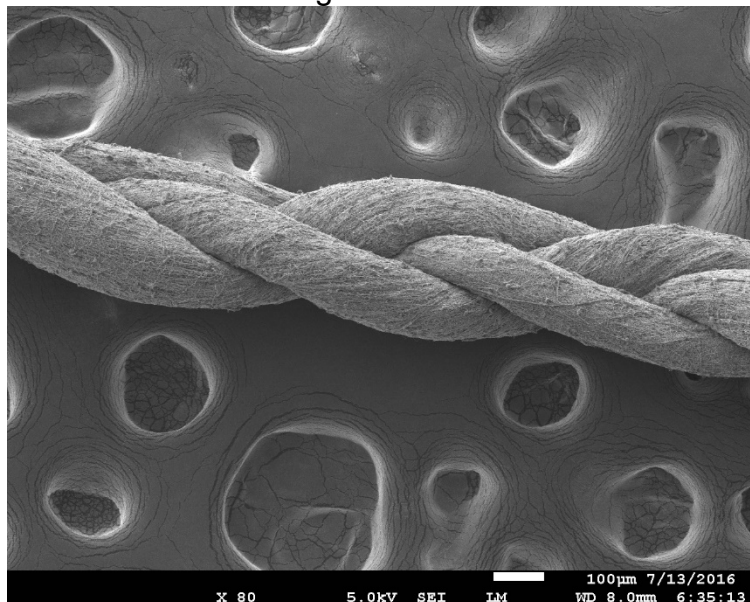


Figure 1: Fully condensed silicon atoms have network connectives of 4 and 5 for (a) an ethane-bridged hybrid material and (b) a 1,3,5-benzene hybrid material, respectively.

POLY 135: Continuous manufacturing of twisted yarns from electrospun polymer fibers

Weerapha Panatdasirisuk², **Shu Yang**¹, *shuyang@seas.upenn.edu*. (1) University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

Electrospinning is one of the most effective and versatile technique to fabricate nano- and microfibers with controlled fiber size and morphology. Despite tremendous effort to utilize electrospun fibers in numerous applications, including tissue scaffolding, energy storage, sensing, and water treatment, the fibers appear as randomly oriented nonwoven fiber mats that can be easily tear apart thus limiting their broader uses and scaling up. Yarns, on the other hand, are produced typically by pulling, grouping, and twisting of single fibers. They are mechanically strong due to the alignment of single fibers, making them knittable to prepare a wide range of complex structures. In this work, we prepared twisted yarns in a continuous fashion by twisting electrospun fibers spun from 2 spinnerets with opposite potential toward a rotating funnel. The polymer jets were solidified and assembled at the funnel before it was continuously withdrawn as a long fiber bundle. The funnel - also offers a support of polymer jets assembly. Polycaprolactone (PCL), a biocompatible polymer is used in our yarn fabrication. The tensile strength of obtained PCL yarns were 4 times higher than that of PCL nonwoven mats obtained from electrospinning. Importantly, we found that the degree of twisting degree influenced the Young's modulus and % strain at break of PCL yarns. Further, we exploited the PCL yarns we fabricated to demonstrated their potential as knittable fabrics knitted together with commercial cotton yarns using a computerized knitting machine. It represents a significant step to bring the nanotechnology to human scales, which will allow us to take advantage of the unique properties of the 3D fibrous materials including high surface area, high porosity, nanoroughness, and mechanical robustness for novel wearable technologies.



Braided nanofiber yarn

POLY 136: Catalyst optimization of covalent organic frameworks by frontier orbital engineering

Christian S. Diercks^{2,1}, c.diercks@berkeley.edu, **Christopher J. Chang**¹, **Omar M. Yaghi**³, **Nikolay Kornienko**⁴, **Song Lin**⁴. (1) *Uc Berkeley Chemistry, Uc Berkeley, California, United States* (2) *Chemistry, University of California Berkeley, Berkeley, California, United States* (3) *Dept. of Chemistry, University of California, Berkeley, Berkeley, California, United States* (4) *Chemistry, UC Berkeley, Berkeley, California, United States*

Up-conversion of carbon dioxide into value-added products is an essential component in the quest for the renewable synthesis of carbon-based fuels. To date, known catalytic systems for this reaction generally suffer from high energy input, poor product selectivity, and short lifetimes. Reticular chemistry of covalent organic frameworks (COFs) has attracted a lot of attention because their large surface areas, the rational design and the organic backbone of the structure hold great promise for the use of this class of materials in heterogeneous catalysis. We report a series of oriented thin films of COFs that effectively reduce CO₂ to CO at low overpotential (550mV) with high selectivity (87%) at high current densities (80mA/mg) which is a significant improvement over the previously reported microcrystalline powder sample. These catalysts are stable for more than 12 hours without any loss in reactivity. The modular synthesis of the structure allows for controlled functionalization of the framework with functional groups of varying inductive effects, without changing the underlying topology of the COF (Fig. 1). Due to the good electronic communication throughout the COF framework, a facile strategy for electronic tuning of the catalytically active cobalt sites in the framework was accomplished. The systematic modification of the electronic structure of the active sites can be monitored by X-ray absorption data on the cobalt L-edge and directly translates into substantial differences in reactivity. This work constitutes the first example of frontier-orbital engineering for the rational catalyst optimization of covalent organic frameworks and exemplifies a powerful example for the notion of covalent chemistry beyond the molecule.

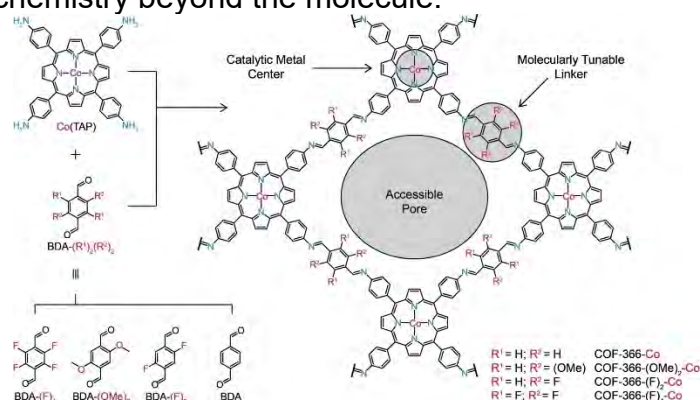
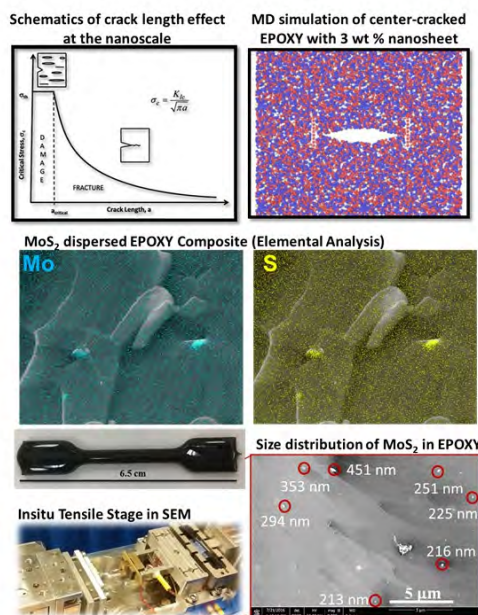


Fig. 1. Design and synthesis of cobalt-porphyrin derived covalent organic frameworks. The molecular nature of the COF backbone allows for systematic modulation of the electronic structure of the catalytically active cobalt center. Due to the porous nature of the framework diffusion of the reactant to the active sites is facilitated.

POLY 137: Nanoscale Toughening Mechanism in MoS₂ Dispersed Epoxy Composite System

John Ryan¹, Samantha Webster¹, Samit Roy², Robert Wheeler¹, **Dhriti Nepal¹**, dhriti.nepal@gmail.com. (1) Materials and Manufacturing Directorate, Air Force Research Lab, Beavercreek, Ohio, United States (2) Aerospace Engineering and Mechanics, University of Alabama, Tuscaloosa, Alabama, United States

Polymer nanocomposites are expected to enhance structural integrity and induce smart sensing capability in ways critical to next-generation materials. However, an understanding of the nature of the fracture and subsequent prediction of material properties is still very premature, owing to a lack of a) characterization techniques to capture the mechanics at sub-100 nm scale and b) accurate models for the estimation of failure modes. Current models based on linear fracture mechanics fail to capture sub-nanometer crack-tip formation or describe the role of nano-inclusion on the fracture toughness of the material. This study incorporates the crack-tip stress field in molecular dynamics simulations to evaluate fracture toughness using MoS₂-epoxy composites as a model system. This allows direct measurement of the near-tip strain field, enabling an understanding of the mechanism of toughness enhancement by nanoparticles. A systematic processing technique was developed to ensure proper dispersion of the nanocomposites of high weight percentage of MoS₂ in DGEBA epoxy polymer matrix. The detailed characterization using FT-IR, DSC, DMA, AFM-IR enabled insights into the nanosheet-polymer network system. High-resolution TEM, SEM, and AFM as well as nano-X-ray computed tomography provided an understanding of 3D dispersion status of these nanosheets. Experiments associated with nanoscale visualization of fracture in the composite are conducted using in-house in situ tensile testing stages placed within SEM and AFM. These experiments provide in-depth knowledge of the influence of flaw size, and platelet size, thickness, and dispersion of nanoparticles on fracture toughness and will be indispensable in guiding the refinement of multi-scale models.

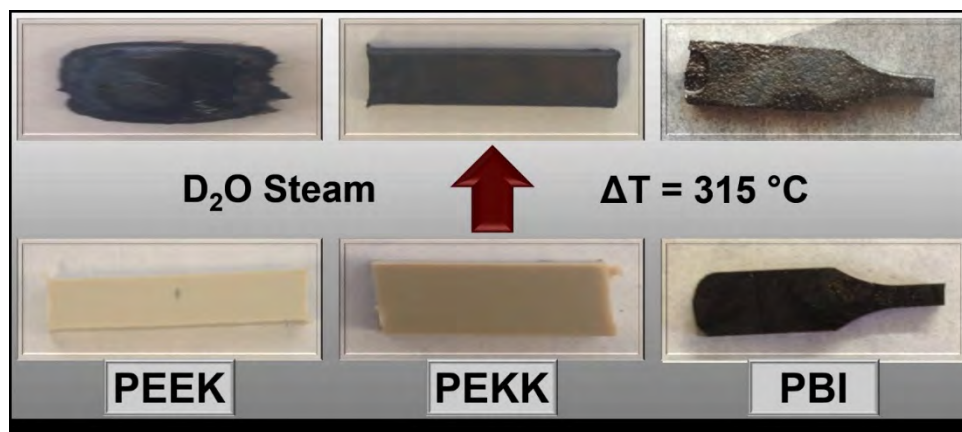


POLY 138: Moisture distribution in PEEK, PEKK, PBI, and their blends: A multinuclear solid-state NMR study

Janet Bluemel, bluemel@tamu.edu, Jacqueline C. Pope. Department of Chemistry, Texas A&M University, College Station, Texas, United States

The group of polyaryletherketones (PAEK) within thermoplastic polymers, including PEEK (polyetheretherketone) and PEKK (polyetherketoneketone) polymers, is of growing interest in a wide range of applications that demand superior mechanical strength and retention of physical properties at high temperatures and pressures. Important applications include downhole materials in oil&gas drilling and fracturing, artificial vertebrae and braces in medicine, and 3D printing. The demand for higher temperature and long term applications keeps growing, along with the quest for improved mechanical performance.

Blends of PEEK and PEKK with polybenzimidazole (PBI) are of interest due to their improved high-temperature stability and wear properties. However, the blends are taking up more water and brines than pure PEEK and PEKK. Water and salts have been identified as the culprits of degradation processes taking place in the polymers. Therefore, it is important to better understand the uptake of water and salts and their location within the polymer networks. The changes of PBI and its PEEK- and PEKK-blends (50:50 wt%) after immersing them in liquid H₂O and D₂O, and exposing them to D₂O steam at elevated temperatures and pressures have been investigated by multinuclear solid-state NMR and IR spectroscopy.^{1,2} Macroscopic morphological and chemical changes on the molecular scale which take place upon high-temperature steam-treatment and the extent and reversibility of the moisture uptake have been determined.^{1,2} Interactions and reactions of water, steam, and aqueous solutions of LiCl and ZnBr₂ with the functional groups of the polymer components have been studied using D₂O in combination with IR, ¹H wideline, ²H, ⁷Li, and ⁷⁹Br MAS, as well as ¹³C and ¹⁵N CP/MAS NMR spectroscopy. Different locations and types of water and protons in the blends will be described and proof will be presented that PBI is mainly responsible for water and salt uptake into the blends.

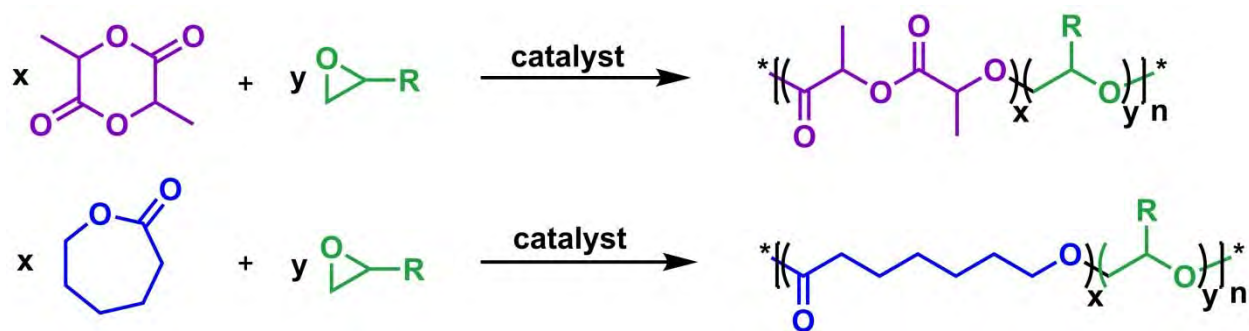


PEEK, PEKK, and PBI Specimens Before and After Steam-Treatment

POLY 139: Copolymerization of epoxides and lactones to ultrahigh molecular weight with an aluminum-chelate catalyst

Malgorzata Chwatko, *malgorzata.chwatko@utexas.edu*, Nathaniel A. Lynd.
Department of Chemical Engineering, University of Texas at Austin, Austin, Texas,
United States

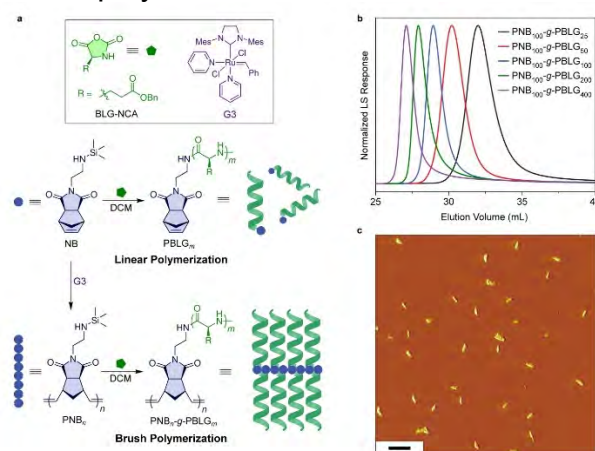
The development of new polymer architectures to meet 21st century needs is driven by advances in synthetic methodology and catalysis. Specifically, as the world moves toward sustainability so should our materials. However, special note should be taken to do so without compromising physical properties. Copolymerization is a classical and powerful strategy for controlling structure property relationships in polymeric materials. In this work, we have discovered a method for the general copolymerization of lactones and epoxides using a simple catalytic route to yield novel degradable materials. The catalyst itself is easy to synthesize and produces ultra-high molecular weight copolymers of lactones and epoxides up to 10 Mg/mol. ϵ -Caprolactone and DL-lactide were chosen as representative lactones, which were each copolymerized with a range of epoxides consisting of ethylene oxide, epichlorohydrin, propylene oxide, and butylene oxide. Reactivity ratios were determined for the copolymerization of lactide and propylene oxide by the method reported by Meyer and Lowry. The reactivity ratios determined were consistent with a gradient copolymer with propylene oxide (PO) being the more preferred monomer, and lactide (LA) being less preferred: $r_{PO} = 2.22 \pm 0.13$, $r_{LA} = 0.21 \pm 0.02$.



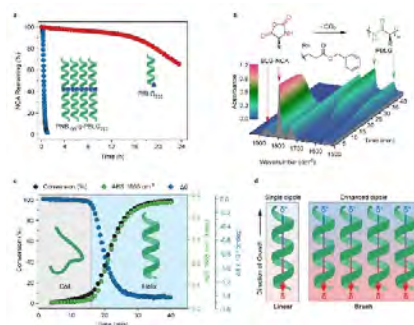
POLY 140: Cooperative polymerization of α -helices induced by macromolecular architecture

Ryan Baumgartner¹, *rbaumga2@illinois.edu*, **Hailin Fu**³, **Ziyuan Song**², **Yao Lin**³, **Jianjun Cheng**². (1) Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (3) Chemistry, University of Connecticut, Storrs, Connecticut, United States

Catalysis observed in enzymatic processes and protein polymerizations often relies on the use of supramolecular interactions and the organization of functional elements in order to gain control over the spatial and temporal elements of fundamental cellular processes. Harnessing these cooperative interactions to catalyze reactions in synthetic systems, however, remains challenging. Here, we report a polypeptide-based macromolecule with spatially organized α -helices that can catalyze its own formation. The system consists of a linear polymeric scaffold containing a high density of initiating groups from which polypeptides are grown, forming a brush polymer. Utilizing various derivatives of these macromolecules, we have shown that changes in secondary and tertiary structure are able to increase the rate of polymerization over 10,000 fold. The parameters that affect the rate are elucidated by a two-stage kinetic model, using principles from nucleation-controlled protein polymerizations, the key difference being the irreversible nature of this polymerization.



(a) Synthetic scheme for linear and brush polymer systems (b) GPC traces of brush polymers (c) AFM phase image of brush polymers.

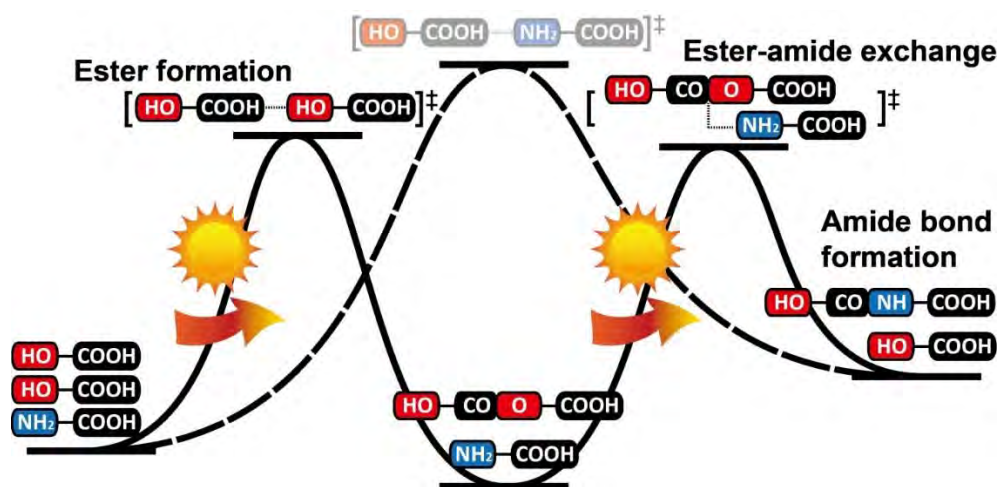


(a) Kinetics of linear and brush polymerizations revealing the greatly enhanced rate in the brush system (b) Time-course IR of the brush polymerization over time (c) Drastic increase in polymerization rate upon spontaneous folding of polypeptides into α -helices (d) Proposed macrodipole involvement in rate enhancement in brush polymer system.

POLY 141: Prebiotic depsipeptide formation from the ester-amide exchange reaction

Sheng-Sheng Yu¹, syu47@gatech.edu, Ramanarayanan Krishnamurthy³, Facundo M. Fernandez², Nicholas V. Hud², Francis J. Schork¹, Martha Grover¹. (1) School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) School of Chem and Biochem, Georgia Tech, Atlanta, Georgia, United States (3) Scripps Rsrch Inst, La Jolla, California, United States

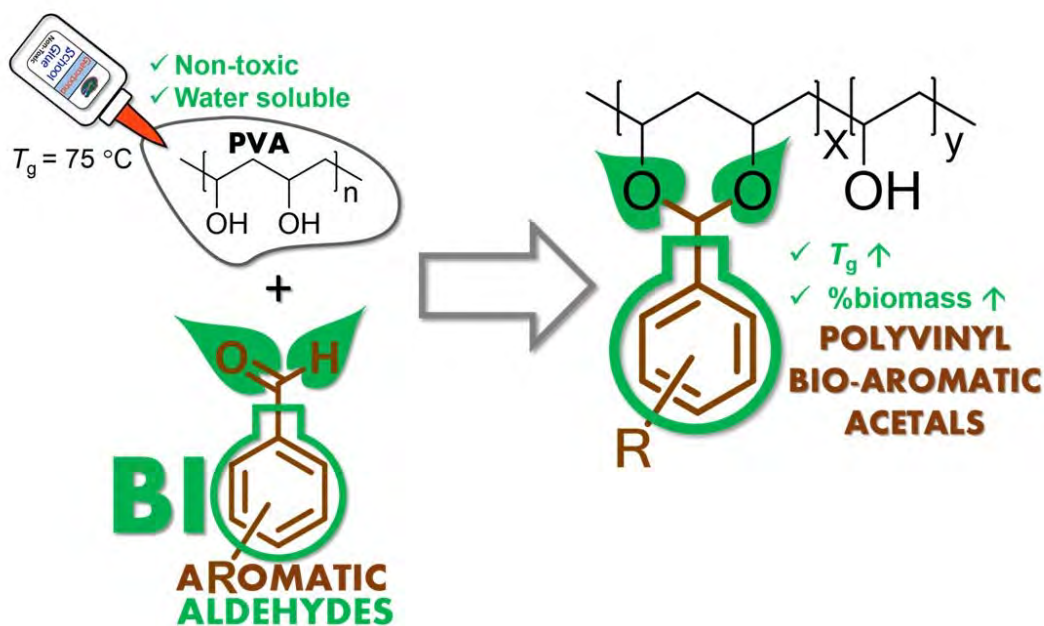
The formation of polypeptides on the early Earth has been a long-standing problem in the field of prebiotic chemistry. Although it is generally accepted that amino acids were present on the prebiotic Earth, the plausible mechanism to form long chain polypeptides is still unclear. Because of the high activation energies and the formation of side products, direct peptide bond formation will not occur unless high temperature or activating agents are used. Here, we found a simple system composed of hydroxy acids and amino acids that is capable of forming peptide bonds under mild conditions. Hydroxy acids form metastable oligoesters in the oscillating (hot dry/cool wet) system and transform into mixed copolymers via the ester-amide exchange reaction. To further understand the kinetic behavior of this copolymerization, we first tracked the growth of initial species from a valine/ lactic acid mixture in a closed system reactor. A mathematical model was developed to simulate the reactions and evaluate the rate constants at different temperatures. We found these reactions can be described by the empirical Arrhenius equation even when the reaction occurred in the solid (dry) state. Further calculations for activation parameters showed that the ester-mediated pathway facilitates amide bond formation by lowering activation entropies. Finally, we combined the experimental and model-based approaches to identify an ideal feeding policy for the growth of long chain polymers. These results not only demonstrate a simple system exhibiting key features for the emergence of peptides at mild conditions, but also provide a theoretical framework that illustrates why the ester-mediated pathway for peptide bond formation would have been more favorable on the early Earth, compared to peptide bond formation without the aid of hydroxy acids.



POLY 142: Commodity plastic mimics from polyvinyl acetals derived from bioaromatic aldehydes and polyvinyl alcohol

Mayra Rostagno, *mayrus61@hotmail.com*, Steven Shen, Ion Ghiviriga, Stephen A. Miller. Department of Chemistry, University of Florida, Gainesville, Florida, United States

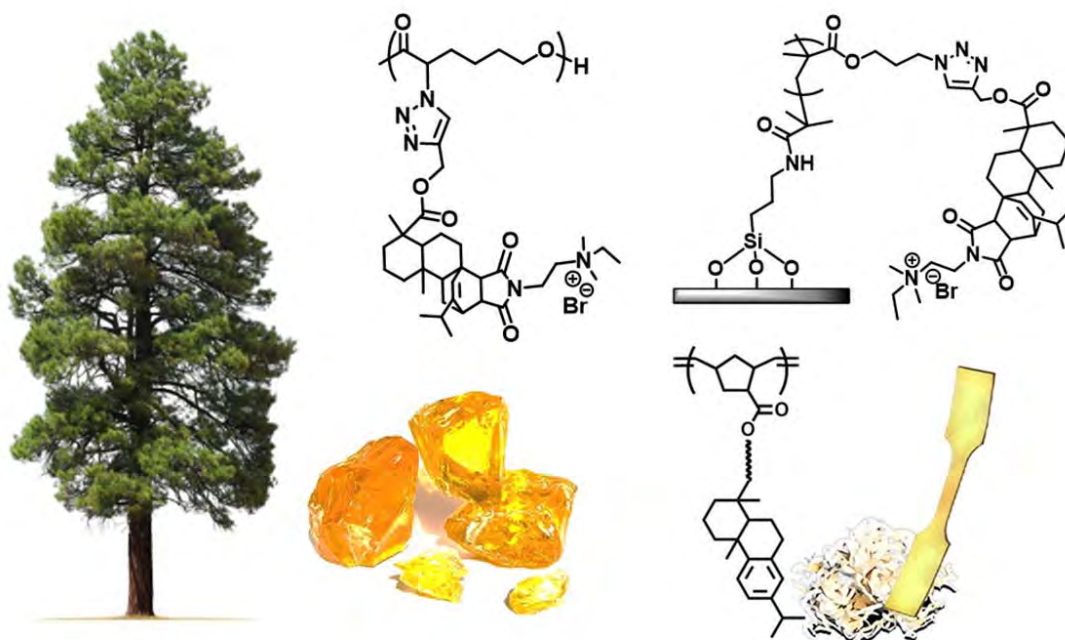
A pressing need exists for new commodity plastics that are both manufactured from renewable resources as well as designed with adequate paths of degradation. To cope with that, a series of polyvinyl aromatic acetals was obtained from the condensation of commercially available polyvinyl alcohol (PVA) and sustainable aromatic aldehydes. The degree of acetalization was determined by ^1H NMR and found to be in the range of 54.1–74.8 %, resulting in calculated number average molecular weights of 38,200 to 46,000 Da. The thermal properties of PVA were substantially improved, polyvinyl aromatic acetals being amorphous and having glass transition temperatures (T_g s) ranging from 114 to 157 °C. Heterogeneous degradation studies at room temperature showed almost complete hydrolysis can be achieved in 24 hours in acidic pH. Furthermore, total hydrolysis of the acetals was achieved under reflux in acidic aqueous solution generating benign aromatic small molecules and biodegradable PVA.



POLY 143: Sustainable antimicrobial biomaterials and biobased plastics from natural biomass

Mitra S. Ganewatta, ganewatt@email.sc.edu, Chuanbing Tang. Dept of Chemistry Biochemistry, University of South Carolina, Columbia, South Carolina, United States

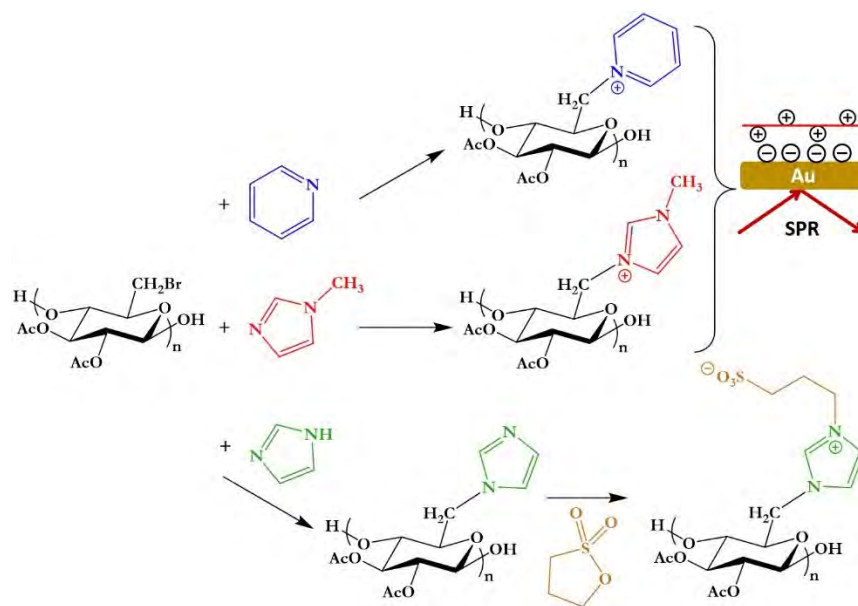
Development of biomaterials and sustainable polymers from natural biomass is widely anticipated as fossil oil reserves dwindle and the environmental problems keep rising. Novel compounds and polymers were synthesized using pine tree resin acids that demonstrated to be effective antimicrobial agents against bacteria including Methicillin-resistant *Staphylococcus aureus*. These chemicals had very low toxicity to mammalian cells proving the effectiveness of them. In addition, sustainable antimicrobial and antibiofilm coatings were developed using the cationic compounds and polymers grafted on surfaces. These surfaces were active against Gram-positive as well as Gram-negative bacterial growth. Interestingly, the surfaces promoted the growth of human dermal fibroblast cells. More recently, ring-opening metathesis polymerization was utilized to synthesize high molecular weight polymers from resin acids. Molecular weights as high as half a million Daltons were prepared. Flexible and mechanically robust films from these resin acid polymers were developed. Thermoplastic elastomers were prepared by combining resin acids and soybean oil derived compounds. Current research includes the development of facially amphiphilic cationic polymers using bile acids for antimicrobial applications.



POLY 144: Efficient, regioselective path to water-soluble polysaccharide ionomers

Shu Liu, *shuliu@vt.edu*, Kevin J. Edgar. Mail Code 0323, Virginia Tech, Blacksburg, Virginia, United States

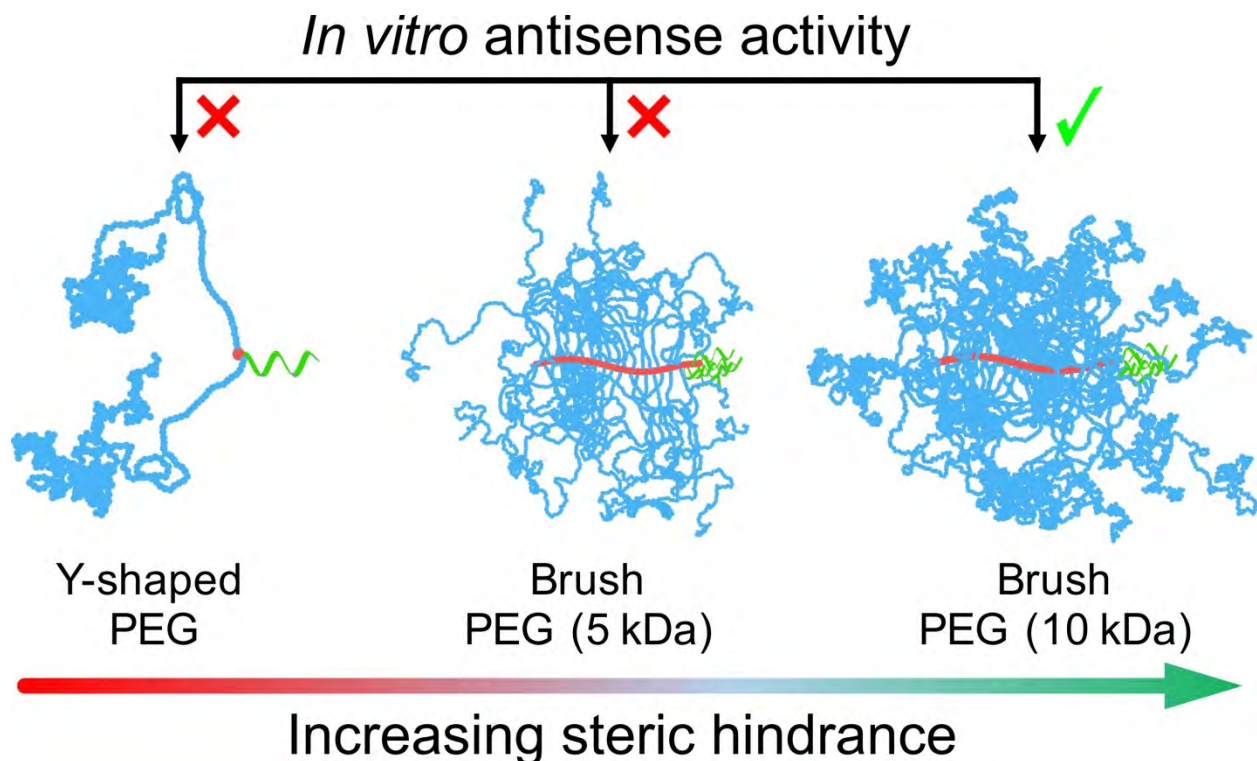
Cationic cellulose and other polysaccharide derivatives are attractive targets for biomedical applications due to their propensity for electrostatically binding with anionic biomolecules, such as nucleic acids and certain proteins. However, relatively few practical synthetic methods have been described for their preparation. Herein, we report a useful and efficient strategy for cationic polysaccharide salt preparation by reaction of 6-bromo-6-deoxycellulose esters or 6-bromo-6-deoxy-curdlan with pyridine or 1-methylimidazole exclusively at the C-6 position, resulting in high degree of substitution (DS). These cationic polysaccharide derivatives bearing substantial, permanent positive charge dissolve readily in water, and bind strongly with a hydrophilic and anionic surface. Also, we applied this simple and efficient strategy for preparing renewable-based copolymers from commercial cellulose esters. The commercial cellulose ester, cellulose acetate (DS 1.8, CA320S), was employed as an exemplary starting material for preparing polysaccharide-based copolymers by a reaction sequence with very high reaction conversions. These modifications can be carried out with essentially perfect regioselectivity and chemoselectivity, and one advantageous example of this new methodology is the synthesis of novel polyelectrolytes starting from uncharged, commercial, inexpensive cellulose esters. Availability of these cationic polysaccharide derivatives will accelerate structure-property relationship studies, i.e. for biomedical application potential including complexation of poly(nucleic acids) for delivery to cell nuclei, delivery of anionic drugs, and epithelial tight junction opening for oral protein delivery.



POLY 145: Improving the biopharmaceutical properties of oligonucleotides by brush-polymer-assisted compaction

Xueguang Lu, lu.xueguang@husky.neu.edu, Xueyan Cao, Dali Wang, Fei Jia, Xuyu Tan, Ke Zhang. *Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States*

Difficult biopharmaceutical properties of oligonucleotide, such as poor enzymatic stability, immunostimulation, and rapid clearance by reticuloendothelial cells, limit their application as therapeutics. Cationic polymers' ability to complex with nucleic acids and delivery them to cells has been extensively explored as a route to therapeutic intervention. Despite significant progress, these materials are still prone to various degree of cytotoxic and immunogenic reactions, which limit their clinical applications. We hypothesize that, if DNA can be made to be selective in binding - only hybridization is allowed but interaction with various proteins is suppressed - then many if not all of the side effects associated with oligonucleotide therapeutics can be bypassed. Herein, we demonstrate that a non-cationic polyethylene glycol brush polymer can provide the DNA with such nanoscale steric selectivity. We show that these unimolecular polymer nanoparticles are capable of entering cells and suppressing gene expression without the need of a cationic polymer co-carrier. The PEG brushes also decrease the immunogenicity and improve the in vivo bio-distribution of embedded oligonucleotide. This new approach has the potential to be applied to essentially all forms of oligonucleotides, i.e. antisense DNA, siRNA, microRNA, aptamers, ribozymes, etc., to improve their biopharmaceutical characteristics.



POLY 146: Complexation of linear DNA and polystyrene sulfonate with cationic copolymer micelles: Effect of polyanion flexibility

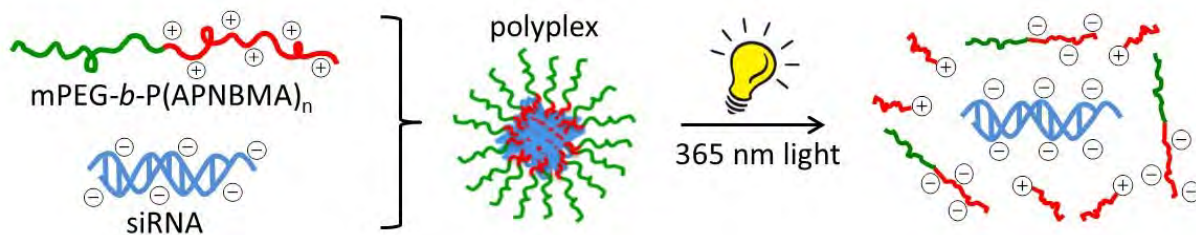
Yaming Jiang¹, jiang640@umn.edu, *Dustin Sprouse*², *Jennifer Lasser*², *Theresa M. Reineke*², *Timothy P. Lodge*^{1,2}. (1) *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States* (2) *Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, United States*

Cationic micelles composed of amphiphilic block copolymers complex with DNA to form micelleplexes, which are attractive vehicles for gene delivery. Compared to model flexible polyanion polystyrene sulfonate (PSS), double stranded DNA (dsDNA) chain is semiflexible, which may affect its ability to complex with cationic particles. Here, the complexation of cationic micelles with linear dsDNA and PSS of similar total charge is compared in buffers of various ionic strengths. The micelles are composed of poly((2-dimethylamino)ethyl methacrylate-*block*-poly(n-butyl methacrylate) chains. The formation of the micelleplexes is monitored via turbidimetric titration as a function of amine group to phosphate (sulfonate) group ratio (N/P or N/S). The size, structure and stability of the resulting micelleplexes were studied by dynamic light scattering and cryogenic transmission electron microscopy. When the polyanion contour lengths are shorter or comparable to the micelle corona thickness, DNA micelleplexes show similar titration curves and structural evolution as the complexes with PSS. When polyanion contour lengths far exceed the radius of the micelles, micelleplexes of DNA show different structures and titration curves from complexes of PSS. We contribute these differences to the different flexibility of the polyanion chains and possible mechanisms are proposed, which may inform future design of micelleplexes as gene delivery vehicles.

POLY 147: Photo-Responsive polymeric formulations to attenuate inflammation in cardiovascular tissues

Chad T. Greco, *cgreco@udel.edu*, Thomas H. Epps, Millicent O. Sullivan. *Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware, United States*

Vascular bypass grafting is a routine treatment for cardiovascular diseases; however, ~50% of bypass grafts fail in the few years following surgery due to cellular inflammatory responses at the suture sites. To address this problem, we synthesized novel diblock copolymers to deliver nucleic acid therapeutics capable of promoting healing in a spatiotemporal manner. A key component of our design is a monomer containing photocleavable *o*-nitrobenzyl moieties linking cationic groups to the polymer backbone so that light irradiation can induce polymer hydrolysis and charge reversal. This monomer was polymerized off a PEG macroinitiator *via* ATRP and then deprotected to form the final material. The polymers self-assemble with anionic nucleic acids in solution to form nanoscale complexes with a PEG “stealth” coating. Application of a photo-stimulus disrupts the electrostatic interactions to trigger the release of bound nucleic acids, such as siRNA. The nanocarriers maintained stability in serum, exhibited robust cellular uptake, and were capable of photo-responsive on/off control over gene expression. These formulations enabled the knockdown of two key functional genes, IL1 β and CDH11, that are implicated in maladaptive responses in human aortic adventitial fibroblasts. The complete knockdown of both genes, in combination, resulted in significant attenuation of TGF- β 1-triggered fibroblast proliferation and differentiation into myofibroblasts, two of the primary hallmarks of fibrosis. Further attenuation over clinically relevant time scales could be achieved by modulating the polyplex dosing regimen. In summary, this photo-responsive system provides a robust framework for addressing key challenges in cardiovascular tissue engineering.



POLY 148: Functionalized star-like ϵ -caprolactone amphiphilic block copolymers for thermoresponsive micellar drug delivery systems

Katherine E. Washington², *kelwashington23@gmail.com*, **Ruvanthi N. Kularatne**², **Yi Xin Ren**², **Michael C. Biewer**³, **Mihaela C. Stefan**¹. (1) Dept Chem UT Dallas, Richardson, Texas, United States (2) Chemistry, University of Texas at Dallas, Heartland, Texas, United States (3) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States

The synthesis of star-like functional polycaprolactones that are thermoresponsive, biocompatible, and biodegradable for applications as micellar drug delivery vehicles for anticancer drugs is reported. The polymers exhibit a lower critical solution temperature (LCST), above which they become insoluble in aqueous solutions, allowing for controlled drug release using external stimuli. The amphiphilic block copolymers are synthesized via ring opening polymerization from functionalized poly(ϵ -caprolactone) monomers with γ -substituents. The hydrophobic block is formed using γ -ethoxy- ϵ -caprolactone, while the hydrophilic block is from γ -2-[2-(2-methoxyethoxy)ethoxy]ethoxy- ϵ -caprolactone (MEEECL). These amphiphilic block copolymers can self-assemble into micelles in aqueous media and encapsulate hydrophobic anti-cancer drugs, such as doxorubicin. The monomers were synthesized with via multi-step syntheses and subsequently used to form the block copolymers. The polymers were prepared via a ring-opening polymerization using tin(II) 2-ethylhexanoate as the catalyst and benzyl alcohol, pentaerythritol, or myo-inositol as the initiator. These initiators have varying numbers of alcohol initiating species allowing for the formation of linear or star-like block copolymers with either 4 or 6 arms. The composition and the molecular weight of the polymers were determined using size exclusion chromatography (SEC) and ¹H NMR. The properties of the various diblock copolymer micelles were investigated. The critical micellar concentration (CMC) was determined by using fluorescence spectroscopy with pyrene as a probe. The LCST was determined through UV-vis spectroscopy and the size and morphology were investigated by dynamic light scattering (DLS) measurements and transmission electron microscopy (TEM). The drug loading capacity and drug loading efficiency, the drug release, and the biodegradability were also examined.

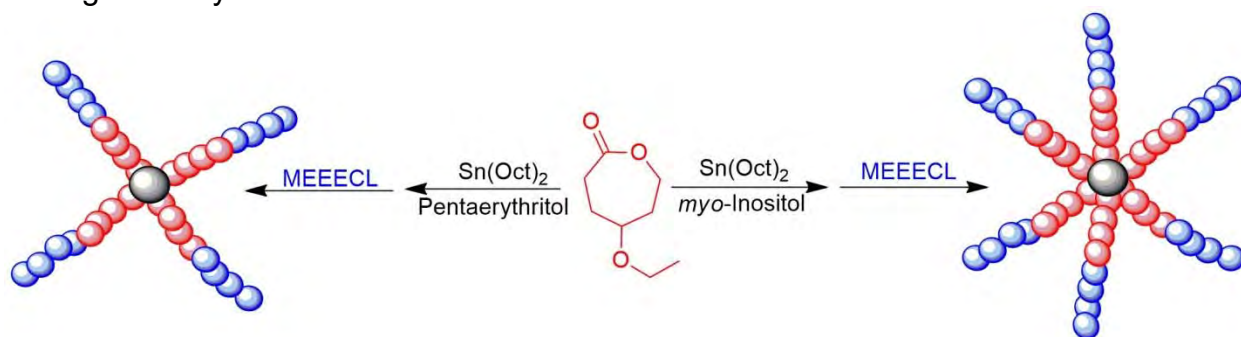
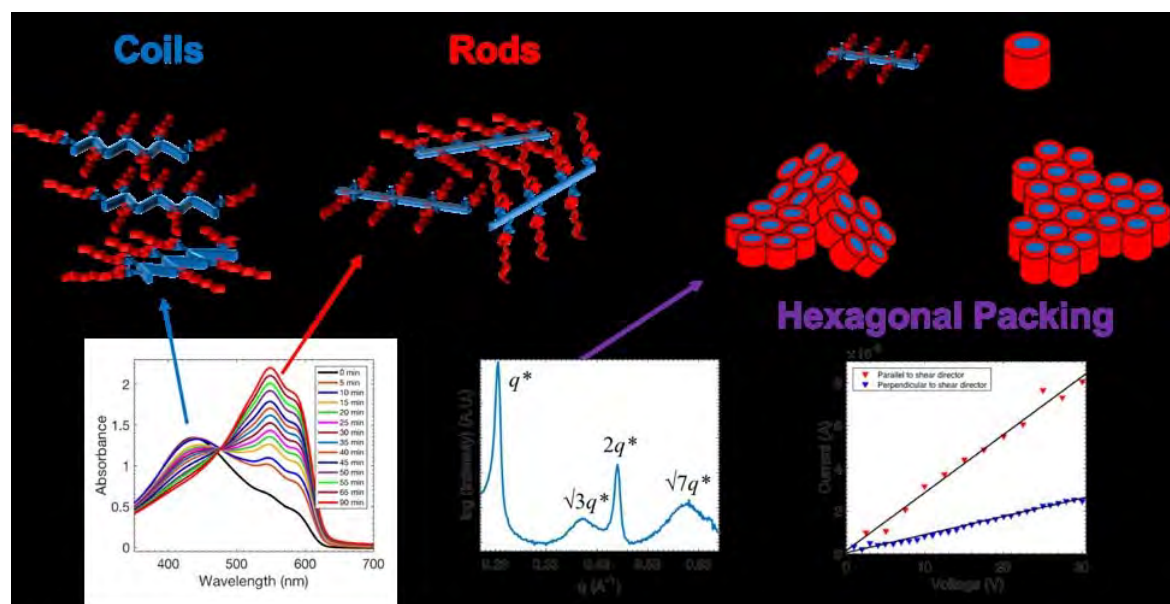


Figure 1. Synthesis of 4- and 6-arm amphiphilic block copolymers from γ -ethoxy- ϵ -caprolactone and γ -2-[2-(2-methoxyethoxy)ethoxy]ethoxy- ϵ -caprolactone (MEEECL).

POLY 149: Multi-scale assembly of polythiophene-surfactant supramolecular complexes

David Bilger², david_bilger@yahoo.com, Amrita Sarkar³, Cameron D. Danesh¹, Manesh Gopinadhan⁵, Greg Braggin¹, Jose Figueroa¹, Thanh Vy Pham¹, Danielle Chun¹, Yashas Rao¹, Chinedum O. Osuji⁴, Morgan Stefik³, Shanju Zhang¹. (1) Dept of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, California, United States (2) Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, San Luis Obispo, California, United States (3) Chemistry, University of South Carolina, Columbia, South Carolina, United States (4) Yale Dept Chemical Engineering, New Haven, Connecticut, United States (5) Yale University, New Haven, Connecticut, United States

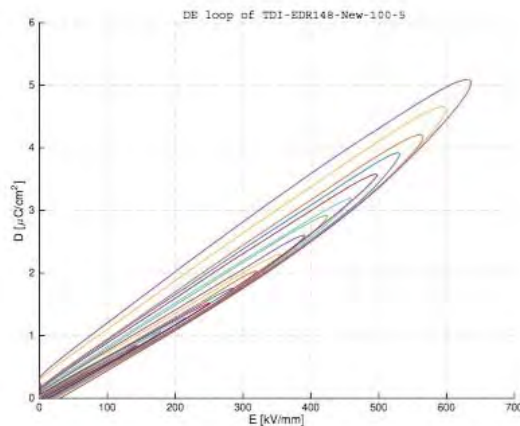
Transitions in the backbone conformation of side-chain functionalized polythiophenes (PTs) have been observed to influence thin-film morphology and performance in organic photovoltaics; however, PT derivatives with ionic side-chain functionality self-assemble poorly when constructed from aqueous solutions. Here, we report on the multi-scale assembly of ionically functionalized poly(3-hexanoatethiophene) derivatives in aqueous quaternary ammonium surfactants by means of small-angle x-ray scattering, four-point probe, polarizing optical microscopy, and ultraviolet-visible absorption and fluorescence spectroscopy. In dilute solution, the incorporation of long surfactant and polythiophene alkyl-chains sterically induces a time-dependent chromism, which is identified to result from a conformational coil-to-rod transition of an intrachain mechanism. When more concentrated, the structural memory of augmented PT aspect ratios promotes the formation of hexagonally-packed lyotropic liquid crystalline solutions. The unique anisotropy in charge transport of aligned liquid crystal films has been observed.



POLY 150: Polyureas for dielectric applications developed through a rational co-design approach

Sydney K. Scheirey¹, sydney.scheirey@uconn.edu, Gregory M. Treich³, Shamima Nasreen², Zongze Li¹, Arun Mannodi-Kanakkithodi⁵, Yang Cao⁶, Rampi Ramprasad⁴, Gregory A. Sotzing⁷. (1) University of Connecticut, Storrs, Connecticut, United States (2) Chemistry, University of Connecticut, Willimantic, Connecticut, United States (3) Institute of Material Science, University of Connecticut, Oakland, New Jersey, United States (4) Unit 3136, University of Connecticut, Storrs, Connecticut, United States

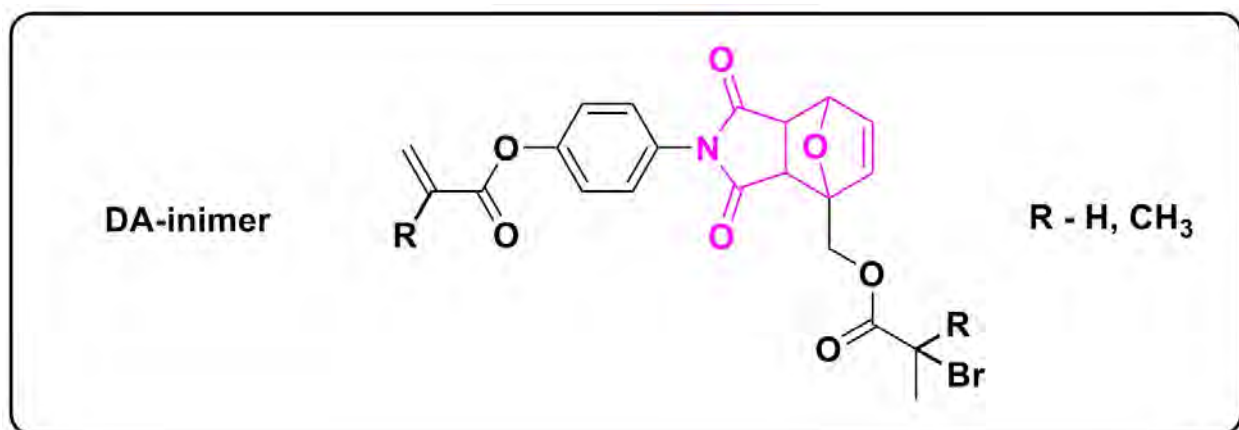
Research in dielectric materials is proving to be increasingly significant as the world shifts its focus towards electrical energy. High energy density capacitors have established their importance in applications consisting of hybrid electric vehicles and insulators. Through the combination of density functional theory (DFT) and experimental design, polymers have been prepared and studied for their dielectric constant and band gap capabilities. Through this rational co-design process, certain polyureas were identified as having promising electrical properties. Specifically, free-standing polymeric films consisting of the polyureas toluene diisocyanate- JEFFAMINE[®], EDR-148 polyetheramine (TDI-EDR148) and methylene diphenyl diisocyanate- JEFFAMINE[®], EDR-148 polyetheramine (MDI-EDR148) have been synthesized. These isocyanates reacted with the ether-containing JEFFAMINE[®], EDR-148 polyetheramine, to form polyureas with molecular weights reaching up to 100,000 g/mol. This relatively high molecular weight for a condensation polymerization allowed quality films to be made of these polyureas at differing concentrations and through different casting techniques. The resulting TDI-EDR148 and MDI-EDR148 polyureas exhibited relatively high degradation and glass transition temperatures (T_g). A dielectric constant value of around 4.5 was obtained from the TDI-EDR148 film while maintaining a loss below 2%. The film also exhibited an energy density greater than 10 J/cm³ and a breakdown strength greater than 600 kV/mm. These new polymers show promise for future thin film capacitors and might compete with the current industry standard biaxially oriented polypropylene (BOPP) which has a dielectric constant of 2.2 and breakdown of 730 MV/m, resulting in a maximum theoretical energy density of 5 J/cm³.



POLY 151: Incorporation of Diels-Alder chemistry into polymer matrices via an inimer approach

Tyler Colt, tacolt@calpoly.edu, Kyle Barcus, Erik Crenshaw, Ryan Rhoads, **Philip J. Costanzo**, phil.costanzo@gmail.com. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

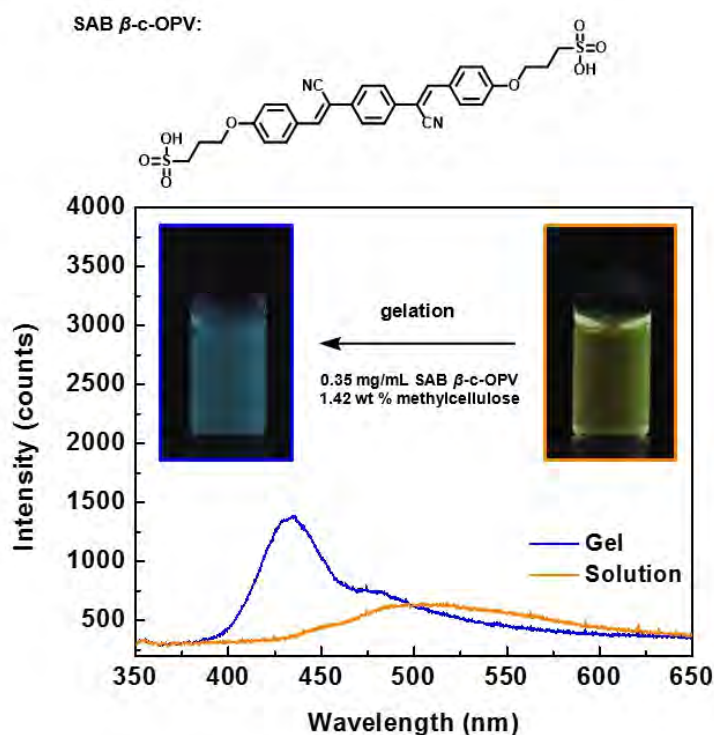
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and light-activated ATRP was utilized to incorporate with an inimer compound to integrate DA linkages at branching points within a branched polymer backbone. Upon the application of a thermal stimulus, the retro-DA was induced and subsequent branch points were reduced to transform a brush architecture into a linear topology. [figure1]



POLY 152: Stimuli responsive β -cyano-oligo(phenylene vinylene) methylcellulose hydrogels

Leandra Forte², *lforte17@wooster.edu*, **Brad Davis**¹, **Joseph Lott**¹. (1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) The College of Wooster, Wooster, Ohio, United States

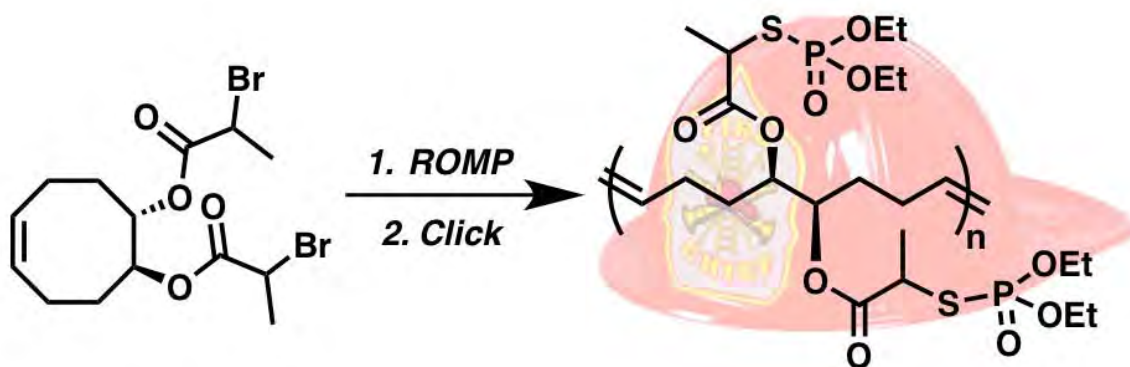
β -cyano-oligo(phenylene vinylene)s (β -c-OPVs) are chromophores that fluoresce brightly in both aggregated states or when molecular vibrations are restricted, yet are non-emissive in solution. Tailorable solubility through tail groups allows this dual emission to be exploited in aqueous systems. A β -c-OPV functionalized with sulfonic acid propoxy groups (SAB β -c-OPV) was synthesized and found to have maximum water solubility of 0.78 mg/mL, with absorbance centered around 362 nm and molar absorptivity of 30,965 L mol⁻¹ cm⁻¹. Frozen aqueous solutions displayed excimer emission around 545 nm with negligible fluorescence at ambient temperature, confirming transference of on-off fluorescence in β -c-OPVs to aqueous environments. A stimuli responsive system was created by incorporating SAB β -c-OPV into methylcellulose solutions and heating them past the lower critical solution temperature to induce gelation. Excimer emission occurred in the solution and emission from isolated molecules was observed in the gels. The shift of peak emission maxima from 517 nm to 436 nm was clearly visible to the eye.



POLY 153: Thio-bromo click approach for developing new, ROMP-based flame-resistant materials

Jonathan Grubb, *jgrubb165@yahoo.com*, Christopher E. Hobbs. Texas A&M University Kingsville, Corpus Christi, Texas, United States

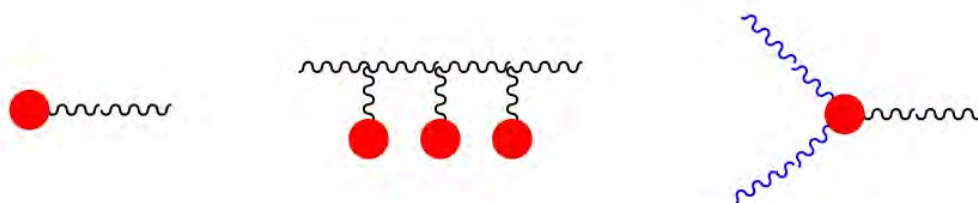
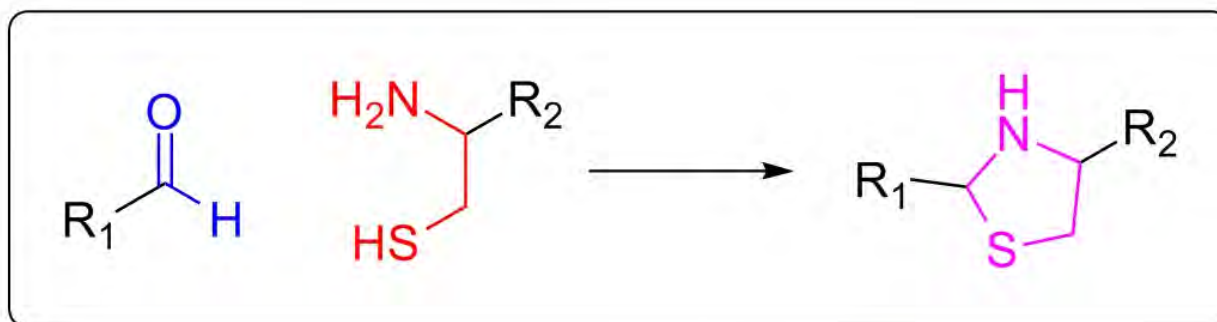
The preparation of a new class of flame-resistant polymeric materials will be described. Ring Opening Metathesis Polymerization (ROMP) was used for the facile preparation of α -bromo ester-containing linear polymers. Flame resistant properties could be instilled in these materials using a post-polymerization installation of phosphate groups through a thio-bromo "click" reaction. The resulting materials were analyzed using common techniques (i.e. vertical flame test) and were shown to exhibit excellent flame resistance and self-extinguishing properties.



POLY 154: Utilization of a cysteine core for the preparation of novel mikto-arm star polymer

Catherine Sarantes, csarante@calpoly.edu, **Karoline Eckhart**, **Clement DeHoe**, **Lucas Souza**, **Austin Ventura**, **Anthony J. Varni**, **Philip J. Costanzo**, phil.costanzo@gmail.com. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

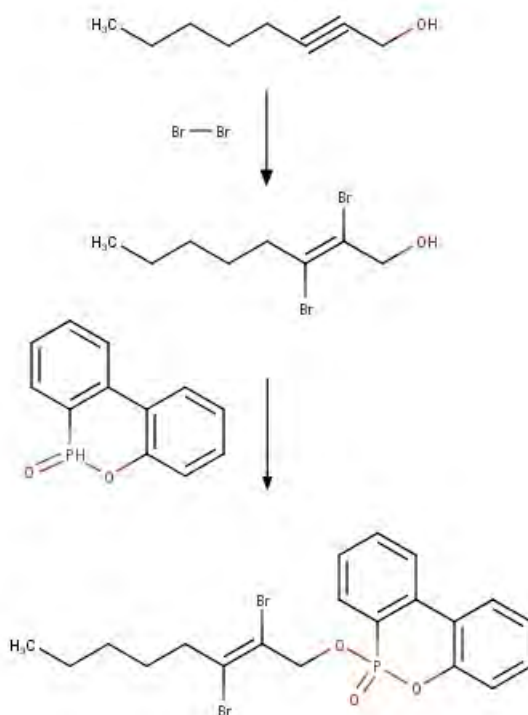
The three distinct functional groups within the cysteine molecule create an synthetic opportunity to create multi-compositional materials. However, the increased functionality is also a synthetic hurdle. We developed a simple and efficient methodology to prepare novel mikto-arm star polymers from a cysteine core. Here, polymers of pre-determined molecular weights were prepared using reversible addition fragmentation transfer (RAFT) and modified to yield a terminal thiol functional group. This mercapto functionality was then incorporated using thiol-ene/yne chemistry to create various compositional arms. [figure1]



POLY 155: Alkynols as a source of flame retardants

Adam Gudbrandson, *agudbrandson@gmail.com*, Bob Howell. Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, Michigan, United States

Alkynols offer an attractive platform for the generation of dual-functional flame retardant for polymeric materials. They contain dual-functionality, a triple bond and a hydroxyl group, that may be readily converted to a variety of compounds with flame retarding properties. In a simple example 1-pentyn-5-ol may first be treated with bromine and then with diphenyl chlorophosphate. The product containing both bromine (for gas-phase activity) and phosphorus (for solid phase activity) should display good flame retardant properties. The carbon foot print of such a material is much smaller than its petroleum counterpart, making the synthesis of these flame-retardants of even more importance.



POLY 156: Self-assembled supramolecular nanosystems for smart diagnosis and targeted therapy of intractable diseases

Kazunori Kataoka^{1,2}, kataoka@bmw.t.u-tokyo.ac.jp. (1) Policy Alternatives Res Inst, Univ of Tokyo, Tokyo, Tokyo, Japan (2) Innovation Center of NanoMedicine, Kawasaki Inst Ind Promotion, Kawasaki, Japan

Nanotechnology-based medicine (Nanomedicine) has received progressive interest for the treatment of intractable diseases, such as cancer, as well as for the non-invasive diagnosis through various imaging modalities. Engineered polymeric nanosystems with smart functions play a key role in nanomedicine as drug carriers, gene vectors, and imaging probes. This presentation focuses present status and future trends of self-assembled nanosystems from block copolymers for the therapy and the non-invasive diagnosis of intractable diseases.

Nanosystems with 10 to 100 nm in size can be prepared by programmed self-assembly of block copolymers in aqueous entity. Most typical example is polymeric micelles with distinctive core-shell architecture. Several micellar formulations of antitumor drugs have been intensively studied in preclinical and clinical trials, and their utility has been demonstrated. Compared with conventional formulations, such as liposomes, polymeric micelles have several advantages, including controlled drug release, tissue penetrating ability and stimuli-sensitivity. The development of smart polymeric micelles that dynamically change their properties due to sensitivity to chemical or physical stimuli is the most promising trend toward nanomedicines, directing to the targeting therapy with high efficacy and ensured safety. Notable anti-tumor efficacy against intractable and metastatic cancer, including pancreatic and brain cancers, of antitumor drug-incorporated polymeric micelles with pH-responding property was demonstrated to emphasize a promising utility of nanomedicines for cancer treatment.

Versatility in drug incorporation is another feasibility of polymeric micelles. Polymeric micelles loaded with siRNA and mRNA have been successfully formulated with relevant properties for nanotherapeutics. Furthermore, loading of imaging reagents makes polymeric micelles with theranostic functions. Appealing enough, our recent result revealed that by installing proper ligands polymeric micelles can effectively crossing the blood-brain barrier to send various therapeutic compounds directly into neural cells in brain parenchyma.

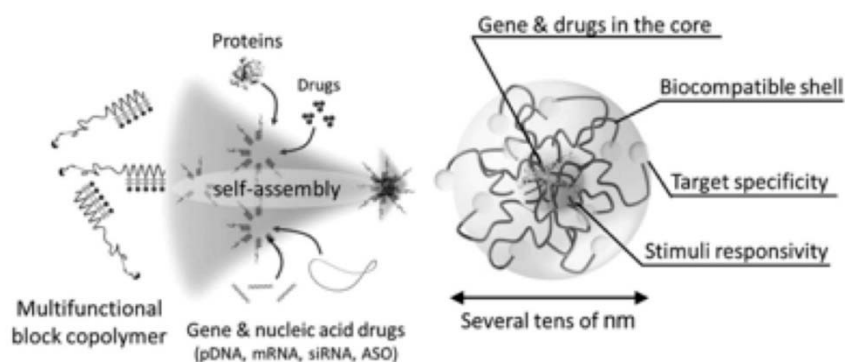
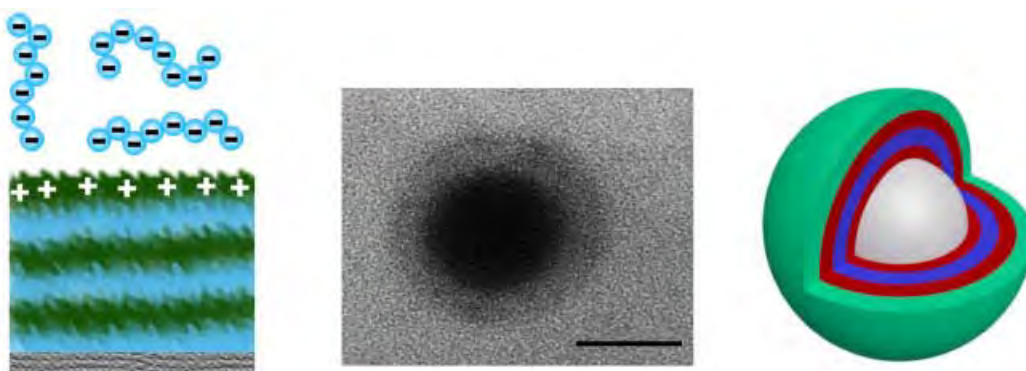


Fig.1 Polymeric micelle as nanocarrier for drug and gene delivery

POLY 157: Electrostatic assembly of nanoparticle systems for controlled and tissue targeted release

Paula T. Hammond^{1,2}, hammond@mit.edu. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Koch Institute of Integrative Cancer Research, MIT, Cambridge, Massachusetts, United States

Layer-by-layer assembly provides an approach that allows complementary secondary interactions to generate a stable thin film coating which can contain a broad range of molecular and macromolecular systems. It can be applied to a range of nanomaterials that are of interest for cancer therapies, from solid nanocrystals that can act as imaging systems to nanometer scale drug containers such as liposomes or polymeric nanoparticles. This kind of approach offers the promise of delivery of a cascade of chemotherapy drugs in sequence, thus allowing for optimized combination therapy of synergistic drugs with therapeutic molecules such as siRNA. The generation of LbL nanoparticles that can directly target a specific tissues such as metastatic tumors, the lungs, or other key organs is dependent on the nature of the outer LbL layer, and the biodistribution of the nanoparticle is highly dependent on net surface charge, degree of hydration, and type of polyelectrolyte bilayer pair that is adsorbed as the final layers on the nanoparticle. Recent work in which these nanoparticle systems are designed for optimized uptake by advanced serous ovarian cancer cells will be discussed, and the use of these approaches to deliver combination siRNA/chemotherapy or drug inhibitor combination therapies or to generate imaging systems and theranostic nanoparticles will be addressed. The potential to target other tissues using designed nanoplex systems is discussed, in particular for the case of targeting cartilage to address the early stages of post-traumatic osteoarthritis. The manipulation of outer surface charge and polymer chain functionality, as well as the ability to design these layered nanoscale complexes to respond to micro-environment cues to achieve controlled biodistribution and uptake to targeted cells in vivo will be described.

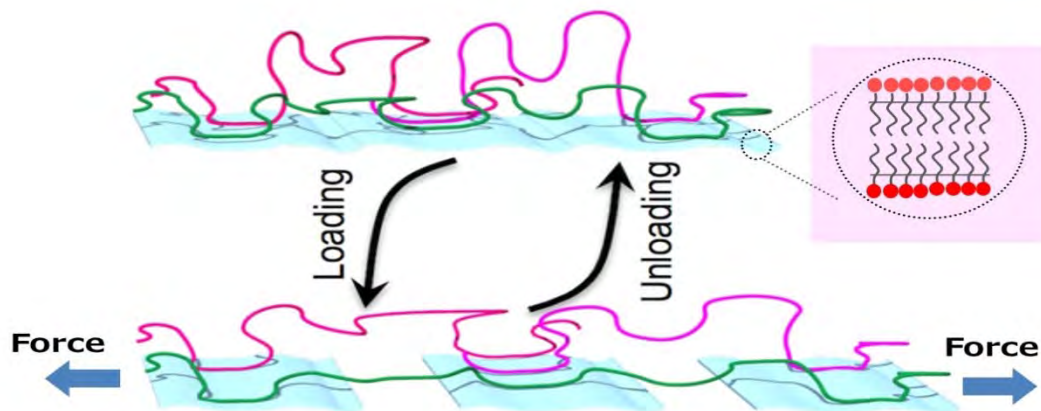


POLY 158: Toughening soft materials with sacrificial bonds

Jian P. Gong^{1,2}, gong@sci.hokudai.ac.jp. (1) Faculty of Advanced Life Science, Hokkaido University, Sapporo, Japan (2) GSS, GI-CoRE, Hokkaido University, Sapporo, Japan

Invention of the double network (DN) hydrogel in 2003 significantly modified the knowledge that hydrogels are weak materials. The extra-ordinary toughness of DN gels is a consequence of the internal fracture of the brittle network to dissipate significant amounts of energy under large deformation and the elasticity of the second network to maintain their original configurations after the deformation. Thus, the covalent bond of the brittle first network serves as true “sacrificial bond”, for the toughness of the DN gels. Many recent works have replaced the covalent bonds with non-covalent bonds to allow the fractured bond to be re-formed in hydrogels. Studies along these lines have successfully produced tough hydrogels with self-recovery after internal rupture.

The double network concept naturally suggests a more general strategy for designing tough soft materials: incorporating, on purpose, a mechanically fragile structure to toughen the material as a whole. This strategy gives more freedom in the molecular design, not limited to double or multiple network systems but also applies to single network system as long as it has sacrificial bond to dissipate energy and can retain original configurations of the material after large deformation. This strategy has been proved effective using ionic bonds in hydrogels. One further goal is to develop tough soft materials with anisotropic mechanical performance resembling to skins, cartilages, muscle, and tendons. Using self-assembly molecules, such as lipid molecules, rod-like macromolecules, block copolymers, to build anisotropic energy dissipation structure would be a strategy. This possibility is demonstrated by a fully anisotropic hydrogels consisting of layered lipid membranes entrapped in the matrix of neutral network. The integrations and interactions of different mechanisms for dissipating energy and maintaining elasticity are essential to the design of tough soft materials.

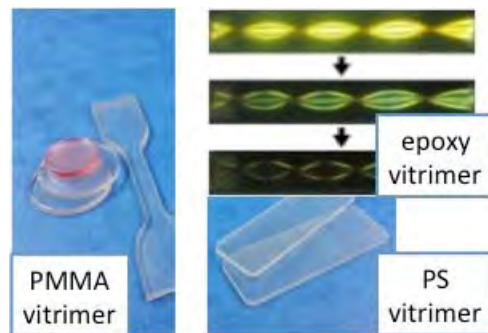


Bilayers as reversible sacrificial bonds

POLY 159: Principles of vitrimer chemistry and physics

Ludwik Leibler, ludwik.leibler@espci.fr. Matière Molle et Chimie, ESPCI Paris, Paris, France

In 2011 we introduced the concept and synthesized, vitrimers, polymer materials that are insoluble and undergo gradual solidification just like amorphous silica. Insoluble whatever the temperature, solid at low temperatures yet processable when heated, vitrimers constitute the third class of polymers along with thermoplastics and thermosets (elastomers). Vitrimers are polymer networks that are able to change their topology without changing the total number of bonds through thermo-activated associative exchange reactions. First vitrimers were made from epoxy resins and used catalyzed transesterification to achieve networks with exchangeable links. Today most plastics and rubbers can be transformed into vitrimers. Since vitrimers can be shaped, assembled, repaired and recycled while showing exquisite chemical and thermomechanical resistance they should rapidly find applications in automotive, electronics, airplane, and coatings industries. Functional vitrimers (e.g. liquid crystalline or responsive and shape memory materials) are also expected to open new exciting applications.



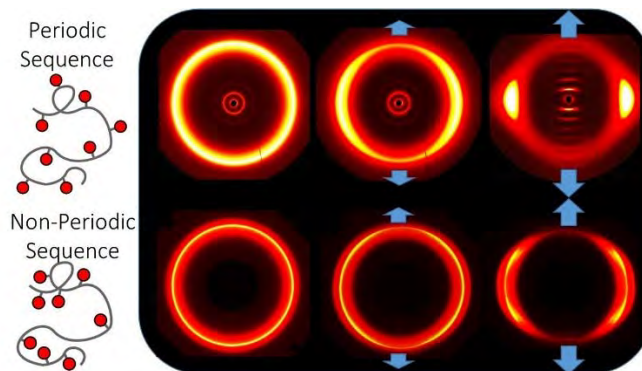
POLY 160: How advances in polymer synthesis have enabled advances in polymer physics

Karen I. Winey, winey@seas.upenn.edu. *Materials Sci. Eng., University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Macromolecules is the premier journal in polymers and has a comprehensive scope that gives equal merit to every aspect of polymer science. The synergy between synthesis, characterization, thermodynamics, properties, simulations and theory has strengthened the field and continually inspires. This crosscutting journal has countless examples that demonstrate how developments in one aspect of the field have motivated another. This talk highlights how advances in polymer synthesis enable advances polymer physics including the role of anionic polymerization on block copolymers, tacticity control for crystallization, and more recently sequence control in associating polymers.

Acid- and ion-containing polymers have specific interactions that produce both hierarchical nanoscale morphologies containing polar aggregates and remarkable bulk properties. Untangling the correlations between the primary structure of such associating polymers and their morphologies and properties has long been a challenge in polymer physics, because most acid- and ion-containing polymers have random sequences of polar and non-polar monomeric units. New synthetic methods can increasingly produce polymers with greater molecular precision that provide greater uniformity of and control over the hierarchical structure morphologies and even yield new morphologies.

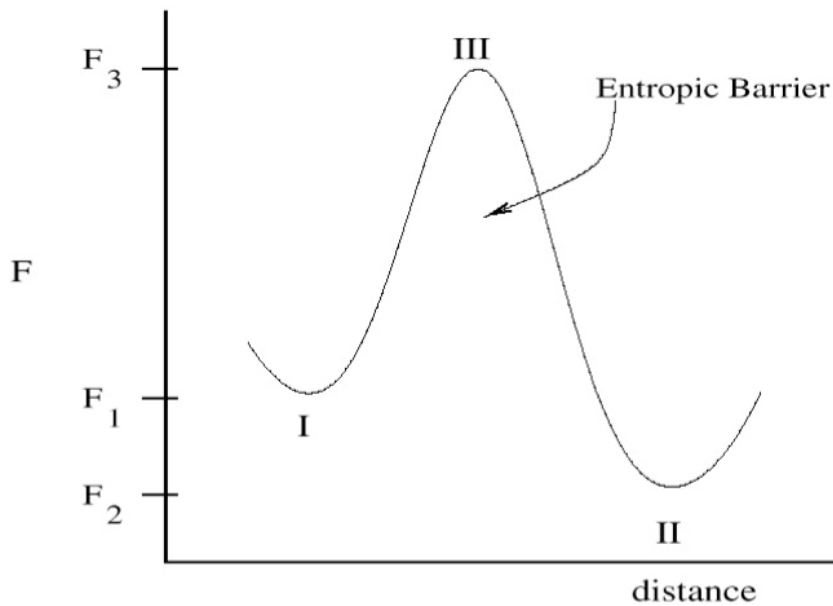
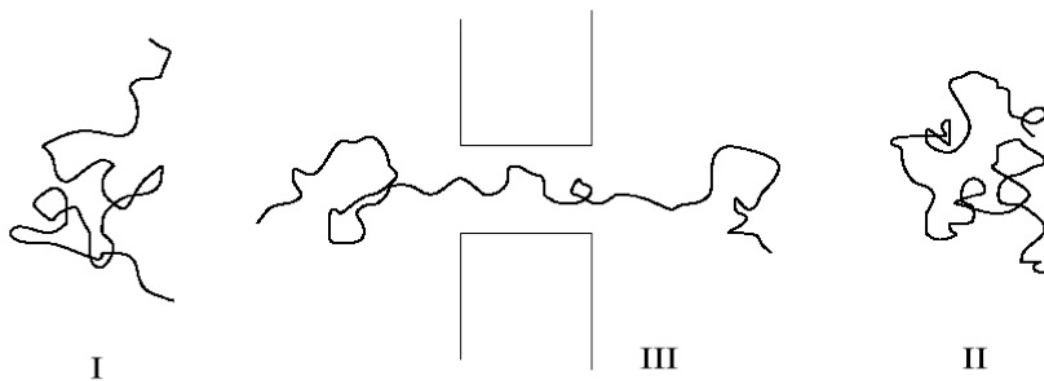
Specifically, we have studied a series of precise polymers synthesized by acyclic diene metathesis (ADMET) chemistry that have functional groups evenly spaced along linear polyethylenes. We have established design rules connecting these precise polymers to particular hierarchical morphologies and have discovered a variety of new morphologies including cubic and layered structures. Using *in situ* X-ray scattering and tensile testing, we've identified three distinct mechanical responses and their corresponding morphology evolutions. These precise polyethylenes have also been studied via molecular dynamics simulations (coarse grained and fully atomistic) to elucidate their morphologies and, more recently their dynamics, which were found to agree with quasielastic neutron scattering results.



POLY 161: Entropic barrier theory of dynamics of macromolecules

Murugappan Muthukumar, *muthu@polysci.umass.edu. Univ of Massachusetts, Amherst, Massachusetts, United States*

Dynamics of macromolecules in structurally heterogeneous media is ubiquitous in many processes in biology and technology. The molecular origin behind this phenomenon was originally attributed to emerge from spatially modulated entropic barriers arising from reduction in conformational entropy of macromolecules due to spatial and topological constraints. Since its inception, the entropic barrier theory has been used during the past three decades in many contexts. We will illustrate the implications of the entropic barrier theory in single-molecule electrophoresis of DNA through protein channels, polymer diffusion in gels, and stochastic resonance.

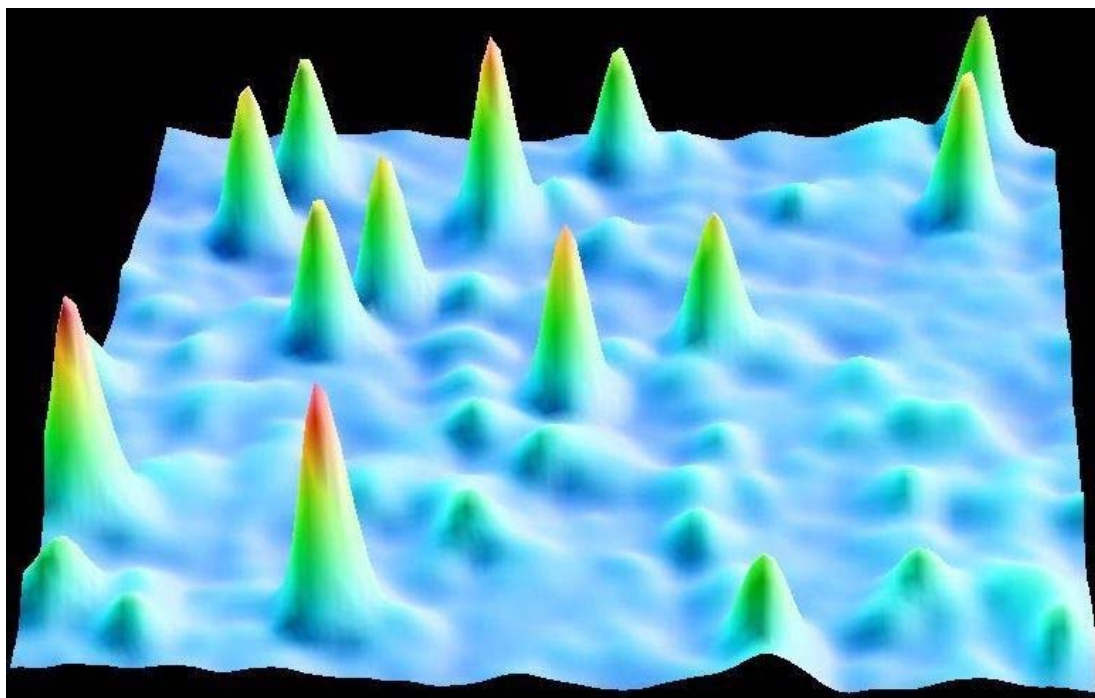


Entropic barrier

POLY 162: Story of single-molecule detection and spectroscopy and the surprises leading to super-resolution microscopy and beyond

W E. Moerner, moerner@stanford.edu. Department of Chemistry, Stanford University, Stanford, California, United States

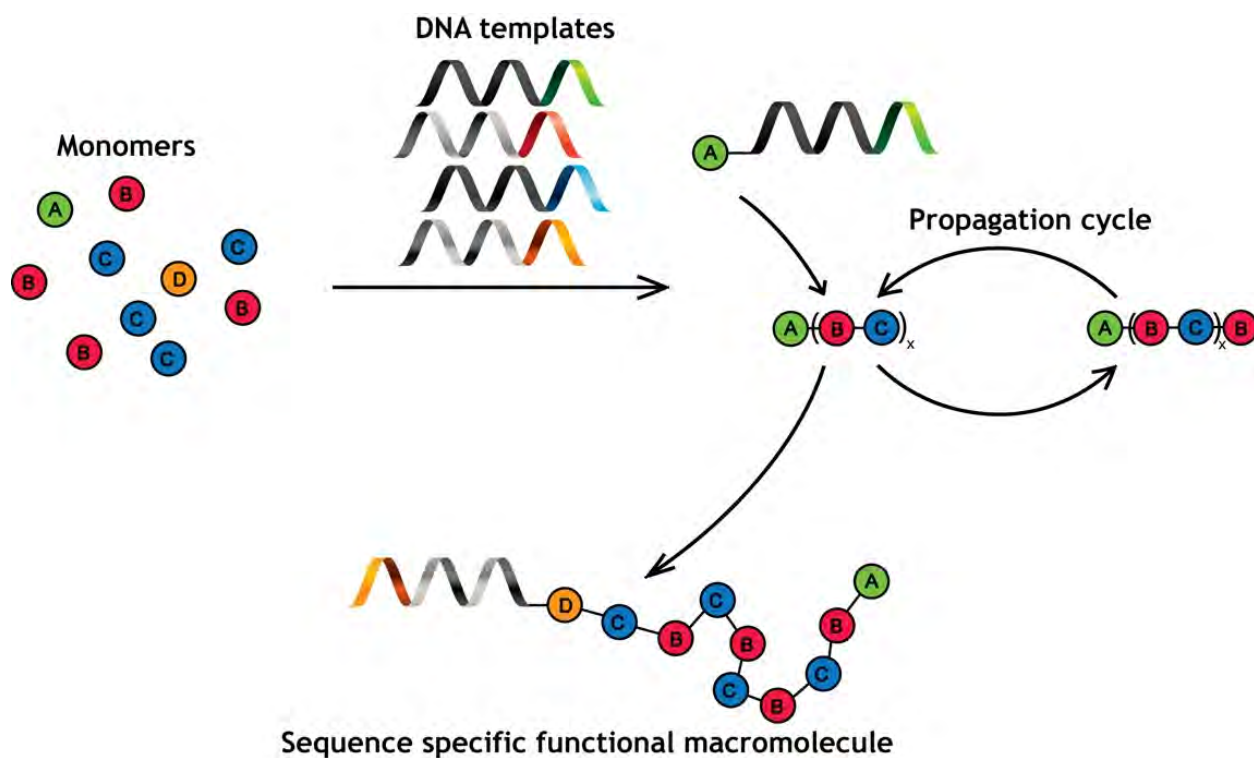
More than 27 years ago at the IBM Almaden Research Center, low temperature high resolution spectroscopy experiments aimed at establishing the ultimate limits to optical storage in solids led to the first optical detection and spectroscopy of a single molecule in the condensed phase. At this unexplored ultimate limit, many surprises occurred where single molecules showed both spontaneous changes (blinking) and light-driven control of emission. In the 1990, optical detection of single molecules at room temperature blossomed in polymers and cells, serving as a local probe of a variety of complex environments without ensemble averaging. Surprises occurred here, too, including blinking and switching of single green fluorescent protein variants. In 2006, several groups showed that the optical diffraction limit of ~ 200 nm can be circumvented with single molecules to achieve super-resolution fluorescence microscopy. Essential to this is the combination of single-molecule fluorescence imaging with active control of the emitting concentration and sequential localization of single fluorophores decorating a structure. Super resolution microscopy has opened up a new frontier in which biological structures and behavior in complex environments can be observed with resolutions down to 20-40 nm and below. Today, even in the “conventional” single-molecule tracking regime where the motions of individual molecules are recorded rather than the shapes of extended structures, much can still be learned about complex nanoscale processes.



POLY 163: Learning from nature to create novel nanomaterials

Rachel K. O'Reilly, *r.k.o-reilly@warwick.ac.uk*. Dept of Chemistry, University of Warwick, Coventry, United Kingdom

Our research targets the design, synthesis and application of uniquely derived polymeric materials, where control over architecture, functionality and reactivity are key. Recently, we have explored ways to exploit the functional nanostructures present in biology – DNA and proteins – to engineer materials with unique properties. For example, direct conjugation allows the useful properties of both synthetic polymers (low cost and relative ease of synthesis, the possibility of a wide range of stimuli-responsive behaviours) and biomolecules (catalysis, information storage) to be combined. We have created temperature-responsive nanoparticles incorporating proteins and complex 3-D DNA structures, and have utilised non-covalent biological interactions to direct self-assembly. A second powerful approach involves mimicking interactions found in Nature, by incorporating nucleobase groups into the side chains of polymers synthesised using conventional controlled radical techniques. Our final avenue of research also makes use of the highly orthogonal nature of nucleobase pairing. We use the hybridisation of complementary functionalised DNA strands to bring reactants together in an order predetermined by a DNA 'programme'. This talk will provide an overview of these three research streams, with a particular focus on our work on DNA templated synthesis.



POLY 164: Supramolecular biomaterials: From fundamentals to advanced healthcare solutions

Eric A. Appel, eappel@stanford.edu. Department of Materials Science & Engineering, Stanford University, Stanford, California, United States

Hydrogels are an important class of biomaterial that have received much attention for tissue engineering and controlled drug-delivery applications on account of their similarity to soft biological tissue and highly tunable mechanical properties. Supramolecular hydrogels are dynamically cross-linked polymer networks exhibiting highly useful properties that are impossible with traditional hydrogels, yet crucial for a wide variety of emerging biomaterials applications. These properties include externally tunable and shear-responsive mechanical properties and self-healing, which allows them to be deployed in a minimally-invasive fashion by catheter delivery or direct injection. These properties have contributed to a rapid gain in interest in the application of these materials for drug delivery and tissue engineering. Herein, we discuss the preparation and application of shear-thinning, injectable hydrogels driven by non-covalent interactions between modified biopolymers (BPs) and biodegradable nanoparticles (NPs). Owing to the non-covalent interactions between NPs and BPs, these hydrogels flow under applied stress and their mechanical properties recover completely within seconds when the stress is relaxed, demonstrating the shear-thinning and injectable nature of the material. Moreover, the hierarchical construction of these biphasic hydrogels allows for multiple therapeutic compounds to be entrapped simultaneously and delivered with differential release profiles in vitro and in vivo. These release characteristics can be independently tuned and can extend over several months, enabling novel long-term treatment strategies. Overall, this presentation will demonstrate the facile synthesis of an injectable hydrogel platform affording minimally invasive application in vivo and controlled release of therapeutics.

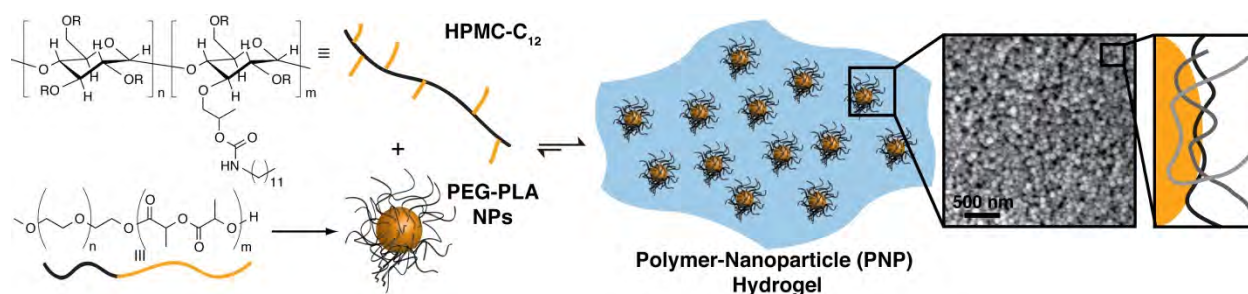


Figure 1: Dynamic, multivalent interactions between polymers and nanoparticles yield PNP hydrogels that are exceedingly simple to prepare, highly modular, syringe injectable, and biocompatible.

POLY 165: Applications of functionalized biodegradable polymers in tissue engineering and regenerative medicine

Kazuki Fukushima¹, kazkittel@gmail.com, Yuto Inoue², Yuta Haga², Masashi Oji², Shunya Takaoka², Chikako Sato², Haruka Tsuchiya², Masaru Tanaka^{3,2}. (1) Department of Polymeric and Organic Materials Engineering, Yamagata University, Yonezawa Yamagata, Japan (2) Yamagata University, Yonezawa, Japan (3) Kyushu University, Fukuoka, Japan

Biodegradable aliphatic carbonyl polymers, such as polylactides, polylactones, and polycarbonates, have been studied for applications in a broad range of resorbable medical devices. With progress in diagnostic and therapeutic technologies for the aged society, the demand for diverse and highly developed biodegradable biomaterials has increased.

We now focus on poly(trimethylene carbonate) (PTMC) analogs with ether substituents for tuning surface hydration, resulting in regulated adhesion of cells and serum proteins (Figure 1). Controlled polymerization techniques by organocatalysts are also used for the safer production of such biomedical materials and the precise formation of block/random/graft copolymers. Our recent interest is directed to amphiphilic block copolymers with a mesogen-like motif for understanding their supramolecular assembly behavior and interaction with biomolecules and cells (Figure 2).

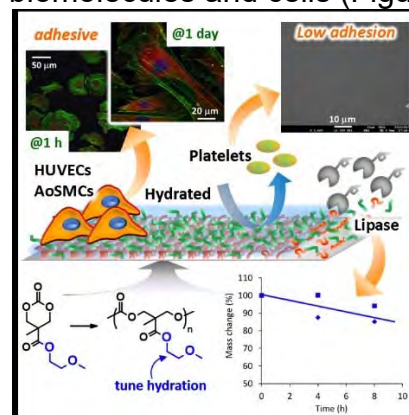


Figure 1. Enzymatically degradable polycarbonate demonstrating low platelet adhesion and good cell adhesion

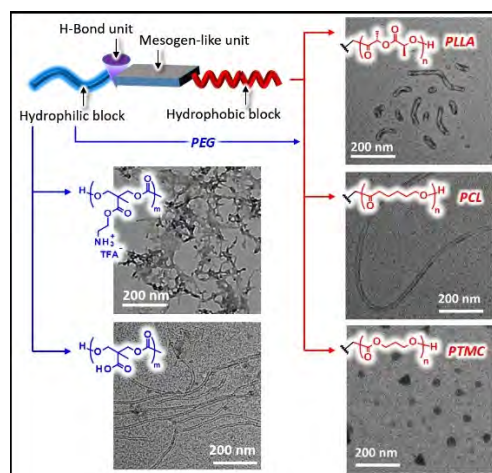
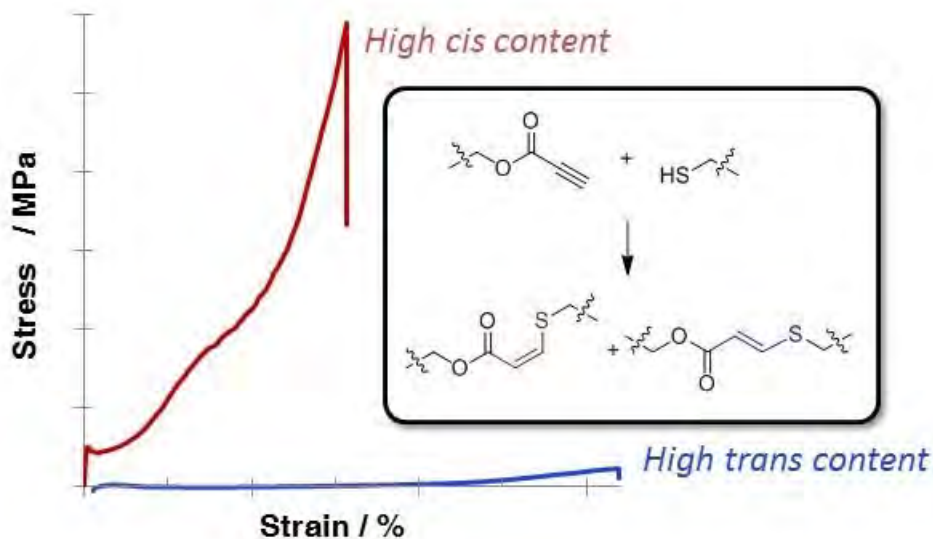


Figure 2. Supramolecular assemblies of amphiphilic block copolymers with an orientation induction unit

POLY 166: Degradable elastomeric biomaterials through stereochemically-controlled synthesis

Andrew P. Dove, *a.p.dove@warwick.ac.uk*. Univ of Warwick, Coventry, United Kingdom

The synthesis of advanced materials for application in biomedical research has received a great deal of attention over recent years. Current state-of-the-art biomaterials typically lack either the mechanical flexibility of modern elastomers and/or degrade in a way that results in loss of mechanical properties. Our research has focussed on the application of stereochemical selectivity in polymer synthesis to create a new class of elastomers through a nucleophilic thiol-yne step-growth addition, in which the mechanical properties are controlled through the stereochemistry of the double bond in the back bone of the polymer - analogous to natural rubber and gutta percha. In this way the chemical composition of the materials can be more readily tuned with a minimal impact on the mechanical properties thus allowing attachment of bioactive molecules and incorporation of units to control degradation.

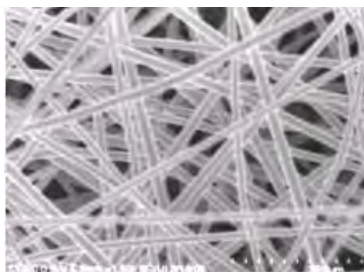


POLY 167: Forty years of spectroscopic studies of polymers at the leading edge from FT-Raman to AFM-IR spectroscopy: Evolution, revolution or back to the future

John F. Rabolt, *rabolt@udel.edu*. University of Delaware, Newark, Delaware, United States

Vibrational spectroscopy has evolved over the past 40 years from a technique used by specialists to one that is used by anyone who is interested in the routine structural characterization of materials. One of the more exciting instrumental developments in the past 5 years is the combination of atomic force microscopy (AFM) and infrared (IR) spectroscopy to overcome the technical limitations of obtaining chemical information at the nanoscale. This new technique, known as AFM-IR, is based on the photo-thermal induced resonance effect (PTIR). It is a powerful tool that provides topographic information that can be correlated with chemical, conformational and molecular orientation information in polymers, in particular, but also can be used to investigate other materials, in general, at a spatial resolution of 50-100 nm.

As an example of the power of this technique, a metastable β -crystalline form of biodegradable and biocompatible poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHx) was fabricated using a combination of solution electrospinning and high-speed collection on a rotary disk with a tapered edge. Using an AFM-IR instrument and low dose selected area electron diffraction (SAED), we have explored the correlation between structure, processing and chain orientation/crystallinity in these single nanofibers and tested the hypothesis that different processing protocols can alter the concentration of the stable α -crystalline form and the metastable β -crystalline form. The ability to obtain IR spectra at high spatial resolutions (50 – 100 nm) has allowed us to probe crystalline populations as a function of nanofiber diameter and as a function of location within the fiber and we have observed, for the first time, the existence of a core-shell structure in a single, 250 nm diameter electrospun nanofiber.

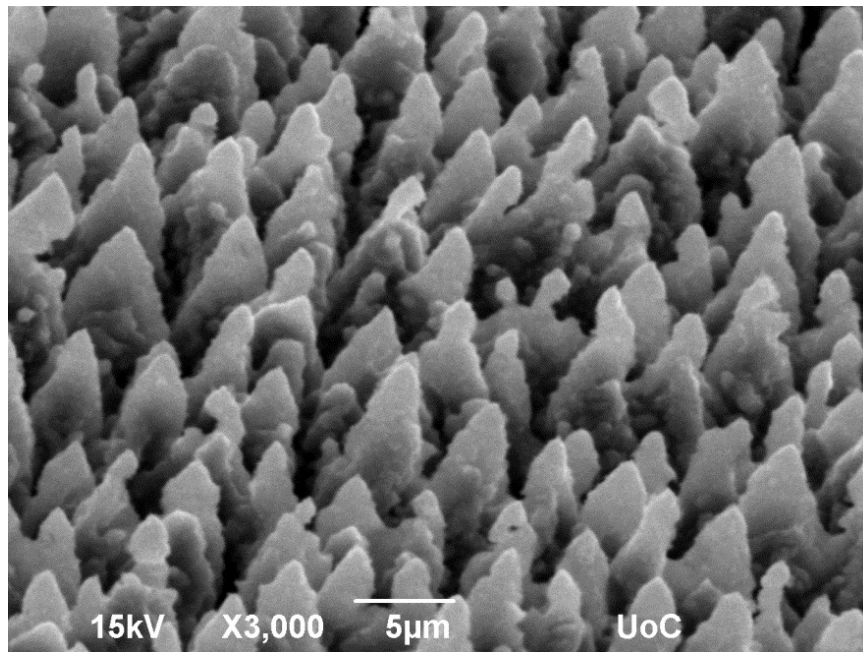


Electrospun Isotactic Polypropylene Nanofibers

POLY 168: Development of multi-functional surfaces with controllable wettability

Melani A. Frysalı^{1,2}, George Kenanakis¹, Georgia Kaklamani¹, Lampros Papoutsakis¹, **Spiros H. Anastasiadis**^{1,2}, spiros@iesl.forth.gr. (1) Inst. of Electronic Structure and Laser, Foundation for Res. Techn.- Hellas, Heraklion Crete, Greece (2) Dept. of Chemistry, Univ. of Crete, Heraklion Crete, Greece

The design of multifunctional surfaces based on biomimetic structures has gained the interest of the scientific community. This is mainly due to potential applications like self-cleaning surfaces, microfluidics, nanomedicine and catalysis. Such biomimetic structures can be achieved by using “smart” coatings, which can respond to external stimuli, such as light, temperature, electric field, pH or solvent selectivity, onto appropriately structured substrates. Novel multifunctional surfaces have been developed, able to alter their wetting properties in response to both temperature and pH as well as light illumination, by combining proper chemistry and surface micro/nano-structuring. For this purpose, dual scale micro/nano-roughened surfaces have been prepared by irradiating Si wafers using ultrafast (femtosecond) laser under a reactive atmosphere; polymeric or inorganic coatings were subsequently introduced to provide the desired functionality. The combination of the hierarchical surface with a ZnO coating and/or a pH- or temperature-responsive polymer results in efficient photo-active properties as well as reversible superhydrophobic / superhydrophilic surfaces in response to the external stimuli. Such surfaces can be optimized to exhibit high or zero water adhesion and/or controllable directionality as well. Moreover, such surfaces can be seeded with human fibroblasts in order to examine the cellular response on both the surface roughness and the surface chemistry.

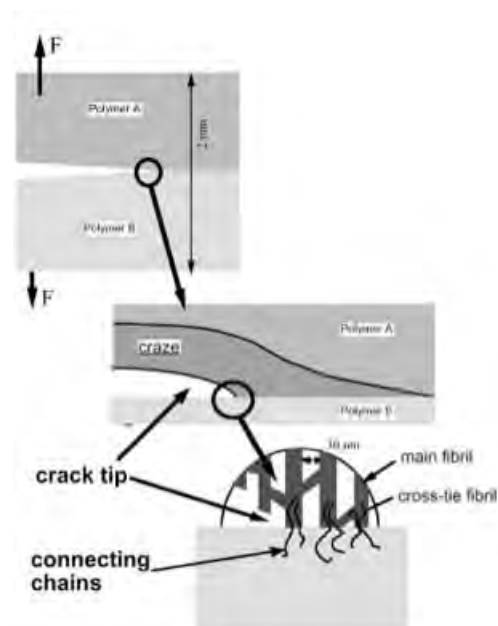


Micro/nano-structured Si surface with a mixed P2VP/PNIPAM (1:1) brush “grafted to” the surface

POLY 169: Developments in polymer adhesion and fracture at IBM Almaden Research Laboratory

Hugh R. Brown, hbrown@uow.edu.au. University of Wollongong, Wollongong, New South Wales, Australia

I will review some of the developments at Almaden in the area of polymer mechanical properties with particular emphasis on the work on crack propagation and fracture, adhesion and friction. These areas have the great advantage that they were partly driven by manufacturing problems but gave fundamental information on important properties of polymeric materials. Developments in some of these areas in the last few years will also be considered.



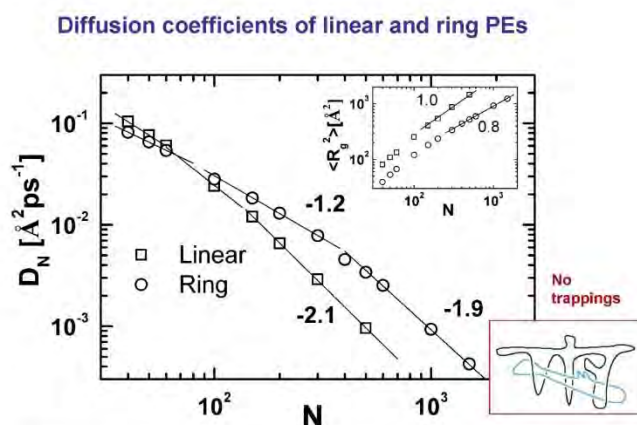
Crack tip at the interface between two glassy polymers

POLY 170: Effects of molecular topology and interface on conformations and dynamics of polymer melts from atomistic molecular dynamics simulations

Do Y. Yoon^{1,2}, doyoon@stanford.edu. (1) Dept of Chemical Engineering, Stanford University, Palo Alto, California, United States (2) Seoul National University, Department of Chemistry, Seoul, Korea (the Republic of)

In the first part, the results of molecular dynamics simulations of linear and ring polyethylene (PE) melts and blends of linear/ring PE melts will be discussed, together with results of lattice-model simulations, focusing on the fundamental effects of molecular topology on conformations and dynamics of polymer melts. For entangled ring PE melts, we observe the time dependence of mean-square monomer displacements and the chain-length dependence of diffusion coefficients to be very similar to entangled linear chains. However, the diffusion coefficients remain larger for the entangled rings than the corresponding entangled linear chains, due to the larger chain length for the onset of entanglement. Severe topological constraints on diffusion coefficients are found only for the rings in the linear chain matrix.

In the second part, the interface characteristics of polystyrene melts in free-standing thin films will be discussed from the molecular dynamics simulations employing an explicit atom force field. The calculated surface tension is in good agreement with experiment, which provides a support for the force field parameters. In the surface region the phenyl-plane normal axis and chain backbone axis are both preferentially oriented along the film surface, in agreement with available experiments. The density profile exhibits an enrichment of phenyls relative to the alkyls at the top low-density surface, but this top surface is followed by a layer of relatively depleted phenyl density of ca. 1 nm thickness. The presence of phenyl depleted region near the free surface of polystyrene films may be related to the most pronounced decrease of glass transition temperatures in thin films of polystyrene as compared with other polymers.



(Hur, Cheol, Winkler, Lacevic, Gee, Yoon, *Macromolecules* 2011, 44, 2311)

POLY 171: Development of silicon-containing polymers for modern micro- and nano-electronics

Qinghuang Lin, qhlin@us.ibm.com. MS 13-241, IBM T J Watson Rsrch Ctr, Yorktown Heights, New York, United States

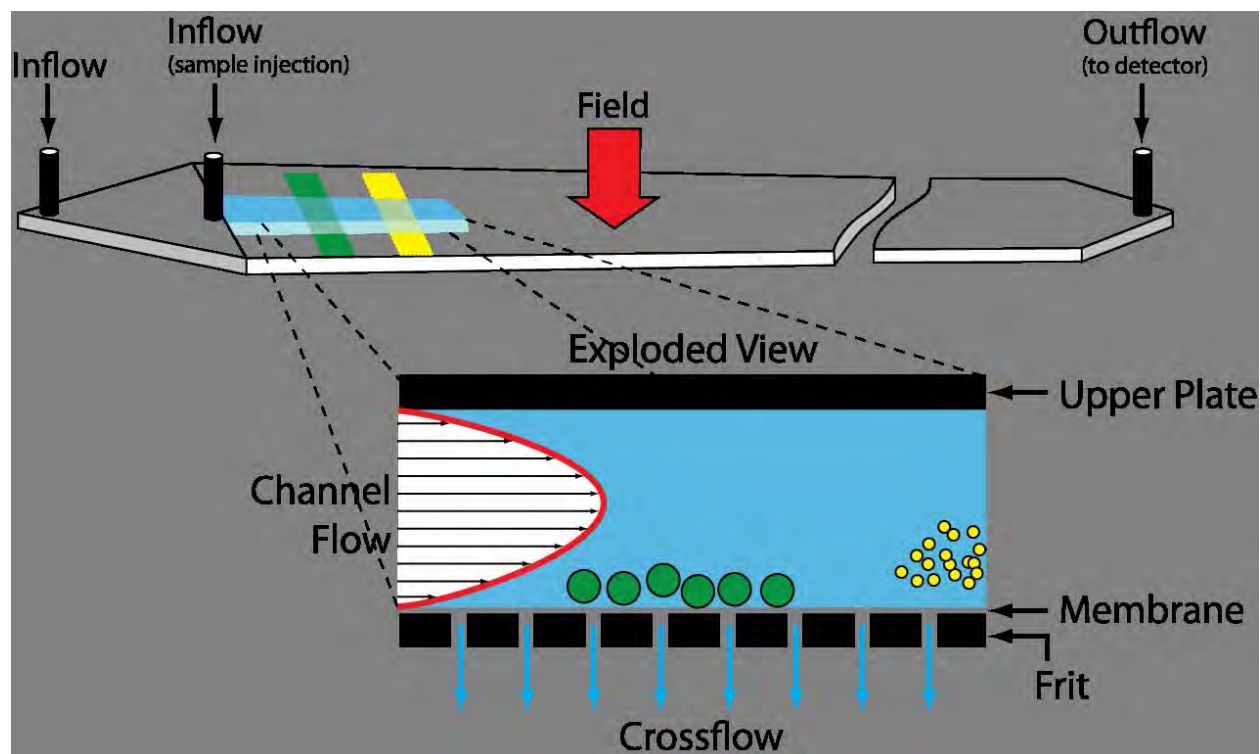
Silicon has been the material of choice for ever smaller, faster and cheaper transistors that have ushered in the Internet Age and the era of Knowledge Economy. In this talk, we will describe the design and synthesis of silicon-containing polymers, with silicon both on the polymer main chain and the side chain, as functional materials for modern micro- and nano-electronics. We will discuss development of these silicon-containing polymers as light-sensitive photoresists, as electrical insulators, and as photo-patternable permanent on-chip electrical insulators. Some of these silicon-containing polymers have been used to manufacture chips that power some of the most powerful or the most popular electronic devices in the world today.



POLY 172: Advances in Asymmetric Flow Field Flow Fractionation (AF4) combined with MALS in the characterization of polymers in solution

Jeffrey A. Ahlgren, jahlgren@wyatt.com. Customer Service and Support, Wyatt Technology Corporation, Goleta, California, United States

Applications in Asymmetric Flow Field Flow Fractionation (AF4) have been growing in number since its commercialization approximately 15 years ago. When coupled with online detectors such as multi-angle light scattering detectors (MALS) and PALS (phase analysis light scattering detectors), molar mass distributions, size distributions, and even charge distributions can now be measured. AF4 can help confirm results determined by classical techniques such as SEC-MALS, and in cases of heavily branched material that becomes entangled in SEC packing material, fractionation by AF4 can result in improved size distribution analysis due to the nature of the fractionation method. Innovations such as hollow fibers have been developed to reduce sample and solvent requirements without loss of signal sensitivity. For sample types prone to entanglement or significant aggregation resulting from sample concentration during focusing steps, specialized channels such as the frit inlet channel have been developed to permit fractionation of these samples without a focusing step that typically is used during FFF methods. Examples of samples which do not fractionate well by SEC but were successfully fractionated by FFF will be presented.



POLY 173: Cognitive macromolecular therapeutics

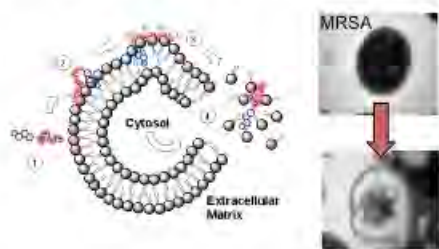
J Hedrick, hedrick@us.ibm.com. IBM Research, San Jose, California, United States

Multi-drug resistant diseases are one of the biggest challenges society is facing in the domain of healthcare. Contraction of a multi-drug resistant disease, whether through a microbial infection or the loss of chemotherapeutic effectiveness, results in an extremely poor patient prognosis given the severely limited treatment options. The rapid resistance development in microbes, for instance, has completely eviscerated the current antimicrobial drug pipeline. The resistance development of a variety of cancer cell lines has rendered treatment with a single therapeutic agent completely ineffective. Instead, chemotherapeutic treatments must rely on a bevy of chemotherapeutic agents and chemosensitizers to achieve remission, most often at the cost of the patient's well-being, owing to significant toxicity.

Traditional, small-molecule drug therapy usually targets highly specific cellular processes or interactions, enabling resistance development through simple mutations in the pathogen's genome. In contrast, macromolecular therapeutics consist of polymeric assemblies that exhibit selective but non-specific interactions with the pathogen, making resistance development extremely difficult. In fact, macromolecular therapeutic agents developed at IBM have shown no resistance development in the treatment of bacteria and viruses, in preliminary *in vitro* studies. Additionally, these agents have been found to be highly effective against drug-resistant bacteria and cancer cell lines, while maintaining very low toxicity towards healthy cells. Given these impressive features, macromolecular therapeutics hold significant promise for disease treatment.

Antimicrobials

Drug resistant bacteria and biofilms are two of the grand challenges of this decade. Central to this challenge is the development of macromolecular therapeutics that preclude resistance. The highly selective mode of action, membrane lysis, mitigates the onset of resistance. Applications range from personal care, wound care to systemic infections.



POLY 174: Development of sustainable alternatives for the next generation of chemicals and materials: Continued progress in development of renewably-sourced materials from DuPont

Henry E. Bryndza, Henry.E.Bryndza@dupont.com. DuPont, Wilmington, Delaware, United States

The development of more sustainable alternatives for the next generation of chemicals and materials is an imperative for the ongoing viability of today's chemicals and materials industries. The depletion of non-renewable resources and the limitations of infrastructure are at odds with the increasing demands for a better quality of life from people all over the world. Moreover, questions about our planet's ability to survive the environmental assault from emerging economies growing in the 21st century the way North America and Western Europe grew in the 20th century all point to the need to find a more sustainable way to grow these foundational industries. This talk highlights DuPont's considerations for sustainable alternatives, the challenges faced with introducing new materials and discusses examples of how disparate technologies have been brought together to commercialize new renewably-sourced products. Illustrations will include recently introduced products as well as new-to-the-world polymer platforms just announced in 2016 that are now ready for collaborative commercialization with customers.



Critical Issues for Commercial Success


Failure modes that must be addressed up-front

Incumbency

- Introducing new materials always involves costs for our customers
- Plan for market entry and penetration is critical for success

Scale

- Most petrochemically-derived materials are produced at large scale
- Must plan for competitive entry of new materials at demonstration scale



New and Improved Products

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POLY 175: Future fabricated with light: Photolithography in 2D leading to CLIP in 3D

Joseph M. DeSimone, desimone@email.unc.edu. University of North Carolina, Chapel Hill, North Carolina, United States

“3D printing” is a misnomer: it is actually 2D printing over and over again. This lecture will describe a new advance in 3D additive manufacturing that is rapid, continuous and no longer layer-by-layer that promises to advance industry beyond basic prototyping to 3D manufacturing. The new Continuous Liquid Interface Production technology (CLIP) harnesses light and oxygen to continuously grow objects from a pool of resin instead of printing them layer-by-layer. The technology was simultaneously introduced to the scientific community as the cover story in the journal Science and on the stages of TED2015. CLIP technology raises the state-of-the-art in 3D fabrication in three ways:

- GAME-CHANGING SPEED: 25-100 times faster than conventional 3D printing
- COMMERCIAL QUALITY: produces objects with consistent mechanical properties
- MATERIAL CHOICE: enables a broad range of polymeric materials



POLY 176: Digital manufacturing at the NNSA's National Security Campus

Daniel E. Bowen, *dbowen@kcp.com. Honeywell Fm T, Kansas City, Missouri, United States*

Additive Manufacturing (AM), in the form of polymer/stereolithography based Rapid Prototyping has been commercially available since the late 1980's. More recently, the technique has migrated from a tool primarily for visualization and prototypes to a technology capable of manufacturing tooling, fixtures, and actual parts from a variety of polymers and metal alloys. This migration has occurred in concert with significant advancements in the capabilities of commercial AM machines, as well as improvements in material physical properties and the understanding of process/physical property relationships.

As such, Additive Manufacturing has the potential to revolutionize manufacturing and is a technique tailor-made for early adoption within the Nuclear Security Enterprise in terms of capability, complexity, and production volume. However, additive manufacturing is critical, even the most critical, but just one aspect within the broader concept of Digital Manufacturing, which also encompasses thinking and designing differently, simulation, and validation. Without these other aspects of Digital Manufacturing, there is little hope that the speed and cost savings promised by AM will be realized. This presentation will discuss the mission of the National Security Campus in the context of advanced manufacturing and AM, and expand upon the theme of Digital Manufacturing.

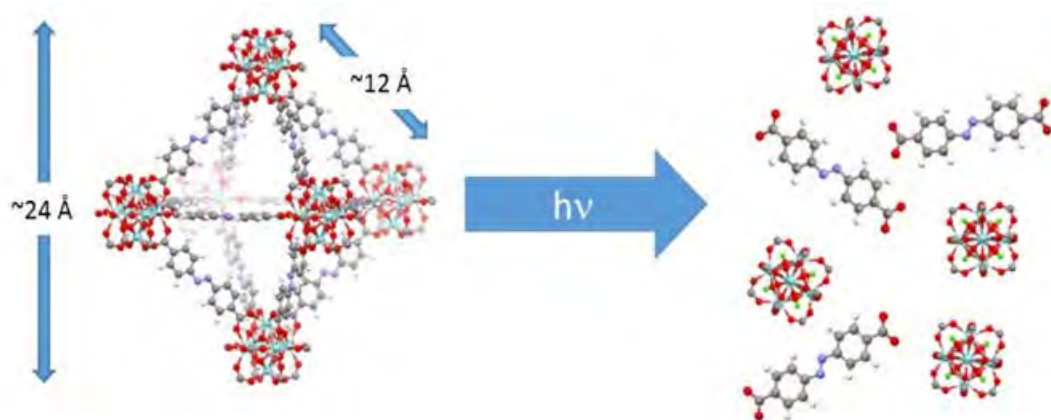


25,000th 3D Printed Development Item

POLY 177: Stimuli-responsive metal organic framework nanoparticles

Amanda J. Morris, ajmorris@vt.edu, Cherie C. Epley. Chemistry, Virginia Tech, Blacksburg, Virginia, United States

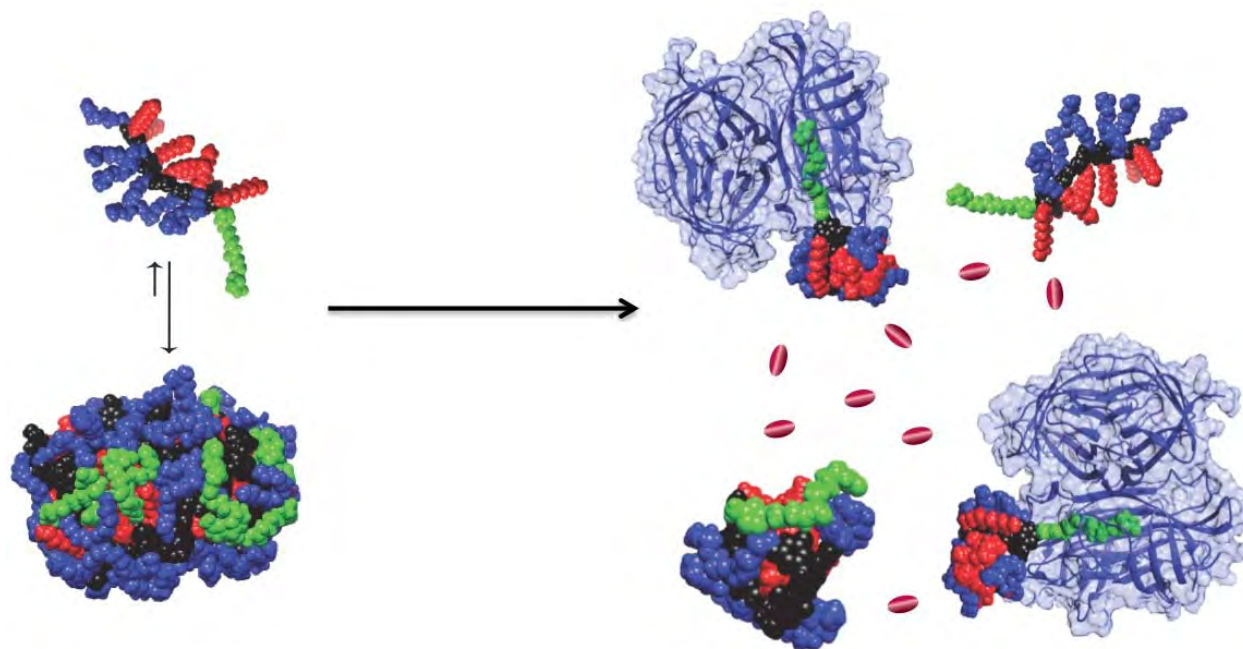
The ability to control via external stimuli the delivery of molecular cargo has the potential to impact a variety of applications – drug delivery, time-release fertilizers, fragrances, and the food packaging industry. In the past photo-caging has generally been accomplished through molecular interactions. Upon light activation, bond scission can release an active molecular species. Ultimately, many of these systems were explored for drug delivery applications. Metal organic frameworks (MOFs), composed of metal nodes connected by multi-dentate organic linkers, provide a 3D, polymeric network that can effectively encapsulate species of interest. Herein, the development of a photo-active, synthetically-tunable MOF nano-cage. The linkers undergo a photo-induced geometry change that causes the overall material to degrade on demand. As the material degrades, encapsulated cargo, in this case molecular dyes and drug molecules, are controllably released. The rate of release can be tuned through both the intensity of light incident on the material and the wavelength of light used to drive the uncaging event (white light vs. monochromatic). Preliminary results concerning the use of the developed MOFs for a new form of photodynamic dynamic therapy (oxygen-independent) will be included.



POLY 178: Atypical responses from polymeric nanoassemblies

Sankaran Thayumanavan, *thai@chem.umass.edu*. Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, United States

Molecular designs that afford tunable supramolecular assemblies are of interest in a variety of applications, including drug delivery, sensing, and diagnostics. When these assemblies are nanoscopic in size and are responsive to specific stimulus, then the interests in these nanoscale scaffolds are even higher. We have developed amphiphilic supramolecular assemblies featuring these characteristics. In addition, these assemblies also can bind guest molecules efficiently and release them in response to specific triggers. Our ultimate goal is to develop design algorithms that lend themselves to predictably design nanoscale assemblies that respond to physical, chemical, or biological stimuli. Fundamental and translational implications of these findings would be numerous. We will report our progress in this area.

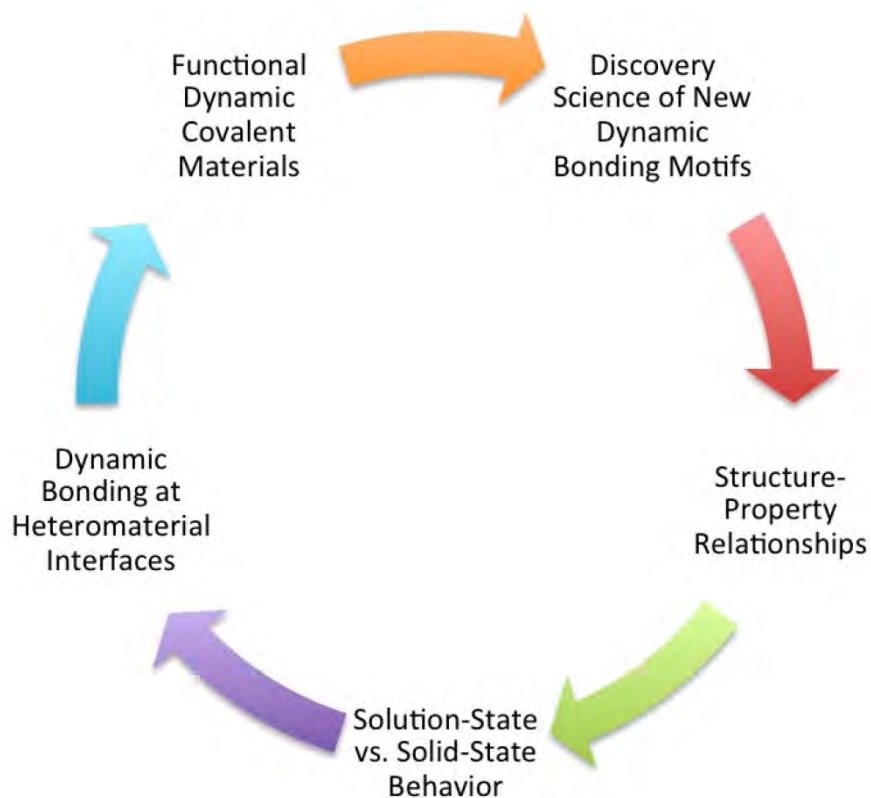


Disassembly of a polymeric nanoassembly in response to a specific protein

POLY 179: Molecular design strategies for smart materials based on new dynamic bonding motifs in polymers

Brett Helms, bahelms@lbl.gov. *The Molecular Foundry, Lawrence Berkeley National Lab, Berkeley, California, United States*

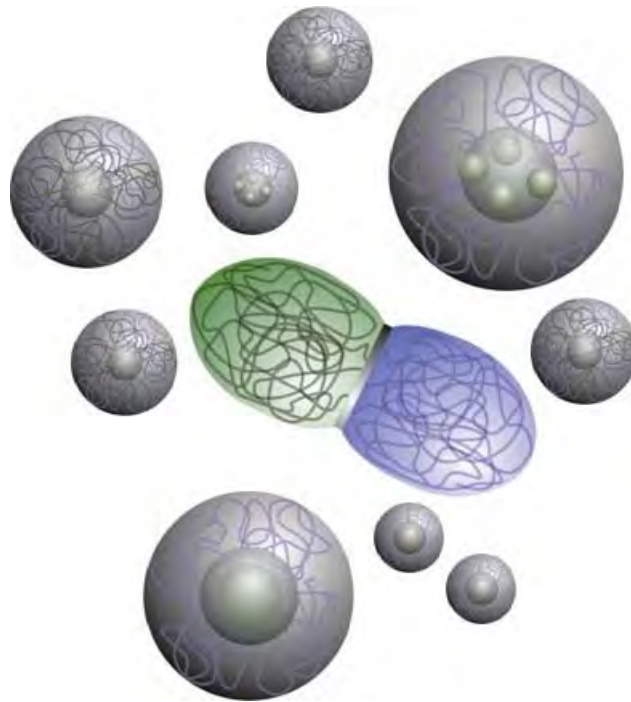
Smart materials incorporating polymers in their design increasingly rely on dynamic bonds to impart useful, reconfigurable character. Here I will describe our recent efforts in understanding and controlling the fundamental physiochemical aspects of such dynamic bonds, with a particular focus on multi-component systems deliberately configured such that a range of competing processes is ultimately responsible for the system's behavior. In some cases, these competitive processes are allowed to proceed in the bulk; in other cases, they are allowed to proceed at an interface. The unique system responses achievable by either scheme suggest that we are only at the beginning of a revolution in smart materials and point to new directions in driven, active matter systems.



POLY 180: Engineering multi-responsive complex coacervate core micelles for biomedical and materials science applications

Ilja Voets, i.voets@tue.nl. Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands

Complex coacervate core micelles (C3Ms) spontaneously form upon co-assembly of two oppositely charged polymers under suitable conditions in aqueous solutions. As micelle formation is driven by electrostatic interactions, C3Ms are multi-responsive nanostructures that readily adapt to changes in charge stoichiometry, pH, ionic strength, as well as external cues, like temperature and light, provided suitable (co)polymers are selected. An overview will be presented of recent work on various types of C3Ms developed for specific biomedical and materials science applications.



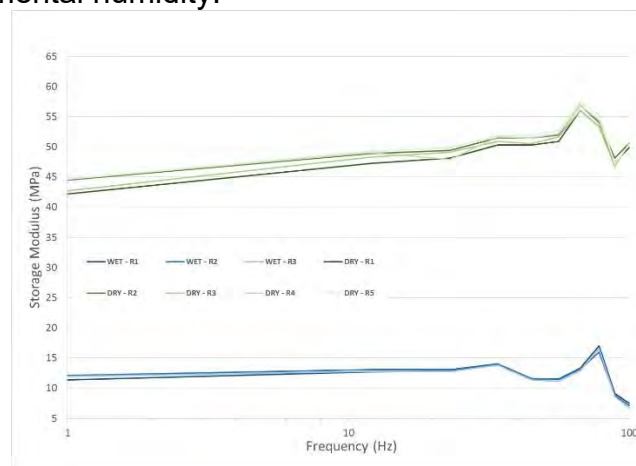
POLY 181: Processing effects on mechanically adaptive response of cellulose nanocrystal composites

Michael Bortner, *mbortner@vt.edu*, Johan Foster, Jacob Fallon, Ben Kolb, Cara Herwig. Virginia Tech, Blacksburg, Virginia, United States

Thermoplastic polymer nanocomposites integrating cellulose nanocrystals (CNCs) have previously been demonstrated to possess mechanically adaptive properties, responding to changes in external environments by a dramatic change in stiffness/modulus. Traditionally, these nanocomposites are generated via solution casting approaches. Thermal processing via melt extrusion can form specific product shapes and/or impart preferential alignment, orientation for targeted mechanical performance.

The focus of this work is to establish the structure-process-property relationships surrounding thermal processing impact on the mechanical response of a thermoplastic urethane polymer containing 10 weight percent CNCs. We investigate monofilament extrusion followed by extrusion based 3-D printing into a desired format. Our work reveals the impact of thermal history of both processes on the mechanical response of CNC composites from a dry state (e.g. <5% relative humidity, RH) to wet state (100% RH), and the corresponding hysteresis following cycling between wet and dry states. Additionally, we reveal the impact of extrusion on CNC orientation and mechanical response.

Preliminary results indicate drastic response with up to 5x reduction in storage modulus between wet and dry states, with comparable relative change over a temperature range of 25-40°C. Following melt extrusion into monofilament form, overall small changes in uniaxial (flow direction) storage modulus (<10%) are observed in the dry state over a broad frequency range. We will present the corresponding impact on wet-state response and hysteresis when cycling between wet and dry states. Additionally, we will deconvolute the separate, competing contributions of CNC orientation and thermal decomposition; the former is expected to substantially increase modulus, while the latter is expected to reduce CNC coupling and decrease both modulus and expected response to environmental humidity.



Frequency dependence of storage modulus response between dry (green) and wet (blue) state.

POLY 182: Self-Assembly and responsiveness of polypeptide-based star and triblock copolymers

*Craig Machado, Ian Smith, Brooke Barnes, **Daniel A. Savin**, dsavin1973@gmail.com.
Chemistry, University of Florida, Gainesville, Florida, United States*

This study involves the bottom-up design and tunability of responsive, peptide-based block copolymers. The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic triblock and star copolymers containing poly(lysine) (PK), poly(leucine) (PL) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. The peptide block in these structures can serve to introduce pH responsiveness (in the case of PK and PE), or can facilitate the formation of elongated or kinetically-trapped structures (in the case of PL.) This talk will present some recent studies in solution morphology transitions that occur in these materials under varying solution conditions.

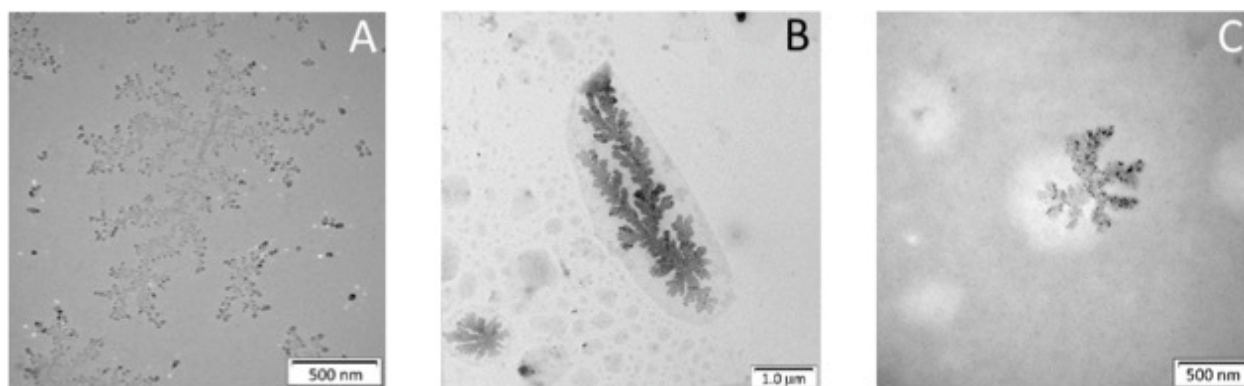


Figure 1. Kinetically trapped structures of PEO-PK-PL triblock polymers.

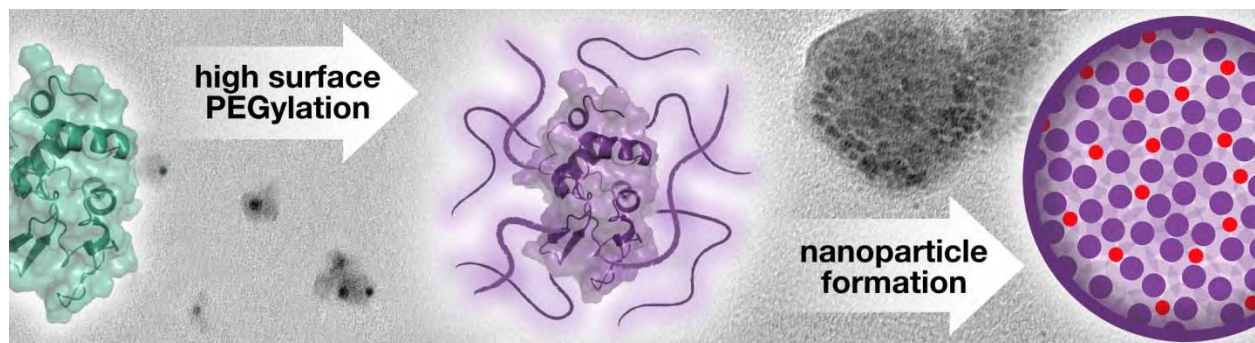
POLY 183: Nanoparticle assembly of surface-modified proteins

Matthias Fach, Lydia Radi, **Peter R. Wich**, peterwich@gmail.com. Institute of Pharmacy and Biochemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

Modern drug delivery systems for therapeutic applications are very similar in size and shape to biological nanostructures with comparable functions, like exosomes or viruses. Polymer-based particles are in particular interesting as drug, vaccine and gene delivery systems because they can be easily chemically modified, but they can lack in biocompatibility and degradability. Alternatives are nature's biopolymers that are readily accessible, can be obtained in high quantity, are structurally well defined and trigger in most cases only a low reaction of the immune system.

Especially proteins have interesting properties as structurally well-defined biopolymers for the formation of nanoparticles. They can have advantages over synthetic polymers when looking at specific areas like biodegradability, non-antigenicity, stability, binding capacity or toxicity. Because of these unique properties, protein-based nanocarriers are promising candidates for the delivery of therapeutics.

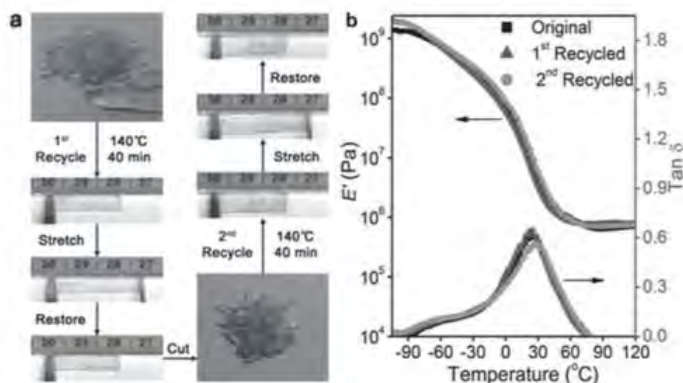
Here, we present a recently developed, universal approach for the preparation of protein-based nanoparticles for the delivery of hydrophobic drugs. It features a new concept for the formation of particles based on the assembly of surface-modified proteins (see Figure). Our method allows the use of solvent evaporation techniques for the formation of stable nanoparticles without denaturation or crosslinking of the proteins. We obtain empty and drug-loaded nanoparticles with a size of around 100 nm that are stable in different physiological environments. The produced nanoparticles are non-toxic and can efficiently deliver the encapsulated drugs in *in vitro* experiments. Additionally, we transferred the method of particle preparation to various proteins in different sizes, showing that this method can be universally applied to any protein of choice. This opens up the potential for multifunctional nano-systems, where the function and structure of the particle material itself might be as important as the therapeutic payload.



POLY 184: Recyclable crosslinked polymer networks via one-step controlled radical polymerization: Full property recovery after multiple melt-reprocessing steps of models for tire rubber and other polymer networks

John M. Torkelson¹, *j-torkelson@northwestern.edu*, **Kailong Jin**², **Lingqiao Li**³. (1) *Chemical and Biological Eng. and Materials Sci. and Eng., Northwestern University, Evanston, Illinois, United States* (2) *Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, United States* (3) *Chemical and Biological Eng., Northwestern University, Evanston, Illinois, United States*

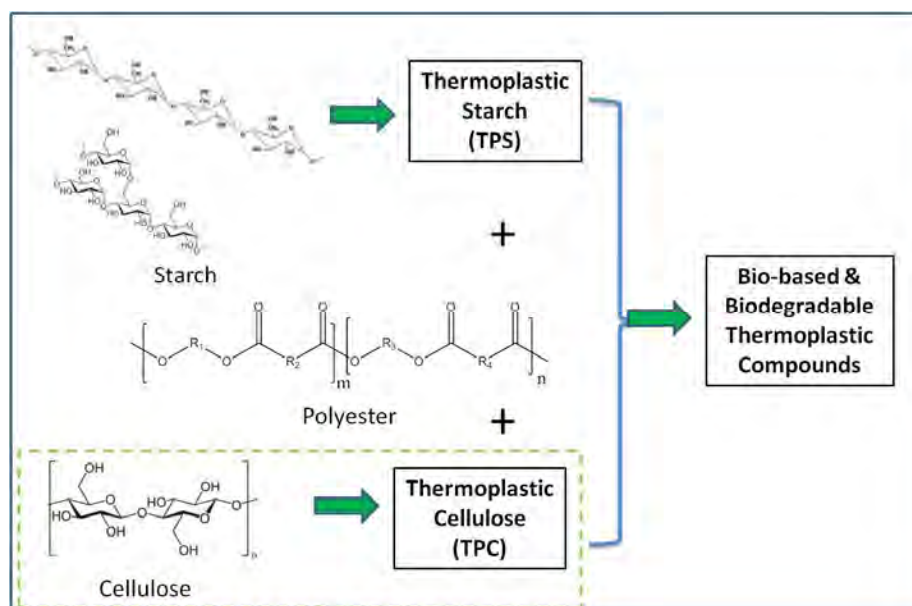
Conventional polymer networks cannot be recycled into high-value products because of permanent, covalent crosslinks. Rubber tires illustrate well the issues ranging from economic loss to environmental problems and sustainability issues that arise with spent, crosslinked polymers. (More than a billion rubber tires are discarded annually worldwide.) A nitroxide-mediated polymerization (NMP) strategy has been developed that allows for one-step synthesis of recyclable crosslinked polymeric materials from any monomers or polymers that contain carbon-carbon double bonds amenable to radical polymerization. The resulting materials possess dynamic alkoxyamine crosslinks that undergo reversible decrosslinking as a function of temperature. As demonstrated with polybutadiene as starting material, and styrene, an appropriate nitroxide molecule and bifunctional initiator for initial crosslinking, a model for tire rubber can be produced by reaction at temperatures comparable to those employed in tire molding. Upon cooling, the crosslinks are made permanent due to the extraordinarily strong temperature dependence of the reversible nitroxide capping and uncapping reaction. Based on thermomechanical property characterization, when the original crosslinked model rubber is chopped into bits and later remolded into the melt state into a well-consolidated material, the resulting material properties at temperature below 373 K indicate full recovery of properties associated with crosslink density after multiple reprocessing steps. Additionally, this simple one-step strategy allows for robust, relatively sustainable recyclability of crosslinked polymers and design of relatively uniform networks for advanced technologies. A more complete description of this strategy and outcomes is provided in a recent publication. Other strategies for melt-state reprocessing of crosslinked polymers will complete or nearly complete recovery of properties will also be discussed.



POLY 185: Compounding of thermoplastic polysaccharides and biodegradable polyesters

Bing Zhou, 04gfzzb02@zju.edu.cn, James H. Wang, Qin Jia. Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai, China

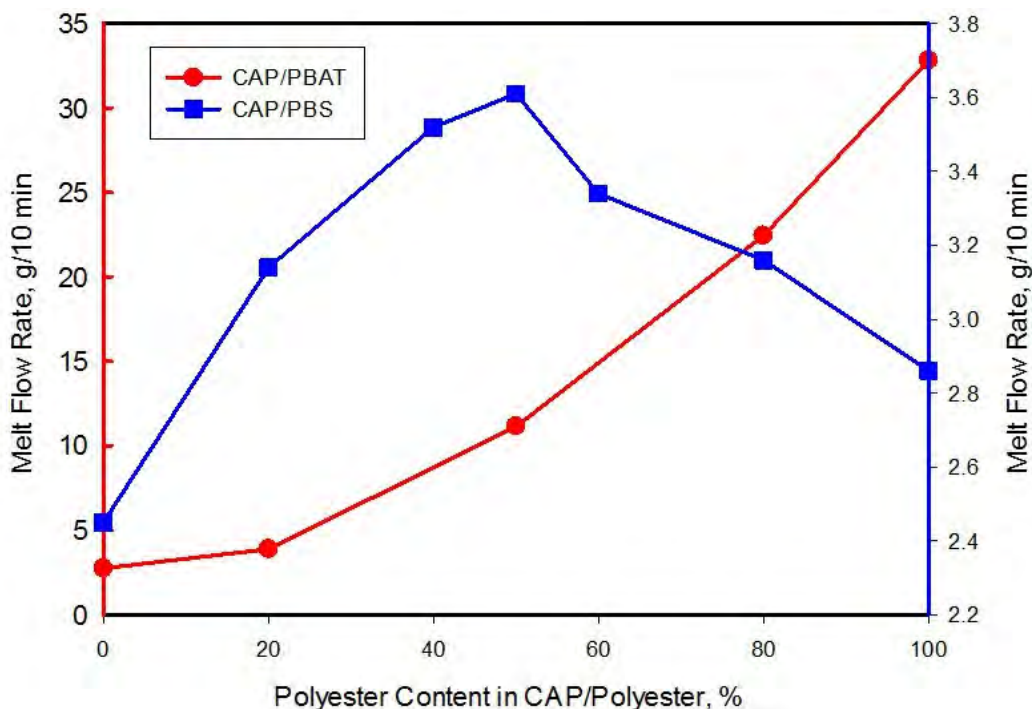
Compounding thermoplastic polysaccharides e.g. thermoplastic starch (TPS) and thermoplastic cellulose (TPC) etc. with biodegradable polyesters could obtain renewable materials with better combination properties than that of each component. However, for the variety of the chemical structures of thermoplastic polysaccharides and biodegradable polyesters, their compatibilities and interactions with each other are really complicated. To get a better understanding, in this study, a set of TPS/polyester binary blends as well as TPS/TPC/polyester ternary blends are prepared and compared. Generally the binary TPS/polyester blends have good ductility, low tensile strength, and high moisture sensitivity, while in the TPS/TPC/polyester ternary blends, by sacrificing some ductility, the tensile strength and modulus can be greatly increased by the presence of the TPC. To determine the mechanical properties of the materials, these blends are converted into thin thermoplastic films. The evaluation of the mechanical properties of the films reveals that the resulting TPS/polyester films have ductility higher than 300%, while the breaking stress of these binary films are as low as 7 MPa. By the addition of TPC to form TPS/TPC/polyester films, the ductility of these ternary films are higher than 110% and it increases with polyester content, while the breaking stress of the films are 20 MPa, about 3 times of binary films. By changing the composition, the above values could be adjusted in very wide range. The mechanical performance of the films is correlated with the microstructures of the films determined by SEM. The findings in this paper provide important insights for developing renewable thermoplastic materials from natural polysaccharides.



POLY 186: Biodegradable polyesters/cellulose esters blends: Thermal and rheological properties important for thermoplastic processing

Yu Bai, yubaipk@gmail.com, James H. Wang, Jun Kuang, Bing Zhou. Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai, China

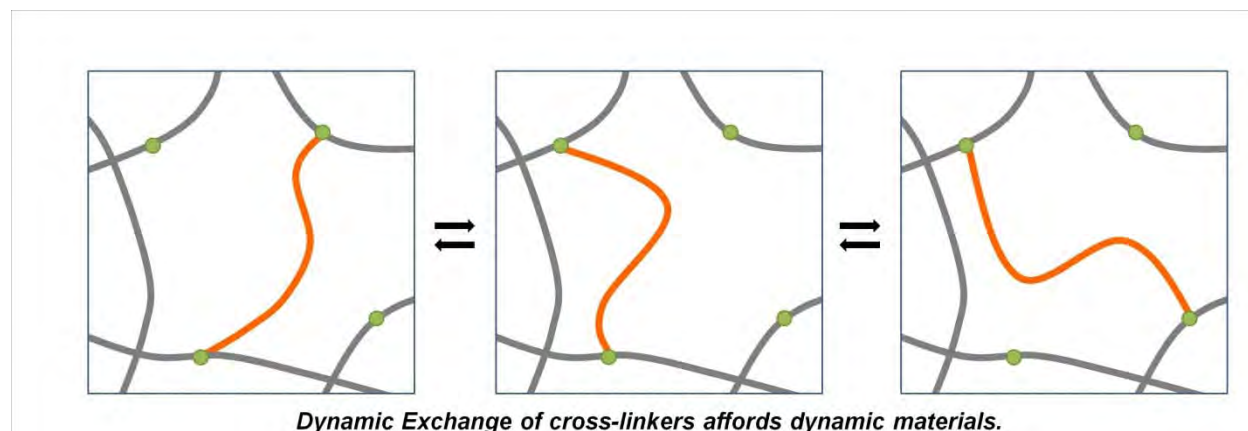
As the world is concerned about global warming and the environmental impact of thermoplastics, there is an increasing interest to explore the utilization of renewable materials such as cellulose for partially replacing commodity polymers from petroleum. Cellulose derivatives, e.g. cellulose esters and ethers, have good mechanical strength and certain thermoplastic properties, but which are not enough for thermoplastic processing. Blends of cellulose acetate propionate (CAP) and biodegradable thermoplastic polyesters, poly(butylene succinate) (PBS) or poly(butylene adipate-co-terephthalate) (PBAT), are prepared and their thermal and rheological properties are investigated in this paper. For CAP/PBS, glass transition temperatures of each polymer component in the blends are the same as those for raw polymers, indicating poor compatibility between CAP and PBS. The increase of PBS crystallization temperature and narrowing of melting and crystallization peaks at the presence of CAP show CAP possibly acts as a nucleation agent. The blends exhibit higher flowability, 3.6 g/10 min, than pure polymers do (<2.9 g/10 min), which helps extend their application in injection molding and film. This is probably due to the weak interface adhesion. On the contrary, CAP/PBAT blends' viscosity satisfy the additivity rule. With the addition of CAP, melting and crystallization peaks for PBAT don't narrow and disappear more quickly than those for CAP/PBS system. This can be ascribed to stronger interaction between CAP and PBAT. All these results have built a basis for further development of suitable thermoplastic materials from cellulose for 3D printing etc.



POLY 187: Renewable silicon-containing cross-linked polymers and tuning their properties

Yoshio Nishimura, *yoshionishimura2015@gmail.com*, Jaeyoon Chung, Zhibin Guan.
University of California Irvine, Irvine, California, United States

The recent trend in materials chemistry towards bottom-up materials design with a focus on small molecule dynamics has allowed scientists and engineers to imbue remarkable macroscopic responses to bulk materials such as self-healing, shape-memory, and malleability. In the last few years these concepts have been applied to epoxy-like thermosets for a new class of dynamic materials called vitrimers, so named due to its glass-like (vitreous) Arrhenian fluidity in a permanently cross-linked organic network. Inspired by our previous discovery that variability in molecular exchange kinetics could directly translate to variability in bulk dynamic properties, we saw the potential of one of covalent bonds containing silicon to deliver similar versatility in dynamic and mechanical properties to vitrimers through minimal molecular perturbation. We have successfully introduced a novel dynamic motif, exchange chemistry of covalent bonds containing silicon, for vitrimer design. The cross-linked polymers were fully reformed after the samples were cut into small pieces and then melt-pressed. This is one of the few examples of materials exhibiting vitrimeric behavior without transition metal catalyst, and thus far the only example of autocatalytic control of the vitrimer topology freezing temperature and the material reprocessing temperature.



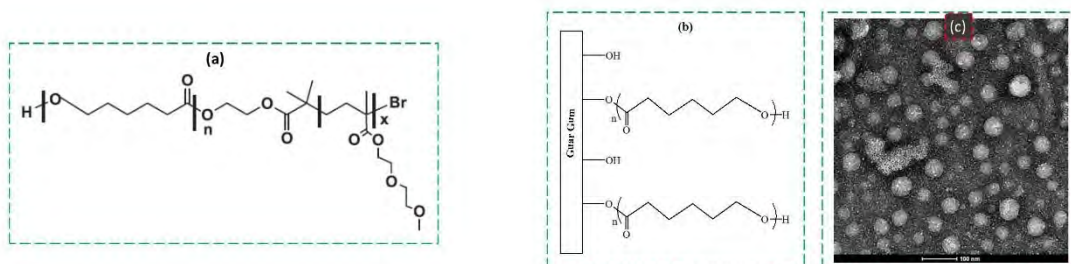
POLY 188: Biodegradable copolymers based on poly(ϵ -caprolactone): From packaging to wastewater treatment applications

Mohammad K. Hassan¹, mohamed.hassan@qu.edu.qa, Hicham Qayouh², Elizabeth Jacob¹, Khadija Zadeh¹, Shaheen A. Al-Muhtaseb³, Mariam A. Al-Maadeed⁴, Mohammed Lahcin². (1) Center for Advanced Materials, Qatar University, Doha, Qatar (2) Laboratoire de Chimie Organométallique et Macromoléculaire – Matériaux Composites, Université Cadi Ayyad, Marrakech, Morocco (3) Department of Chemical Engineering, Qatar University, Doha, Qatar (4) Office of VP for Research, Qatar University, Doha, Qatar

Synthetic polymers exhibit interesting properties, such as mechanical strength and high wear resistance, made them good candidates to replace other materials like glass and wood. However, they generate large volume of waste and huge amount of CO₂ during their production and dumping. Substitution of petroleum-based plastics with bio-based plastics is a promising alternative to reduce CO₂ footprint and the pressure on landfills from the synthetic non-degradable plastic waste, both are crucial for sustainable environments.

This work presents our efforts to develop and characterize various types of biodegradable materials for packaging, drug delivery, and wastewater treatment applications. The materials include copolymers of poly(ϵ -caprolactone) with poly[oligo(ethylene glycol)methyl ether methacrylate] and with Guar Gum, and its thermoplastic polyurethane based on L-lysine diisocyanate and 1,4-butanediol. Synthesis of the biopolymers and their morphology, thermal, mechanical, dynamic mechanical, and dielectric characteristics will be presented.

In addition, measurements of the low critical solution temperature of the poly(ϵ -caprolactone)-*b*-poly[oligo (ethylene glycol) methyl ether methacrylate] amphiphilic copolymers in aqueous medium using UV-visible spectroscopy will be discussed. Behavior of the copolymers studied by transmission electron microscopy, dynamic light scattering, and adsorption experiments indicate their potential to remove colloidal organic impurities from wastewater, without changing the pH of the water.

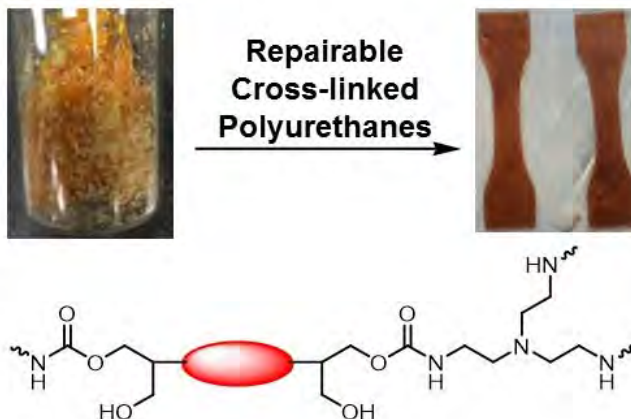


Chemical structure of copolymers of poly(ϵ -caprolactone) with poly[oligo (ethylene glycol) methyl ether methacrylate] (a) and with Guar Gum (b); and TEM of the former in aqueous solution (c).

POLY 189: Stress relaxation and reprocessability of cross-linked polyhydroxyurethanes

David J. Fortman^{1,3}, djf243@cornell.edu, **Jacob P. Brutman**², **Marc A. Hillmyer**², **William R. Dichtel**³. (1) Department of Chemistry & Chemical Biology, Cornell University, Ithaca, New York, United States (2) Department of Chemistry, University of Minnesota - Twin Cities, Minneapolis, Minnesota, United States (3) Department of Chemistry, Northwestern University, Evanston, Illinois, United States

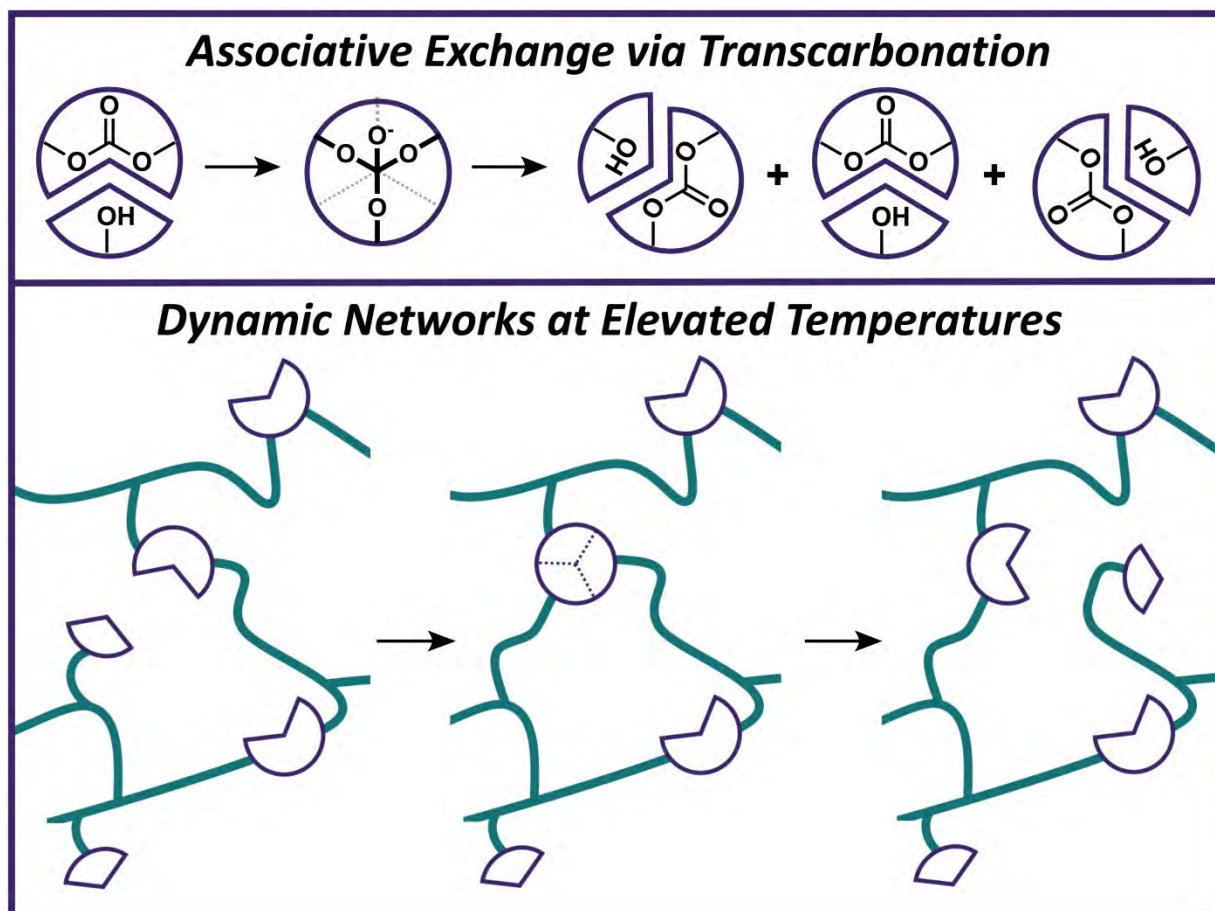
Vitrimers are an emerging class of polymeric materials that display thermoset-like mechanical properties at service temperatures and reprocessability at elevated temperatures. We have recently reported cross-linked polyhydroxyurethane networks derived from bis(6-membered cyclic carbonates) and polyamines as a new class of polymer networks that show vitrimer-like behavior at elevated temperatures, which we attribute to associative transcarbamoylation reactions occurring within the hydroxyurethane networks. These networks exhibit tensile properties competitive with traditional thermosets at room temperature, and recover approximately 75% of their as-synthesized values after elevated temperature reprocessing. We will present further investigation into the effects of cyclic carbonate ring size, cross-linking density, and monomer structure on the stress relaxation behavior, thermal stability, and reprocessability of polyhydroxyurethane networks, and demonstrate how these studies inform the design of future reprocessable and sustainable polymeric materials enabled by the dynamic nature of urethane linkages.



POLY 190: Polycarbonate vitrimers from bis(cyclic carbonates) and polyols

Rachel L. Snyder¹, rlsnyder@u.northwestern.edu, **David J. Fortman**^{1,2}, **William R. Dichtel**¹. (1) Chemistry, Northwestern University, Evanston, Illinois, United States (2) Chemistry & Chemical Biology, Cornell University, Ithaca, New York, United States

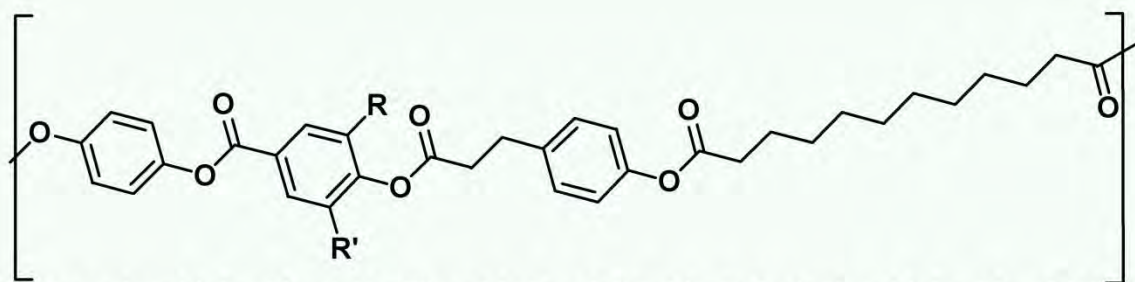
Thermosets display excellent mechanical strength imparted by covalent crosslinking of polymer chains; however, these materials traditionally contain static linkages that preclude all post-synthetic reprocessing. Vitrimers are a new class of crosslinked polymers that address reprocessability by incorporating linkages that undergo thermally activated, associative exchange reactions, such that networks are mechanically robust at service temperatures, yet processible at elevated temperatures. From the ring-opening polymerization of bis(cyclic carbonates) with polyfunctional alcohols, we have developed a new class of polycarbonate vitrimers, which show Arrhenius-type stress relaxation at elevated temperatures in the presence of Lewis acid catalysts. We will present our investigation of the effects of network structure on the mechanical properties, dynamics, and reprocessability of this novel set of materials.



POLY 191: Renewable aliphatic-aromatic copolyesters based on phloretic acid

Massoud J. Miri, *mjmsch@mail.rit.edu*, Michael E. Bloom, Jeferson F. Vicentin, Joseph M. Marsico, Tullio S. Geraci, Daniel S. Honeycutt. School of Chemistry and Materials Science, Rochester Institute of Technology, Rochester, New York, United States

We have synthesized highly renewable, thermoplastic copolyesters with a wide range of melting temperatures. Among the comonomers applied to obtain terpolyesters and tetrapolyesters were lignin derivatives, such as vanillic acid, syringic acid, p-coumaric acid and phloretic acid. Phloretic acid as principle comonomer resulted in the best combination of polymerization behavior and polymer properties. Bulk polymerizations were performed as two-stage transesterifications. The effects of the number of methoxy groups of comonomers and the monomer content on the glass transition temperature and melting temperature was established. The copolyesters were further characterized by ^1H NMR, ^{13}C NMR, TGA, solution viscometry, GPC, and hot-stage microscopy.

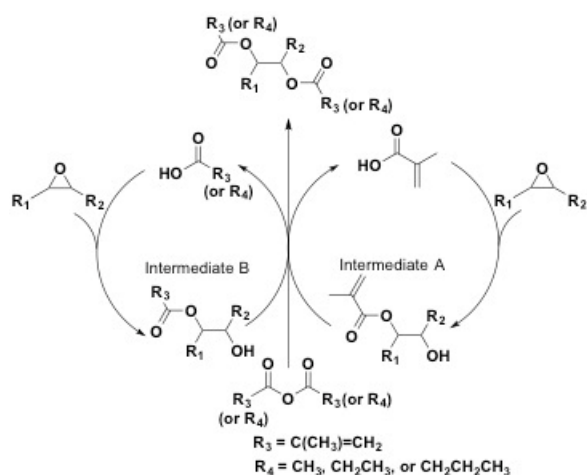


Benzoic acid: $R = R' = \text{H}$, Vanillic acid: $R = -\text{OCH}_3$, $R' = \text{H}$; Syringic acid: $R = R' = -\text{OCH}_3$

POLY 192: Structure-property relationships in modified highly functional bio-based thermosets

Arvin Z. Yu, *arvinzillionyu@yahoo.com*, Jonas M. Sahouani, Dean C. Webster.
Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States

Dual methacrylated epoxidized sucrose soyate (DMESS) have previously been synthesized from epoxidized sucrose soyate (ESS). DMESS showed lowered resin viscosity compared with the single methacrylated product (MESS). However, due to its highly functionalized nature, the resulting thermosets were found to be very brittle. In order to increase ductility and maintain low viscosity, ester groups were incorporated into the resin. The synthesis is a one-pot process involving the addition of two anhydrides mixed prior to addition. The resins were characterized using Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), gel permeation chromatography (GPC), and viscosity measurements. The resins were mixed with varying amounts of styrene and cured using peroxyesters as initiators. The extent of cure was determined by gel content using Soxhlet extraction and confirmed using FTIR. The thermal and mechanical properties were evaluated using thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and tensile testing.



POLY 193: Mechanically stiff 3D printed biomimetic hydrogel for chondrogenesis and cartilage tissue production

Elizabeth Aisenbrey, *elizabeth.aisenbrey@colorado.edu*, **Stephanie J. Bryant**,
Chemical and Biological Engineering, University of Colorado, Boulder, Colorado, United States

Hydrogels laden with mesenchymal stem cells (MSCs) are promising for the treatment of cartilage defects; however, hydrogels suitable for cell culture require a low modulus, and therefore are not able to support normal joint loads. This work develops novel cell-laden hydrogels that are mechanically strong, promote chondrogenesis, and support cartilage tissue growth. We developed an *ex vivo* cartilage defect model in which a mechanically supportive poly(ethylene glycol) PEG hydrogel, with a modulus similar to that of native cartilage ($E=1\text{MPa}$) was photopolymerized *in situ*. After 28 days of dynamic loading, the hydrogel-filled plug protected the surrounding tissue while the unfilled defect led to tissue degeneration (Figure 1A[SJB1]). To develop a hydrogel that has a similar modulus to cartilage, but also supports differentiation and tissue growth, we propose independently designing the stiff structure from the soft cellular component. A degradable soft photoclickable thiol-norbornene PEG hydrogel was designed to which cartilage-like extracellular matrix (ECM) molecules functionalized with thiols are incorporated to create an environment that recapitulates key physiochemical cues in native cartilage (Figure1B). After 9 weeks, the encapsulated MSCs formed a cartilage ECM predominantly made of collagen II, resulting in increased modulus and concomitant PEG degradation (Figure1C). The stiff structure is designed with a cathedral-like structure to capture the orientation of the collagen fibers natively. As a proof of conception, 3D printed structures using digital projection photolithography to create pillar structures were implanted in an *ex vivo* cartilage defect and infilled with a soft hydrogel (Figure1D). Future work will combine the 3D structure with the aforementioned infilled MSC-laden hydrogel to evaluate its effect on tissue production while simultaneously protecting the surrounding cartilage tissue.

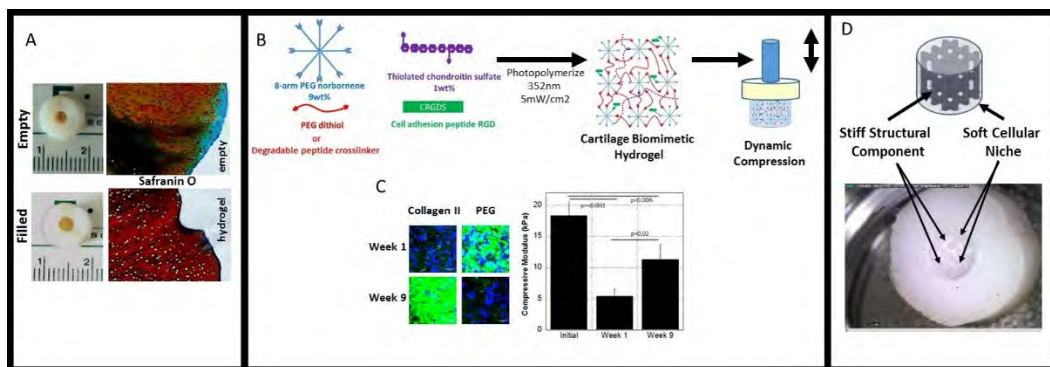
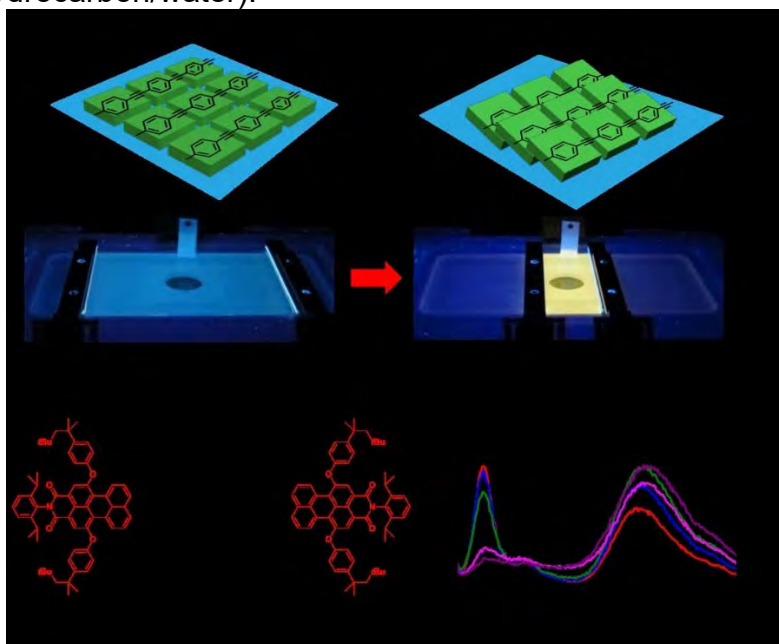


Figure 1. A) Porcine osteochondral explants after 4 weeks of dynamic compression (1hr/day) and glycosaminoglycans (red) B) PEG cartilage hydrogel C) Collagen II, PEG and nuclei (blue) immunohistochemistry and compressive modulus of MMP7-degradable hydrogel. D) 3D printed structure implanted in a cartilage defect and infilled with soft hydrogel.

POLY 194: Exciton migration in conjugated polymers at the amphiphilic interfaces

Byungjin Koo, *byungjin@mit.edu*, Timothy M. Swager. MIT, Cambridge, Massachusetts, United States

Exciton migration to emissive defects in conjugated polymers is a robust signal amplification strategy for optoelectronic sensors. Herein we present two approaches to form emissive low-energy defects in poly(phenylene ethynylene)s (PPEs) and demonstrate the energy migration at the amphiphilic interfaces. The first approach is to utilize a novel interpolymer assembly. We synthesized PPEs with designed amphiphilic side chains via Sonogashira couplings and they form monolayers at the air-water interface. The compressed polymer monolayers assemble into what we call incline-stack conformation as a result of the high anchoring propensity of the side chains to a water subphase. This assembly generates excimer emission with improved quantum yields and we observe the exciton transfer from backbone (cyan emission) to interpolymer excimer bands (yellow emission) upon the compression of monolayers. The yellow interpolymer assembly is transferred to the glass substrate via Langmuir-Blodgett technique and this assembly undergoes reorganization and shows yellow-to-cyan fluorescence transduction upon exposure to solvent vapors. The second approach is to employ emissive dyes as an end-group. We end-functionalized the PPEs (ending with Ar-Pd-I) with the acetylene-terminal perylene monoimide in one-pot synthesis. The reaction conditions for perylene incorporation will be discussed. The compression of the polymer monolayers at the air-water interface induces energy transfer from backbone (cyan emission) to perylene (red emission). Applying the exciton migration scheme in water is realized at the micelle-water interface and in the complex emulsions (fluorocarbon/hydrocarbon/water).



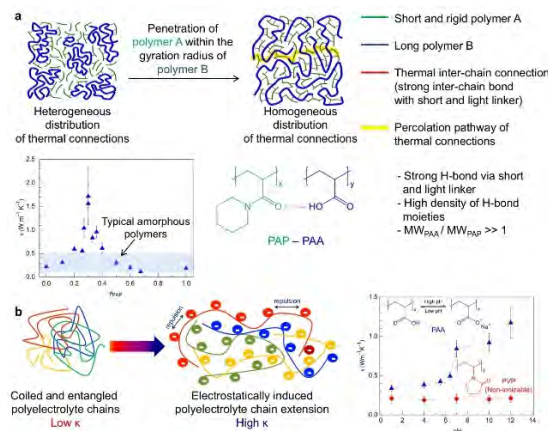
Two approaches to form low-energy emissive sites for exciton migration and dual-fluorescence chemical sensors

POLY 195: Molecular engineering of polymers to realize high thermal conductivity in amorphous systems

Apoorv Shanker², apoorvsh@umich.edu, Gun-Ho Kim³, Chen Li⁴, Kevin Pipe⁴, Jinsang Kim^{1,2}. (1) Materials Science and Engineering, University Michigan, Ann Arbor, Michigan, United States (2) Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States (3) Mechanical and Nuclear Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of) (4) Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, United States

Structural defects such as chain entanglements & voids, & weak Van der Waals inter-chain interactions result in low thermal conductivity ($\kappa = 0.1\text{-}0.5\text{Wm}^{-1}\text{K}^{-1}$) in polymers which limits their use in applications that require to dissipate heat quickly (e.g., power electronics). Common methods to enhance polymers' κ like compositing with high- κ fillers and chain alignment suffer with numerous disadvantages such as unwanted physical properties, high cost etc. For practical applications, high κ polymers that are more compatible with conventional manufacturing processes are desired. Here, we demonstrate two design strategies to engineer the polymer chains' morphology & inter-chain interactions to realize high κ in all-polymeric amorphous systems.

In the first approach, we employed hydrogen bonds between a short rigid polymer chain (Poly(*N*-acryloyl piperidine), PAP) and a long flexible one (Polyacrylic acid, PAA) to form inter-polymer complex in which the longer PAA chains were held in extended chain conformation. In addition to improving intra-chain thermal transport through the extended PAA chains, H-bonds also strengthened inter-chain heat transfer resulting in significant enhancement in κ with value as high as $1.5\text{Wm}^{-1}\text{K}^{-1}$ achieved in nanoscale thin films. In the second approach, we employed linear electrostatic repulsion field along the polymer backbone to induce chain extension. Controlled ionization of a weak polyelectrolyte (PAA, $\text{pK}_a \sim 6$) resulted in a tunable charge density on the polymer chain which induced changes in chain conformation from 'coiled-up' at low pH to 'extended' above the pK_a value. κ in typical spin-cast film increased linearly with the degree of PAA ionization, reaching up to $\sim 1.2\text{Wm}^{-1}\text{K}^{-1}$ in film with >90% ionization.



a, H-bonded inter-polymer complex and measured κ of spin-cast PAP:PAA films at various monomer mole fractions of PAP (ϕ_{PAP}). **b**, Coulombic repulsion induced chain expansion and κ of PAA and a non-ionizable polymer PVP as a function of polymer solution pH.

POLY 196: Directed structure manipulation of conjugated polymers with external fields

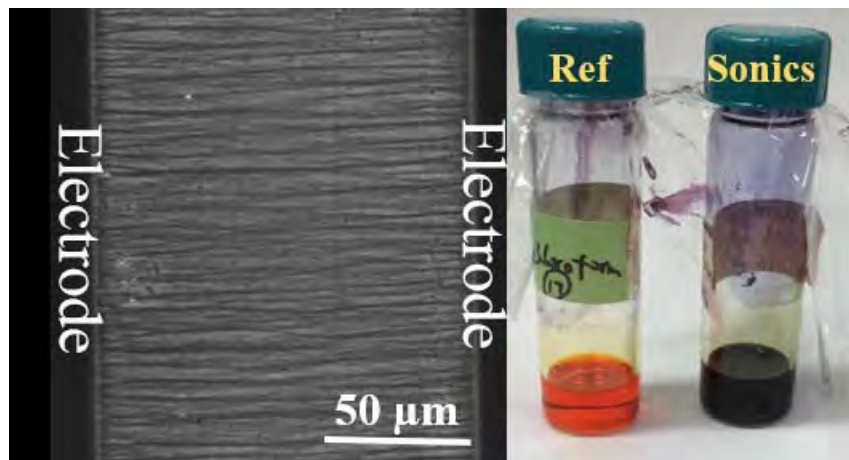
Yuyin Xi, xiyuyin@uw.edu, Lilo D. Pozzo. Chemical Engineering, University of Washington, Seattle, Washington, United States

Due to the conductive nature and great tuning ability from the perspective of material design, conjugated polymers serve as excellent candidates for flexible and large scale electronic devices processing. However, there is still a large room to further improve the performance by engineering and optimizing their nano-scale structure. In this work, the effect of applying electric and acoustic (pressure) fields on conjugated polymers in solutions have been investigated.

It was shown that conjugated polymers can be uni-directionally aligned over nanometer and micrometer scales by an external AC electric field. Optimum amplitude and frequency are identified for alignment by utilizing optical microscopy, small angle neutron scattering (SANS) and atomic force microscopy (AFM). Other affecting parameters, including concentration, solvent quality, and details of the molecular structure of the polymers were systematically studied. It was found by x-ray diffraction (XRD) that, in general, the p-p stacking direction was along the fiber growth axis. The leading alignment mechanism was proposed to be dielectrophoresis occurring during the polymer crystallization process. Both the electrical and mechanical properties were enhanced, as probed by dielectric spectroscopy and rheology.

External application of acoustic waves is yet another powerful way to effectively modify and accelerate the assembly of conjugated polymers into nanowires and sheets. SANS and UV-vis spectroscopy were utilized to explore the conformation of conjugated polymers after ultrasound application in solution. Good solvents, such as chloroform (CF), chlorobenzene (CB), and 1,2-dichlorobenzene (DCB), were used. It has been found that the concentration, sonication time, polymer side chain and backbone units all played a role and affected the polymer structure.

These results demonstrate that external fields are effective mechanisms to direct conjugated polymers into forming desired structures. These approaches also have strong potential to be economically integrated into large scale processing of organic electronics.

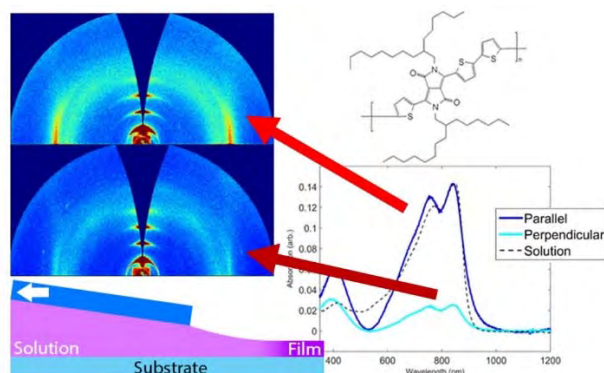


Electric field aligned P3HT (left) and sonication effect on P3HT solutions(right)

POLY 197: Direct, single-step alignment of semiconducting polymer thin films and factors influencing their deposition via solution shearing

Leo Shaw², leoshaw@stanford.edu, Pascal Hayoz⁴, Hongping Yan^{1,2}, Ying Diao³, Julia Reinspach², John W. To², Michael Toney¹, Thomas Weitz⁵, Zhenan Bao². (1) SSRL, Menlo Park, California, United States (2) Chemical Engineering, Stanford University, Stanford, California, United States (3) Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (4) GMV/BE, BASF Schweiz AG, Basel, Switzerland (5) Physics of Nanosystems, Faculty of Physics, Ludwig-Maximilians-Universitaet Muenchen, Munich, Germany

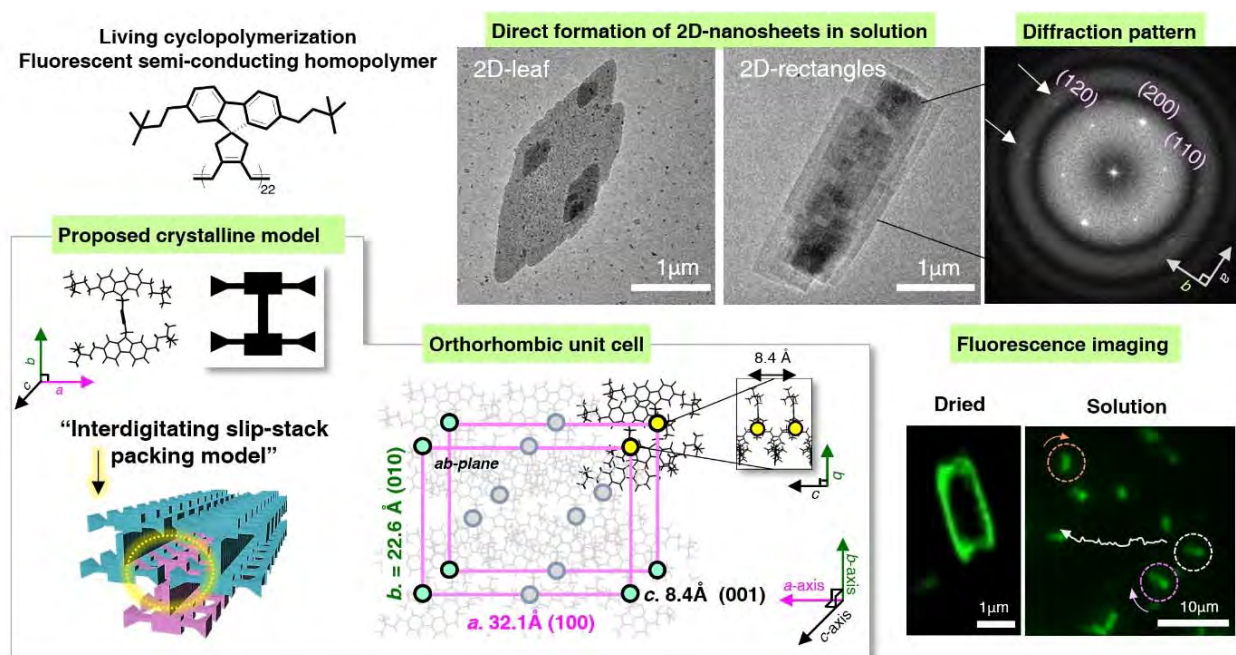
Organic semiconductors (OSCs) have properties that allow them to fill application spaces beyond silicon, specifically those of flexible, wearable, implantable, and biodegradable electronics. More widespread deployment of these technologies is dependent on industrially viable fabrication processes, such as roll-to-roll printing. Solution shearing is a deposition technique that not only can be easily adapted to such processes, but also has been demonstrated to produce highly aligned and high crystalline small molecule OSC thin films. In-plane alignment of OSCs in the active layers of electronic devices can impart desirable properties, such as reduced device cross-talk due to charge transport anisotropy, polarized light absorption or emission, and enhanced charge transport performance because of better ordering. We have observed the alignment of a diketopyrrolopyrrole-terthiophene donor-acceptor polymer deposited directly from solution without surface templating or complex pre- or postdeposition processing; a dichroic ratio up to ~ 7 was achieved. The degree of alignment in the thin films were tuned by controlling the coating speed and was found to be a competition between the shear alignment of polymer chains in solution and stochastic nucleation. Unlike previous reports however, no charge transport anisotropy was observed. Coupled with the observed anisotropy in X-ray diffraction data and the relative degrees of crystallinity in these films, these results are consistent with polymer alignment in both the amorphous and crystalline regions of the films. Alignment is directly influenced by deposition parameters like temperature and substrate treatment or chemical parameters like alkyl side-chain length. Furthermore, solvent choice had a complex effect on film deposition, sometimes yielding no alignment. Our work shows that solution shearing can be used to tune in-plane polymer alignment in a single-step process without substrate patterning or postdeposition treatments.



POLY 198: Direct formation of large area two-dimensional nanosheets from fluorescent semi-conducting homopolymer with new orthorhombic crystalline orientation

Sanghee Yang, sangheeyang@icloud.com, Inho Choi, Suyong Shin, Tae-Lim Choi.
School of Chemistry, Seoul National University, Seoul, Korea (the Republic of)

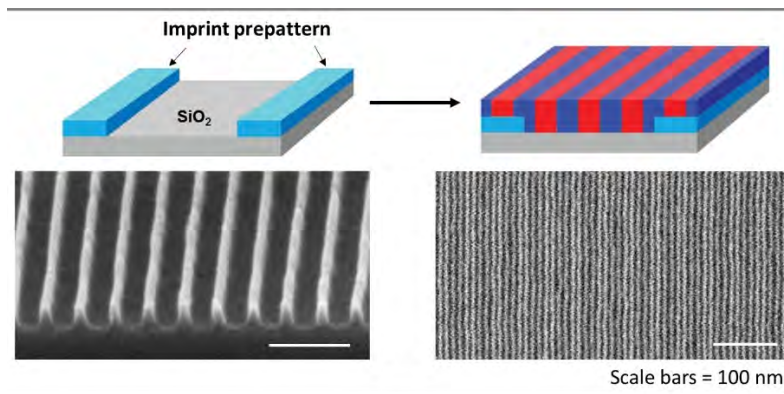
Self-assembly of semi-conducting polymers has been widely investigated due to intriguing optoelectronic properties for the application. Among various methods to assemble nanostructure using the semi-conducting polymers, direct self-assembly methods into two-dimensional (2D) nanostructures have proven difficult because of strong supramolecular interactions between conjugated polymers. Therefore, the amphiphilic block copolymer with post-treatment such as changing chemical environments was required for formation of 2D-nanostructures. Here, we report the synthesis of conjugated homopolymer by living cyclopolymerization of 1,6-heptadiyne having fluorene moiety and its *in situ* assembly behavior of large-area 2D-fluorescent semi-conducting nanostructures. Using high-resolution visualization methods, such as AFM and TEM, we observed rectangle-, raft-, and leaf-shaped 2D-sheets. Interestingly, we proposed a unique slip-stack packing model and orthorhombic unit cell with interdigitating between fluorene side-chains based on the crystallinity information obtained from XRD and HR-TEM. The fluorescence of 2D-nanosheets enabled the super-resolution fluorescent imaging, thereby allowing for the real-time monitoring of the individual nanostructures in solution.



POLY 199: Directed self-assembly of 5 nm block copolymer lamellae enabled by nanoimprint lithography

Austin Lane¹, austinplane@gmail.com, **XiaoMin Yang**², **Michael J. Maher**³, **Gregory Blachut**¹, **Yusuke Asano**¹, **Yasunobu Someya**¹, **Stephen Sirard**⁴, **Akhila Mallavarapu**⁵, **Christopher J. Ellison**³, **Carlton G. Willson**^{1,6}. (1) McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas, United States (2) Seagate Technology, Fremont, California, United States (3) Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States (4) Lam Research, Austin, Texas, United States (5) Department of Mechanical Engineering, University of Texas at Austin, Austin, Texas, United States (6) Department of Chemistry, University of Texas at Austin, Austin, Texas, United States

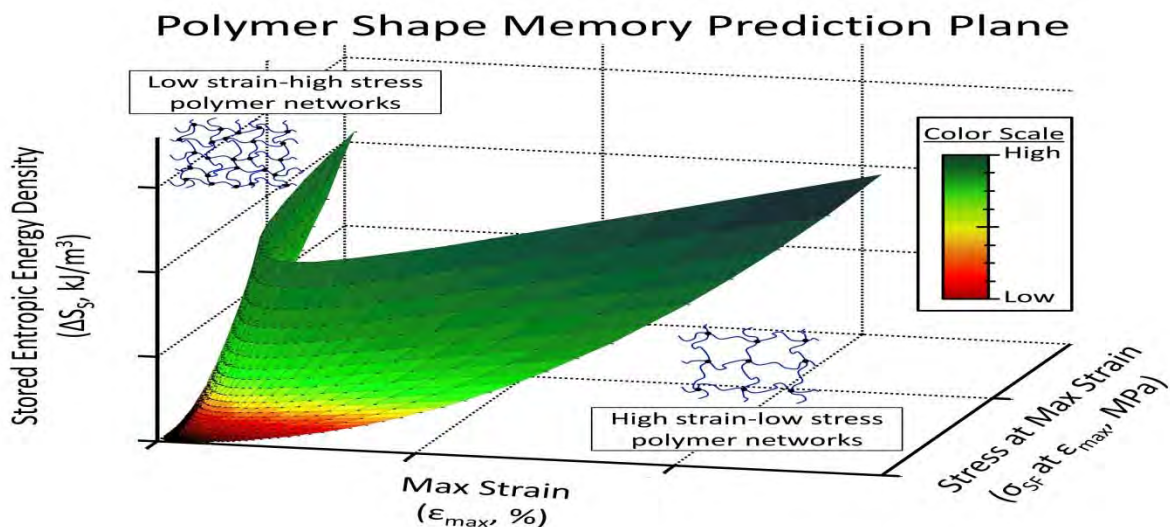
Although many block copolymer (BCP) systems are suitable for nanopatterning applications, lamellar BCPs capable of forming perpendicular 5 nm features are especially valuable because the feature sizes naturally produced by these materials rival the resolution of the most advanced patterning processes used in semiconductor manufacturing today. By pushing the limits of chemical incompatibility between polymer blocks, we have recently demonstrated the self-assembly of 5 nm line/space patterns in thin films using poly(5-vinyl-1,3-benzodioxole-*block*-pentamethyldisilylstyrene) (PVBD-*b*-PDSS, $L_0 = 10$ nm). When assembled on top of guiding structures patterned by nanoimprint lithography (NIL), highly ordered 5 nm BCP lamellae were produced over large areas. This approach combines chemo- and grapho-epitaxy directed self-assembly (DSA) processes with thermal annealing to produce aligned BCP structures. The cross-linked NIL resist structures were modified by plasma etching prior to BCP deposition, and systematic variation of the height of the NIL guidestripes demonstrated that topography plays an important role in promoting defect-free self-assembly. Cross-sectional analysis using STEM and electron energy loss spectroscopy (EELS) revealed key process parameters responsible for promoting vertical through-film structures. To fabricate relevant structures for microelectronics applications, sophisticated etching techniques were developed to selectively remove one block and produce high aspect ratio etch masks from the initial BCP film. The resulting 5 nm structures could be then transferred into an underlying film by a subsequent reactive ion etching (RIE) process. These results represent a significant advancement for demanding patterning applications such as fabricating high areal density NIL templates for bit-patterned media.



POLY 200: Quantitative predictions of shape memory effects in polymers

Christopher C. Hornat, *chornat@g.clemson.edu*, Ying Yang, Marek W. Urban. *Material Sci Engineering, Clemson University, Clemson, South Carolina, United States*

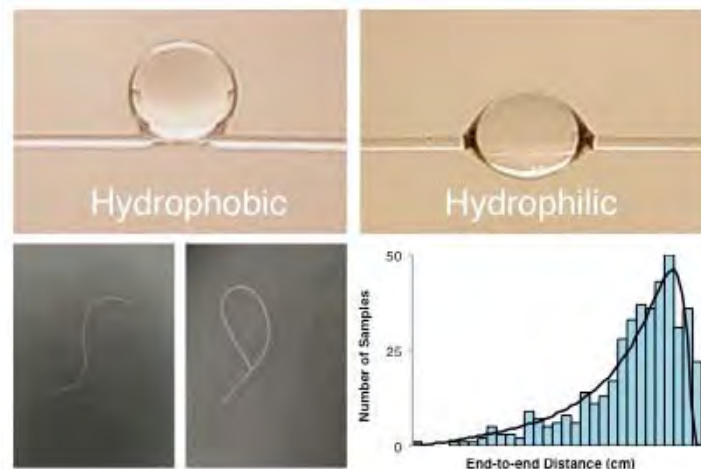
Shape memory polymers offer unique properties that are critical to the future of advanced materials. In an effort to effectively predict shape recovery, these studies utilized dynamic and static forces during dynamic mechanical analysis (DMA) to quantify shape memory effects (SME) in polymers. These studies identified the basis for glass transition temperature-based (T_g) SME and showed unique shape memory transitions that are macroscopically manifested by directional extension and subsequent retraction in thermoplastic and thermosetting polymers. While viscous components of the network at the onset of the T_g are responsible for material's extension, the retractions result from stored conformational entropy as a result of crosslink density and/or chain entanglements. This behavior was quantified in terms of stored (ΔS_s) entropic energy density, which combines stress and strain aspects of shape recovery. In contrast to traditional strain recovery and fixation ratios, the proposed approach encompass the maximum strain (ϵ_{max}), stress (σ_{SF} at ϵ_{max}), and energy storage (ΔS_s) by considering polymer architecture, molecular weight, molecular weight distribution, and viscoelastic behavior, thus allowing quantitative assessments of the SME from a single DMA experiment. This concept can be extended to determine the SME in glassy and amorphous inorganic materials for any material that exhibits the T_g and the rubbery plateau above the T_g .



POLY 201: Semi-flexible string conformational analysis towards an experimental hydrophobic-folding model system

Roxanna Kiessling², RKiessling18@students.claremontmckenna.edu, Collin Barraugh², Babak Sani¹. (1) Chemistry, Claremont McKenna, Pitzer & Scripps Colleges, South Pasadena, California, United States (2) Claremont McKenna College, Claremont, California, United States

We study two-dimensional folding with elastomers extruded into strings, $\sim 100\mu\text{m}$ wide and centimeters long. These strings are large enough for convenient experimental observation, and flexible enough to access a large number of folded conformations. We acoustically excite the strings at the air-water interface and optically image them to quantify conformational parameters. Semi-flexible or rigid strings produce histograms of end-to-end distances that are consistent with semi-flexible chain modelling, with well-defined persistence lengths. The choice of polymer (PDMS, polydimethylsiloxane) enables hydrophobicity patterning along the length of the string with ultraviolet-ozone radiation. We use water droplet-on-fiber contact angle measurements to assess the degree and longevity of string hydrophilicity introduced via this exposure. We have demonstrated that the UV-patterning of the string has a direct impact in its folding conformational statistics. We envision this system as a tunable experimental means of studying and designing complex folding pathways, with possible applications to molecular (bio)polymer folding problems.

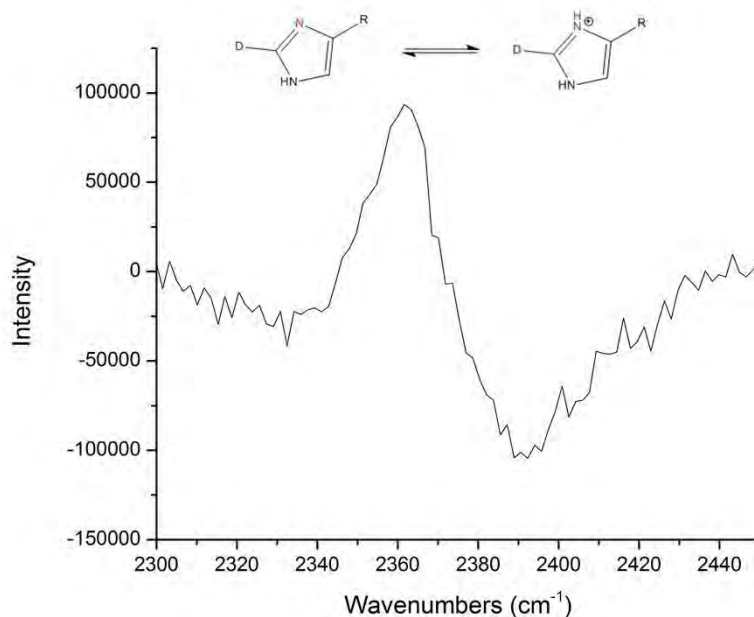


Top: A $1\mu\text{L}$ water droplets on untreated hydrophobic (**Left**), and UV-treated hydrophilic (**Right**) strings. **Bottom Left:** Optical images of 6cm string conformations at the water's surface. **Bottom Right:** Distribution of end-to-end distances of a string at the air-water interface, between acoustic excitations. Distribution was fit to a semi-flexible chain-model (Winkler, 2.7cm persistence length).

POLY 202: pKa determination of a his residue in a self-assembling peptide using Raman spectroscopy

Brett Pogostin², *bpogostin@haverford.edu*, Casey H. Londergan¹, Karin S. Akerfeldt².
(1) Department of Chemistry, Haverford, Pennsylvania, United States (2) Chemistry, Haverford College, Rockland, Delaware, United States

Semonogelin I (Sgl) is a protein found in human semen that is known to form a hydrogel. Previous studies found that a 13 amino acid residue segment of this larger protein self-assembles into an extended β -sheet based hydrogel at pH 7-9. It is hypothesized that a histidine residue near the C-terminal end of the peptide sequence may explain this pH dependence due to the proximity of the pKa of histidine to the pH of the hydrogelation observed. The current project aims to determine the pKa of this histidine using Raman spectroscopy. Previous studies have found that this method could be used to determine the pKa of deuterated L-carnosine by observing a shift in a C-D stretch from 2360 to 2390 cm^{-1} between the deprotonated and protonated forms of histidine. Thus, it was hypothesized that the same method could be used to determine the pKa of histidine within a peptide sequence, and potentially one that self assembles into a hydrogel. Initially, we investigated shorter peptide derivatives of the original sequence. We are currently increasing the length of the peptide in a stepwise manner in order to determine how far we can take this method. Ultimately, we are interested in evaluating the feasibility of using this method to determine the pKa of a histidine residue within the framework of a hydrogel with the aim of determining to what extent the protonation state of histidine is responsible for triggering hydrogelation.

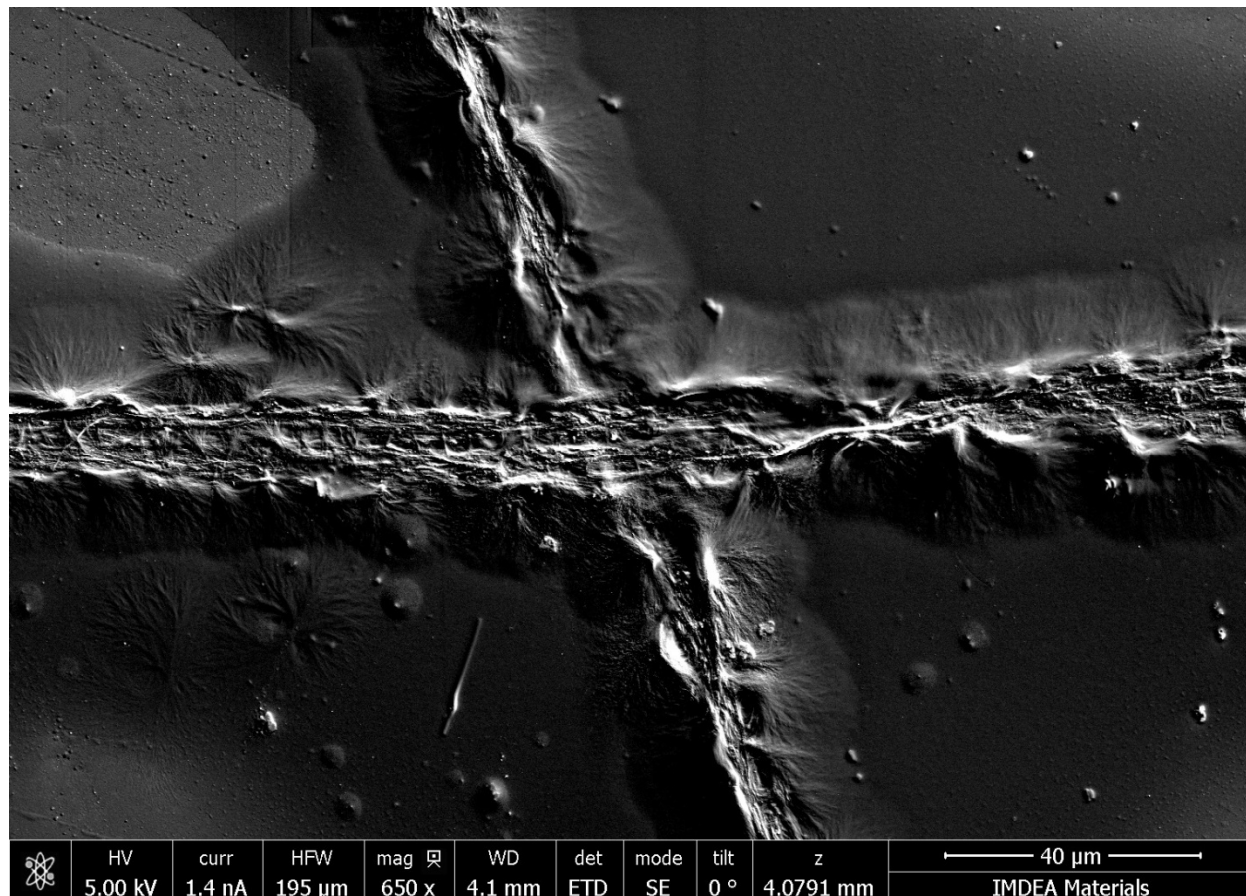


A Raman difference spectrum between generated by titrating a histidine containing tripeptide from pH 4.5 to 10. The maximum at 2360 cm^{-1} and the minimum at 2390 cm^{-1} are attributed to the deprotonated and the protonated forms of histidine, respectively.

POLY 203: Aligned spherulites of conjugated polymers induced by carbon nanotubes

Karina J. Reynolds¹, *kjgreynolds@me.com*, **Shanju Zhang**². (1) Chemistry and Biochemistry, California Polytechnic State University, Highlands Ranch, Colorado, United States (2) Dept of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, California, United States

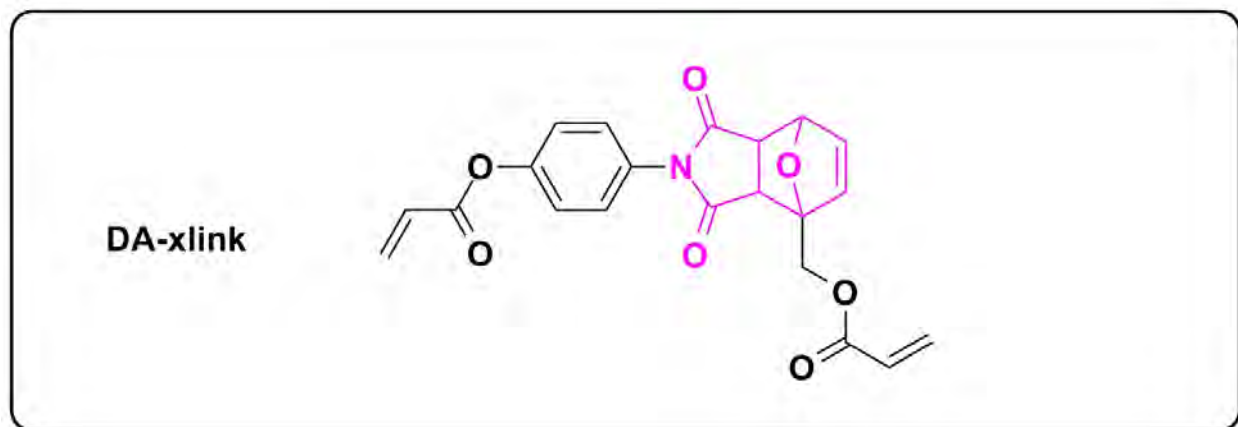
Macroscopic alignment of conjugated polymers is pivotal in utilizing unique anisotropy of optoelectronic properties for various emerging applications of flexible devices. However, it is challenging to fabricate aligned crystalline structures of conjugated polymers in large areas. Here we report on the first evidence of aligned spherulites of poly(3-butalthiophene) (P3BT) around the carbon nanotube fibers using solvent annealing methods by means of polarized optical microscopy, differential scanning calorimetry, electron scanning microscopy, X-ray diffraction, Raman spectroscopy and four-point probe resistance tester. P3BT forms crystalline spherulites without fibers under the same condition. We study the effect of various factors such as concentration, type of solvent, temperature, evaporation rate, annealing time, etc. on the structural evolution. The thermal properties and electrical conductivities of aligned spherulites are tested. A theoretical model is proposed to interpret this new structure and the mechanism behind its influence on charge transport.



POLY 204: Thermally responsive materials with dynamic topology based upon Diels-Alder chemistry

Cecilia Gregory, *cegregor@calpoly.edu*, *Emily Wilborn*, **Philip J. Costanzo**, *phil.costanzo@gmail.com*. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

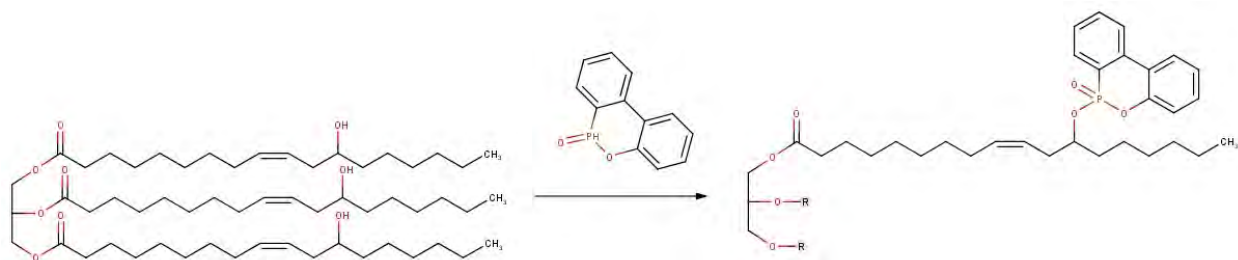
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and RAFT polymerization techniques were employed to prepare star-like structures with DA linkages at a central core. Upon the application of a thermal stimulus, the retro-DA was induced and star-like structures were reduced to a linear topology.[figure1]



POLY 205: Thermal and flammability properties of epoxy resin containing flame retardants derived from castor oil

Eric Ostrander, *Ostra2ea@cmich.edu*. Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States

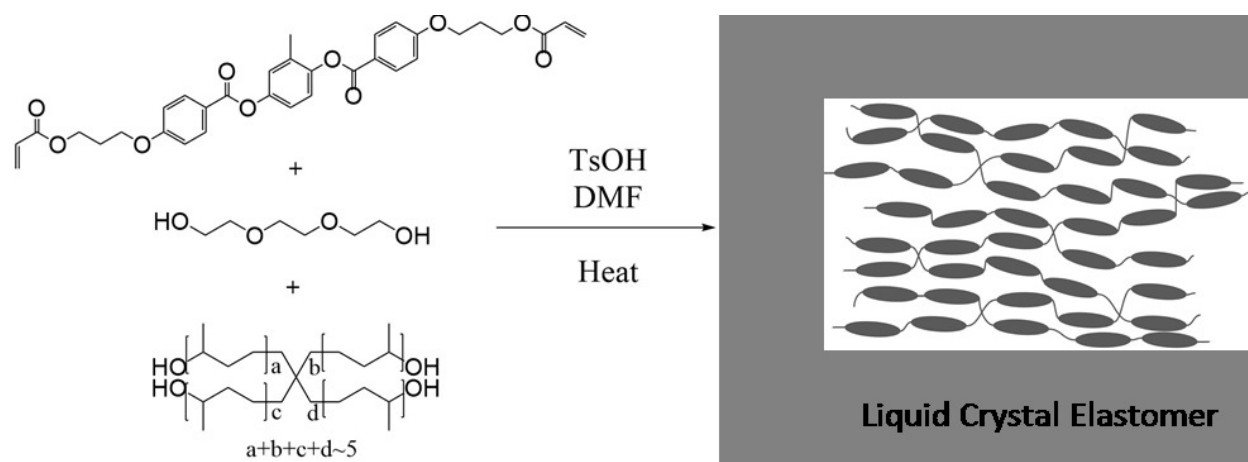
Castor oil is a nonedible seed oil available in large quantities annually. It contains both unsaturation and hydroxyl functionality which may be utilized for the generation of compounds with good flame retarding properties. Treatment of castor oil with a series of phosphorus compounds generates phosphorus esters and introduction of bromine at the unsaturation generates a compound containing both bromine and phosphorus. All the phosphorus esters display good flame retarding properties in DGEBA epoxy resin. Unexpectedly, the inclusion of bromine does not enhance flame retardancy. In fact, in some cases, the presence of bromine is antagonistic to the flame retarding action of the phosphorus esters.



POLY 206: Modular liquid crystal elastomer synthesis: Acid catalyzed oxa-Michael addition

Cameron Earl¹, cearl@caltech.edu, **Zuleikha Kurji**^{1,2}, **Julia A. Kornfield**¹. (1) Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States (2) Washington State University, Pullman, Washington, United States

Incorporating functional groups into liquid crystal elastomer (LCE) networks can help amplify microscopic properties to the macroscopic scale. In 2015, the Yakacki group at the University of Colorado at Denver reported the synthesis of a tailorable and programmable LCE using a two-stage thiol acrylate Michael addition and photopolymerization. This synthesis is highly modular; nearly any diacrylate, and any di- and tetra-thiol can be used to make an elastomer so new functional groups may be introduced to the system by adding new thiol- or acrylate-functionalized monomer to tailor the LCE's properties. Thiols, however, are difficult to synthesize and di- and tetra-functional thiols are hard to find commercially. Most low molecular weight thiols also have an extremely low odor threshold (around 0.011 ppm). In contrast, however, terminal alcohols are effectively odorless, more shelf-stable, and available commercially in much larger varieties. Taking advantage of the oxa-Michael addition mechanism, these terminal alcohols may provide a viable substitute for the thiol monomers to create a system with even greater modularity. Here we report that through a qualitative screening process, triflic and tosyl acid catalysts were found to successfully catalyze the polymerization and crosslinking of a model diacrylate with di- and tetra-functional terminal alcohols. Both traditional heating and microwave radiation were able to activate the reaction. FTIR spectroscopy is being used to first confirm the oxa-Michael reaction, and to monitor reaction kinetics over time.



POLY 207: Syntheses, structures and functions of AIE polymers

Ben-Zhong Tang, tangbenz@ust.hk. Dept Chem, Hong Kong U Sci Tech, Kowloon, Hong Kong

Polymers with aggregation-induced emission (AIE) are widely studied recently because of their good solubility, processability, and high emission efficiency in the aggregated states. In this talk, the research efforts directed to AIE polymers including the design and syntheses, structures and topologies, as well as functionalities and applications will be introduced. The synthetic approaches for the construction of AIE polymers include chain polymerizations, step polymerizations, as well as post-modification of polymers. Through such versatile polymerization approaches, a vast array of AIE macromolecules with various chemical and topological structures can be easily accessed such as linear or zigzag shaped oligomers and polymers, star-shaped oligomers, dendrimers and hyperbranched polymers, conjugated microporous polymers, as well as crystalline supramolecular polymers. Combining the AIE characteristic with the desired traits of the polymeric materials will endow the resulting macromolecules with fascinating functionalities and they have found applications in optoelectronic devices, chemo/biosensing and biological imaging.



Syntheses, structures and functions of AIE polymers

POLY 208: Polymer chemistry of graphenes and graphene nanoribbons

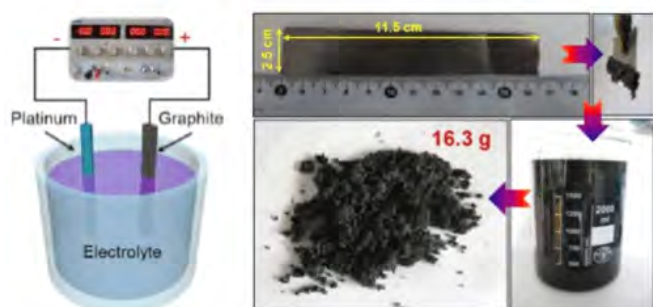
Klaus Muellen, muellen@mpip-mainz.mpg.de. Max Planck Institute for Polymer Research, Mainz, Germany

Carbon materials are of immense practical importance, but are often known as structurally ill-defined “black stuff” such as soot. Graphenes and graphene nanoribbons (GNRs), their geometrically restricted cutouts, are new additions to the carbon family which are widely praised as multifunctional wonder materials and rich playgrounds for physicists. Indeed, graphenes hold enormous promise as materials for energy technologies. Further, GNRs are regarded as a new generation of semiconductors superior to i) silicon in view of the required miniaturization of printed circuits and superior to ii) classical conjugated polymers due to better band structure control. Above all, however, graphene as a two-dimensional polymer and GNRs are true challenges for materials synthesis.

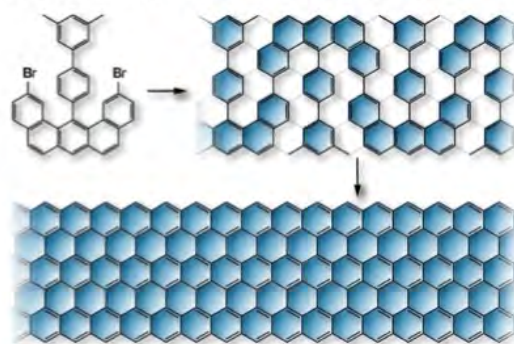
Herein, we approach graphene fabrication in two steps. “Top-down” protocols such as electrochemical exfoliation are applied for batteries, fuel cells and photodetectors. In the “bottom-up” synthesis of GNRs, repetitive cycloaddition reactions in solution are shown to afford multiply branched polyphenylene polymers which then serve as precursors for perfectly “graphitized”, solution-processable GNRs as long as 600 nm. An alternative on-surface synthesis utilizes immobilization of suitable monomers and in-situ STM-control of the polymerization to secure structural perfection.

It is thus a synthetic breakthrough which leads to new materials science and physics such as single-molecule field effect transistors from GNRs and even spintronics. The present fundamental study is far away from robust technologies, but an attempt can be made at predicting some future trends.

Top-down electrochemical exfoliation



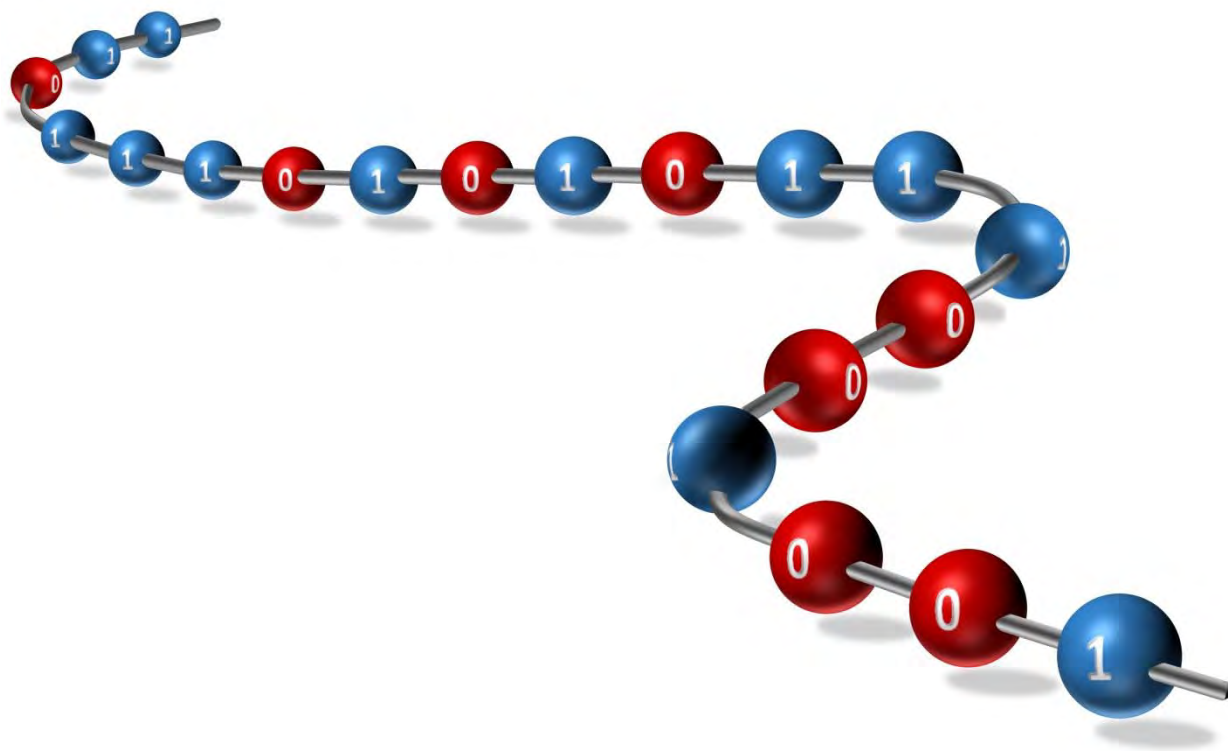
Bottom-up chemical synthesis



POLY 209: Digital polymers: A new class of man-made macromolecules

Jean-Francois Lutz, jflutz@unistra.fr. Precision Macromolecular Chemistry, Institut Charles Sadron, Strasbourg, France

Digital polymers are synthetic macromolecules that allow molecular storage of information. For instance, a binary sequence can be inputted in a polymer chain using two monomers that are intentionally defined as 0 and 1 bits. Typically, a readable sequence is synthesized using multistep-growth protocols that allow exact placement of the coded monomer units in the chains. Using such strategies, our group has recently described the synthesis of different class of digital polymers, including polyphosphodiesters, poly(alkoxyamine phosphodiester)s, poly(alkoxyamine amide)s, poly(triazole amide)s and polyurethanes. In all cases, the digital information stored in the polymer can be efficiently read using tandem mass spectrometry. In addition, dynamic polymers (e.g. alkoxyamine-based structures) allow erasing of information. The relevance of these different macromolecules for applications in the field of data storage, long-term storage and product identification will be discussed in this presentation.

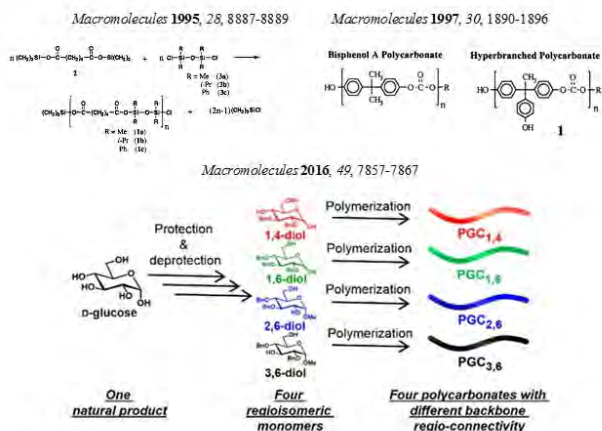


Schematic representation of a digital polymer. The blue and red spheres symbolize monomer units.

POLY 210: Historical evolution of degradable polymers in the Wooley laboratory: From poly(silyl ester)s to natural product-based polycarbonates

Karen L. Wooley, wooley@chem.tamu.edu. 3255 TAMU, Texas AM University, College Station, Texas, United States

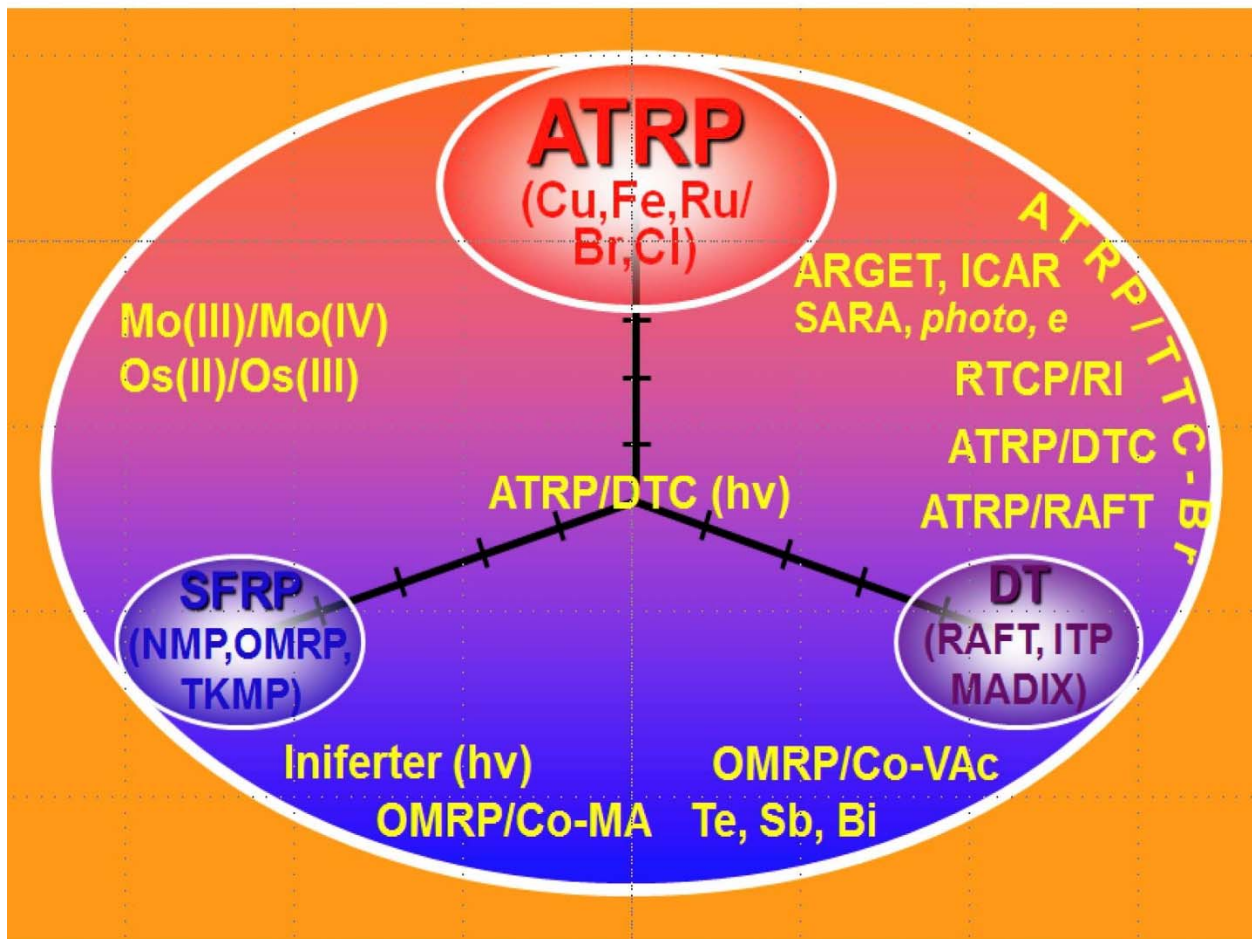
Karen L. Wooley's first publication of her independent career appeared in *Macromolecules* in 1995, and she has published a total of 50 articles in *Macromolecules* (1992 – 2016). Reaching a total of 50 publications in *Macromolecules* during this year prior to the 50th-year celebration of *Macromolecules* is an interesting coincidence that will be highlighted by selection of a series of those publications that describe the historical evolution of degradable polymer systems designed and developed in the Wooley laboratory. That initial publication in 1995 described poly(silyl ester)s as a new family of hydrolytically-degradable polymers with tunable stabilities. Several other reports of variations in the synthetic methods, compositions, structures, degradation kinetics and other properties followed. This presentation will progress from the poly(silyl ester)s to comparative studies of linear vs. hyperbranched polycarbonates that were explored in the 1990's and 2000's, and will conclude with the recent shift to natural product-based building blocks for the construction of polycarbonates.



POLY 211: Reversible deactivation radical polymerization after nearly 50 years

Krzysztof Matyjaszewski, *km3b@andrew.cmu.edu*. CMU, Pittsburgh, Pennsylvania, United States

First examples of controlling radical polymerization can be traced back to 1960s. Currently, in reversible deactivation radical polymerization (RDRP), there are three basic mechanisms based on: (i) spontaneous reversible deactivation of radicals with stable radicals such as nitroxides (NMP) or transition metals (OMRP), (ii) a catalyzed reversible deactivation with transition metal complexes, such as atom transfer radical polymerization (ATRP), and (iii) degenerative transfer processes such as RAFT, MADIX, or iodine transfer polymerization processes are most often used. Some recent developments in RDRP will be presented.

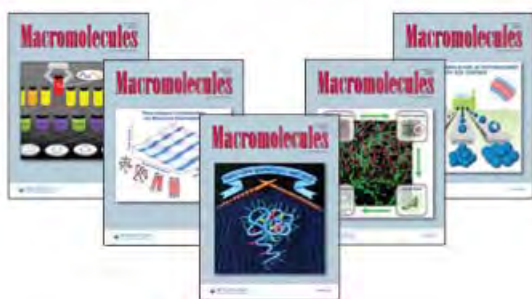


POLY 212: 50 Years of macromolecules: A perspective

Timothy P. Lodge, *lodge@umn.edu*. Dept Chem Koltoff Smith Halls, University of Minnesota, Minneapolis, Minnesota, United States

The ACS journal *Macromolecules* began publishing in 1968, and is now in its 50th year. From the outset it was intended to report the best fundamental research in polymer science, covering a broad topical range from synthesis to characterization, from solutions to bulk, from surfaces to thin films, from structure to properties, from biological macromolecules to synthetic materials, and from computer simulation to theory. It has always maintained a strictly independent editorial team, with Editors and Associate Editors who are active researchers and leaders in the field, and strived for rapid and rigorous peer review. It has grown in size from 115 original articles in Volume 1, to about ten times that number in Volume 50. It has consistently led the field in the number of citations, and now exceeds 100,000 per year. This talk will reflect on a selected subset of scientific areas in which tremendous progress has been made, from a historical perspective. A common theme that pervades these topics is the exciting interplay among synthesis, new characterization tools, and advances in theoretical and computational methods. Also included will be discussion of most published authors and most influential papers. Some of the major developments in scientific publishing, and particularly the ways they continue to evolve and influence our field, will be identified.

Macromolecules



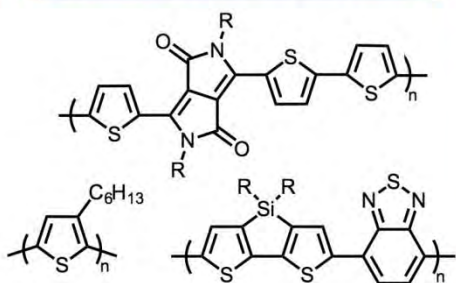
POLY 213: Diffusion-Ordered NMR Spectroscopy (DOSY) of conjugated polymers

Lisa M. Kozycz, lisa.kozycz@utoronto.ca, **Craig J. Hawker**, **Michael L. Chabinyc**.
University of California Santa Barbara, Goleta, California, United States

We have developed a new method to investigate the size, shape and aggregation of conjugated polymers using diffusion-ordered NMR spectroscopy (DOSY). A major limitation of many high-performance conjugated polymers is their limited solubility in common organic solvents, making them difficult to fully characterize in solution. Since molecular weight is intrinsically linked to device performance, it is critical to be able to measure polymer chain length easily and reliably. Using our method, polystyrene equivalent molecular weights can be calculated from a single DOSY measurement, using less material and shorter acquisition times than conventional size-exclusion chromatography (SEC) measurements. Furthermore, the solvent and temperature of the DOSY experiment can be easily changed to adapt to various polymer solubilities, in contrast to SEC set-ups, which are not easily modified. Concentration dependent measurements on multiple molecular weights of the same polymer are used to determine the polymer scaling law, which describes the behavior of the polymer in solution (eg. random coil vs. rigid rod). This novel approach provides a method for gaining information critical to understanding structure-property-performance relationships for conjugated polymers in organic electronics in a simple, non-destructive way.

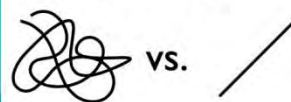
¹H DOSY NMR:

- concentration <0.5 mg/mL
- any solvent or temperature
- acquisition time ~60 seconds



Polystyrene
equivalent
molecular weight

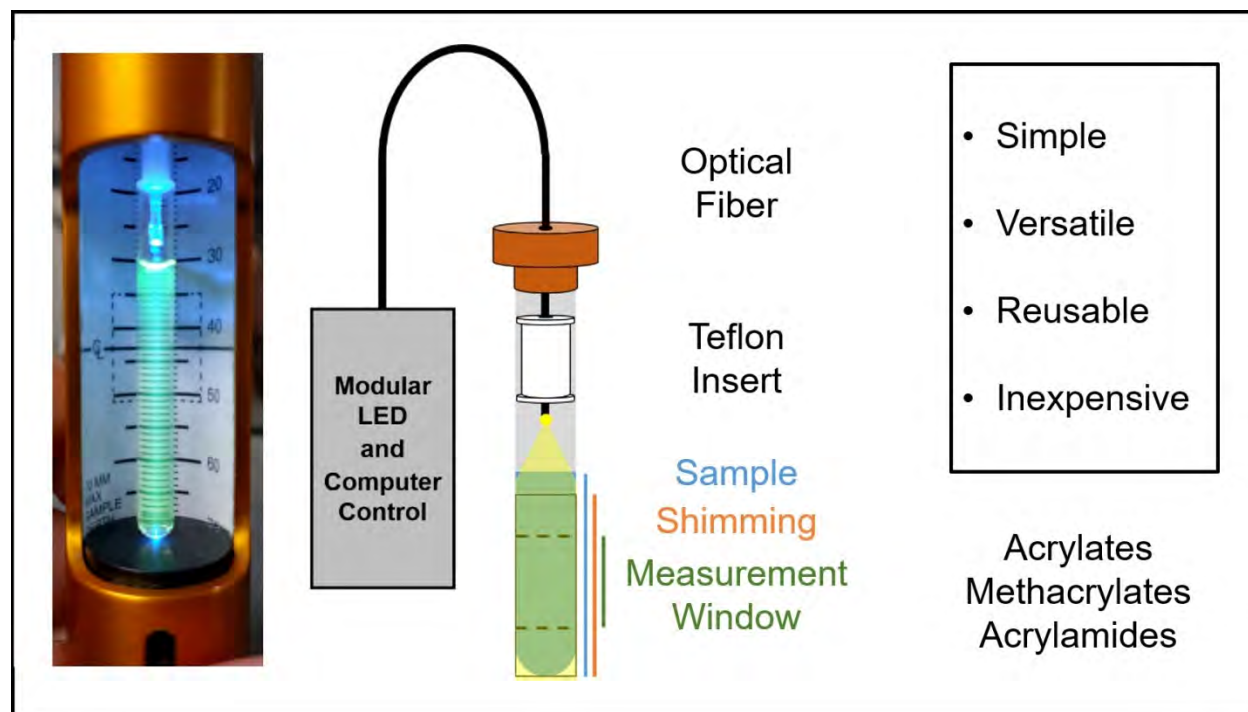
$$D_0 \sim M^\nu$$



POLY 214: Fiber-coupled NMR: A simple and versatile approach to study controlled photopolymerizations in real time

Neil Dolinski², neilverse@gmail.com, Zachariah A. Page⁴, Fabian Eisenreich¹, Stefan Hecht PhD¹, Javier Read De Alaniz⁵, Craig J. Hawker³. (1) Dept Chemistry Hu Berlin, Berlin, Germany (2) Materials, UCSB, Santa Barbara, California, United States (3) Univ of California, Santa Barbara, California, United States (4) University of California Santa Barbara, Goleta, California, United States (5) Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California, United States

The use of light in controlled polymerizations has been of increasing interest to the broad polymer science community in recent years. A facile method to study such photopolymerizations using *in situ* nuclear magnetic resonance (NMR) spectroscopy is presented. Guiding light from modular LEDs into an NMR sample using optical fibers and Teflon inserts allowed for monitoring of propagation kinetics, 'on'/off' behavior, and initiation by chain transfer agents. The all-in-one illumination and measurement has impressive speed and sensitivity, ideal for rapid polymerizations, while avoiding cumbersome aliquot-based techniques. Additionally, through the use of 2 dimensional diffusion order spectroscopy, molecular weight can be tracked as a function of time and conversion. Polymerizations of several monomers with different catalysts and excitation wavelengths highlight the versatility of the presented method. Given the simplicity and modularity of the setup, general availability of NMR spectroscopy, and low cost of the components, this methodology has the potential to broadly impact the polymer community.



POLY 215: PFPE-based polymeric ^{19}F MRI agents: A new class of contrast agents with outstanding sensitivity

cheng zhang^{1,2}, cheng.zhang2@uqconnect.edu.au, Hui Peng¹, Simon Puttick^{1,2}, Debra Searles^{1,3}, Andrew whittaker^{1,2}. (1) Australian Institute for Bioengineering and Nanotechnology, Brisbane, Queensland, Australia (2) ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Brisbane, Queensland, Australia (3) School of Chemistry and Molecular Biosciences, Brisbane, Queensland, Australia

^{19}F magnetic resonance imaging (MRI) is a powerful noninvasive molecular imaging technique for the detection of important diseases. The major challenge of ^{19}F MRI is signal attenuation caused by the reduced mobility of probes with increased fluorine content. Here we report the synthesis of perfluoropolyether (PFPE) end-functionalised homopolymer of oligo(ethylene glycol) methyl ether acrylate (poly(OEGA)_m-PFPE) for the development of highly sensitive ^{19}F MRI contrast agents (CAs). The structural characteristics, conformation/aggregation behaviour, ^{19}F NMR/MRI properties were studied in detail. Dynamic light scattering and molecular dynamics simulations were conducted and demonstrated that the poly(OEGA)₂₀-PFPE polymer undergoes single-chain folding in water while polymers with less OEGA content experience multiple-chain aggregation. Long ^{19}F T₂ relaxation times were obtained (> 85 ms) and no obvious decrease was observed with increasing fluorine content up to ~30 wt %. Moreover, the signal-to-noise ratio increases linearly with increasing concentration of fluorine. In a comparative study, partly-fluorinated statistical copolymers containing trifluoroethyl acrylate (TFEA) were also prepared. The ^{19}F T₂ of the TFEA-based polymers dropped dramatically with an increase in fluorine content. Cell uptake and NMR performance within the cells was also examined, showing robust uptake of all PFPE-based polymers and high in-cell mobility of fluorinated polymer segments. To date, this is the first report of the synthesis of polymeric PFPE-based CAs and our results show that the PFPE-based polymers are an exciting new class of ^{19}F MRI CAs with extremely high fluorine content and outstanding sensitivity.

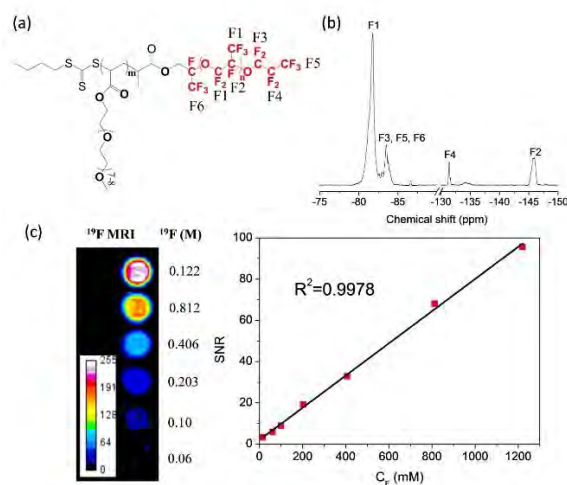
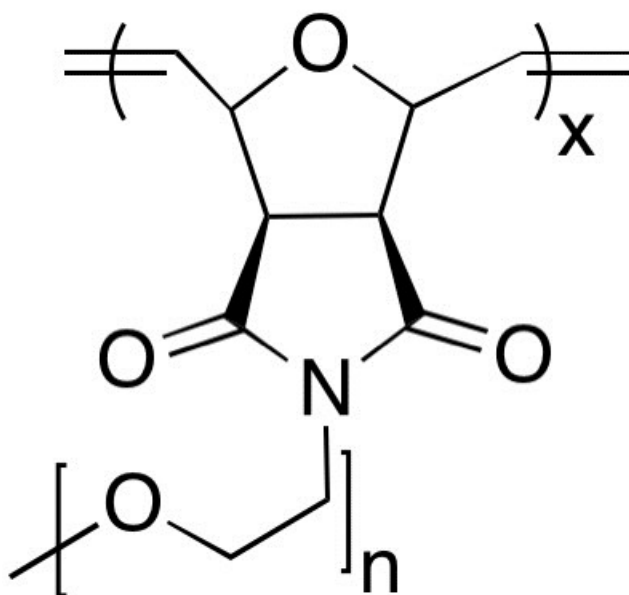


Figure. (a) The chemical structure of the poly(OEGA)-PFPE polymer. (b) The ^{19}F NMR spectrum of the poly(OEGA)-PFPE in PBS/D₂O (V/V 90/10). (c) Left: ^{19}F MRI in PBS (4 ml); right: ^{19}F MRI SNR versus concentration of fluorine in solution.

POLY 216: Decoupling of segmental motion and ionic conductivity in oligomeric ethylene oxide functionalized dicarboxide oxanorbornene polymers

Dean A. Waldow¹, waldowda@plu.edu, Alexei P. Sokolov², Yangyang Wang³. (1) Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States (2) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (3) Center for Nanophase Materials Sci., Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Understanding ionic conductivity mechanisms in polymers is important to the design of solid polymer electrolytes for lithium ion batteries. Polymers based on dicarboximide oxanorbornene monomers were synthesized by ring-opening metathesis polymerization with a Grubbs third generation catalyst. These polymers were chosen to study the decoupling of ionic motion from segmental motion due to their fairly rigid and bulky backbone. They have been synthesized with varying lengths of oligomeric ethylene oxide (EO) side chains (2, 3, 4, 8 and 12 units) with polydispersities typically less than 1.1. Ionic conductivity and relevant segmental dynamics were characterized with dielectric spectroscopy with varying levels of added bis(trifluoromethane)sulfonamide lithium salt (LiTFSI). The polymers were found to have high LiTFSI solubilities. Dielectric spectroscopy results demonstrate five to six orders of magnitude of decoupling of ionic conductivity from segmental motion when compared to typical values at the glass transition temperature for a polymer with strongly coupled dynamics. Quasi-elastic neutron scattering (BASIS) was also used to characterize the segmental dynamics as a function of salt concentration for the homopolymer with two ethylene oxide units, which is one of the polymers with high levels of decoupling.



POLY 217: Light scattering without refractive index increment. A new approach to calibrate SEC-light scattering setups

Wolfgang Radke¹, wradke@pss-polymer.com, Jasmin Preis¹, Simona Lavric². (1) PSS Polymer Standards Service, Mainz, Germany (2) Melamin d.d, Kocevje, Slovenia

Size exclusion chromatography (SEC) with light scattering detection (SEC-LS) has become a popular method for polymer characterization. In contrast to conventional SEC, SEC-LS can provide absolute molar masses at each elution volume, allowing determining true molar mass distributions and molar mass averages.

SEC-LS requires application of a light scattering instrument in conjunction with a concentration detector, typically a RI detector. The primary information obtained by the detectors are voltages, which have to be converted to the respective physical properties.

Presently, calibration of SEC-light scattering detectors follows two approaches. Either a reference liquid of known Rayleigh ratio or well-characterized polymer standards are used for calibration.

If calibration is performed using a polymer standards, usually the molar mass and the specific refractive index increment, dn/dc , of the standard needs to be known.

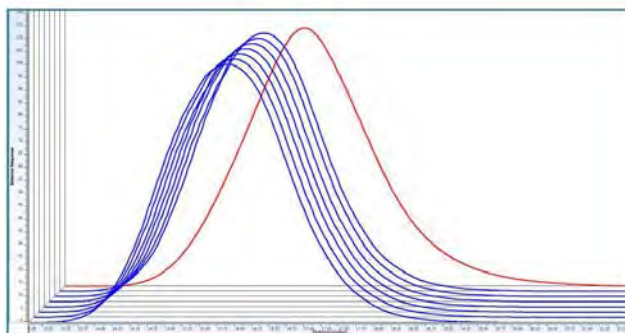
For molar mass determination of unknown analytes, knowledge of their refractive index increment, dn/dc is also required

Unfortunately the correct refractive increment is often unknown in the solvent applied, or its determination is difficult, e.g. in mixed solvents or in solvents containing salts or additives.

The present contribution will describe an alternative approach to calibrate an SEC-LS setup and to determine the molar mass of a unknown analytes, requiring neither the refractive index increment of the sample, nor of the polymer used for calibration. Only the molar mass of the calibrant and the concentrations of the calibrant and the unknown samples are required.

The new calibration approach does not require any refractive index increment, Consequently, experimental difficulties arising from preferential solvation as they are present in ternary systems (mixed solvent, salt containing eluents) are eliminated..

Besides the theoretical approach, the contribution will provide experimental results, proofing the suitability of the new approach.

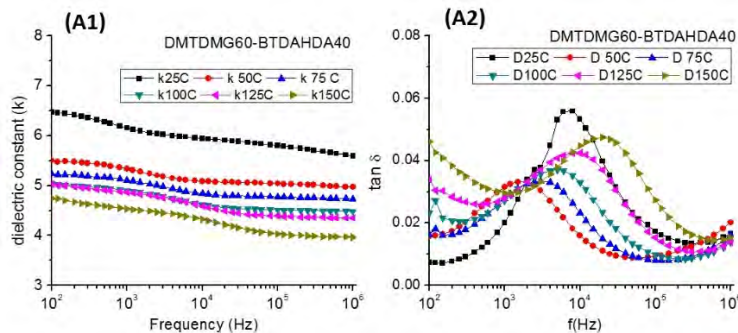


POLY 218: Polyimide-Tin(poly)ester hybrid films as dielectric materials

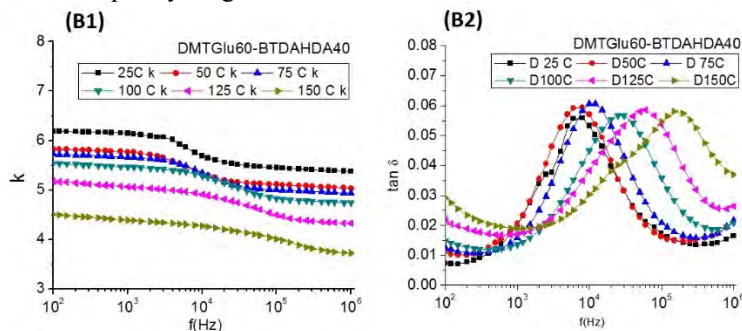
Shamima Nasreen¹, *shamima.nasreen@uconn.edu*, Gregory M. Treich², Matthew L. Baczkowski², Matthew Tefferi³, Sydney K. Scheirey², Yang Cao³, Gregory A. Sotzing¹.

(1) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Polymer Program, University of Connecticut, Storrs, Connecticut, United States (3) Department of Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States

There are many challenges to discover high energy density dielectric materials with low loss for modern energy storage applications. One such challenge is to improve the dielectric constant of the material while maintaining good film quality. Previously, it has been found that tin (poly)esters exhibit large dielectric constants. However, there are difficulties in their processing as free standing films. Organic polyimides historically have shown excellent film formation with moderate dielectric constants. Herein, polyimide/tin (poly)ester hybrid films were made by blending a polyimide with the organometallic tin polyesters poly (dimethyltin 3,3-dimethylglutarate) (pDMTDMG) and Poly (dimethyltin glutarate) (p(DMTGlu)). Films were obtained by varying the blend ratios of the tin (poly)ester from 10% to 90% with the polyimide moiety and by optimizing different casting conditions. These hybrid free standing films exhibit dielectric constants close to that of the tin polyesters with the average values ranging from ca. 5.9-6.2, and a low loss ca. 1-2% over a frequency range of 10^2 - 10^6 Hz. These are much higher than the polyimide having a dielectric constant of ca. 3.5. Among these organic-organometallic hybrid systems, the blend of 60% pDMTDMG and pDMTGlu with 40% polyimide shows the most effective film properties with a band gap of 5.0 eV. The film quality was further investigated with microscopic techniques to determine the morphology, while X-Ray Diffraction patterns were used to observe the crystallinity of these hybrid films.



Dielectric constant, k, (A1) and their corresponding loss, $\tan \delta$, (A2) of pDMTDMG60-BTDAHDA40 film in different temperatures over a frequency range 10^2 - 10^6 Hz



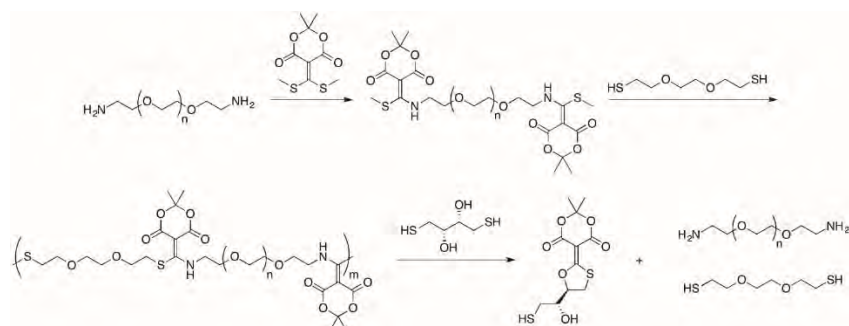
Dielectric constant, k, (B1) and their corresponding loss, $\tan \delta$, (B2) of pDMTGlu60-BTDAHDA40 film in different temperatures over a frequency range 10^2 - 10^6 Hz

POLY 219: Chemically degradable polymers for applications in nano and biotechnology

Igor Kolesnichenko¹, igorvkoles@utexas.edu, **Cedric Ginestra**¹, **Malgorzata Chwatko**³, **James Reuther**¹, **Nathaniel Lynd**⁴, **Eric V. Anslyn**². (1) Chemistry, The University of Texas at Austin, Austin, Texas, United States (2) A1590 NHB 5.114, UTexas Chem and Biochem, Austin, Texas, United States (3) University of Texas at Austin, Austin, Texas, United States (4) Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States

An important goal of organic chemistry has centered on the development of methods to assemble and disassemble molecular modules. The wide scope of easily reversible reactions opens a door to this manipulation of modules. The focus of this work is the development of a simple molecular tether to reversibly bind amines and thiols in aqueous conditions at neutral pH. Described, herein, are the details of reactions using a Meldrum's acid-derived conjugate acceptor and its utility in polymer chemistry, an area that could greatly benefit from the introduction of reversible covalent bonds (RCBs). Polymers have become a mainstay in many everyday objects, but oftentimes they are difficult to dispose of once they have served their purpose. Introduction of a chemically cleavable linker within polymer chains could prove to be a way to solve this problem. Additionally, RCBs could potentially open avenues to drastically widen the applications of polymers. A current focus of pharmaceutical companies is the attachment of polyethylene glycol (PEG) groups to drugs and proteins to aid with improving water solubility and increasing hydrodynamic radius. However, one of the problems that can arise is the bioaccumulation of high molecular weight PEG chains within the body. One of the focuses of this work is the development of high molecular weight PEG chains that can be chemically triggered to break down into smaller units, which can be excreted.

Furthermore, we sought to exploit this interesting RCB in the area of nanotechnology. The current goal in microchip and microprocessor development is to introduce smaller and smaller (<1 nm) features to thin films to increase information storage capabilities. Herein, we present a novel diblock copolymer, with the two blocks tethered together by a chemically cleavable RCB unit. Thin film coating of this microphase-separating copolymer, followed by chemically triggered removal of the linker was utilized to achieve etching of the thin film at the molecular (Angstrom) level.

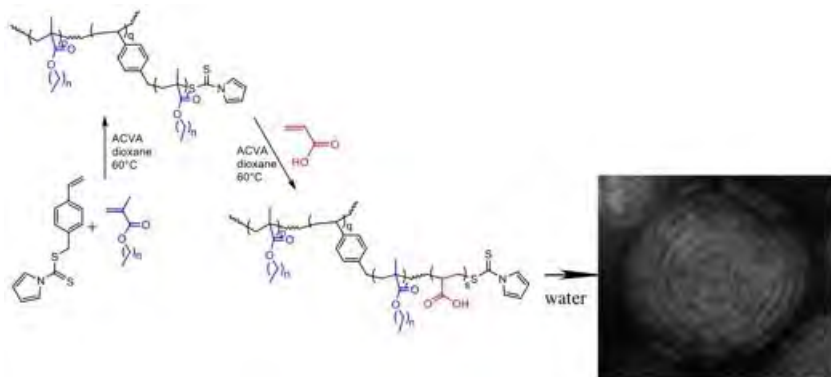


Synthesis of high molecular weight PEG chains and their chemically triggered degradation to low molecular weight units.

POLY 220: Particles formed from poly(butyl methacrylate)-co poly(acrylic acid)

Stephen Rimmer², *s.rimmer@bradford.ac.uk*, Sarah L. Canning³, Mark Geoghegan¹.
(1) Univ of Sheffield, Sheffield, United Kingdom (2) Chemistry, University of Bradford, West Yorkshire, west Yorkshire, United Kingdom (3) Chemistry, University of Sheffield, Sheffield, South Yorkshire, United Kingdom

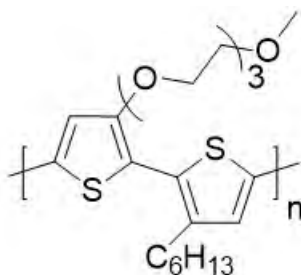
Poly(butyl methacrylate)-co-poly(acrylic acid)s have been prepared using RAFT methodology with either block, graft, random or block-highly branched architectures. Block copolymers were prepared by conventional sequential polymerization the two monomers using RAFT. Graft copolymers with butyl methacrylate backbones were prepared by a grafting-from approach that involved generation of poly(butyl methacrylate)s with pendant dithioate esters followed by RAFT polymerization of acrylic acid from the backbone. The dithioate esters were added to the backbone by using a phase transfer process involving nucleophilic substitution of methylene styryl repeat units. Modification using phase transfer catalysts in mixed aqueous/organic media was shown to be more effective than homogeneous solution modification methods. Highly branched block copolymers were prepared using self-condensing RAFT polymerization. The process involved copolymerization of butyl methacrylate with a styryl dithioate ester followed by further chain extension with acrylic acid. Morphologies observed after dispersion in water were shown to be critically dependant on architecture and in some cases involving the highly branched polymers lamella structures, onion micelles, were observed. The observation of onion-like structures was unexpected and cannot be explained by arguments involving packing of hydrophobes, as has been put forward for morphologies observed with block copolymers. The onion-like structures could be used to complex and deliver a charged dye with the possibility of controlled release of a number of positively charged species.



POLY 221: Triethylene glycol monomethyl ether substituted polythiophenes for organic electronic applications

Dushanthi S. Dissanayake⁴, dushanthi.dissanayake@gmail.com, Samodha S. Gunathilake³, Jia Du³, Taniya M. Pathirana³, Elena Sheina⁶, Enrique Gomez², Mihaela C. Stefan¹, Michael C. Biewer⁵. (1) Dept Chem UT Dallas, Richardson, Texas, United States (2) Penn State University, University Park, Pennsylvania, United States (3) Chemistry, University of Texas at Dallas, Richardson, Texas, United States (4) Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, United States (5) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States (6) pHase2 Microtechnologies Inc, 1425 Forbes Avenue, Suite 302, Pittsburgh, Pennsylvania, United States

Poly(alkylthiophene)s mainly poly(3-hexylthiophene) (P3HT) is attractive as a semiconducting polymer in various applications such as organic field effect transistors, organic photovoltaic devices and sensors. P3HT shows better solubility in organic solvents, and has good conductivities in doped or oxidized state, but are not stable overtime. However, poly(alkoxythiophene)s such as poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) (P3MEET) has been reported with increased conductivity upon doping and were stable over time but can be insoluble in organic solvents due to α,β' coupling between thiophene rings. Here we report a polymer of bithiophene units composed of 3HT and MEEET synthesized via McCullough method to address the issues associated with both poly(alkylthiophene)s and poly(alkoxythiophene)s. This polymer reveals a range of promising optical, electrical and thermal properties such as better ordering in solid state, reduced band gap, better thermal stability and most importantly high conductivity upon doping with iodine vapor which persisted for days.



poly[3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene]

POLY 222: New route to phosphonium monolithic framework: Synthesis, thermal stability and film morphology

Xiaoyan Yang, xiaoyay@g.clemson.edu, Yimei Wen, George Chumanov, Rhett Smith. Chemistry, Clemson University, Central, South Carolina, United States

A phosphonium organic network was prepared from a homemade monomer. The polymerization yields polymeric monolith and the structure was examined by IR. The versatile method shows the ability to tailor properties by applying different starting material. TEM and SEM images indicate the reaction formed layered structure. The amorphous polymer is thermally stable up to 370 °C in air and has char yield (40%) at 800 °C in N₂. The polymer is stable after soaking in 6 M NaOH solution at 60 °C for 24 h. The water uptake is 10.63% and the specific BET surface area is 9 m² g⁻¹. The surface was examined by AFM and the RMS roughness is within 5 nm. These properties indicate the potential application in CO₂ capture and alkaline fuel cell membrane.

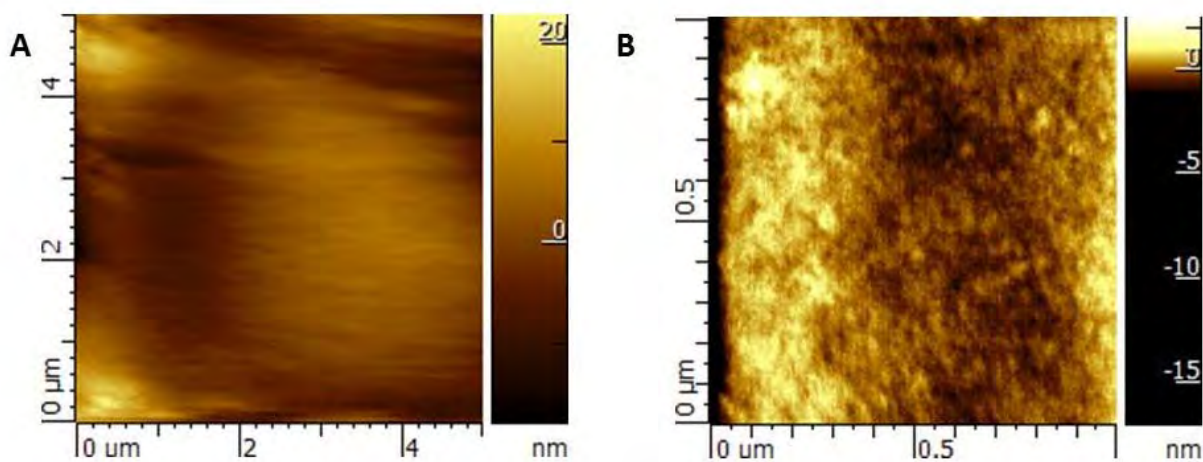
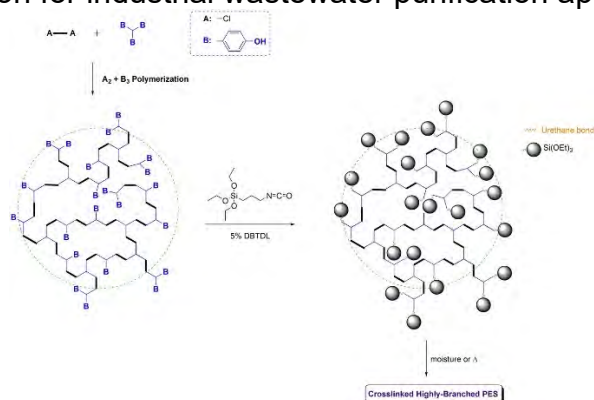


Figure 1. AFM 2D height images of polymer film: 5 μm×5 μm (A) and 1 μm×1 μm (B).

POLY 223: Synthesis and characterization of highly branched, functional poly(arylene ether sulfone)s

E. Billur Sevinis Ozbulut², sevinis@sabanciuniv.edu, Aybige Ozturk², Ipek Sacligi², Turkan Ormanci Acar³, Derya Imer³, Ismail Koyuncu³, Yusuf Z. Menceloglu^{1,5}, Serkan Una^{4,5}. (1) Faculty of Engineering Natural Sciences, Sabanci University, Istanbul, Turkey (2) Faculty of Engineering and Natural Sciences, Material Science and Nanoengineering, Sabanci University, Istanbul, Turkey (3) Environmental Engineering, Istanbul Technical University, Istanbul, Turkey (4) Nanotechnology Research and Application Center, Sabanci University, Tuzla, Istanbul, Turkey (5) Integrated Manufacturing Technologies Research and Application Center & Composite Technologies Center of Excellence, Sabanci University, Istanbul, Turkey

Polysulfone based polymers are commonly employed in high performance membrane applications for water purification purposes. In certain applications for industrial wastewater recovery, operation conditions such as high pH and high temperature are known to negatively influence the membrane performance. In this study, highly branched, functional poly(arylene ether sulfone)s (HB-PES) were synthesized via the A_2+B_3 polymerization. It is well-known that despite their multitude of end-groups, hyperbranched or highly branched polymers typically show poor thermo-mechanical properties compared to their linear analogues. In order to develop HB-PES films and membranes with enhanced thermo-mechanical properties or water-dispersibility, various strategies were developed to introduce functional groups such as silane, acrylate or phenolate functionality on polymer chain ends, which were characterized by FT-IR and NMR spectroscopies, SEC, DMA, DSC and stress strain tests. Acrylate and silane functionalities allowed the ability of crosslinking in the presence of moisture, UV light or heat. The thermal and chemical resistance of the organic-inorganic composite film produced from these novel silane functional HB-PESs was specifically investigated. In an attempt to develop ultrafiltration and nanofiltration membranes with enhanced thermal and mechanical properties, silane or acrylate functional HB-PESs were incorporated into the linear PES-based membranes produced by the phase inversion process followed by a post-crosslinking step. Moreover, phenolate functional HB-PESs were found to be dispersible or soluble in water depending on the number of terminal groups, which enabled the fabrication of thin film composite (TFC) membranes by interfacial polymerization for industrial wastewater purification applications.



Synthesis of functional poly(arylene ether sulfone)s

POLY 224: Can the overall molecular architectures of synthetic polymers be characterized ?

Rana Gurarslan², **Alan E. Tonelli**¹, alan_tonelli@ncsu.edu. (1) TECS, North Carolina State University, Cary, North Carolina, United States (2) TECS, NCSU, Raleigh, North Carolina, United States

Currently the best method for characterizing polymer microstructures is provided by high resolution ¹³C-NMR observations of their solutions, which may be sensitive to microstructures encompassing 1 or 2nm of the polymer backbone. However, due to the short-range structural sensitivity of NMR and other spectroscopic probes, they can only identify and quantify local microstructural features, but are unable to locate them along or among polymer chains. We need only look at the one-to-one correspondence between the primary structures and biological functions of proteins to recognize a similar need to characterize complete individual chain architectures, *i.e.*, macrostructures, of synthetic polymers. The present situation for synthetic polymer structural characterization is akin to being able to only determine the composition and possibly amounts of neighboring amino acid pairs or triplets in proteins, rather than their complete primary structures. Any potential experimental probe of synthetic polymer macrostructures must be sensitive to their complete chain architectures, including the types, quantities, and backbone locations of their shorter-range microstructures. The Kerr-Effect, or birefringence electrically induced in dilute polymer solutions can be highly sensitive to overall polymer macrostructures. This results from the magnitudes and directions of the overall macroscopic dipole moments and anisotropic polarizability tensors of polymer chains averaged over all of their myriad conformations. Because potential complete chain macrostructures are virtually innumerable, we suggest ¹³C-NMR be used to determine the types and amounts of short-range microstructures, and the agreement between observed and estimated Kerr-Effects used to locate them.

Can a locally sensitive probe like NMR be used to determine Polymer Macrostructures?

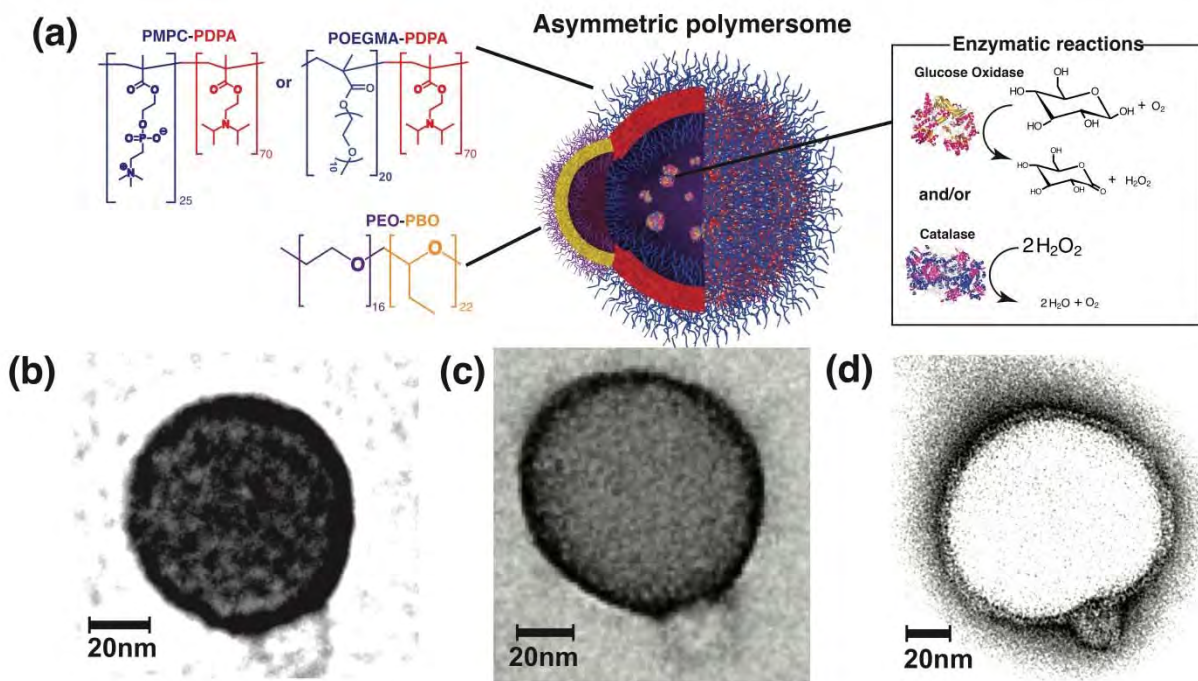
NO!



POLY 225: Glucose-tactic asymmetric polymersomes

Giuseppe Battaglia, *g.battaglia@ucl.ac.uk*. Chemistry, University College London, London, United Kingdom

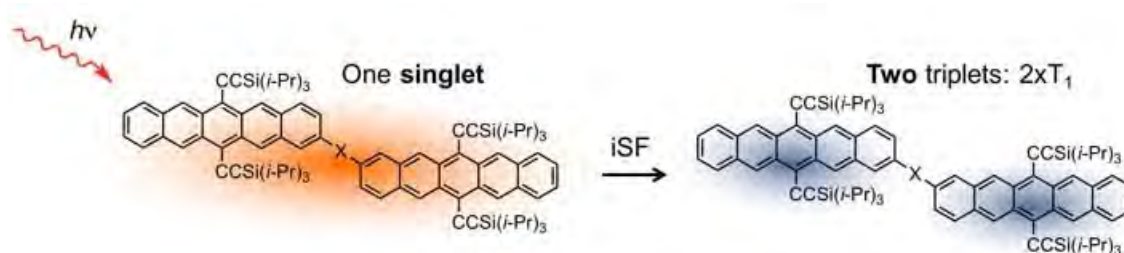
One of the most promising tasks is the ability to engineer nanoscopic carriers that can autonomously navigate within tissues and organs, accessing nearly every site of the human body guided by endogenous chemical gradients. Here I will discuss the design of a fully synthetic, organic, nanoscopic system that exhibits attractive chemotaxis driven by enzymatic conversion of glucose. I will show we achieve this by encapsulating glucose oxidase, alone or in combination with catalase, into nanoscopic and biocompatible asymmetric polymer vesicles (known as polymersomes). I will demonstrate that these vesicles self-propel in response to an external gradient of glucose by inducing a slip velocity on their surface, which makes them move in an extremely sensitive way towards higher concentration regions. Such a chemotactic behaviour is critical to control several operations including anomalous distribution within blood vessels as well as very interesting collective behaviour that leads to both the formation of clusters and swarms. I will finally demonstrate that the chemotaxis enables a four-fold increase in penetration to the brain compared to non-chemotactic systems and this opens up a completely new way to deliver drugs within a human body.



POLY 226: Design strategy for efficient intramolecular singlet fission in oligoacenes

Elango Kumarasamy², elango3403@yahoo.co.uk, Luis Campos¹. (1) Chemistry, MC3124, Columbia University, New York, New York, United States (2) chemistry, Columbia University, New York, New York, United States

Singlet fission (SF), a process where a singlet exciton is converted into two triplet excitons constitute an important concept in third generation solar cells that could improve the efficiency of a single-junction solar cell beyond Shockley-Queisser limit. Elucidating the mechanism behind SF has generated much interest and in organic molecules, intermolecular-SF (xSF) has been extensively investigated. The efficiency of xSF is a function of multiple factors and presents significant challenge to decouple the effects of electronic structure versus intermolecular packing, thus hindering a fundamental mechanistic understanding. To circumvent this challenge, intramolecular-SF (iSF) has been explored, where the SF is an inherent property of the molecule and allows for rapid characterization by ultrafast spectroscopic techniques. This talk will highlight the design and synthesis of iSF materials based on acenes, which have allowed us to elucidate structure-property relationships and design rules, paving the way to a deeper understanding of the iSF mechanism.

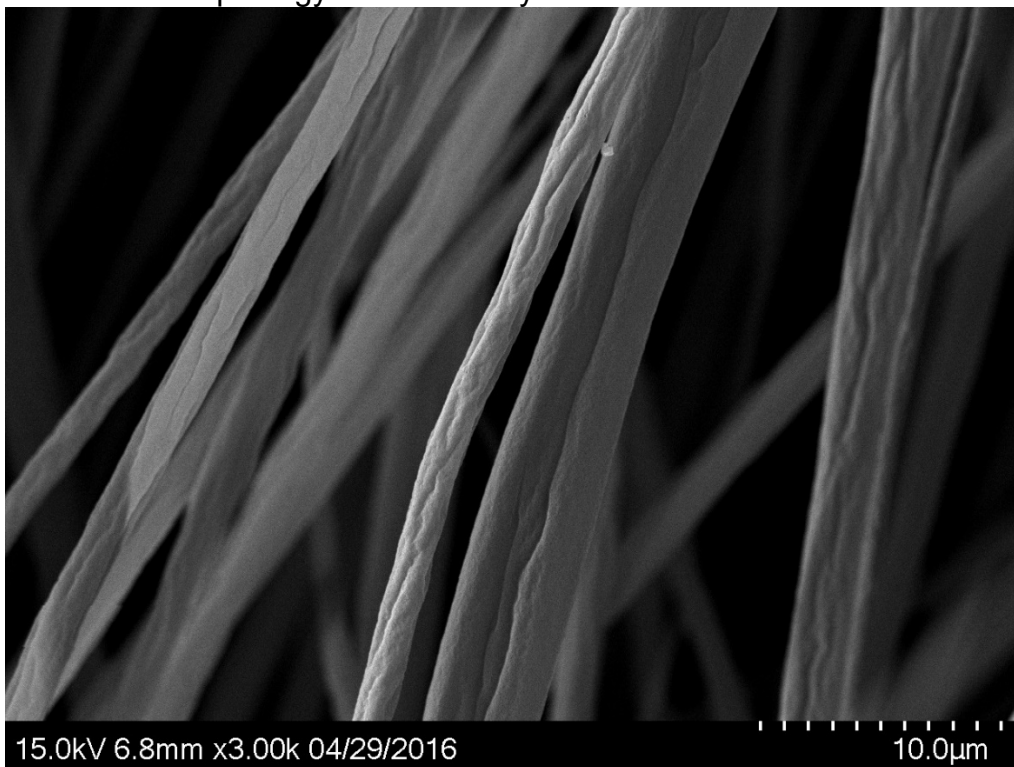


POLY 227: Electrspun phase separating block-copolymer fibers for biological applications

Sandra Camarero-Espinosa, *s.camareroespinosa@uq.edu.au*, Justin Cooper-White.
Tissue Engineering and Microfluidics, Australian Institute for Bioengineering and Nanotechnology, Brisbane, Queensland, Australia

Block copolymers are smart materials capable of separating into well-defined phase structures, offering interesting properties such as well-defined surface chemistries. These novel materials find applications in a broad range of fields as gas separating membranes, substrates for catalysis or tissue engineering substrates. However, fabrication of 3-dimensional fibrous materials with well-defined phase separations usually requires tedious processes such as annealing, co-extrusion or spinning with combination of solvents that drive the phase separation.

Here, we present a simple, one-step method for the fabrication of as-spun phase separating fibers consisting of polystyrene-*b*-poly(ethylene oxide) with a structure that spans homogeneously along the material. Fibers with a core-shell, body center cubic (BCC) or gyroid structures can be prepared at glance by just introducing small modifications on the solution concentration or flow rate during the spinning process. Moreover, the surface chemistry of these fibers can also be tuned in a spatially controlled manner by chemical modification of the polyethylene oxide phase, via end-group functionalization and click-chemistry. We thus synthesized and fabricated phase separating fibrous scaffolds presenting different biological cues (peptide sequences) that represent an interesting platform to study and tune biomaterial-cell interactions that determine cell morphology and ultimately cell fate.

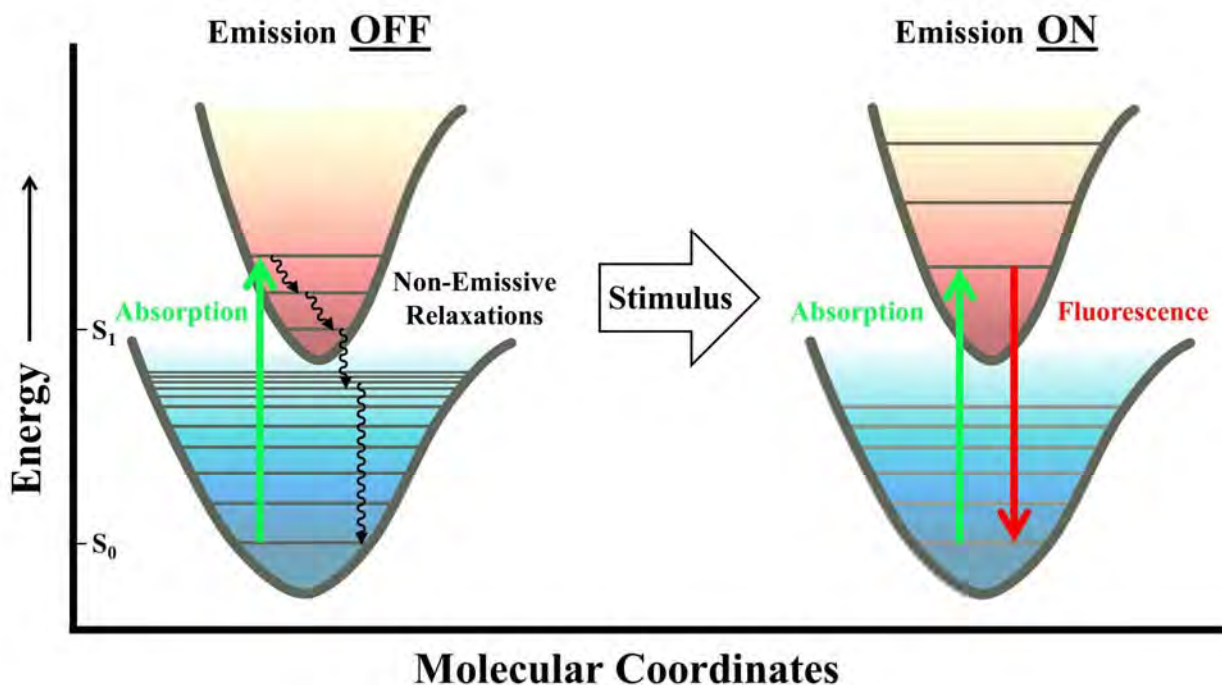


As-electrospun phase separating fibers

POLY 228: Functional molecular vibrations for stimuli responsive polymers

Joseph Lott, joseph.r.lott@usm.edu. University of Southern Mississippi, Hopkins, Minnesota, United States

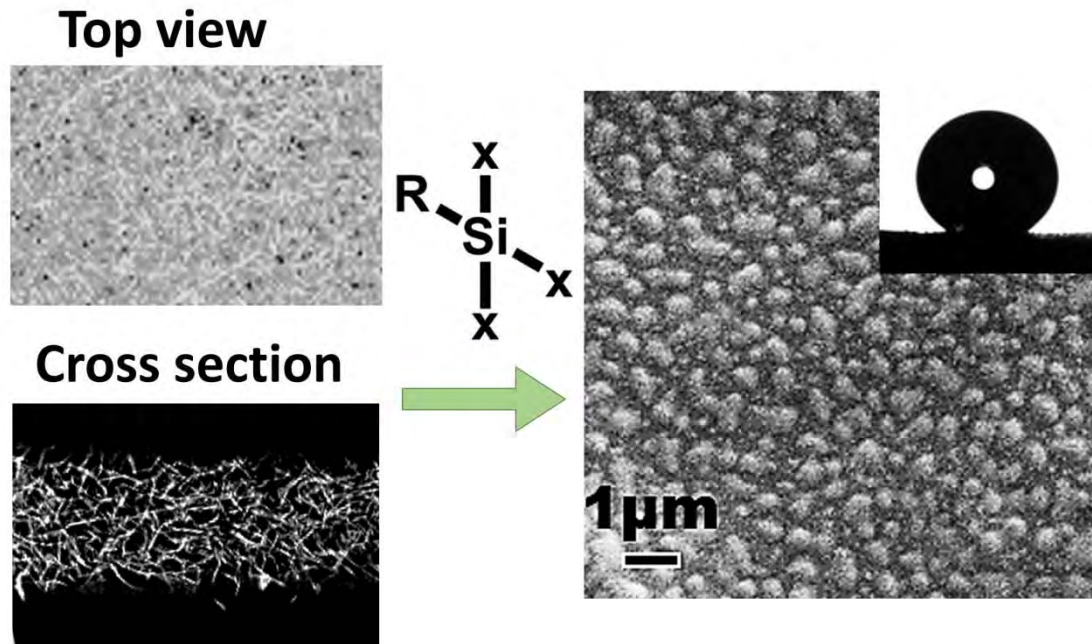
An innovative approach to optically active stimuli responsive polymers is presented. The materials are based on precisely engineered 'molecular reporters' that exhibit vibrationally-dependent emission intensity. For these molecules, no fluorescence is observed when molecular motions are unhindered, yet when vibrational freedom is impinged, fluorescence emission is turned on. Owing to the many stimuli that can be used to perturb the vibrational (and therefore the fluorescence) ability of the small molecules, innovation over a broad portfolio of polymer-based systems is enabled. Demonstrations of this concept include optical responses triggered by gelation, curing of epoxies, and traversing the glass transition. Additionally, piezochromic and mechanochromic stimuli responses are covered.



POLY 229: Bio-Inspired porous amphiphobic materials through surface step-growth polymerization

Stephanie Oyola-Reynoso¹, Jiahao Chen¹, Boyce Chang¹, Ian Tevis^{1,2}, **Martin Thuo**¹, *mwangi.m@gmail.com*. (1) Materials Science & Engineering, Iowa State University, Ames, Iowa, United States (2) Safi-Tech, Ames, Iowa, United States

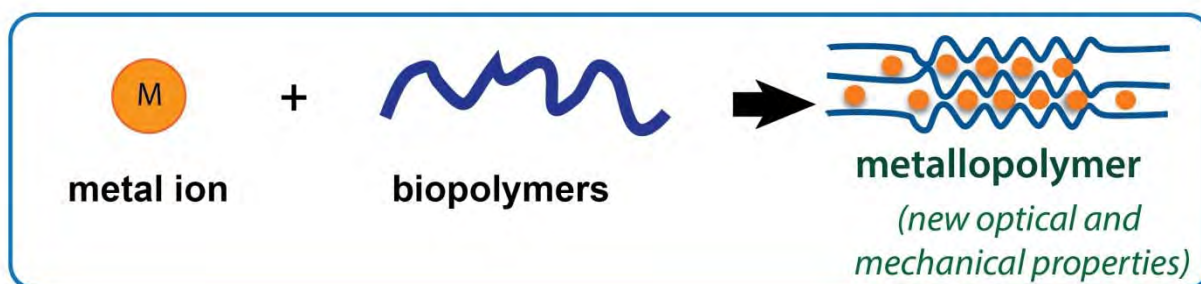
Chemical grafting of small molecule reagents onto polymeric fibrous materials, has been extensively used to modify their surface properties. Inherently adsorbed surface water, however, complicates our current assumptions that such molecules often form monolayers. We hypothesized, and demonstrated, that adsorbed water is a valuable comonomer for polyvalent labile reagents (monomers). Surface energy mismatch between the reagents' non-reactive tails and the water leads to concomitant self-assembly allowing for stochastically distributed rate-limited particles to form across the surface. This process leads to hydrophobic particles forming on a porous material, herein demonstrated with paper and mixed-polymer fabrics. Mechanistic understanding in the formation of these materials, their characterization and applications will be discussed.



POLY 230: Controlling mechanical properties of polymeric materials using photo-active metal coordination interactions

Alexis Ostrowski, *alexiso@bgsu.edu*. Department of Chemistry, Bowling Green State University, Bowling Green, Ohio, United States

We have designed new materials that integrate the photochemistry of metal-coordination complex into polymers. The inclusion of transition metal ions allowed for new photoreactivity in the polymers where the bonding interactions, and thus polymer cross-linking, was controlled with light. Depending on the type of metal and coordinated ligand, coordination complexes offer a diversity of reactivity due to the changing metal-ligand binding interactions (energy, geometry etc.). We have integrated such metal-coordination bonding into polysaccharide-based materials to create photoresponsive gels. These gels showed changes in mechanical properties and pore size after light irradiation, and could be used as scaffold materials for tissue engineering. We also created model polymer materials to understand how we could influence and control material properties by tuning the metal ion and ligand. We showed that by changing the geometry of ligand coordination, we could control the mechanical properties of the resulting materials. In addition, such metallopolymers showed reversible photoreactivity, where light irradiation led to softening of the materials.

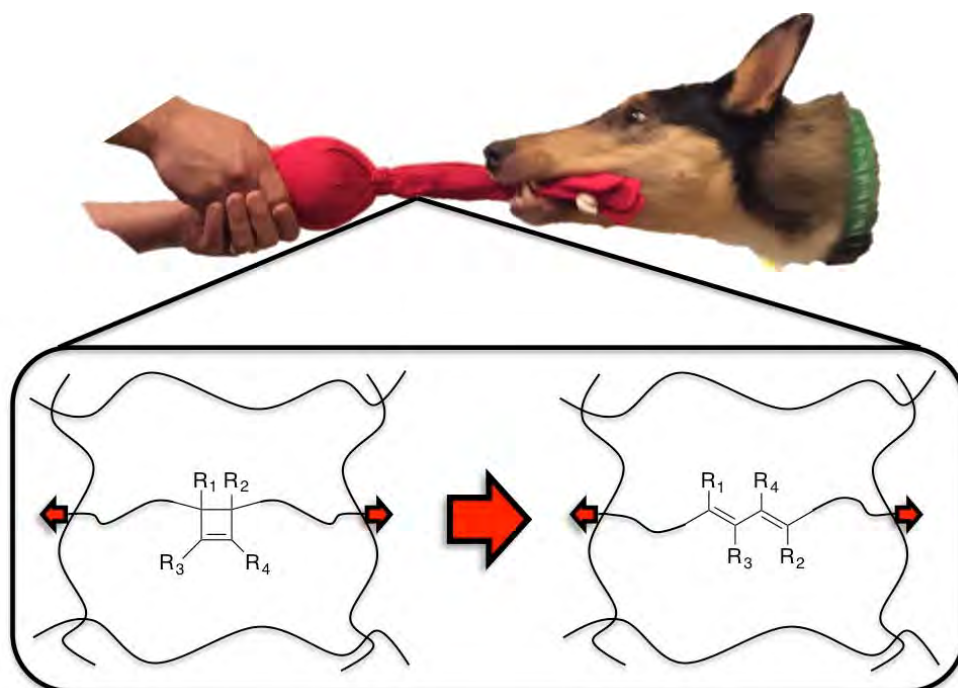


The addition of transition metal ions to polymers was used to create new materials with unique optical and mechanical properties

POLY 231: Examining the mechanical reactivity of substituted cyclobutene mechanophores

Cameron L. Brown, *clb68@duke.edu*, **Tatiana B. Kouznetsova**, **Brandon Bowser**, **Stephen Craig**. *Department of Chemistry, Duke University, Durham, North Carolina, United States*

Materials often fail as a result of the mechanical loads they experience during use. On the molecular level, forces within polymers are distributed unevenly throughout the material, and some polymer subchains experience greater stress than others. In some cases, the forces experienced by these overstressed subchains can trigger chain scission events. Chain scission in turn might nucleate the formation of a microcrack that subsequently propagates, ultimately leading to material failure. In recent years, force reactive functional groups, or mechanophores, have emerged as the basis of a potential strategy for not only signaling, but also combatting this destructive cascade. The strategy comprises embedding mechanophores along the polymer backbone or within cross-links, so that otherwise destructive force within an overstressed subchain trigger a constructive, rather than a destructive, response. Examples of potentially constructive responses include mechanically activated catalysis, mechanochromism, self-healing / self-strengthening, and small molecule release. In this work, we examine the mechanical reactivity of cyclobutene-based mechanophores and their utility towards developing stress-reporting and stress-responding materials.



POLY 232: Light on an upward trajectory: Sensitized light upconversion in polymers

Yoan C. Simon, *Yoan.Simon@usm.edu. Adolphe Merkle Institute, University of Fribourg, Marly, Switzerland*

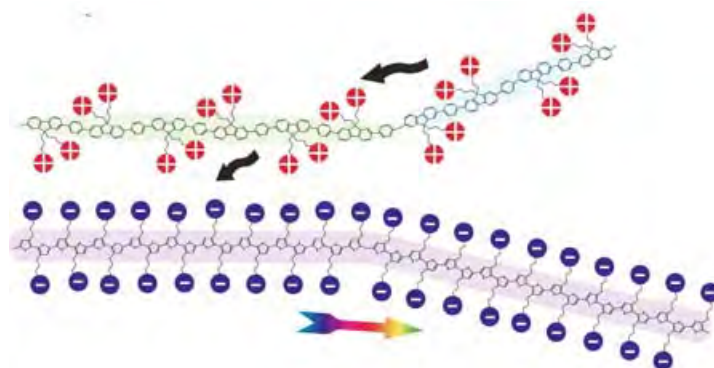
From solar harvesting to sensing, there is a need to capture low-energy electromagnetic radiations and turn them into light of higher energy, a process otherwise known as light upconversion (UC). Specifically, sensitized UC via triplet-triplet annihilation (TTA) is a promising photophysical process which has been known for decades but only resurged recently in the solid state. Interestingly, TTA-UC relies on a complex cascade of energy transfers between two chromophores with carefully matched electronic levels. One of the limiting factors for this cascade is the inherent reduced mobility in polymers. This contribution will cover our latest realizations in the to overcome these limitations and sketch out the guiding principles upon which they are founded. Multiple systems will be presented such as upconverting (nano)particles, organogels, and nanostructured mixes. This presentation will serve to establish some of the structure-property relationships of upconverting polymeric materials.



POLY 233: Conjugated polyelectrolytes as light harvesting antenna

Carmen Segura, *cjsegura@ucsc.edu*, Alexander Ayzner. *Chemistry and Biochemistry, UC Santa Cruz, Santa Cruz, California, United States*

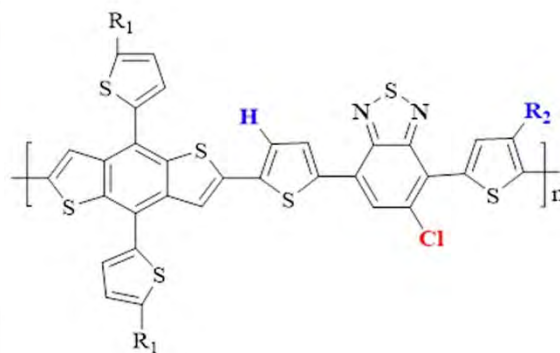
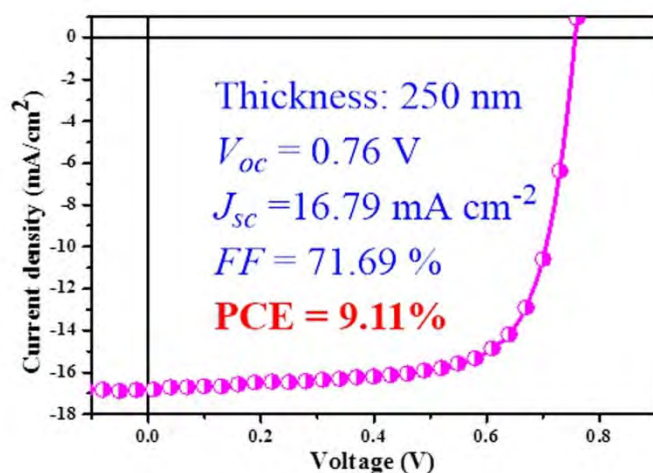
Inspired by natural light harvesting systems that were fine-tuned by nature through billions of years of evolution, the focus of this research aims to mimic nature's approach of capturing solar energy by constructing a self-assembled, artificial light-harvesting antennae capable of efficient electronic energy transfer. To do this, we have begun working with a pair of oppositely charged conjugated polyelectrolytes (CPEs) – the energy donor, which is a cationic poly(fluorene-co-phenylene) (PFPI), and the acceptor, which is an anionic regioregular poly(alkylcarboxylthiophene) (PTAK). This study focuses on the role that surfactants have on the solution structure and optical properties of CPE complexes, with the goal of controlling complex formation with a ternary ionic surfactant agent. The interaction between the CPEs and an negatively charged surfactant sodium dodecyl sulfate (SDS) at concentrations above and below critical micelle concentrations were studied in aqueous solution by UV-visible absorption, steady state fluorescence spectroscopy, dynamic light scattering and small-angle X-ray scattering. We find that CPE complex-surfactant interactions lead to surfactant-concentration-dependent spectroscopic behavior and changes in the hydrodynamic sizes of the complexes. We further investigated the binding competition between the anionic PTAK and anionic SDS with the cationic donor CPE, PFPI. We find that SDS can be used to unbind the CPE complex, depending on the relative charge ratio of cationic CPE/ anionic CPE/ SDS system. This leads to drastic changes in the solution structure and electronic energy transfer efficiencies.



POLY 234: Chlorination: A facile method for high-performance polymer solar cells

Feng He, *hefeng0801@gmail.com*. Chemistry, South University of Science and Technology of China, Shenzhen, Guangdong, China

Halogenation is an effective way to tune the energy levels of organic semiconducting materials. To date, fluorination of organic semiconducting materials to fabricate polymer solar cells (PSCs) has been used far more than chlorination; however, fluorine exchange reactions suffer from low yields and the resulting fluorinated polymer always comes with higher price, which will greatly hinder their commercial applications. Herein, we designed and synthesized a series of chlorinated donor-acceptor (D-A) type polymers, in which benzo[1,2-b:4,5-b]dithiophene and chlorinated benzothiadiazole units are connected by thiophene π -bridges with an asymmetric alkyl chain. These chlorinated polymers showed deep highest occupied molecular orbital energy levels, which promoted the efficiency of their corresponding PSCs by increasing the device open circuit voltage. The asymmetric alkyl chain on the thiophene moieties gave the final polymer sufficient solubility for solution processing and strong π - π stacking in films allowed for high mobility. Although the introduction of a large chlorine atom increased the torsional angle of the polymer backbone, the chlorinated polymers maintained high crystallinity and a favorable backbone orientation in the blended films. These factors contributed to respectable device performances from thick-film devices, which showed PCEs as high as 9.11% for a 250 nm-thick active layer. These results demonstrate that chlorination is a promising method to fine tune the energy levels of conjugated polymers, and chlorinated benzothiadiazole may be a versatile building block in materials for efficient solar energy conversion.

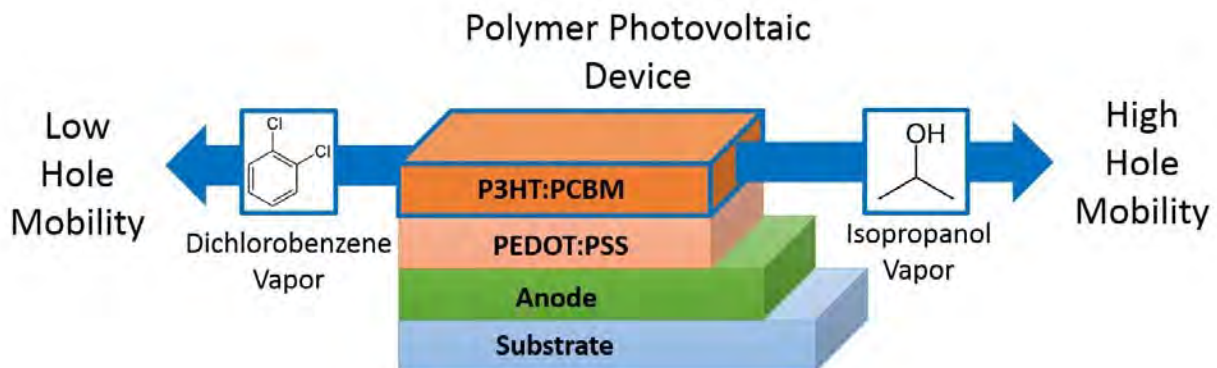


The chlorinated polymers exhibit high crystallinity, good mobility, favorable backbone orientation, and respectable device performances from the thick-film devices (PCE up to 9.11%), which demonstrates that chlorination is a promising approach for high efficient polymer solar cells with affordable process.

POLY 235: Effect of solvent vapor annealing on crystallinity and hole mobility in P3HT:PCBM polymer photovoltaics

Levi Moore¹, levi.m.moore@eagles.usm.edu, **Mithun Bhattacharya**¹, **Qi Wu**¹, **Sang Gil Youm**², **Evgueni E. Nesterov**², **Sarah E. Morgan**¹. (1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States

Many efforts have been made in the processing of organic photovoltaic devices to increase performance, including thermal annealing and solvent vapor annealing, wherein a photovoltaic active layer film is exposed to a solvent vapor-saturated atmosphere. Solvent vapor annealing was used in order to manipulate the morphology and performance of P3HT:PCBM polymer organic photovoltaic (OPV) devices. OPV active layers were annealed with a good solvent (dichlorobenzene), no solvent (air), or a poor solvent (isopropanol). Devices annealed with isopropanol vapors exhibited a higher hole mobility than the air control devices, which showed higher hole mobility than air- or dichlorobenzene-annealed devices, as calculated from dark-current measurements and fitting using the Mott-Gurney square law. These changes in performance are attributed to the changes in nanomorphology effected by solvent vapor annealing. Morphologies of films annealed solely with solvent vapor annealing, and in tandem with thermal annealing, were studied with UV-Vis spectroscopy, atomic force microscopy (AFM), and grazing incidence wide-angle x-ray scattering (GIWAXS). AFM analysis shows phase-separated domains on the order of exciton diffusion lengthscales. Coherence lengths of crystalline P3HT lamellae were determined by Scherrer analysis of the GIWAXS patterns, and followed the trend of DCB < air < IPA.



POLY 236: Enhancing charge transport in redox active polymers through molecular design

Kenneth Hernandez-Burgos², kenhndz@illinois.edu, Mark Burgess¹, Etienne Chenard¹, Nagarjuna Gavvalapalli¹, Rajeev Assary³, Jeffrey Moore², Joaquin Rodriguez Lopez². (1) Chemistry, University of Illinois at Urbana-Champaign, Champaign, Illinois, United States (2) School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (3) Argonne National Laboratory, Argonne, Illinois, United States

Non-aqueous Redox Flow Batteries (NRFBs) are emerging devices for electric grid storage applications. A major challenge in redox flow batteries is enhancing the ionic conductivity across the membrane while preventing the crossover of the anolyte and catholyte. Recently, we reported that using redox active polymers (RAPs) in combination with size exclusion membranes, in contrast to ion selective membranes, provides a viable alternative that addresses these challenges and enables NRFBs. The electron transfer kinetics of large polymer redox mediators with hundreds to thousands of redox active centers in solution are not well understood. In addition, the existence of a preceding chemical step that mediates the redox chemistry of RAPs in solution highlights the importance of charge hopping on these polymer. In order to gain a better understanding of the electrochemical properties of RAPs, we use a systematic molecular design approach to investigate the impact of backbone and redox-pendant electronic interactions on the performance of viologen RAPs (fig. 1). We used different electrochemical techniques to study the redox properties, charge transfer kinetics and self-exchange of electrons through redox active dimers and their equivalent polymers. Stark contrast was observed between the electrochemical properties of viologen dimers and their corresponding polymers. Our studies provide insights on how the modulation of RAP inter-pendant interactions decisively impacts charge transfer. While polymers with optimized macroscopic reversibility were obtained, the microscopic trends describing small molecule electrochemistry did not hold for polymers, showing anti-Marcus effects that require further investigation.

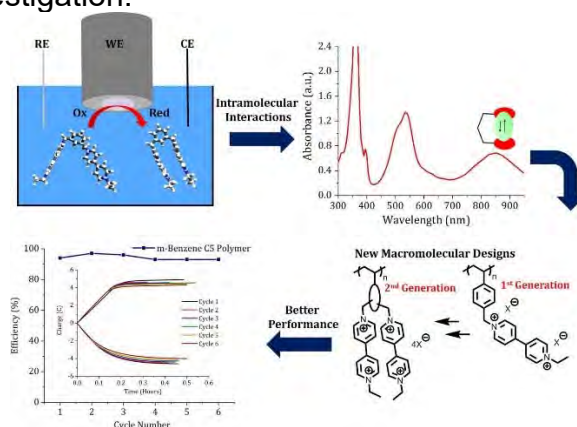


Figure 1. Schematic representation that shows the work flow for this project. We used a systematic molecular design approach in combination with spectroelectrochemical techniques to design and characterize new redox active polymers for energy storage applications.

POLY 237: Multi-grafting lithium polyacrylate as high-performance polymer binder for lithium-ion battery

Pengfei Cao¹, caopengfei686@gmail.com, Michael Abdelmalak³, Eric Stacy², Bingrui Li¹, Tao Hong², Jagjit Nanda³, Alexei P. Sokolov^{2,1}, Tomonori Saito¹. (1) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States (3) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Developing sustainable energy storage technologies has been attracting significant attentions due to the ever-growing energy needs and depleting fossil fuels. Increasing the energy density of the lithium-ion battery (LIB) is highly required due to their expanding applications from portable electronics to large-scale emerging applications, such as an electric vehicle that requires longer driving distance upon a single charging. Theoretically, using silicon instead of the traditional graphite on anode can raise the capacity up to 10 times higher, while the significant volume change during lithiation and delithiation seriously limits the long cycle life of the silicon anode.

In this project, a multiphase graft copolymer of lithium polyacrylate was synthesized and tested as a polymer binder for silicon-based anode in lithium-ion battery. A macro RAFT-CTA was synthesized by amidation reaction of carboxylic acid terminated RAFT-CTA with primary amine on chitosan in aqueous solution, and the following RAFT polymerization of acrylic acid allows the synthesis of well-defined comb-like copolymers, i.e., chitosan-*graft*-PAA. Further titration of the chitosan-*graft*-PAA with lithium hydroxide results the comb-like copolymer with chitosan as a backbone with lithium polyacrylate as the side chains. Multi-grafting lithium acrylate with different grafting densities and side chain lengths can be synthesized. The effect of different polymer binders, such as PVDF, PAA, LiPAA and chitosan-*graft*-PAA and chitosan-*graft*-LiPAA, on the electrochemical performance is assessed, and galvanostatic test result demonstrated that the comb-like copolymer exhibit the better cycling performance compared with the linear analogue.



POLY 238: Drifting proton transport by nanophase separation induced intrinsic electric field in polymer electrolyte material under anhydrous state

Yidong Hu, huyidong@t.shu.edu.cn, Liuming Yan, Baohua Yue. Department of Chemistry, Shanghai University, Shanghai, China

High proton conductivity is a fundamental property of polymer electrolyte material for application in proton exchange membrane fuel cells operated under high-temperature and water deficient environment. In this work, a nanophase separated polymer electrolyte material is designed with enhanced proton transport drifted by intrinsic electric field. The material consists of both acidic and alkaline motifs which are separated into acidic and alkaline domains resulting nanophase separated morphology. Though neutralization reaction occurs in the interface between the acidic and the alkaline domains, chemical equilibrium (homogeneous) does not establish because of space separation. Such inhomogeneity induces space charge distribution and thus intrinsic electric field which promotes the proton transport.

This design is realized by grafting acidic and alkaline hydrophilic sidechains (provide motifs) onto hydrophobic polysulfone backbone (provides mechanical integration). An elaborate balance among these three components, which is optimized by multiscale molecular simulation, is established by controlled radical polymerization. The nanophase separated material is synthesized as follows: First, polysulfone backbone is functionalized with chloromethyl groups via Blanc chloromethylation reaction. Then, poly(vinyl phosphonic acid)-*block*-poly(vinyl triazole) sidechains are grafted using controlled radical polymerization. The nanophase separated morphology is achieved by precise control of functionalization degree and polymerization degrees of poly(vinyl phosphonic acid) and poly(vinyl triazole) sidechain (**Figure 1**).

The structures and morphology are characterized by NMR spectroscopy and high resolution SEM. Good agreement is observed between the multiscale molecular simulation and SEM observation. Impedance spectroscopy reveals extraordinary improvement of proton conductivity in the nanophase separated material compared with all composing components. In addition, synergetic effects are observed for mechanical properties and chemical and thermal stabilities. Finally, the application behaviors in fuel cells are characterized with satisfactory results.

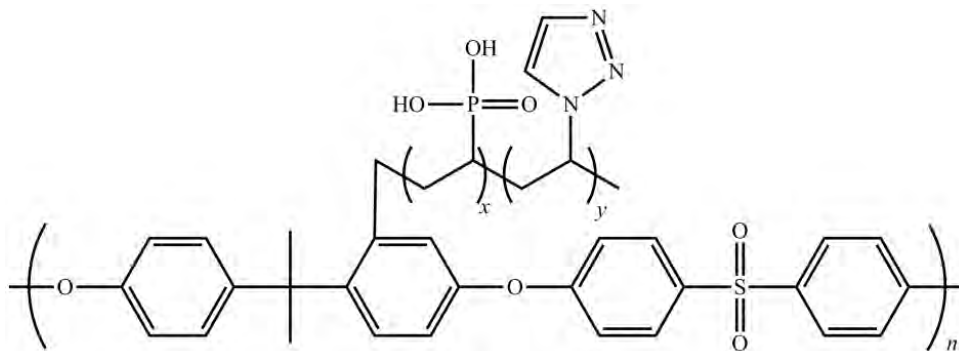
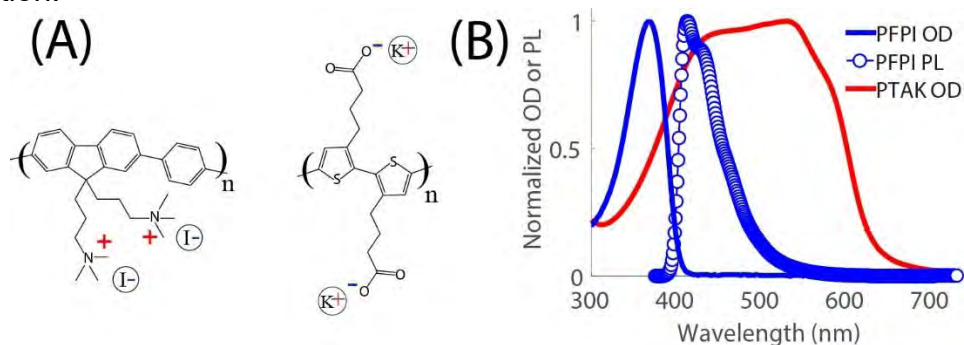


Figure 1 Schematic structure of the nanophase separated polymer electrolyte material

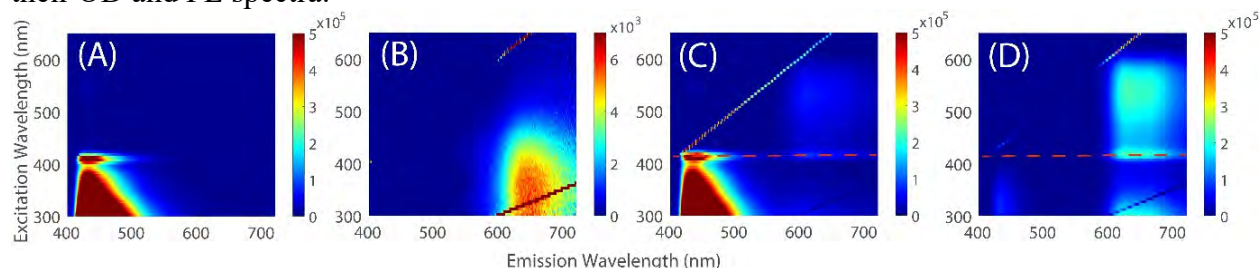
POLY 239: Photophysical changes driven by complexation of oppositely charged conjugated polyelectrolytes

William R. Hollingsworth¹, wrhollin@ucsc.edu, Carmen Segura², Jonathan Balderrama³, Nathaniel Lopez¹, Pamela Schleissner⁴, Alexander Ayzner¹. (1) Chemistry and Biochemistry, UC Santa Cruz, Santa Cruz, California, United States (4) Chemistry and Biochemistry, UC Santa Cruz Dept. of Chemistry, Santa Cruz, California, United States

Conjugated polyelectrolytes' solubility, tunable absorption spectrum, large absorption cross section and tendency toward self-assembly make them an attractive class of materials to act as a light-harvesting and electronic energy transport layer in modular systems aimed at mimicking photosynthesis. Their photophysical properties are highly dependent on the complicated interplay between the polymer back-bone microstructure and on inter- and intra-chain aggregation. If conjugated polyelectrolytes are to be used in light harvesting applications then we must develop an understanding of how the formation of ionically bound donor-acceptor complexes effects their photophysical properties. I will discuss recent characterization of stable, oppositely-charged conjugated polyelectrolyte complexes by steady-state and time-resolved photoluminescence. These complexes exhibit rapid energy transfer from donor to acceptor and a > 2 order-of-magnitude increase in acceptor quantum yield. This increase is unrelated to energy transfer from the donor, and is instead brought about by a planarization of the acceptor backbone as it templates to the donor upon complexation.



Structures of the polyfluorene (a) and polythiophene (b) conjugated polyelectrolytes, as well as their OD and PL spectra.

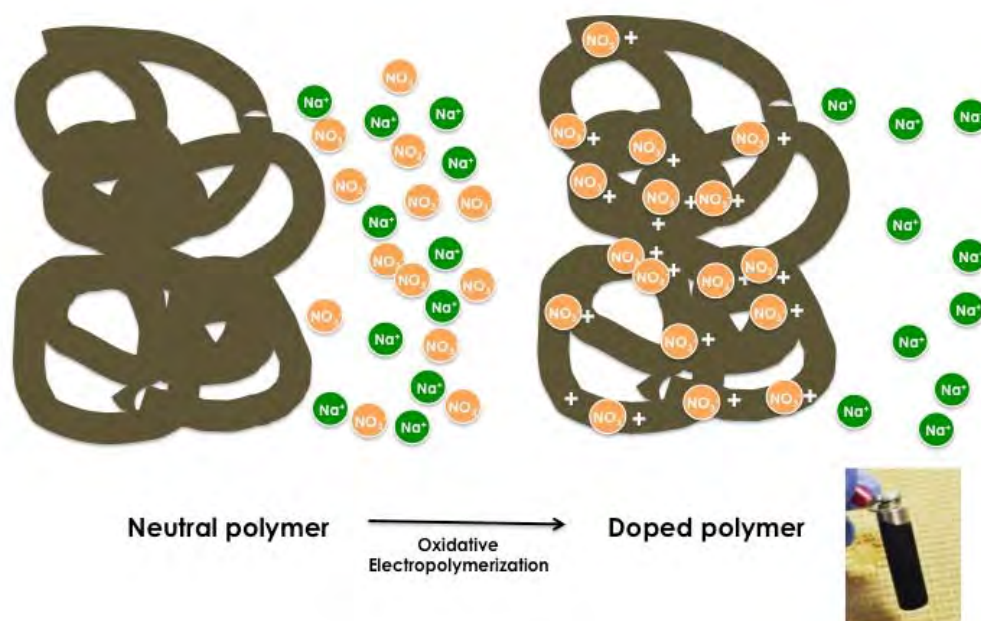


2D photoluminescence maps of polyfluorene in solution (a), polythiophene in solution (b), a 1:0.01 monomole ratio of polyfluorene to polythiophene (c), a 1:0.25 monomole ratio of polyfluorene to polythiophene (d).

POLY 240: Application of polypyrrole-based selective electrodes in electrochemical impedance spectroscopy to determine nitrate concentration

Monica C. So¹, mso@csuchico.edu, Meghdad Hajimorad², Hadil Mustafa², Saqer Alhloul³. (1) Chemistry and Biochemistry, California State University Chico, Chico, California, United States (2) Electrical and Computer Engineering, California State University Chico, Chico, California, United States (3) East Washington University, Cheney, Washington, United States

Nitrate is a commonly found nitrogen species in the environment, especially in agricultural regions. Since excessive nitrate accumulation has negative impacts on the environment, the quantitative monitoring of nitrate levels in the field is a critical component of precision agriculture. Researchers recently showed the application of plasticized polyvinyl chloride electrodes in conjunction with electrochemical impedance spectroscopy (EIS) to monitor nitrate levels. In this work, we show that nitrate doped polypyrrole (PPy(NO₃⁻)) electrodes also have the potential of serving as nitrate sensors in EIS applications. To the knowledge of the authors, PPy(NO₃⁻) electrodes have not been used before to monitor nitrate levels using EIS. Using a metric extracted from the low-frequency EIS behavior of our PPy(NO₃⁻) electrodes, we also show the potential of realizing a nitrate sensor whose output response spans about 100 times for an input dosage range of 30–6200 ppm. This may lead to the future development of low-power and responsive nitrate sensors for large-scale field deployment.

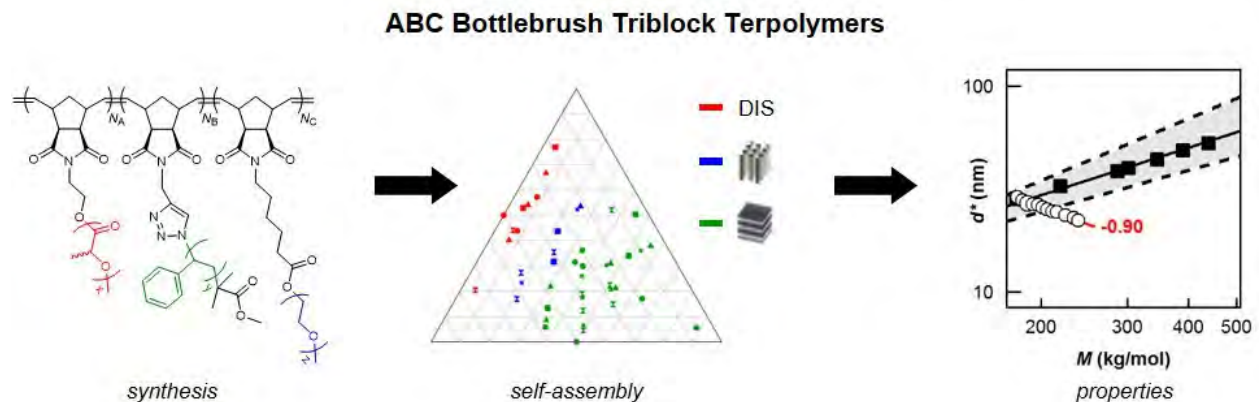


Nitrate anions move in from solution to compensate for the positive charges formed on the polymer chain during doping.

POLY 241: Consequences of low- χ design in block copolymer self-assembly

Alice Chang, *abc@caltech.edu*, Robert H. Grubbs. California Institute of Technology, Pasadena, California, United States

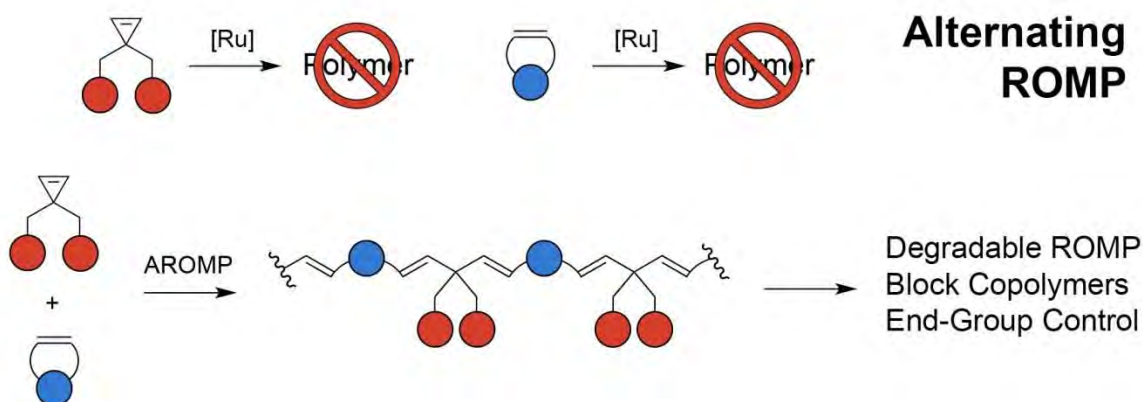
We performed the first systematic study of the phase behavior of ABC bottlebrush triblock terpolymers. Along the way, we discovered a new lamellar morphology with unusual consequences for polymer properties and scaling behavior. We synthesized a series of ABC triblock terpolymers having grafted polylactide (L), polystyrene (S), and poly(ethylene oxide) (O) side chains. Partial mixing of L and O end blocks due to low- χ design produces a new morphology (LAM_P) with mesoscopic ACBC connectivity, counter to all known examples for ABC triblock terpolymer self-assembly. For ABC triblock terpolymers, the standard model demands periodic domains with ABCB repeat units (*i.e.*, LAM₃). In our system as designed, however, we can decouple the domain connectivity from the synthesized block connectivity. Other consequences of partial mixing in LAM_P include a dramatic decrease in domain spacing with increasing molecular weight under certain conditions. LAM_P has been characterized by small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). Self-consistent field theory (SCFT) for brush polymers supports the experimental model and affirms the importance of χ . Recently, we have extended these insights into low- χ design from ABC triblock terpolymers to polymer blends. To the best of our knowledge, these phenomena are unprecedented in block copolymer self-assembly. This discovery introduces a new tool for controlling polymer structure and properties in future materials design.



POLY 242: Development and applications of living alternating ring-opening metathesis polymerization of cyclopropenes

Benjamin R. Elling¹, bre28@stanford.edu, Yan Xia³, Jessica Su². (1) Chemistry, Stanford University, Stanford, California, United States (2) Chemistry, Stanford University, Stanford, California, United States (3) MC 5080, Stanford University, Stanford, California, United States

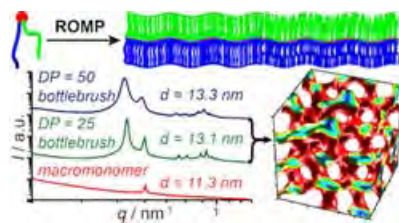
In our investigation of the ring-opening metathesis polymerization (ROMP) of cyclopropenes (CPs), we developed a class of CPs that do not undergo homopropagation but selectively undergo alternating polymerization with low-strain cyclic olefins. This system produced polymers with controlled molecular weights, low dispersities, and regular microstructures, as evidenced by NMR spectroscopy and MALDI-TOF MS. We further developed the system to copolymerize CPs with dioxepins to produce polyacetals/ketals that degrade readily into small molecules under acidic conditions. The controlled nature also allowed for the synthesis of block copolymers and end group control.



POLY 243: Graft-through synthesis and assembly of Janus bottlebrush polymers from A-branch-B diblock macromonomers

Ken Kawamoto³, ken_k@mit.edu, Mingjiang Zhong^{2,5}, Karim R. Gadelrab², Li-Chen Cheng², Caroline A. Ross¹, Alfredo Alexander-Katz², Jeremiah A. Johnson⁴. (1) MIT, Cambridge, Massachusetts, United States (2) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (4) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States (5) Chemical Engineering, Yale University, New Haven, Connecticut, United States

The design, synthesis, and characterization of bottlebrush block copolymers made through the ring-opening metathesis polymerization of A-branch-B diblock macromonomers are presented. The self-assembly of polystyrene/polydimethylsiloxane bottlebrushes was carefully studied in the bulk and in thin films. Lamellar, hexagonal cylindrical, and gyroid phases were observed and modeled. The unique A-branch-B bottlebrush structure provides unique advantages in the context of bottlebrush polymer self-assembly, including access to the first examples of the gyroid phase.

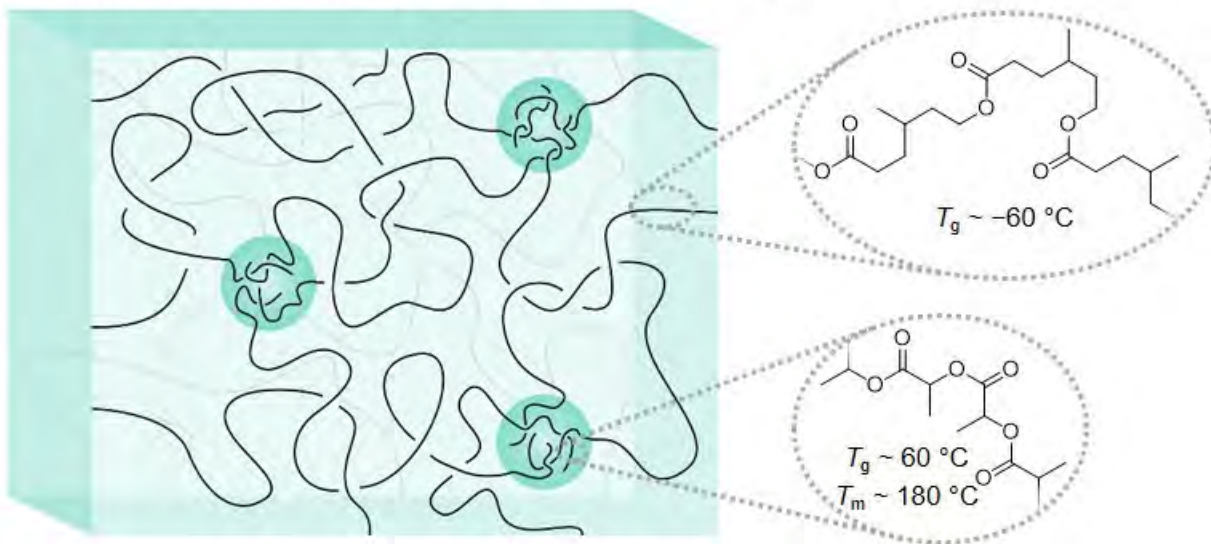


POLY 244: Strong aliphatic polyester thermoplastic elastomers

Annabelle Watts, leex7085@umn.edu, Marc A. Hillmyer. University of Minnesota, Minneapolis, Minnesota, United States

Thermoplastic elastomers (TPEs) made of ABA block polymers exhibit properties that compete with vulcanized natural rubber, while allowing for the materials to be reprocessed. Most commercially produced TPEs are made from petroleum-derived monomers such as styrene and butadiene due to their abundance, and exhibit impressive mechanical properties and good thermal stability. Aliphatic polyester-based TPEs have been studied to meet the need for sustainable polymers that can replace non-degradable and petroleum-derived materials. Though much work has been done in creating TPEs that have an aliphatic polyester backbone, there are still challenges in finding a system that is readily synthesized and exhibits mechanical properties that compete with styrenic TPEs. This work focuses on the synthesis and characterization of a new aliphatic polyester block polymer system which has polymerization conditions that are both thermodynamically and kinetically favorable. The rubbery B midblock provides access to a highly entangled rubber network. Creep and residual strain in the material are suppressed when the hard A end blocks are isotactic poly(lactide). The system reported in this talk demonstrates elastomeric properties that are competitive with styrenic TPEs.

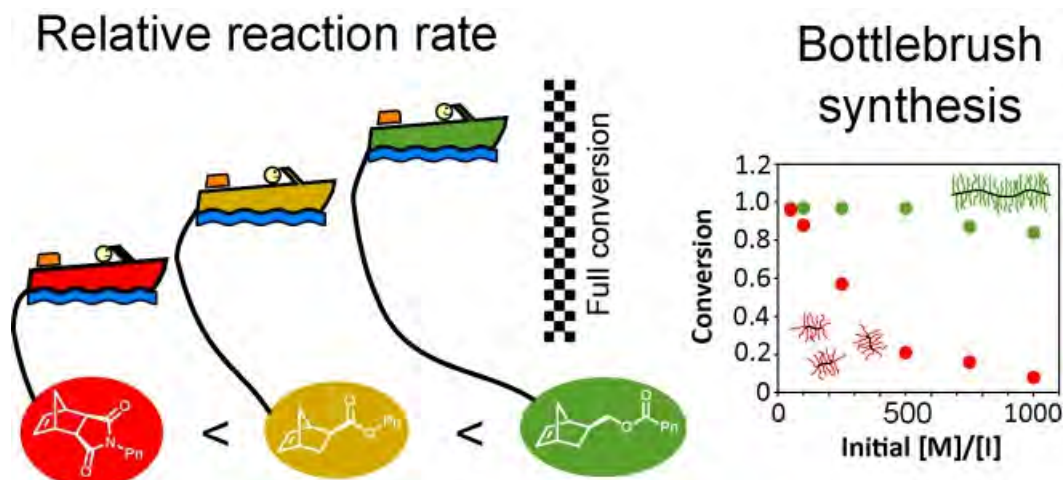
Tough and Sustainable Thermoplastic Elastomers



POLY 245: Synthesis and characterization of bottlebrush polymers: The importance of the Anchor Group

Scott Radzinski^{1,2}, scr014@vt.edu, Jeffrey Foster^{1,2}, Robert Chapleski Jr², Diego Troya², John Matson^{1,2}. (1) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

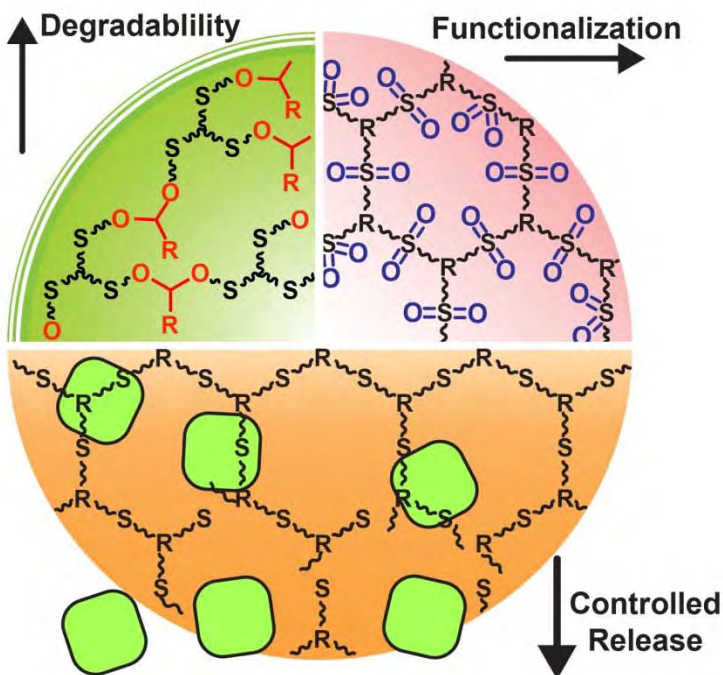
Bottlebrush polymers are macromolecules with densely grafted polymeric pendent groups attached to a polymeric backbone. These polymers are prepared using one of four synthetic strategies: grafting-from, grafting-to, transfer-to and grafting-through. The grafting-through process typically uses ring opening metathesis polymerization (ROMP) to synthesize the bottlebrush polymers with perfect grafting density. We evaluated the effect of anchor group chemistry—the configuration of atoms linking the polymer to a polymerizable norbornene—on the kinetics of ROMP of polystyrene and poly(lactic acid) MMs initiated by $(\text{H}_2\text{IMes})(\text{pyr})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (Grubbs 3rd generation catalyst). We observed a variance in the rate of propagation of >4-fold between similar MMs with different anchor groups. This phenomenon was conserved across all MMs tested, regardless of solvent, molecular weight (MW), or repeat unit identity. The observed >4-fold difference in propagation rate had a dramatic effect on the maximum obtainable backbone DP, with slower propagating MMs reducing the maximum bottlebrush MW by an order of magnitude (from ~106 to ~105 Da). Experimental and computational studies indicated that the rate differences likely resulted from a combination of varying steric demands and electronic structure among the different anchor groups. Based on these data, the optimal anchor was chosen for a one pot two-step process in synthesizing large MW bottlebrush polymers with tunable sidechains and backbone DPs to yield well defined structures.



POLY 246: Thiol-ene/yne photopolymerization – Simple reactions to yield complex materials

Douglas V. Amato¹, douglas.amato@eagles.usm.edu, **Derek L. Patton**². (1) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Campus Box #10076, University of Southern Mississippi, Hattiesburg, Mississippi, United States

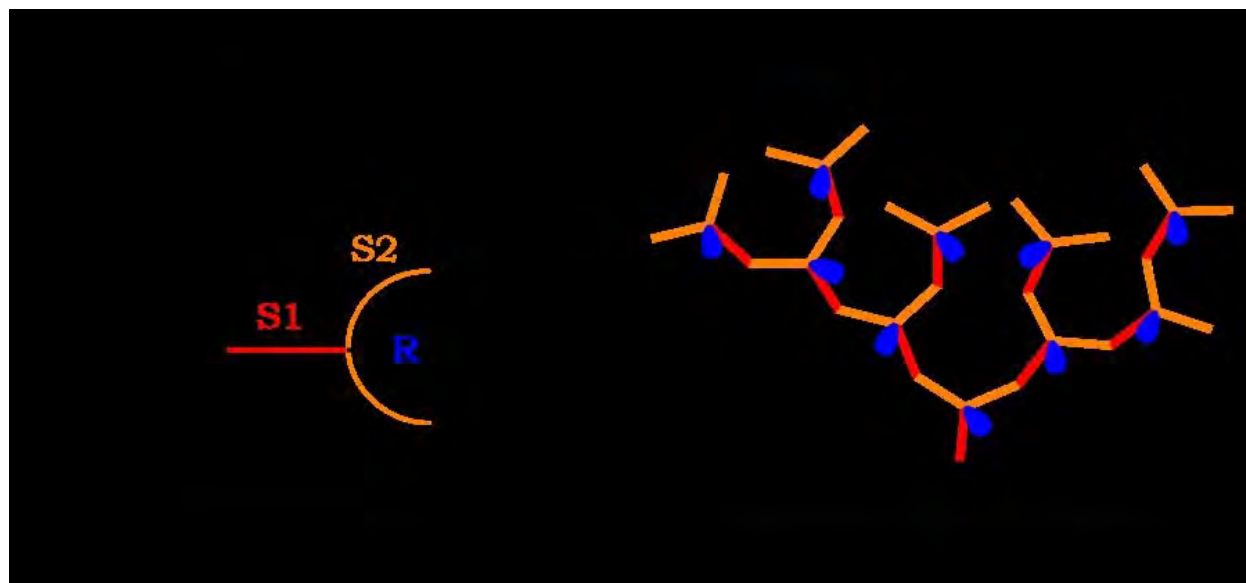
We demonstrate the utility of thiol-ene/yne photopolymerizations as a simple and efficient tool to fabricate multifunctional materials as either droplets or bulk materials. Thiol-ene/yne mediated miniemulsion polymerization has led to functional nanoparticles with tunable thermal/mechanical properties and high loading of essential oil derivatives (50 wt%). Encapsulation of essential oils resulted in nanoparticles with potent biocidal activity (10^5 reductions in bacteria population) against a library of pathogenic bacteria. Next, thiol-ene chemistry was used to fabricate complex/degradable microparticles with even greater loading capacity (90%) and conversion dependent release kinetics of omniphilic dyes. Microparticles cured at high conversion (90%) resulted in long-term retention (>30 days) of dyes while low conversion resulted in rapid release (minutes). Lastly, we synthesized acetal containing monomers from intrinsically antimicrobial aldehydes. Upon polymerization, the acetals are inert and fully incorporated within a stable thiol-ene network. However, exposure to aqueous/humid environments, results in rapid degradation of acetal linkage which releases the aldehyde in its active form effectively eradicating both gram-positive (*S. aureus*) and gram-negative (*E. coli*, *P. aeruginosa* and *B. cenocepacia*) bacteria with negligible activity towards human cells.



POLY 247: Chain-growth CuAAC polymerization: A versatile strategy to produce hyperbranched polymers with well-defined structures in one-pot

Xiaosong Cao¹, xcao@nd.edu, Yi Shi², Weiping Gan¹, Hannah Naguib¹, Xiaofeng Wang¹, Robert Graff¹, Haifeng Gao¹. (1) Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States (2) Chemistry and Biochemistry, University of Notre Dame, South Bend, Indiana, United States

Abstract: As an emerging new technique, chain-growth polymerization of AB_m monomers using the efficient copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction has enabled the synthesis of structurally defined hyperbranched polymers in solution. In this presentation, we demonstrate the high versatility in the monomeric design by proposing a modular AB₂-R monomer structure that was composed of three structural motifs (one alkynyl group, two azido groups, and a dangling R group) connected by two space linkers (S1 and S2). The influence from the structural parameters of S1, S2, and R groups on the polymerization kinetics, the molecular weights, and the DB was systematically studied. Subsequently, we further expanded the monomer library with a series of orthogonal functionalizable monomer which enabled efficient and quantitative post-modification of hyperbranched polytriazoles. These explorations may offer new thoughts to fulfill sophisticated nanostructures and functions



POLY 248: Water-Soluble ion-containing poly(ether ester)s for extrusion 3D printing

Allison Pekkanen, apekk@vt.edu, Callie Zawaski, Christopher B. Williams, Timothy E. Long. Virginia Tech, Blacksburg, Virginia, United States

Fused deposition modeling (FDM) is a prevalent form of 3D printing with a large historical precedence for thermoplastic elastomers, commonly including ABS and polycarbonate. Although the study of these polymers is widespread, there is a lack of research to develop new materials for FDM, making research into novel materials extremely valuable.

Poly(ether ester)s represent a promising class of water-soluble polymers, with previous research utilizing these systems in ion exchange and battery applications. In this previous work, poly(ether ester)s are synthesized with low molecular weight poly(ethylene glycol) (PEG) and dimethyl 5-sulfoisophthalate (SIP) to achieve a family of ionic PEGs with varying counter cation. While the precedence of these materials exists in literature, higher molecular weight PEG, as well as ion exchange to evaluate divalent counterions, offers additional functional handles for potential modifications. In this work, water-soluble poly(ether ester)s are synthesized and characterized for their use in low-temperature FDM. The poly(ether ester)s undergo ion exchanges to further enhance their rheological properties. In particular, the exchange to divalent counter cations induces a sharp increase in melt viscosity, which is key to successful printing (Figure 1). Interestingly, this exchange does not affect the room-temperature properties of the material, indicating that a change in counterion does not affect the properties of the final printed part. Extrusion 3D printing of poly(ether ester)s with a calcium counter cation is achieved at 70 °C, creating parts that exhibit fine features without stringing between gaps. Furthermore, the angle at which these parts can be printed exceeds that of ABS, indicating the integrity of the final printed part. These copolymers represent a class of materials suitable for low-temperature FDM while also imparting water solubility onto the printed part.

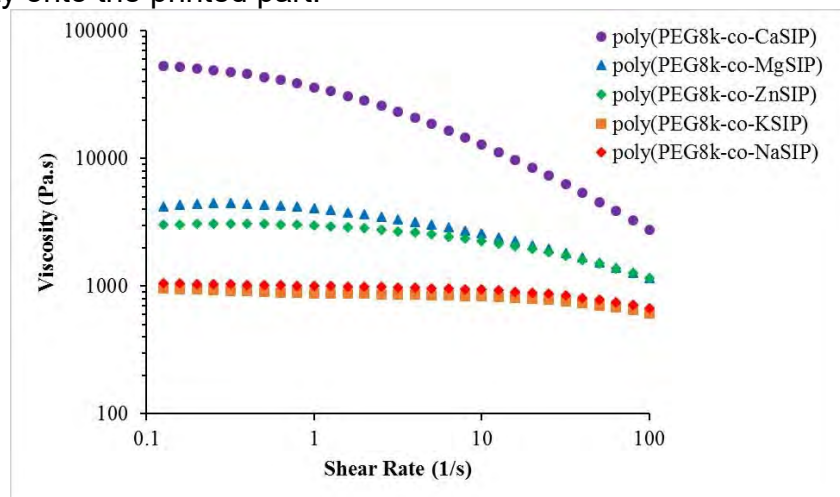
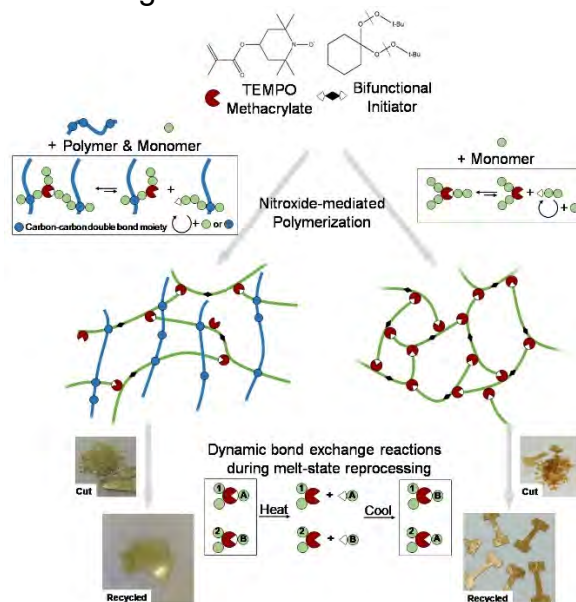


Figure 1. Rheological characterization reveals enhanced viscosity for polymers with divalent counter cations, which determines the printability of the polymer.

POLY 249: Recyclable cross-linked polymer networks via one-step controlled radical polymerization

Kailong Jin¹, *kailongjin2012@u.northwestern.edu*, **Lingqiao Li**¹, **John M. Torkelson**^{1,2}.
(1) *Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, United States* (2) *Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States*

Conventional polymer networks cannot be recycled into high-value products because of permanent, covalent cross-links. Rubber tires illustrate well the issues ranging from economic loss to environmental problems that arise with spent, cross-linked polymers. Here, we developed a one-step strategy using nitroxide-mediated polymerization (NMP) to synthesize recyclable network polymers with dynamic alkoxyamine cross-links that allows for reprocessing in the melt state through repeated bond formation and dissociation. With this method, we use stable nitroxide radicals containing a polymerizing moiety (carbon-carbon double bond) as both radical regulators during reaction and branch units on the polymers or cross-linker chains. We also use bifunctional initiators to generate chains with radical sites on both sides to connect the nitroxide branch units, resulting in cross-linked polymer. This NMP-based approach can be applied to any monomers or polymers that contain at least one carbon-carbon double bond that is amenable to radical polymerization. For example, through this strategy, we designed a network polymer using polybutadiene and styrene monomer as a model for recyclable tires, showing full property recovery after multiple melt-reprocessing recycles; we also produced polymer networks from monomers with good reprocessability and relative uniformity. With nitroxide groups serving as thermally reversible cross-links and simple functionalization of monomers, this one-step strategy provides for both robust, sustainable recyclability of cross-linked polymers and design of networks for advanced technologies.

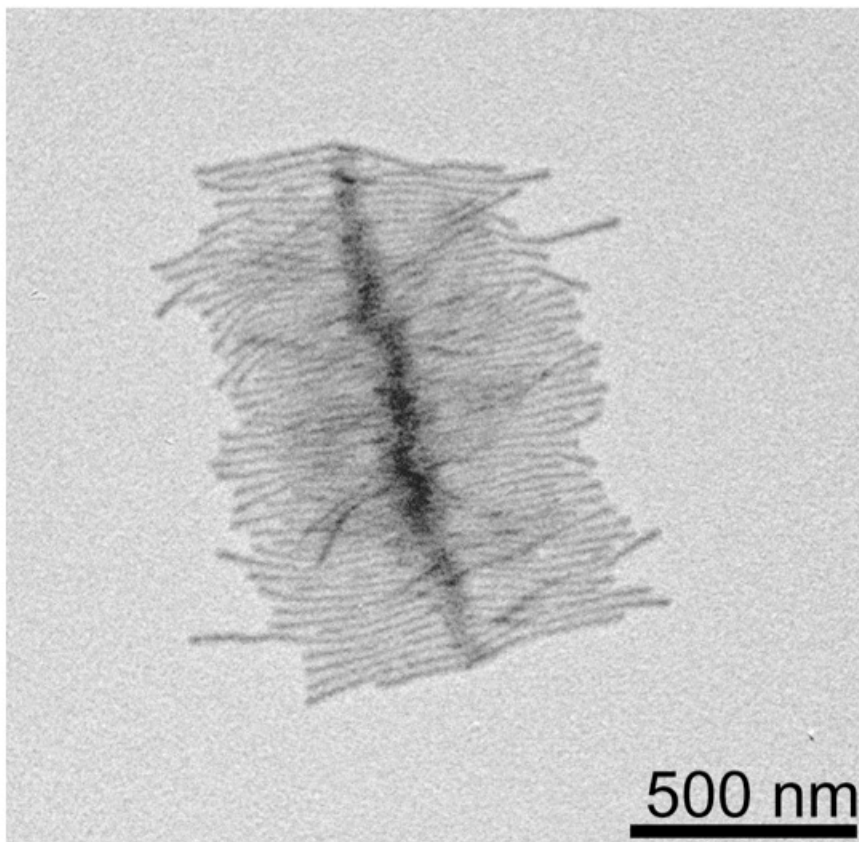


Network formation through bulk NMP and network reprocessing through rearrangements of dynamic alkoxyamine covalent bonds.

POLY 250: Living crystallization-driven, seeded growth approaches to functional supramolecular materials

Ian Manners, *ian.Manners@bristol.ac.uk*. Univ of Bristol Sch of Chemist, Bristol, United Kingdom

Although chemical synthesis has evolved to a relatively advanced state, the ability to prepare uniform samples of materials of controlled shape, size, and structural hierarchy on a length scale from 10 nm – 100 microns is still in its relative infancy and currently remains the virtually exclusive domain of biology. In this talk a promising new route to well-defined 1D and 2D materials within this size regime, termed “living crystallization-driven living self-assembly” (CDSA), will be described. The “seeded growth” characteristic of living CDSA means that the process can be regarded as a type of “living supramolecular polymerization” that is analogous to living covalent (e.g. anionic) polymerizations of molecular monomers and also to biological “nucleation-elongation” processes such as amyloid fiber growth. Living CDSA was discovered as a result of an investigation of the solution self-assembly behavior of block copolymers with crystallizable polyferrocenylsilane (PFS) metalloblocks but has now been extended to an array of block copolymers with crystallisable organic blocks, including pi-conjugated or biodegradable materials, and also to molecular amphiphiles that form pi-stacked supramolecular polymeric assemblies. Potential applications exist in areas from nanoelectronics to delivery vehicles.



POLY 251: Living supramolecular polymerization of perylene bisimide J-aggregates

Wolfgang J. Wagner^{1,2}, wolfgang.wagner@uni-wuerzburg.de, **Vladimir Stepanenko**^{1,2}, stepanenko@chemie.uni-wuerzburg.de, **Frank Wuerthner**^{1,2}, wuerthner@chemie.uni-wuerzburg.de. (1) Institut für Organische Chemie, Universität Würzburg, Würzburg, Bayern, Germany (2) Center for Nanosystems Chemistry and Bavarian Polymer Institute, Universität Würzburg, Würzburg, Bayern, Germany

Supramolecular polymers of π -conjugated molecules have recently attracted attention in material science because they exhibit well-defined structures, self-healing abilities and intriguing optoelectronic functions. Although the thermodynamics of supramolecular polymerization has been widely studied, the kinetics of this process is still not well-known. Remarkably, kinetic effects in supramolecular systems are essential playing an important role in the structure and functions of the self-assembled aggregates. One strategy to control the kinetics of an aggregation process is the seeded polymerization approach, which consists of the induction of supramolecular polymerization of kinetically trapped building blocks by addition of seeds (small aggregates acting as nuclei). In our previous studies we have successfully applied the seeded supramolecular polymerization concept in perylene bisimide (PBI) dye aggregates. In the present work, we demonstrate that this approach can be also employed to transform kinetically trapped dimethoxy-substituted PBI (**MeO-PBI**) non-fluorescent H-aggregates into highly fluorescent J-aggregates by an unprecedented living supramolecular polymerization mechanism. This is an innovative concept to control the kinetics of supramolecular polymers and to obtain out of equilibrium polymers with low polydispersity, narrow size distribution, and photofunctional properties.

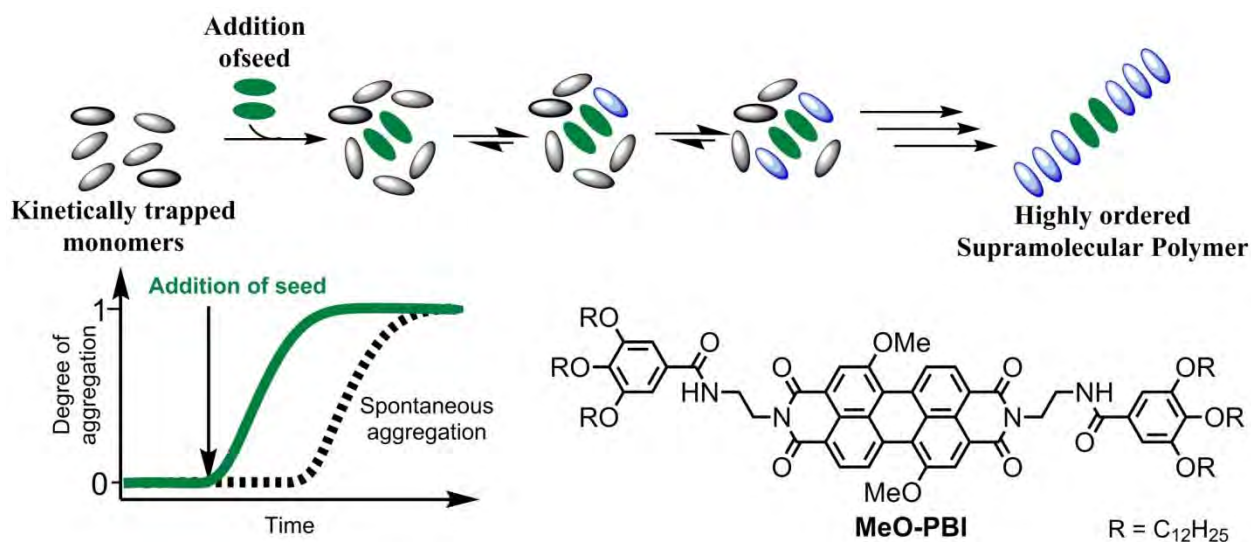
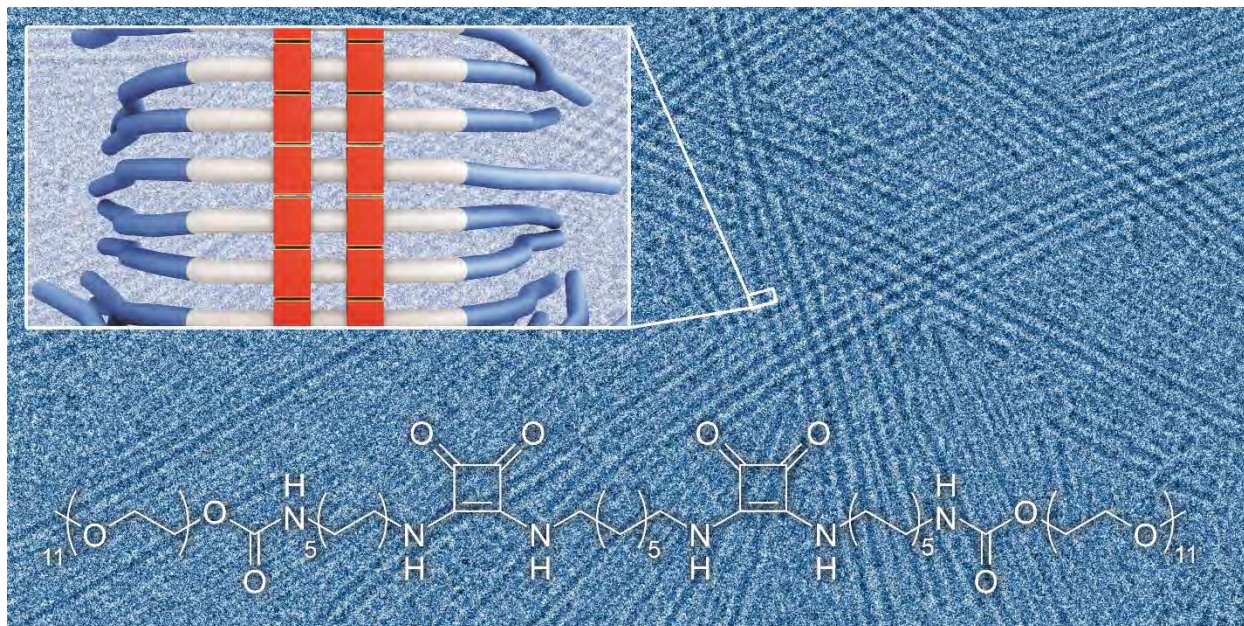


Figure 1. Illustration of the concept of seeded polymerization and molecular structure of **MeO-PBI**.

POLY 252: Probing hydrogen bond-aromaticity coupling in squaramide-based supramolecular polymers

Roxanne Kieltyka, *r.e.kieltyka@chem.leidenuniv.nl*. Universiteit Leiden, Leiden, Netherlands

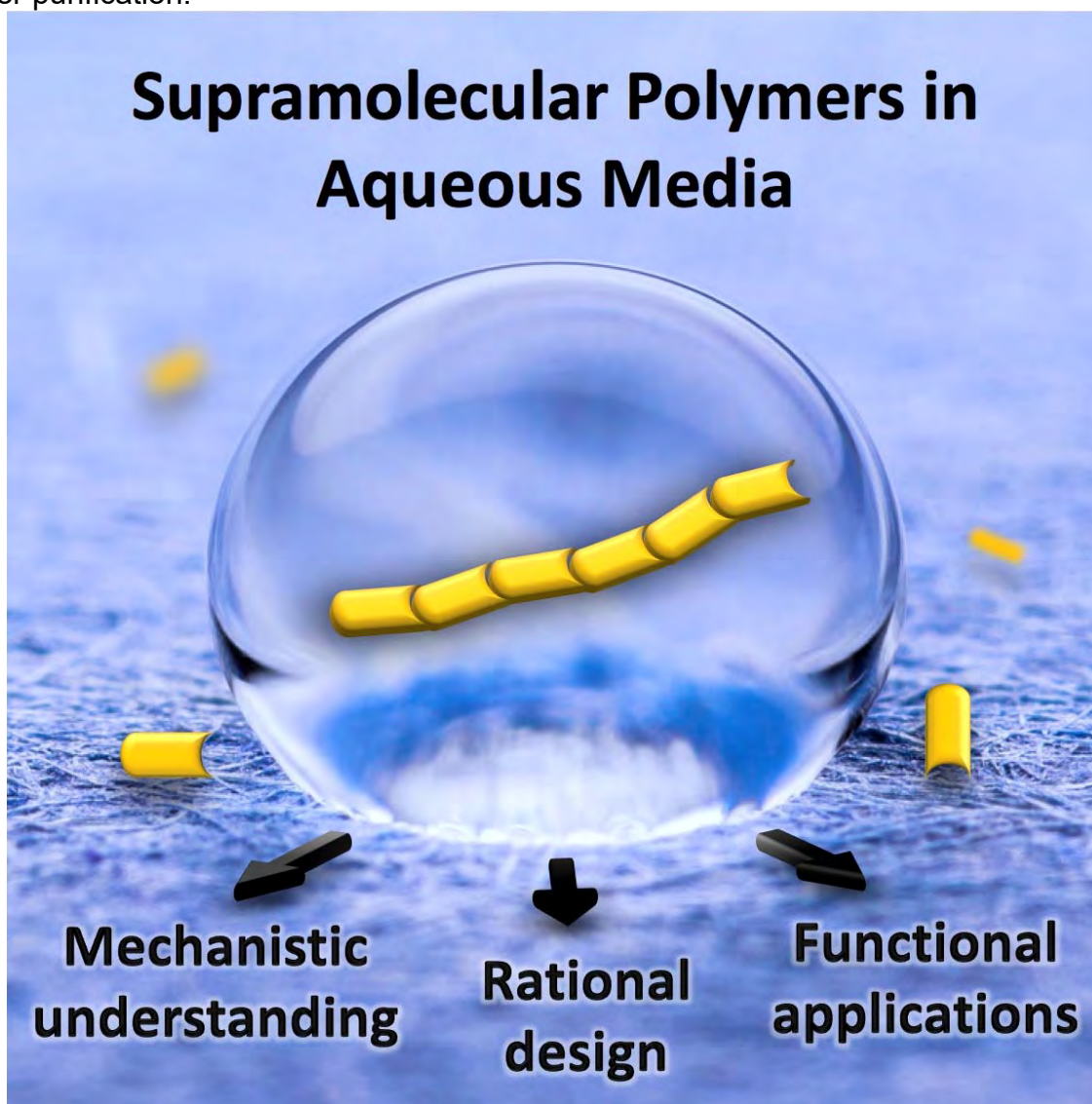
The interplay between aromaticity and hydrogen bonding in the self-assembly of squaramide-based supramolecular polymers is explored. Partially aromatic bis(squaramide) bolaamphiphiles were designed to self-assemble through a combination of hydrophobic, hydrogen-bonding and aromatic effects into high aspect ratio fibrils. Strong hydrogen bonding and aromatic gain of the monomer was observed using a combination of experimental (UV-vis, IR) and computational (NICS, HOMA) techniques. A significant increase in thermodynamic stability and a striking difference in the morphology of the self-assembled bis(squaramide) bolamphiphiles was observed in comparison to isosteres that cannot access the aromatic gain-hydrogen bonding effect. We have further examined the effect of modulating the hydrogen-bonding strength of the bolaamphiphilic monomer by using thionated squaramides; significant differences in the self-assembly behaviour of the monomers are observed.



POLY 253: Supramolecular polymers in aqueous media: From mechanisms to materials

Boris Rybtchinski, *boris.rybtchinski@weizmann.ac.il*. Weizmann Institute of Science, Rehovot, Israel

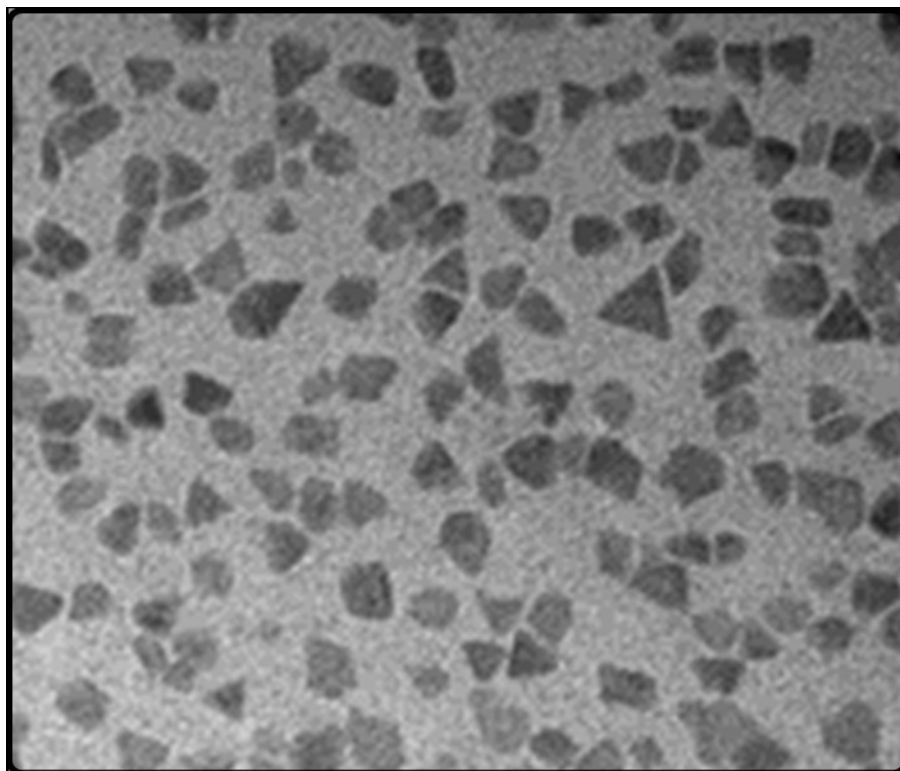
We will present our recent thermodynamic and kinetic studies on supramolecular polymerization in water, and emerging approaches to rational design of noncovalent polymers. In particular, we will address the influence of strong hydrophobic interactions on the polymerization mechanisms, highlighting kinetic trapping and supramolecular isomerism in noncovalent polymers. We will also present our results on aqua materials based on entangled noncovalent polymers, focusing on supramolecular membranes for water purification.



POLY 254: Zerovalent metallosupramolecular polymers for the in situ nucleation of platinum nanoparticles

Lucas Montero de Espinosa, *lucas.montero@unifr.ch*, Luis Olaechea, Christoph Weder. *University of Fribourg, Adolphe Merkle Institut, Fribourg, Switzerland*

Metallosupramolecular polymers (MSPs) are a subclass of supramolecular polymers in which the monomeric units are connected through metal-ligand complexes. MSPs are typically assembled via the coordination of multifunctional macroligands with metal salts; however, very few works have investigated MSPs based on zerovalent metal complexes. Building on our previous work on Pt(0)-containing MSP networks, we have developed a synthetic framework for the synthesis of linear MSPs in which chain extension takes place through Pt(0)(alkyne)₂ complexes. These polymers can be prepared by ligand exchange between Pt(0)(styrene)₃ and a diphenyl acetylene-terminated telechelic core such as poly(ethylene-co-butylene) or poly(tetrahydrofuran). The materials thus prepared are stable under ambient conditions and display elastomer-like properties. However, heating these MSPs over a characteristic threshold temperature causes the dissociation of the Pt(0)(alkyne)₂ complex, which leads to the formation of Pt(0) nanoparticles (NPs) in the polymer matrix as confirmed by TEM. This contribution will discuss the structure-property relationships found in these materials and a model study with non-polymeric Pt(0) complexes, which showed that the decomplexation temperature, i.e. the threshold temperature for NP formation, depends strongly on the ligand structure. In summary, these materials offer a novel approach for the in situ preparation of Pt nanoparticles in polymeric matrices that does not involve the reduction of a metal salt.



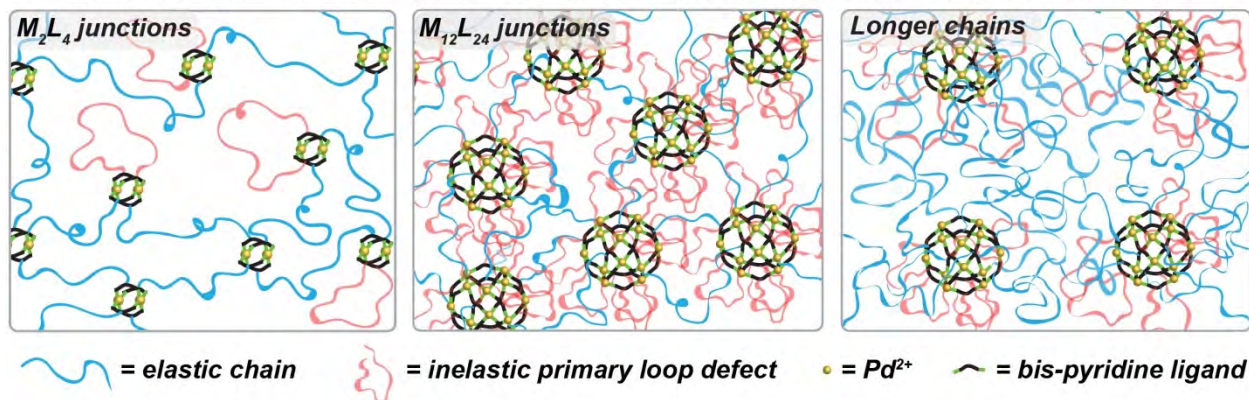
TEM micrograph of Pt NPs obtained by thermal treatment of zerovalent MSPs

POLY 255: Network structure-property relationships in polymer metal-organic-cage gels

Aleksandr V. Zhukhovitskiy^{7,3}, alexzhuko@berkeley.edu, Julia Zhao³, Mingjiang Zhong^{8,3}, Eric G. Keeler^{3,9}, Eric Alt², Paul Teichen¹⁰, Robert G. Griffin⁴, Michael J. Hore¹, Adam Willard⁵, Jeremiah A. Johnson⁶. (1) Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, Ohio, United States (2) MIT, Cambridge, Massachusetts, United States (3) Chemistry, MIT, Cambridge, Massachusetts, United States (4) NW14-3220, MIT Francis Bitter Magnet Lab, Cambridge, Massachusetts, United States (5) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (6) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States (7) Chemistry, University of California, Berkeley, Berkeley, California, United States (8) Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States (9) Francis Bitter Magnet Laboratory, MIT, Cambridge, Massachusetts, United States

Synthetic polymer gels are a platform class of soft materials, whose viscoelasticity has enabled numerous technologies: from absorbents, contact lenses and biomedical implants, to scaffolds for tissue engineering, cell cultures, and drug delivery. Yet, despite their utility, synthetic polymer gels don't yet rival the functional sophistication of biogenic polymer gels like mucous, cartilage, and the extracellular matrix. What these biogenic gels possess that synthetic polymer gels typically lack is dynamic and multi-tier structural hierarchy. In an effort to advance synthetic polymer gels in this regard, we set out to explore polymer metal-organic-cage (polyMOC) gels, whose junctions are nanoscopic cages formed via the dynamic subcomponent self-assembly of polymer end-groups with metal ions: specifically, poly(ethylene glycol) terminated with bis-pyridine ligands and Pd^{2+} . The present discussion will begin to unravel the complex hierarchical network structure and dynamics in these polyMOC gels, as well as elucidate the effects of polymer size and architecture and absolute junction stoichiometry on the network structure and the resulting mechanical properties of the gels.

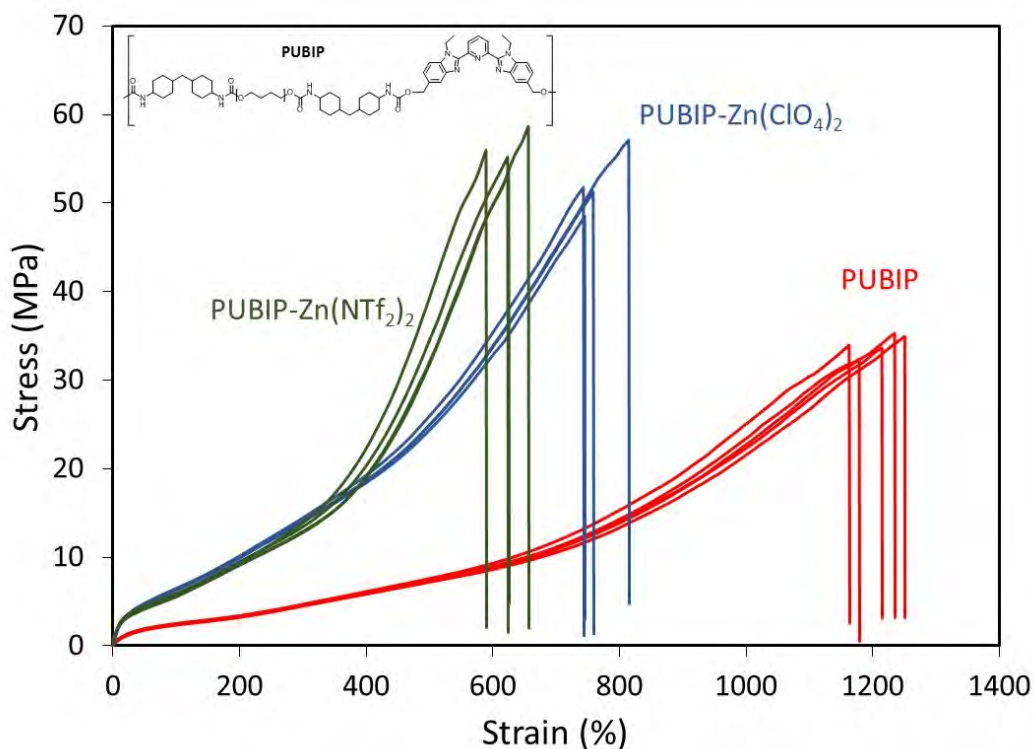
Effects of junctions and polymer size/architecture on overall network structure:



POLY 256: Metallo-Supramolecular crosslinked elastomers

Robert H. Lambeth³, *robert.h.lambeth2.civ@mail.mil*, Alice M. Savage¹, Frederick L. Beyer². (1) MSTB, U.S. Army Research Lab, Belcamp, Maryland, United States (2) U.S. Army Research Laboratory, Rising Sun, Maryland, United States (3) US Army Research Lab, Aberdeen Proving Ground, Maryland, United States

Supramolecular polymers are an important class of materials whose properties depend on reversible bonds that disassociate and reassociate in response to various stimuli. Metal-ligand based supramolecular bonds are particularly interesting because the strength of the bond is easily tuned by varying the metal, ligand structure and/or counterion. In addition, metal-ligand complexes are ionic in nature and have a strong driving force for phase segregation from the surrounding material enabling further manipulation of material properties. The influence of metal-ligand bond strength, phase segregation of the metal-ligand complex, and counterion effects on the physical and mechanical properties of soft elastomers will be discussed. These effects were studied in side-chain functionalized poly(acrylates) crosslinked with 2,6-bis(*N*-alkylbenzimidazolyl)pyridine (BIP) where the metal-ligand bond strength primarily affected the properties of the polymer at high temperatures and strains. Polyurethanes were also prepared where a difunctional BIP ligand was used as a chain extender. The polymer was crosslinked with Zn(II) salts bearing different counterions and distinct differences in the physical and mechanical properties were observed.

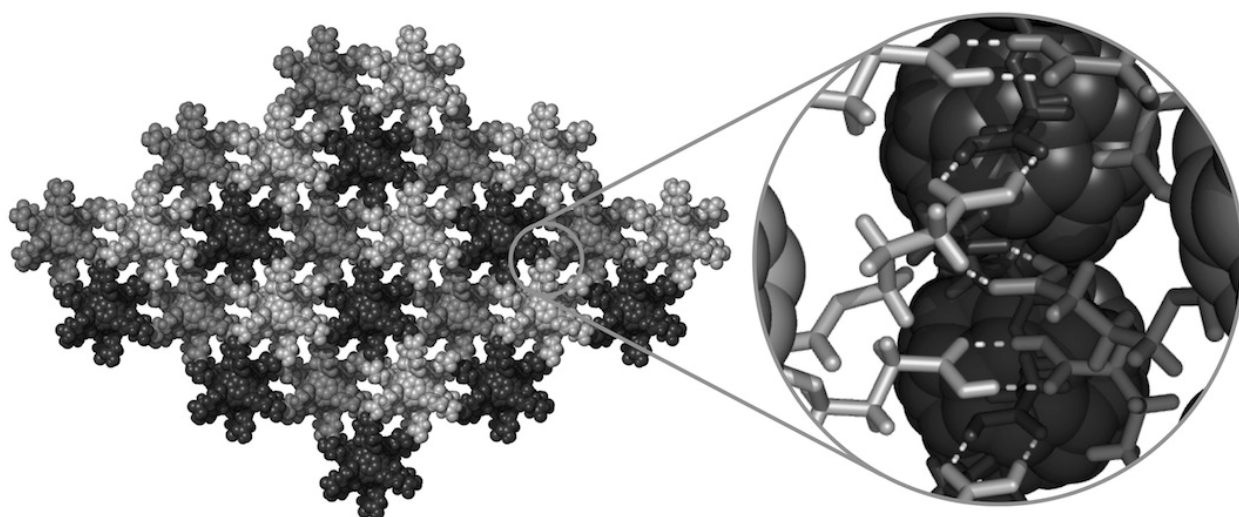


POLY 257: Porous functional nanostructures mediated by directed supramolecular interactions

Florian Beuerle, *florian.beuerle@uni-wuerzburg.de*. Institute of Organic Chemistry & Center for Nanosystems Chemistry (CNC), University of Wuerzburg, Wuerzburg, Germany

Porous materials possessing spatially well-arranged functionalities are promising candidates for applications in the fields of heterogeneous catalysis, sensing, gas storage or separation, membranes, or optoelectronics. Efficient synthesis of these complex molecular architectures is usually achieved by cross-linking of small organic building blocks under dynamic conditions with metal-organic or covalent organic frameworks (MOFs and COFs) as well as molecular cage compounds being prototype examples of current interest for suchlike functional materials. In contrast, the formation of robust porous structures by means of supramolecular interactions between rigid organic molecules might be a promising alternative thus combining low-weight materials with easy processing. However, the crystallization of stable organic structures possessing permanent porosity is still quite challenging and only a limited number of examples for supramolecular crystals retaining porosity in the solid state under activation conditions have been reported so far. Furthermore, supramolecular interactions might play a key role for the formation of defined morphologies of functional materials on larger size regimes.

Here I report on our most recent investigations on the implementation of octahedral [60]fullerene hexakisadducts as connectivity centers in porous supramolecular frameworks as well as the spontaneous self-assembly of dye-containing COF crystallites into tubular nanostructures with inner tube diameters of around 100 nm.



Porous hydrogen-bonding frameworks based on [60]fullerene frameworks possessing twelve carboxylic acid groups

POLY 258: Dynamic, multistimuli-responsive polymers based on metal-stabilized, dynamic covalent imine bonds

Fátima García, Janis Pelss, Han Zuilhof, **Maarten Smulders**,
maarten.smulders@wur.nl. Laboratory of Organic Chemistry, Wageningen University,
Wageningen, Netherlands

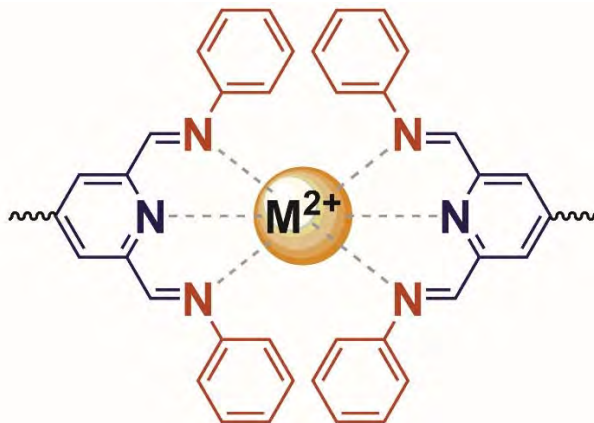
The incorporation of reversible bonds in covalent polymers has enhanced polymer materials to become adaptive, leading to 'smart' functional materials that are, e.g., self-healing or stimuli-responsive. Next to non-covalent interactions, recently also dynamic covalent bonds have been used to prepare such smart polymer materials, as this type of bond combines intrinsic reversibility with the robustness of covalent bonds. Herein, we extend the use of dynamic imine bonds to the construction of hydrolytically stable, multi-responsive coordination polymers. To this aim we combine imine bonds and metal-ligand (M–L) bonds to obtain dynamic polymer materials that are responsive *via* their imine and their M–L bonds, as well as through both types of interactions in concert.

As key binding motif we rely on a tridentate pincer ligand bearing a 2,6-diiminopyridine moiety, which can coordinate to octahedral metal ions in a 2:1 fashion. As such, this pincer can be considered as the dynamic covalent structural analogue of the classic terpyridine ligand.

We show by various techniques (NMR, DOSY, UV/vis and viscometry) that selective end-functionalization of macromonomers with this motif leads to the formation of stable, multistimuli-responsive main-chain coordination polymers: the resulting polymer material was found to be responsive to a range of stimuli (choice of metal: Zn²⁺ versus Eu³⁺; addition of metal scavenger; transimination by a diamine or an alkoxyamine; addition of acid), giving access to five different macromolecular states with distinct material properties.

We also show how this pincer motif can be integrated in a C₃-symmetrical molecular scaffold to afford self-healing materials. The extent of self-healing was found to be strongly dependent on the nature of the selected metal ion.

Our approach, based on dynamic metal-stabilized imine complexes, thus offers a novel route towards dynamic polymer materials with functionalities that can be finely tuned by a range of external stimuli.

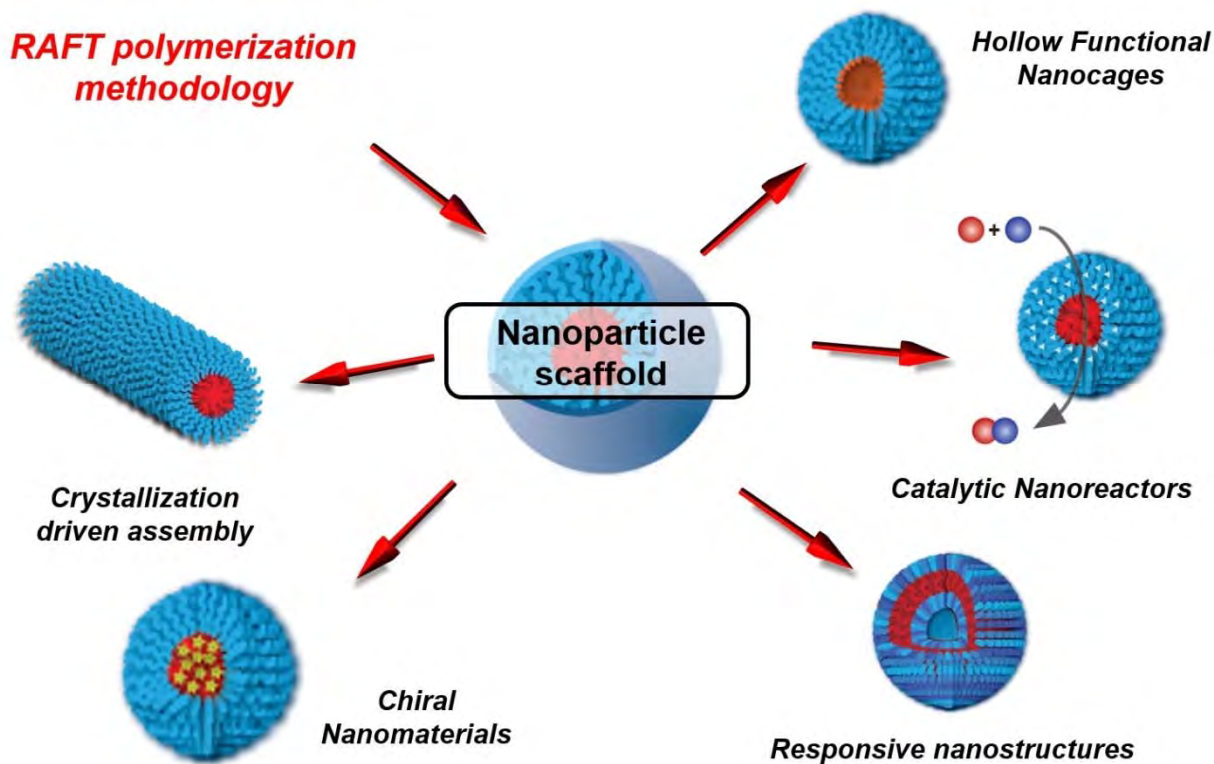


General structure of the imine-based pincer structures reported herein.

POLY 259: Hybrid nanomaterials

Rachel K. O'Reilly, *r.k.o-reilly@warwick.ac.uk*. Dept of Chemistry, University of Warwick, Coventry, United Kingdom

The development of novel routes towards the preparation of hybrid nanomaterials is of great interest as it allows access to materials with novel properties. Of particular interest is the exploration of synthetic polymers with biomolecules and biomaterials. This presentation will describe recent work in the synthetic development and characterisation of such hybrid materials and their application.

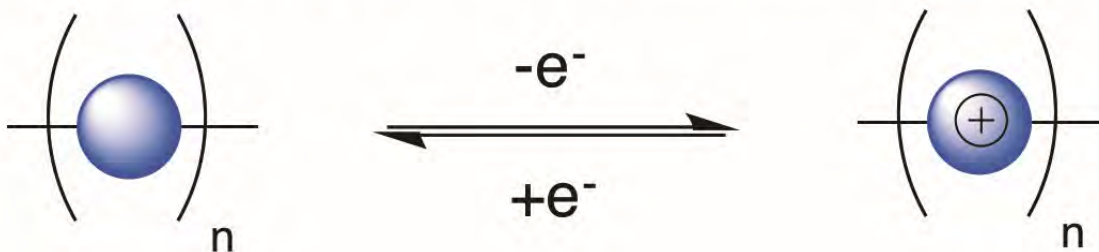


POLY 260: Design and synthesis of polymers for next generation energy storage technologies

Brett P. Fors, bpf46@cornell.edu. Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States

The development of efficient electrical energy storage technology will be a key enabler of renewable energy source utilization. This presentation will detail the design of next generation organic cathode materials for batteries and supercapacitors. These new polymeric cathode materials are synthesized from readily available starting materials and show highly efficient energy storage capabilities.

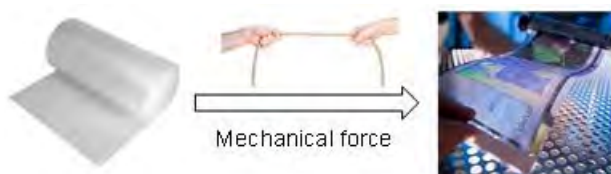
Efficient and Highly Reversible Cathode Material



POLY 261: Mechanochemical generation of conjugated polymers from non-conjugated polymers

Zhixing Chen, Jaron A. Mercer, Noah Z. Burns, **Yan Xia**, yanx@stanford.edu.
Chemistry, Stanford University, Stanford, California, United States

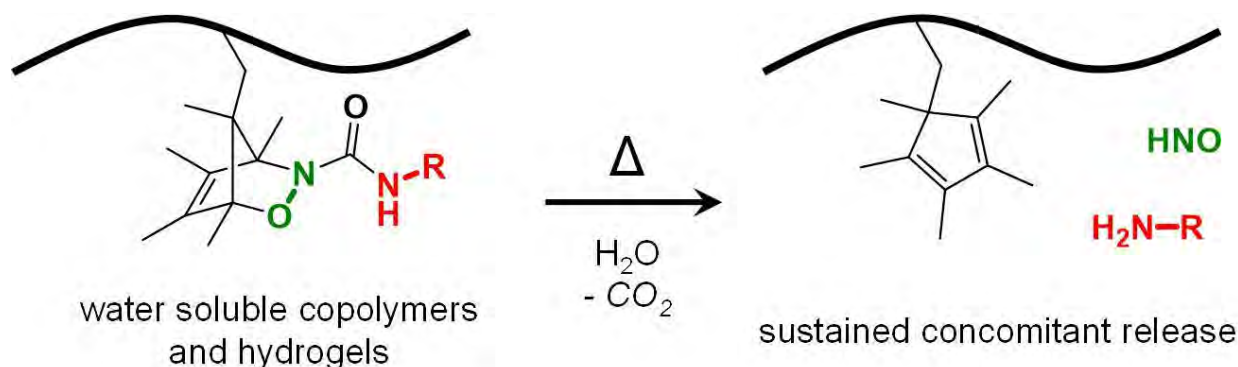
The recent advent of polymer mechanochemistry enables a new paradigm of design for force-responsive materials. Conjugated polymers represent a major class of functional materials with distinct optical, electronic, thermal, and chemical properties from non-conjugated polymers, and mechanochemical generation of conjugated polymers can open new avenues for mechanically responsive materials. However, this goal has several formidable design challenges. We present our design to meet all these challenges and the first example of mechanochemical generation of polyacetylene from poly(ladderene) precursors. Spectroscopic, optical, microscopic, and electronic characterizations supported the generation of polyacetylene with uniform all *trans* configurations and high conjugation length.



POLY 262: Polymers for thermal and mechanochemical release of nitroxyl (HNO) and other small molecule payloads

Derek Church³, Saghar Nourian¹, Chang-Uk Lee³, Melissa Ryskamp³, Ashlynn Vander Meer³, Neal A. Yakelis², John P. Toscano¹, **Andrew J. Boydston³**,
boydston@chem.washington.edu. (1) Johns Hopkins Univ, Baltimore, Maryland, United States (2) Chemistry, Pacific Lutheran University, Federal Way, Washington, United States (3) Chemistry, University of Washington, Seattle, Washington, United States

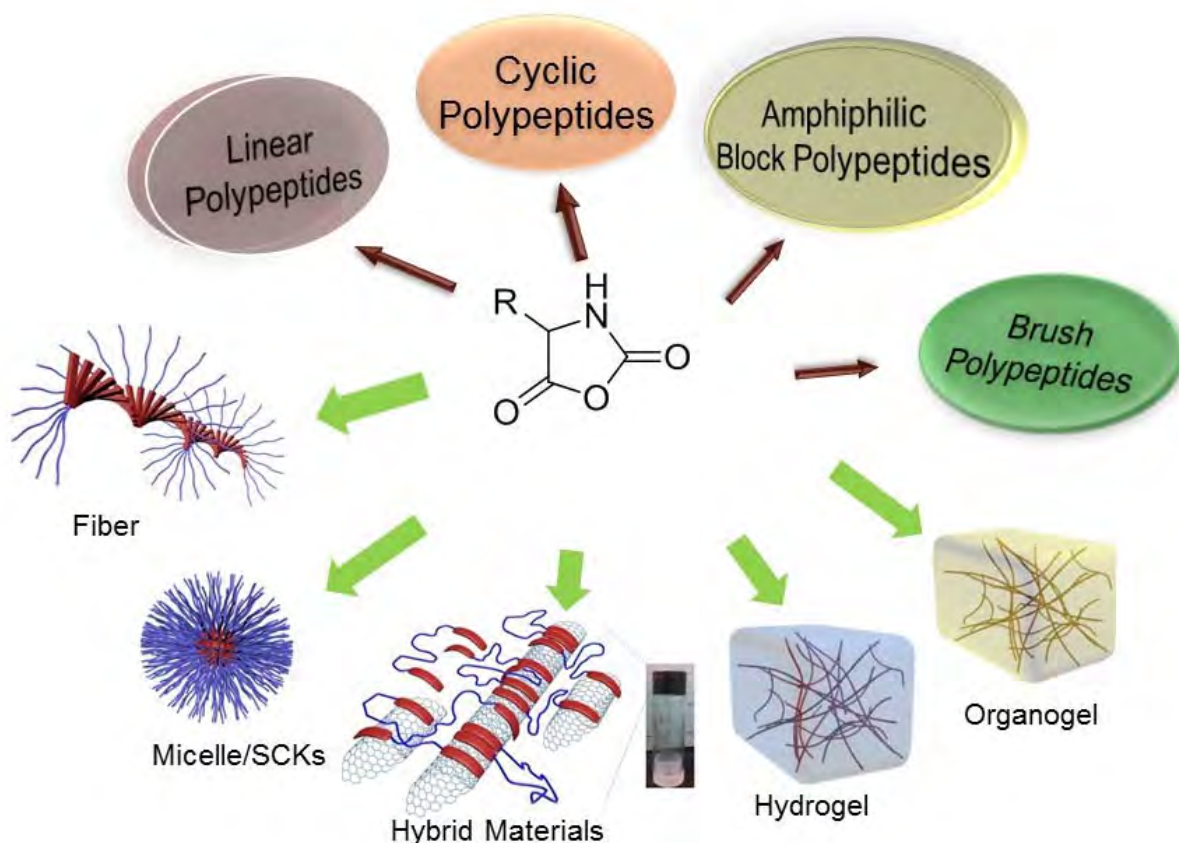
Our research team has evaluated oxazines that are capable of triggered release of nitroxyl (HNO) and other small molecules in response to either thermal or mechanical impetus. Specifically, We demonstrate concomitant release of HNO and small molecule organics from amphiphilic poly(norbornene)-based copolymers. This key function was achieved by incorporation of thermally-labile oxazine units within random and block copolymer architectures. Upon thermolysis, we observed generation of HNO and release of a small molecule conjugate. Importantly, the release kinetics of HNO and a UV-active small molecule reporter were found to be 1:1, signifying an ability to monitor HNO production indirectly or to simultaneously release organic therapeutics with HNO. We also observed mechanochemical triggering of oxazine moieties contained within polymer main chains and bridging crosslink segments, which were accessed by modifying the sites of attachment within the polymer-oxazine conjugate.



POLY 263: Functionally-versatile polypeptide materials

Jingwei Fan¹, Xun He¹, Rachel Letteri¹, Tan Nguyen¹, Jiong Zou¹, **Karen L. Wooley**², wooley@chem.tamu.edu. (1) Texas A&M University, College Station, Texas, United States (2) 3255 TAMU, Texas AM University, College Station, Texas, United States

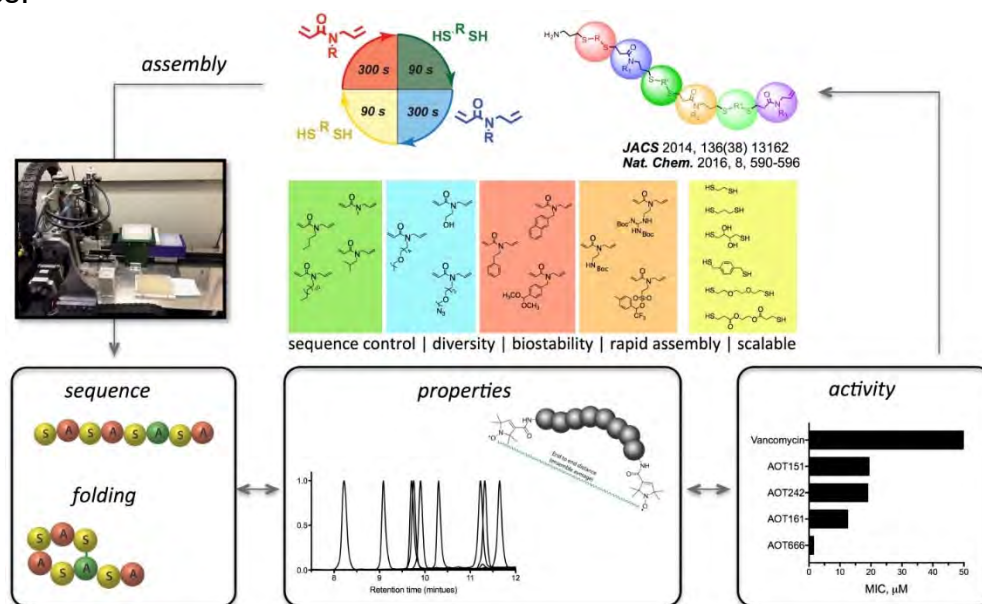
This presentation will highlight our efforts toward the synthesis of well-defined polypeptide-based materials and investigation of their properties and potential applications. Ring-opening polymerization of N-carboxyanhydride monomers allows for the construction of block polymers, molecular brushes and other architectures. Many of those unique polymer structures exhibit interesting properties, including (hydro)gelation abilities. By combining peptide-based block copolymer hydrogelators and photo-thermally-active carbon nanotubes, soft conductive materials can be reversibly photo-generated, allowing for rapid and spatially-defined construction of conductive patterns (> 100 S/m).



POLY 264: Bioinspired sequence-defined oligomers and their biological applications

Christopher A. Alabi, caa238@cornell.edu. *Chemical Engineering, Cornell, Ithaca, New York, United States*

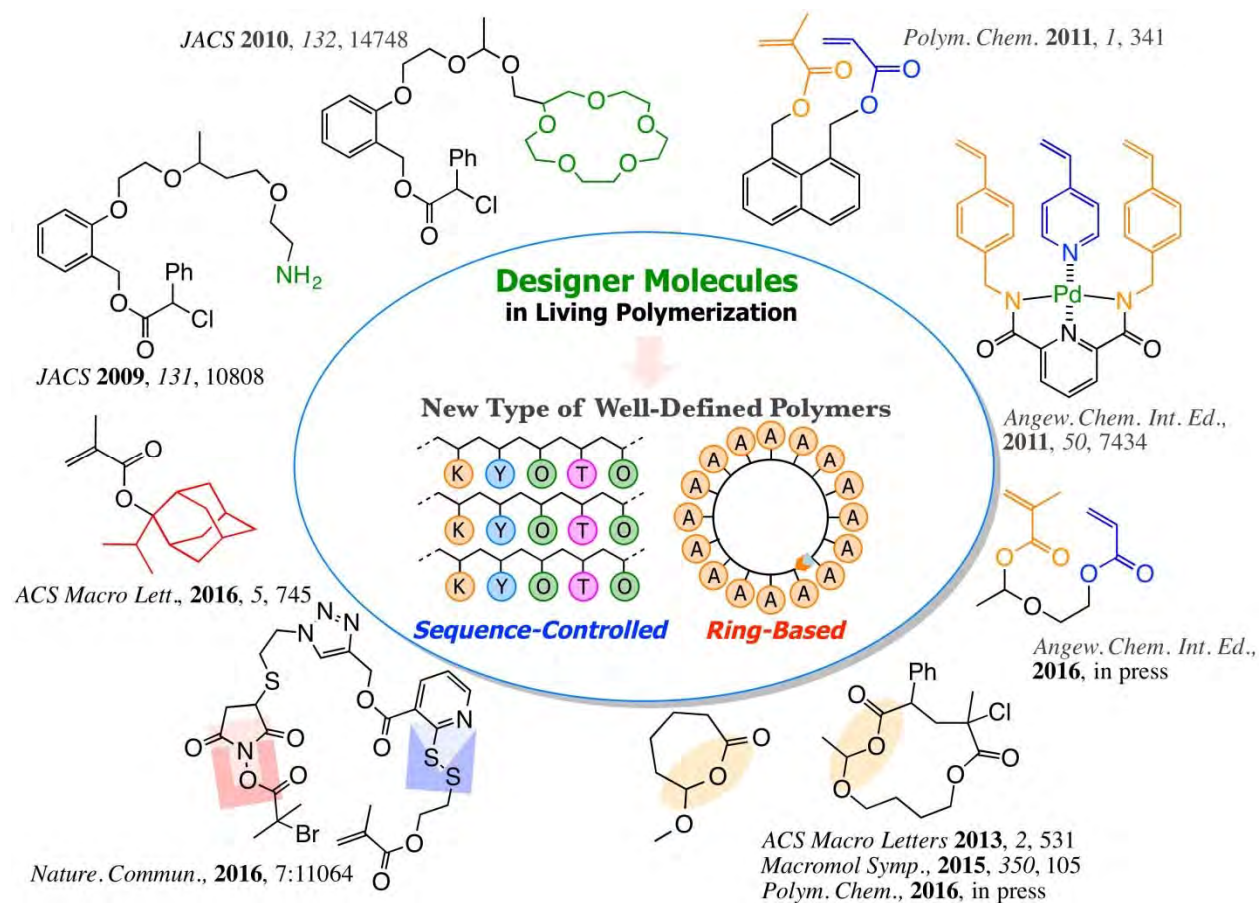
Precise control over the primary sequence of a macromolecule has several exciting scientific and technological implications. Control over primary sequence and conformation can lead to the formation of new folded secondary and tertiary structures. The latter can enable the development of new synthetic enzymes, scaffolds for molecular encoding and data storage, synthetic affinity ligands, sequence responsive materials, programmable biomaterials and much more. However, only few examples of synthetic primary sequence control have been reported due to numerous practical challenges. Motivated by the technological implications and the need for sequence-control and structural diversity in polymer research, we present a versatile methodology for the synthesis of a new class of sequence-defined oligomers. This approach involves the sequential use of functional *N*-allylacrylamide and dithiol monomers to iteratively assemble sequence-defined oligothioetheramides (oligoTEA) on a liquid fluororous support with tunable pendant and backbone functional groups. The combination of fast solution-phase reaction kinetics with a robust fluororous solid-phase extraction (FSPE) technology allows for the efficient assembly of molecularly encoded synthetic oligoTEAs with broad structural diversity. Strategic placement of complementary reactive monomers during the oligoTEA assembly process facilitates the synthesis of a wide variety of enzymatically stable synthetic sequence-defined architectures. A few examples of precisely coded and covalently folded macromolecules will be presented along with a new low-resolution characterization technique for analyzing the macromolecular conformation of flexible systems. Some novel bioactive sequences will be presented and used to investigate the effect of backbone sequence on chemical and biological properties.



POLY 265: Designer molecules toward advanced polymerizations: Control of sequence and topology for vinyl polymers

Makoto Ouchi, ouchi@living.polym.kyoto-u.ac.jp. Sawamoto Lab, Dept of Polymer Chemistry, Kyoto University, Kyoto, Japan

Biopolymers such as DNA and proteins are expressing their functions based on sequence and position of functional groups in the pendant groups as well as shape (topology) of the main chain. On the other hand, for synthetic polymers, control of the chain length and terminal groups is now possible using living polymerizations, but that of topology and sequence is still extremely difficult. Our efforts have been directed to control of side-chain sequence and main-chain topology for vinyl polymers via creative design of molecules (i.e., initiators and monomers) in polymerizations to lead to construction of new type of “well-defined polymers” as well as development of functions derived from the controlled structure.



POLY 266: α,ω -Difunctional polyethylene telechelics through functional group tolerant catalysis

Stefan Mecking, *stefan.mecking@uni-konstanz.de*. Department of Chemistry, University of Konstanz, Konstanz, Germany

Polyethylene telechelics with two reactive endgroups are attractive building blocks, but their limited accessibility to date is a strong limitation. This contribution discusses two convenient novel routes to strictly linear α,ω -difunctional polyethylene telechelics. Via direct selective insertion polymerization, in a mixture of ethylene and a functional comonomer the latter is incorporated exclusively in endgroups while the crystallizable backbone is composed only of ethylene. For the case of vinyl furane comonomer, a fidelity in both initiating and terminating endgroups of > 90 % are achieved. A mechanistic understanding rationalizes these findings and identifies the generic requirements for such a selective monomer reactivity.

An alternative approach is the chain doubling of fatty acid feedstocks. From common plant oils, by an iterative sequence of olefin metathesis and selective isomerization ultra-long chain building blocks are obtained. For example, from erucic acid in once cycle C_{48} α,ω -dicarboxylic acid is obtained in high yield and purity by this scalable method.

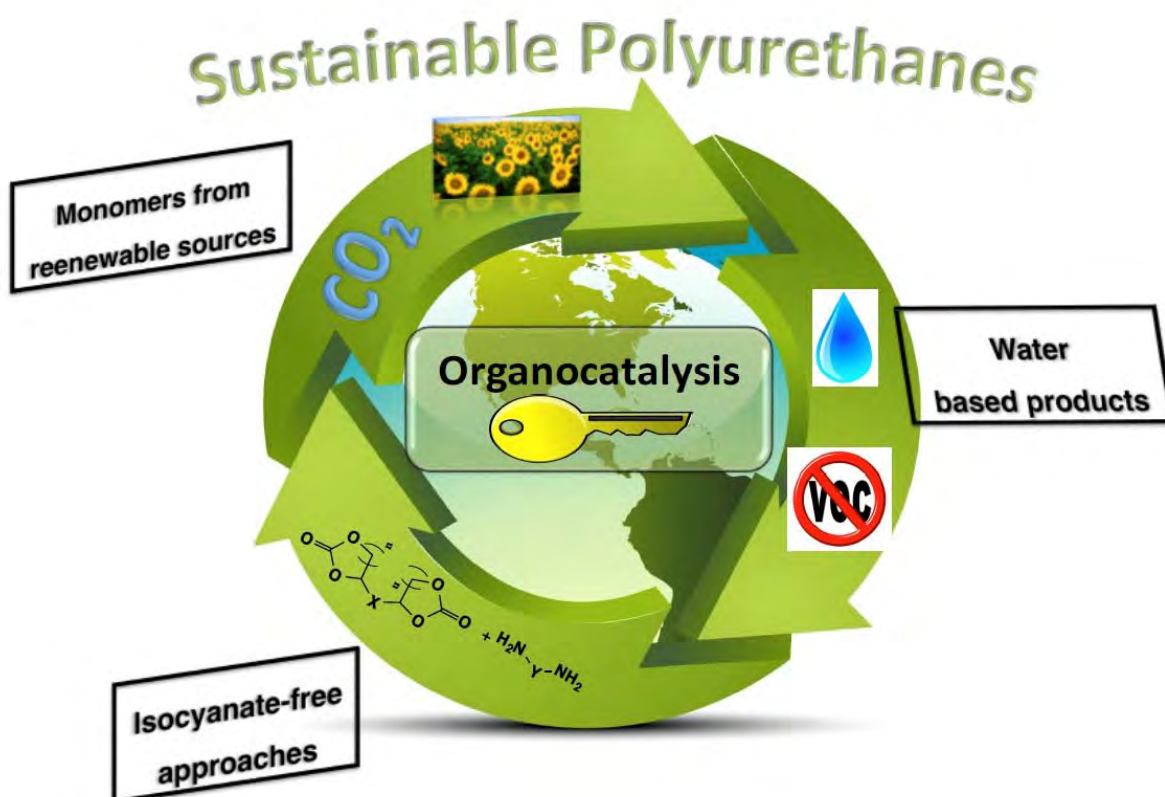
The properties of these telechelics and further their utilization for polymer materials synthesis are discussed.



POLY 267: Organocatalyzed synthesis of polyurethanes

haritz sardon, *haritz.sardon@ehu.es*, Amaury Bossion , Alexander Yuen . POLYMAT , University of Basque Country, UPV/EHU, San sebastian, Spain

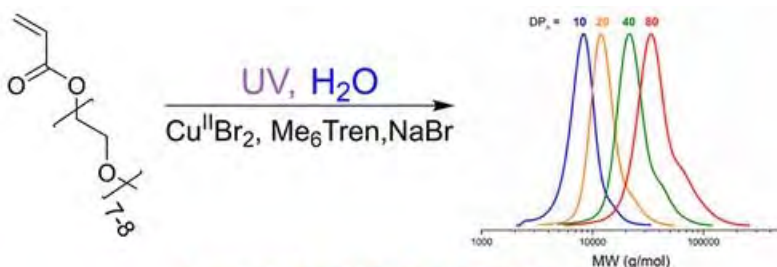
Polyurethanes (PUs) constitute one of the most important classes of polymeric materials with applications ranging from high-performance structural applications to nanomedicine. From a green and sustainable chemistry standpoint, the current challenge in the polyurethane's industry is to switch to more greener approaches for the polyurethane production. Critically, important highlights for the future of polyurethanes will be the utilization of more benign organocatalysis instead of conventionally used tin-based catalyst, the move from toxic isocyanates to isocyanate free approaches, to replace petroleum-based reagents with biobased and/or to make the transition from organic solvent-based to water-based PUs. In this work different polymerization approaches will be describes for the synthesis of more sustainable polyurethanes, paying a special attention to the use of organocatalysis.



POLY 268: Aqueous copper(II) photoinduced polymerization of acrylates: Low copper concentration and the importance of sodium halide salts

Glen R. Jones³, glen.jones@warwick.ac.uk, Richard Whitfield², Athina Anastasaki¹, David M. Haddleton³. (1) University of California, Santa Barbara, Coventry, United Kingdom (2) Chemistry, University of Warwick, Coventry, United Kingdom (3) Department of Chemistry, University of Warwick, Coventry, West Midlands, United Kingdom

Photoinduced metal-mediated radical polymerization is a rapidly developing technique which allows for the synthesis of macromolecules with defined molecular weight and narrow molecular weight distributions, although typically exhibiting significant limitations in aqueous media. Herein we demonstrate that the presence of alkali metal halide salts, in conjunction with low copper concentration and UV irradiation, allows for the controlled polymerization of water-soluble acrylates in aqueous media, yielding narrow molecular weight distributions and high conversions. Despite the aqueous environment which typically compromises polymer end group fidelity, chain extensions have also been successfully performed and different degrees of polymerization were targeted. Importantly, no conversion was observed in the absence of UV light and the polymerization could be switched “on” and “off” upon demand, as demonstrated by intermittent light and dark periods and thus allowing access to spatiotemporal control.

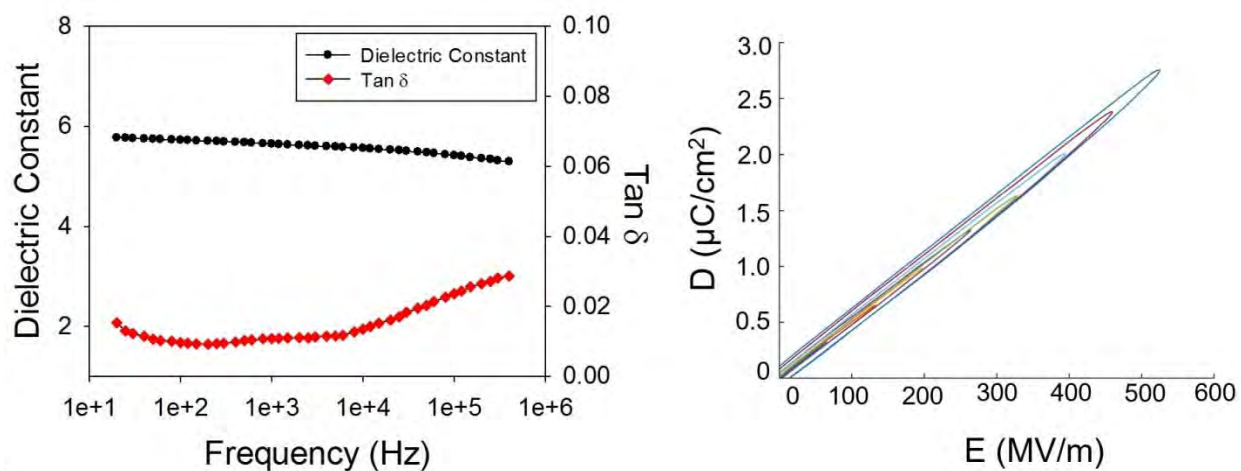


Low [Cu] + NaBr :
Controlled polymerization in Water

POLY 269: Synthesis, characterization, and analysis of a novel polythiourea for dielectric applications aided by molecular dynamics and density functional theory

Gregory M. Treich³, gregory.treich@uconn.edu, Mayank Misra¹, Shamima Nasreen², Mattewos Tefferi⁵, Arun Mannodi-Kanakkithodi⁴, Rampi Ramprasad⁴, Yang Cao⁵, Gregory A. Sotzing². (1) Chemical Engineering, Columbia University, New York, New York, United States (2) Chemistry, University of Connecticut, Willimantic, Connecticut, United States (3) Institute of Material Science, University of Connecticut, Oakland, New Jersey, United States (4) Materials Science and Engineering, University of Connecticut, Storrs, Connecticut, United States (5) Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States

Recently, research of dielectric materials has accelerated as the world has pushed from coal and gas power to electricity. New materials are essential for modern electronics to store more energy and work more efficiently while decreasing size and weight. A rational co-design approach between computational predictions, polymer synthesis, and electrical characterization has resulted in a novel polythiourea with promising dielectric properties made from a rigid aromatic block and a flexible ether-containing block, among several other polymers. This polymer has a dielectric constant above 5.5 with an energy density of ca. 10 J/cm³, over twice the dielectric constant and double the maximum energy density of the current industry standard, biaxially oriented polypropylene (BOPP). To further understand the fundamentals behind this polythiourea, density functional theory (DFT) coupled with machine learning was used to simulate the polymer in a crystalline state and compute properties from that structure. Molecular dynamics (MD) was also used to simulate dynamic chain movements and model the polythiourea in an environment and structure that more closely resembles reality. These insights should assist future researchers in understanding how best to design a molecule for their preferred dielectric applications.

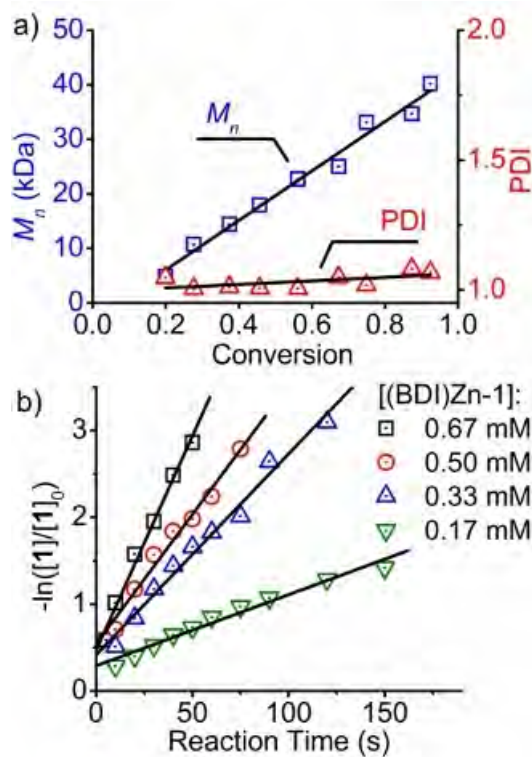
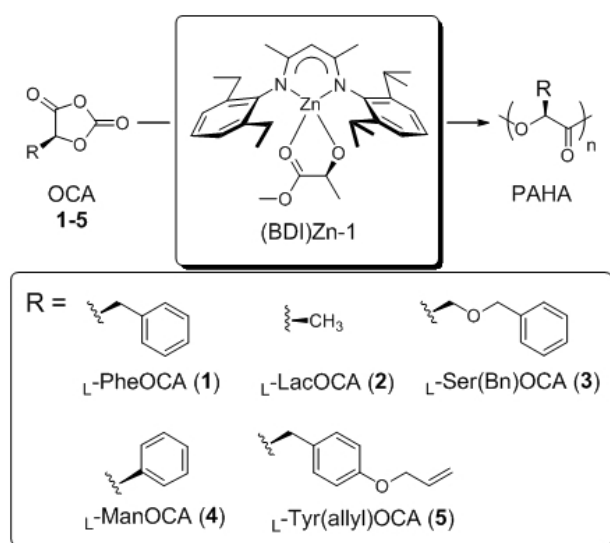


Dielectric constant and loss alongside D-E hysteresis loop for a new polythiourea presented in this work.

POLY 270: Controlled ring-opening polymerization of O-carboxyanhydrides using organometallic catalysts

Rong Tong², rtong@vt.edu, Jianjun Cheng¹. (1) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States

O-Carboxyanhydrides (OCAs) have recently emerged as a class of viable monomers which can undergo ring-opening polymerization (ROP) to prepare poly(α -hydroxyalkanoic acids) with functional groups that are typically difficult to achieve via the ROP of lactones. Organocatalysts for the ROP of OCAs, such as dimethylaminopyridine (DMAP), may induce undesired epimerization of the α -carbon in polyesters resulting in the loss of isotacticity. Herein, we report the use of one β -diimine zinc catalyst for controlled ROP of various OCA without epimerization (Figure 1). Both homopolymers and block copolymers with controlled molecular weights, narrow molecular weight distributions and isotactic backbones can be readily synthesized. The M_n of resulting poly(PheOCA) showed a linear correlation with the conversion of PheOCA, agreeing with the expected values (Figure 2a). The polymerization proceeded with first-order dependence on OCA concentration (Figure 2b). Derived from the kinetic data of four different concentrations of (BDI)Zn-1, the order in Zn catalyst concentration was determined to be 1.21 from the slope of the fitted lines, indicating that the ROP of PheOCA likely proceeds through monometallic enchainment step. In addition, we used (bpy)Ni complex as the cocatalyst that leads to the controlled polymerization of high molecular-weight polyesters.



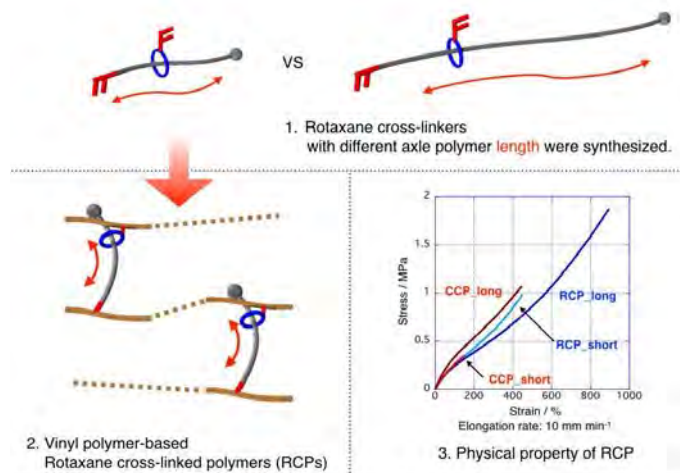
POLY 271: Synthesis of vinylic macromolecular rotaxane cross-linkers endowing network polymers with toughness

Jun Sawada, *jsawada@polymer.titech.ac.jp*, Daisuke Aoki, Toshikazu Takata.
Chemical Science and Engineering, Tokyo Institute of Technology, Meguro, Tokyo, Japan

Rotaxane cross-linked polymers (RCPs) having the rotaxane structures at the cross-link points have been attracting considerable attention due to the unique properties, such as high swellability, extensibility and well stress-relaxing ability, caused by the movable cross-link points. However, the whole mechanism of the generation of such excellent properties and function of RCPs are not clarified yet, because of the structural complexity of RCP. Therefore, structure-definite rotaxane cross-linker (RC) is necessary to close in on the nature of RCP. In this work, we have developed novel RCs with the definite structure to clarify how the movable length of the components at the cross-link points affects the property of the corresponding RCPs.

RCs with different axle lengths were synthesized. Pseudo[2]rotaxane initiator possessing a methacrylate group-containing wheel component was used for diphenyl phosphate (DPP)-catalyzed living ring-opening polymerization of *d*-valerolactone. Degree of polymerization was easily controlled, as 25 and 50 in this time, by changing the feed ratio of $[M]/[I]$. The polymerization was followed by the end-cap reaction and introduction of another methacrylate group into the axle component to afford RC. RCPs and CCPs were obtained by the radical polymerizations of *n*-butyl acrylate in the presence of a small amount of RCs and CCs, respectively.

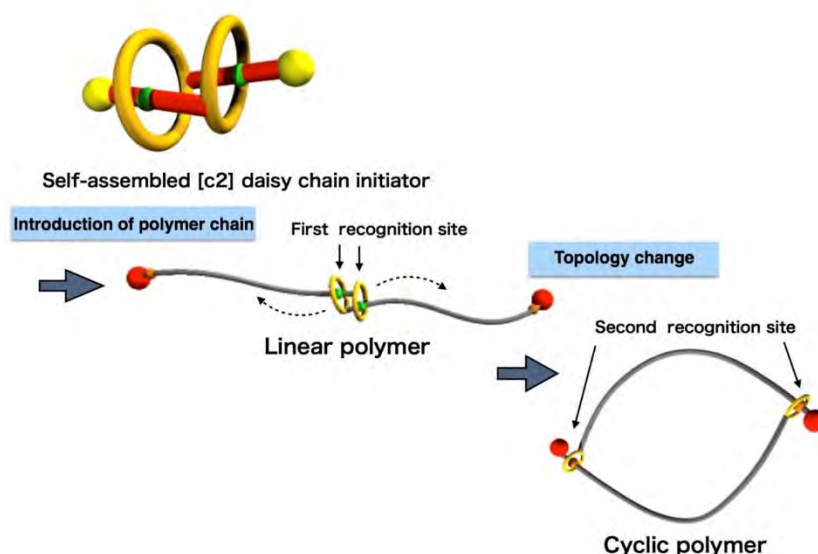
Physical properties of RCPs and CCPs were evaluated by swelling test, and tensile test. RCPs showed higher swellability than CCPs, suggesting the equalizing cross-link structure caused by the movable cross-link points of RCPs. We call this phenomenon 'equalizing effect'. As for the mechanical properties, it should be noted that the toughness of RCPs were much bigger than those of CCPs. The results can be explained by avoiding stress concentration due to the equalizing effect. Moreover, RCP synthesized with longer RC showed larger swellability and toughness than that of RCP synthesized with shorter RC. It was also suggested that longer movable area of RCP gave larger equalizing effect.



POLY 272: Topology transformation from linear polymer to cyclic Polymer: Effective synthesis of cyclic polymer utilizing [c2]daisy chain dimer

Daisuke Aoki, daoki@polymer.titech.ac.jp, Toshikazu Takata. Tokyo institute of technology, Tokyo, Japan

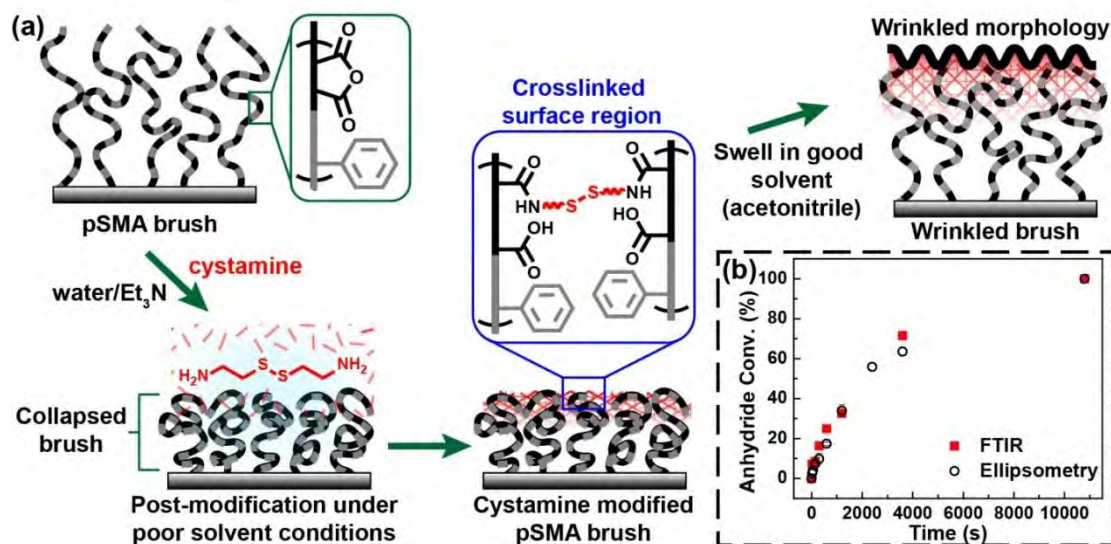
Recent advance of polymer chemistry makes it possible to synthesize various type of polymers in a large scale. However, synthesis of cyclic polymer has been limited due to difficulties in preparation and purification because of their unique topology having no chain ends. In order to synthesize cyclic polymer effectively and easily, cyclization process is the key, i.e. when and how cyclization should be conducted effectively. If the cyclization spontaneously and selectively occurs even in high concentration, it would be ideal process for the effective syntheses of cyclic polymers. To solve the problem of the cyclization process, we focused on a molecular self-assembly, a key concept in supramolecular chemistry where molecules adopt a defined arrangement spontaneously and selectively. Here, we would like to describe the effective synthetic method of cyclic polymer, where 1) cyclization process spontaneously and selectively occurred according to the self-assembly of [c2]daisy chain dimer as pseudo[2]rotaxane dimer, 2) polymer chain growth easily started from [c2]daisy-chain dimer by the living polymerization initiated by the [c2]daisy-chain dimers 3) topology transformation of the rotaxane-linked polymer having the [c2]daisy chain dimer as a junction point from linear to cyclic was induced by changing the position of wheel component (Figure). By this method, small circle surrounded by the two wheels at the center of polymer chain in the linear polymer was expanded by the topology transformation from linear to cyclic changing the movable junction point from first recognition site to second recognition site. Since elaborate synthesis in high dilution and special purification by preparative GPC were not required through all steps, we believe that the present work will enable over 100 g scale synthesis of various cyclic polymers and related versatile applications.



POLY 273: Wrinkling polymer brush surfaces via postpolymerization modification

Cassandra Reese³, cassandra.reese@eagles.usm.edu, **Wei Guo**³, **Li Xiong**³, **Christopher M. Stafford**¹, **Brad S. Lokitz**², **Olga Ovchinnikova**², **Anton levlev**², **Derek L. Patton**³. (1) NIST, Gaithersburg, Maryland, United States (2) Bldg 8610 MS 6494, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) School of Polymers and High Performance Mater, The University of Southern Mississippi, Hattiesburg, Mississippi, United States

Buckling instabilities (wrinkles, creases, and folds) are ubiquitous in soft materials and can be exploited to define the shape, morphology, and function of complex systems – as exemplified by nature in the wrinkling of skin or folding of brain tissue. Following nature's lead, strain-induced wrinkling of polymer thin films has emerged as a powerful bottom-up approach to engineer surfaces that exhibit complex ordered and disordered patterns at multiple length scales. Herein, we highlight out recent efforts to exploit ultrathin polymer brush surfaces (<100nm) with wrinkled and creased morphologies using a simple postpolymerization modification (PPM) approach. Poly(styrene-alt-maleic anhydride) (pSMA) polymer brushes were synthesized via surface-initiated polymerization and then postmodified (crosslinked) under poor solvent conditions. Exposure of the partially crosslinked brushes to good solvent conditions preferentially swells the non-crosslinked regions to induce the buckling instability. Swelling ratio measurements were determined to investigate the onset of buckling of pSMA brush films. Additionally, time of flight secondary ion mass spectroscopy (TOF-SIMS) was utilized to obtain depth profiles of pristine pSMA and pSMA at discrete postmodification reaction times. The pSMA were exposed to sequential postmodification reactions to enable wrinkle-to-crease morphological transitions while endowing the brush with additional chemical functionality.

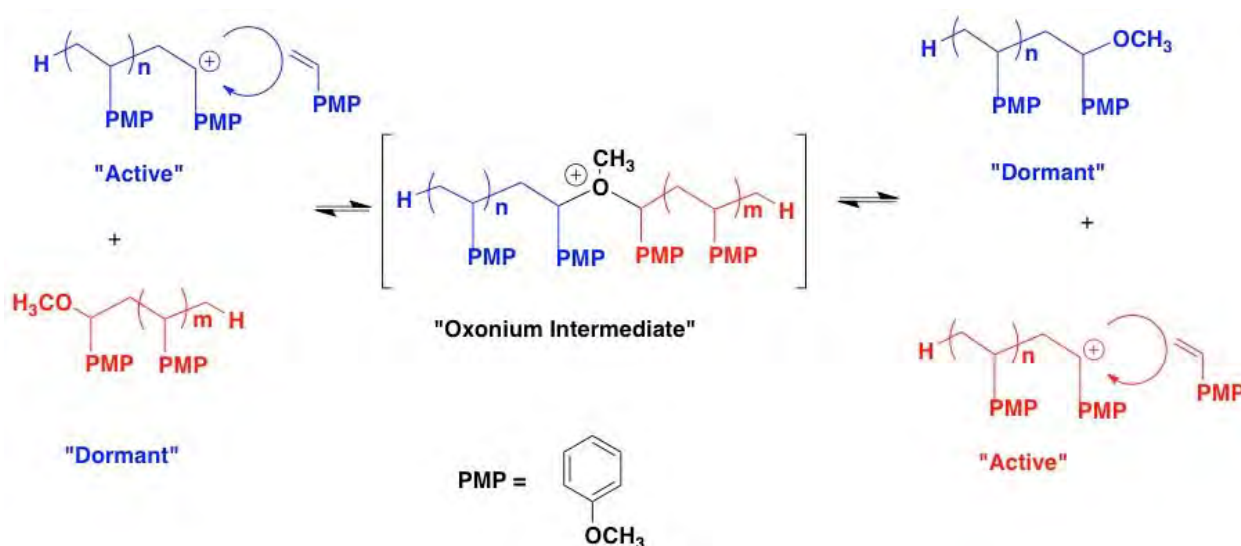


(a) Synthetic strategy to wrinkled polymer brush surfaces (b) Anhydride conversion versus cystamine reaction time determined by FTIR and ellipsometry

POLY 274: Methanol-mediated living cationic polymerization of 4-methoxystyrene via oxonium intermediate

Alka Prasher³, *ahk23@wildcats.unh.edu*, **Stephanie R. Liffland**⁴, **David A. Nicewicz**², **Wei You**¹. (1) University of North Carolina, Chapel Hill, North Carolina, United States (2) Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, United States (3) Department of chemistry, University of North Carolina, Chapel Hill, North Carolina, United States (4) Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, United States

Herein we report a metal-free, acid initiated living cationic polymerization of 4-methoxystyrene. The molecular weight and dispersity of the synthesized poly(4-methoxystyrene) are controlled by the concentration of methanol. We propose that methanol acts as a reversible chain-transfer agent, analogous to reversible addition fragmentation chain-transfer (RAFT) polymerization, regulating the equilibrium between the propagating active cation chain and the resulting oxonium intermediate (Scheme 1). The molecular weights of the synthesized polymers were in good agreement with theoretical molecular weight assuming that each molecule of methanol generates one polymer chain. A study using alcohols of different nucleophilicity indicated that the molecular weight and dispersity of the synthesized polymers varies inversely with the nucleophilicity of the alcohol additive.



Scheme 1 Living cationic polymerization of 4-methoxystyrene via oxonium intermediate

POLY 275: Stereocomplex formation of poly(*N*-methyl-*N'*-(2-isopropyl-6-methylphenyl) carbodiimide and effect of regioregularity of isopropyl pendant scaffold towards complexation

Dumindika Siriwardane², dxs124830@utdallas.edu, Oleg V. Kulikov¹, Bruce M. Novak³. (1) Chemistry, UT Dallas, Richardson, Texas, United States (2) Chemistry, University of Texas at Dallas, Richardson, Texas, United States (3) School of Natural Sciences Mathematics, University of Texas at Dallas, Richardson, Texas, United States

Here we report the formation of stereocomplex from poly(*N*-methyl-*N'*-(2-isopropyl-6-methylphenyl)) carbodiimide. This chiral polymer (predominantly P or M helix) shows change of specific optical rotation with thermal annealing and it retains chirality persistent. Our understanding behind this phenomena is the formation of stereocomplex between complementary strands of polymer bearing aromatic rings with *o*-isopropyl groups. Inspired by the leucine zipper motifs that act as dimerization regions in proteins, we were curious to look deeper into the role the isopropyl group could play in aggregation. We have investigated this complexation by synthesizing various derivative forms of homo polymers and block co-polymers by altering the regioregularity of isopropyl scaffold. AFM, SEM, p-XRD, SAXS, and solid state ¹³C NMR were used to determine the structure and property of these complexes.

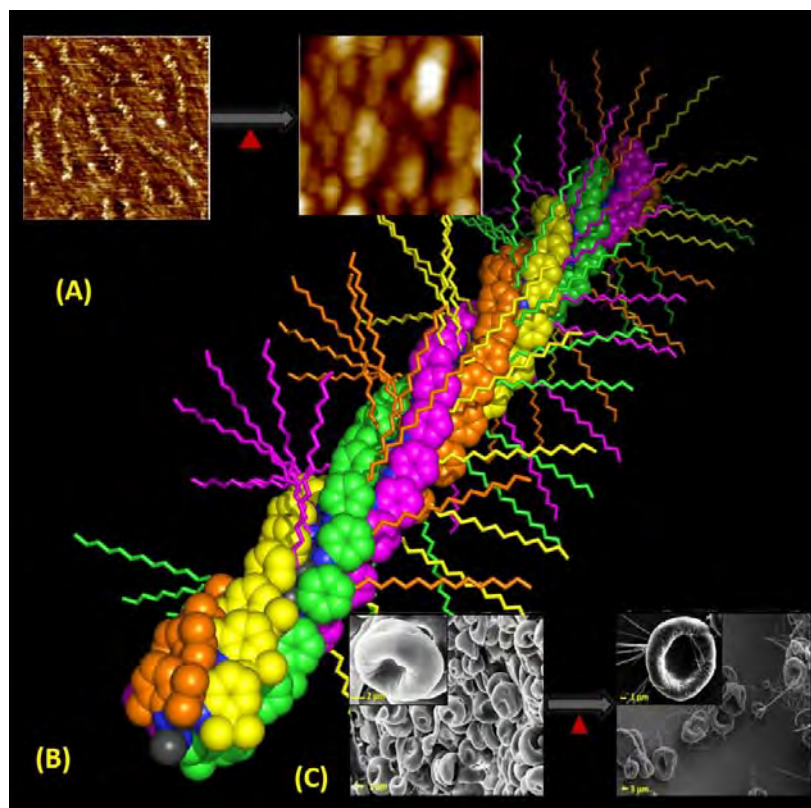


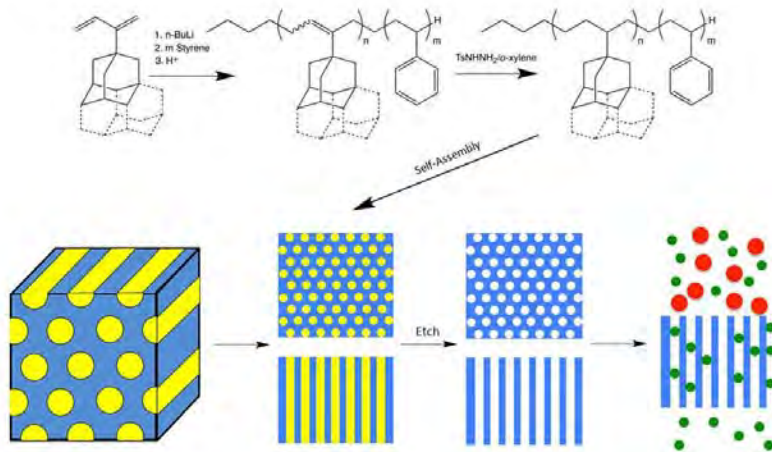
Figure 1. (A) AFM images (B) Cartoon (C) SEM images for block co-polymer of poly(*N*-methyl-*N'*-(2-isopropyl-6-methylphenyl))carbodiimide-*b*-poly(*N*-phenyl-*N'*-octadecyl)carbodiimide

POLY 276: Synthesis and characterization of diamondoid substituted block copolymers

Connor Hill¹, hill1545@vandals.uidaho.edu, Mark F. Rolfe. (1) Chemical and Materials Engineering, University of Idaho, Moscow, Idaho, United States (2) Chemical and Materials Engineering, University of Idaho, Moscow, Idaho, United States

Diamondoids are a unique class of hydrocarbons, whose cage-like structure can be superimposed on a diamond lattice. Their high crystallinity relative to molecular weight has the potential to yield interesting and industrially applicable macromolecular architectures, particularly in the form of diblock copolymers. Previous work indicates that diamondoids functionalized for polymerization exhibit self-assembled nanostructures through microphase segregation. Calculation of unusually high χ interaction parameters for diamondoid block copolymers suggests that phase feature sizes could be as small as 5nm. Feature sizes in current nanopatterning applications that utilize directed self-assembly are often limited by the χ parameter of commonly used monomers, while the use of etched diblock copolymers for microporous membranes is often limited by the mechanical stability of the remaining matrix block. Block copolymers of functionalized diamondoids have great potential to overcome both of these limitations.

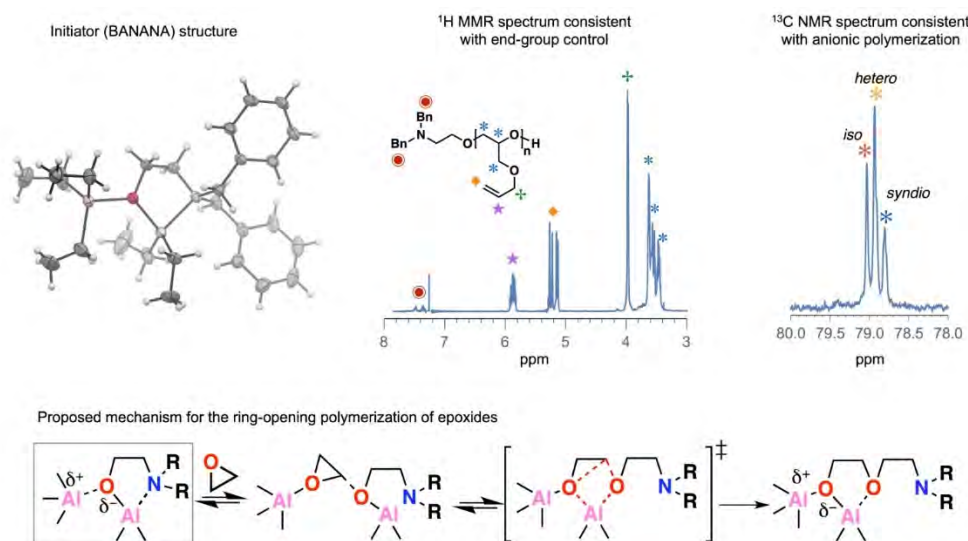
This research project will be divided into three objectives: synthesis of diamondoid monomers, living anionic polymerization of monomers, and characterization of microphase segregation in resultant films. 2-(1-Adamantyl)-1,3-butadiene monomer has been successfully synthesized through reaction of 1-Acetyladamantane with excess vinyl Grignard reagent and dehydration of the subsequent tertiary alcohol. This process is to be used for the synthesis of diamantane and triamantane substituted dienes as well. Block copolymers of the proposed diamondoid monomers with polystyrene will be synthesized by living anionic polymerization and further hydrogenated with *p*-toluenesulfonhydrazine. Films from these block copolymers will then be created by means of spin or dip-coating. Annealing studies will reveal the potential microphase segregation, which will be compared to the well-characterized polystyrene-*block*-polyisoprene system.



POLY 277: Design and synthesis of new initiators for the ring opening polymerization of epoxides inspired by the Vandenberg catalyst

Nathaniel A. Lynd, nate.lynd@gmail.com. Department of Chemical Engineering, University of Texas at Austin, Berkeley, California, United States

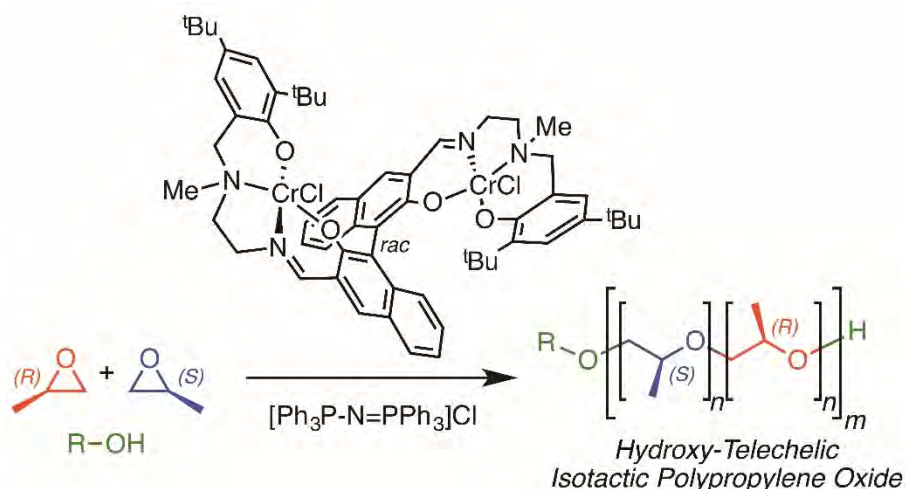
The development of new polymer structures driven by innovation in polymerization catalysis is key to disruptive advances in applied and fundamental polymer science. Expansion of the scope of structural possibilities in polymeric materials enhances the diversity in terms of architecture, composition, and stereochemistry that drives our knowledge of polymer physics, and properties available for new applications. In heterocyclic monomer systems, the driving force for incorporation of distinct monomers into a polymer chain is derived largely from an indiscriminate ring-strain which imparts significant versatility for the synthesis of new functional materials. Heterocyclic monomers can be polymerized via a variety of traditional ionic and catalytic approaches which each exhibit various advantages from a materials design perspective. In order to combine the advantages of a both an ionic and a catalytic approach, we looked to the historical Vandenberg catalyst as our ansatz for the development of new organoaluminum initiators. In this presentation, I will propose a structure and mechanism of polymerization for the Vandenberg catalyst, and present the synthesis of new initiators that contain key structural elements of the proposed Vandenberg catalyst structure. While some features of the Vandenberg catalyst could be replicated (e.g., isoselectivity), and new capabilities could be introduced (e.g., control of molecular weight and end-group functionality), the performance in terms of polymerization rate could not be improved upon using our defined molecular catalysts. Serendipity then led to the identification of a new class of polymerization initiators that operate via a distinct mechanism that is characteristically anionic in nature, provides control over molecular weight, chain-end functionality, and proceeds at a similar polymerization rate as the Vandenberg catalyst: The bis-(alkane-aluminum)-N-alkoxides, or BANANAs.



POLY 278: Isospecific, chain shuttling polymerization of propylene oxide using a bimetallic chromium catalyst: A new route to semicrystalline polyols

Matthew Childers, matthew.childers@pnnl.gov, Lilliana S. Morris, Geoffrey W. Coates.
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States

Hydroxy-telechelic poly(propylene oxide) (PPO) is widely used industrially as a midsegment in polyurethane synthesis. These polymers are produced from racemic propylene oxide using chain shuttling agents and double-metal cyanide catalysts to produce atactic polymers. Unlike atactic PPO, isotactic PPO is semicrystalline with a melting temperature of approximately 67 °C. Currently there is no practical route to hydroxy telechelic isotactic PPO using racemic propylene oxide as the monomer. In this work, hydroxy telechelic isotactic PPO is synthesized from racemic propylene oxide with control of molecular weight using isoselective bimetallic catalysts in conjunction with chain shuttling agents. The discovery of an easily accessible bimetallic chromium catalyst is reported for this transformation. Diol, triol, and polymeric chain shuttling agents are used to give hydroxy telechelic isotactic PPO of varying functionality and structure.



POLY 279: Chromonic liquid crystal hydrogels

Ruvini Kularatne¹, ruvini331@gmail.com, Taylor H. Ware². (1) Bioengineering, The University of Texas at Dallas, Dallas, Texas, United States (2) Bioengineering, The University of Texas at Dallas, Richardson, Texas, United States

Stimuli-responsive hydrogels have emerged as a class of materials that can be programmed to change shape and topography in response to changes in environmental conditions. This stimulus response in hydrogels is typically isotropic in nature. In this work, we report on the synthesis of anisotropic, mechanically active hydrogels using the self-assembly of the lyotropic chromonic liquid crystals (LCLC). Unlike conventional lyotropic LCs, LCLCs can be macroscopically aligned using patterned surfaces. In this work, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) is used to synthesize a polymerizable LCLC mesogen, ionic dimethacrylate derivative of perylene-3,4,9,10-tetracarboxylic diimide (PDI). The anisotropic hydrogels were generated through the radical polymerization of chromonic reactive mesogens (PDI) in their nematic state with n-isopropylacrylamide (NIPAM). The presence of NIPAM and the molecular ordering due to the presence of chromonic liquid crystal imparts anisotropic thermoresponsive behavior to the hydrogel. This anisotropic swelling in the chromonic hydrogel can be programmed. We discuss hydrogel sheets that actuate at temperatures that are compatible with living organisms (figure 1). This shape change behavior of the hydrogel will be discussed and will be correlated to the polymer network structure, morphology and liquid crystalline phase. Finally, we discuss the introduction of chiral dopants to create surfaces capable of reversible changes in topography.



Figure 1: Reversible, 3D shape changes of the chromonic hydrogel with temperature

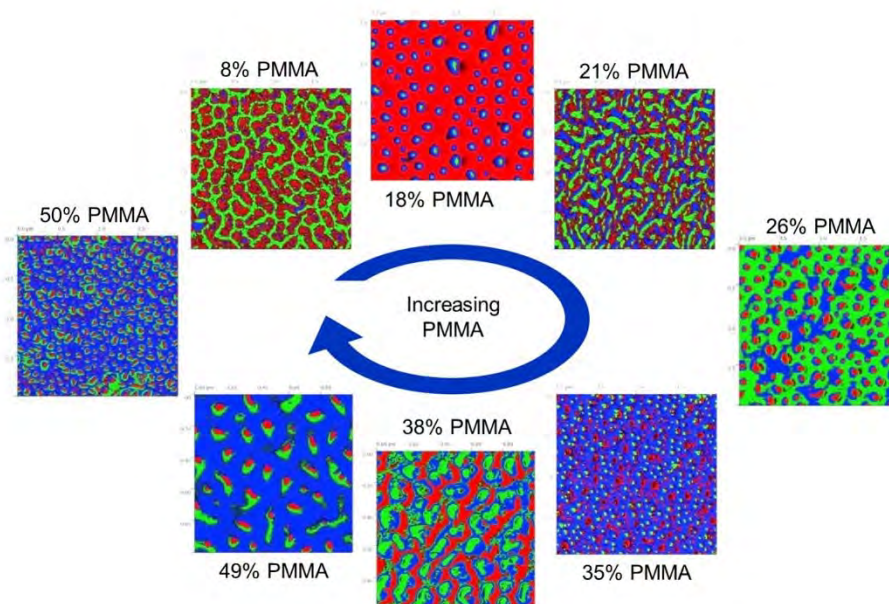
POLY 280: Self-Assembly and phase behavior in mixed polymer brushes

Chester K. Simocko², chester.simocko@sjsu.edu, **Amalie L. Frischknecht**¹, **Dale Huber**¹. (1) Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico, United States (2) Department of Chemistry, San Jose State University, San Jose, California, United States

Polymer self-assembly has been utilized to create nanoscale features which can then be controlled by micron sized templates, leading to well-defined and long-range ordered phases. While block copolymers are the traditional system to study this behavior, mixed-polymer brushes also self-assemble into distinct phase regimes.

Mixed-polymer brushes offer several advantages over traditional spin-coated block copolymer systems. Since the polymers are directly attached to the surface, they are more mechanically and chemically robust. Also the surface does not need to be planar; since the brushes grow from the surface, any surface geometry can be used. Finally, features such as right angles, which are difficult to replicate for block copolymer systems, should be readily accessible with a mixed-polymer brush system.

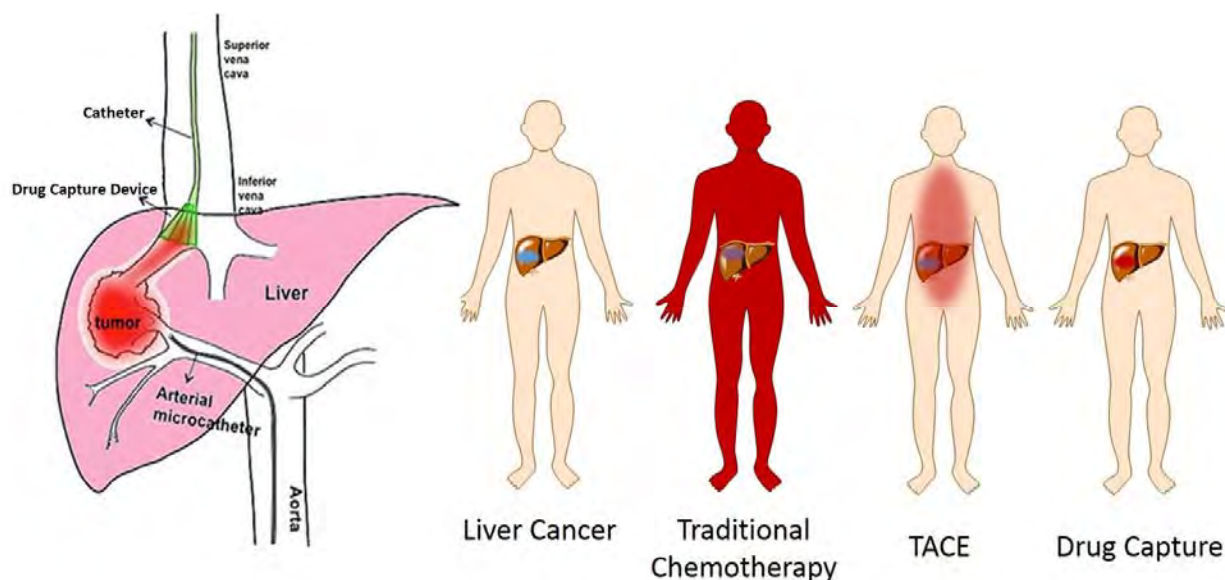
We have synthesized ternary polymer brushes consisting of polystyrene (PS), poly (methyl methacrylate) (PMMA), and poly (4-vinyl pyridine) (P4VP). By using self-consistent field theory (SCFT) and experimental results, we have been able to predict a complete phase diagram, identify seven unique phase behaviors, and model both lateral and vertical phase separation of this system. Both the experimental and theoretical results strongly agree; all phases observed experimentally correlate with the theoretical models.



POLY 281: Materials for drug capture: Filtering off-target chemotherapy agents from the bloodstream

Michael D. Schulz¹, mdschulz@caltech.edu, **Carl Blumenfeld**¹, **Steven Hetts**², **Robert H. Grubbs**¹. (1) Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States (2) Radiology, University of California, San Francisco, San Francisco, California, United States

The systemic, off-target toxicity of chemotherapy is a well-known problem in oncology. In an effort to overcome this challenge, many approaches have been developed to deliver chemotherapy directly and exclusively to the tumor. One of these approaches is transarterial chemoembolization (TACE), a procedure in which chemotherapy is introduced via catheter directly into the artery supplying the tumor. Despite this site-specific delivery, a portion of the chemotherapy dose still enters systemic circulation and causes off-target damage. To address this issue, we are developing materials that are capable of capturing this residual chemotherapy from the blood stream. Ultimately, this material will be used to construct a device that can be deployed via catheter “downstream” from the tumor, enabling excess chemotherapy to be sequestered before entering systemic circulation. Our approach uses DNA-functionalized surfaces, which enables the capture of DNA-targeting chemotherapy drugs. In order to improve the cost and scalability of this system, we developed simple methods of covalently attaching genomic DNA to a variety of surfaces. We have further demonstrated that this approach is capable of sequestering doxorubicin, cisplatin, and epirubicin—three common chemotherapy agents—from solution at clinically relevant concentrations. The efficacy of these materials was demonstrated in PBS, human serum, and blood, indicating that this approach is likely viable *in vivo*. Moreover, the kinetics of drug capture are rapid: We observed >95% reduction of doxorubicin concentration in human serum in <10 minutes. The efficacy of these materials indicates that drug capture is indeed a viable strategy for mitigating the harmful side-effects associated with chemotherapy.

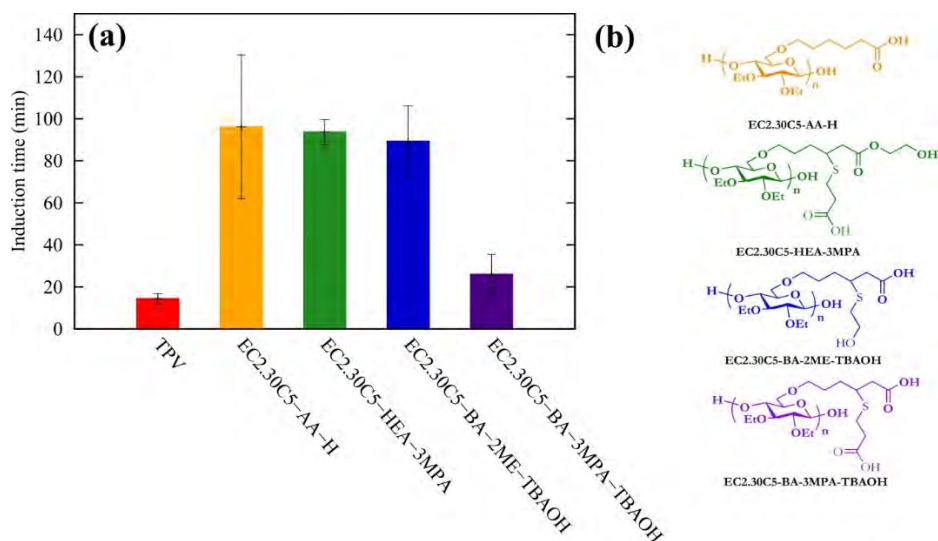


POLY 282: Multifunctional cellulose ether derivatives for high performance amorphous solid dispersions prepared by olefin cross-metathesis and thiol-michael addition

Yifan Dong², yifand@vt.edu, Laura I. Mosquera-Giraldo⁴, Lynne Taylor¹, Kevin J. Edgar³. (1) Purdue University, West Lafayette, Indiana, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (3) Mail Code 0323, Virginia Tech, Blacksburg, Virginia, United States (4) Department of Industrial and Physical Pharmacy, Purdue, West Lafayette, Indiana, United States

Modification of cellulose by esterification and etherification has been very useful to enhance its solubility and processibility. However, the range of commercially available cellulose derivatives is very limited due to the harsh conditions for etherification (strong alkaline) and esterification (strong acidic). Olefin cross-metathesis (CM) is a powerful synthetic tool with high efficiency, great selectivity and very mild reaction conditions. By appending olefin-terminated branches onto cellulose backbone as metathesis “handles”, we were able to apply CM with a variety of olefins like acrylic acid,¹ different acrylates²⁻³ and acrylamides.⁴ Furthermore, since all CM products are α,β -unsaturated acids/esters, we also investigated elaboration of α,β -unsaturation through thiol-Michael addition.⁵ Using an excess of thiol and amine, functionally diverse thiols can undergo complete Michael addition, eliminating α,β -unsaturation and offering an extra functionality. Moreover, given the stable cellulose ether backbone, acrylate ester can be further saponified to recover a carboxyl group, affording two carboxylic acids per original olefinic reactive site. This tandem olefin CM/thiol-Michael modification allows a broad range of polysaccharide derivatives with tunable functionalities and architectures for applications including ASD.

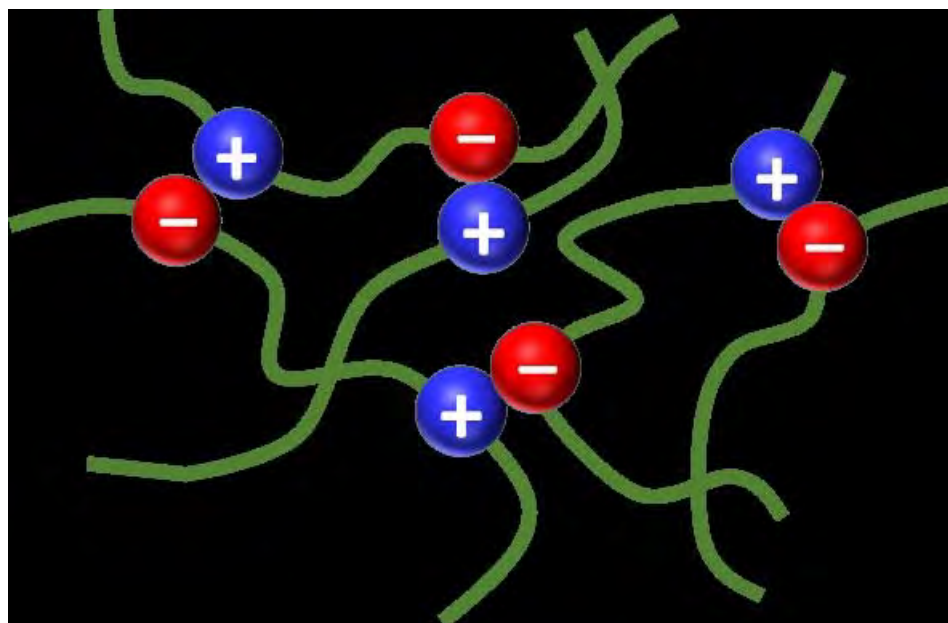
Our previous work has proven the success of CM for modification of commercial cellulose ethers (e.g. EC, MC and HPC) and microcrystalline cellulose into amphiphilic ASD candidates. In this work, we will share our recent progress in design and optimization of polymer structures using these new tools, detailed structure-property studies and drug crystallization inhibiting results.



POLY 283: Synthesis and characterization of organic ion-pairs as dynamic bonds for stimuli-responsive polymers

Guodong Deng², gd28@zips.uakron.edu, Kevin A. Cavicchi¹. (1) University of Akron, Akron, Ohio, United States (2) Polymer Engineering Dept, University of Akron, Akron, Ohio, United States

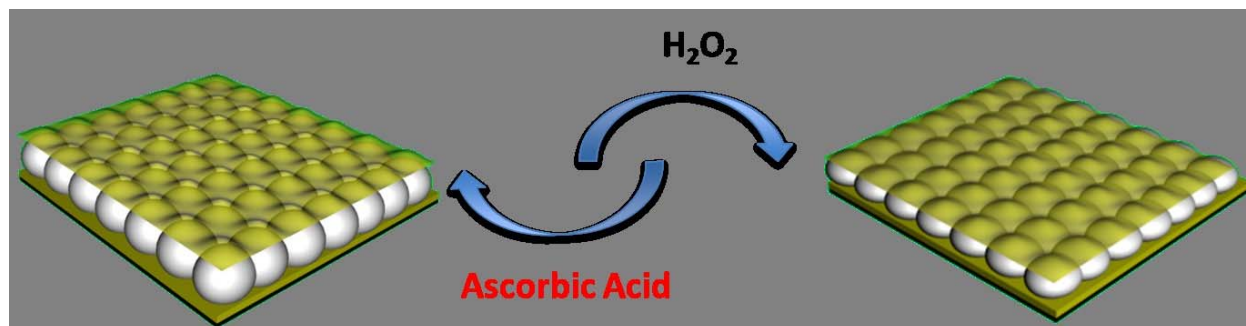
Novel materials that can reversibly adapt to their environment are important as functional materials. In polymer networks, dynamic bonding of the crosslinks, which can break and reform under an external stimuli (e.g. heat or mechanical stress) are of interest for functional material properties, (e.g. self-healing or shape memory). One general route to introduce dynamic bonds is through non-covalent interactions. Ion-pairing, is another potential non-covalent dynamic bond that has not been fully investigated especially when compared to other interactions like hydrogen bonding and metal-ligand interactions. In this work, ionically crosslinked networks of a poly(butyl acrylate) elastomer by vinyl benzyl tri-n-octyl ammonium/phosphonium styrene sulfonate ion pairs were prepared as model system to study the thermo-mechanical properties as a function of the network parameters, including ion-pair chemistry and crosslink density. Results of rheological behavior, mechanical and thermal properties of these materials will be comprehensively studied compared to other ionic systems, such as ionomers with pendant counter ions.



POLY 284: Optical devices constructed from smart microgels for sensing

Qiang M. Zhang¹, zhang_qiang_333@sina.com, Samuel Mugo³, Michael Serpe². (1) Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada (2) E3-44 Gunning Lemieux Chem Centre, University of Alberta, Edmonton, Alberta, Canada (3) Physical Sciences Department, MacEwan University, Edmonton, Alberta, Canada

Ferrocene-modified poly (N-isopropylacrylamide) - based microgels were synthesized, characterized and used to construct optical devices (etalons). The response of the microgels and etalons to H₂O₂ was investigated, and we show that both the microgel diameter, and the optical properties of the etalons, depended on the solution concentration of H₂O₂ from 0.6 mM to 35 mM. This behavior is a direct result of the oxidation of ferrocene, which influences the microgel diameter. This was also demonstrated by electrochemical-mediated oxidation/reduction of ferrocene using cyclic voltammetry. These materials could be used to monitor H₂O₂ that is generated from enzymatic reactions. Specifically, we show that the H₂O₂ generated from the oxidation of glucose catalyzed by glucose oxidase could be quantified. Finally, the devices can be reused multiple times via a regeneration process. This investigation illustrates the versatility of the etalon system to detect species of broad relevance, and how they could potentially be used to quantify products of biological reactions.



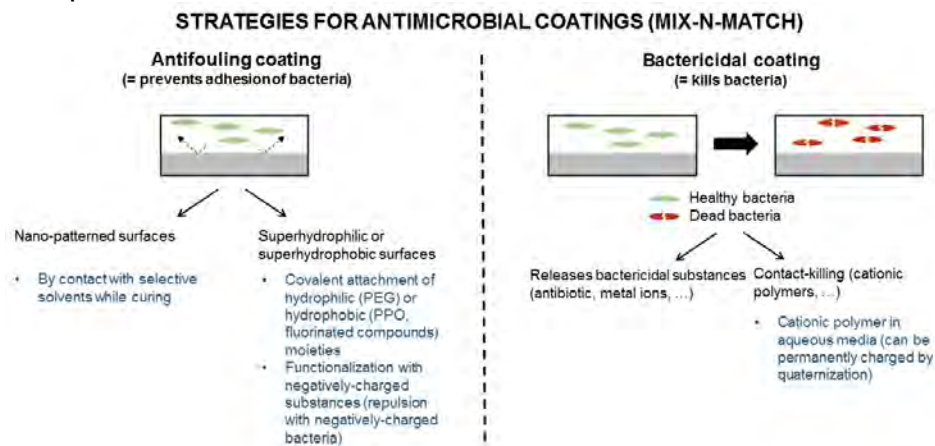
POLY 285: Antifouling aminoplast coatings and their layer-by-layer deposition technique

Mareva Fevre¹, marevafevre@gmail.com, **Xin Ding**², **Rudy Wojtecki**¹, **Yi-Yan Yang**², **J Hedrick**¹. (1) IBM Almaden Research Center, San Jose, California, United States (2) Inst Bioengr Nanotech, Singapore, Singapore

The prevention of pathogen (cross-)contamination or colonization remains an ongoing global healthcare challenge, both medically and financially. It is estimated that, each year, in the US alone, approximately 2 million people suffer from nosocomial infections, 4.5% of which lead to death. Bacteria attachment at the surface of implants or catheters is a serious post-surgery complication. Diagnosis and treatment are tricky, mostly owing to the complexity of biofilms' composition and difficulty to fully eradicate them, as well as the recent emergence of antibiotic resistant bacteria strains. Therefore, the development of antimicrobial coatings preventing bacterial adherence has emerged as a critical scientific and technologic challenge other the past decades.

We recently reported on a new class of recyclable thermosets and coatings based on 1,3,5-hexahydro-1,3,5-triazines (HTs), namely poly(hexahydrotriazines) (PHTs). Given the ability of HTs to bind antimicrobial metals and the synthetic diversity of the related PHT materials that allow incorporating anti-fouling polymers such as PEG, we investigated PHT-based coatings that could be used to achieve a dual action for both defending against bacterial adhesion and attacking any that bind. We showed that silver-coated PHT materials exhibit excellent antifouling properties against *P. aeruginosa*, while ammonium and PEG-modified films efficiently prevent the adhesion of *S. aureus*.

In another strategy, branched poly(ethylenimine) was deposited on glass substrates and crosslinked with glyoxal using a facile and environment-friendly layer-by-layer spray coating deposition technique. The coatings were modified by the chemical incorporation of PEG, negatively-charged moieties, fluorinated compounds and with poly(propylene oxide) (PPO). In the latter case, the hydrophobic nature of the modifier induced "micro-precipitation" of domains of the coatings leading to texturing of the surface. Functionalized BPEI/glyoxal materials successfully inhibited the attachment of bacteria at the surface, with up to 90% reduction of the metabolic activity of *S. Aureus* after a 7-day incubation period.

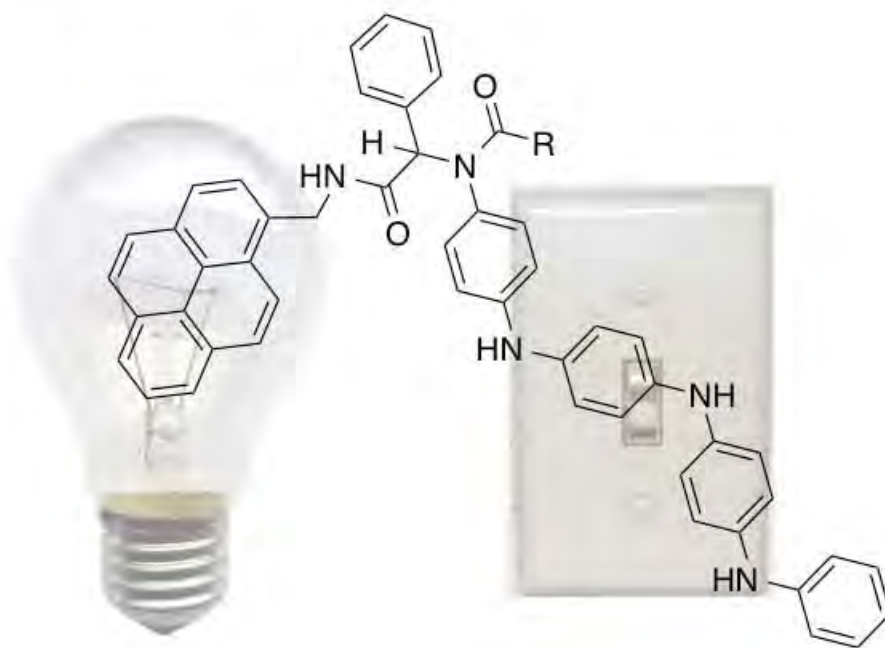


POLY 286: Polymeric sensors for 6-D super-resolution microscopy: Advanced fluorogenic materials for measuring redox reactions at surfaces and in solution

Justin Cole, *justinpcole11@gmail.com*, Ashley Hanlon, Erik B. Berda. Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

6-D super-resolution microscopy allows for the visualization of fluorogenic processes smaller than the wavelength of light. Advanced fluorogenic dyes and responsive polymeric materials will allow us to probe chemical processes on a nanometer scale using super-resolution microscopy. This talk will discuss our progress towards building efficient redox-active polymer-based dyes, tuning them for specific systems, and using these materials to measure redox processes.

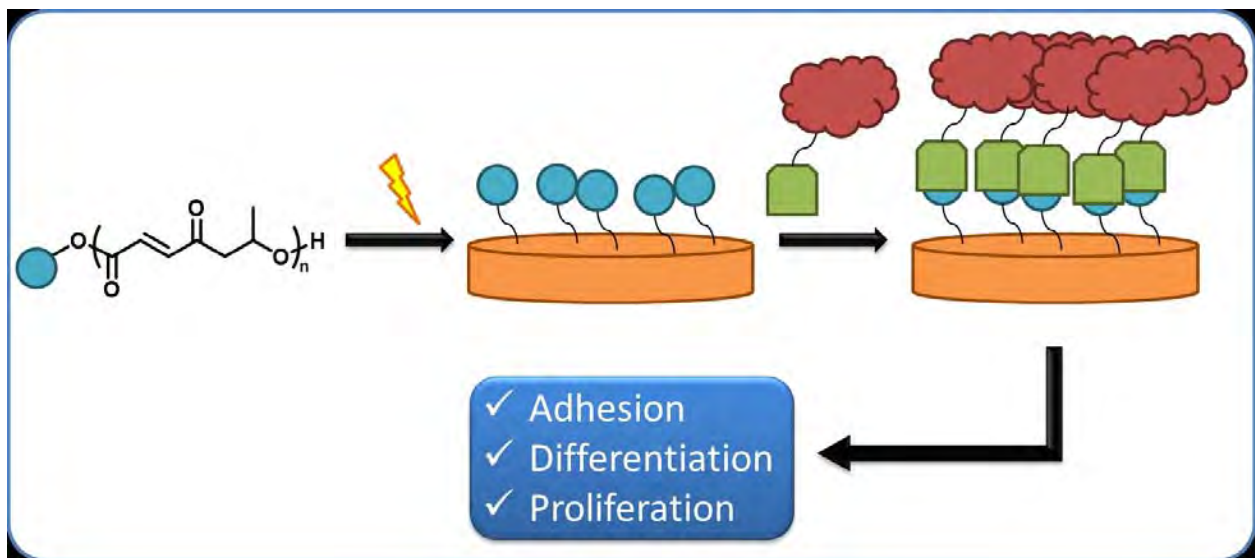
Fluorogenic sensors based on tandem tetraaniline "switch" and pyrene fluorophore



POLY 287: Functionalized poly(propylene fumarate) for 3D printed bone growth scaffolds

James Wilson, *J.Wilson.3@warwick.ac.uk*, Alex Kleinfehn, Shannon Petersen, Yusheng Chen, Matthew Becker. Department of Polymer Science, University of Akron, Akron, Ohio, United States

Poly(propylene fumarate) (PPF) has been widely researched for use in 3D printed scaffolds for future *in vivo* applications as a consequence of the polymer backbone exhibiting both alkene crosslinking ability and degradable ester functionality. Through controlled crosslinking the moduli of the scaffold can be tuned to be comparable with bones in the human body. A new facile method has been developed to produce both homopolymers and block copolymers of PPF with new functionalities incorporated into the polymer chain. These new functionalities are able to undergo post-polymerization modification using 'click'-type addition chemistry either before or after 3D printing. The addition of proteins to the surface of the printed scaffold has been fully characterized, with the aim of improving the regrowth of critical size bone defects in conjunction with the degradation of the scaffold. Furthermore, as a consequence of the ability to incorporate a range of different functionalities, multiple non-competing post-polymerization modifications can be carried out on the same scaffold to attach different proteins to the surface.



POLY 288: Vesicle-to-worm transition provides a new high-temperature oil thickening mechanism

Matthew J. Derry, *m.derry@sheffield.ac.uk*, Oleksandr Mykhaylyk, Steven P. Armes.
Department of Chemistry, University of Sheffield, Sheffield, United Kingdom

Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization of benzyl methacrylate (BzMA) in mineral oil enables the *in situ* synthesis of diblock copolymer spheres, worms or vesicles.¹ Polymerization-induced self-assembly (PISA)²⁻⁴ occurs when using a soluble poly(stearyl methacrylate) (PSMA) macromolecular chain transfer agent (macro-CTA) to polymerize BzMA monomer to yield an insoluble second block, thus forming sterically-stabilized PSMA-PBzMA diblock copolymer nanoparticles. For a given copolymer, the final morphology is dictated by the mean degree of polymerization (DP) of the stabilizer block, the DP of the core-forming block and the copolymer concentration. In the present study, we report that PSMA₁₃-PBzMA₉₆ vesicles undergo a vesicle-to-worm transition on heating to 150 °C (see Figure 1), as judged by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Variable temperature ¹H NMR spectroscopy indicates that this transition is the result of surface plasticization of the core-forming block by hot solvent, effectively increasing the volume fraction of the stabilizer block and so reduces the packing parameter for the diblock copolymer chains. The rheological behavior of a 10% w/w copolymer dispersion in mineral oil is strongly temperature-dependent: the storage modulus increases by five orders of magnitude on heating above the critical gelation temperature of 135 °C, because the non-interacting vesicles are converted into weakly interacting worms. Detailed analysis of the SAXS data indicate that each vesicle produces on average three worms. Such vesicle-to-worm transitions offer an interesting new mechanism for the high-temperature thickening of oils.

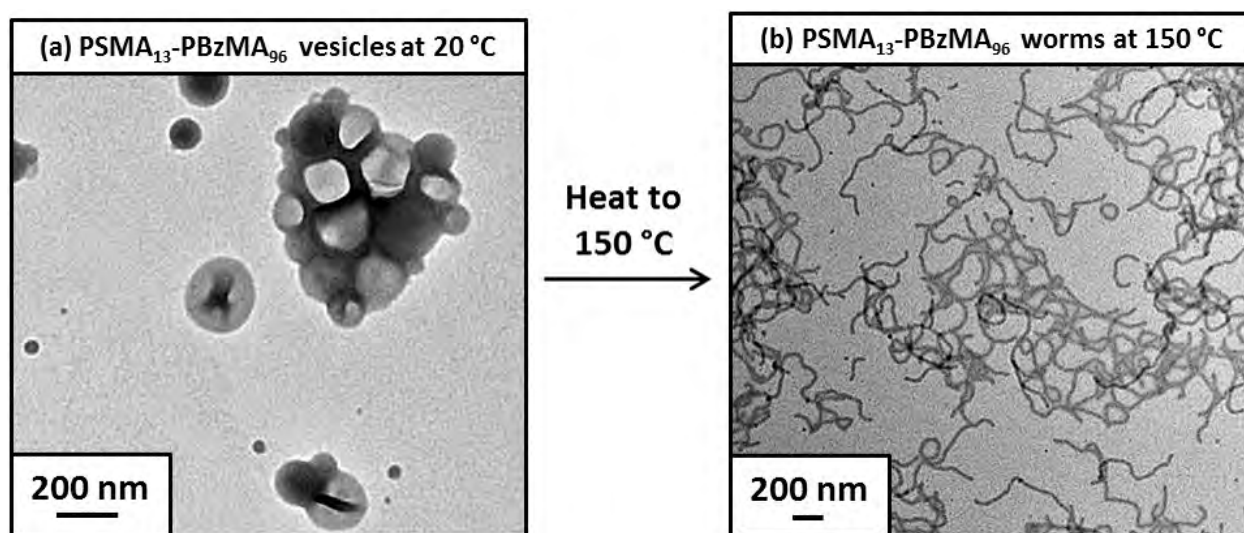
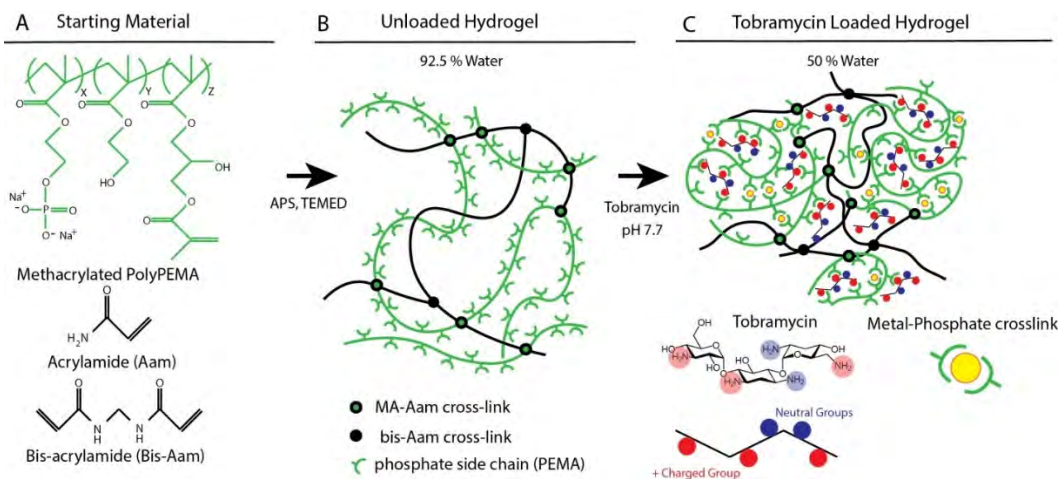


Figure 1. Transmission electron micrographs obtained for (a) 0.1% w/w PSMA₁₃-PBzMA₉₆ vesicles at 20 °C and (b) the highly anisotropic worms formed by the same vesicle dispersion on heating up to 150 °C.

POLY 289: Tough antibiotic-eluting double network hydrogels

Russell Stewart, *russell.stewart@utah.edu*, Dwight Lane. University of Utah, Salt Lake City, Utah, United States

Aquatic caddisworm silk is a tough multi-network natural fiber. The major toughening mechanism resides in serial Ca^{2+} -phosphoserine (pS) crosslinked nano-domains that comprise H-fibroin, the major structural protein in the fibers. Reversible strain induced rupture of the Ca^{2+} -crosslinked domains at a critical stress results in pseudo-plastic strain softening. When unloaded, refolding of the Ca^{2+} -crosslinked domains, directed by an elastic covalent network, resulted in nearly full recovery of fiber stiffness and strength. To mimic the natural toughening mechanism in a synthetic hydrogel, a simple H-fibroin polyphosphate analog was created by copolymerizing 2-(methacryloyloxy) ethyl phosphate (MOEP) and methacrylic acid. Methacrylate groups were grafted onto the carboxyl sidechains. The phosphate-graft-methacrylate prepolymer was crosslinked into hydrogels by polymerization with acrylamide. When incubated with Ca^{2+} ions, the double network (DN) hydrogels shrank to ~50% of their initial volume. Above a critical phosphate sidechain density, the Ca^{2+} loaded DN hydrogels qualitatively replicated the strain-rate dependent yield, toughness, and self-recovery properties of the natural silk fibers. The enhanced toughness was attributed to unfolding of clustered phosphate- Ca^{2+} crosslinks at a critical stress that mimicked the natural pS/ Ca^{2+} crosslinked b-domains. The polyphosphate DN hydrogels also shrank to 50% of their initial volume when incubated with tobramycin (tob), a polycationic aminoglycoside antibiotic. The tob-crosslinked hydrogels eluted tob at concentrations above the *Psuedomonas aeruginosa* minimum bacteriocidal concentration for >50 days. Hydrogels loaded with sub-stoichiometric Ca^{2+} concentrations relative to the concentration of phosphate sidechains, then loaded with tob, had mechanical properties similar to articular cartilage and provided sustained release of high concentrations of tob. The results suggest the polyphosphate-co-acrylamide DN hydrogels have potential as antibiotic eluting prosthetic biomaterials.

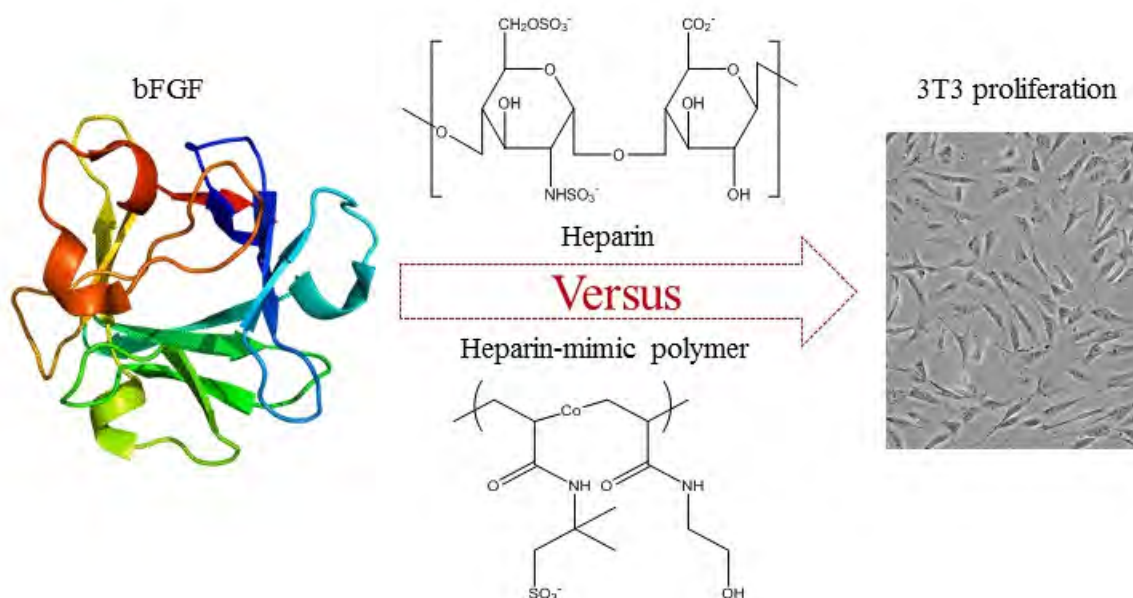


Tough Ca^{2+} -phosphate crosslinked DN hydrogels provide prolonged release of aminoglycoside antibiotics.

POLY 290: Polysulfonates with complex architectures as heparin mimics

bray caroline², *c.p.bray@warwick.ac.uk*, Raoul Peltier², Hyungsoo Kim¹, Antonio Mastrangelo³, Sebastien Perrier². (1) Mail Drop 152B, The Lubrizol Corporation, Wickliffe, Ohio, United States (2) University of Warwick, Coventry, United Kingdom (3) Lubrizol Limited, Derby, United Kingdom

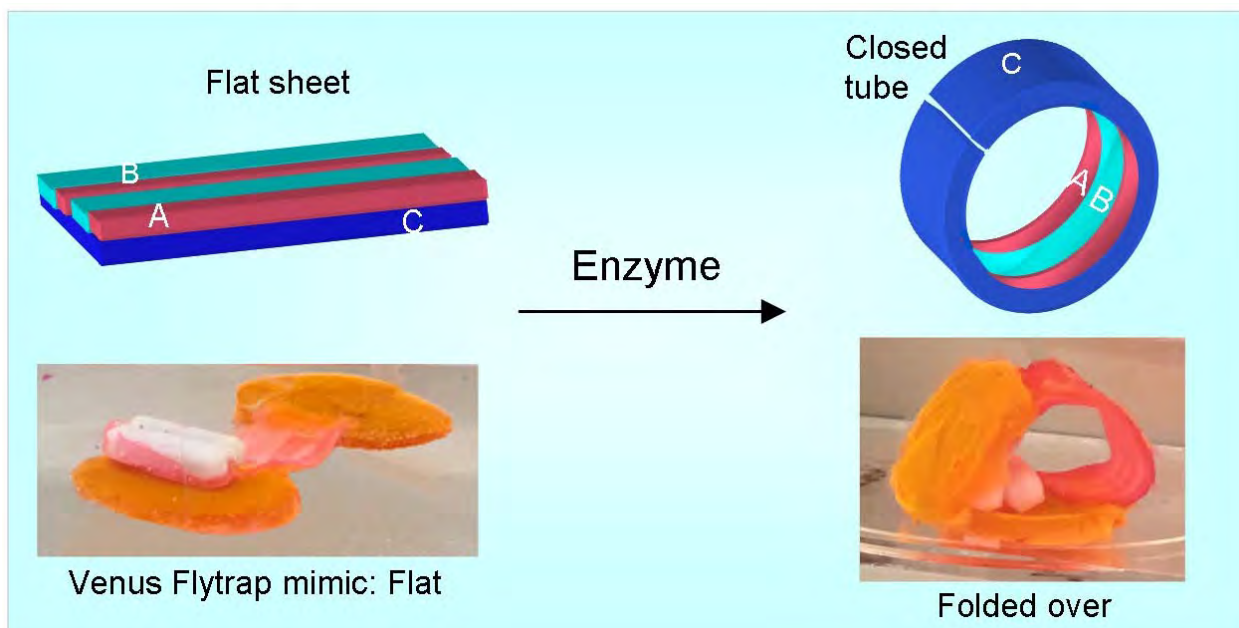
Polysulfonated polymers have recently attracted a lot of attention for various biological applications, this is due to their structural similarity with heparin. Here, we have studied the use of reversible addition-fragmentation chain-transfer (RAFT) polymerization to control the polymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) in aqueous solution, and obtained a range of well-defined homo- and block-polymers with various architectures. Excellent control over the polymerization enabled the synthesis of high-order multiblock polymers, as well as core cross-linked star copolymers with alternating AMPS and *N*-hydroxyethyl acrylamide (HEAm). The resulting materials have been evaluated for their ability to stabilize basic Fibroblast Growth Factor (bFGF), and promote the growth of fibroblast cells.



POLY 291: Nature-inspired hydrogels that change shape in response to external stimuli or to specific biomolecules

Srinivasa R. Raghavan, *sraghava@umd.edu*. *Chemical Biomolecular Engineering, University of Maryland, College Park, Maryland, United States*

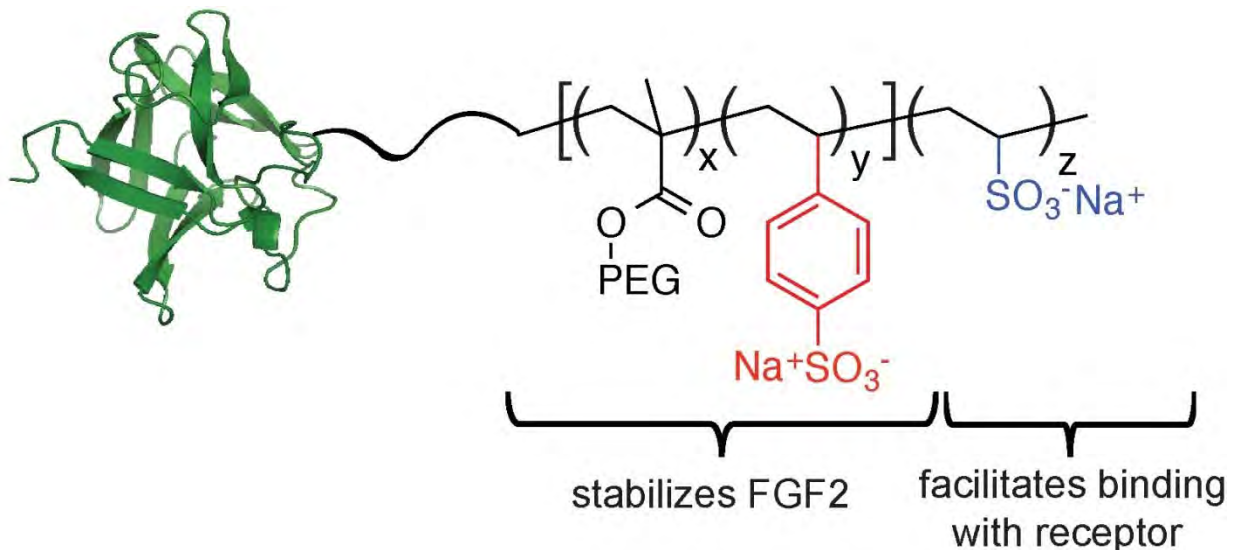
Materials found in nature frequently show an ability to change their shape or external morphology under different conditions. For example, the leaves of plants like the Venus fly trap transform from an open to a closed shape when an insect sits on it. Inspired by these natural systems, we have attempted to create hydrogels that undergo a change in their shape in response to external stimuli such as pH, temperature, light, or solvent quality. Towards this end, we have developed a method for creating hybrid hydrogels that comprise different gel types juxtaposed in predetermined zones or patterns. When such a hybrid gel is exposed to the stimulus of interest, only the portions of the hybrid that are responsive to the stimulus are affected. This introduces differential stresses in the material, which ultimately results in radical changes in shape. For example, we have made self-folding hydrogel sheets, where an initial flat sheet curls up into a folded tube under the action of the appropriate stimulus. An additional challenge in this area is to design gels that are responsive to specific solutes (e.g., proteins or enzymes, or small molecules such as glucose or fructose). In this regard, we have designed a hybrid gel containing specific regions of a degradable biopolymer. When exposed to a specific enzyme, the biopolymer regions are degraded, causing the overall gel to change its shape. This transformation in the gel is highly specific and occurs with very low (millimolar) concentrations of the biomolecule. Such shape-changing gels could have potential applications in biosensing, drug delivery and tissue engineering.



POLY 292: Synthesis of a superagonist heparin-mimicking block copolymer-FGF2 conjugate

Samantha Paluck², samantha.paluck@gmail.com, Thi H. Nguyen³, Jonghan P. Lee⁴, Heather D. Maynard¹. (1) UCLA, Los Angeles, California, United States (2) Chemistry and Biochemistry, UCLA, Roswell, Georgia, United States (3) Chemistry and Biochemistry, UCLA, Los Angeles, California, United States

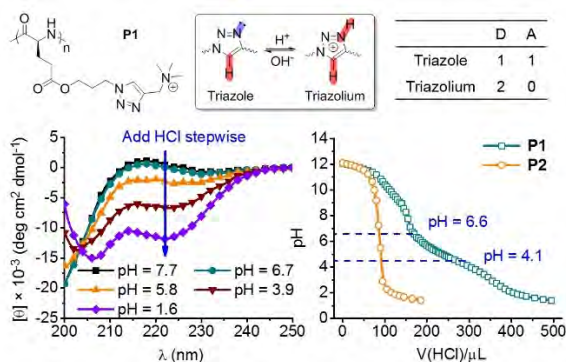
Fibroblast growth factor 2, or FGF2, is a heparin-binding protein involved in a variety of biological functions such as angiogenesis, cellular migration and stem cell self renewal. Because of its ability to stimulate these cellular functions, FGF2 is useful for applications in wound healing and tissue regeneration. However, the ability to increase the activity of FGF2 and stabilize it to storage are critical for its clinical success. Heparin, a highly sulfated glycosaminoglycan is known to both stabilize FGF2 and is also required for protein binding to fibroblast growth factor receptors. In this talk, we will report a heparin-mimicking block copolymer that was designed to both stabilize FGF2 and facilitate binding with its receptors. The heparin-mimicking block copolymer was covalently conjugated to FGF2 through disulfide exchange between a pyridyl disulfide end group on the polymer and an exposed cysteine on the protein. The resulting conjugate remained active after storage at 4C and 23C for 7 days, whereas free FGF2 showed loss in activity. The conjugate was also tested for receptor binding abilities and showed increased receptor binding when compared to FGF2 alone in both a cell based assay and a receptor based enzyme-linked immunosorbant assay (ELISA). Furthermore, the conjugate was shown to stimulate endothelial cell migration and tubulogenesis statistically better than FGF2 in *in vitro* based assays. Together, these data suggest that the heparin-mimicking block copolymer conjugate could be useful in therapeutic applications to replace FGF2.



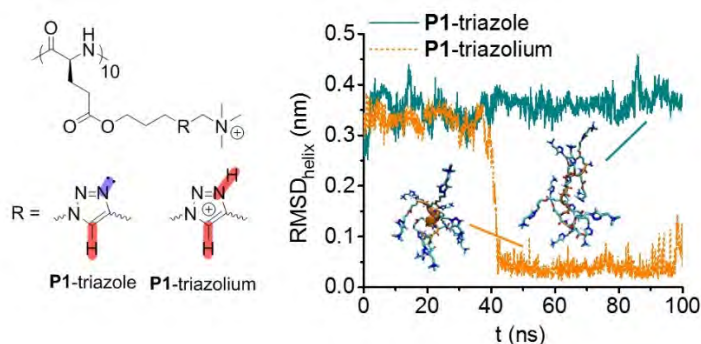
POLY 293: Triazole polypeptides: Regulation of polypeptide conformation through side-chain hydrogen bonding patterns

Ziyuan Song³, zsong5@illinois.edu, Rachael A. Mansbach², Ryan Baumgartner¹, Andrew Ferguson³, Jianjun Cheng³. (1) Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (3) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Molecular forces play an important role in protein folding and function, correlating the static conformation and the dynamic feature of proteins. The impact of these forces on the conformation, however, is not well studied due to the structure complexity of proteins. Herein we use polypeptides, synthetic analogs of proteins, to demonstrate the hydrogen bonding (HB) pattern of side-chains has a profound effect on backbone conformation. While polypeptides bearing side-chains with both HB donating and accepting ability adopt random coil structure, similar polypeptides missing either ability exhibit α -helical conformation. 1,2,3-Triazole, altering its HB patterns through protonation, was incorporated in polypeptide side-chains to reversibly alter the secondary structure of backbones in response to the change of pH. Molecular dynamics simulation shows the water molecules serve as the medium to connect the side-chain HB groups and backbone peptide bonds. This work not only provides fundamental understanding on HB in protein structure, but also affords interesting conformation-switchable polypeptide materials.



Chemical structure, hydrogen bonding pattern analysis, circular dichroism spectra, and titration curve of triazole polypeptides

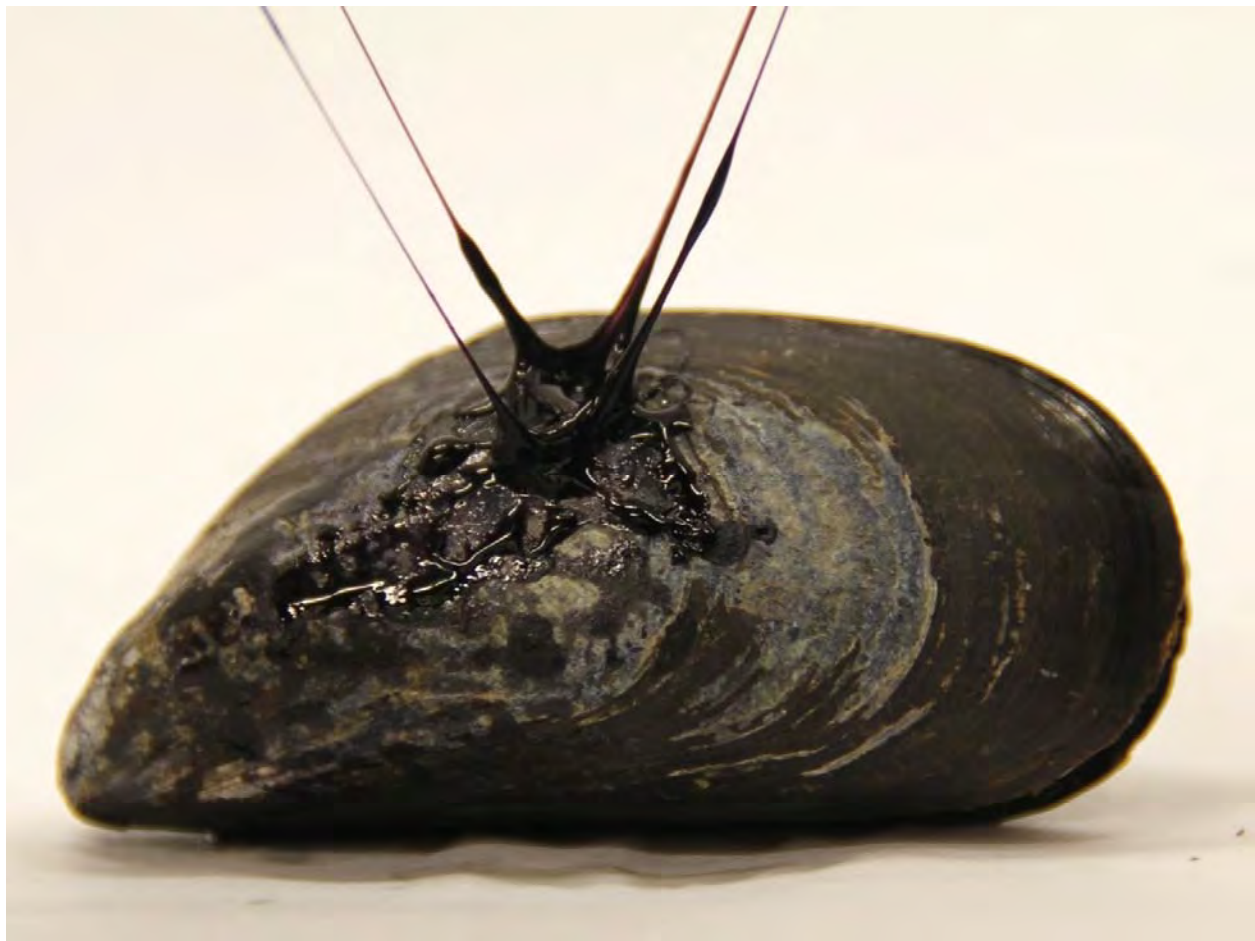


Molecular dynamic simulation of triazole polypeptides

POLY 294: Bio-inspired metal-coordination dynamics: An easy way to engineer gel viscoelastic mechanics

Niels Holten-Andersen, *holten@mit.edu*. *Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States*

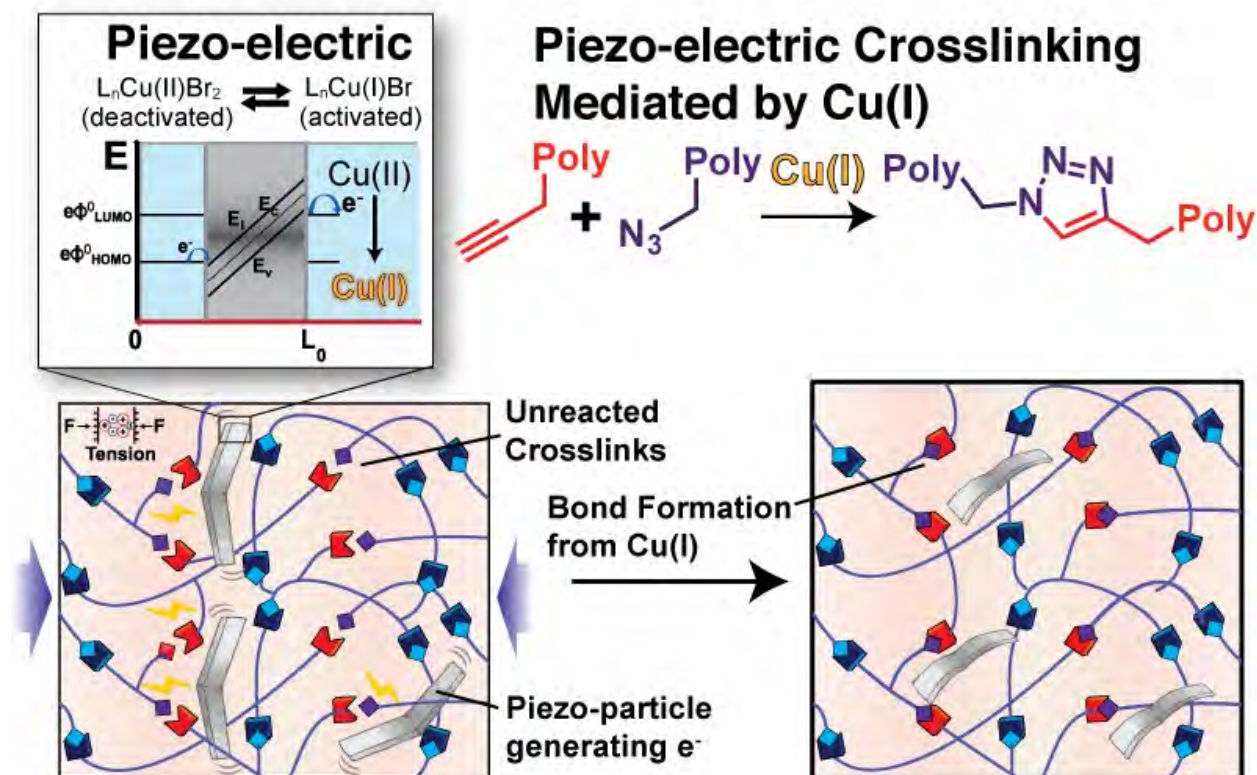
Growing evidence supports a critical role of metal-coordination complex crosslinking in soft biological material properties such as underwater adhesion and self-healing. Given their exploitation in such desirable material applications in nature, bio-inspired metal-coordinate complex crosslinking no doubt provides unique possibilities to further advance synthetic polymer materials engineering. Using bio-inspired metal-binding polymers, initial efforts to mimic these material properties have shown promise. In addition, novel opportunities for new fundamental insights on how polymer network mechanics can be strongly coupled to supramolecular crosslink dynamics are also emerging. Early lessons from studies of these supramolecular chemo-mechanical couplings will be presented.



POLY 295: Crosslinking acrylate-containing polymers by downstream piezoelectric reduction

Emily Sanders, emilycaitlinsanders@gmail.com, Hemakesh Mohapatra, Aaron P. Esser-Kahn. Chemistry, University of California, Irvine, Irvine, California, United States

Reinforcing a polymer by mechanical disruption is a concept that has yet to be deeply probed. We have recently seen that atom-transfer radical-polymerization (ATRP) can be controlled by the piezoelectric reduction of Cu(II) to Cu(I) by BaTiO₃. To expand this idea beyond ATRP, we tested the copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) with the piezo-reduction. We synthesized both azide- and alkyne-containing acrylate polymers by radical addition-fragmentation chain transfer (RAFT) polymerization. These materials can be strengthened by the inclusion of piezoelectric nanoparticles in copolymers that contain azide and alkyne moieties. When a shearing force is applied, the piezoelectric nanoparticles eject an electron that reduces Cu(II) to Cu(I) and CuAAC chemistry occurs. We monitored this reaction by IR and NMR and observed the expected changes in the spectra. Mechanical testing further demonstrated the structural changes as a result of crosslinking. These polymers will provide a novel platform for studying material responses to mechanical stress, and can be used for a variety of engineering applications.



A graphical representation of how the downstream reduction of piezoelectric particles can be coupled to copper(I)-catalyzed alkyne-azide cycloaddition chemistry.

POLY 296: Superhydrophobic coatings from Treated diatomaceous earth

Frank D. Blum¹, fblum@okstate.edu, **Bhishma R. Sedai**¹, **Helanka Perera**¹, **Abhijit Paul**¹, **Bal K. Khatiwada**², **Hamid Mortazavian**¹. (1) Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States (2) Chemistry, University of the Ozarks, Clarksville, Arkansas, United States

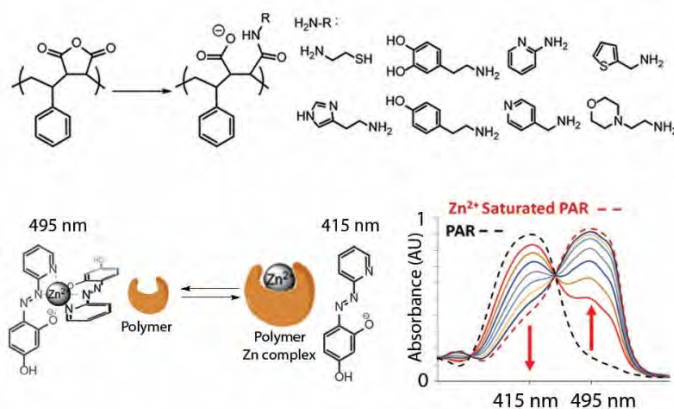
Superhydrophobic coatings were made using fluorosilane treated diatomaceous earth with different polymeric resins/binders. These coatings have been characterized with contact angle measurements, scanning electron microscopy and calorimetry. Contact angles greater than 150° were attainable if the particles were sufficiently coated with fluorinated coupling agents and also if there were enough particles in the coatings. The critical particle loadings depended on the resin/binder system used. The behavior of these surfaces mimics that from, for example, the lotus leaf as they had low surface energies and also appropriate nano-micro structures.



POLY 297: Protein-mimetics materials based on styrene-maleic anhydride copolymers

Anton A. Smith^{1,2}, aaas@berkeley.edu, **Shawn M. Darnall**¹, **Aaron Hall**¹, **Melissa Puga**¹, melissa_puga@live.com, **Ting Xu**¹. (1) Material Sci Eng, UC Berkeley, Berkeley, California, United States (2) Department of Chemistry, Aarhus University, Aarhus, Denmark

The advent of controlled radical polymerizations has narrowed the gap between synthetic and natural macromolecules. Synthetic polymers with structures and functions previously exclusive to biomacromolecules are now within reach of modern polymer chemistry. Through a judicious choice of monomers and postfunctionalization techniques we have used natural proteins as inspiration for biomimetic polymers. Specifically, the alternating copolymer of styrene and maleic anhydride offers an interesting platform for a facile synthesis of protein mimetics. These polymers, endowed with pendant groups akin to those of amino acids found in the active site of metal binding proteins, have been probed for metal binding capability. This has led to polymer libraries with a high heavy metal binding capacity, without the liability of oxidation of sulfides, a feature limiting the use of intracellular metal binding proteins outside their native environment. Moreover, the platform allows for the inclusion of pendant groups on these biomimetic polymers outside the grasp of biology, allowing the use of unnatural binding motifs to overcome the limitations of the chemistry of nature. Additionally, using RAFT polymerization it is possible to combine the advanced architectures possible through RAFT polymerization. Furthermore, an understanding of polymerization kinetics allows a degree of control over the distribution of monomers in the polymers, through the compositional drift endemic to the polymerization. This allows a facile synthesis of complex polymers, such as gradient to block copolymers depending on the experimental conditions chosen. The control architecture as well as pendant groups attached through postfunctionalization expand the possibilities of biomimetic polymers and materials. Altogether; we work to explore the gap between synthetic and natural polymers through the facile synthesis of vast biomimetic polymer libraries possible, in combination with the control of architecture possible through RAFT polymerization.



Styrene-maleic anhydride copolymers modified combinatorially and tested for heavy metal binding affinity.

POLY 298: Accessing poly(olefin)-block-poly(thiophene) copolymers via one-pot living polymerizations

Amanda Leone¹, akleone@umich.edu, Kendra Souther², Anne J. McNeil³. (1) Chemistry, University of Michigan, Ann Arbor, Michigan, United States (2) Chemistry, University of Michigan - Ann Arbor, Ann Arbor, Michigan, United States (3) University of Michigan, Dexter, Michigan, United States

Block copolymers self-assemble into morphologies unobtainable by their corresponding homopolymers. Block copolymers consisting of conducting and insulating segments have been used to tune conducting polymer morphology and improve physical and optoelectronic properties. However, their syntheses commonly require multiple catalysts and purification steps. We have identified a single catalyst capable of consecutively undergoing two distinct polymerization mechanisms to generate poly(thiophene)-*block*-amorphous poly(1-hexene) copolymers in one-pot in a living manner. The challenge with this approach is rooted in tuning a single catalyst for multiple, living polymerizations. Therefore, we are currently developing a hybrid single-catalyst, one-pot synthetic approach for block copolymerization through in-situ catalyst modification. Preliminary results suggest copolymers with targeted insulating block topologies e.g., branched (amorphous), linear (semi-crystalline), etc. will be accessible via this method, enabling systematic evaluation of polythiophene's optoelectronic response to variation in the insulating block topology, crystallinity, and molecular weight. Ultimately we aim to apply these methods to a variety of monomers to facilitate block copolymer synthesis and material analysis.



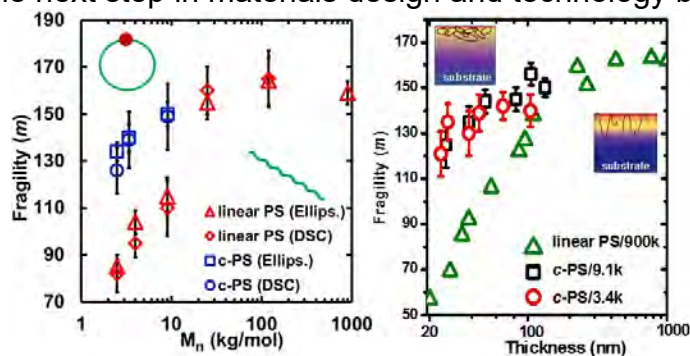
POLY 299: Distinct thermophysical and interfacial properties associated with low molecular weight cyclic polystyrene in bulk and confined states: T_g , fragility, and thin film stability

Lanhe Zhang², lanhezhang2012@u.northwestern.edu, Ravinder Elupula³, Scott M. Grayson³, John M. Torkelson^{2,1}. (1) Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, United States (2) Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States (3) Chemistry Department, Tulane University, New Orleans, Louisiana, United States

Cyclic polymers represent an exciting class of topologically distinctive polymers. The influence of “end-to-end” tethering and the unusual conformational properties associated with cyclic topologies have prompted studies of bulk properties such as viscosity, T_g , and crystallization. On the other hand, very few studies have investigated properties of ring polymers in confined films.

High purity cyclic polystyrene (c-PS) was obtained via ATRP and “click” chemistry with high monodispersity and nearly quantitative conversion of the linear precursor. In the absence of chain ends, bulk c-PS samples exhibit very weak T_g - and fragility-MW dependences compared to linear PS. In stark contrast to the substantial T_g -confinement effects in linear PS supported on silica, low MW c-PS exhibits a nearly complete suppression of this confinement effect. Due to its very limited conformational mobility, the cyclic topology strongly restricts polymer-substrate interactions. Therefore, the near elimination of the T_g -confinement effect in c-PS originates mainly from a very weak perturbation to T_g near the free surface (in comparison to linear PS). Upon nanoscale confinement, linear PS films have been shown to have significantly reduced fragility compared to bulk. Despite having similar bulk fragility as high MW linear PS, low MW c-PS films show major suppression in fragility reduction with decreasing thickness. Due to a lack of chain ends, properties associated with the low MW ring structure are not prone to be perturbed by either MW reduction or confinement. This result indicates a strong correlation between the susceptibility of fragility perturbation and the susceptibility of T_g perturbation, caused by chain topology and/or by confinement.

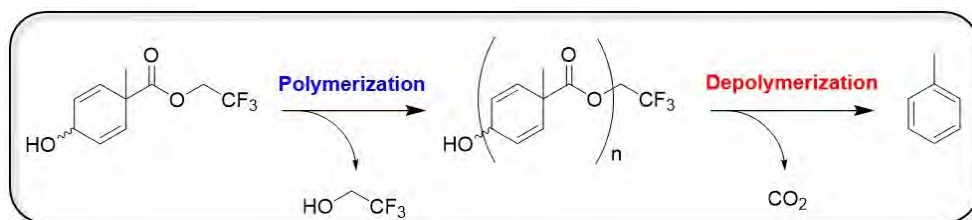
Lastly, c-PS thin films exhibit superior thermal stability against dewetting compared to their linear analogues, making novel cyclic polymer architectures attractive materials for practical usage. Taking advantage of different chain topologies and their specific attributes may be the next step in materials design and technology breakthrough.



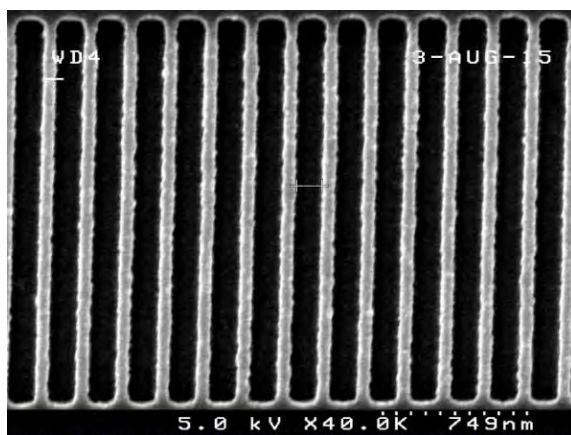
POLY 300: Unzipping polyester as a new photoresist material

Wontae Joo¹, wtjoo864@gmail.com, Austin Lane², Di Liu¹, Kensuke Matsuzawa², Ryan A. Mesch¹, Wade Wang², Benjamin Cassidy¹, Andrew Dick², Scott T. Phillips³, Carlton G. Willson². (1) Chemistry, The University of Texas at Austin, Austin, Texas, United States (2) Dept Chem Eng, Univ Texas Austin, Austin, Texas, United States (3) Pennsylvania State University, University Park, Pennsylvania, United States

The preparation and study of a self-immolative, aromatizing polyester for use in a new photoresist design is described. It was challenging to meet the long list of requirements that the new material must meet for this end use. The new polymer, a polyester was successfully prepared by two distinctively different synthetic routes and fully characterized. The polymer “unzips” upon irradiation with short wavelength light, driven by an aromatization reaction that releases carbon dioxide and toluene. When the polymer is blended with a matrix resin, such as m-cresol novolac, the generation of the small molecules changes the solubility of the matrix. A single photochemical event results in breaking many, many covalent bonds, hence the formulated system demonstrates high sensitivity of the sort seen in chemically amplified resists (CARs). However, in principle, the new resist does not suffer from the bias and image blur that are characteristic of the CAR design because the key, unzipping reaction does not require acid diffusion and the reaction once initiated is confined to a single chain. The novolac resist formulation is a positive tone electron beam resist with sensitivity very much higher than that of common resists such as PMMA and ZEP in which the solubility change is generated by chain scission.



Polymerization and Depolymerization of Unzipping Polyester

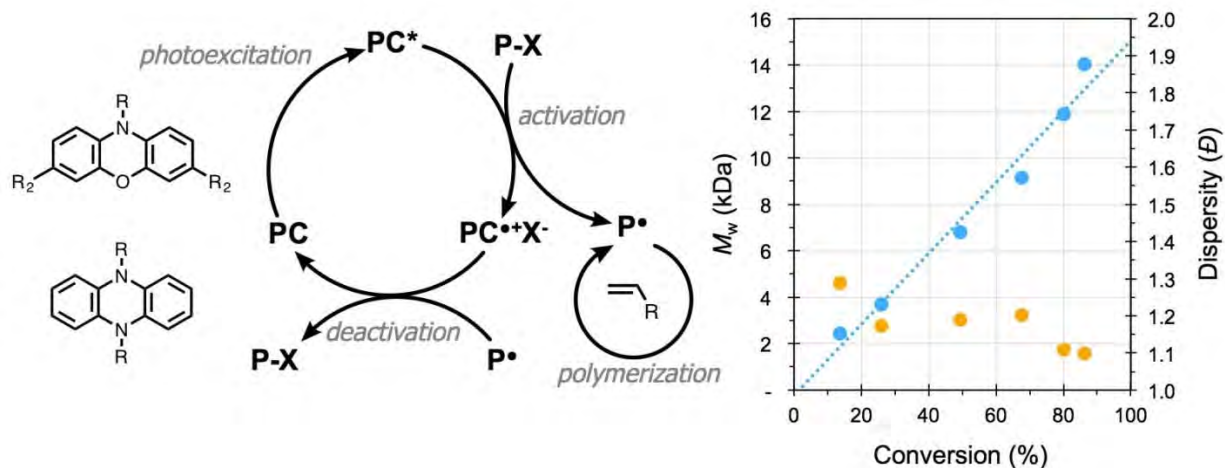


Electron Beam Lithography of Unzipping Polyester

POLY 301: Organocatalyzed atom transfer radical polymerization via photoredox catalysis

Ryan M. Pearson², rpearson98@gmail.com, Garret Miyake¹. (1) University of Colorado Boulder, Boulder, Colorado, United States (2) Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado, United States

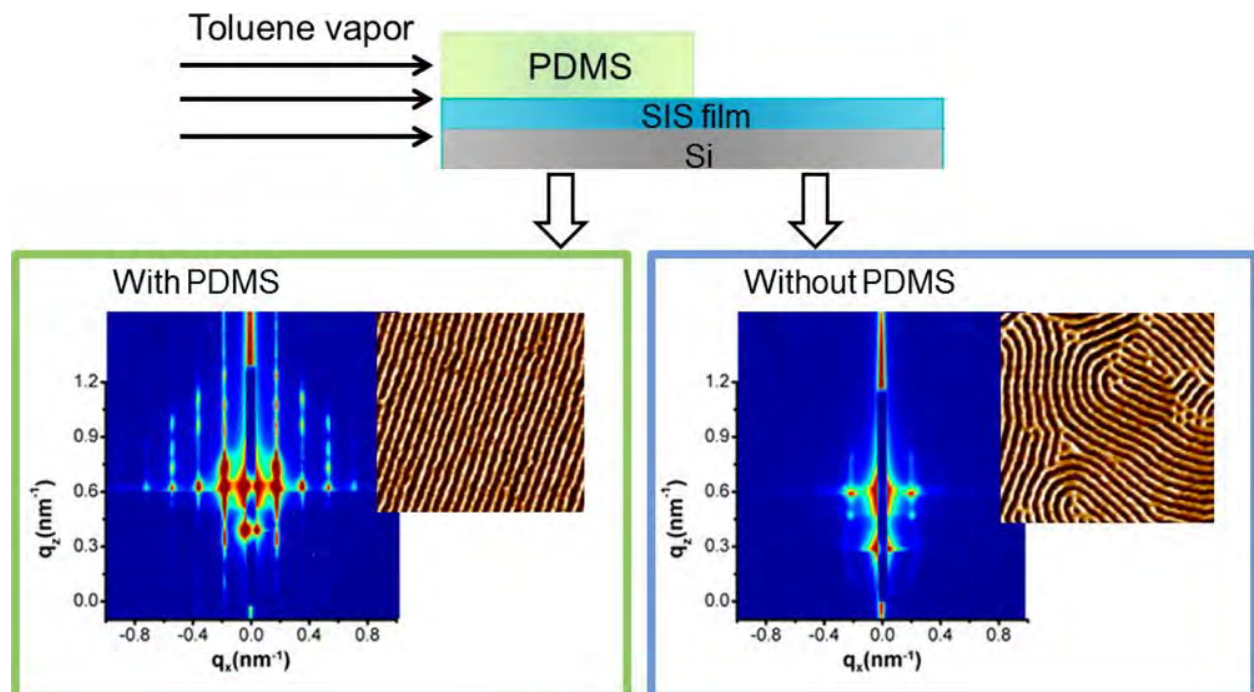
Two classes of highly reducing organic photoredox catalysts, N,N' diaryl phenazines and N-aryl phenoxazines have been synthesized and employed in organocatalyzed atom transfer radical polymerization (ATRP) for the production of well-defined polymers using visible light. The redox potentials and absorption profiles are readily tuned allowing us to gain further insight into the polymerization mechanism and achieve greater control over the polymerization for the synthesis of macromolecules with predictable molecular weights and low dispersities.



POLY 302: Simple, generalizable method towards highly aligned functional polymeric films

Zhe Qiang, zq7@zips.uakron.edu, Kevin A. Cavicchi, Bryan D. Vogt. University of Akron, Akron, Ohio, United States

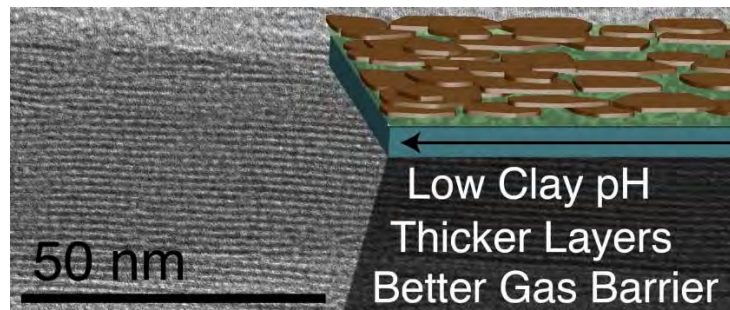
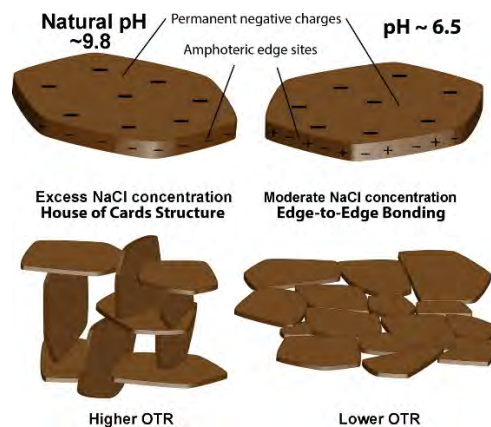
Macroscopic alignment of block copolymer domains in thin films is desired for many applications, such as cell responsive surfaces or optical polarizers. Alignment generally requires specialized tools that apply external fields, shear force gradient, or produce topological patterned substrates. This requirement limits the broad academic application of aligned BCPs. Here, we describe a simple modification of commonly utilized solvent vapor annealing (SVA) process for macroscopic alignment of BCPs. Adhering a flat, crosslinked elastomer pad to the BCP film leads to differential swelling between the elastomer pad and BCP to produce a shear force that aligns the ordered BCP domains. The impact of processing parameters including physical properties of PDMS pad, on the quality of alignment quantified by the Herman's orientational factor (S) is systematically examined. Moreover, this SVA-S process has been successfully applied to align a wide variety of BCP and composite systems. With addition of carbon precursors in the system, highly aligned large-pore mesoporous carbon films can be fabricated using SVA-S method. This highly aligned mesoporous carbon films exhibit a more narrow pore size distribution compared to unaligned analogous. Moreover, the electrical conductivity becomes anisotropic with nearly 40% difference between parallel and perpendicular directions of the cylindrical mesopores. Additionally, highly aligned polystyrene-*b*-polydimethylsiloxane (PS-*b*-PDMS) can be used to produce directional silica lines. Using a bilayer film, the center-to-center distance of these features was effectively halved. Similarly, by sequential shear-alignment of two distinct layers, a rhombic array of silica nanolines was fabricated.



POLY 303: High oxygen gas barrier multilayer thin films through pH and ionic strength manipulation of montmorillonite clay

Yixuan Song², *dorianxuan@tamu.edu*, **David Hagen³**, **Jaime C. Grunlan¹**. (1) Texas A M Univ, College Station, Texas, United States (2) Materials Science and Engineering, Texas A&M University, College Station, Texas, United States (3) Mechanical Engineering, Texas A&M University, Bryan, Texas, United States

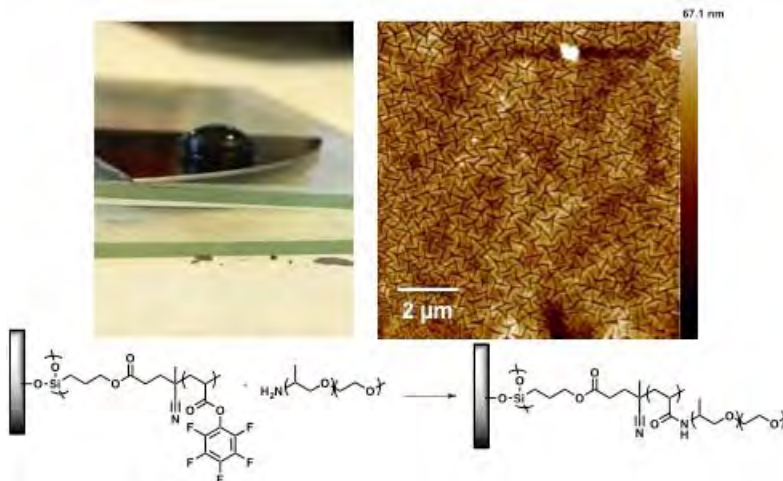
With a highly tortuous and ordered nanobrick wall structure, polyelectrolyte-montmorillonite (MMT) clay multilayer nanocoatings can dramatically reduce the oxygen transmission rate (OTR) of polymer film used in various packaging applications (e.g., PET and oriented polypropylene) by several orders of magnitude. In an effort to produce high oxygen barrier with fewer deposition steps, pH and ionic strength of the MMT aqueous suspension were altered. A 10 bilayer (BL) polyethylenimine (PEI)/MMT film, assembled with pH 4 clay, exhibited 5X reduction in OTR relative to a similar thin film assembled with unaltered clay (pH ~ 10). In a related approach, NaCl was used as an “indifferent electrolyte” to alter the rheological behavior of the MMT suspension. An “edge-to-edge” bonding network is formed with moderate NaCl concentration, leading to greater film thickness, better clay coverage (and alignment) and ultimately better oxygen barrier. An 8 BL PEI/MMT multilayer coating, assembled with 5 mM NaCl in the aqueous clay suspension, exhibited an order of magnitude reduction in oxygen permeability relative to its salt-free counterpart. These strategies reduce the number of layers necessary for high gas barrier, potentially making these multilayer films interesting for commercial packaging applications.



POLY 304: Controlling and manipulating crease formation in polymer brush platforms

Karson Brooks², ksbrooks@uga.edu, Mir J. Razavi³, Xianqiao Wang³, Jason J. Locklin¹. (1) Univ of Georgia Riverbend Rsch, Athens, Georgia, United States (2) Chemistry, University of Georgia, Athens, Georgia, United States (3) Engineering, University of Georgia, Athens, Georgia, United States

Precisely controlling the topography in thin film coatings is advantageous as morphology plays a large role in surface characteristics, such as wetting and adhesion. Previously, we reported a way to fabricate nanoscale surface creases using micro-contact printing to perform post-polymerization modification (PPM) on reactive polymer brush surfaces with a high degree of control over crease size and shape. Using poly(pentafluorophenyl acrylate) brushes, surfaces that are highly susceptible to nucleophilic attack by primary amines, creases are formed upon reaction with oligomeric and polymeric amine-bearing molecules under confinement due to substantial stresses generated upon reaction and the formation of a bilayer system that contains a significant modulus mismatch. In this talk, we will report a detailed investigation of this phenomena using further analysis of the experimental variables including polymer miscibility and end-group reactivity. Isolation and manipulation of these variables provide further insight into the factors governing buckling instabilities and crease formation in reactive thin film platforms.



POLY 305: Tuning CO₂-philicity in highly permeable polymeric membranes for gas separation

Tao Hong², *thong1@vols.utk.edu*, **Hongbo Feng**², **Sophia Lai**¹, **Shannon M. Mahurin**¹, **De-en Jiang**³, **Brian K. Long**², **Jimmy W. Mays**^{2,1}, **Alexei P. Sokolov**^{2,1}, **Tomonori Saito**¹.
(1) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Chemistry, University of Tennessee Knoxville, Knoxville, Tennessee, United States (3) University of California, Riverside, Riverside, California, United States

Due to the extensive use of fossil fuels, the global CO₂ emissions have increased steadily over the past several decades, contributing to unpredictable climate changes. Passive membrane CO₂ separation technology is considered as a promising approach to mitigate the issue. However, materials with high CO₂ permeability and good gas selectivity are needed for use in these membranes, and no one current materials can meet these requirements. Traditional gas separation membranes based on size-sieving mechanism are not efficient for separation of CO₂, because its size is similar to that of N₂ and O₂, other main components of the flue gas. Our work is based on the incorporation of CO₂-philic groups, e.g. amidoxime and polyethylene oxide, into high permeable polymer matrix, e.g. polydimethylsiloxane and poly (1-trimethylsilyl-1-propyne), to achieve a better gas solubility selectivity in order to increase the overall gas separation performance. Varying the degree of functionalization in our membranes with CO₂-philic groups resulted in a tunable gas separation performance, and some representative membranes demonstrated performance above the Robeson upper bound line (Figure 1), which indicates their advanced performance over the majority other current membranes. It is especially important that the Robeson upper bound is crossed at high CO₂ permeability that is crucial for treatment of enormous flue gas volumes. A variety of characterization techniques, e.g. gas sorption, rheology, quartz crystal microbalance and broadband dielectric spectroscopy measurements are performed to elucidate the key parameters necessary for achieving excellent performance of the synthesized membranes. Moreover, the employed Density Functional Theory and Grand Canonical Monte Carlo calculations of CO₂-polymer interactions provide further insight for the permeation mechanism in the polymeric membranes, as well as offering a guide for future membranes development.

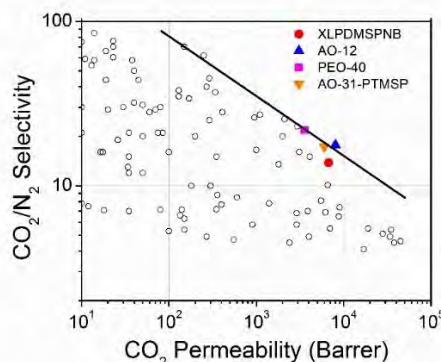
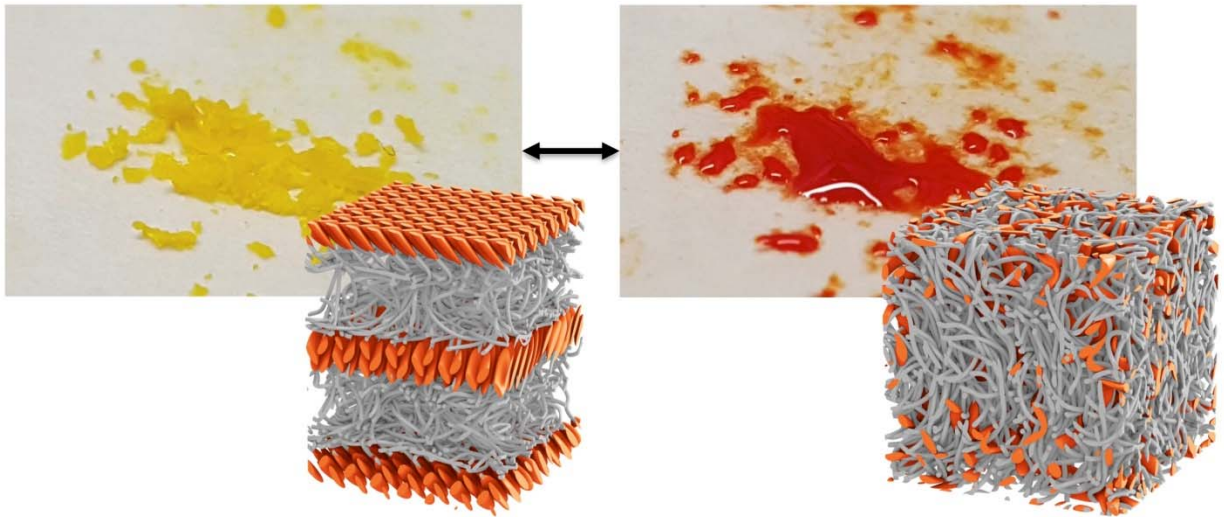


Figure 1. Representative data of developed polymeric membranes in Robeson plot.

POLY 306: Self-Assembly of exfoliated monolayer crystals as photoswitchable soft matter

Runye H. Zha^{1,2}, *helen.zha@berkeley.edu*, José A. Berroca², Ghislaine Vantomme², Ronald Gosens³, Bas de Waal³, Egbert W. Meijer^{2,3}. (1) Department of Materials Science & Engineering, University of California, Berkeley, Berkeley, California, United States (2) Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands (3) Macromolecular Science and Technology, Eindhoven University of Technology, Eindhoven, Netherlands

Molecules that bridge the gap between block copolymers and liquid crystals have become a recent field of interest, as these molecules can exhibit both polymeric and small molecule self-assembly behavior. Here, we present a class of well-defined functionalized oligodimethylsiloxanes that form multi-domain nanomaterials with different morphologies based on the balance between self-assembly forces. Of particular interest is the assembly of supramolecular materials that consist of crystalline monolayers exfoliated by regularly spaced liquid domains. These materials have highly ordered molecular organization as well as high molecular mobility and thus exhibit fascinating properties. Using photoisomerizable azobenzene motifs, we apply this exfoliated monolayer crystal morphology towards the synthesis of materials with dramatic light-driven phase transformations for photolithography or adhesive applications.



POLY 307: N-annulated perylenes. Outstanding scaffolds to build up functional supramolecular polymers

Luis Sánchez, *lusamar@ucm.es*, Julia Buendía, Elisa E. Greciano, Jorge S. Valera, Yeray Dorca, Rafael Gómez. *Química Orgánica I, Universidad Complutense de Madrid, Madrid, Spain*

The construction of supramolecular structures with specific size, shape and function by self-assembly is ubiquitous in chemistry, materials science and biology. The interaction of molecules by non-covalent forces generates supramolecular polymers that can show properties (optical, chiroptical, mechanical, etc...) not presented by the isolated block molecules. *N*-annulated perylene derivatives are very useful π -conjugated platforms to attain processable materials with highly anisotropic electronic properties. The decoration with suitable functional groups allows the utilization of such scaffolds to build up functional supramolecular polymers. Herein, we present a number of supramolecular polymers constructed from *N*-annulated perylene carboxamides that form luminescent organogels (**1**), act as self-assembling atropisomers (**2**) or can be used for living supramolecular polymerization.

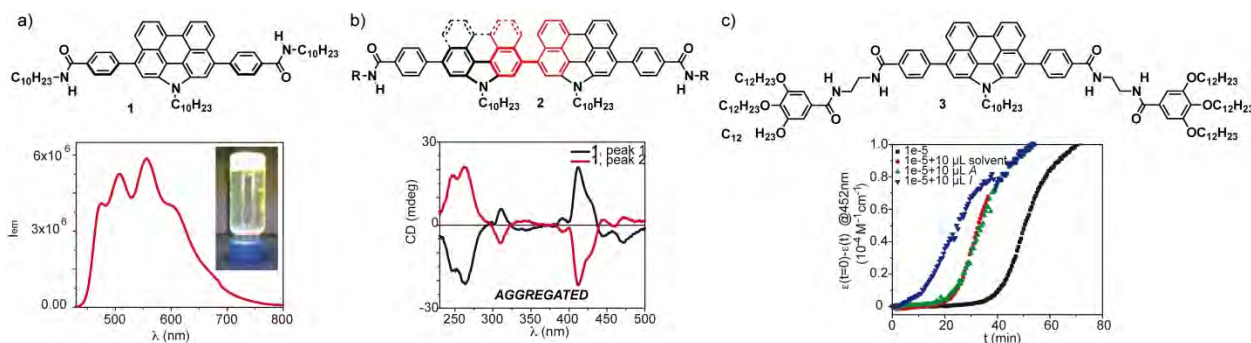
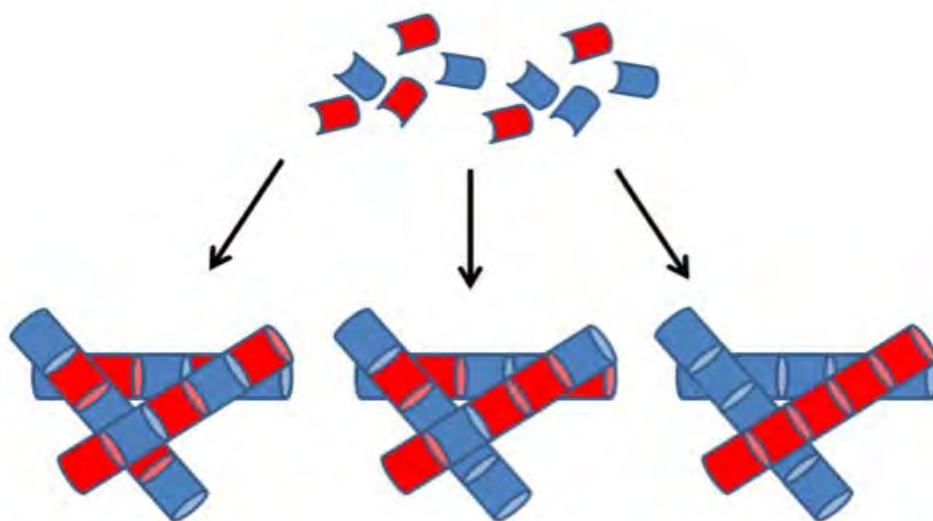


Figure 1. Chemical structures of different *N*-annulated perylenecarboxamidas utilized to build up supramolecular polymers exhibiting high luminescence (a), atropisomerism (b) and living supramolecular polymerization (c).

POLY 308: Controlling the assembly of multicomponent supramolecular gelator systems

Emily Rose Draper², Catherine Colquhoun⁴, Emily Cross¹, **Dave Adams**³,
d.j.adams@liverpool.ac.uk. (1) DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GLASGOW, LIVERPOOL, United Kingdom (2) School of Chemistry, University of Glasgow, Glasgow, United Kingdom (3) UNIVERSITY OF GLASGOW, Glasgow, United Kingdom (4) University of Leeds, Leeds, United Kingdom

Multi-component low molecular weight gelators can be used to prepare gels with a higher degree of complexity and information content than single component systems. However, controlling how the different components behave in the presence of one another is difficult. For example, if one component gels first, it is unclear how, if at all, the second component modifies the network that is growing. Once the first network has formed, the second network must grow in the presence of the first; again, it is not clear if this has any effect. Here, we will discuss our work on two component systems and show examples of self-sorting, as well as co-assembly. We focus on controlling this assembly, and the effect of the different possibilities on the final properties of the gels.

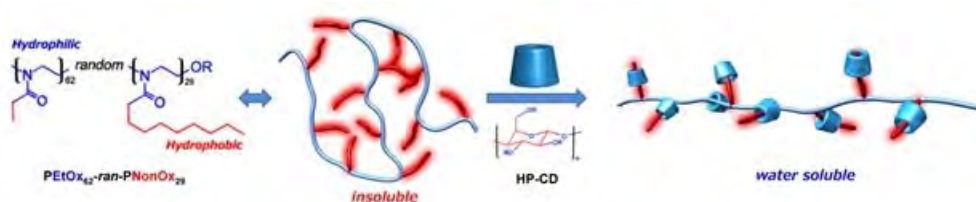


POLY 309: Supramolecular control over thermoresponsive polymers

Richard Hoogenboom, *richard.hoogenboom@ugent.be*. Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium

Thermoresponsive polymers facilitate the development of a wide range of applications in multiple areas spanning from construction or water management to lab-on-a-chip technologies and biomedical sciences. The combination of thermoresponsive polymers with supramolecular chemistry, inspired by the molecular mechanisms behind natural systems, is resulting in adaptive and smart materials with unprecedented properties. In this contribution, we will first demonstrate the utilization of thermoresponsive poly(2-oxazoline)s as basis for smart polymeric sensors. This first part will deal with thermoresponsive copolymers based on 2-ethyl-2-oxazoline and 2-nonyl-2-oxazoline (see Figure). By shielding the hydrophobic nonyl side chains with supramolecular host-guest complexation with cyclodextrins, not only the phase transition temperature can be tuned but also large hysteresis (up to 40K) is observed. This hysteresis results from the formation of a meta-stable soluble state based on cyclodextrin host-guest complexation. When heating this solution above its phase transition temperature at 50 °C, the hydrophobic association of the free nonyl side chains prevents redissolution until the solution is cooled down to the original phase transition of the polymer without cyclodextrin, which is around 10 °C. Importantly, this large hysteresis window could be exploited as memory function for the thermal history of the solution.

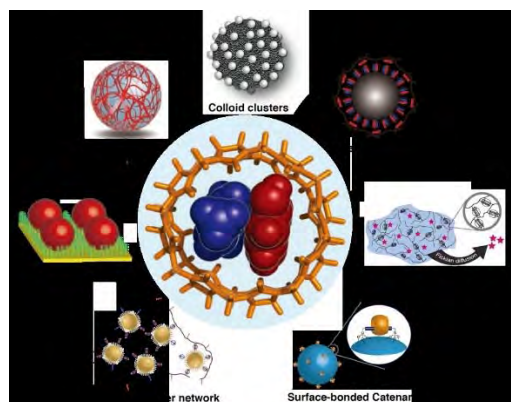
Secondly, a crosslinked polymer hydrogel decorated with dialkoxynaphthalene as electron-rich supramolecular guest molecules are reported to swell upon complexation with the tetracationic cyclobis(paraquat-*p*-phenylene) electron poor macrocyclic host. Combining this hydrogel with a thermoresponsive polymer that contains a stronger binding electron rich tetrathiafulvalene host in solution allows shuttling of the macrocyclic host between the solution and the hydrogel. As such, this multicomponent supramolecular system reveals heating induced swelling of the hydrogel and cooling induced shrinkage.



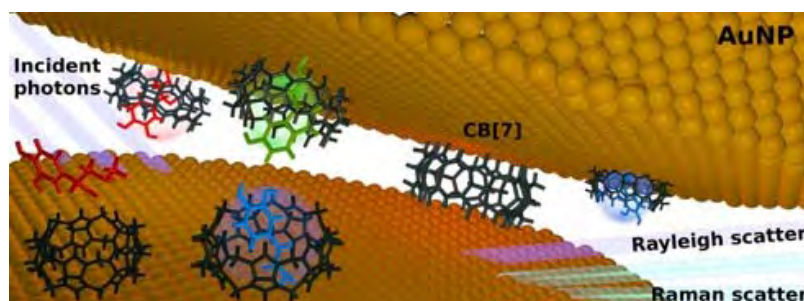
POLY 310: Control of functional materials and supramolecular network dynamics at both the molecular and colloidal length scales

Oren A. Scherman, *oas23@cam.ac.uk. Univ Cambridge Melville Lab, Cambridge, United Kingdom*

Cucurbit[*n*]urils (CB[*n*]) are macrocyclic molecules made of glycoluril monomers linked by methylene bridges, where *n* is the number of glycoluril units. CB[*n*] are excellent host molecules as they form stable yet dynamic complexes with guest compounds in aqueous media with extremely high affinity. The larger homologue CB[8] is capable of simultaneously accommodating two guests to form either 1:1:1 heteroternary or 2:1 homoternary complexes with association constants up to 10^{15} M^{-2} through multiple non-covalent interactions.^[1] Our group has exploited CB[8]'s unique host-guest binding properties as a linking motif to prepare supramolecular polymers, micelles, hydrogels, microcapsules, hierarchical structured colloids and colloid/polymer hybrid materials.^[1-5] The interactions of CB[*n*] with gold colloids has also been an area of interest within the group. The use of CB[*n*] as a molecular ruler to control the aggregation of Au NPs and subsequently bind and detect analyte molecules at room temperature within their cavity is a major area of research in the group.⁶ Simple, robust CB[7]-AuNP constructs have shown the ability to detect neurotransmitters through the formation of 1:1 complexes using SERS. Moreover, this system is capable of performing quantitative multiplexing in biological media such as urine.⁷ In this lecture I will highlight recent advances we have made in controlling dynamic functional materials and sensors based on CB-mediated host-guest interactions.



Functional materials based on CB[8]-mediated host-guest interactions at interfaces.

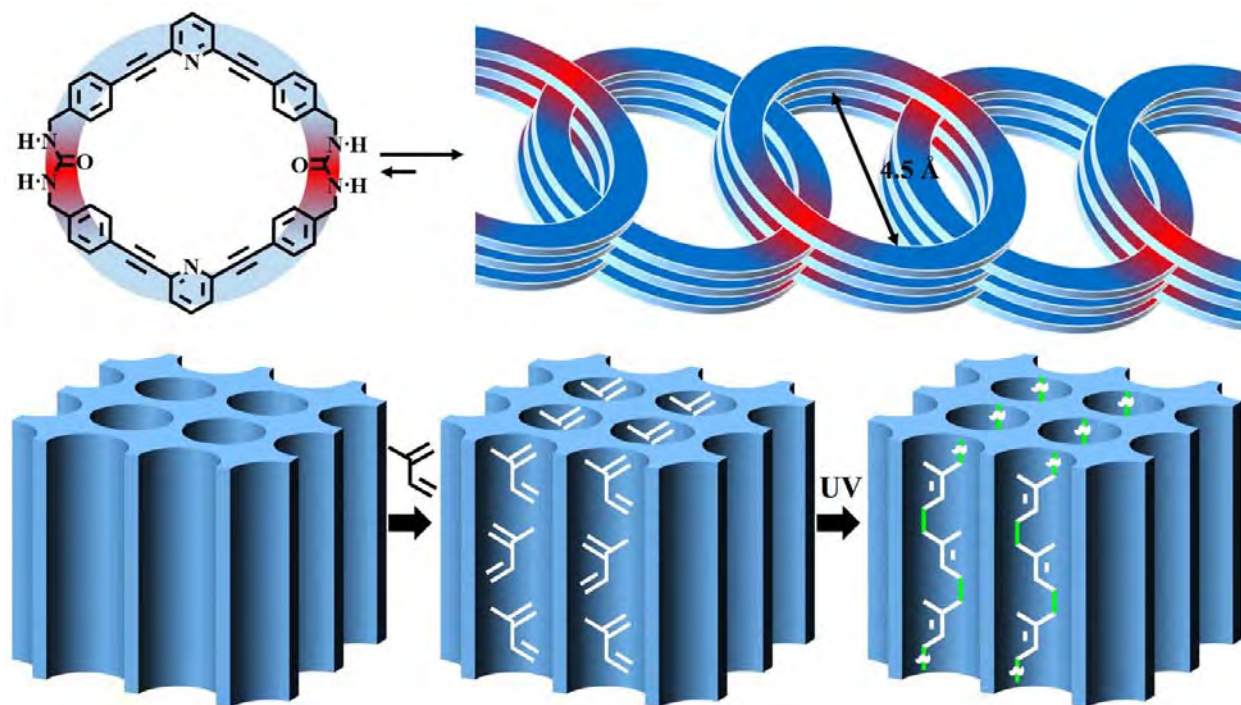


(Left) Multiplexing of neurotransmitters in CB[7]-Au NP aggregates. (Right) Single molecule detection at RT.

POLY 311: Functional materials from self-assembled *bis*-urea macrocycles

Linda S. Shimizu, SHIMIZLS@mailbox.sc.edu, Sahan R. Salpage, Bozume Som, Ammon J. Sindt. Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States

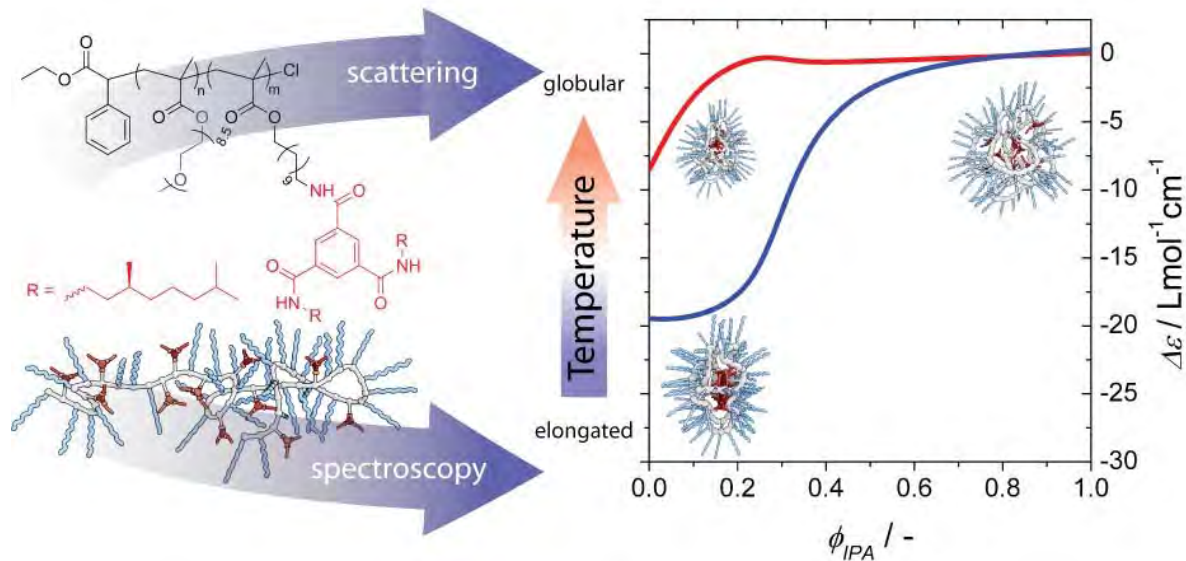
Porous materials are applicable to nanofluidics, to catalysis, and to gas storage and can be used as controlled nanoenvironments to stabilize reactive species or facilitate selective reactions. Our group has focused on macrocyclic building blocks that are constructed from urea groups and organic C-shaped spacers. These building blocks are remarkably robust and assemble in high fidelity. Simple 1-dimensional channels are advantageous for studying basic processes of transport and diffusion. This talk explores the optimal design of these building blocks and examines the applications of these homogeneous channels as confined environments for photocycloadditions and polymerization reactions. Small pores and channels offer a handle for influencing selectivity of reactions performed in their nanoenvironments. The ~ 4.5 Å diameter channels of pyridyl-phenylethynylene *bis*-urea macrocycles facilitated the photoinitiated and stereoselective oligomerization of isoprene to afford *trans*-1,4 polyisoprene with low dispersity. The larger ~ 9 Å diameter channels of the assembled phenylethynylene *bis*-urea macrocycles were able to absorb a wide range of coumarin, chromone, substituted styrene and vinyl-pyridines. UV-irradiation of these host-guest complexes induced selective photodimerizations and polymerizations in these nanochannels.



POLY 312: Impact of solvency and secondary structure on the conformation of single chain polymeric nanoparticles

Gijs ter Huurne, Lafayette de Windt, Anja Palmans, Egbert W. Meijer, Ilja Voets, i.voets@tue.nl. Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands

Single polymeric chains can be 'folded' into single chain polymeric nanoparticles (SCPNs) to prepare functional water-soluble nanostructures through intramolecular assembly of pendant structuring motifs. Here we present an overview of our recent work on SCPNs focusing on the delicate interplay between solvency and helical secondary structure on the conformation of water-soluble copolymers with pendant chiral benzene-1,3,5-tricarboxamides (BTAs) as revealed by scattering methods and circular dichroism spectroscopy.

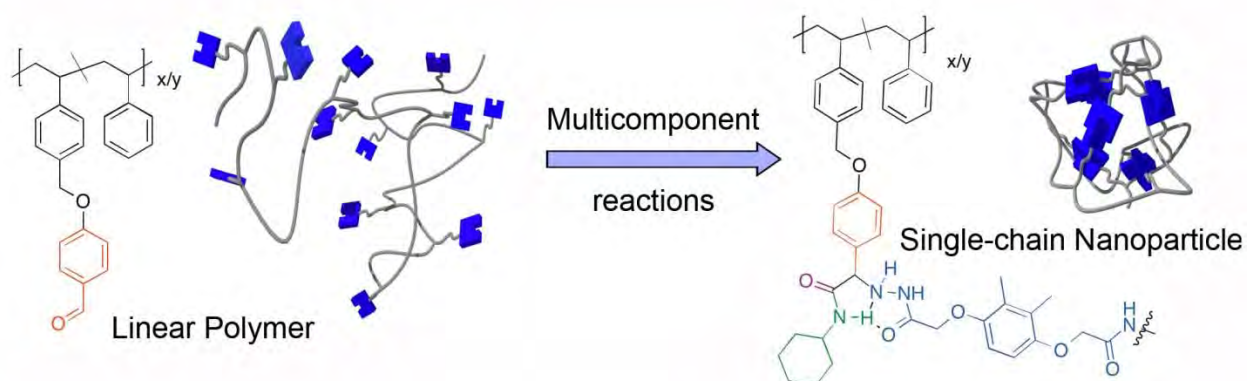


Impact of the secondary structure arising through intramolecular assembly of pendant chiral benzene-1,3,5-tricarboxamides (BTAs) on the conformation of oligo(ethylene glycol) methyl ether methacrylate-based polymers. Reproduced with permission. Copyright 2013 American Chemical Society.

POLY 313: Single-chain nanoparticles with sequenced defined segments via multicomponent reactions

Erik B. Berda², erik.berda@unh.edu, Justin Cole¹. (1) Chemistry, University of New Hampshire, Durham, New Hampshire, United States (2) Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

Our group is interested in mimicking the tertiary structure of proteins, albeit in a rudimentary fashion, using single-chain nanoparticles (SCNP) containing sequence defined segments. SCNP synthesis is a simple process in principle: an organic transformation is used to effect the intramolecular cross-linking of a linear polymer chain to afford an architecturally defined nanomaterial. This presentation will discuss our recent efforts using multicomponent reactions to install peptide or depsipeptide segments in SCNPs. The segments, we've discovered, readily aggregate via hydrogen bonding to form aggregates or well-defined folding regimes.



Schematic representation of single-chain nanoparticle synthesis using multicomponent chemistry

POLY 314: Controlled self-assembly of peptidic Au(I)-metalloamphiphiles into 1D nanorods in water

Benedict Kemper, *Benedict.Kemper@uni-mainz.de*, Pol Besenius. Johannes Gutenberg Universität Mainz, Institute of Organic Chemistry, Mainz, Germany

The aim of the work presented herein is to couple Au(I) complexes to small peptide building blocks in order to prepare new C_3 -symmetrical metalloamphiphiles as supramolecular monomers. These molecular building blocks are based on dendritic β -sheet encoded peptide amphiphiles and induce supramolecular polymerization into 1D nanorods. The control of the self-assembly of these dendritic Au(I)-metalloamphiphiles results from the interplay of intermolecular non-covalent attractive interactions between the peptidic backbones - mainly hydrogen bonding and the hydrophobic effect - as well as steric and electrostatic repulsive forces of the dendritic side chains. The degree of the self- and disassembly in water as well as the morphology and size of the resulting anisotropic (bio)organic-inorganic hybrid materials will be discussed.

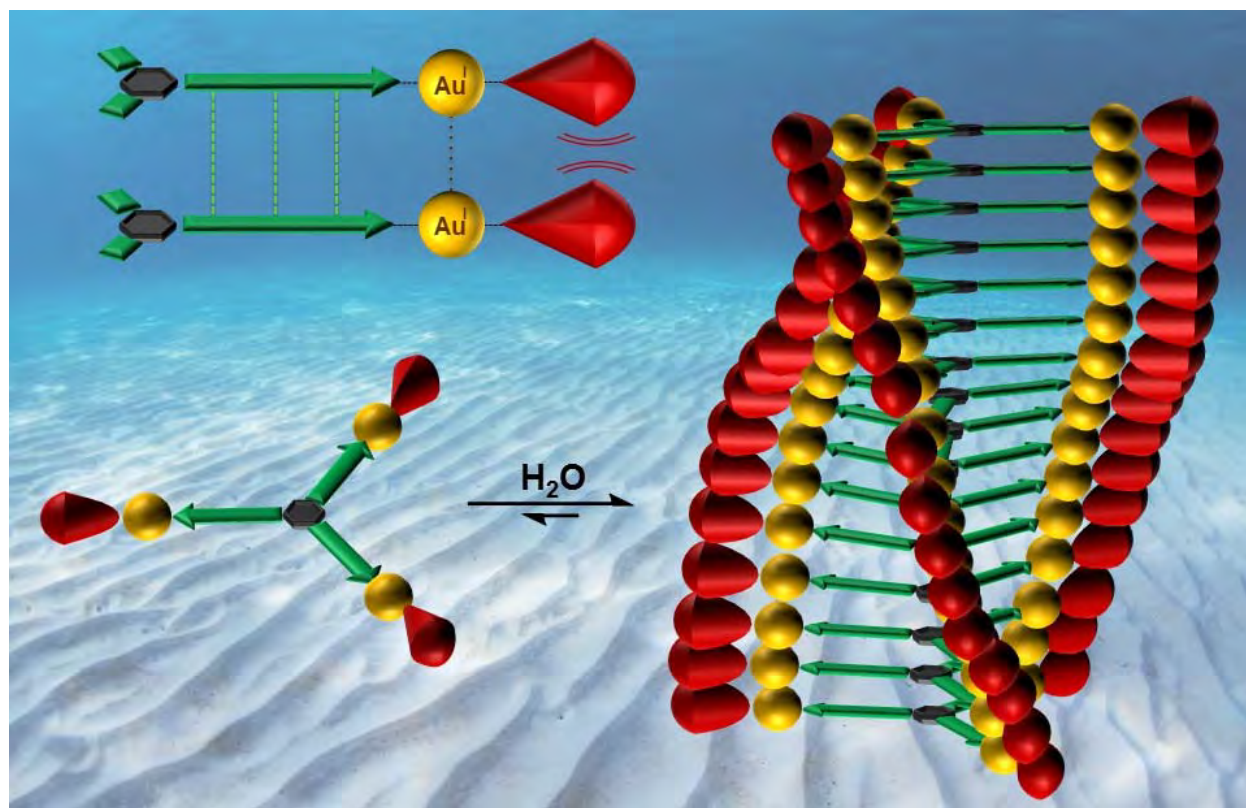
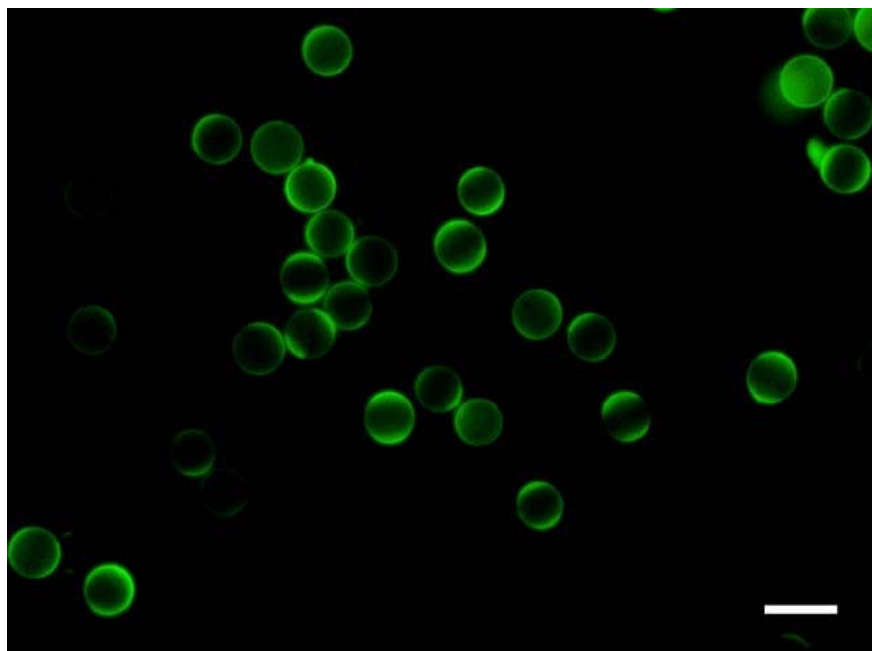


Figure 1: Driving forces (upper left) and schematic representation of the self-assembly of the Au(I) metalloamphiphilic supramolecular monomers (top view) into 1D nanorods (side view) in water.

POLY 315: Photo- and magnetoresponse self-assembly of nanoparticles

Bart Jan Ravoo, *b.j.ravoo@uni-muenster.de*. Organic Chemistry Institute, WWU Muenster, Muenster, Germany

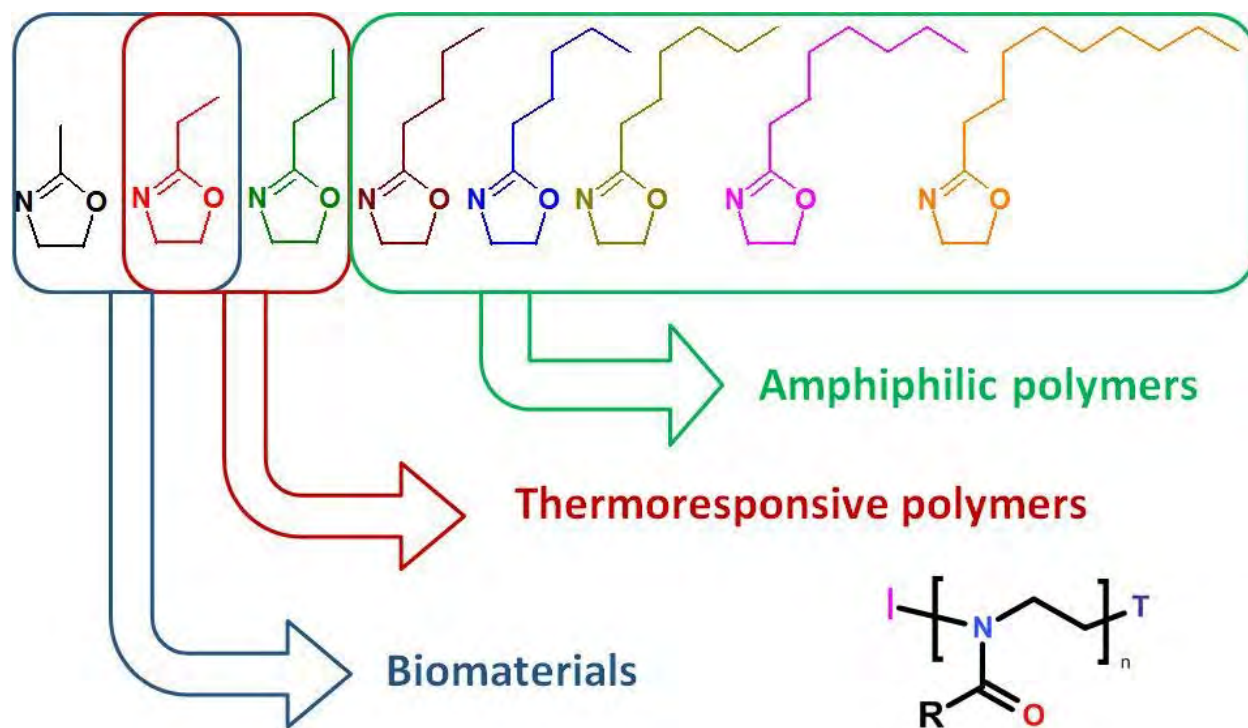
Self-assembly is emerging as a superior method to prepare adaptive and responsive nanomaterials. In this contribution, we will highlight our newest findings concerning the preparation of photoresponsive and magnetoresponse materials by self-assembly. These materials are photoresponsive since the particles interact through photoresponsive host-guest interactions of cyclodextrins and azobenzenes. Moreover, they are magnetoresponse since they contain superparamagnetic nanoparticles. We have prepared “magnetic vesicles” that self-assemble in microscale linear aggregates in a magnetic field. A noncovalent and photoresponsive cross-linker can stabilize the metastable linear aggregates, which can be photoisomerized between an adhesive and a nonadhesive configuration. Thus, the hybrid material responds to magnetic field as well as to light and a stable self-assembled structure can only be obtained in a magnetic field in the presence of the noncovalent cross-linker. Furthermore, we explored arylazopyrazoles (AAPs) as a new light-responsive motif. Compared to azobenzenes, AAPs offer quantitative photoisomerization in both directions and longer half-life times of the E-isomer. Derivatives of AAPs were readily synthesized enabling easy post-functionalization and water solubility. AAPs were applied in photoresponsive clustering of nanoparticles. Moreover, we have prepared Janus silica particles (diameter 6 micron) by sandwich microcontact printing of an ATRP initiator and subsequent growth of polymer brushes exclusively in the printed caps of the Janus particles. Moreover, we have shown that AAPs can be included in the polymer brush caps, and that the resulting “guest” Janus particles form linear aggregates in the presence of superparamagnetic “host” nanoparticles coated with cyclodextrins. These anisotropic aggregates can be manipulated with a magnetic field.



POLY 316: Poly(2-oxazoline)s as functional biomaterials

Richard Hoogenboom, *richard.hoogenboom@ugent.be*. Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium

The living cationic ring-opening polymerization of 2-oxazolines has been studied in great detail since its discovery in 1966. The versatility of this polymerization method allows copolymerization of a variety of 2-oxazoline monomers to give a range of tunable polymer properties that enable, for example, hydrophilic, hydrophobic, fluorophilic, as well as hard and soft materials. However, this class of polymers was almost forgotten in the 1980s and 1990s because of the long reaction times and limited application possibilities. In the new millennium, a revival of poly(2-oxazoline)s has arisen because of their potential use as biomaterials and thermoresponsive materials, as well as the easy access to defined amphiphilic structures for (hierarchical) self-assembly. Recent developments from our research that illustrate the potential of poly(2-oxazoline)s will be discussed in this lecture, including the preparation of defined high-molar mass polymers as well as functional biomaterials.



POLY 317: Training the old dog new tricks: The applications of the Biginelli reaction in polymer chemistry

Lei Tao, leitao@mail.tsinghua.edu.cn. Chemistry Department, Tsinghua University, Beijing, China

Recently, our group reassessed multicomponent reactions (MCRs) from the angle of click reaction, and developed a new type click reaction: multicomponent click (MCC) reaction, i.e. some highly efficient and atom economy MCRs can also be considered as click reaction (Figure 1).

Figure 1. The multicomponent click reactions

Same as traditional two components click reactions, MCC reactions can also be used as efficient coupling tools. Moreover, it is easy to introduce new functional groups through MCC reactions due to their multicomponent nature. Here, the Biginelli reaction has been chosen as a representative MCC reaction, and the applications of the Biginelli reaction in polymer chemistry, including the synthesis of new functional polymer, polymer post-modification, new combinatorial system for polymer synthesis^{1,2,3} have been discussed.

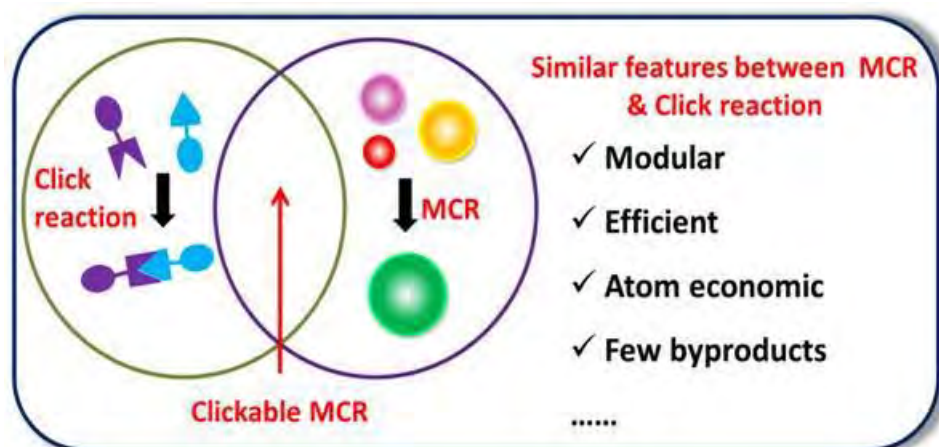
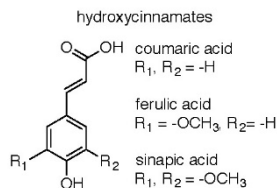


Figure 1. The multicomponent click reactions

POLY 318: Biomass-derived polymers incorporating hydroxycinnamates

Andrea M. Kasko, *akasko@ucla.edu*. 410 Westwood Plaza, Department of Bioengineering, Los Angeles, California, United States

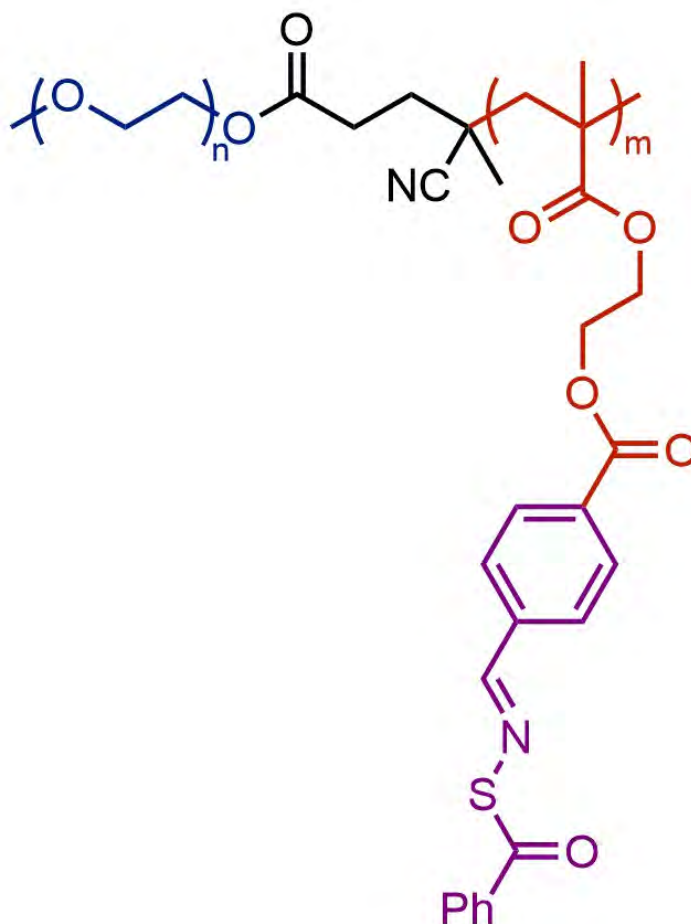
As the second most abundant natural polymer after cellulose, lignin provides an ideal platform for the development of novel polymeric and composite materials. Lignin is isolated from plant materials through the industrial processing of lignocellulosic biomass during the production of paper or ethanol. While the polysaccharide components of biomass are well-utilized, lignin is considered a low value byproduct and has little commercial use. In 2011, the worldwide pulp and paper industry produced 50 million tons of lignin but only 2% was used commercially and the rest was burned as a low value fuel. An opportunity therefore exists to utilize lignin as widely available low value carbon source to produce new commodity and high performance polymeric materials. Monolignols (the monomers that form lignin) and their derivatives (including hydroxycinnamates, a biosynthetic precursor to monolignols) are particularly attractive because they possess an aromatic group, which is quite uncommon in other natural polymers. Introduction of aromatic units into polymers typically improves their thermal and mechanical properties (compared to aliphatic polymers). We developed a series of monomers based on hydroxycinnamates, and incorporated them into polymers via condensation polymerization. Approximately 40 different polymeric structures were synthesized, with a broad range of molecular weights and molecular weight distributions. The resultant polymers exhibit good thermal stability and were typically amorphous (although a few samples exhibited a melting point). However, the polymers generally exhibited very limited solubility in common organic solvents (excluding DMF). These results suggest that hydroxycinnamate-based copolymers may find use in applications where thermal stability and solvent resistance are desired. Furthermore, these results indicate that lignocellulose may be useful as a new feedstock for commodity polymeric materials.



POLY 319: Polymeric materials for delivery of hydrogen sulfide (H₂S), a biologically relevant signaling gas

John B. Matson^{2,3}, jbmatson@gmail.com, Jeffrey Foster^{1,3}. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (3) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

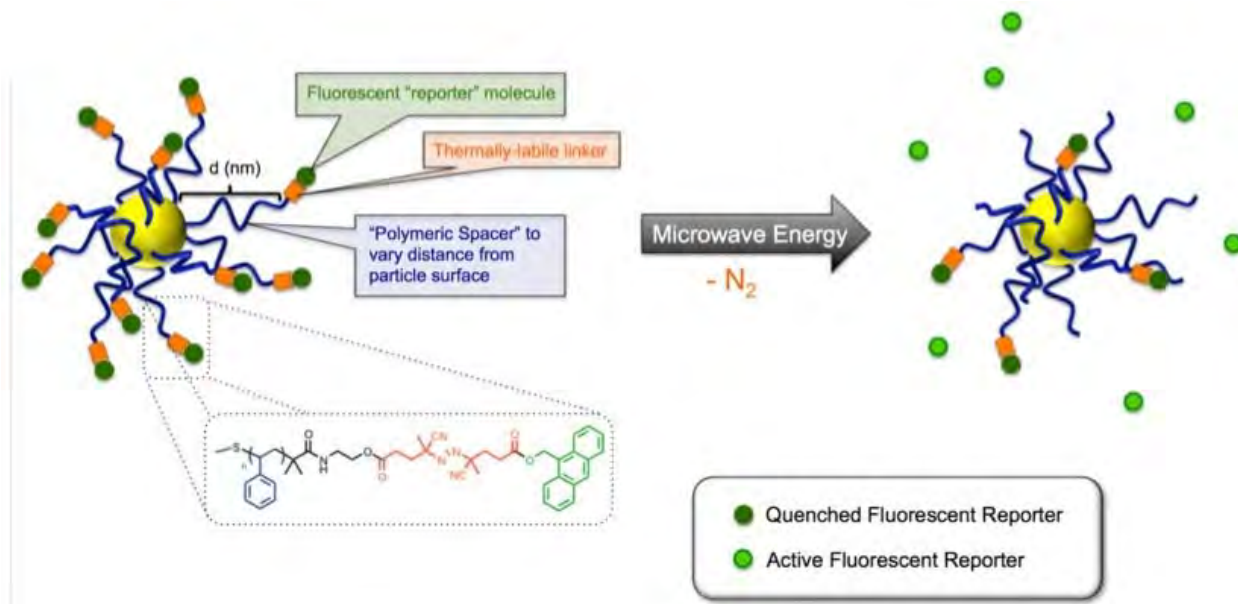
Despite its reputation as a foul-smelling and toxic pollutant, H₂S is a vital biological signaling agent, and it is of interest as a therapeutic for a variety of diseases and conditions. This work focuses on developing polymers for the sustained and controlled delivery of hydrogen sulfide (H₂S). Small molecule H₂S donors are compounds that can be triggered to decompose with release of H₂S in response to a biological trigger. H₂S donors used in this work including *S*-aroylthiooximes and *N*-thiocarboxyanhydrides, which are appended onto amphiphilic polymer frameworks to form H₂S-releasing assemblies, including micelles and vesicles. H₂S release rates can be controlled by changing the type of assembly as well as the mobility of the H₂S-releasing hydrophobic block. These polymers are relevant as both biological tools and as potential therapeutics, including in cancer, wound-healing, and cardiovascular disease.



POLY 320: New strategies for polymer functionalization: From multifunctional homopolymers to polymeric thermometers

Charles A. Figg, Tomohiro Kubo, R. N. Carmean, Christopher P. Kabb, **Brent S. Sumerlin**, sumerlin@chem.ufl.edu. Department of Chemistry, University of Florida, Gainesville, Florida, United States

This presentation will describe our recent work in developing new approaches for postpolymerization functionalization, specifically focusing on strategies that allow two distinct functional groups to be installed at one site along a polymer chain. We exploited the chemoselective nature of cyanuric chloride [2,4,6-trichlorotriazine (TCT)] to obtain ω,ω -heterodifunctionalized semitelechelic polymers, as well as multifunctional homopolymers (i.e., homopolymers that contain two distinct functional groups on each monomer unit). We will also describe our recent work that involved using telechelic polymers to probe the surface-localized hyperthermia of metal nanoparticles under microwave irradiation. This approach indicated the temperature near the surface of the nanoparticles was nearly 70 °C higher than the bulk solution temperature, but decreased rapidly with radial distance. This finding provides opportunities in the area of catalysis and processing and provides fundamental insight into the phenomenon of microwave heating.

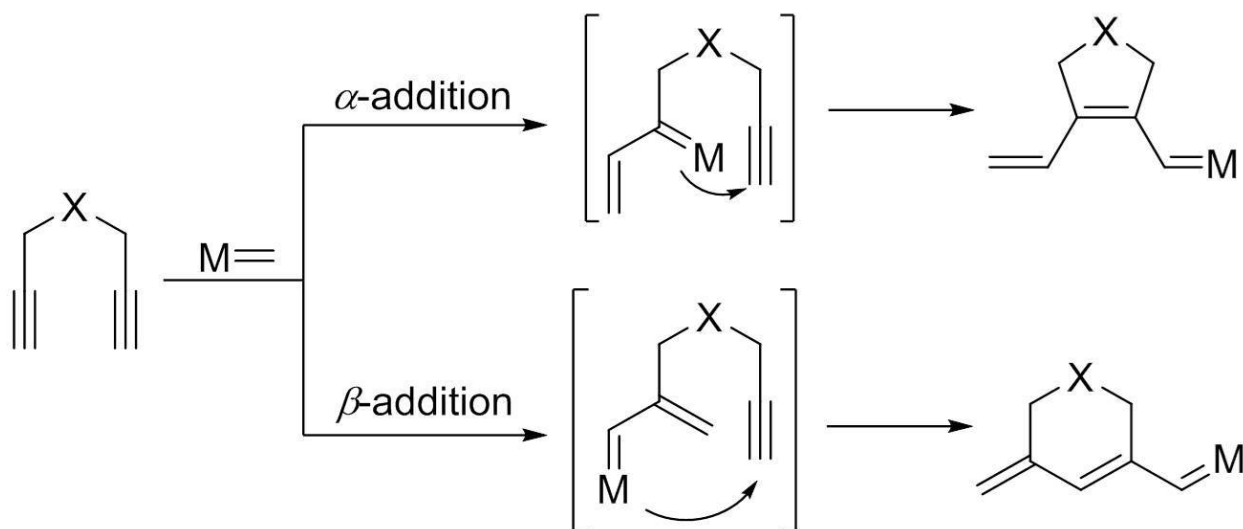


POLY 321: Cyclopolymerization using Grubbs catalyst

Tae-Lim Choi, *tlc@snu.ac.kr*. School of Chemistry, Seoul National University, Seoul, Korea (the Republic of)

Olefin metathesis provides a versatile synthetic method to produce small, medium and large molecules. Over the past two decades, wide ranges of the molecules have been prepared by various types of olefin metathesis, such as cross metathesis (CM), ring-closing metathesis (RCM), ring-opening metathesis (ROM) reactions. Ru-based Grubbs catalysts have popularized the reaction because the catalysts are not just highly active but also very easy to handle with good functional group tolerance. Now the metathesis polymerization of olefin monomers is one of the most common ways to construct numerous polymer architectures and nanostructures. On the other hand, only a few study reported the polymerization of alkyne-containing molecules, which can efficiently produce conjugated backbone.

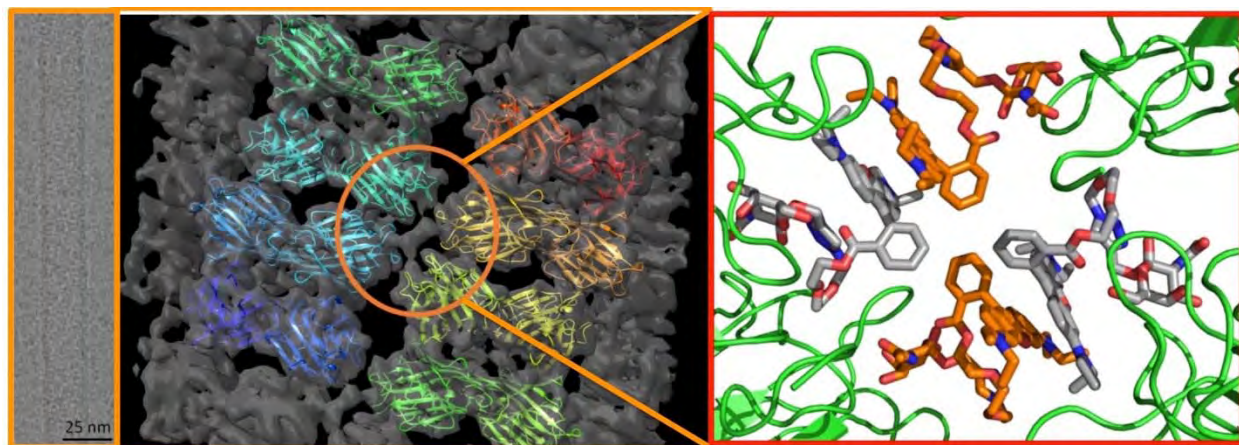
So far especially in polymerization, olefins are the main functional group for the monomer. Here, we will describe alkyne polymerization by olefin metathesis using Grubbs catalysts. Also, our strategy to achieve controlled cyclopolymerization to prepare polymers with desired molecular weights and narrow polydispersity indices will be discussed. (Fig. 1) We studied the cyclopolymerization of 1,6-heptadiyne derivatives, which is another olefin metathesis polymerization, using Ru-based Grubbs catalysts. In the history of cyclopolymerization of diynes, these catalysts had shown poor activity and resulted in no polymer, whereas Mo-alkylidenes had achieved the efficient cyclopolymerization. We focused on the control of reaction conditions to improve the efficiency of polymerization utilizing common Grubbs catalysts, instead of the catalyst engineering. As a result, it was disclosed that severe dependence on various factors, such as the solvent, temperature, dissociative ligands, and even steric effect, could alter the efficiency of polymerization.



POLY 322: Carbohydrate-based macromolecular self-assemblies and their biological functions

Guosong Chen, guosong@fudan.edu.cn. Dept of Macromolecular Sciences, Fudan University, Shanghai, China

Carbohydrates are the most abundant organic species in the world and also one of most important biological macromolecules with nucleic acids and proteins. The self-assembly of DNA and proteins make a significant contribution to our lives and they have been employed to make functional self-assembled materials. Compared to the development of DNA and proteins, our knowledge and manipulation to the self-assembly of carbohydrates as well as their functionality are quite limited. The major obstacle is the complicated chemical structure of oligosaccharides, i.e. perplexing glycoforms and microheterogeneity on proteins, which make the research a problematic and long-term task. Under this circumstance, macromolecular self-assembly might provide an alternate insight to this problem. In this talk, I will present: 1) development of precise protein array with regular shape at mm scale controlled by protein-carbohydrate interaction; 2) construction of polymeric vesicles mimicking *glycocalyx*, structure, self-assembly and immunological functions; 3) control of macromolecular self-assembly by chemical reactions related to sugars.

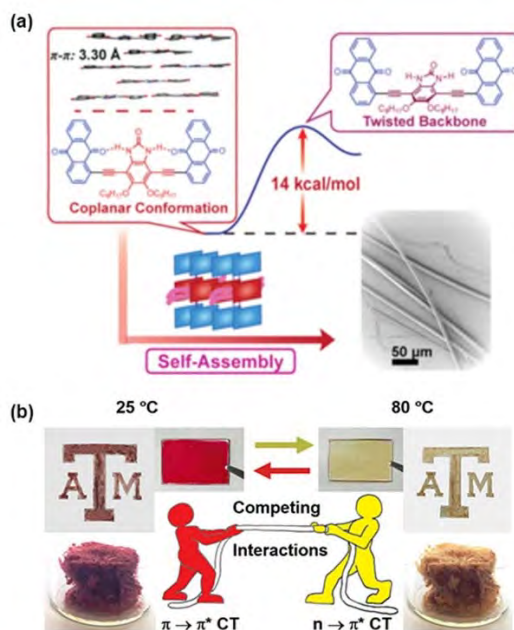


POLY 323: Harnessing non-covalent interactions for functional organic and polymeric materials

Lei Fang¹, fang@chem.tamu.edu, **Tianyu Yuan**¹, **Congzhi Zhu**², **Mark A. Olson**³. (1) Texas A M University, College Station, Texas, United States (2) Dept of Chem, Chemistry Bldg Rm 204, Texas AM University, College Station, Texas, United States (3) Tianjin University, Tianjin, China

Non-covalent bonds play a crucial role in governing the intrinsic molecular properties, self-assembly, and solid-state characters of organic/polymeric materials. In the first part of the talk, I present the active conformational control in a conjugated system using intramolecular H-bonds, to achieve tailored molecular, supramolecular, and solid-state properties. The H-bonding functionalities are fused to the backbone and precisely pre-organized to enforce a fully coplanar conformation of the π -system, leading to short π - π stacking distances, controllable molecular self-assembly, and solid-state growth of one-dimensional nano/micro-fibers. This investigation demonstrates the efficiency and significance of intramolecular non-covalent approach in promoting conformational control and self-assembly of organic molecules.

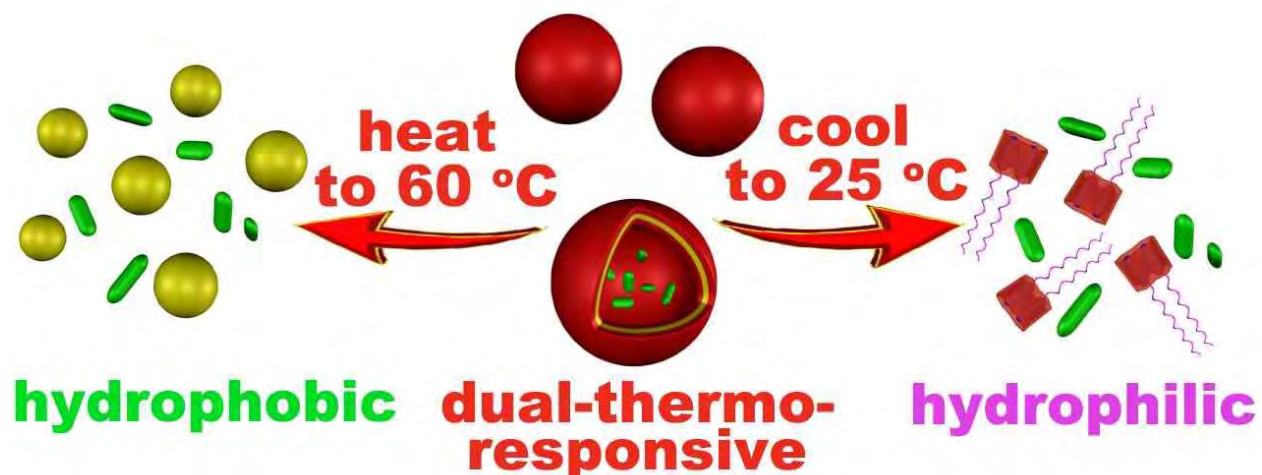
In the second part of this talk, the design and synthesis of a new class of thermochromic supramolecular materials is presented. These water-processable supramolecular materials are composed of a bis-bipyridinium acceptor, a p-electron rich naphthalene derivative donor, and halogen counterions. Long helical nanofibers can be assembled in water, gelating at room temperature. Inked designs, thin films and aerogels are solution-processed to exhibit thermochromic behavior based on competing $p \rightarrow p^*$ and $n \rightarrow p^*$ charge transfer (CT) interactions. By using different p-electron rich donors and counterions, we demonstrated that both the colour observed at room temperature and at high temperatures could be tailored. Our results open up the door to develop novel amphiphile-based thermochromes with water processability and a large tunable colour palette.



POLY 324: Functional materials constructed by the combination of traditional polymers and host-guest molecular recognition motifs

Feihe Huang, *fhuang@zju.edu.cn*. Department of Chemistry, Zhejiang University, Hangzhou, China

We are interested in constructing functional materials by the combination of traditional polymers and host-guest interactions. For example, we prepared supramolecular gels by crosslinking a PMMA polymer with pendent dibenzo[24]crown-8 (DB24C8) units by using two bisammonium salts with different end groups based on the host-guest interactions of DB24C8 units and secondary ammonium salt moieties, exhibiting excellent self-healing properties. A supramolecular cross-linked network was constructed from a fluorescent conjugated polymer and a bisammonium salt cross-linker driven by DB24C8/secondary ammonium salt host-guest interactions, and demonstrated to act as a multiple fluorescent sensor. We developed a novel amphiphilic diblock copolymer with a supramolecular polymer block and a traditional polymer block. The block chain length ratio of the diblock copolymer could be adjusted with no need to do intricate organic and/or polymer syntheses, inducing the formation of various assembled morphologies and functions. We fabricated a dual-responsive supra-amphiphilic polypseudorotaxane from a water-soluble pillar[7]arene and an azobenzene containing random copolymer construct. Additionally, we constructed the first pillararene-based gemini-type supra-amphiphilic [3]pseudorotaxane from a water-soluble pillar[10]arene and a paraquat-containing poly(N-isopropylacrylamide). This macromolecular [3]pseudorotaxane showed unique dual-thermo-responsiveness.

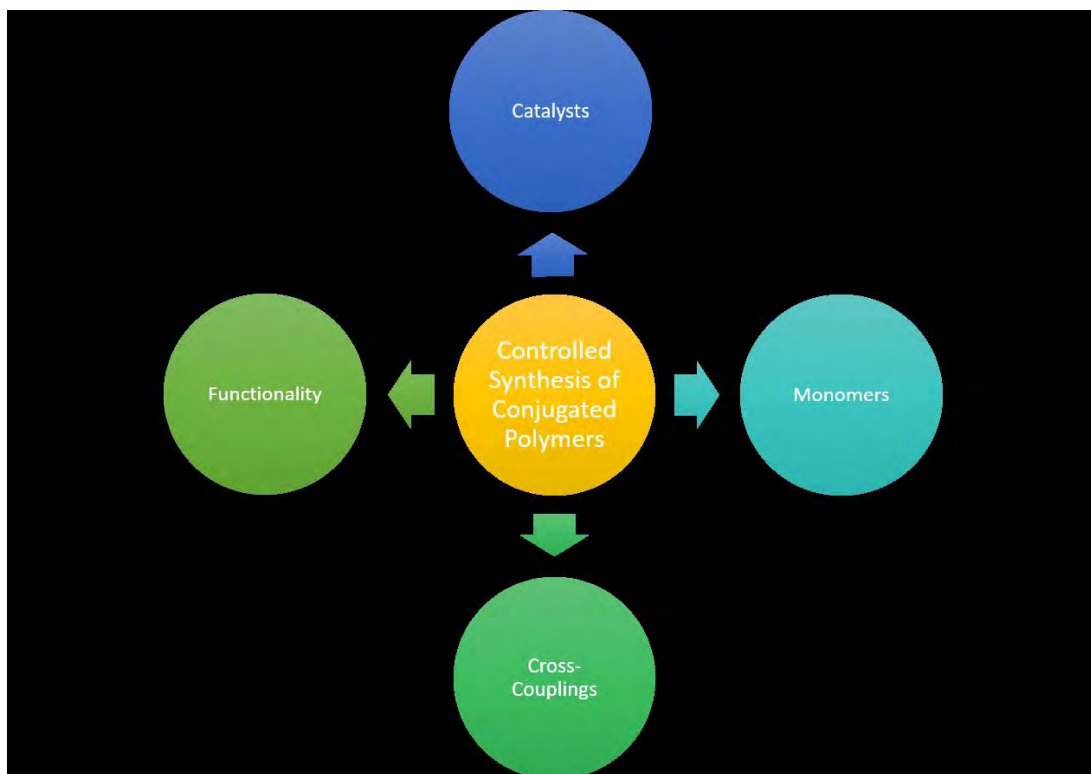


POLY 325: Diversifying catalysts, monomers, cross-coupling strategies and functional groups in the controlled synthesis of conjugated polymers

Yunyan Qiu¹, yunyanq@andrew.cmu.edu, Kevin J. Noonan², Tomasz Kowalewski³. (1) Chem Dept, Carnegie Mellon Univ, Pittsburgh, Pennsylvania, United States (2) Box 63, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (3) Dept of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

The ability to precisely incorporate monomers into polymeric materials grants polymer chemists access to a variety of complex architectures. These materials are commonly prepared by living chain-growth polymerization techniques which have revolutionized the field of polymer synthesis. Catalyst-transfer polycondensation (CTP) is one of those chain-growth methods to afford well-defined conjugated polymers. Serving as active components in most of optoelectronic devices, conjugated polymers prepared by CTP exhibit improved device performance due to uniform polymeric structures. Some promising features CTP can provide include control over size and microstructure, good chain end fidelity and the construction of sophisticated polymeric frameworks with functionality.

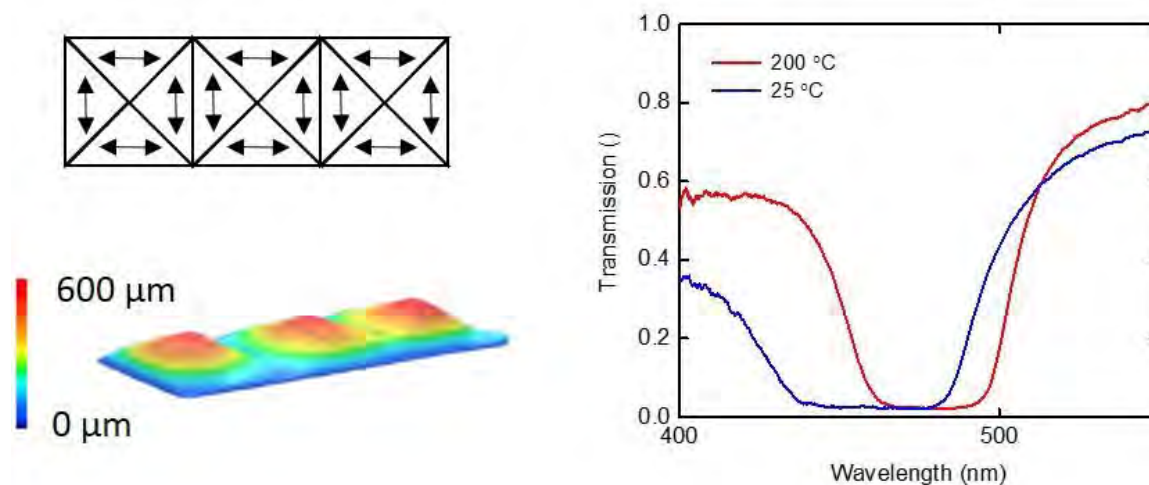
The frontier of CTP research now focuses on (a) understanding the exact mechanism, (b) monomer scope expansion by rational design of catalysts and conjugated monomers, and (c) obtaining conjugated materials with structural diversity. This talk details some of our endeavor towards diversifying the choice of catalysts, monomers, cross-coupling reactions and functional groups available in CTP process.



POLY 326: Bioinspired stimuli-responsive materials: Concurrent shape and color change in programmed cholesteric liquid crystal elastomers

Michelle T. Leslie^{3,1}, mtl49@case.edu, Gary E. Wnek², LaShanda T. Korley⁴, Timothy J. White¹. (1) Materials and Manufacturing Directorate, Air Force Research Laboratory, Centerville, Ohio, United States (2) Case Western Reserve Univ, Cleveland, Ohio, United States (3) Macromolecular Science & Engineering, Case Western Reserve University, Shaker Heights, Ohio, United States (4) Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, Ohio, United States

Biological systems employ anisotropy to enable selectivity in motion, transport, or add functionality, like structural color. Resembling the structure-function relationships found in nature, cholesteric liquid crystals (CLCs) are inherently and selectively reflective, and shown to exhibit stimuli-induced changes in coloration particularly in compositions prepared with low-molar mass liquid crystals. Here, we report on the ability to pattern and imprint both color and shape (topography) change in monolithic elements prepared from cholesteric liquid crystalline elastomers. The materials examined here are of the main-chain subclass, synthesized via photopolymerization of an acrylate formulation. The spatial anisotropy was initiated via photoalignment of dye molecules on substrate surfaces. Within the presentation, we will elucidate subtle nuances in the fundamental nature of the mechanics that differentiate the stimuli-response of these materials from nematic liquid crystalline elastomers. The ability to simultaneously and concurrently regulate the color as well as the direction of reflected light could open up interesting applications in textiles, optics, and sensing.

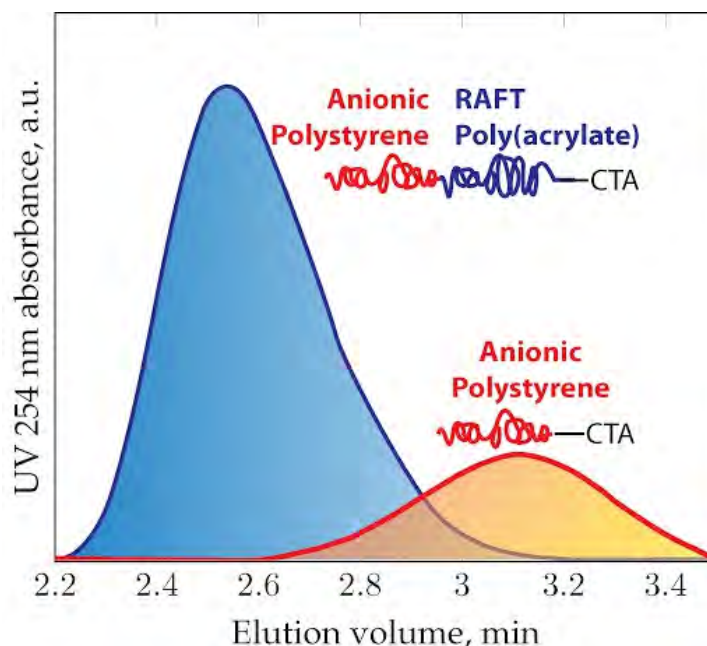


The imprinted director orientation and corresponding shape (topography) and color change response as a result of thermal stimulus.

POLY 327: Towards commercially scalable processes for polymers produced by sequential anionic and RAFT polymerization

Michael Forrester³, mf1@iastate.edu, **William Bradley**⁴, **Nacu Hernandez**², **George A. Kraus**¹, **Eric W. Cochran**¹. (1) Iowa State Univ, Ames, Iowa, United States (2) Iowa State University, Ames, Iowa, United States (3) Chemical Engineering, Iowa State University, Ames, Iowa, United States (4) Chemistry, Iowa State University, Ames, Iowa, United States

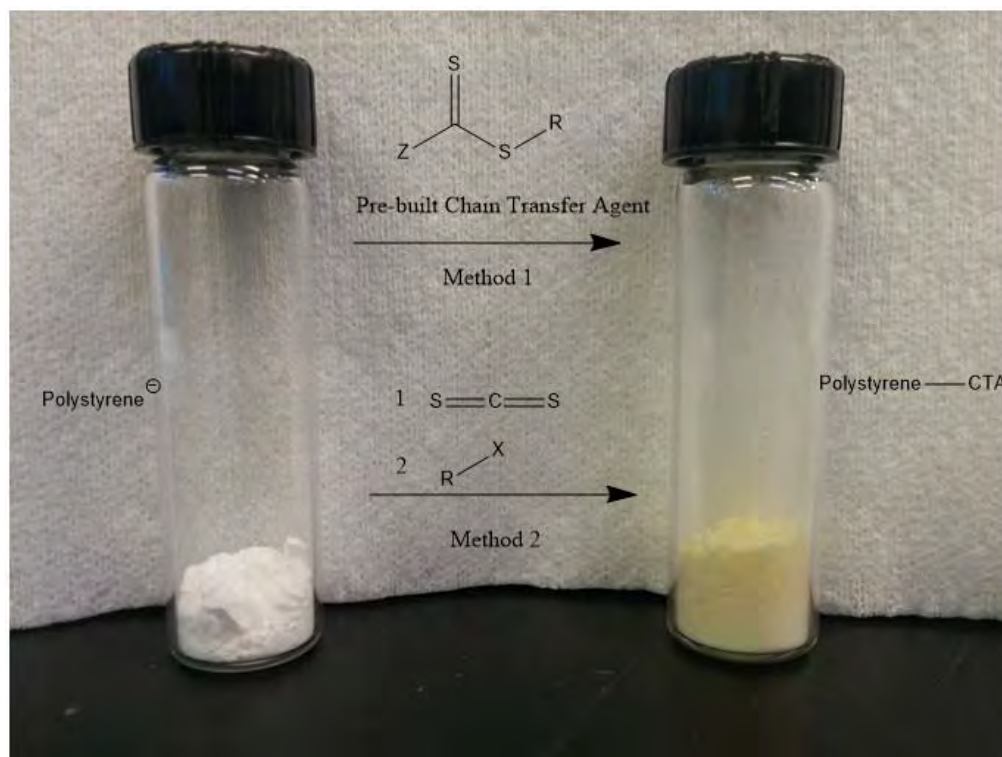
In this contribution we present strategies for scalable methods of merging living anionic and RAFT polymerization, which enable the commercial production of a far more diverse array of block copolymers than presently available. Anionic polymerizations can rapidly achieve exceedingly high conversions of styrenic and diene monomers, and are used extensively in the industry to make a variety of styrenic block copolymers. Unfortunately, (meth)acrylic monomers are too reactive at non-cryogenic temperatures to be feasible with this chemistry. On the other hand, reversible addition-fragmentation chain transfer (RAFT) polymerization achieves good conversion and well-defined (meth)acrylic polymers and block copolymers. Moreover, RAFT is very flexible with regard to solvent choice, is highly tolerant of impurities and supports a large palette of monomers. However, RAFT features sluggish propagation rates for vinyl aromatics and does not adequately control dienes. In this work we examine two different methods for producing anionic-RAFT macro-CTAs. In the first, chain transfer agent could be pre-synthesized and coupled to the living anionic chain. Alternatively, a chain transfer agent could be constructed using the living chain end as the precursor for the synthesis of the final macro-CTA. Following this reaction an acrylate/methacrylate monomer can be used to achieve a styrenic(diene)/(meth)acrylate block copolymer.



POLY 328: Scalable synthesis of macroCTAs from living anionic polystyrene

William Bradley, *wbrad@iastate.edu*, Michael Forrester, Nacu Hernandez, George A. Kraus, Eric W. Cochran. Iowa State University, Ames, Iowa, United States

In this contribution we report the efficient and scalable combination of living anionic polymerization of styrene with the reversible addition-fragmentation chain transfer (RAFT) polymerization of acrylics. The living anionic polymerization of styrene and dienes has been a commercial process for decades and forms the basis for a major component of the thermoplastic elastomers industry. However, the application of anionic polymerization to acrylics has proven to be challenging and has remained limited to dienes and styrenics. On the other hand, controlled radical polymerizations such as RAFT are compatible with a broad range of acrylics, but struggle to polymerize vinyl aromatics over commercially viable time scales. We have explored the end-group chemistry of living anionic polystyrene to develop a polystyrene macro-chain transfer agent (macroCTA) and have identified a number of novel methodologies that hold promise as scalable routes for the marriage of anionic and RAFT polymerization. These methodologies are challenging due to undesirable side reactions with living anionic polystyrene. This talk will illustrate how we have overcome these difficulties, achieving macroCTAs that have proven to be excellent RAFT agents for polymerization of acrylics and realize approximately 80% to 95% coblock efficiency in the transition from living anionic polystyrene to a RAFT polymerized n-butylacrylate polymer.

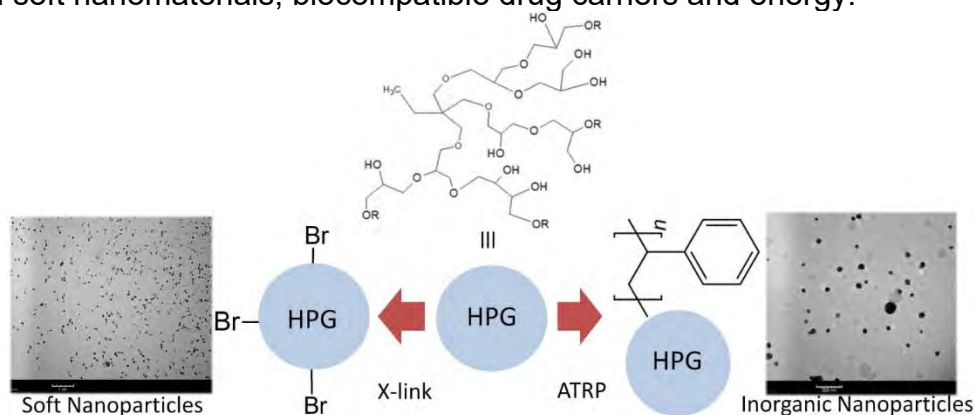


Polystyrene not capped compared to macroCTA capped polystyrene on the right. Capping of polystyrene is performed in various methods.

POLY 329: Synthesizing Hyperbranched Polyglycerol (HPG) derivatives for use in templating hard inorganic nanostructures, biocompatible soft nanoparticles and structure-preserving binder materials for batteries

James Icozzia¹, jicozzia3@gatech.edu, **Zhiqun Lin**². (1) *Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States* (2) *School of Material Sci Engr, Georgia Institute of Technology, Atlanta, Georgia, United States*

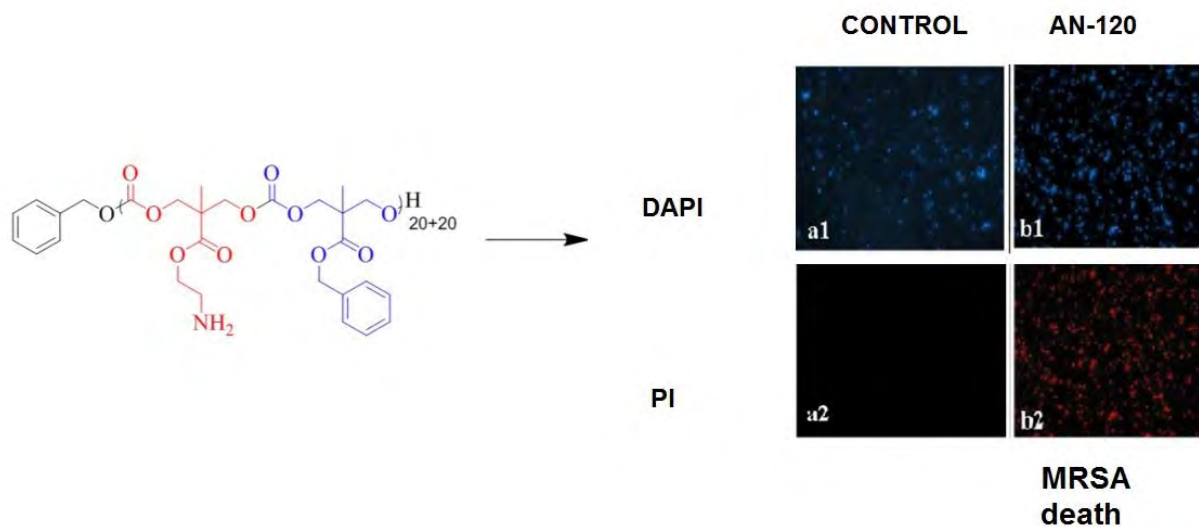
Hyperbranched polyglycerols (HPG) are heavily branched polyether polyols possessing many hydroxyl groups similar to perfect dendrimeric structures. Unlike dendrimers, HPG can be produced in simple one-pot reactions. Improvements in HPG polydispersity and size control make HPG an attractive alternative to dendrimers. These hydroxyl groups are amenable to different chemical modifications. In this work, HPG is esterified to produce ATRP macroinitiators for templating inorganic nanoparticles of various types (Au, Ag, Fe₃O₄ and others), leaving-group loaded HPG for the production of static and stimuli-responsive crosslinked polymeric nanoparticles and a novel binder in lithium ion batteries. In the first work, well-defined HPG-b-polystyrene (HPG-b-PS) is used to template hard functional materials including Au, Ag and Fe₃O₄ nanoparticles. Polyglycerol coordinates precursor anions within the inner portion of the HPG-b-PS structure where they are converted to the respective inorganic nanoparticles with sizes between 15 and 100 nm. The covalently-tethered PS capping layer keeps the nanoparticles dissolved in solution, preventing aggregation. In the second work, HPG is brominated to enable easy conversion to reactive HPG derivatives amenable to either photo or chemical crosslinking. Azide-capped HPG is used to make static UV-crosslinkable polymer nanoparticles. Chemical crosslinking via functional bipyridine derivatives is also used to produce redox and light-responsive polymer nanoparticles. In the third work, a novel hyperbranched poly(ethylene glycol) methyl ether methacrylate (HPG-b-PEGMEM) is employed as a novel structure-preserving binder in lithium batteries possessing a ZnFe₂O₄ active material. It is believed that this gel-like binder reduces pulverization of the active material under repeated cycling. The aim of this work is to improve the cycle lifetime and stability at lower charge capacities. To date, stable charge capacities as high as 650 mAhg⁻¹ have been achieved up to more than 300 cycles. These works demonstrate the wide applicability of HPG-based materials whereby simple chemical modifications can enable its use in diverse areas including hard and soft nanomaterials, biocompatible drug carriers and energy.



POLY 330: Synthesis of biodegradable polycarbonate nanostructures with selective lysis against gram positive bacteria

alekhya nimmagadda¹, animmagadda@mail.usf.edu, Jianfeng Ca². (1) Chemistry, USF, Tampa, Florida, United States (2) Dept of Chemistry, University of South Florida, Tampa, Florida, United States

The resistance developed by the bacteria toward antibiotics has become a major concern in public health. There has been a significant interest in the development of antimicrobial cationic polymers due to the ease and low-cost of manufacture compared to host-defense peptides (HDPs). Herein, we report the design and synthesis of amphiphilic polycarbonates containing primary amino groups. These polymers exhibit potent antimicrobial activity and excellent selectivity to Gram-positive bacteria, including multi-drug resistant pathogens. Fluorescence and TEM studies suggest that these polymers are likely to kill bacteria by disrupting bacterial membranes. These polymers also show low tendency to elicit resistance in bacteria. Their further development may lead to new antimicrobial agents combating drug-resistance.



POLY 331: Promising approach to developing eco-friendly, sustainable and dual-cure coatings

Ozlem Akdogan, oakdogan@emich.edu. Engineering Technology, Eastern Michigan University, Ypsilanti, Michigan, United States

Vegetable oil is fascinating bio-based resource that is used for myriads of chemical and specialty products including coatings and is at the center of my research. Bio-based chemicals have a very long history of being used in adhesive, sealant and coatings industry due to their versatility and nontoxic properties. Promoting bio-based chemicals in terms of design, formulation and synthesis are the key elements of this research.

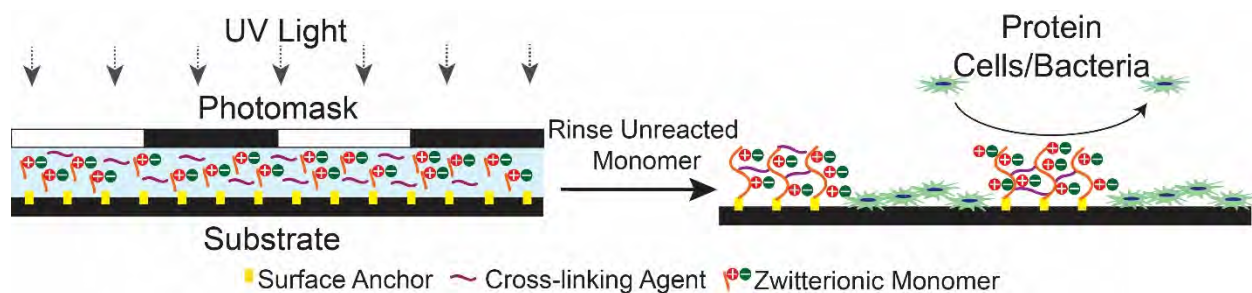
The research focuses on synthesis and characterization of polyester acrylate oligomers derived from epoxy resin (ER), itaconic acid (IA) (bio-based material), and glycidylmethacrylate (GMA). This novel polyester acrylate is then be blended with Acrylated epoxidized soybean oil (AESO) in varying proportions. This polymer blend containing both hard and soft materials, and containing both acrylate and hydroxyl groups has been used to formulate dual-cure coating systems. Dual-cure systems –that will cure by both radical polymerization (acrylate) and step-growth polymerization (-OH + -NCO) mechanism have been formulated by addition of varying amount of aliphatic polyisocyanate crosslinker. The wet films of the coatings were applied and cured under different conditions - only by thermal cure (step-growth), only by UV-cure and dual-cure. Cure study has been done using FT-IR spectroscopy (Peak area ratio method) to study the effect of cure type on properties of coatings. The differential scanning calorimetric technique (DSC) is used to investigate their mechanical properties as a function of cure type. Effect of composition and cure type on various film properties such as adhesion, flexibility, pencil and pendulum hardness, and impact resistance, and solvent resistance has been studied.



POLY 332: Engineering zwitterionic polymers that control cell adhesion and direct neurite growth to improve cochlear implants

Braden Leigh, *braden-leigh@uiowa.edu*, *Elise Cheng*, *Marlan R. Hansen*, *Allan Guymon*. *Univ of Iowa, Iowa City, Iowa, United States*

Biomedical devices typically accumulate fibrous tissue on their surfaces during the first several weeks after implantation, i.e. the foreign body response (FBR). This fibrosis is particularly problematic for neural prosthetics, such as the cochlear implant. When electrode arrays become encapsulated in the dense avascular fibrotic tissue, the applied current, which stimulates the spiral ganglion neurons (SGNs), or inner ear neurons, is attenuated, thereby causing significant broadening of the current and lower signal resolution. Nonspecific adsorption of proteins to device surfaces marks the implant as foreign and instigates scar tissue formation. Zwitterionic polymers, or materials with an equal number of positive- and negative-charged atoms on each repeat unit, are a new class of material that show great promise in resisting nonspecific protein adsorption to mitigate the FBR. In this work, photopolymerization was used to covalently graft sulfobetaine methacrylate (SBMA) and carboxybetaine methacrylate (CBMA), two zwitterionic monomers, to glass surfaces. X-ray photoelectron spectroscopy (XPS) was used to confirm the successful grafting of both zwitterionic polymers. The physicochemical properties of the surface respond to changes in aqueous solution concentration of the zwitterionic monomers. These surfaces show a strong resistance to protein adsorption which correlates to changes in contact angle while varying solution concentrations. Further, parallel line pattern surfaces were fabricated to evaluate the efficacy of these materials to spatially control cell adhesion and growth. Fibroblasts, oligodendrocytes, astrocytes, Schwann cell, and spiral ganglion neurons (SGNs) all exhibit a strong repulsion to zwitterion-coated regions on both patterned and unpatterned surfaces. Interestingly, zwitterionic micropatterns formed using photopolymerization direct the regrowth SGN neurites. Neurite extensions grow directly between zwitterion-coated bands avoiding interaction with the functionalized regions. While SGN neurites extend along SBMA stripes, CBMA patterns significantly improve alignment compared to SBMA patterns. These results lay the foundation for next generation cochlear implants and other neural prosthetics.

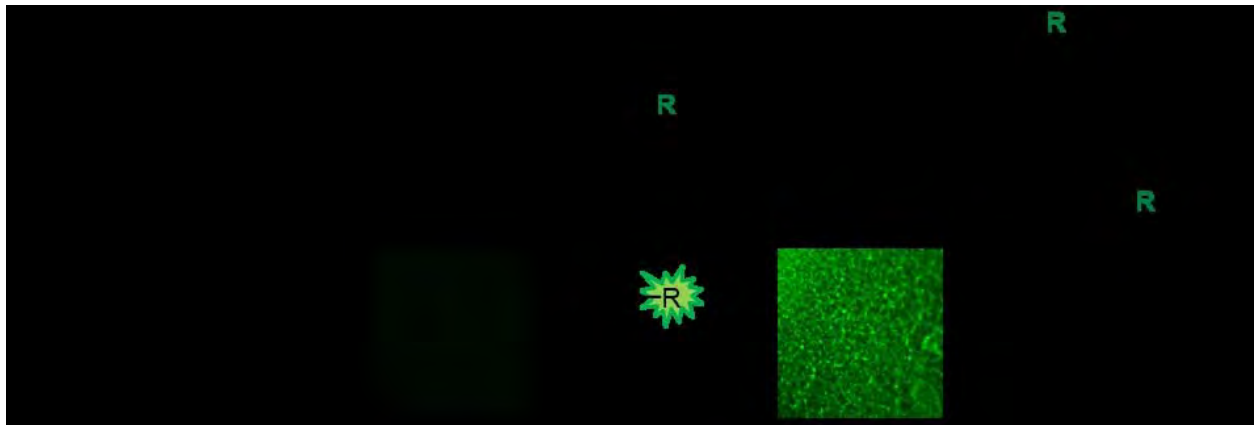


Schematic of the photografting/patterning process.

POLY 333: Modification of alkene-containing copoly lactide scaffolds for biomedical applications

Pranav Kalelkar¹, k13pranav@gmail.com, **Rachit Agarwal**³, **Andres Garcia**³, **David M. Collard**². (1) Chemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (3) Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

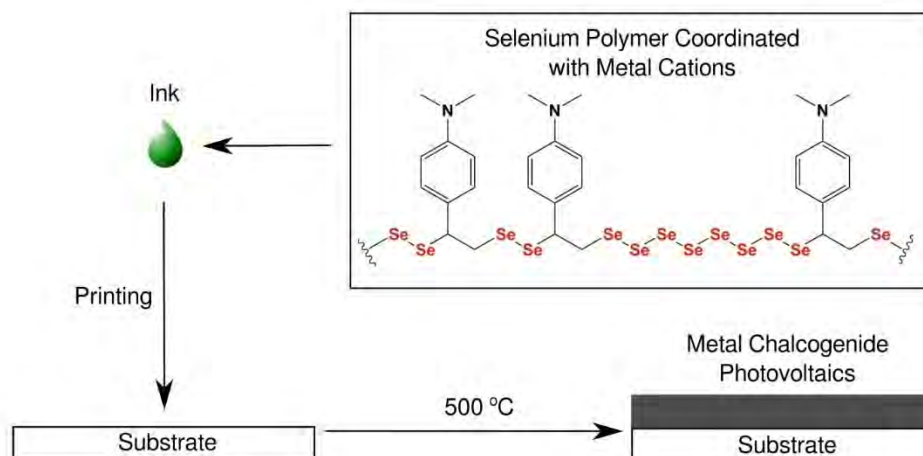
Every year, approximately six million people suffer from major bone injuries that require bone grafting procedures. Challenges associated with current implants used to promote bone repair include host rejection, risk of transmission of infection, and limited supply. A new copoly lactide that contains electrophilic α,β -unsaturated ester linkages can be processed into 3-D scaffolds. The addition of thiols to the alkenes allows for the attachment of biological molecules such as RGD-containing adhesive peptides that facilitate the recruitment of bone progenitor cells. We will explore protein adsorption, cell attachment, and the bone mineralization capacity of scaffolds fabricated out of such modified peptide-bearing copoly lactides.



POLY 334: Chalcogen polymers for completely solution-processed inorganic photovoltaics

Trevor R. Martin¹, martintr@uw.edu, Hugh Hillhouse², Christine K. Luscombe¹. (1) Materials Science and Engineering, University of Washington, Seattle, Washington, United States (2) Molecular Engr and Sciences Rm 123, University of Washington, Seattle, Washington, United States

This work focuses on developing novel chalcogen polymers to synthesize nanocrystals and crystalline thin films for printed photovoltaics applications. We have invented new polymers that consist primarily of linear chains of sulfur or selenium atoms. To our knowledge, polymeric materials with this chalcogen backbone structure have not been previously demonstrated and therefore, there are many opportunities for important discoveries within this field. Specifically, this work has utilized these polymers to develop routes for solution-processing metal-chalcogenide materials in ways that were previously impossible. Chalcopyrite materials such as $\text{CuInS}_x\text{Se}_{2-x}$ (CISSe), the gallium alloy variant $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_y\text{Se}_{2-y}$ (CIGSSe), and the earth-abundant kesterite material $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ (CZTSSe) have tunable bandgaps that are ideally suited for thin-film photovoltaics (PV) applications, high absorption coefficients due to direct bandgaps, and are extremely stable. However, these materials are conventionally manufactured using expensive and complicated vapor-phase reaction procedures or high-temperature, vacuum-based deposition methods. Our preliminary work has shown that chalcogen polymers can also be functionalized to directly coordinate with metal cations. This resulting hybrid organic-inorganic polymer can be printed onto a substrate and heated to initiate a chemical reaction that produces a metal-chalcogenide material such as CISSe. This new synthetic method provides a pathway towards making PV materials via a simple, completely solution-processed, low-temperature fabrication procedure. If successful, this technique would constitute the first viable means to produce low-bandgap chalcogenides without additional vapor-phase reactions or high-temperature sputtering depositions.

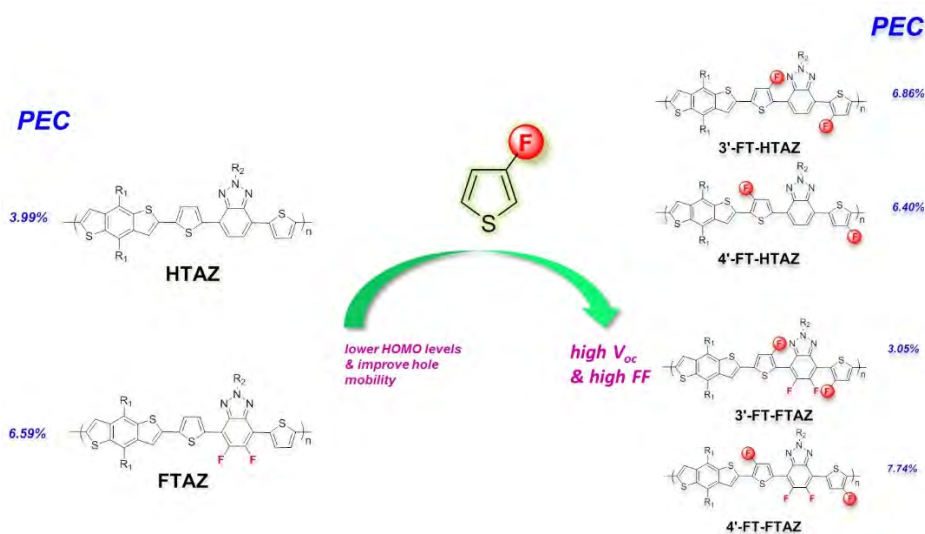


POLY 335: Fluorinated thiophenes in PBnDT-TAZ for bulk heterojunction solar cells: The impact of fluorination

Qianqian Zhang, *qianqzh@gmail.com*, Liang Yan, Wei You. Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States

Fluorination of conjugated polymers has been a widely adopted approach to tune optoelectronic properties of conjugated polymers, aiming for enhancing the power conversion efficiency (PCE) of their solar cells. Most fluorinated donor-acceptor (D-A) polymers have the fluorine atoms placed on the acceptor units; for example, in the well-studied PBnDT-FTAZ, two fluorine atoms are substituted onto the benzotriazole (TAZ) unit. Compared with the non-fluorinated counterpart (PBnDT-HTAZ), PBnDT-FTAZ shows one order of magnitude higher hole mobility in its bulk heterojunction (BHJ) blend with phenyl-C61-butyric acid methyl ester (PC₆₁BM), which directly translates into a remarkable improvement in fill factor (FF) of its BHJ device, leading to the observed efficiency of 7% (vs. 4% for PBnDT-HTAZ).

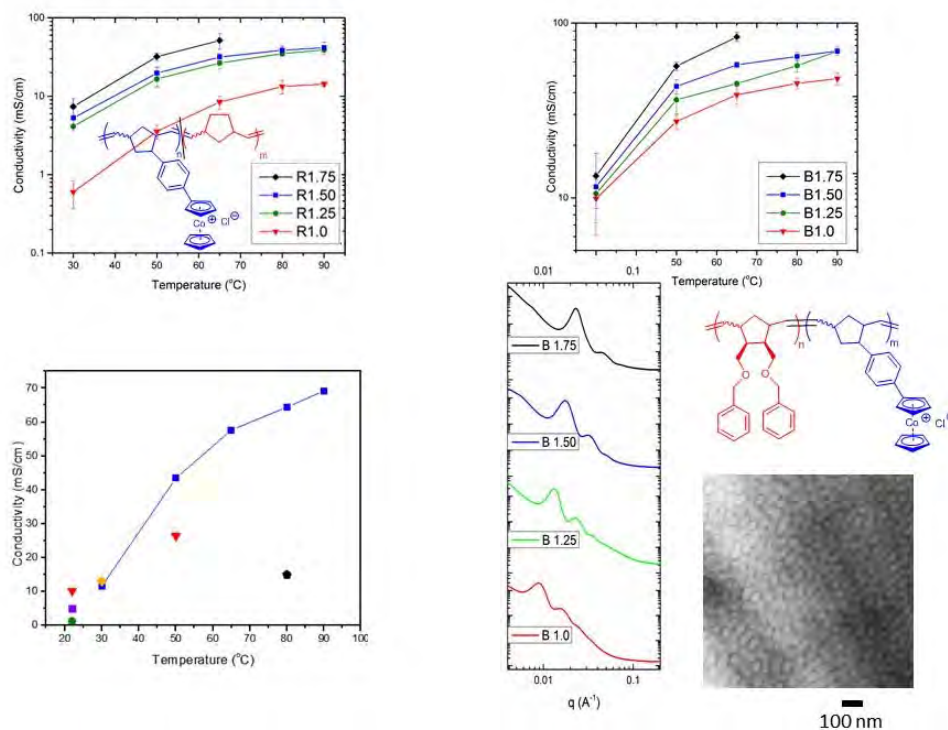
In this study, we intend to direct our attention to the fluorination of the two connecting thiophene units between the TAZ unit and the BnDT unit. Four structurally related polymers based on PBnDT-HTAZ were then designed and successfully synthesized, featuring thiophene units fluorinated at different positions and/or fluorinated TAZ units. It was found that the fluorination positions on thiophene units (3 vs 4 position) have a strong impact on the reactivity of monomers, the conformation and twisting angles between adjacent units, the energy levels of the new polymers and the aggregation of polymer chains. More interestingly, the fluorination of thiophene units can efficiently deepen the HOMO level and increase hole mobility of these new polymers. When these newly designed polymers were tested for their photovoltaic performance, remarkably high V_{oc} (as high as 0.99 V) and high fill factor were achieved owing to the deep HOMO levels and high hole mobility, respectively. The synthetic chemistry to control the fluorination positions at thiophene units and the strategy of incorporation of fluorinated thiophene units to improve the efficiency of PSCs developed in this study will provide the community useful material design guidance.



POLY 336: Introducing cobaltocenium to Alkaline Anion Exchange Membrane Fuel Cells (AAEMFC)

Haomiao Yuan, haomiao@mail.pse.umass.edu, **Tsung-Han Tsai**, **Bryan Coughlin**,
Polymer Science and Engineering, University of Massachusetts Amherst, Amherst,
Massachusetts, United States

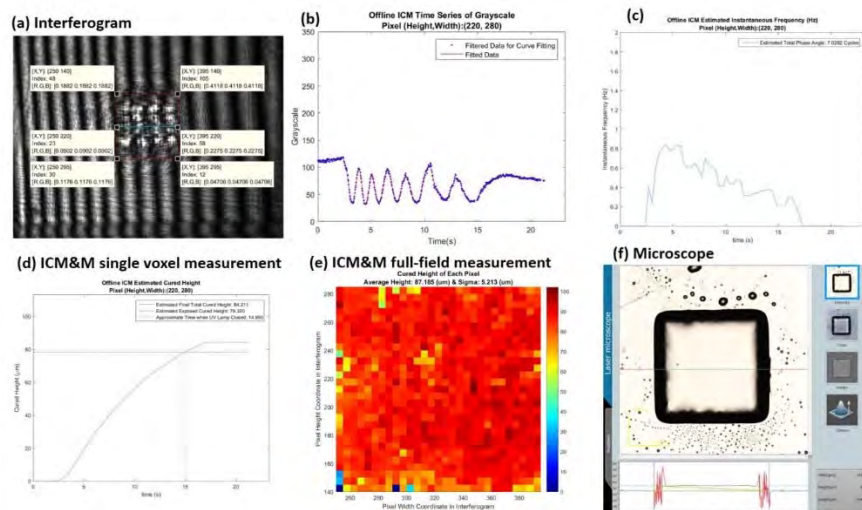
Cobaltocenium derivatives are good candidates for alkaline anion exchange membrane (AAEM) because of their excellent thermal, alkaline and electro-chemical stabilities under fuel cell operational conditions. However, there has not yet been an efficient method incorporate cobaltocenium cation into polymers that possess alkaline stable structures Here, cobaltocenium-containing monomers with different chemical structures were synthesized. The carbon-carbon bond linkages between cobaltocenium and polymerizable olefin ensure alkaline and thermal stabilities. Monomers were copolymerized with comonomers to afford amphiphilic polymers with precisely controlled ion exchange capacities over a wide range. Different polymer architectures were prepared such as random copolymer, block copolymer and crosslinked networks. The polymers were fabricated into thin robust membranes. The solvent processibility of the non-crosslinked membranes shows a great advantage during membrane fabrication. The ion conductivity of these membranes were measured and showed promising results for use as alkaline anion exchange membrane fuel cell applications.



POLY 337: Real-time metrology for photopolymer additive manufacturing with exposure controlled projection lithography

Xiayun Zhao, *zhaoxiayun@gmail.com*, David W. Rosen. Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

As additive manufacturing (AM) is poised for growth and innovations, there is tremendous current interest in polymeric and soft matter additive manufacturing due to their great processability and properties which could enable applications across numerous industrial sectors. Measurement science has been identified as a research priority to accelerate the commercialization and adoption of polymers AM. The Exposure Controlled Projection Lithography (ECPL) is an additive manufacturing process, in which liquid photopolymer monomers cross-link into solid polymeric part with controlled ultraviolet irradiation projected from beneath a stationary and transparent substrate. It is promising for fabrication of micro optics components. Due to the complex chemical kinetics and physics interactions in photopolymerization process, unavailable in-situ metrology and unmeasurable time-varying disturbances such as oxygen inhibition and light source fluctuations, a common practice in AM process planning relies heavily on experimental characterization, statistics models and multiphysics simulation in an open-loop control mode, which cannot effectively control the grey-box process. To improve the process accuracy and precision with closed-loop control, a real-time process metrology for the ECPL, including sensor model, calibration procedure, data mining algorithms, and measurement characterization. Experimental results show that the ICM&M method can provide a cost-effective real-time full-field measurement for ECPL cured heights with excellent accuracy and reliability, and decent capability of estimating lateral dimensions. The scientific and engineering outcomes from this research will help enhance modeling of nonlinear photopolymerization processes, and provide a paradigm of real-time measurement feedback control for generic polymer additive manufacturing processes.

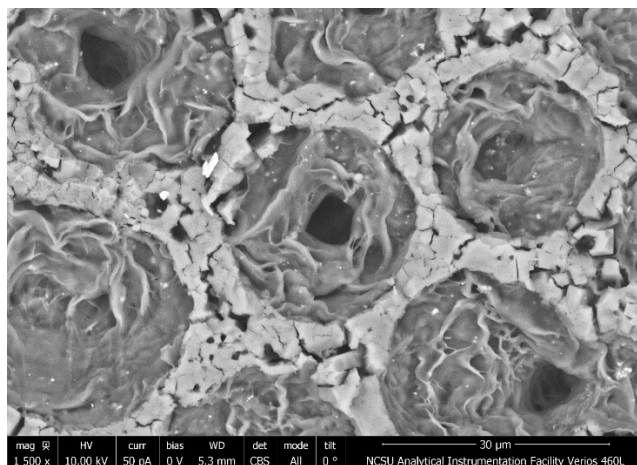


Demo of implementing ICM&M for an ECPL cured part

POLY 338: Nanoscale considerations responsible for diverse macroscopic phase behavior in substituted isobutyl-POSS/poly(ethylene oxide) blends

Yavuz Caydamli¹, yavuzcaydamli@gmail.com, Erol Yildirim¹, Jialong Shen¹, Xiaomeng Fang¹, Melissa A. Pasquinelli¹, Richard J. Spontak^{2,3}, Alan E. Tonelli¹. (1) TECS/Fiber and Polymer Science, North Carolina State University, Raleigh, North Carolina, United States (2) Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States (3) Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States

Incorporation of polyhedral oligomeric silsesquioxane (POSS) molecules into polymer matrices presently constitutes a significant and convenient means by which to prepare hybrid organic/inorganic polymer blends possessing a wide range of interesting and useful properties. In this study, we systematically compare the phase behavior of monofunctional isobutyl POSS molecules possessing different surface chemistry with that of non-functional octaisobutyl POSS in the presence of poly(ethylene oxide) (PEO). At some concentrations of octaisobutyl POSS, macroscopic surface features previously reported for POSS covalently bonded to different polymers are observed for the first time with non-covalently bonded POSS. Complementary calculation of interaction energies from *ab initio* computer simulations is utilized to elucidate the molecular-level mechanism responsible for such observations. Each of the monofunctional POSS molecules with either allyl, aminopropyl or maleamic acid substitution exhibits distinctly different phase behavior in PEO, as discerned from both polarized light microscopy (PLM), laser-scanning confocal microscopy (LSCM) and scanning electron microscopy (SEM) conducted in both planar and cross-sectional views. As above, each of these systems is further analyzed by molecular simulations to permit quantitative comparison and explain their noticeably different behavior in PEO. To establish important structure-property relationships for these unique blends, their thermomechanical properties have been likewise measured and related to their phase behavior. A surprising result from this study is that the surface topography of the blends is largely governed by the viscosity of the POSS/PEO solution prior to casting, irrespective of the polymer molecular weight. This result opens a new and unexplored avenue by which to fabricate POSS-containing polymers with tunable phase behavior and bulk properties.



POLY 339: Stable entrapment of cholesteric 1D photonic domains in Liquid Crystalline Random Terpolymer (LCRTP) architecture with dual covalent and physical networking sites: A platform towards elastomeric 1D photonic material

Lalit H. Mahajan¹, *lalit.mahajan@uconn.edu*, **Dennis Ndaya**³, **Prashant B. Deshmukh**³, **Manesh Gopinadhan**², **Chinedum O. Osuji**², **Rajeswari Kasi**^{3,1}. (1) Polymer Program, University of Connecticut, Storrs, Connecticut, United States (2) Yale Dept Chemical Engineering, New Haven, Connecticut, United States (3) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States

We report a molecular engineered random terpolymer platform comprising 1D photonic cholesteric mesophases (half pitch length: 150-200 nm) in conjunction with microphase segregated PEG domains. Furthermore, we report for the first time, bulk material consisting of entrapped helical 1D photonic domains with the coexistence of microphase segregated domains retaining photonic reflection and improved mechanical features provided by dual level networks: a) optimal interchain UV-crosslinking with thiol-ene chemistry (b) physical junction points provided by microphase segregated domains. To this end, we synthesize poly(norbornene) based LCRTP architecture bearing side chains containing cholesteryl mesogens (NBCh₉), cyanobiphenyl mesogens (NBCB₁₂/NBCB₆) and semicrystalline PEG (Mn = 2000 g/mol) (NBPEG) by Ring Opening Metathesis Polymerization (ROMP). Compression molding of LCRTP material at 90 °C and subsequent quenching yields the film with stabilized cholesteric mesophase capable of reflecting visible light. Judicious selection of amounts of cholesteric and smectogenic/nematogenic monomers lead to molecular level interaction between liquid crystalline domains to obtain a change in pitch length of cholesteric helices exhibiting red-shift in the reflection wavelength as compared to random copolymer control sample of NBCh₉ and NBPEG (processed at 90 °C). For the retention of optical reflection after crosslinking, it is very important to optimize the extent of crosslinking so that delicate helical mesophases are not disrupted. Sample with optimized crosslinker content (1.75 wt %, 1.75 XL) exhibited retention of optical reflection along with improved mechanical features studied by Dynamic Mechanical Analysis. Interestingly, 1.75 XL sample exhibited one way shape memory properties based on T_{cl} (liquid crystalline clearing temperature) due to dual networking sites. The combination of structural control by molecular level design and mechanical integrity by physical and chemical crosslinking offers a versatile platform for development of functional stimuli responsive materials, optical sensors and actuators.

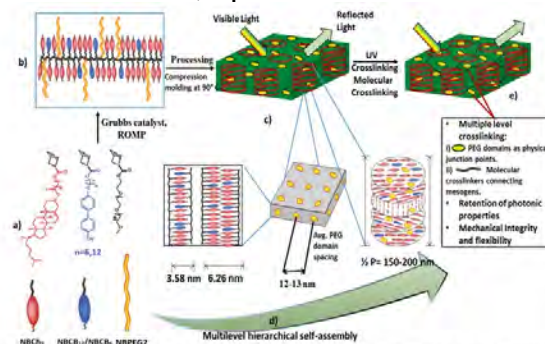
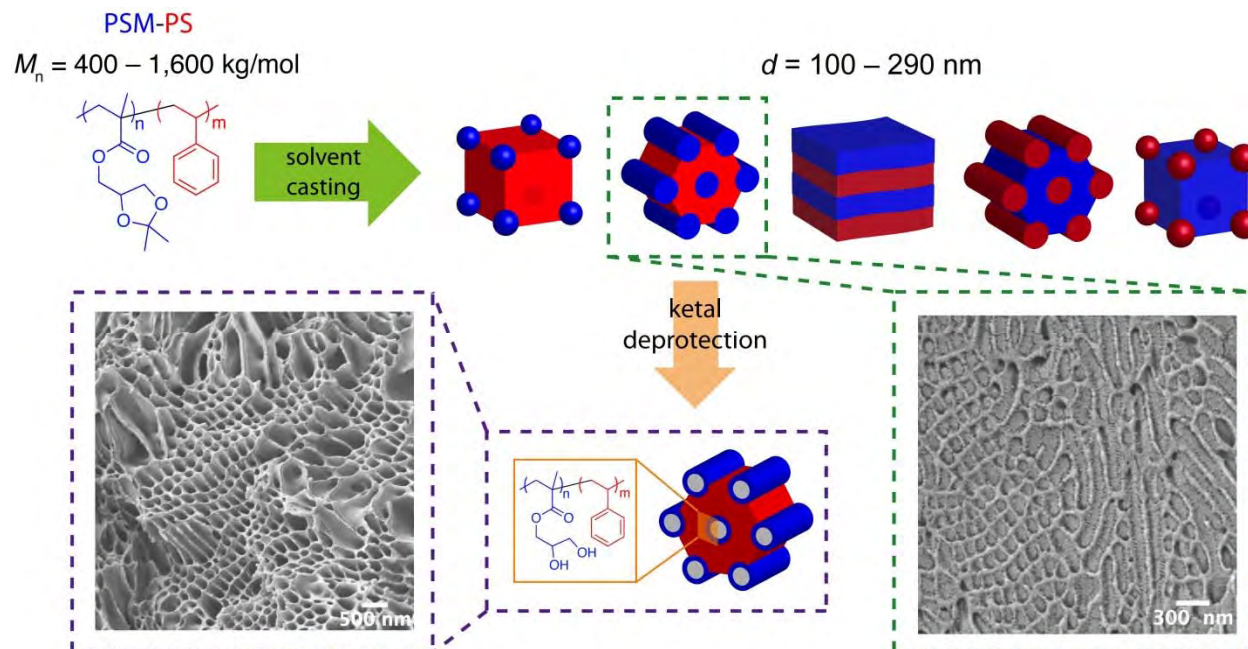


Figure. Schematic illustration of entrapping multilevel hierarchical self-assembly by means of physical and molecular crosslinking. a,b) Monomers and Architecture c) Processing and self-assembly d) Multilevel hierarchical assembly at room temperature e) Entrapment of 1D photonic domains by dual cross-linking.

POLY 340: Nanoporous materials from ultrahigh molecular weight linear block copolymer precursors

Jose Kenneth Mapas, *jkdmapas@gmail.com*, **Javid Rzayev**, *Department of Chemistry, SUNY Buffalo, Buffalo, New York, United States*

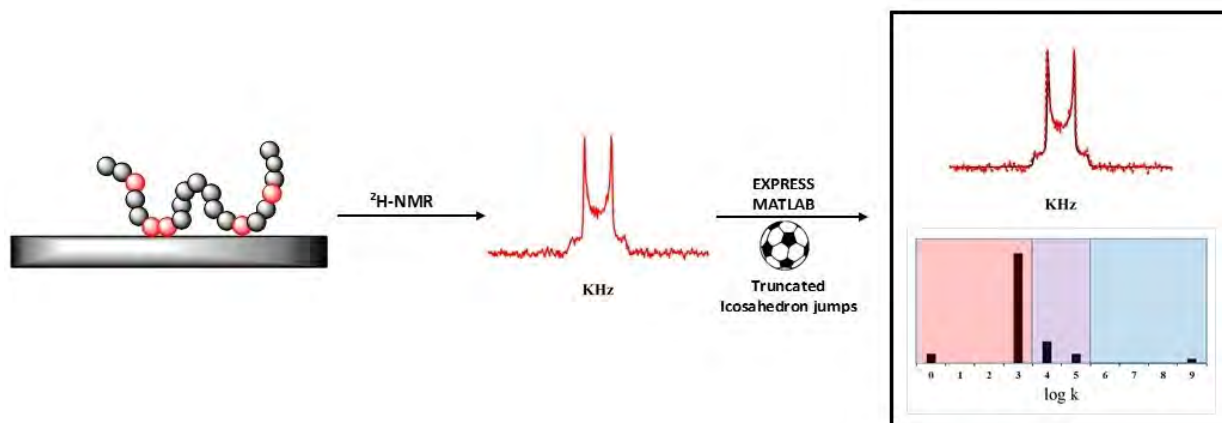
Nanoporous materials were produced from self-assembled ultrahigh molecular weight polystyrene-*b*-poly(solketal methacrylate) (PS-PSM) block copolymers using mild selective deprotection conditions. Through the combination of a Cu(0)-mediated controlled radical polymerization and reversible addition-fragmentation chain transfer polymerization protocols, block copolymers with molecular weights $> 10^6$ g/mol having moderate dispersities were produced. Solvent casting of the copolymers with varying compositions and molecular weights led to the formation of well-ordered periodic nanostructures with domain spacings as large as 290 nm as evaluated by SEM and ultra-small-angle x-ray scattering techniques. Rapid and selective acid-catalyzed deprotection of ketal groups in the PSM block provides a handle to control pore wall functionality producing nanoporous membranes with a polystyrene matrix and hydrophilic pores.



POLY 341: Segmental dynamics of poly(styrene-stat-methyl methacrylate-d₃) in bulk and at very small amounts on silica

Ugo N. Arua¹, ugo.arua@okstate.edu, Madhubhashini Madduma Arachchilage^{1,2}, Frank D. Blum¹. (1) Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States (2) Chemistry, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

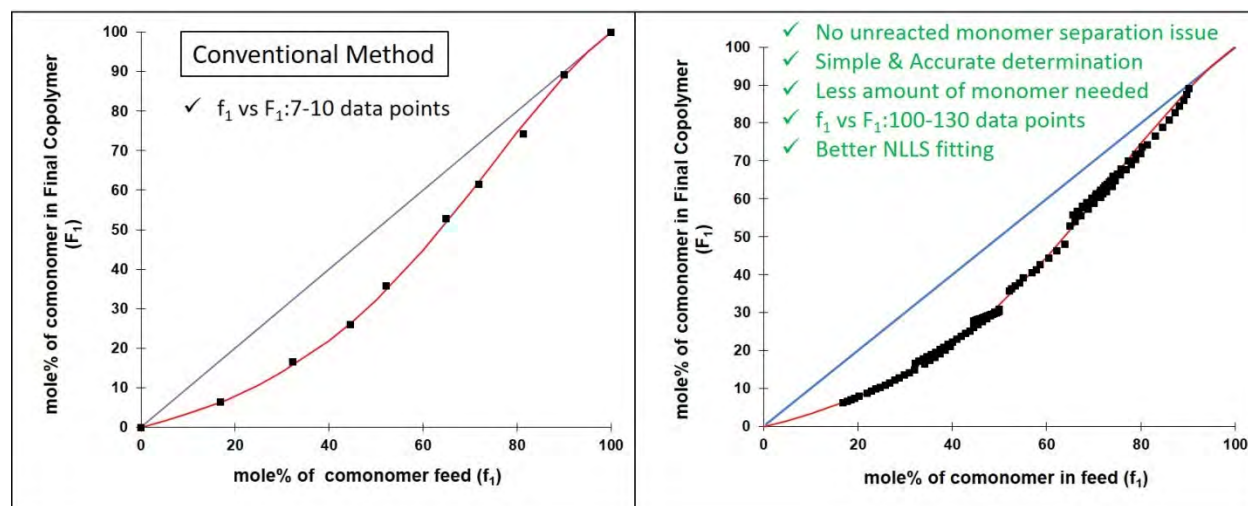
Solid state deuterium (²H) NMR spectroscopy was used to study the segmental dynamics of poly(styrene-stat-methyl methacrylate-d₃) copolymers both in bulk and adsorbed on the surface of silica. Copolymers of different compositions were synthesized (from 100% - 10% methyl methacrylate-d₃). Adsorbed copolymers at small adsorbed amounts (1 and 2 mg/m²) were prepared. Spectra were collected as a function of temperature and the effect of polymer composition and adsorbed amount was observed. Simulations of the line shapes of the resulting spectra were made based on the soccer ball (truncated icosahedron) model, which is a good approximation to small angular jump motions, to categorize motions with fast, intermediate and slow jump rates. We find that, at small MMA contents and small adsorbed amounts, the MMA-d₃ segments show a disproportionate amount of more restricted dynamics. These results indicate how different mers in random copolymers may segregate at interfaces.



POLY 342: Simple and accurate determination of reactivity ratios of chain copolymerization following terminal model by *in-situ* $^1\text{H-NMR}$ technique

DIBYENDU DEBNATH², dd68@zips.uakron.edu, Jessi Baughman³, Robert A. Weiss¹, Coleen R. Pugh². (1) Polymer Engineering, University of Akron, Akron, Ohio, United States (2) Department of Polymer Science, The University of Akron, Akron, Ohio, United States (3) Chemistry, The University of Akron, AKRON, Ohio, United States

We propose a new method for the determination of reactivity ratios of monomers in a chain copolymerization that follows terminal model kinetics. We assume that the monomers consumed during copolymerization are accumulated in the polymer backbone without undergoing any side reactions. We used $^1\text{H-NMR}$ spectroscopy as a tool to follow the monomer consumption with time, and hence accurately determined the reactivity ratio from non-linear least square (NLLS) fitting of Mayo-Lewis plot. We considered 100 to 130 data points for better NLLS fitting of Mayo-Lewis plot, whether conventional method does fitting with 7 to 10 data points. The data points were obtained from *in-situ* NMR spectroscopy experiments of different feed compositions of monomers. The methodology was validated using styrene (St) and methyl methacrylate (MMA) as a model system. We obtained $r_{\text{St}} = 0.58 \pm 0.02$ and $r_{\text{MMA}} = 0.49 \pm 0.02$, which is similar to other literature reports following conventional methods. Our methodology requires very low quantities of monomer, unlike conventional methods. Additionally, with this methodology we can bypass a number of practical issues that appear in conventional methods, such as separation of unreacted monomer, which is especially when it aggregates with polymer; inaccurate determination of unreacted and consumed monomer due to lack of consideration of the relaxation times of the protons of interest. We copolymerized N,N-dimethylacrylamide (DMA) with 2-(N-ethylperfluorooctanesulfonamido)ethyl acrylate (FOSA) and with 2-(N-ethylperfluorooctanesulfonamido)ethyl methacrylate (FOSM). With our unique methodology, we successfully determined the reactivity ratios of two separate copolymerization systems as $r_{\text{DMA}} = 0.93 \pm 0.04$, $r_{\text{FOSA}} = 1.42 \pm 0.07$ and $r_{\text{DMA}} = 1.13 \pm 0.03$, $r_{\text{FOSM}} = 3.51 \pm 0.08$.



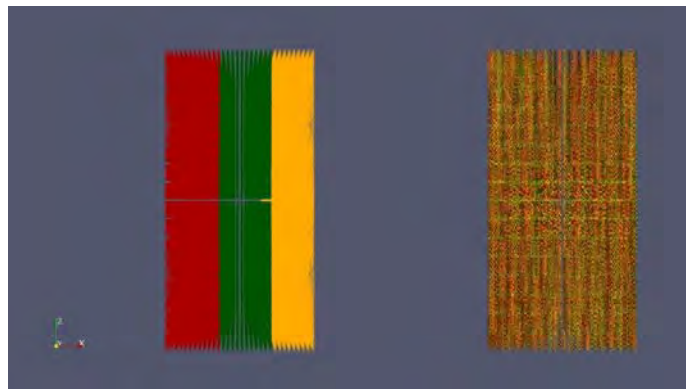
POLY 343: Calculating initial lattice configurations to enhance computational efficiency for polydisperse polymer simulations

Wanxing Xu, *wanxingxu@mymail.mines.edu*, John R. Dorgan. *Chemical and Biological Engineering Department, Colorado School of Mines, Golden, Colorado, United States*

Computer simulation as a scientific tool has been implemented for problems in virtually every field of scientific research. Polymer science has particularly profited by the use of computational simulations that are capable of predicting molecular scale properties. Monte Carlo (MC) is an extremely powerful tool to study the structural and thermodynamic properties of polymer melts. Much experimental evidence demonstrates that polydispersity plays a significant role in the physics of polymer melts. Despite its fundamental role in the behavior of polymers, polydispersity has not yet been fully extended to systems typical of industrial polymers.

A new algorithm is developed to place polymer chains of differing length into an initial configuration on a face-centered-cubic lattice. Simulations with no flow biasing are performed on two different initial configurations to show differences in reaching equilibrated configurations. Monte Carlo simulations presented here are performed on a fully occupied face-centered cubic lattice by using the p-COMOFLO algorithm, a variant of the cooperative motion algorithm of Pakula. This algorithm allows for a realistic polymer melt density by modeling lattices at full density.

System properties including the chain size, segmental density distributions and chain-end density distribution are investigated as function of Monte Carlo time. The simulation results show that the initial configuration generated by this new algorithm comes to equilibrium significantly faster with respect to chains size, segmental densities, and chain end densities. At equilibrium, the longer chains reside away from the walls and the shorter chains are preferred near the walls. Meanwhile, there is a preference for chains ends to locate at the wall. This newly developed algorithm offers the advantage of speeding up computational equilibrium and thus less computational time is needed. Accordingly, it represents an important advancement in pursuing the simulation of systems of true practical importance.



Visualization of Mapping Three Different Chains to the Lattice Using Two Different Placement Methods

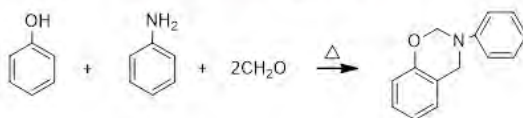
POLY 344: Effect of organically modified montmorillonite on polymerization and thermal degradation mechanisms of polybenzoxazine

Aysegul Hisar Telli, *aysglhsr@gmail.com*, *Jale Hacaloglu*. *Chemistry, Middle East Technical University, Ankara, Turkey*

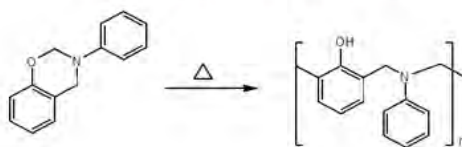
The polymer/layered silicate nanocomposites have received significant attention, owing to their remarkable mechanical, thermal, and physical-chemical properties compared with virgin polymer and conventional (microscale) composites. Montmorillonite, known as clay, has two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina, is naturally hydrophilic and the stacks of clay platelets are held tightly together by electrostatic forces. The preparation of a composite out of untreated clay is not very effective as most of the clay cannot interact with the matrix, the clay must be treated before it can be used to make a nanocomposite. By exchanging the ions present in between the layers with various organic cations, montmorillonite clay can be compatibilized with a wide variety of matrix polymers.

In the present work the effects of organically modified montmorillonite (OMMT), Cloisite 10A, involving dimethyl benzyl hydrogenated tallow ammonium as the organic modifier, on curing and thermal characteristics of polybenzoxazine based on phenol and aniline, PPa. The mono substituent benzoxazine monomer, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, was synthesized by solventless method and characterized by Fourier transform infrared, (FTIR), nuclear magnetic resonance (NMR) and direct pyrolysis mass spectrometry (DP-MS) techniques. The pure benzoxazine monomer and benzoxazine monomer in the presence of OMMT were polymerized by applying a step-wise curing program. The disappearance of the exothermic ring opening polymerization peak in the differential scanning calorimetry (DSC) curves of the polymer and composite were confirmed polymerization of the monomers by the applied curing program. The morphology of the nanocomposite was evaluated by X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). Thermal characteristics of polybenzoxazine and its composite were investigated by thermogravimetric analysis (TGA), DSC and DP-MS techniques.

Schema 1. Synthesis of Benzoxazine



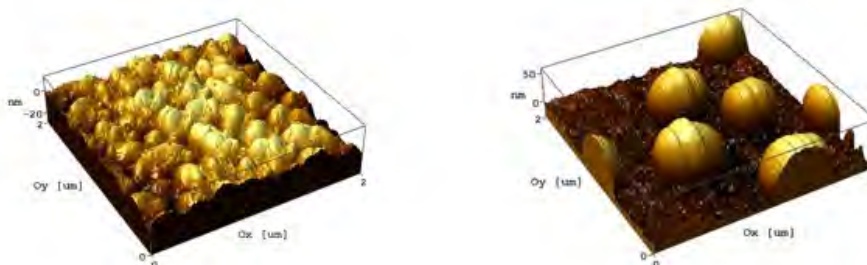
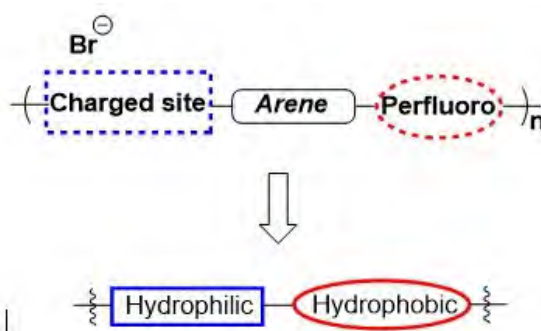
Schema 2. Polymerization of Benzoxazine



POLY 345: Hydrophilic-hydrophobic hybrid polymer involving perfluoro- with tetraarylphosphonium moieties: Synthesis, film morphology and electrochemical properties

Wang Wan², wan2@g.clemson.edu, Xiaoyan Yang², Rhett Smith¹. (1) Clemson University, Clemson, South Carolina, United States (2) Chemistry, Clemson University, Central, South Carolina, United States

A novel polymer having both a hydrophilic phosphonium site and a hydrophobic perfluoro-group was designed and successfully prepared by palladium-catalyzed P–C coupling reaction. In the polymer, hydrophilic and hydrophobic segments were arranged alternatively on the backbone. Anion exchange of bromide for ditriflamide polyelectrolyte tremendously improved thermal stability (5% degradation by TGA) from 234 °C to 460 °C and chemical stability under alkaline condition. Therefore, these polyelectrolytes were tested for ion conductivity and as electrode components in battery and in fuel cell applications. The film morphology was influenced by structural variation and has been investigated by AFM, SEM and critical surface energy were measured related to both main chain and counterion



AFM images ($2 \times 2 \mu\text{m}$) of dip cast films of polymeric bromide (left) and polymeric ditriflamide (right) by using acetone solvent

POLY 346: CdSe/CdS-Conjugated polymer core-shell hybrid nanoparticles by a grafting-from approach

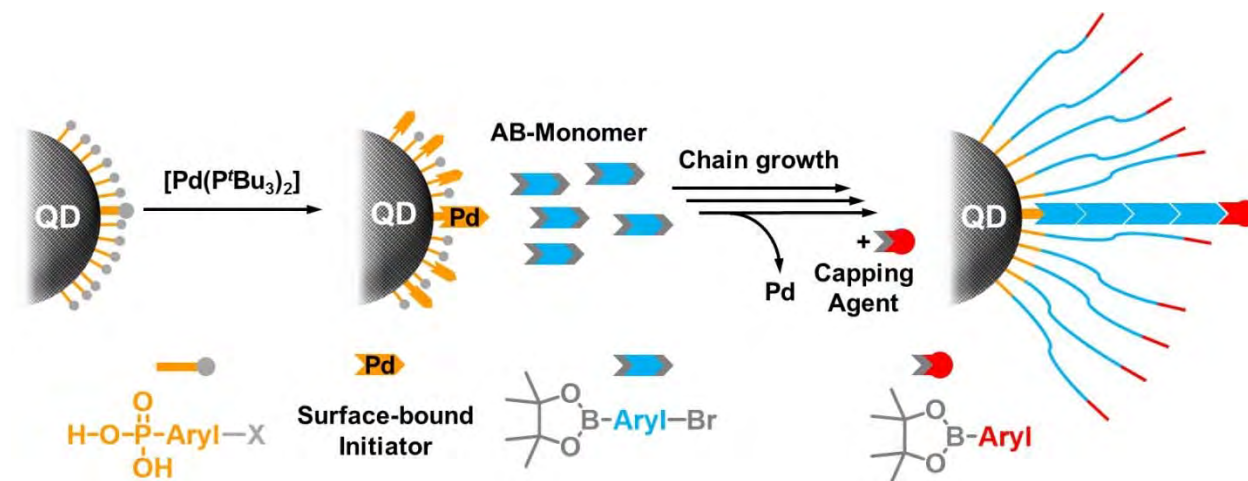
Steffen Huber¹, steffen.huber@uni-konstanz.de, **Tjaard deRoo**¹, **Denis Seletskiy**², **Alfred Leitenstorfer**², **Stefan Mecking**¹. (1) Department of Chemistry, University of Konstanz, Konstanz, Germany (2) Department of Physics, University of Konstanz, Konstanz, Germany

Hybrid nanoparticles consisting of II-VI semiconductor nanocrystals and organic conjugated polymers are increasingly relevant and have potential application in light emitting devices, photovoltaics and bioimaging applications.

For the functionalization of particles with polymer grafting-from approaches are the method of choice and allow for a covalent attachment of polymer with defined chain length and high grafting densities. However, conjugated polymers are normally obtained by step-growth reactions which are incompatible with grafting-from approaches. Here, we report on a grafting-from approach by controlled Suzuki-Miyaura coupling polymerization which yields CdSe/CdS nanocrystals with semiconducting polymers grown from their surface.

High quality CdSe/CdS core-shell nanocrystals are synthesized and functionalized with halo-aryl-phosphonic acids. They serve as organic precursors for three-coordinated surface bound Pd(II) Suzuki-Miyaura initiator complexes which are obtained by the reaction with a Pd(0) source. These immobilized initiators can then be used to grow conjugated polymers from the nanocrystal's surface. A key issue in terms of the scope of the method and the bandgaps accessible is a sufficiently high reactivity of the surface bound initiators, matched to the given monomer of interest. Successful polymerization from the nanocrystal's surface is concluded from MALDI-TOF mass spectrometry of stripped-off polymer.

The synthesized particles feature a bright photoluminescence and preliminary photoluminescence experiments indicate an effective energy transfer from the polymer to the nanocrystal.



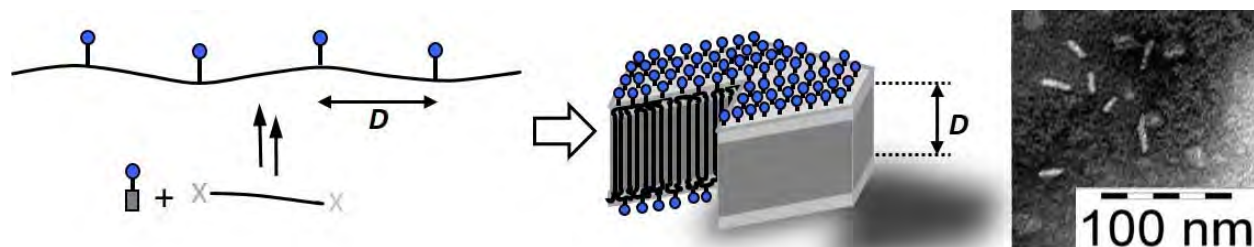
POLY 347: Anisotropic nanocrystals from precisely long-spaced ionomers

Christina Rank, christina.rank@uni-konstanz.de, Stefan Mecking. Department of Chemistry, University of Konstanz, Konstanz, Germany

Anisotropic nanoparticles with defined shape and surface chemistry are of general interest as building blocks for superstructure formation. In contrast to inorganic nanoparticles, anisotropic polymer nanoparticles are still barely investigated. In most cases, phase separation of immiscible segments of block copolymers is used to generate anisotropic surfaces but the shape of these particles often remains spherical or dumbbell-like.

We report a different approach by directly encoding the crystal shape and surface chemistry in the microstructure of the polymer by precisely spaced ionic groups on a crystalline polyethylene-like polymer backbone. By post-polymerization dispersion of the ionomers in water the ionic groups align at the surface of the crystalline polyethylene core and self-stabilize the particle in water. The distance of the ionic groups on the polymer backbone determines the thickness of the platelet-like nanocrystals.

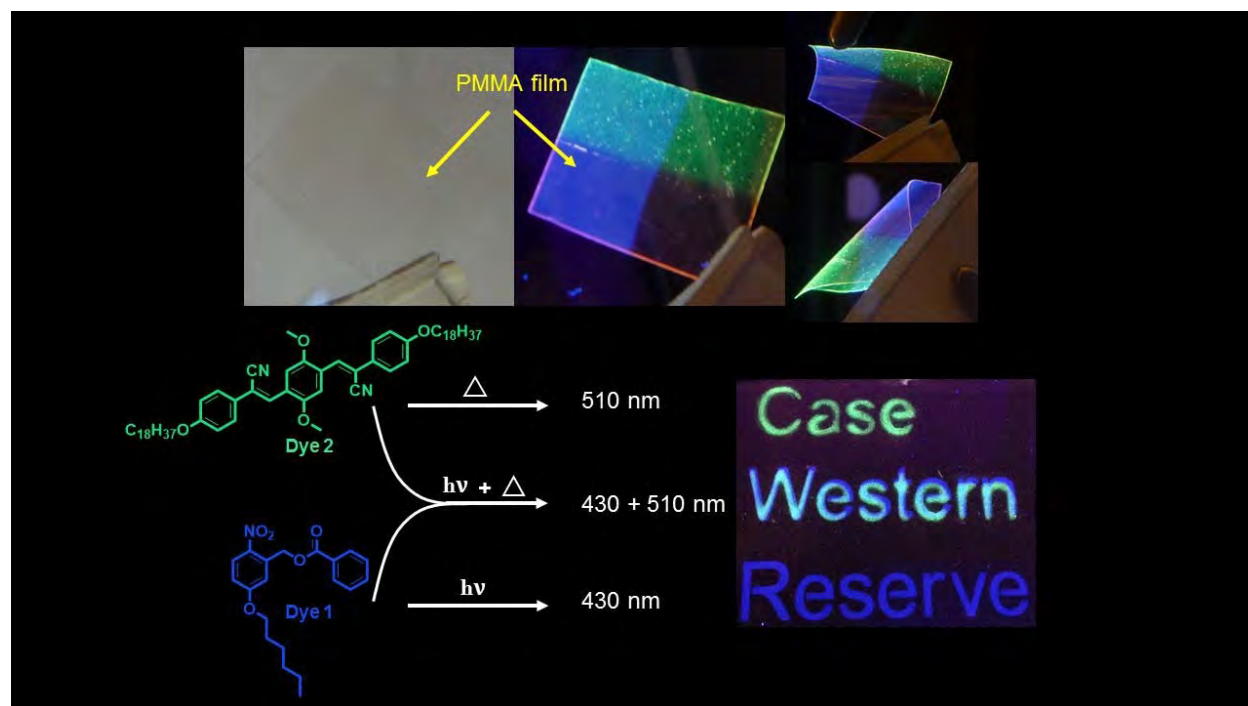
Classical polycondensation was used to prepare precisely spaced ionomers from ultra long-chain aliphatic monomers and small co-monomers which can be functionalized prior or after polymerization. The ultra long-chain monomers are readily obtained from unsaturated fatty acids by repetitive self-metathesis and isomerization of the double bond. The modular layout of the polycondensation reaction offers the opportunity to design size and surface chemistry of the nanoparticles with reasonable synthetic effort by varying the length of the spacer and the ionic groups.



POLY 348: Dual-patterning optical data storage in polymer films with orthogonally responsive dyes

Peiran Wei¹, Pwx182@case.edu, Bowen Li², Al d. Leon¹, Emily Pentzer¹. (1) Chemistry, Case Western Reserve University, Cleveland, Ohio, United States (2) chemistry, Case Western Reserve University, Cleveland, Ohio, United States

Much research efforts have gone into the development of novel approaches and new materials for next generation of optical data storage (ODS) devices.^{1,2} Current technologies use one-photon-absorption or two-photon-absorption processes to write binary data by locally changing the optical properties of the medium.¹⁻⁴ Further improving storage capacity will be realized by decreasing the diameter of the data storage units, or extending data units to the third dimension. In this work, we present a simple and scalable method for increasing the data storage units by using orthogonally stimuli-responsive small molecule dyes in a film of commodity polymer. We developed a novel ODS system that can be written with thermal treatment, light treatment, or both, to give three different colors visible under UV irradiation, with resolution down to 300 μm . The flexible polymer film remains colorless and transparent under ambient light after this dual patterning or and retains the stored data after polishing with sandpaper. Such a straightforward and scalable method enables polymer films to store quaternary information instead of binary data (0, 1, 2, 3 vs. 1, 1), which has a potential of doubling information density in ODS systems.

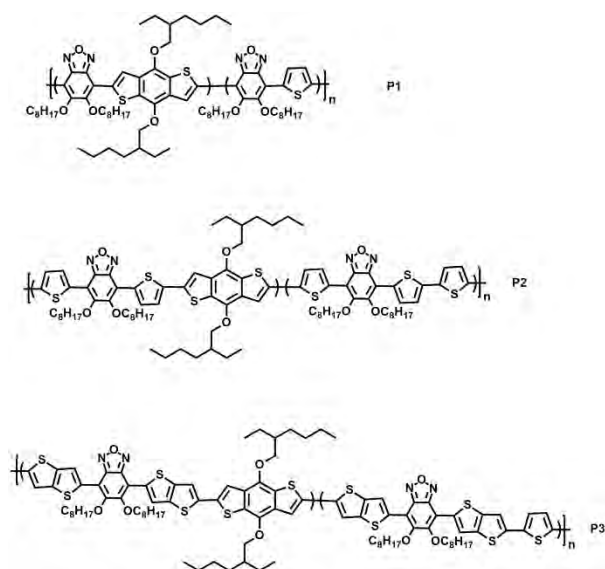


PMMA film doped with UV and heat responsive dyes and activated orthogonally

POLY 349: 2,1,3-Benzooxadiazole, thiophene and benzodithiophene based random copolymers for organic photovoltaics: Thiophene versus thieno[3,2-b]thiophene as π -conjugated linkers

Seza Goker¹, sezagoker@gmail.com, Gonul Hizalan¹, Ece Aktas¹, Seda Kutkan¹, Ali Cirpan², Levent Toppare³. (1) Chemistry, Middle East Technical University, Ankara, Turkey (2) Department of Chemistry, Middle East Technical University, Cankaya Ankara, Turkey (3) Middle East tech Univ, Ankara, Turkey

Molecular design and device optimization played a significant role for the rapid development in the field of PSCs over the past decade.¹ One of the most efficient strategies to achieve superior photovoltaic properties is the donor-acceptor approach. Low-band-gap polymers having extended absorption in the longer wavelengths with an increased device efficiency are obtained via donor-acceptor approach. Its planar structure, strong π - π intermolecular interactions, regioregularity, easy modification and high hole mobility makes benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) one of the most successful electron-donor units for semiconducting polymers.^{2,3} BDT-based conjugated polymers gave high performance photovoltaic devices with PCBM since its symmetric structure could enhance the electron delocalization and interchain interaction.⁴ On the other hand, 2,1,3-Benzooxadiazole (BO) is one of the strong electron withdrawing moieties widely used in PSCs due to its planar, rigid geometry, ease of preparation, excellent stability and optoelectronic characteristics. 5,6-Bisalkoxy-substituted BO based conjugated polymers reveal better solubility than that of their unsubstituted counterparts. These inspired us to synthesize polymers comprising benzooxadiazole unit as electron acceptor and benzodithiophene, thiophene moieties as electron donor building blocks bridged by different heteroaromatic rings (Scheme 1). Thiophene and thienothiophene units were selected as the conjugated linkers. The syntheses, electrochemical and spectroelectrochemical characterizations of the polymers were performed.

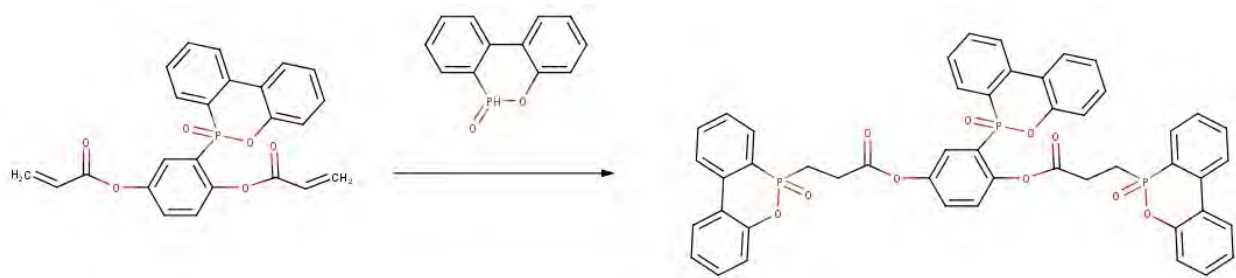


Scheme 1

POLY 350: Multifunctional phosphorus flame retardants for polymeric materials from benzoquinone

Aeshah Alrubayyi, *alrub1as@cmich.edu*. Central Michigan University, Mount Pleasant, Michigan, United States

Phosphorus flame retardants from renewable biomaterials offer effective, nontoxic alternatives to organobromine compounds which are stable in the environment, tend to bioaccumulate and may pose a risk to human health. Benzoquinone readily undergoes Michael addition of phosphite to generate a phosphorus-substituted hydroquinone. This hydroquinone derivative can be converted to the *bis*-acrylate by treatment with acryloyl chloride. Phosphite addition to the unsaturation of the *bis*-acrylate generates trifunctional phosphorus compounds. These compounds display good thermal stability and may serve as effective flame retardants in a variety of polymeric systems.

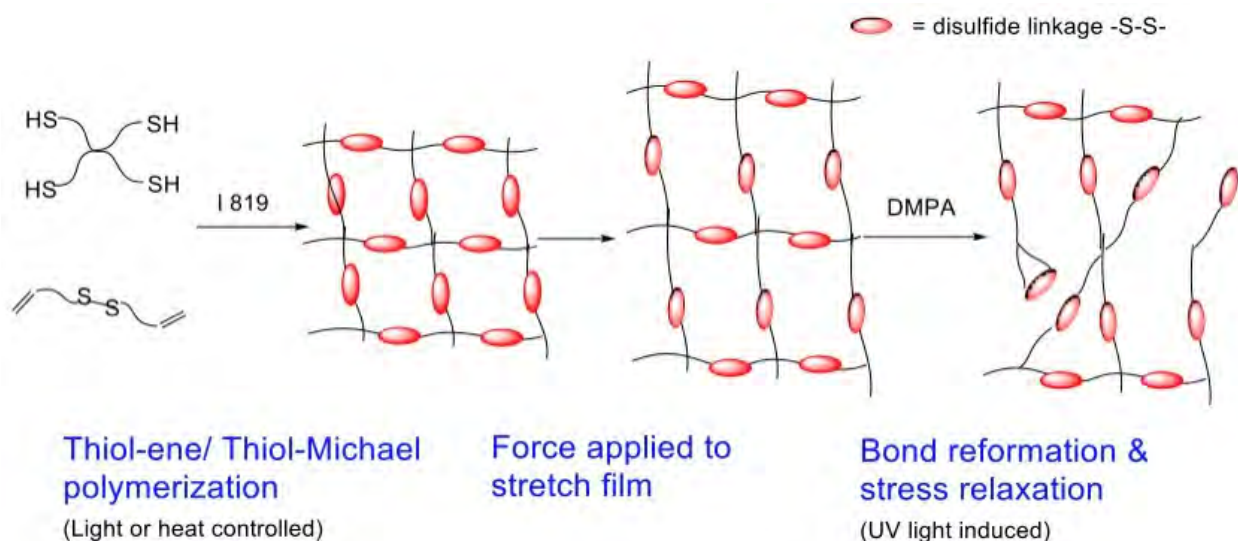


POLY 351: Photochemical controlled disulfide based thiol-ene/thiol-Michael covalent adaptable network development and application

Xun Han, *x.han85@gmail.com*, Xinpeng Zhang, Nancy Sowan, Lewis Cox, Sijia Huang, Christopher Bowman. UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States

Covalent adaptable networks (CANs) incorporate dynamic covalent bonds that undergo rearrangement in response to the application of a particular stimuli. These dynamic systems enable the CAN materials to possess novel properties such as self-healing, recycling, and stress relaxation. In recent decades, various types of dynamic bond rearrangements, such as metal-catalyzed transesterification, Diels-Alder reactions, imine exchange, and addition-fragmentation, have been implemented in CAN materials development. As one type of dynamic covalent bonds, disulfide bonds initiate rearrangements stimulated by heat, light, pH, etc., and consequently, emerge as promising candidates for dynamic materials.

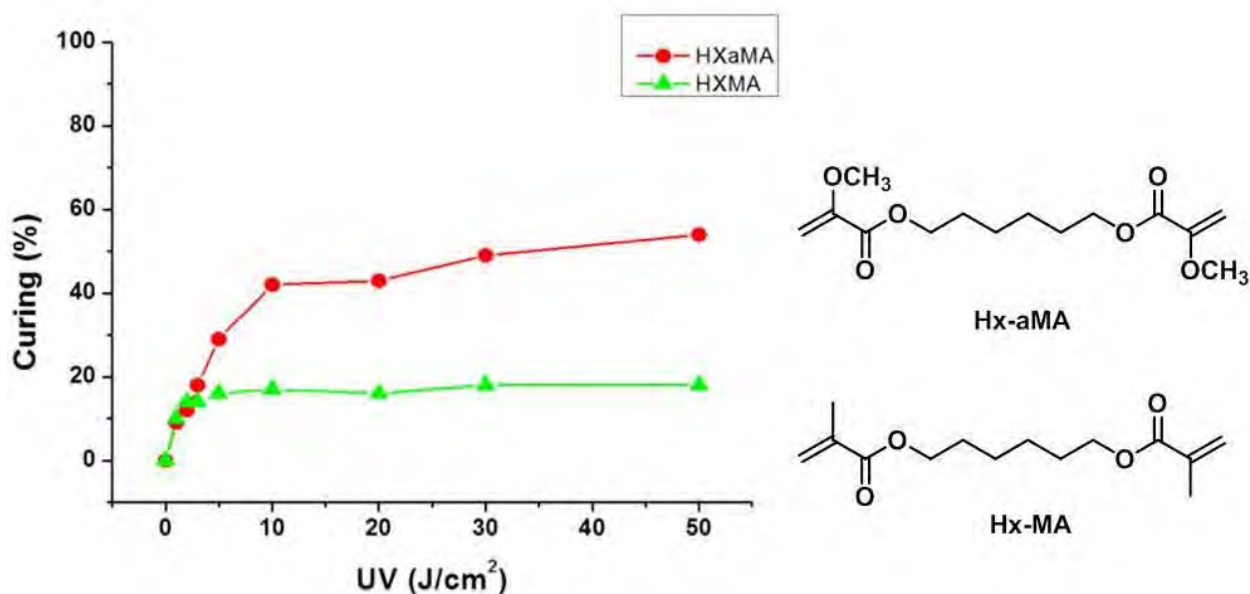
Here, we designed and synthesized disulfide-containing vinyl monomers and further applied them in constructing photo thiol-ene/thiol-Michael polymer networks. Addition of a radical initiator enables photo induced disulfide bond exchange, thus achieving spatial and temporal control over reformation of the basic polymer films. Various types of instruments including FT-IR, NMR, DMA, MTS, tensometer, etc. were employed to characterize and evaluate the performance of these photoresponsive polymers. They exhibited highly efficient stress relaxation behavior with stress reduction of up to 80% in photoplasticity experiments. The application of these CANs in impression imprinting materials was demonstrated. The effect of implementing the disulfide-contained monomers in reducing polymerization shrinkage stress in purely acrylate polymerization was also evaluated.



POLY 352: Photoreactivity of α -methoxyacrylate containing reactive mesogens and their synthesis

Hyein Jung^{1,2}, gpdl@kRICT.re.kr, Jungshin Park¹, Jinsoo Kim¹, Yun-Ho Kim¹, Eunyoung Kim², Jae-Won Ka¹. (1) Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of) (2) Yonsei University, Seoul, Korea (the Republic of)

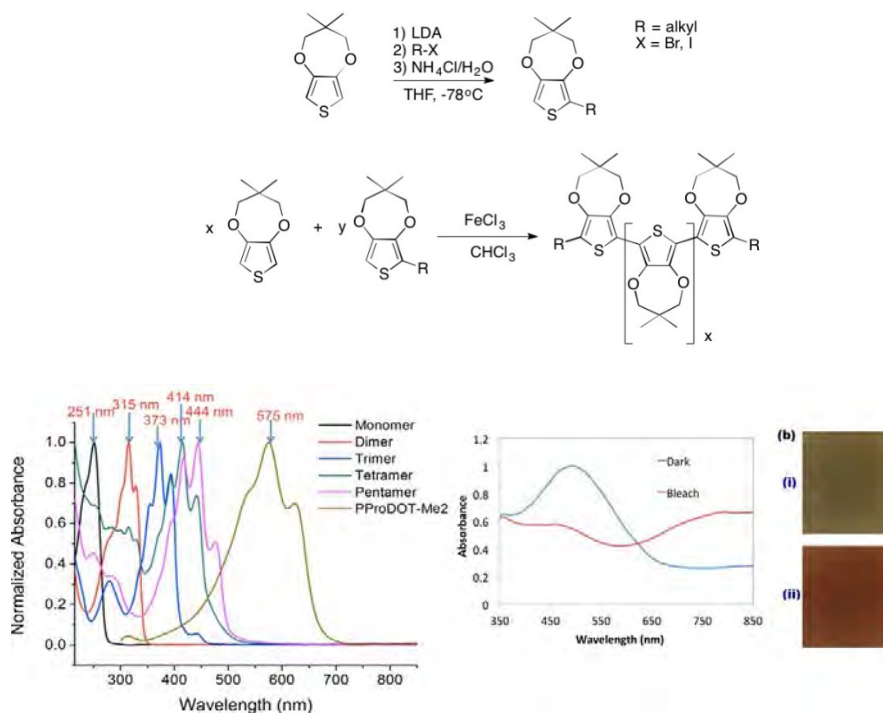
Reactive mesogens (RMs) are liquid crystalline materials with polymerizable end groups. Polymerization of reactive mesogens with two or more polymerizable groups leads to densely crosslinked networks in which the liquid crystalline order is permanently fixed. RMs have been extensively studied and used for a wide range of display applications such as mobile phones, monitors, televisions, etc. Recently using the PS-VA (polymer-stabilized VA) included RMs at industry, it is important to be able to UV curable at low energy. However, previous reported acrylate or methacrylate RMs are need to high energy photo-irradiation or photoinitiator because of their low photoreactivity under the curing UV light (365 nm). In order to improve photoreactivity, we introduced α -methoxyacrylate instead of acrylate or methacrylate. In this report, we'll present synthesis of biphenyl, terphenyl, naphthalene cored α -methoxyacrylate RM by esterification reaction and photoreactivity of them.



POLY 353: Oligomeric 3,4-propylenedioxythiophene dyes for achieving color neutrality with electrochromic devices

omer A. Yassin¹, omer.yassin@uconn.edu, Michael T. Otley¹, xiaozheng zhang², Mengfang Li², Gregory A. Sotzing^{1,2}. (1) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Polymer Program, Institute of Material Science, University of Connecticut, Storrs, Connecticut, United States

Electrochromic devices are an everyday part of our life. It is continuously growing field due to its current and potential applications for architectural, vehicular, and aircraft windows, skylights, sun- roofs, eyeglasses, and numerous types of displays. Whether its purpose is for energy conservation or just aesthetics, these switchable devices have a promising future. Neutral colors (grey or black) are highly desirable for these applications. However, the ability to design strongly absorbing (black) electrochromic polymers (ECPs) that can be switched to a highly transmissive state is challenging due to the requirement of designing a polymer that absorbs the entire visible region homogeneously. Herein, we have demonstrated the ability to achieve color neutrality by tuning the absorption wavelength using a copolymer-electrochromic oligomer dye approach. The absorption spectra measurements and excited state calculations demonstrated a dependence on chain length similar to what is expected of finite polyene systems. Electroactive monomer, 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me₂) was used to synthesize various homo-oligomers of increasing conjugation length that generate different electrochromic dyes. The theoretical calculations provided insight into the electronic properties of these molecules. These electrochromic dyes, if end- capped, could be used with other electrochromic oligomers and/or polymers to complement each other to achieve a desired color or neutrality.

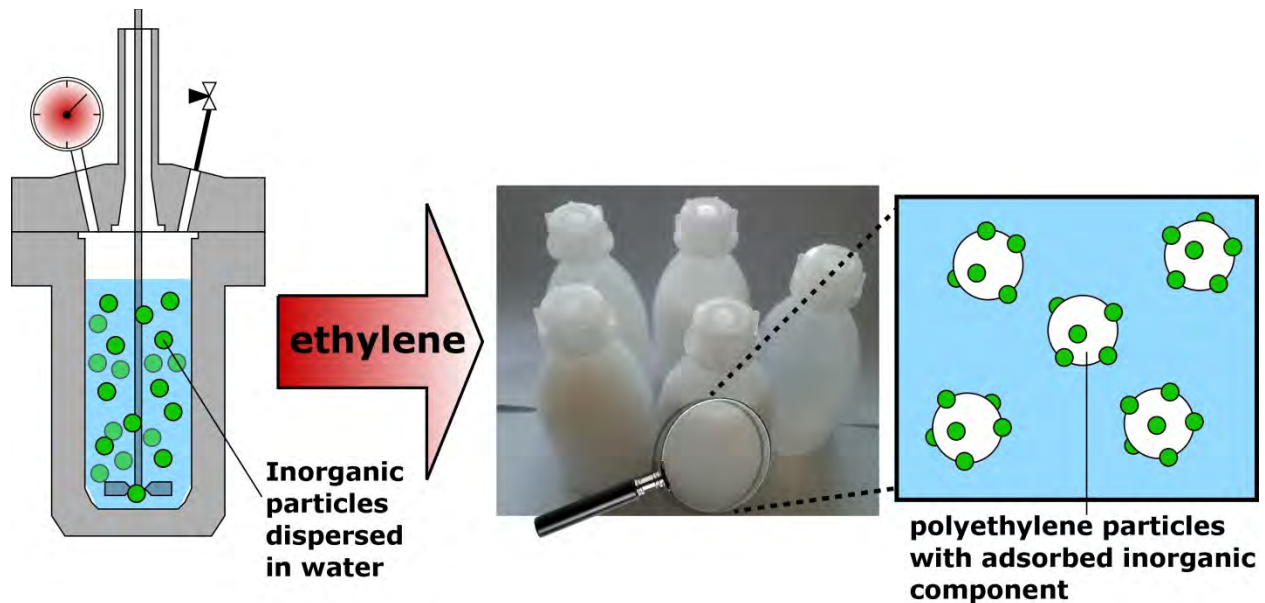


POLY 354: In-situ stabilization of polyolefins in aqueous systems by inorganic particles

Tobias Morgen, tobias.morgen@gmx.de, **Stefan Mecking**, Department of Chemistry, University of Konstanz, Konstanz, Germany

Polyolefin nanocomposites containing inorganic components show improved properties in various applications. A common route to nanocomposites is their preparation from composite nanoparticle dispersions. Usually, aqueous dispersions from heterophase polymerization are employed. However, for the case of polyethylene, free-radical emulsion polymerization requires high pressures and catalytic aqueous polymerizations have become available more recently only.

We report on the synthesis of aqueous, Pickering stabilized dispersions of polyethylene. The added inorganic particles effectively stabilize the polyolefin particles formed and also support particle formation during the aqueous polymerization reaction. The morphology and composite nature of the particles were confirmed via transmission electron microscopy and spectroscopic methods.

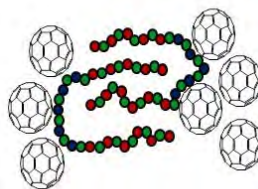
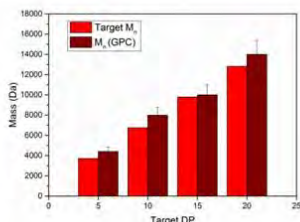
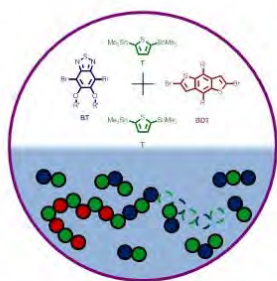


POLY 355: Structure-property relationships of conjugated polymers

Samuel S. Lawton², s.s.lawton@warwick.ac.uk, **David M. Haddleton**¹. (1) Chem Dept, Coventry, United Kingdom (2) Chemistry, University of Warwick, Coventry, United Kingdom

Inspired by the growing demand for economically viable and renewable energy sources, organic photovoltaics (OPVs) are attracting significant attention. With efficiencies exceeding 10 %, donor/acceptor blends or bulk heterojunction (BHJ) devices are amongst the most promising and nearing commercialization. However, many of the recent advances in performance are not fully understood, thus a better understanding of the structure-property relationships of donor polymers is required to accelerate advancement in the field.

This work will describe the synthesis of various donor polymers and analysis of their structure and properties by NMR, SEC, UV/Vis and electrochemical techniques as well a correlation with device efficiencies. We are working to maximize processability and efficiency of the donor polymer in the BHJ whilst gaining a more detailed understanding of the role donor structure plays in device efficiency.



Condensation

Control

Manipulation

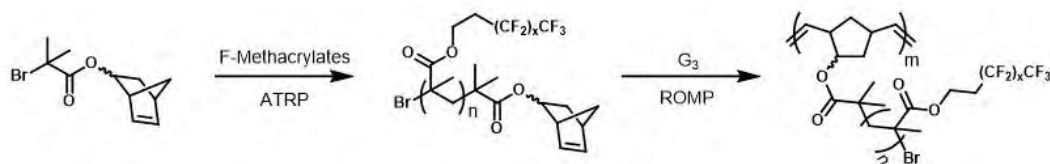
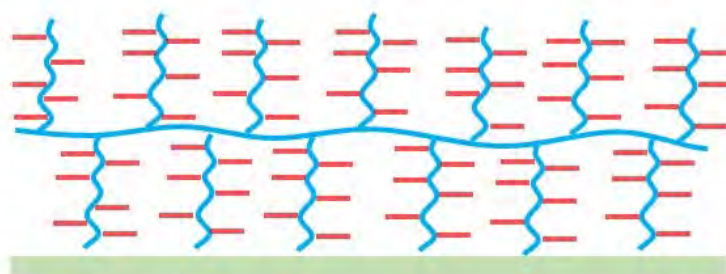
Application

POLY 356: Fluorinated polymethacrylate bottlebrush enables outstanding water- and oil-repellent surfaces

Yingdong Luo¹, luoy@ornl.gov, Kunlun Hong². (1) The center for nanophase materials sciences, Oak Ridge National Lab, Knxoville, Tennessee, United States (2) Bldg 8610 MS 6494, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Due to serious environmental and health concerns, the production of materials which generate perfluorooctanoic acid (PFOA) during degradation and the direct usage of PFOA are restricted in EU and US. Poly(fluoroalkylacrylates) with side chains of more than eight fluorinated carbon atoms are ideal materials for functional coatings with low surface energy. Degradation of these polymers could potentially generate similar toxic pollutants to PFOA. A less biohazardous material alternative is highly desirable. Polymers with lower fluorinated carbon atoms are less persistent in food webs and have less bioaccumulative potentials. However, it's challenging to increase the moderate wetting performance of these materials.

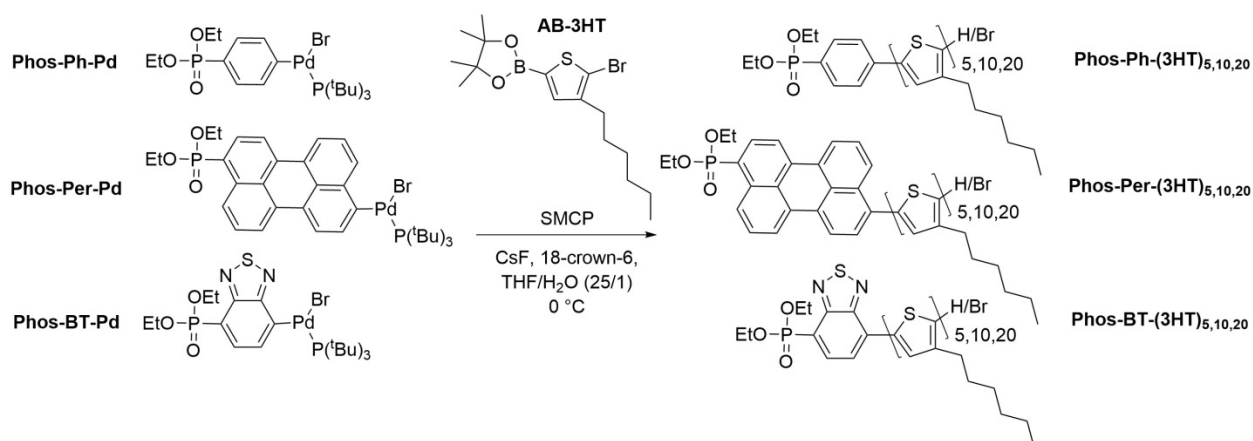
Bottlebrush architecture of polymers in thin films could tune the orientation of polymer chains. Fluorinated bottlebrush polymers have rarely been studied due to synthetic challenges. In this study, we synthesized fluorinated bottlebrush (co)polymers through ATRP and ROMP, then evaluated effects of the arm chain length (fluorinated methacrylate), side chain length (macromonomer) and bottlebrush backbone length of these bottlebrush polymers toward high performance coating materials. By dynamic contact angle measurements, bottlebrush architecture showed high water contact angle and outstanding water- and oil-repellent performance.



POLY 357: Phosphonate functionalized poly-3-hexylthiophenes by controlled Suzuki-Miyaura coupling polymerization for interface modification in hybrid solar cells

Arthur Groh¹, arthur.groh@uni-konstanz.de, **Philipp Ehrenreich**², **Lukas Schmidt-Mende**², **Stefan Mecking**¹. (1) Department of Chemistry, University of Konstanz, Konstanz, Germany (2) Department of Physics, University of Konstanz, Konstanz, Germany

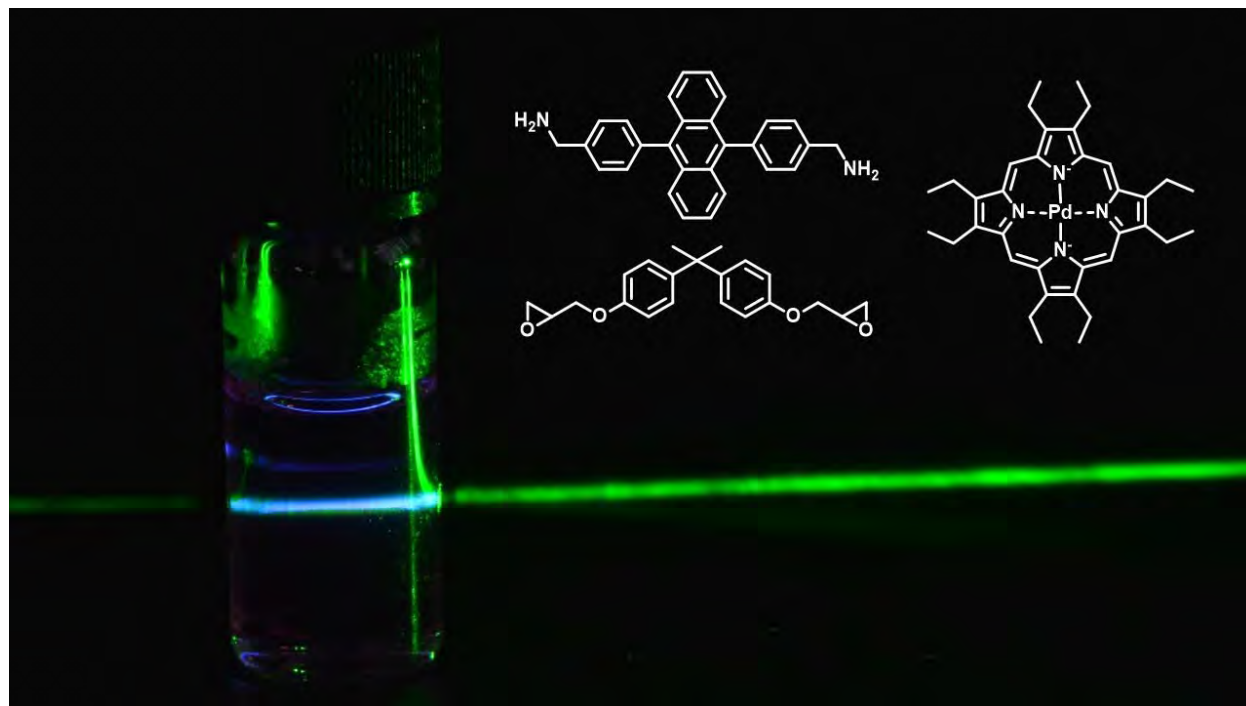
In hybrid solar cells (HSCs) the inorganic/organic interface plays a crucial role for the power conversion efficiency (PCE) via the phase compatibility, energy level alignment and the interfacial dipole orientation. Here, we present a method for the synthesis of defined polymeric interfacial modifiers. Functionalized Pd(II) initiators were isolated and used, with AB-type bromo-thiophene-boronic acid ester monomers, in a controlled Suzuki-Miyaura Coupling polymerization (SMCP). By varying the initiator to monomer ratio regio-regular oligo- to polythiophenes with chain lengths from 5 to 50 repeat units with a narrow molecular weight distribution and defined functionalized end groups are obtained. The ability of diethyl phosphonates to bind strongly via condensation with titania surfaces was exploited for the utilization as interfacial modifiers in titania/P3HT HSCs. The influence of the chain length and the electron deficient aryl-phosphonate end groups on the PCE is rationalized.



POLY 358: Triplet-Triplet annihilation upconversion in epoxy-amine networks

Abigail K. Williams¹, *abigail.jentsch@eagles.usm.edu*, **Joseph Lott²**, (1) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) University of Southern Mississippi, Hopkins, Minnesota, United States

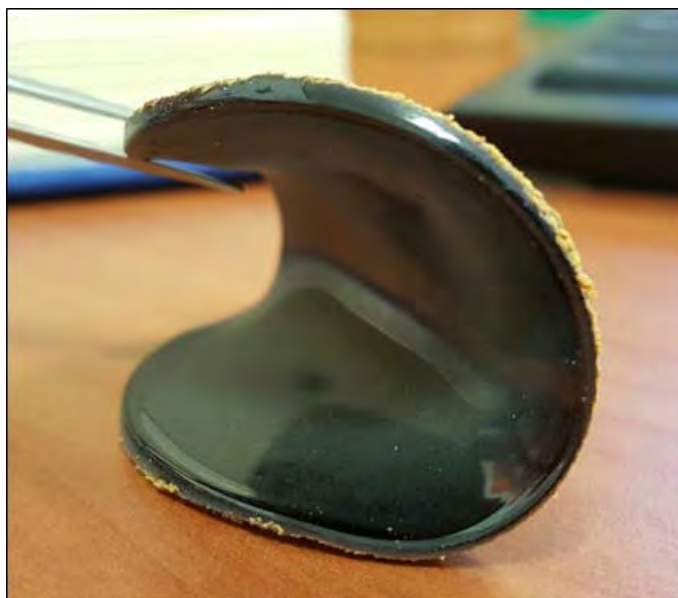
Photon upconversion through triplet-triplet annihilation can convert low energy photons from non-coherent, low-power light sources into higher energy photons. As such, TTA-UC can be used in a variety of applications, most notably photovoltaic devices. However, for such applications mechanically robust materials with high glass transition temperatures (T_g) are preferred. Currently, upconversion efficiencies in these rigid materials are low due to poor solubility of required chromophores and inefficient energy transfer between sensitizer and emitter molecules. In this work, we utilize well known epoxy-amine chemistry to covalently incorporate chromophores into a mechanically robust polymer matrix. Synthesis of functionalized 9,10-diphenylanthraene derivatives and their UC performance in conjunction with palladium octaethylporphyrin (PdOEP) in solution are presented. The preparation of epoxy-amine networks containing PdOEP and covalently incorporated emitters are outlined. Chromophore concentrations were systematically varied and direct and upconverted fluorescence measurements are presented. The reactive strategy used to incorporate the functionalized DPA molecules allows for high chromophore concentrations to be realized with limited undesirable effects from aggregation and self-quenching. Optimal design parameters for this quick, cost-effective method of making glassy materials capable of TTA-UC are discussed.



POLY 359: Flexible sulfur copolymer film via inverse vulcanization technique

Vijay Wadi, Shahrukh Khawaja , **Saeed Al Hassan**, *alawan@hotmail.com*. The Petroleum Institute, Sarasota, Florida, United States

Recent development in inverse vulcanization technique attracted many researcher in developing new advanced materials using elemental sulfur. Here in we report the simple and scalable preparation of the sulfur rich highly flexible polysulfide film via inverse vulcanization technique. The films were prepared by reacting elemental sulfur with diallyl disulfide, a garlic extract at 165 C for 15 to 20 min and the resulting mixture was cured in a petri dish for 24 h. The film were obtained by removing from petri dish, the average film thickness was around 1 mm. The presence of disulfide bond in diallyl disulfide also increases the total sulfur content in the final film (65 to 94 wt %). The reaction between sulfur and allyl disulfide was confirmed by NMR and FTIR spectroscopy. High flexibility of the films could be due to the presence of freely rotating aliphatic linkage between carbon bonds. DSC confirms the low T_g of the films (-10 C to -21 C) depending on the amount of diallyl disulfide. SEM images showed the uniform and smooth surface morphology of the films. The mechanical property of the films studied in UTM further supports the flexibility of the films. Abundant natural availability and over 7 million tone excess annual production of elemental sulfur by petroleum refining and simple method of preparation makes sulfur films a potential candidate for future sulfur lithium battery and mercury adsorption research.

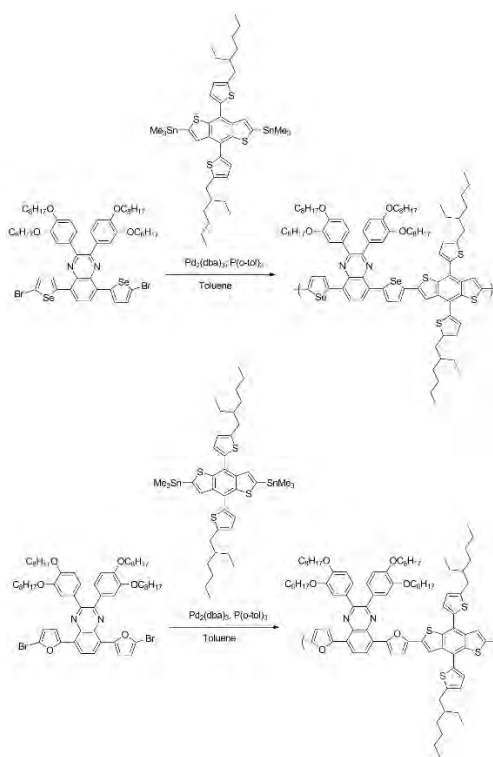


Flexible sulfur copolymer film

POLY 360: Syntheses, electrochemical and spectroelectrochemical characterizations of quinoxaline-based conjugated polymers for organic photovoltaics

Mustafa Yasa², e161920@metu.edu.tr, Seza Goker¹, Yasemin Arslan Udum⁴, Gorkem E. Gunbas^{1,2}, Levent Toppare^{3,2}. (1) Chemistry, Middle East Technical University, Ankara, Turkey (2) Polymer Science and Technology, Middle East Technical University, Ankara, Turkey (3) Middle East tech Univ, Ankara, Turkey (4) Graduate School of Natural and Applied Sciences, Gazi University, Ankara, Turkey

Donor-Acceptor (D-A) type conjugated polymers are very popular for potential applications such as organic light emitting diodes, solar cells, electrochromic devices and organic field effect transistors.^{1,2} In literature, there are several studies of organic solar cells of quinoxaline-based conjugated polymers. Quinoxaline is a strong electron-withdrawing unit resulting in promising acceptor features. Alkoxybenzene groups are introduced to this acceptor moiety for solution processability of quinoxaline comprising copolymers.^{3,4} The incorporation of selenophene into the polymer backbone as the π -bridge results in low band gap polymers as compared to sulfur and oxygen containing counterparts. In the meantime, furan based polymers have lower HOMO energy level than thiophene counterparts due to high electronegativity of oxygen compared to sulfur atom⁵. Hence, selenophene and furan units were selected as π -bridges. In this study, quinoxaline and benzodithiophene based conjugated polymers were synthesized via Stille polycondensation reaction. Electrochemical and spectroelectrochemical studies were performed. The structures of the polymers were illustrated in Scheme 1.



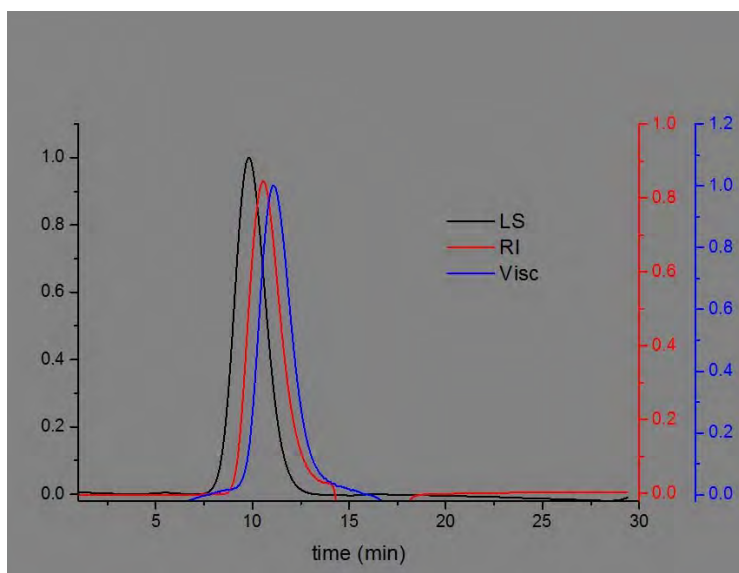
Scheme 1.

POLY 361: Analysis of polyamides with GPC using triple detectors

Reza Farasat, farasat721@gmail.com. Technical, Tosoh Bioscience LLC, King of Prussia, Pennsylvania, United States

The polyamides, most specifically, nylons are common materials in everyday life which produce large quantities of scrapes and wastes contaminating the environment. One solution for decreasing the waste is plastic recycling. Due to aforementioned caveats, the ability to accurately and precisely characterize polyamide materials is essential. One common method for polyamide characterization is the determination of molar mass averages and distributions. Triple detectors can be used to get most comprehensive information in this regard.

In this work a low dead volume GPC System, equipped with a dual flow refractive index detector (RI), coupled in series to a light scattering and a viscometer was used to analyze the three different polyamide samples. The analysis was carried out by a Size Exclusion Chromatography (7.8 mm ID × 30 cm; 13 μm) column with rigid, porous, polymer beads showing minimal shrinkage or swelling in polar organic solvents. Hexafluoroisopropanol (HFIP) was used as the mobile phase and a solvent. The number, weight, and z-average molar mass values (M_n , M_w , and M_z) were determined by two methods such as (1) conventional column calibration and (2) light scattering. The conventional calibration curve was created at 40°C by using narrow molecular weight Poly (methyl-methacrylate) (PMMA) standards. GPC-MALS was calibrated by a PMMA standard ($M_w = 12,500$ g/mol) with dn/dc of 0.213. The intrinsic viscosity was determined for the multiple injections of all three Polyamides. The results indicate overall stability of the peak parameters and reproducibility of the RI detector housed within the EcoSEC GPC System. A stable RI detector baseline is essential as it directly impacts the accuracy and reproducibility of the molecular weight data extrapolated from the GPC elution profile. In this work we report successful analysis of Polyamide samples by triple detectors.



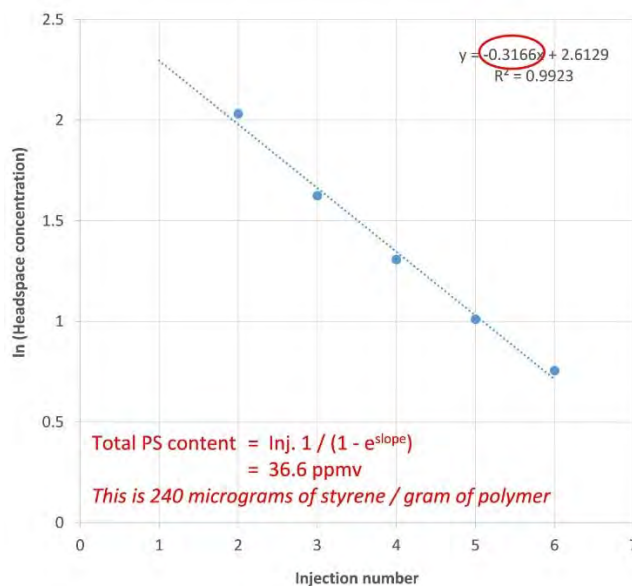
POLY 362: Rapid screening of packaging for residual monomers using SIFT-MS

Vaughan S. Langford¹, **Barry J. Prince**², barry.prince@syft.com, Daniel B. Milligan², Mark Perkins³, Terry Wilks⁴, Terry Potter⁵. (1) Syft Technologies Limited, Christchurch, New Zealand (2) Syft Technologies, Christchurch, New Zealand (3) Anatune, Cambridge, United Kingdom (4) Quantum Analytics LLC, Foster City, California, United States

Residual monomers can be a contamination and leaching issue for molded or extruded plastic products. For the pharmaceutical and food industries, leaching from packaging can result in contamination of product. Application of rapid analysis enables wider testing and therefore improved quality control.

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) enables direct, real-time monitoring of volatile compounds and therefore facilitates better quality control. Unlike traditional chromatography-based techniques, there is no requirement to separate compounds prior to analysis. This leads to a number of benefits. Not only can challenging compounds, such as formaldehyde, ammonia and small sulfur compounds, be analyzed without derivatization or pre-concentration, but these analyses can be completed in seconds.

By coupling advanced autosampler technology to SIFT-MS instruments, analyses can be entirely automated, fully realizing the potential of the fast SIFT-MS-based measurements. Further, by utilizing the autosampler's advanced software features, techniques that are cumbersome with chromatography can be turned into practical, economic methodologies, in some cases realizing a ten-fold increase in throughput. In this paper, a range of automated headspace techniques will be demonstrated, including rapid headspace method optimization and multiple headspace extraction (MHE) methods. These and other high-throughput SIFT-MS applications will be illustrated using residual monomer analysis from polymers such as polyacetal, polypropylene, and polystyrene.

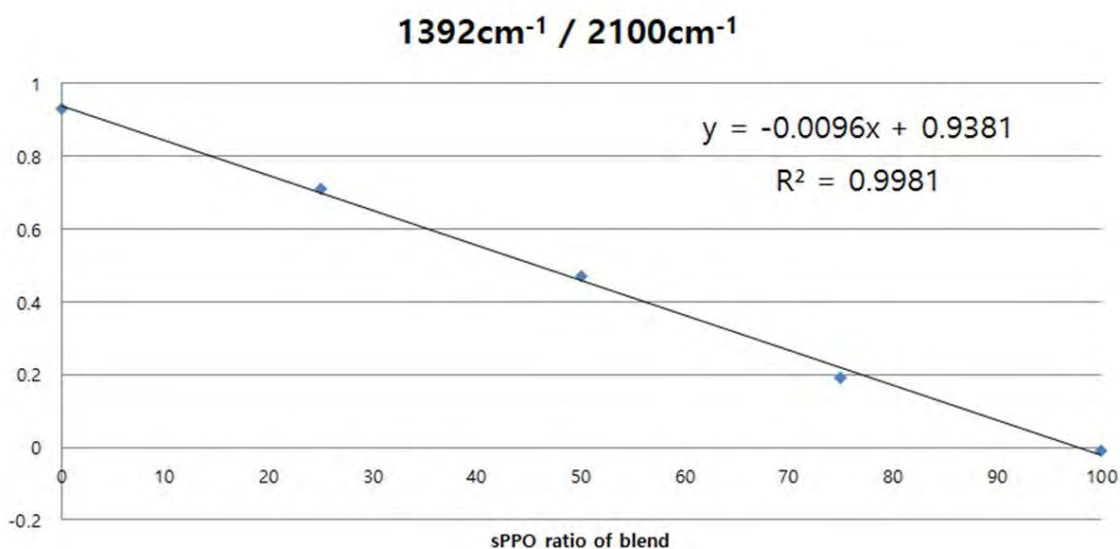


POLY 363: FTIR characterization of co-deposited LbL film of sPPO and sPS copolymer with PDDA

Chang G. Cho, *cgcho@hanyang.ac.kr*, H. S. Ryu, Alam Heo. Dept. of Organic & Nano Engineering, Hanyang University, Seoul, Korea (the Republic of)

Layer-by-layer (LbL) deposition is carried out by alternately depositing positively and negatively charged polyelectrolytes, and this method has become a very versatile method in preparing very thin polyelectrolyte multilayer composite film. During the deposition the polyelectrolyte self-assembles and self-organizes on an oppositely charged substrate via electrostatic or hydrogen bonding interactions, so it is possible to include nanoparticles and biological molecules of different shapes as far as the objects are charged. Similarly, two kinds of anionic polyelectrolytes (or cationic polyelectrolytes) can be used together after mixing, in order to induce a post reaction in the LbL film, in a real application.

In this study, a highly sulfonated poly(phenylene oxide) (sPPO) was prepared from PPO, and used as the major component in the negatively charged polyelectrolyte mixture. Also polystyrenesulfonic acid copolymer containing azide moiety (sPS-az) was prepared, and used together with the sPPO, as the minor component in the negatively charged polyelectrolyte mixture. The mixed polyelectrolyte solution was co-deposited with a cationic polyelectrolyte, poly(dimethyldiallylammonium chloride) (PDDA) in order to make LbL film which is crosslinkable by UV. Formation of LbL film was studied by UV/vis spectroscopy, and the composition of the film was characterized by FTIR. The result was interpreted and correlated with the differences in the solubility parameters of the two anionic polymers.

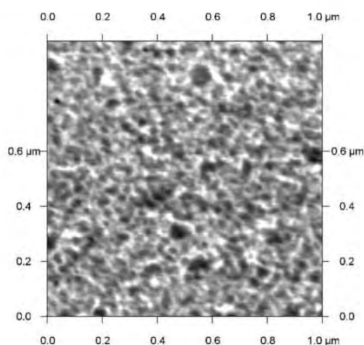
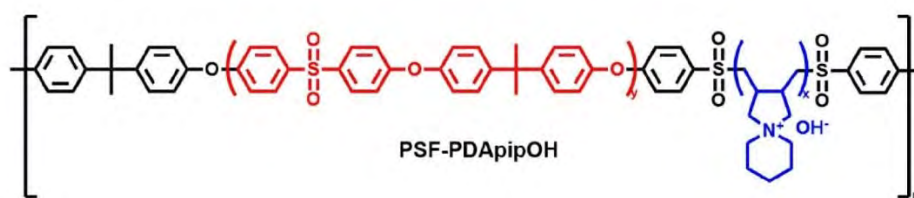


Calibration curve on the ratio of sPPO/sPS-az from FTIR absorption at 1392 cm⁻¹ / 2100 cm⁻¹

POLY 364: Polysulfone-poly(diallylpiperidinium hydroxide) multiblock copolymers containing alkaline stable spirocyclic quaternary ammonium cations for alkaline exchange membranes

Brendan J. Graziano^{1,2}, *b-graziano@onu.edu*, **Derek J. Strasser**¹, **Daniel M. Knauss**¹.
(1) Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, United States (2) Donald J. Bettinger Department of Chemistry & Biochemistry, Ohio Northern University, Ada, Ohio, United States

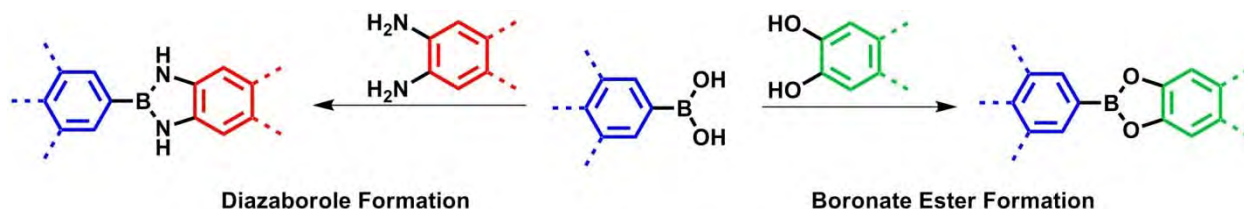
Herein we report the first hydrophobic/hydrophilic multiblock copolymer membranes containing poly(diallylpiperidinium hydroxide) with a polysulfone matrix. Using bis(4-fluorophenyl) disulfide as a single component UV iniferter, telechelic poly(diallylpiperidinium chloride) prepolymers were obtained. The poly(diallylpiperidinium chloride) prepolymers were then activated for nucleophilic aromatic substitution by oxidation of the 4-fluorophenyl sulfide end groups to 4-fluorophenyl sulfone. Following ion metathesis to hexafluorophosphate, the poly(diallylpiperidinium hexafluorophosphate) prepolymers were condensed with bisphenol A and bis(4-fluorophenyl) sulfone generating the multiblock copolymers. The multiblock copolymers were solution cast, in the hexafluorophosphate form, from DMAc resulting in robust, colorless, and transparent membranes. Tapping mode AFM indicated microphase separation. The multiblock polysulfone-poly(diallylpiperidinium hydroxide) copolymers were shown to be highly conductive, reaching 102 mS/cm at 80 °C with 45% water uptake. Thermal decomposition of the multiblock copolymer materials were shown to be stable over 300 °C with 5% weight loss observed at 331 °C in the hydroxide form. Ultimately, the base stability of both the poly(diallylpiperidinium hydroxide) and multiblock copolymer membranes was evaluated. Homopolymer stability was observed in proton NMR after 1000 hours at 80 °C in a 1M KOH/ methanol-d₄ solution. Membranes were found to maintain at least 92% of their hydroxide conductivity after being treated in 80 °C, 1M KOH for 5 days.



POLY 365: Investigating the Dynamic Assembly of Boronate Esters and Diazaboroles for the Formation of Frameworks and Polygons

Vasileios Droghkaris¹, vdroghkaris@wesleyan.edu, **Brian H. Northrop**². (1) Chemistry, Wesleyan University, Middletown, Connecticut, United States (2) Department of Chemistry, Wesleyan University, Middletown, Connecticut, United States

Highly symmetric structures that can be dynamically assembled from boronic acid building blocks have attracted great interest. Covalent Organic Frameworks (COFs), which have potential uses in gas storage, catalysis and optoelectronics, represent a prominent example of such highly symmetric materials formed through dynamic self-assembly. Recently, discrete analogues of infinitely periodic COFs have gained attention and have been shown to have properties that are distinct from those of COFs, such as reversible and controllable aggregation. These discrete assemblies (Covalent Organic Polygons - COPs) have potential for use as porous liquid crystals and microporous two dimensional membranes. We are currently developing routes to new discrete porous boronate ester assemblies while also investigating how different functionalization can influence the aggregation and properties of the assemblies. Furthermore, the condensation of boronic acids with diamines to form diazaboroles offers a potentially useful alternative means of building frameworks and polygons, though dynamic diazaborole assembly has not yet been thoroughly investigated. Studying the interactions of these building blocks and how they affect the stability and crystallinity of the assemblies will provide insights into the development of new porous materials.

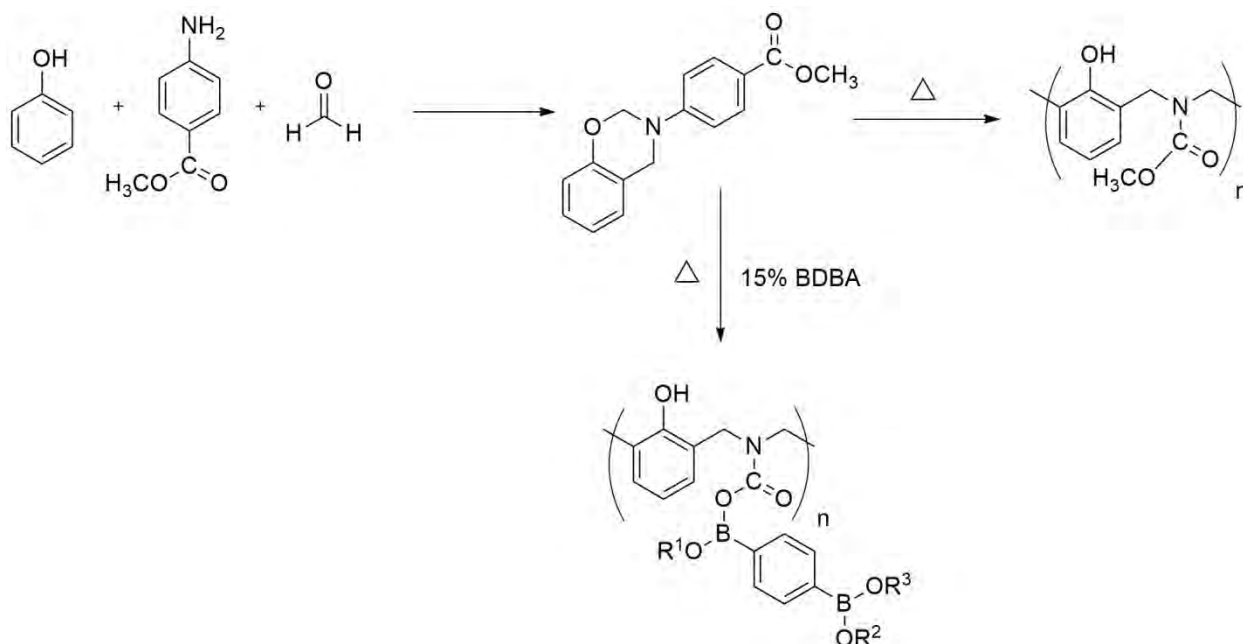


POLY 366: Effect of aromatic boronic acid on characteristics of polybenzoxazine based on phenol and *p*-amino methyl benzoate

Halil Ipek¹, ihalil@metu.edu.tr, **Jale Hacaloglu**². (1) Middle East Technical University, Ankara, Turkey (2) Chemistry, Middle East Technical University, Ankara, Turkey

During the last decades, polybenzoxazines with various advantageous, that overcome the shortcomings of traditional phenolic and epoxy resins such as releasing condensation by-products and using acid or base catalysts for polymerization, have received significant attention both academically and industrially. They exhibit excellent properties such as high thermal stability, glass transition temperature and modulus and low water absorption and dielectric constant. In addition they have near-zero shrinkage upon curing. Benzoxazine monomers can easily be prepared either in solution or in liquid phase from reactions of phenols, amines and their functional derivatives and formaldehyde.

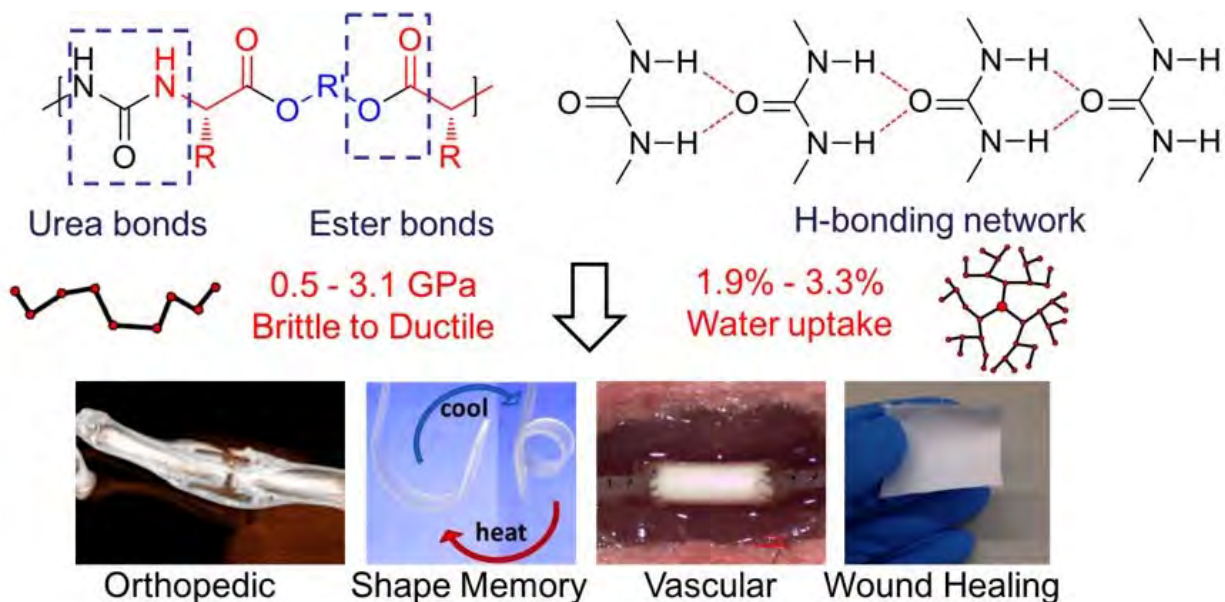
In this study, our main aim is to prepare composites of polybenzoxazine with improved thermal characteristics by incorporation of aromatic diboronic acid, benzene-1,4-diboronic acid, (BDDBA). For this purpose, firstly, the benzoxazine monomer based on phenol and *p*-amino methyl benzoate, (Pab) was synthesized and characterized by FTIR, NMR and Mass Spectrometry techniques. The thermal polymerizations of pure benzoxazine monomer, (PPab) and benzoxazine monomer in the presence of 15 wt% BDDBA, (PPab/BDDBA) were achieved by multi-step curing program. The disappearance of the exothermic ring opening polymerization peak in the differential scanning calorimetry, DSC, curves of the polymers confirmed polymerization of the monomers by the applied curing program. Thermogravimetry Analyses, TGA, and direct pyrolysis mass spectrometry, DP-MS, were applied to investigate the thermal characteristics of the polymer samples.



POLY 367: Structure-property-processing-application relationship of amino acid-based poly(ester urea)s

Jiayi Yu¹, jy30@zips.uakron.edu, **Matthew Becker**². (1) Polymer Science, The University of Akron, Cuyahoga Falls, Ohio, United States (2) University of Akron, Akron, Ohio, United States

A new class of amino acid-based poly(ester urea)s (PEUs) were developed with tunable mechanical properties, water uptake ability and degradation rates. Our previous *in vitro* and *in vivo* studies have shown the great potentials of this 1,6-hexanediol *L*-phenylalanine based PEU in the surgical repair of bone defects. My work details the synthesis of a series of PEUs possessing a variation in diol chain length, in branch density, in filler content and studies how these subtle structural differences influence the mechanical properties and *in vitro* biodegradation rates. The results show that the elastic moduli covers a wide range of values from 0.5 GPa – 3.1 GPa which overlap with several currently clinically available biodegradable polymers. The amount of degradation varies from 1% – 5% over 16 weeks. Compared with poly(*L*-lactic acid), PEUs degrade more quickly and the rate can be tuned by changing the diol chain length, branch density and filler content. Based on these tunable physical properties, these materials can be selected, processed into different forms (extruded/injection molded tubes, 3D printed scaffolds, electrospun nanofiber sheets/tubes, etc.) and used as orthopedic materials, shape memory materials, tissue adhesives and wound dressing materials.

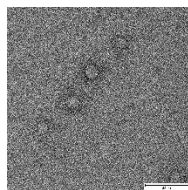


POLY 368: From exhaust gas to drug delivery: Nano carriers based on carbon dioxide and tailored epoxide building blocks

Markus Scharfenberg¹, *mscharfe@uni-mainz.de*, **Holger Frey**². (1) Johannes Gutenberg University Mainz, Mainz, Germany (2) Chemistry, University of Mainz, Mainz, Germany

Carbon dioxide (CO₂) is an attractive carbon source for materials synthesis with respect to resource utilization, as it is nontoxic, renewable, sustainable and readily available in large quantities and high purity. In combination with tailored epoxides, multifunctional polymers can be synthesized. The resulting materials are promising for a variety of applications, such as ceramic binders, adhesives, coatings, and packaging materials as well as for biomedical functions, since they are biodegradable into nontoxic compounds.^[1] Increasing demand for more versatile biomaterials has also revived the interest in aliphatic polycarbonates for biomedical purposes, for which their degradability, low glass transition temperature, and elasticity, previously perceived as their major drawbacks, may turn into advantages.

In this work, we have synthesized different kind of amphiphilic non-ionic polyether polycarbonates directly from carbon dioxide (CO₂) and tailored epoxide building blocks in a solvent-free synthesis. PEG and mPEG were used as macro-transfer agents/initiators.^[2] These aliphatic surfactants are biocompatible and biodegradable. Their potential as emulsifiers were investigated and confirmed. Beside this, novel multifunctionalized surfactants were prepared to stabilize the nano carriers in aqueous solution. Furthermore, these surfactants were used for modification with fluorescence dyes to investigate cellular uptake. The functionalized as well as the unfunctionalized surfactants were fully characterized by FT-IR, NMR, SEC and DSC measurement, and their CMCs were determined. Beside these methods, TEM and DLS measurements were performed to investigate their structure in aqueous solution and hereby their potential for drug delivery. In addition to that, the drug release was examined by in vitro studies.



POLY 369: Hyperbranched polymers for the disruption of quorum sensing in *Pseudomonas aeruginosa*

William Martin¹, *w.martin@bradford.ac.uk*, **Joey Shepherd**². (1) Chemistry, University of Bradford, Bradford, United Kingdom (2) School of Clinical Dentistry, University of Sheffield, Sheffield, United Kingdom

Bacterial biofilms are complex mixed communities of bacteria which can form on almost any surface. They are a particular problem in the biomedical field as they frequently colonise medical devices such as indwelling catheters and prosthetics, and they are difficult to treat with conventional therapies as they are not sensitive to traditional treatments such as antibiotics, due to their complex architecture. In order to form biofilms, bacteria use Quorum Sensing (QS), which involves the use of molecular signals sent and received by the bacteria forming and maintaining the biofilm. Gram negative organisms, such as *Pseudomonas aeruginosa* which frequently colonises chronic wounds and is also the main pathogen in the lungs of cystic fibrosis patients, use homoserine lactone (HSL) in the QS process. HSL is released by bacteria and binds to the LasR receptor both internally and in neighbouring bacteria, initiating further signalling and cascades of pathogenic factors involved, for example, with bacterial adhesion the surface and release of virulence factors.

Hyperbranched polymers are ideally suited to functionalisation of the multiple end groups with covalently bound compounds, and this approach has previously been used for the delivery of bioactive molecules in wound dressings. This poster will describe the synthesis of hyperbranched polymers with HSL analogues covalently attached to them. The ability of these materials to disrupt the QS process will be discussed.



Highly branched poly(*N*-isopropyl acrylamide) modified with HSL analogues

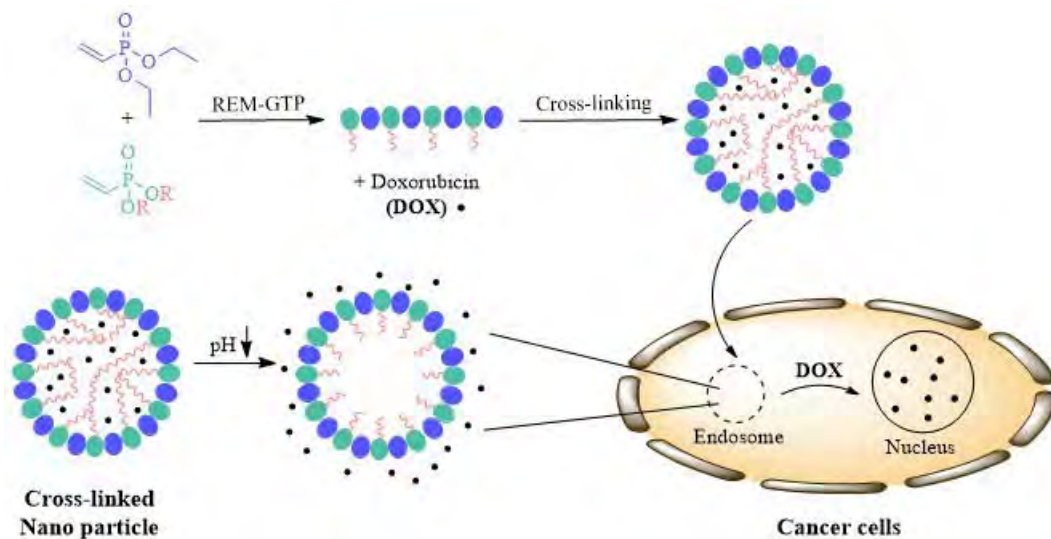
POLY 370: Smart polymers - drug delivery with polyvinylphosphonates

Christina Schwarzenböck, christina.schwarzenboeck@makro.ch.tum.de, Bernhard Rieger, Technische Universität München, WACKER Lehrstuhl für Makromolekulare Chemie, Munich, Germany

Rare Earth Metal-Mediated Group Transfer Polymerization (REM-GTP) is a method to generate polymers with defined molecular weights and narrow polydispersities. Its unique character allows the synthesis of copolymers as well as the introduction of a broad range of functionalities to the chain end.

This living polymerization type can be used for a variety of *Michael*-type acceptor monomers. Especially interesting phosphorus containing monomers are the vinylphosphonates, because their polymers exhibit water solubility, a tunable lower critical solution temperature and biocompatibility.

Very recently our group succeeded to apply these fascinating properties and develop a new type of multiresponsive nanocarriers for the use in the field of targeted drug delivery. We synthesized novel temperature and pH sensitive drug delivery vehicles as a potent tool in cancer therapy. Especially promising for these biomedical applications are cross-linked nano particles, since their formation is, in comparison to micelles, not concentration dependant and their properties are well tunable. In case of polyvinylphosphonates, it is possible to adjust the temperature sensitivity *via* variation of the used monomer ratios. Furthermore, the desired pH response can be achieved through the modification of the linker units. These highly tunable properties make these smart polymers very attractive for a broad range of drug delivery applications and are therefore a fascinating opportunity for a tailor-made next generation cancer therapy.

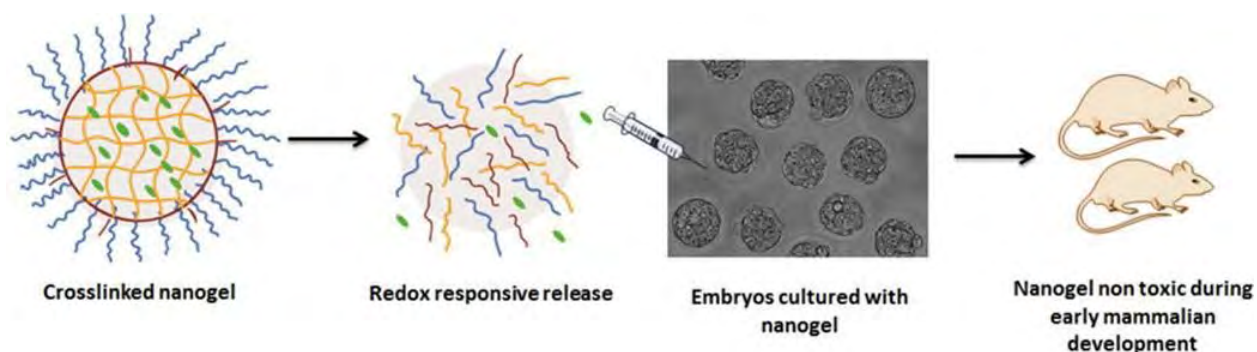


Drug delivery into cancer cells with polyvinylphosphonates.

POLY 371: Polyglutamic acid based GRAS nanogels for drug delivery

priyaa prasad², emailpriyaa@gmail.com, Mijanur Rahaman Molla², Wei Cu², Mine Canakc², Barbara Osborne², Jesse Mager², Sankaran Thayumanavan¹. (1) Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, United States (2) Chemistry, University of Massachusetts Amherst, Sunderland, Massachusetts, United States

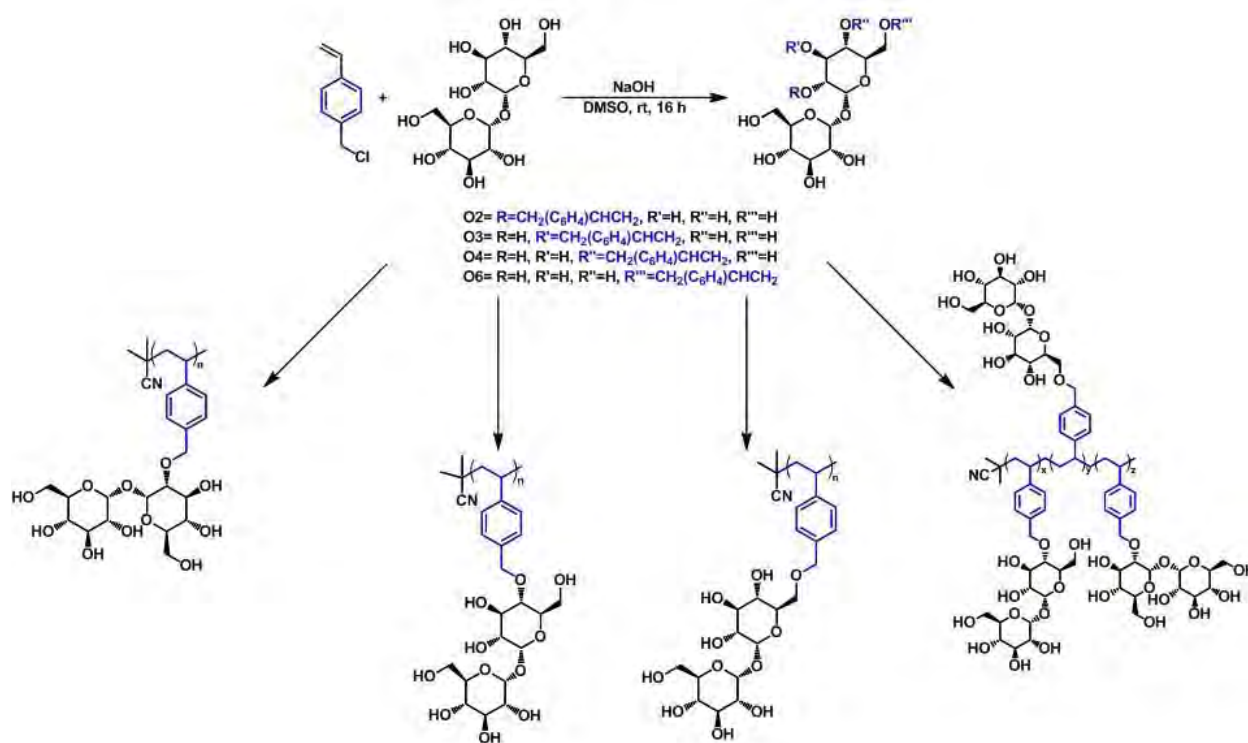
One of the major hurdles in developing drug delivery systems is accounting for all significant requirements of a delivery vehicle including stable encapsulation, target specificity, stimuli responsiveness and more importantly biocompatibility. We have developed a polymeric nanogel system based on GRAS (generally recognized as safe) components. These nanogels that are composed of a Glutamic acid based polyamide polymer backbone show redox responsive release and high *in vitro* cellular viability on HEK 293T, HeLa, MCF 7 and A549 cell lines. The toxicity of these nanogels was further evaluated with a highly sensitive assay using mouse preimplantation embryo development, where blastocysts were formed after four days of *in vitro* culture and live pups were born when morulae/early blastocysts were transferred to the uteri of surrogate recipients. These results suggest that the designed GRAS nanogels are non-toxic during mammalian development and do not alter normal growth or early embryo success rate.



POLY 372: Conformational effect of trehalose monomers and polymers on protein stabilization

Marco Messina², marcosmessina@aol.com, Jeong Hoon Ko², Zhongyue Yang¹, Jane M. Strouse¹, Kendall N. Houk¹, Heather D. Maynard¹. (1) UCLA, Los Angeles, California, United States (2) Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States

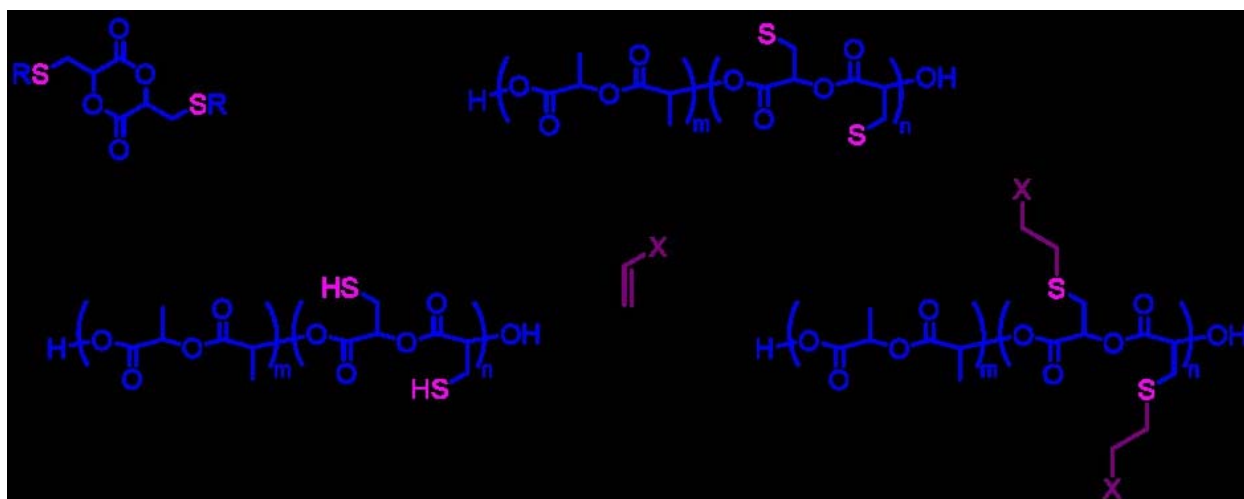
There is considerable interest in protein therapeutics and proteins as chemical and biochemical reagents. However, proteins are unstable and aggregate when exposed to outside stressors such as heat, pH changes, and desiccation. To prevent aggregation and prolong protein activity, sugars such as trehalose are frequently added as excipients. Herein, we report the synthesis and characterization of four trehalose monomer regioisomers containing a vinylbenzyl ether moiety at either the O2, O3, O4, or O6 position. Computational analysis of these regioisomers suggested that they all adopt the native conformation of trehalose but differ in their conformational flexibility. Polymers were synthesized via free radical polymerization containing each monomer separately as well as one polymer containing all regioisomers. The stabilization capability of each polymer was then tested with a model protein. The synthesis and stabilization ability of these polymers will be discussed.



POLY 373: Fabrication of biodegradable surfaces of modified poly(lactic acid) for biomedical applications

Pranav Kalelkar, k13pranav@gmail.com, David M. Collard. Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

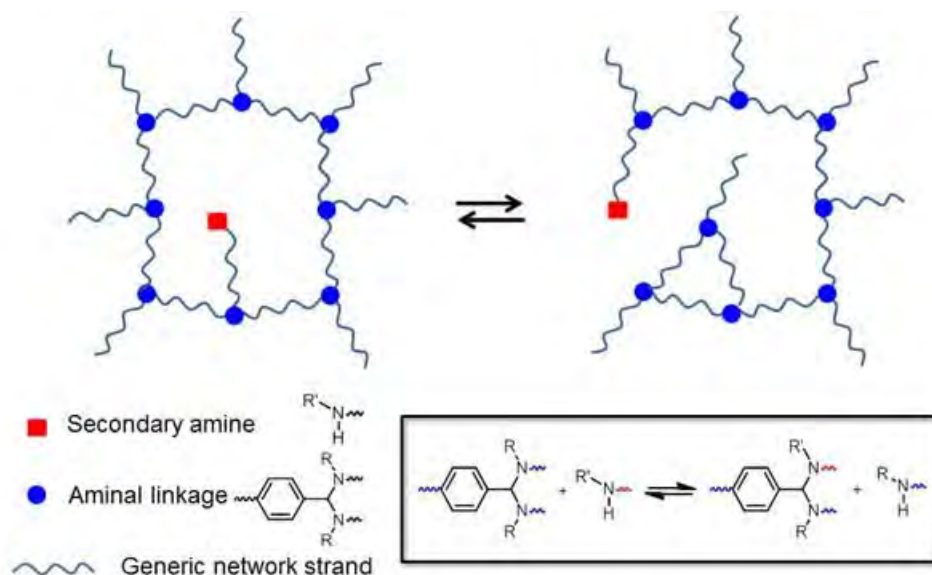
Poly(α -hydroxy acid)s (PHAs), such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and their copolymers (e.g., PLGA), are aliphatic polyesters that are biocompatible, biodegradable and bioresorbable. These properties, together with the ability to fabricate them into 3-D scaffolds, renders them attractive candidates for biomedical applications. However, the absence of reactive functional groups limits their applications in this field. To overcome this limitation, we have prepared two new copolymers of PLA that contain either α,β -unsaturated esters or thiol-containing side chains. These functional side chains allow for the attachment of biological molecules such as peptides and proteins through nucleophilic addition of thiols to electron-deficient alkenes, the thiol-ene reaction, or disulfide formation.



POLY 374: Investigation of the dynamic aminal bond exchange towards the design and synthesis of polyaminal polymers

Albert Chao¹, achao2@lsu.edu, **Donghui Zhang**². (1) Chemistry, LSU, Baton Rouge, Louisiana, United States (2) 437 Chemistry Materials Building, Louisiana State University, Baton Rouge, Louisiana, United States

Designing polymers comprised of dynamic aminal bonds represents a new strategy towards synthesizing re-moldable and self-healing materials. In this study, model aminal compounds have been prepared by condensation of secondary amines (e.g., piperidine, morpholine) and mono aldehydes (e.g., formaldehyde, benzaldehyde). ¹H NMR spectroscopic analysis revealed that these aminal compounds undergo dynamic exchange in solution at room temperature. Addition of a catalytic amount of trifluoroacetic acid accelerates the transamination at room temperature, whereas a catalytic base decelerates the reaction. However, at elevated temperature (e.g., 70 °C), addition of base also facilitates the transamination in the polymers. Both linear and cross-linked polymers comprised of aminal bonds have been prepared by condensation polymerization of secondary diamines with di or trialdehydes in organic solvents. Thermal and mechanical properties of these polymers were characterized by TGA and DSC and tensile measurements.



POLY 376: Encoding function in protein-oligonucleotide precision biopolymers

Weina Liu^{2,1}, *weina.liu@uni-ulm.de*, *Tanja Weiß*. (1) *Max Planck Institute for Polymer Research, Mainz, Germany* (2) *Organic Chemistry, Ulm University, Ulm, Germany*

Nature controls structure, interactions and function of its biopolymers such as polypeptides, proteins and DNA thus achieving large molecular weight compounds as well as precise and often complex monomer sequences. While synthetic polymerization, inevitably produce polymers with sequence and molecular mass distributions. Although considerable progress has been made for precise polymerization by sequence-controlled reaction, yet this reaction is limited to oligomers because of decreasing yield with sequence length. Based on the advances in bioengineering, recombinant proteins can be produced with rational designed sequences and structures, which have been denoted as “monodispersed polymers”, previously. In this work, we propose a synergistic approach combining the polyamide backbone of denatured protein human serum albumin (dHSA) with grafted single strand DNA(ssDNA) side chains, which provides access to high molecular weight yet retaining monodispersity of the protein precursor. The polyamide backbone of the formed copolymer dHSA-ssDNA could be covalently loaded with functionalities like anti-cancer drug doxorubicin. In addition, a series of functional molecules (chromophore, GFP, cell targeting peptide) which were pre conjugated to complementary ssDNA, and afterwards non-covalently loaded on dHSA-ssDNA scaffold via the dsDNA hybridisation to form a family of functional protein-DNA hybrid copolymers with precise molecule structure. Furthermore, Y shape DNA linker was loaded onto dHSA-DOX-ssDNA, which demonstrated that the copolymer could be functionalized simultaneously by covalently and non-covalently loading. In addition, the introduced Y shape DNA linker provided potential for further prolongation and crosslinking of network formation.

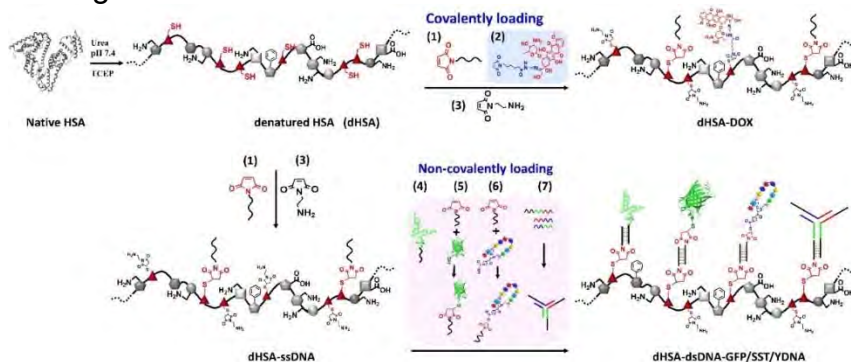


Fig. 1 Scheme of copolymer dHSA-ssDNA and functional molecules covalently, or non-covalently loading.

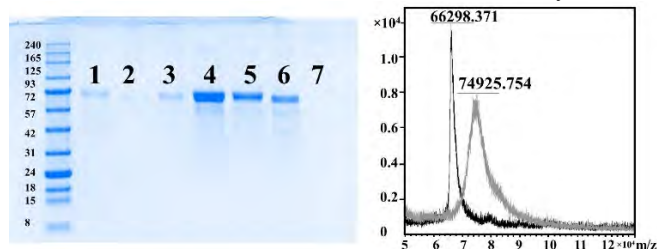
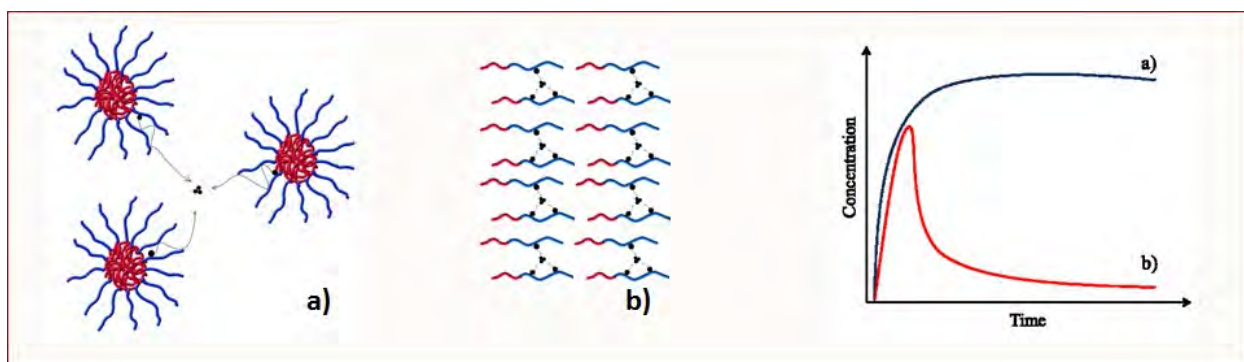


Fig. 2 SDS-Page gel of dHSA-ssDNA fractions from HPLC separation with ion exchange column, and MolDi-ToF spectra shows the molecule mass of fraction 4, compared to native HSA.

POLY 377: Poly(acrylic acid) based block copolymers as excipients for enhancing solubility of poorly water soluble drugs

Anatolii Purche², purch004@umn.edu, William S. Boyle², Theresa M. Reineke¹. (1) Chemistry, University of Minnesota, Vadnais Heights, Minnesota, United States (2) Chemistry, University of Minnesota, Twin Cities, Minneapolis, Minnesota, United States

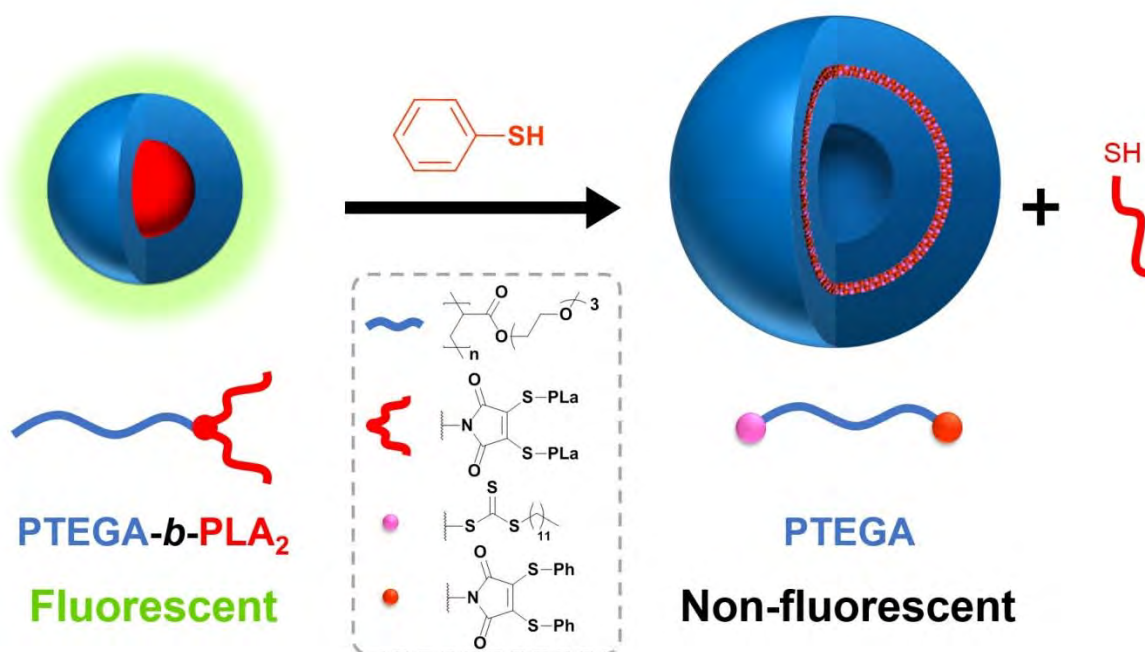
Oral administration is the most preferable route of drug delivery, especially during prolonged therapy of chronic diseases. Unfortunately, many effective pharmaceuticals are poorly water-soluble, which leads to decreased bioavailability and shelf life. One of the ways to improve drug solubility and efficacy is to prepare an amorphous solid dispersion (ASD) with a polymer excipient. It is important that the polymer matrix of an ASD will stabilize the drug in the amorphous state and maintain its supersaturated concentration long enough in the dissolution media. Some of the commercial polymeric systems have shown a positive impact on drug dissolution, but most of them are difficult to characterize due to high polydispersity and system complexity. This makes it difficult to understand the structure property relationships and to quantify the effect of drug-polymer specific interactions. Also, most of the available excipients that improve dissolution of poorly water-soluble drugs tend to form nano-aggregates in the solution. Thus here, block copolymers are explored, which self-assemble into micelle-like structures, as excipients for dissolution of two representative drugs: probucol and phenytoin. Reversible addition-fragmentation chain transfer (RAFT) polymerization was used as a controlled polymerization technique to obtain well-defined block-copolymers of polystyrene and poly(acrylic acid). The polymers were characterized by nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC). A set of four different block copolymers with different molecular weights were synthesized to determine the effect of nano-aggregation in ASD on dissolution of selected drugs. Caco-2 cell permeability assay was applied to determine drug bioavailability from obtained formulations.



POLY 378: Dual effect of thiol addition on fluorescent polymeric micelles: ON-to-OFF emissive switch and morphology transition

Anne B. Mabire¹, *a.b.m.mabire@warwick.ac.uk*, Mathew Robin¹, Helen Willcock^{1,2}, Anaïs Pitto-Barry¹, Nigel Kirby³, Rachel K. O'Reilly¹. (1) Chemistry, University of Warwick, Coventry, United Kingdom (2) Loughborough University, Loughborough, United Kingdom (3) Australian Synchrotron, Clayton, Victoria, Australia

Widely commercialized for imaging and biological applications, fluorescent dyes are often large molecules containing aromatic rings and have a low solubility. Dithiomaleimide (DTM) was found to be a highly emissive fluorescent functionality and was used to label proteins, polymers and nanoparticles. The DTM motif can also be incorporated into a block copolymer as a part of a dual initiator for ring opening polymerization (ROP) and reversible addition-fragmentation chain transfer polymerization (RAFT). In this case, the amphiphilic block-dye-block copolymer is constituted of poly(D,L-lactide) (PLA) as the hydrophobic segment and poly(triethyleneglycol monomethyl ether methacrylate) (PTEGA) as the hydrophilic segment. The self-assembly of this amphiphilic block copolymer into spherical micelles in water ensures the location of DTM functionality at the micelles' core/shell interface. The reactivity of the DTM functional group was used to induce a morphology transition from spherical micelles to vesicles, simultaneously with an ON-to-OFF fluorescence emission switch. This transition is the result of a thiol exchange reaction, which occurs in the presence of an excess of thiol in the environment; the PLA segment is substituted with thiophenol. The transition was observed *via in situ* SAXS measurements, showing a morphology change within 10 min, which is consistent with fluorescence spectroscopy results. The vesicles' formation was also confirmed by multi-angle laser light scattering.



POLY 379: Fabrication and ‘orthogonal’ modification of multi-functional nanogels for targeted therapy

Laura Chambre¹, *lchambre2008@my.fit.edu*, **Bugra Aktan**¹, **Rana Sanyal**¹, **Amitav Sanyal**^{1,2}. (1) Chemistry, Bogazici University, Istanbul, Turkey (2) Center for Life Sciences and Technologies, Bogazici University, Istanbul, Turkey

Nanogels are potential candidates for applications in biomedical areas such as drug delivery, tissue engineering, protein encapsulation and bioimaging platforms. Such applications often necessitate multi-functionalization of nanogels with various appropriately functionalized small molecules and/or ligands (Figure 1). In this study, poly(ethylene glycol) methacrylate based maleimide and N-hydroxy succinimide (NHS) containing carbonate bearing copolymers, obtained using controlled polymerization techniques like atom-transfer radical polymerization and reversible addition-fragmentation chain transfer polymerization, were crosslinked with dithiols to yield reactive nanogels. To demonstrate the multi-functionality of these nanogels, a cyclic peptide based targeting group and a fluorescent label were conjugated in aqueous media. In vitro studies demonstrated preferential internalization of targeting group containing nanogels by breast cancer cells. Lastly, to increase the functionality of these nanogels, their post-gelation modification with doxorubicin, an anticancer drug was carried out to target tumor cells.

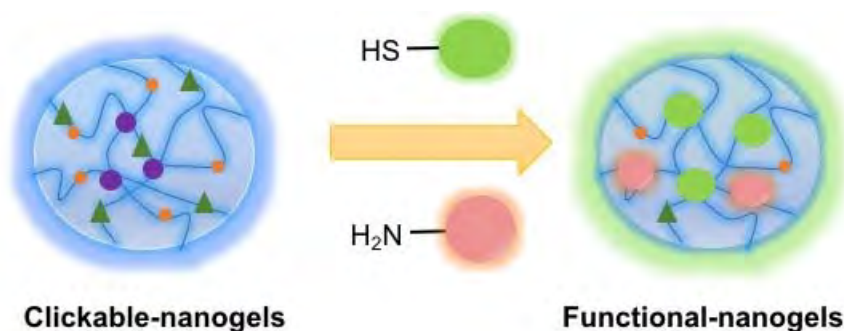
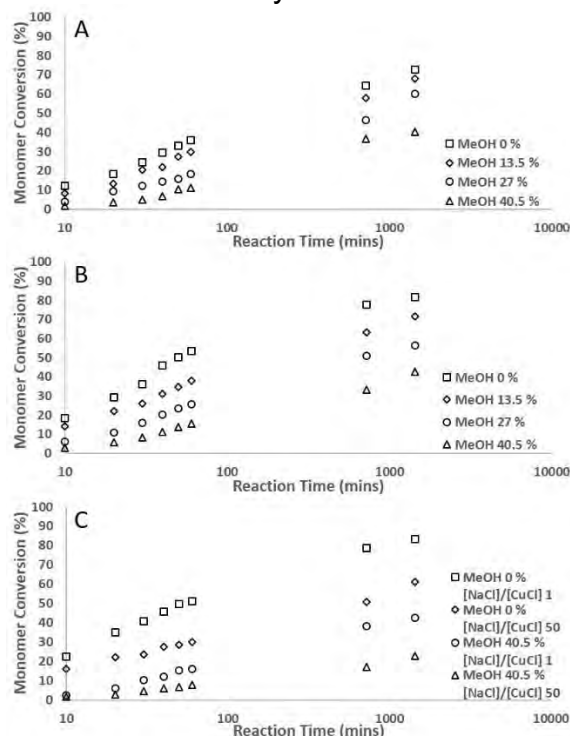


Figure 1. Multi-functionalization of nanogels

POLY 380: Atom transfer radical polymerization of sodium polystyrene sulfonate under aqueous conditions: Controlling an uncontrollable reaction

Paul Balding^{1,2}, pbalding3@gatech.edu. (1) Chemistry and Biochemistry, Georgia Tech, Atlanta, Georgia, United States (2) Louisiana State University, Baton Rouge, Louisiana, United States

Various reaction conditions in the atom transfer radical polymerization (ATRP) of sodium polystyrene sulfonate (NaPSS) from protic media were investigated. Synthetic control depended on pH, cosolvent methanol to water composition MeOH (v/v %), added deactivator species relative to copper catalyst concentration $[\text{NaCl}]/[\text{CuCl}]$, copper catalyst to initiator concentration ratio $[\text{C}]/[\text{I}]$, deactivator type and ligand type. The polymerization was tracked over time using ^1H NMR to determine the percentage monomer conversion and thus the overall reaction kinetics. Higher conversions were achieved as the pH was increased from 6 to 13, with the highest conversion of 99.5 % calculated at a pH 13, $[\text{C}]/[\text{I}]$ of 1.3, $[\text{NaCl}]/[\text{CuCl}]$ of 10, a bidentate ligand copper complex and with no added methanol. Polymer size and polydispersity (PDI) were obtained through gel permeation chromatography coupled multi angle static light scattering. Molecular weight was found to increase by an order of magnitude at higher pH values of 12-13 compared to 6-7. Increasing MeOH composition (v/v %) caused a decrease in molecular weight while $[\text{C}]/[\text{I}]$ values below one produced multimodal peaks, an indication of poor reaction control. PDI was relatively low, 1.05-1.15 under desirable conditions which were when $[\text{NaCl}]/[\text{CuCl}]$ was increased and MeOH was at intermediate values between 0 and 40 % by volume.

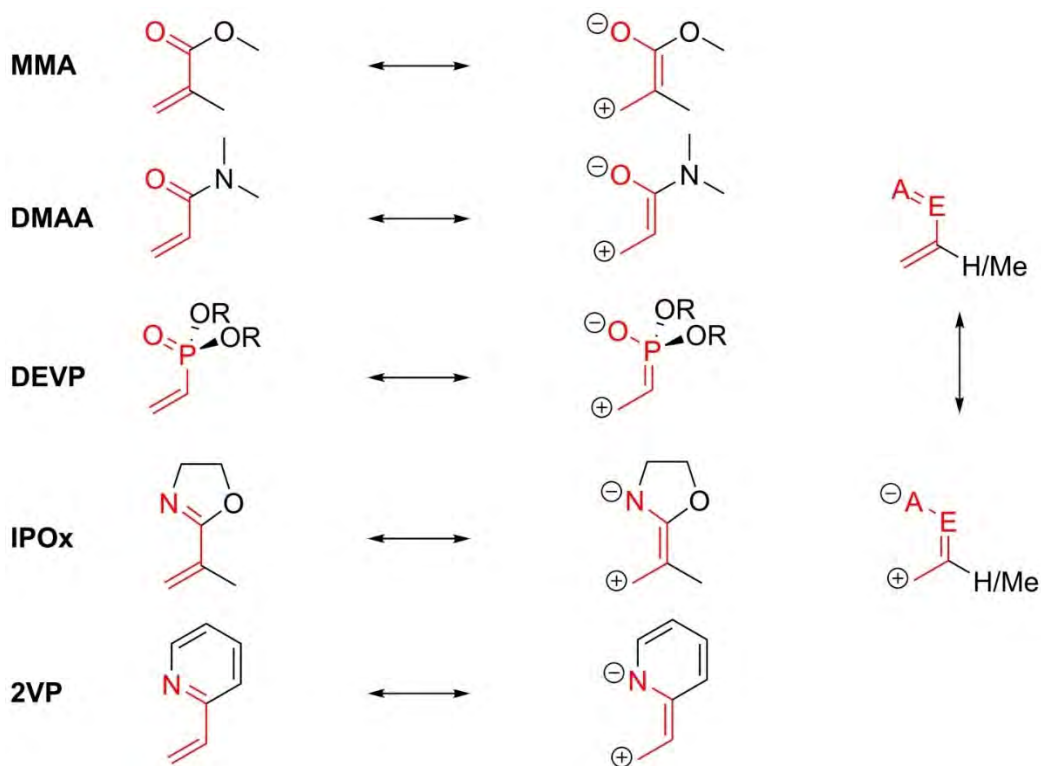


Monomer conversion as a function of methanol content and time. Increased MeOH composition (v/v %) decreased the reaction kinetics regardless of the amount of added deactivator species.

POLY 381: Catalytic precision polymerization of polar monomers: Rare earth metal-mediated synthesis of homopolymers and polymer brushes

Philipp Pahl, philipp.pahl@makro.ch.tum.de, **Benedikt S. Soller**, **Bernhard Rieger**.
WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München,
Munich, Germany

Rare earth metal-mediated group transfer polymerization (REM-GTP) was originally discovered in the early 1990s for the polymerization of methyl methacrylate (MMA). In the following years REM-GTP was expanded to a variety of different meth(acrylates) and meth(acrylamides). Just recently, interest in this field emerged for the polymerization of different *Michael*-type acceptor monomers, having new heteroatom functionalities. Beyond the known (meth)acrylates, now a variety of monomers from vinyl phosphonates to *N*-coordinating 2-vinylpyridine (2VP) and 2-isopropenyl-2-oxazoline (IPOx) can be polymerized by lanthanide complexes using REM-GTP. Besides the living character of this technique allowing the precise adjustment of the molecular weight with very narrow molecular weight distributions, the catalyst geometry enables stereospecific polymerizations thus giving access to tailor-made materials. In combination with living cationic ring-opening polymerization, PIPOx produced by REM-GTP can be converted to high precision nano scaled molecular brushes with defined backbone and poly(2-oxazoline) side chains.



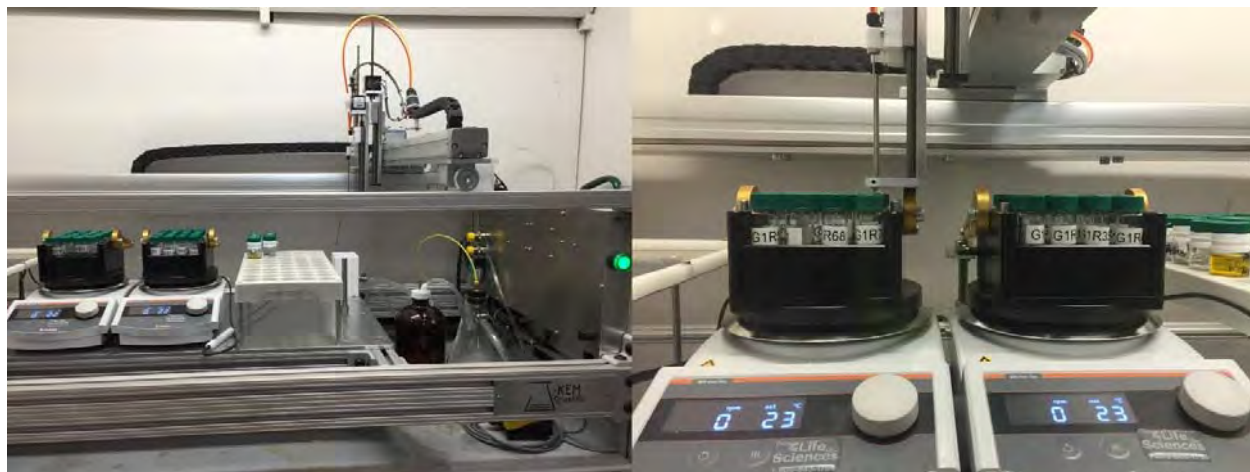
Overview of polar monomers suitable for REM-GTP and general structure of *Michael*-type monomers

POLY 382: High swelling acrylate elastomers with a RAFT crosslinker by high-throughput approach

Jehoon Lee, jl144@zips.uakron.edu, Kevin A. Cavicchi. University of Akron, Akron, Ohio, United States

High swelling materials have been studied as potential application of hydrogels and oil absorbents. Previous studies on these primarily focused on introducing an electrolyte or by solution polymerization. In this study, high swelling elastomers were synthesized via a direct one-pot polymerization with a reversible addition fragmentation chain-transfer (RAFT) crosslinker in neat polymerization.

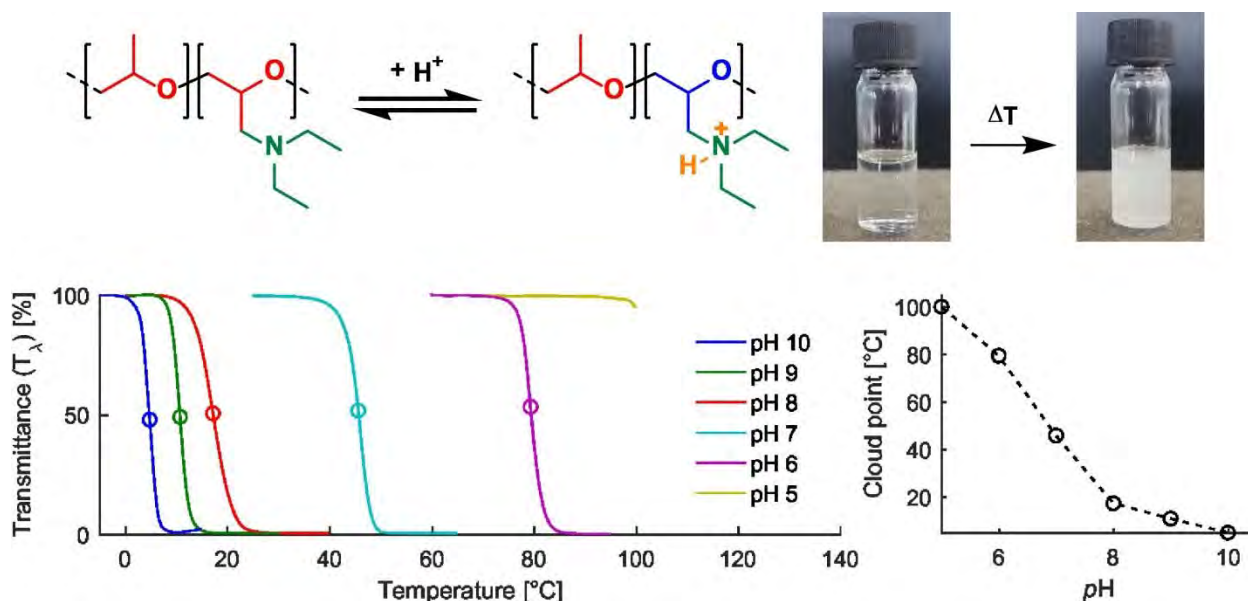
3,4-divinylbenzyl trithiocarbonate (DVBTC) was first synthesized via a one-pot reaction and used as a dual chain-transfer and crosslinking agent to prepare acrylate elastomers to target a range of crosslink densities using high-throughput polymerization robot. The crosslink density of the gels were measured by swelling and rheology and showed a monotonic increase of the crosslink density with RAFT crosslinker concentration. Phase diagram investigation of the different composition will be followed and shape memory testing will be demonstrated as an application.



POLY 383: Amino functional poly(propylene oxide)

Jan Blankenburg^{1,2}, blankenburg@uni-mainz.de, **Jana Herzberger**^{1,2}, **Holger Frey**¹. (1) Chemistry, University of Mainz, Mainz, Germany (2) Graduate School Materials Science in Mainz, Mainz, Germany

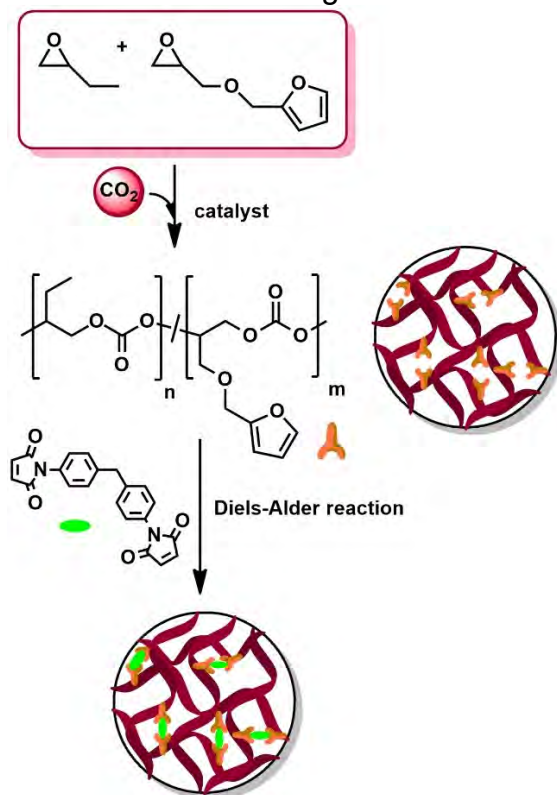
Poly(propylene oxide) (PPO) is widely used for the production of polyurethane foams and nonionic surfactants. Despite its importance in industry and its similar structure to poly(ethylene glycol) (PEG), only a small number of multifunctional PPO is known. The new class of multi amine functionalized PPO polymers were synthesized by the anionic ring opening polymerization (AROP) of propylene oxide (PO) and *N,N*-diethyl glycidyl amine (DEGA). The use of PPO macro initiators with one or two hydroxyl functionalities in an AROP of DEGA yielded PPO-*b*-PDEGA block and triblock copolymers. These block copolymer structures showed dispersities below 1.1. A synthesis route for the copolymerization of PO with DEGA in random fashion was developed to obtain random copolymers with different contents of amine functionalities and dispersities below 1.1. This synthesis strategy also made the synthesis of PolyDEGA possible, which had not been achieved before by AROP. The detailed characterization of the polymers was performed by size exclusion chromatography (SEC), ¹H-NMR spectroscopy, mass spectrometry (MS) and differential scanning calorimetry (DSC). The synthesized block copolymers and random copolymer structures showed thermo-responsive behavior in aqueous solution by exhibiting a cloud point. In neutral aqueous solutions, the LCST increases with increasing ratio of DEGA in the polymer. Due to the amine group, the pH of the solution has a strong impact on the cloud temperature. By changing the pH, the cloud point of a polymer solution could be tuned between 0 °C and 100 °C. These thermo- and pH-responsive properties were studied by turbidity measurements. The strong pH- and thermo-responsive behavior makes multi amine functional poly(propylene oxide) an interesting smart material.



POLY 384: Novel aliphatic polycarbonate elastomers based on CO₂ and epoxides

Lena Kunze, lkunze@uni-mainz.de. Organic Chemistry, Johannes Gutenberg-University, Mainz, Rheinland-Pfalz, Germany

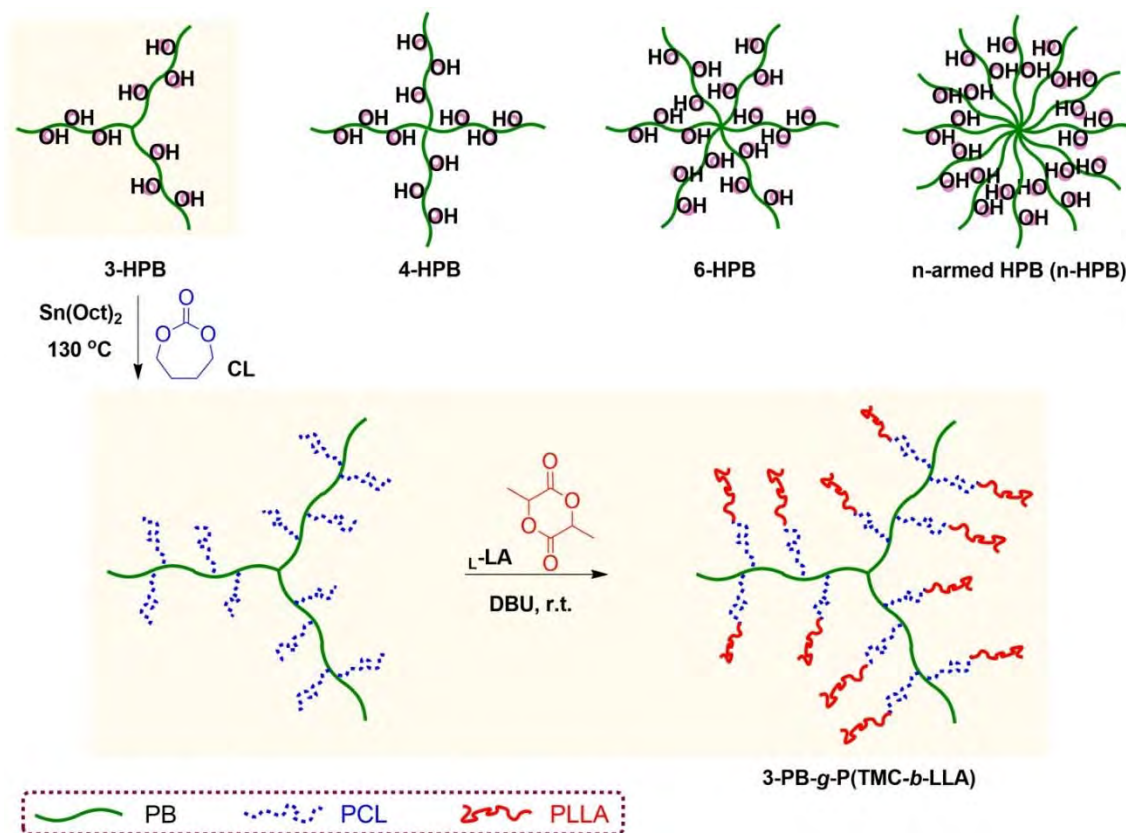
Since the discovery of the immortal polymerization 1969 carbon dioxide (CO₂) is utilized as a comonomer in the ring-opening-polymerisation (ROP) of epoxides to obtain aliphatic polycarbonates (APCs). CO₂ represents a renewable carbon source which is easily available in high purity. Novel degradable aliphatic polycarbonate terpolymers were synthesised without polyether defects via catalytic polymerization of CO₂ and functional epoxide monomers. In addition, the novel polymers were cross-linked via Diels-Alder reaction. Catalytic polymerization of CO₂ with 1,2-propylene oxide (PO), 1,2-butylene oxide (BO) and furfuryl glycidyl ether (FGE) afforded the corresponding co- and terpolymers poly(1,2-propylene carbonate) (PPC), poly(1,2-butylene carbonate) (PBC) and poly(1,2-butylene carbonate-co-furfuryl glycidyl ether carbonate) (P(BC-co-FGEC)). Terpolymers with low FGE-contents could be achieved. The polymerisation proceeded at low temperatures and high CO₂ pressure utilizing the binary catalytic system of (*R,R*)-(salen)-CoCl/[PPN]Cl. Thermal and elastic properties of the obtained polycarbonates were compared. Thermo-reversible cross-linking of P(BC-co-FGEC) was performed utilizing a bifunctional maleimide as cross-linking agent. The linear polymers were characterized by NMR and FT-IR spectroscopy as well as DSC, SEC and TGA measurements. PBC and the terpolymers were additionally characterised by rheologic measurements before and after cross-linking. Due to the low glass transition temperature (*T_g*) of the BO-based terpolymer, it is expected to be applicable as a potential elastomeric material after cross-linking.



POLY 385: Synthesis of star-comb double crystalline copolymers of ϵ -caprolactone /L-lactide: Effect of main-chain structure on crystallization behavior

Xuefei Leng, lengxuefei@dlut.edu.cn. Dalian University of Technology, Dalian, Liaoning, China

A series of highly branched star-comb poly(ϵ -caprolactone)-*block*-poly(L-lactide) (scPCL-*b*-PLLA) were successfully achieved using star-shaped hydroxylated polybutadiene (HPB) with designed number of arms and hydroxyl groups as macroinitiator by simple “graft from” strategy. These star-comb double crystalline copolymers were first synthesized and expected to illustrate the influences of the main chain structure. The crystallization behaviors of scPCL-*b*-PLLA with different topologies were investigated by means of wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and polarized optical microscopy (POM) analysis. It is shown that the comb branched architectures greatly promote the crystallization behavior of both PCL and PLLA compared with their equivalent linear counterparts. The crystallinity and crystallization rate raised from linear to anchored copolymers, but decreased with the number of HPB arms increased due to the dense branching topology. The structure-property relationship was discussed systematically in this work.



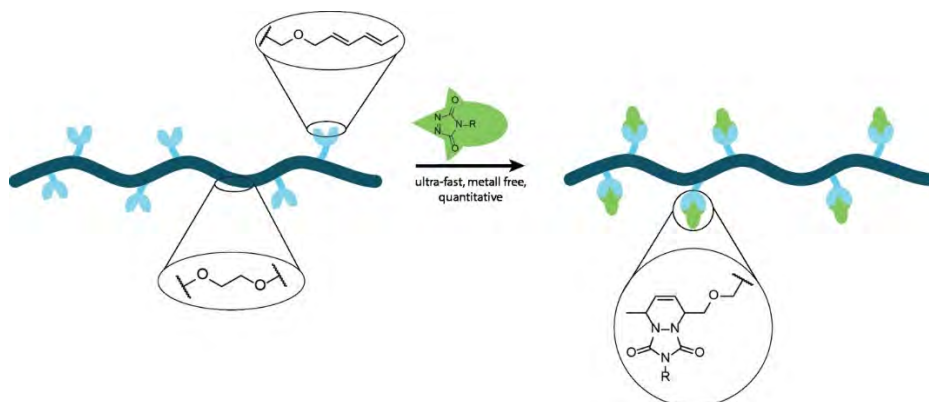
The synthesis of star-comb diblock copolymers of ϵ -caprolactone /L-lactide with different main-chain structure.

POLY 386: Diene functional polyethers: A versatile platform for triazolinedione click chemistry: New multi-functional PEGs for pharmaceutical purposes and clickable polyethers

Tobias Johann^{1,2}, tobias.johann@students.uni-mainz.de, **Holger Frey**¹. (1) Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany (2) Max Planck Graduate Center, Mainz, Germany

Poly(ethylene glycol) (PEG) is highly established for pharmaceutical, cosmetic and medical applications. PEG is known as the “gold standard” biocompatible water-soluble polymer due its very low toxicity and immunogenicity. One drawback of PEG is the limited number of functional groups per polymer. To overcome this issue, multi-functional polyethers can be synthesized by ring opening polymerization of epoxide derivatives. A broad toolkit of epoxides has been developed to tailor the properties of the polymer and to introduce functional groups, e.g., catechols, hydroxyl groups, cyanides, double bonds, amines and furans. Especially functional moieties that can be addressed via “click” reactions like Diels-Alder (DA) reactions are favorable due to their mild reaction conditions and highly efficient reactions. Furan moieties have been proven to be suitable for [4+2] cycloaddition with maleimides. A major drawback is the usually occurring retro Diels-Alder reaction at elevated temperatures, and in some cases conversion of the furan moieties is not quantitative. To overcome this issue, 4-substituted 1,2,4-triazoline-3,5-diones (TADs) can be used instead. TADs are known to be highly reactive dienophiles with reactivity up to 3000 times faster than other common dienophiles, such as maleimides.

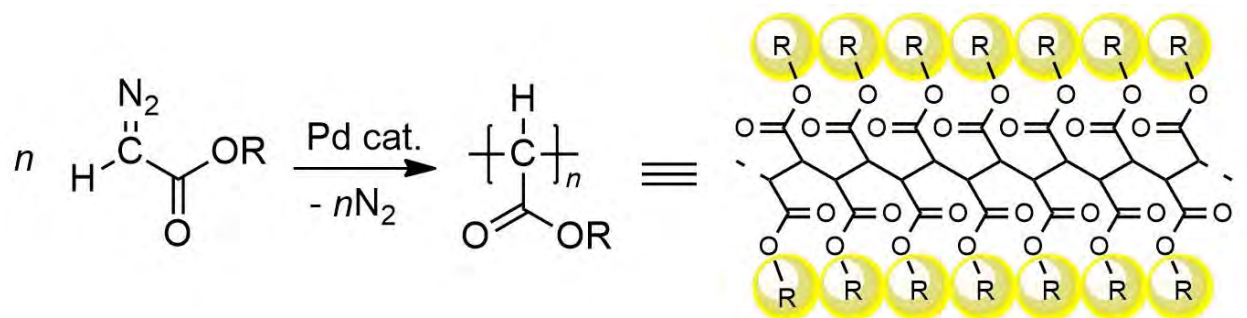
We report the synthesis of hexa-2,4-diene glycidyl ether (HDEGE), a novel diene functional epoxide monomer, which is suitable as a diene compound for DA “click” reactions. Polyethers based on HDEGE, ethoxyethyl glycidyl ether (EEGE), propylene oxide (PO) and ethylene oxide (EO) were prepared via the monomer activated technique to obtain copolymers with varying HDEGE content. The HDEGE moieties were further reacted with 4-phenyl-1,2,4-triazole-3,5-dione (PhTAD) and 4,4'-(4,4'-diphenylmethylene)-bis-(1,2,4-triazoline-3,5-dione) (BisTAD) as a dienophile, leading to quantitative, irreversible functionalization within a few seconds and in case of BisTAD to highly crosslinked networks. In conclusion, multi-functional polyethers containing HDEGE have been shown to be a promising platform for ultra-fast, metal free and quantitative functionalization under mild conditions.



POLY 387: Advances in Pd-initiated polymerization of diazoacetates: From variety of functional groups, living polymerization system, to high stereoregularity

Hiroaki Shimomoto, *shimomoto.hiroaki.mx@ehime-u.ac.jp*, Eiji Ihara. Department of Materials Science and Biotechnology, Ehime University, Matsuyama, Ehime, Japan

Polymerization of diazoacetates is a useful method for preparing C-C main chain polymers bearing an ester substituent on each main chain carbon atom [poly(substituted methylene)s]. However, the substituents introduced into the side chain were limited to hydrophobic groups, and controlled and stereospecific polymerization has not been achieved so far. Recently, we have successfully synthesized poly(substituted methylene)s with hydrophilic groups including hydroxy group and oligo(ethylene glycol) units; the resulting polymers were found to show higher hydrophilicity compared to the corresponding vinyl polymer counterparts. In addition, we have succeeded in controlling the polymerization of diazoacetates for the first time by employing cyclophosphazene-containing diazoacetates as monomers. Furthermore, we have found that the polymerization using a new initiating system, amidinate/Pd, proceeds with significantly higher stereoregularity compared to those with previously reported Pd-based initiating systems.

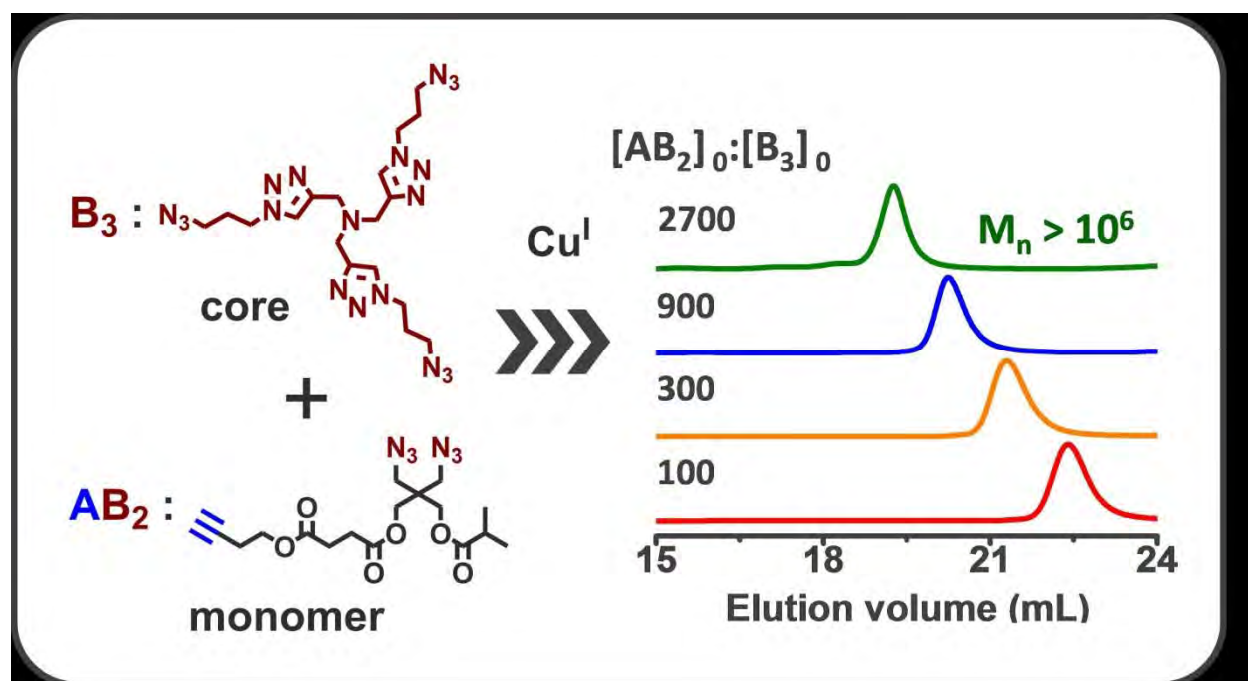


- ✓ Variety of functional groups
- ✓ Living polymerization
- ✓ High stereoregularity

POLY 388: One-Pot synthesis of hyperbranched polymers with over a million molecular weight and low polydispersity

Xiaosong Cao¹, xcao@nd.edu, **Yi Shi**², **Xiaofeng Wang**¹, **Robert Graff**¹, **Haifeng Gao**¹.
(1) Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States (2) Chemistry and Biochemistry, University of Notre Dame, South Bend, Indiana, United States

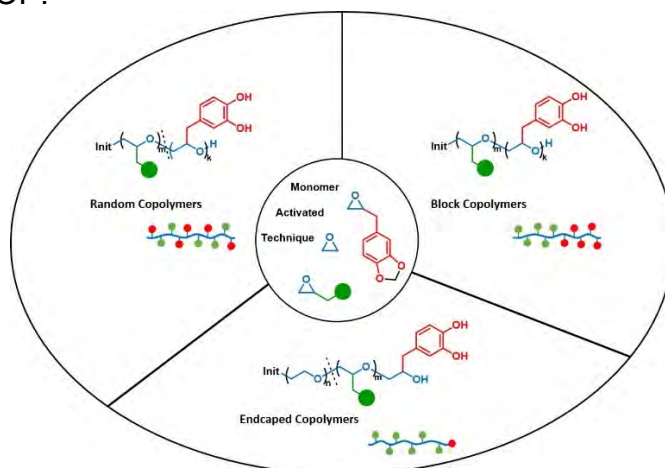
Hyperbranched polymers (HBPs) have found various applications in catalysis, biomaterials, microelectronics and nanomedicines, due to their three-dimensional structure, cavernous interior and large number of peripheral functionalities. From synthetic point of view, it remains a challenge to achieve HBPs with both high molecular weight and uniform structure in a one-pot reaction. This poster presents our first one-pot one-batch synthesis of hyperbranched polymers with over a million molecular weight and low polydispersity in the copper-catalyzed alkyne-azide cycloaddition (CuAAC) polymerization of AB₂ monomer in the presence of a novel ligand-based B₃ core. This tris-triazoleamine-containing B₃ molecule complexed with Cu^I catalyst efficiently and activated the azido reactivity in both B₃ and B₃-containing polymers, leading to a linear increase of polymer molecular weights with the feed ratio of [AB₂]₀: [B₃]₀ at full monomer conversion. By using this method, hyperbranched polymers with molecular weight $M_n = 1.01 \times 10^6$ and polydispersity $M_w/M_n = 1.06$ was achieved within 4 hours.



POLY 389: Safrole Oxide (SFO): A novel functional epoxide monomer for the introduction of Catechol moieties into multifunctional Poly(ethylene glycol) via monomer activated technique

Olga Linker¹, ollinker@uni-mainz.de, **Tobias Johann**^{1,2}, **Holger Frey**¹. (1) Institute of Organic Chemistry, University of Mainz, Mainz, Germany (2) Max Planck Graduate Center, Mainz, Germany

Poly(ethylene glycol) (PEG) is the most important representative of the class of aliphatic polyether due to its outstanding properties. Its high aqueous solubility is unique among the polyether, which are usually not water-soluble. PEG exhibits a low immunogenicity, antigenicity and toxicity. It is the gold standard of biocompatible polymers in medical, pharmaceutical and cosmetic applications. Diverse surfaces, drugs or biomolecules can be modified by covalent attachment of PEG chains, which is known as “PEGylation”. This strategy improves the biomedical and pharmaceutical properties of drugs. Some “PEGylated” pharmaceuticals are already approved by the American Food and Drug Administration (FDA). The drawback of PEG for some applications is the low number of functional groups of the polymer. To achieve multifunctionality, ethylene oxide can be copolymerized with various functional epoxides, leading to multifunctional PEG. In recent years, PEG with catechol termini have been used to impart antifouling properties to surfaces, to fabricate composite materials and to stabilize nanoparticles. PEG modified with catechol moieties can form supramolecular polymer networks in the presence of iron ions. In this work we present the synthesis of a novel catechol-containing monomer safrole oxide (SFO). SFO is obtained in a one-step reactions and enables the incorporation of surface-active catechol moieties into a variety of hydrophilic and biocompatible polyether architectures by copolymerization. Via cleavage of the protecting groups, the polymer-attached catechol functionalities are liberated and available for surface attachment or metal complexation. SFO has been copolymerized with ethylene oxide using the monomer activating technique. This method enables the copolymerization with a variety of comonomers and therefore the incorporation of divers functional groups, which could not be introduced via the well-established classical approach of the AROP.

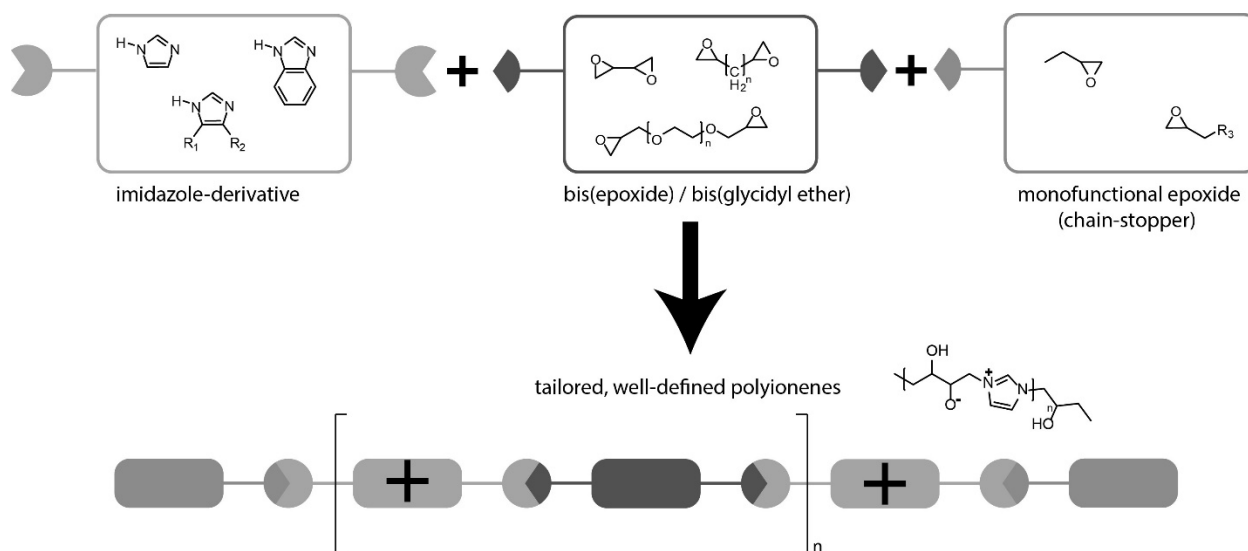


Multifunctional poly(ethylene glycol) with catechol moieties via monomer activated technique.

POLY 390: Tailored imidazolium-containing polyionenes: Polymer additives for electrochemical deposition processes and copper plating

Arthur D. Ziegler, ziegler@uni-mainz.de, Holger Frey. Chemistry, University of Mainz, Mainz, Germany

In recent years, polycations and especially imidazolium-containing polycations, often closely linked to poly(ionic liquid)s (PILs), have gained increasing interest in polymer research as well as materials science. The range of application for cationic imidazolium moieties is diverse, ranging from catalysts based on N-heterocyclic carbenes (NHCs) to ionic conductors to surface interactions. The so-called “Damascene Process” is widely used for manufacturing microelectronic devices, using electrochemical deposition of copper on photolithographically designed multilayer structures. Electrochemical deposition is an important field of research, also with respect to the multifunctional additives employed. Polyionenes are polycations with charges localized in the polymer backbone. This class of polymers shows interesting features in their hybrid-characteristics for copper-plating. Unfortunately, industrially used polyionenes are often highly branched structures, leading to issues regarding their characteristics. We synthesized novel polyionenes via polyaddition of imidazoles and bis(epoxide)s. This versatile, yet relatively unexplored method can be used for rather well-defined polyionenes. To date, detailed characterization of multiple charged polymers remains challenging and requires special characterization methods. Common methods such as SEC or MALDI-ToF often fail when it comes to polyelectrolytes due to the special nature of multiple charged compounds and the resulting aggregation behavior. We also present a strategy to control the molecular weight by using a chain-stopper and characterization via ^1H NMR spectroscopy.



Examples of monomers used for polyaddition of imidazole-derivatives with bis(epoxide)s resulting in well-defined polyionenes.

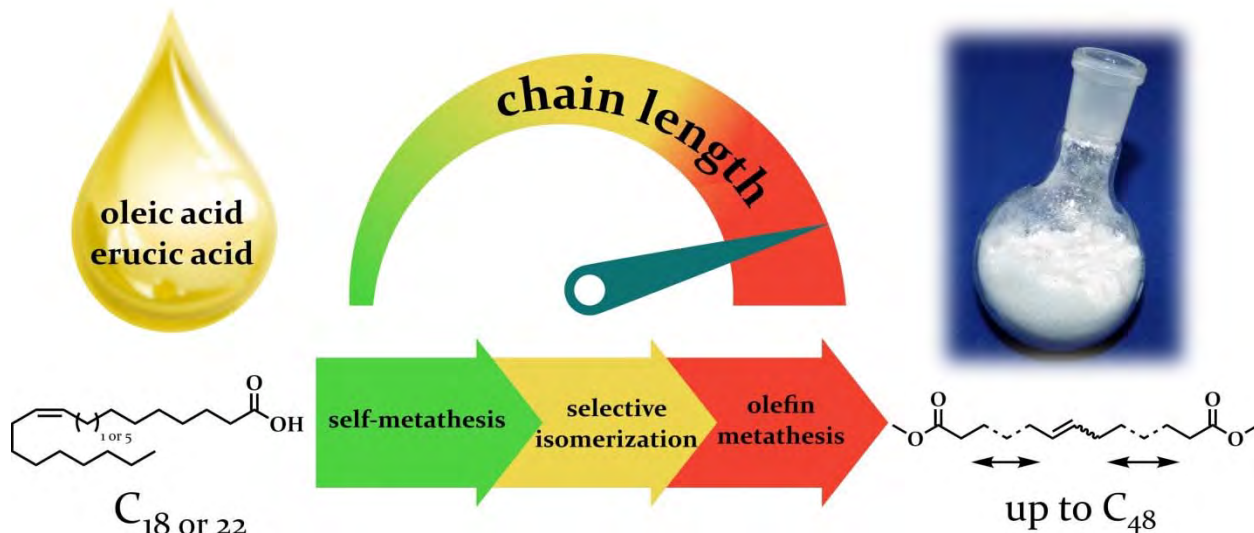
POLY 391: Chain multiplication of fatty acids

Manuel Haeussler, manuel.haeussler@uni-konstanz.de, Timo Witt, Stefan Mecking.
Department of Chemistry, University of Konstanz, Konstanz, Germany

Ultra Long-chain α,ω -difunctional building blocks represent an interesting class of substrates and are often found in nature as structure-bearing elements. For instance, they occur as ceramide – a major component of the *stratum corneum* of the epidermis layer of the human skin, and they are part of the cellular walls of several algae species (algaenans) but also of plants (cutin and suberin). Further, such chain lengths correspond to the typical lamella thickness of polymer crystals, rendering them relevant for convenient access to nanocrystals and to high-melting polymers.

The preparation of long-chain α,ω -difunctional building blocks is possible by various approaches to date. However, conventional routes *via* traditional organic synthesis require elaborate multi-step reactions and involve stoichiometric side products. A more straightforward approach is the utilization of fatty acids from plant oils as they inherently provide a long aliphatic methylene sequence. A major drawback of most state-of-the-art techniques though is that the maximum chain length accessible is in the same range as the fatty acid used.

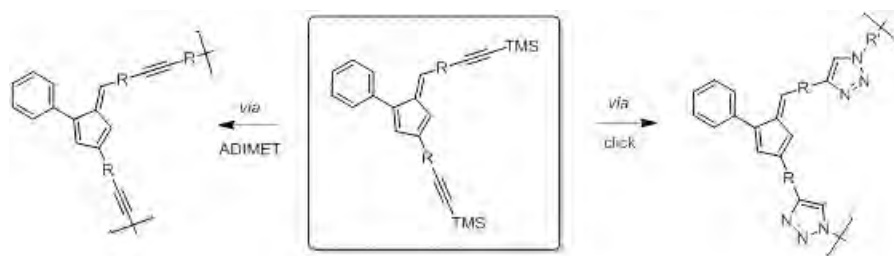
We report a novel approach for the chain-length multiplication of monounsaturated fatty acids by a combination of two catalytic transformations, namely olefin metathesis and double-bond isomerization. With this unique process, ultra long-chain α,ω -difunctional building blocks with a doubled methylene sequence are obtained. Starting from readily available oleic acid (18:1) and erucic acid (22:1) this translates to the formation of C₃₂ or C₄₈ building blocks. As a possible application of such ultra long-chain compounds the preparation of high-melting polyesters (up to $T_m = 120\text{ }^\circ\text{C}$) is reported. Furthermore such well-crystallizable compounds offer themselves for the preparation of thermoplastic elastomers or polymer nanocrystals.



POLY 392: Synthesis and applications of dialkyne functionalized fulvenes

Andrew Peloquin², andrewpeloquin@gmail.com, **Nicholas P. Godman**^{2,1}, **Gary J. Balaich**², **Scott T. Iacono**^{2,1}. (1) Chemistry Research Center, United States Air Force Academy, Colorado Springs, Colorado, United States (2) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States

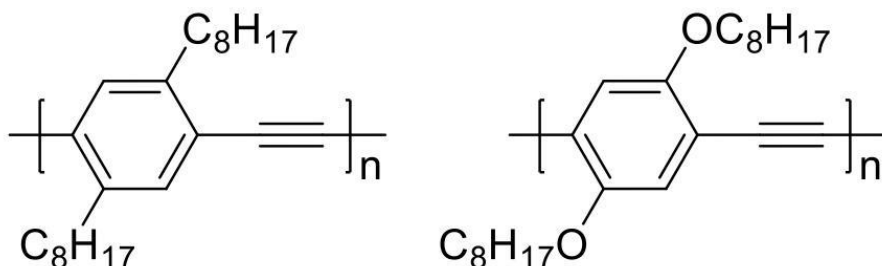
Substituted pentafulvene compounds have been shown to possess donor- π -acceptor behavior and low band gap for application in light harvesting materials. However, little research has been made on incorporating intact fulvene moieties in a polymer backbone. Currently, our efforts focus on the design of dialkyne functionalized fulvene monomers, which can be polymerized by both acyclic diyne metathesis polymerization (ADIMET) and 1,3-dipolar cycloaddition-mediated 'click' strategies without disrupting the fulvene core. Due to the amendable nature of our fulvene synthesis strategies and the diversity of dialkynes and diazides available, polymers with highly tunable properties can be obtained.



POLY 393: Side group effects on aggregation properties of conjugated polymers

Yajing Yang², yangyajing19900902@gmail.com, Kirk S. Schanze¹. (1) Chem Dept, University of Florida, Gainesville, Florida, United States (2) university of florida, Gainesville, Florida, United States

Over the past several decades, conjugated polyelectrolytes (CPEs) have drawn much attentions as versatile materials with particular focus in biochemical detection systems due to their water solubility. In spite of the potential advantages, their properties can be limited by a low fluorescence quantum yield or unpredictable response due to a strong propensity to aggregate in aqueous media. In a previous poly-P-phenylenethynylene (PPE) type polyelectrolytes study, we discovered that aggregation could be reduced simply by changing the linkage atom from oxygen to carbon between the side chain and the conjugated backbone. Yet, the reasons were not clear. To further study this difference in aggregation behavior, two pairs of neutral conjugated polymers were synthesized which feature the same conjugated backbone and side group but with different linkage atoms (P-C and P-O). The photophysical properties were fully characterized both in different organic solvents and on films. Solvent mixture experiments between “good solvents” and “poor solvents” were also performed. P-O formed a more aggregated structure than P-C in “poor solvents”. The DFTB+ calculations indicated that the reason for their different aggregation properties can be attributed to the conformational control by the substituent groups. The oxygen substituent tends to form a more co-planar structure while carbon substituent prefers a twisted confirmation.

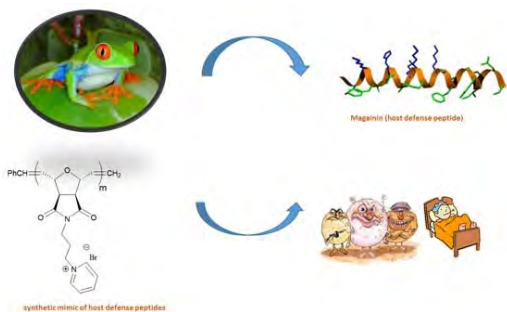


POLY 394: Synthesis of DABCO based cationic polymers with ROMP technique and examination of antibacterial activity

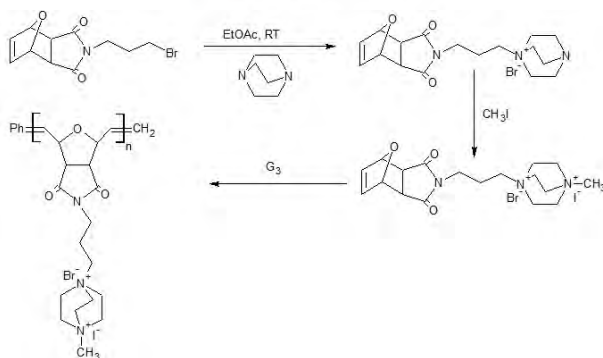
Aylin KAYMAZ², aylinpak39@gmail.com, **Tarik EREN²**, Seyda Bucak¹. (1) Chemical Engineering, Yeditepe University, Istanbul, Turkey (2) Chemistry, Yildiz Technical University, Istanbul, Turkey

Bacterial infection is a global problem and has become more important especially in the last decades due to rising death rates. The main reason for that is the increased resistance of bacteria to the drugs. The new generation antibiotics are quite important for fighting against the bacteria. Basically, there are two main categories of new generation antibiotics: the host defense peptides and their synthetic analogues of host defense peptides. Hydrophobic and hydrophilic (cationic functionality) groups play a role to the molecule in antibacterial action. It is also well known that amphiphilic polymers disrupt the cell membranes of the bacteria and can realize the cell death.

This paper focuses on the synthesis of such a polymer. The synthesized polymer has a cationic structure which gives it the advantage of having high interaction with the anionic surfaces of the bacteria. Due to that increased interaction, the cationic groups are expected to destroy the cell membranes of the bacteria and hence realize the death of the bacteria. In the scope of this work, the monomers containing DABCO and pyridine have been used to synthesize polymers with molecular weights of 3000 g/mole and 10000 g/mole with Ring Opening Metathesis Polymerization method. During the antimicrobial tests realized, the hemolytic concentration of DABCO based polymers have been measured as higher than 400 µg/mL, while the MIC value is lower than 4 µg/mL.



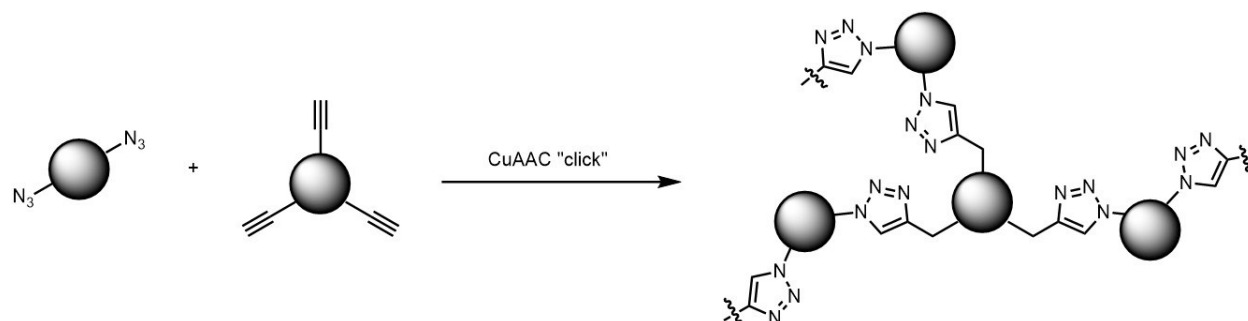
Scheme 1. Synthetic mimic of host defense peptides



POLY 395: Click chemistry toward stable reverse osmosis membranes for water desalination

Breanne L. Hamlett², *bhamlett6@gatech.edu*, **M.G. Finn²**, **Ryan P. Lively¹**, **Benjamin McCool³**. (1) *Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States* (2) *Chemistry, Georgia Institute of Technology, Newnan, Georgia, United States* (3) *ExxonMobil, Annandale, New Jersey, United States*

While current water desalination membranes, made of polyamide composites, perform at high levels, they are chemically unstable to defouling and cleaning agents, including NaOCl, HCl, and NaOH. In this work, triazoles are used to create chemically stable main chain functional group linkages. Given their chemical and oxidative stability, ease of synthesis, and the fast reaction rate of the copper catalyzed azide alkyne cycloaddition (CuAAC) "click" reaction, triazoles are potentially an excellent linker in interfacial polymerization and membrane formation. Representative triazoles were subjected to various conditions mimicking water pretreatment processes. Conditions were developed for interfacial CuAAC "click" polymerization. Additionally, polymers of intrinsic microporosity (PIMs), whose highly contorted and rigid structure leads to inefficient packing in the solid state and thus creating micropores (< 2 nm) and a large, accessible surface area, have demonstrated excellent gas and solvent separation properties when compared to other materials. PIM-like monomers containing spirocenters have been functionalized with "clickable" azide and alkyne groups and investigated in interfacial polymerization. Overall, this work brings new, robust, and scalable chemistry to water purification, based on CuAAC "click" chemistry. Monomer design can be readily tuned to influence bulk properties, because azides and alkynes can be introduced easily. Ultimately, this will lead to polymers with excellent chemical resistance and thermal stability as ultra-thin membranes via interfacial polymerization.

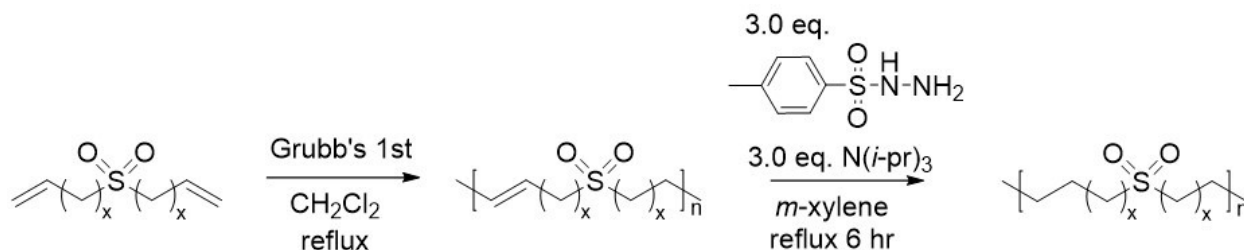


General scheme of CuAAC "click" polymerization

POLY 396: Synthesis of high melting precision aliphatic polysulfones via ADMET polymerization

Michael H. Bell, bellmichael3@gmail.com, Grace Hester, Taylor W. Gaines, Kenneth B. Wagener. Dept. of Chemistry, University of Florida, Gainesville, Florida, United States

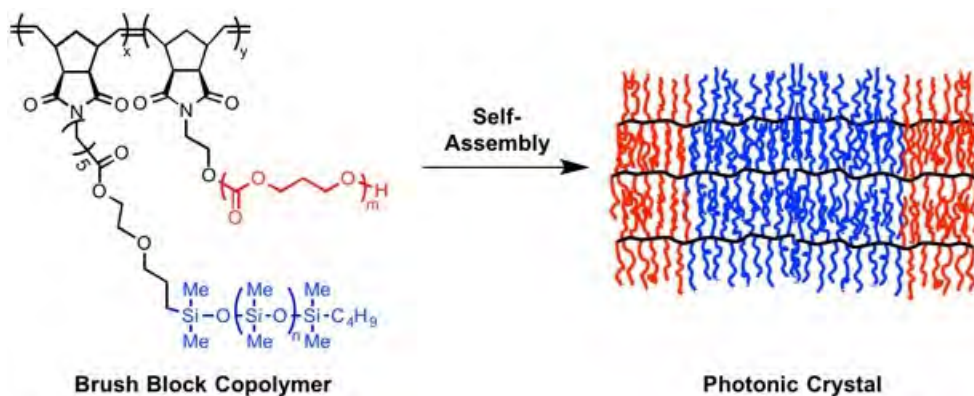
Polyethylenes make up a vast majority of commercially used plastics throughout the world. The addition of functional groups to polyethylene can extend its applications to include tougher thermoplastics, self-healing polymers, and permselective membranes. Acyclic diene metathesis (ADMET) polymerization offers an unprecedented opportunity to synthesize precision linear functional polyethylene polymers. Presented here is the synthesis and characterization of sulfone containing polyethylene polymers synthesized via ADMET polymerization. The synthesized polymers were precise in functional group spacing. The precise location of the sulfone groups, which were not tactic, within the polyethylenes increased crystallinity, promoted secondary bonding, and raised T_m . Interestingly, polysulfones exhibited an increase in melting temperature with increased sulfone content. Melting temperatures as high as 175°C were achieved, a 45°C increase over linear polyethylene.



POLY 397: Self-Assembly of brush block copolymer photonic crystals featuring low T_g side chains

Allegra L. Liberman-Martin, *alibermanmartin@gmail.com*, Crystal Chu, Alice Chang, Robert H. Grubbs. *California Institute of Technology, Temple City, California, United States*

Brush block copolymers, which feature polymeric side chains grafted to a linear backbone, display interesting properties due to their dense functionality, low entanglement, and ability to rapidly self-assemble to highly ordered nanostructures. Using ruthenium-mediated ring opening metathesis polymerization (ROMP) of norbornene-functionalized macromonomers, our group has demonstrated the synthesis of brush block copolymers that behave as photonic crystals. Previous work has shown that the frequency of reflected light can be tuned by varying the backbone degree of polymerization or blending in polymer additives. However, the impact of side chain properties on self-assembly and photonic behavior remains poorly understood. Herein, we report a series of block copolymers featuring poly(dimethylsiloxane) (PDMS) and poly(trimethylene carbonate) (PTMC) side chains. These components were selected to investigate photonic crystal self-assembly for a brush block copolymer featuring side chains with low glass transition temperatures ($T_g = -125\text{ }^\circ\text{C}$ for PDMS, and $T_g = -15\text{ }^\circ\text{C}$ for PTMC). The morphologies and photonic properties of these materials will be discussed.

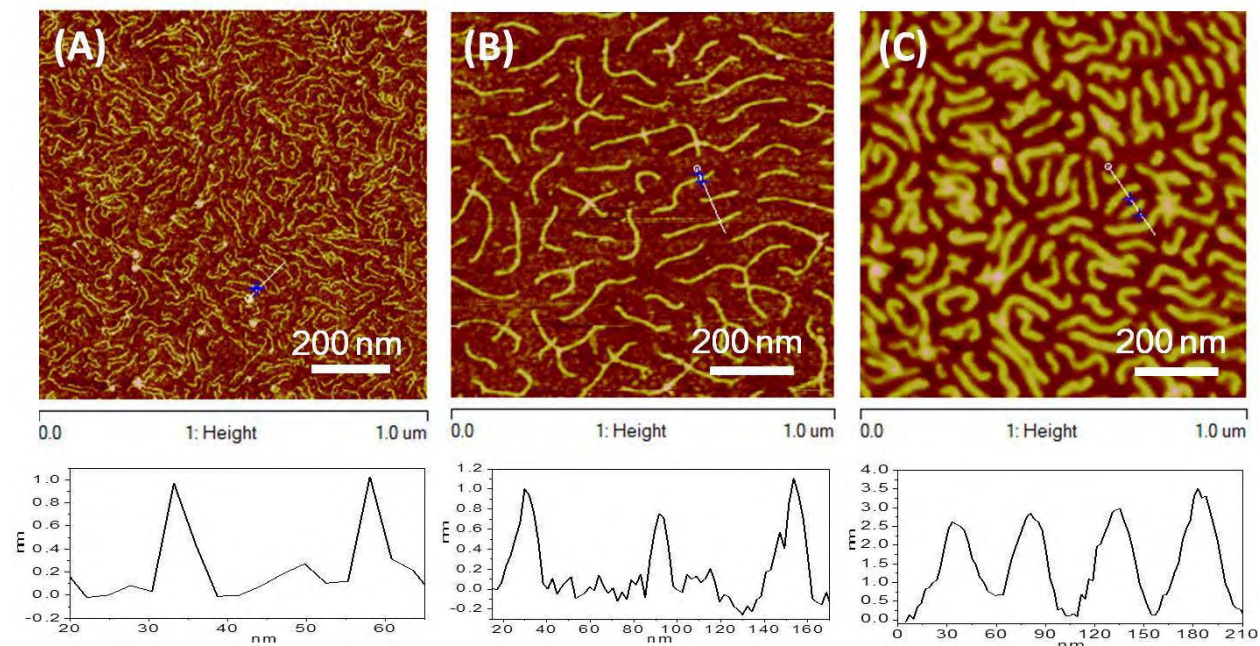


POLY 398: Synthesis of molecular brushes with ultrahigh grafting density using accelerated CuAAC coupling-onto strategy

Yi Shi, Yi.Shi.27@nd.edu, Weiping Gan, Xiaosong Cao, Haifeng Gao. Chemistry and Biochemistry, University of Notre Dame, South Bend, Indiana, United States

This poster presents our recent progress in the synthesis of cylindrical molecular brushes with tunable and ultrahigh grafting density (up to 1.4 side chains per backbone carbon) by accelerated CuAAC coupling-onto strategy. Two kinds of polymer backbone (polycarbonate and polymethacrylate with two or three pendant azido groups) and various alkynyl-terminated SCs with different compositions and molecular weights, including ay-PMA, ay-PS, ay-PEO, ay-PtBA-*b*-PS, and ay-PDMA, were applied to synthesize molecular brushes with different properties. Moreover, the comparison of the dimensions of molecular brushes with different grafting density was also performed by AFM using the same test condition. These molecular brushes could be potentially applied in releasing guest molecule.

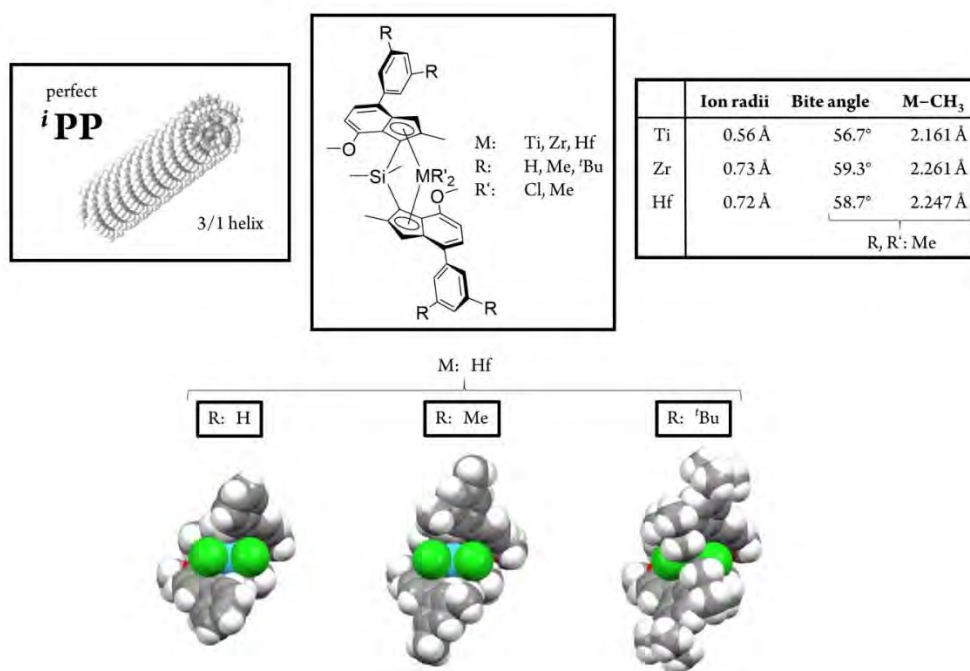
Cylindrical molecular brushes with different grafting density



POLY 399: Ultra-rigid indenyl-based group IV metallocene complexes for nearly perfect *i*PP catalysis

Martin Machat, martinmachat@gmx.net, Bernhard Rieger. WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Munich, Germany

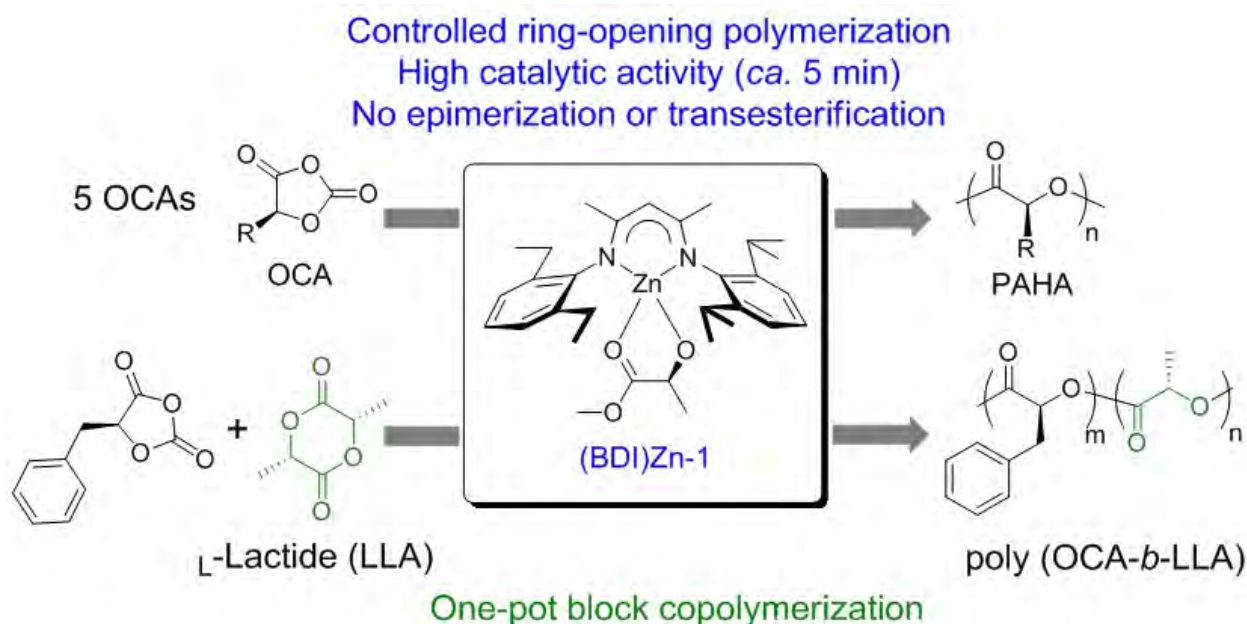
More than five decades ago the coordinative polymerization of olefins passed the threshold of an exclusively hyped research topic evoking one of the most important industrial catalytic processes to date. Facilitated by the unique efficiency of *Ziegler-Natta* catalysis, polypropylene has ascended to one of the most widely known commodity plastics in everyday life and the potential of this polymer is far from being completely exhausted. Precise catalytic control in the polymerization of propene is key to developing new materials with outstanding properties based on this easily accessible and largely available monomer unit. In 2012, our research group discovered the state of the art homogenous metallocene catalyst for ultra-high molecular weight polypropylene with almost perfect stereo- and regioselectivity. This strictly isotactic polymer, possessing the highest known melting transition for untreated *i*PP (*ex reactor*), is not just the result of striving for perfection, but also gains novel insight into key substituents for this outstanding precision in polymerization catalysis. The impact of this crucial substitution pattern on the polymer properties and the catalytic performance is enlightened in a comparative study examining this benchmark system together with two novel, related metallocene complexes. Further focus is directed towards varied group IV metal centers (M: Ti, Zr, Hf) and their decisive differences in fundamental metallocene chemistry as well as the catalytic behavior in the polymerization of propene. In this context, the structural and chemical determination of the metal-carbon bond in alkylated metallocene complexes plays a central role in continuative investigations.



POLY 400: Controlled ring-opening polymerization of O-carboxyanhydrides using β -diiminate zinc catalyst

Ruibo Wang, *rwang41@illinois.edu*, Jianjun Cheng. *Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States*

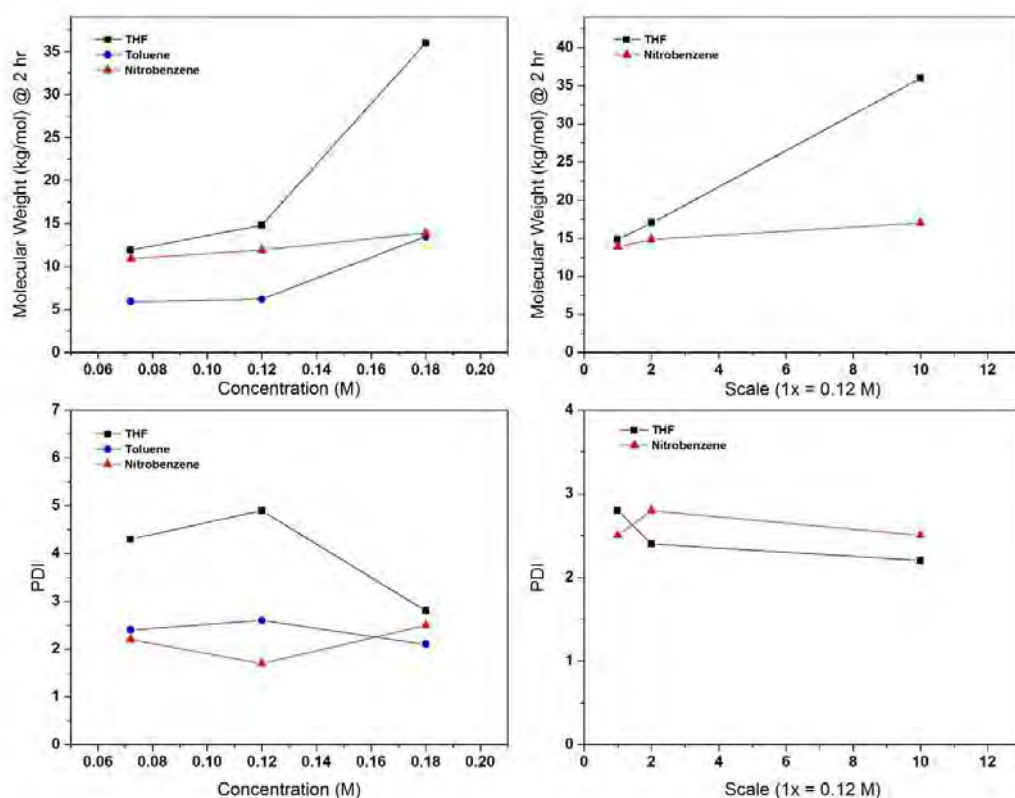
O-Carboxyanhydrides (OCAs) have recently emerged as a class of viable monomers which can undergo ring-opening polymerization (ROP) to prepare poly(α -hydroxy acids) with functional groups that are typically difficult to achieve via the ROP of lactones. Organocatalysts for the ROP of OCAs, such as dimethylaminopyridine (DMAP), may induce undesired epimerization of the α -carbon in polyesters resulting in the loss of isotacticity. In this work, we report the use of (BDI-IE)Zn(OCH(CH₃)COOCH₃) ((BDI)Zn-1, (BDI-IE) = 2-((2,6-diethylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene), for the controlled ROP of various OCAs without epimerization. Both homopolymers and block copolymers with controlled molecular weights, narrow molecular weight distributions and isotactic backbones can be readily synthesized. (BDI)Zn-1 also enables controlled copolymerization of OCAs and lactide, facilitating the synthesis of block copolymers potentially useful for various biomedical applications. Preliminary mechanistic studies suggest that the monomer/dimer equilibrium of the zinc catalyst influence the ROP of OCAs, with the monomeric (BDI)Zn-1 possessing superior catalytic activity for the initiation of ROP in comparison to the dimeric (BDI)Zn complex.



POLY 401: Microwave-assisted polyarylene: Synthesis, characterization, and optimization

Stephen M. Budy, sbudy@smu.edu, David Y. Son. Chemistry, Southern Methodist University, Dallas, Texas, United States

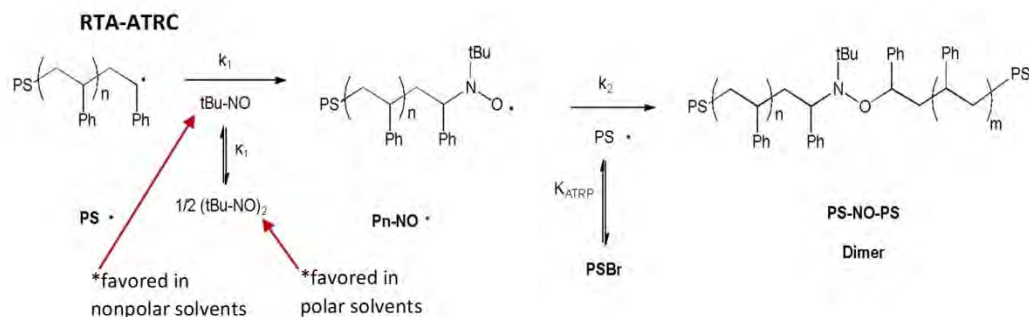
A series of Diels–Alder polyarylene polymers were synthesized via microwave-assisted step-growth polymerization. Optimization of 1,4-bis(2,4,5-triphenylcyclopentadienone)benzene with 1,4-diethynylbenzene using a variety of solvents, concentration, and time was achieved. The polyarylene polymers were characterized by ^1H NMR, FTIR, TGA, DSC, DMA, and GPC. Thermal analysis showed little change in the series of polymers for onset of decomposition ($T_d = 550\text{ }^\circ\text{C}$). Polar solvents (e.g., tetrahydrofuran and nitrobenzene) worked well for microwave-assisted polymerization, however, nonpolar/aromatic solvents (e.g., toluene and xylene) also afforded lower molecular weight polyarylene polymers/oligomers. Molecular weights were monitored over time affording well over 100 kg/mol and dispersities more difficult to control in the range 1.9 to 20.1. Further work will involve scaling up the polymerization reactions and also using a variety of different monomers.



POLY 402: Expanding the scope of radical traps in RTA-ATRC reactions by using solvent mixtures and additives

Eric S. Tillman, *etillman@bucknell.edu*, **Maya Arce**, *marce@scu.edu*. *Chemistry and Biochemistry, Santa Clara University, Santa Clara, California, United States*

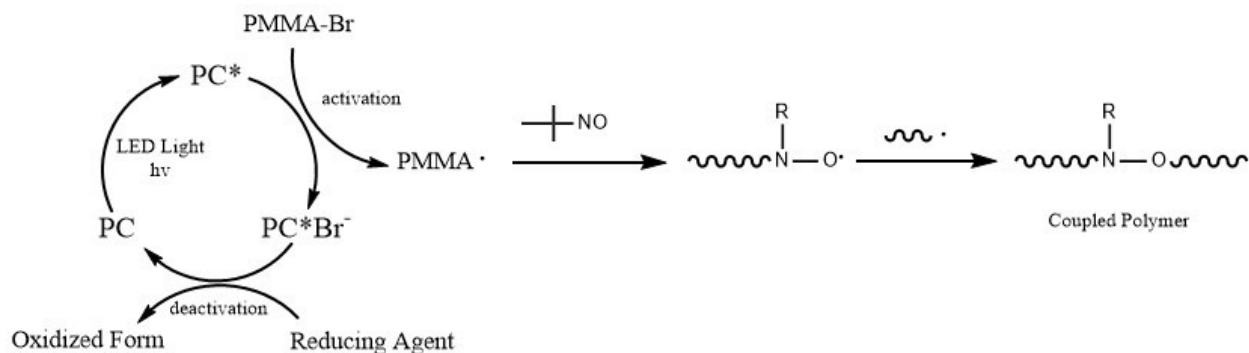
The rate of radical trap-assisted atom transfer radical coupling (RTA-ATRC) of polystyryl radicals (PSBr) has been studied as a function of solvent composition and the inclusion of additives. The extent of coupling was found to be initially higher in solvent mixtures of polar (THF) and non-polar (hydrocarbons) compared to either pure solvent, but polar solvents showed similar results at higher extents of coupling (~70% and higher). The enhanced performance of mixed solvents is attributed to a balancing act between KATRP values (favored in more polar solvents) and the monomeric form of the radical trap (favored in non-polar solvents). Additives, such as β -cyclodextrin in particular, show great promise in stabilizing the radical trap in monomeric form to enable a greater rate of coupling across all solvents.



POLY 403: Photocatalyzed chain end coupling reactions of brominated polymers

Eric S. Tillman, **Ching Pan**, cpan@scu.edu, **Jessica Wu**, jpwu@scu.edu. Chemistry and Biochemistry, Santa Clara University, Santa Clara, California, United States

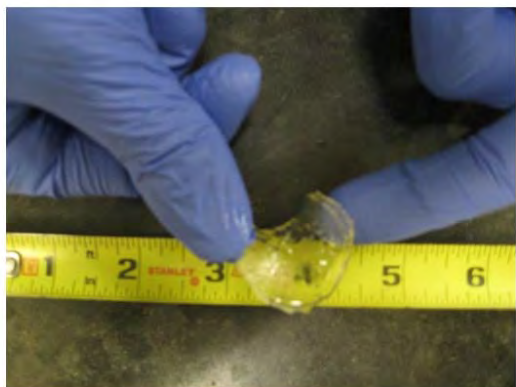
Monobrominated poly(methylmethacrylate) (PMMA-Br) can be synthesized through photoredox processes employing aromatics organic compounds as a small photocatalysts (PCs) in a metal free, organocatalyzed atom transfer radical polymerization (O-ATRP). The same photoredox process was modified and deprived of monomer to generate PMMA dimers through photocatalyzed radical trap-assisted atom transfer radical coupling (RTA-OATRC). This reaction sequence expands the scope of photocatalyzed atom transfer reactions, reducing or eliminating the usage of metals in post-polymerization sequences.



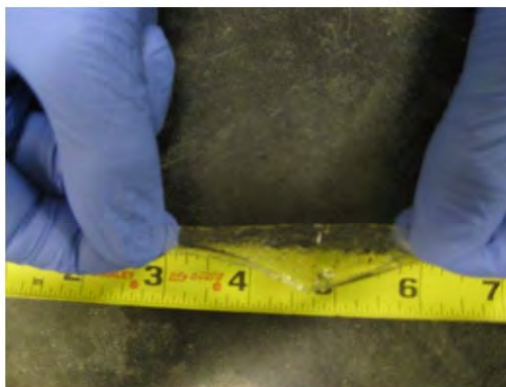
POLY 404: High-strain elastomeric networks from thiol-ene chemistry

Andrew J. Guenthner¹, andrewguenthner@gmail.com, **Jacob C. Marcischak**¹, **Timothy S. Haddad**³, **Josiah Reams**², **Michael D. Ford**⁴, **Joseph M. Mabry**¹. (1) Aerospace Systems Directorate, Air Force Research Laboratory, Lancaster, California, United States (2) ERC Inc., Lancaster, California, United States (3) Air Force Research Laboratory, ERC Incorporated, Edwards AFB, California, United States

Most thiol-ene networks exhibit limited strain to failure capability due to the use of small molecule monomers, leading to relatively high cross-link densities. In this work, we show that the use of telechelic prepolymers with a degree of polymerization around 50 and small molecule chain extender / cross-linker combinations may be utilized to produce elastomeric networks with a large molecular weight between cross-links, and consequently a strain to failure of several hundred percent. The prepolymers were made by a single-step reactive treatment of commercially available hydrogenated hydroxyl-terminal polybutadienes. The chain extenders consisted of di-functional aliphatic thiol compounds, while the cross-linker consisted of an aliphatic tetrathiol. The systems were thermally cured at 60 °C for a period of several days with the aid of a peroxide initiator. The successful creation of these networks extends the range of physical properties available to thiol-ene networks and demonstrates that these networks are feasible replacements for many types of urethane elastomers that require the use of hazardous isocyanate curatives.



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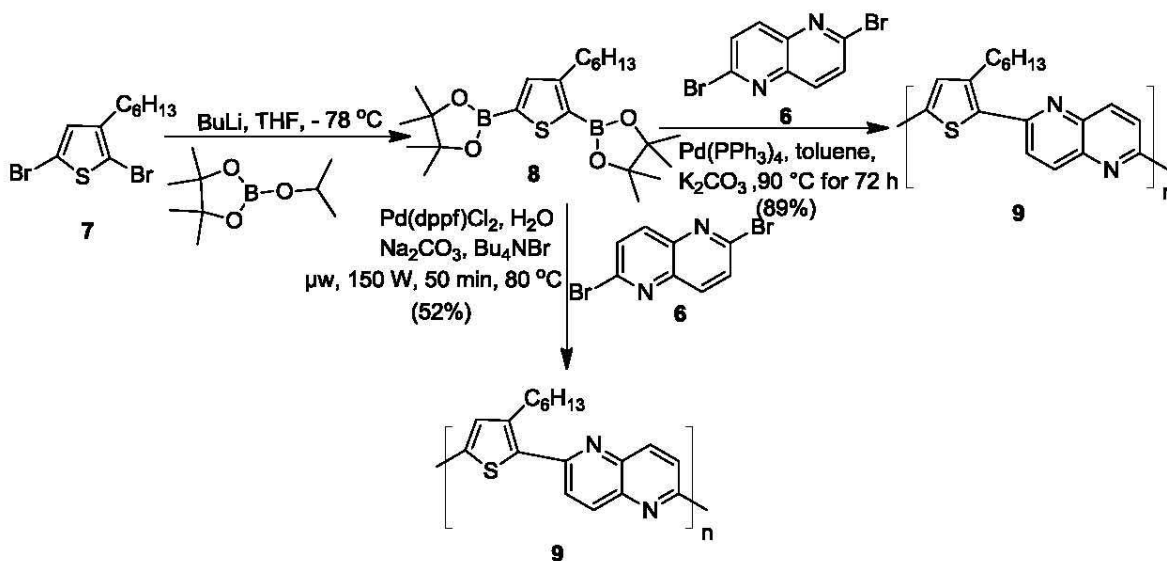


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POLY 405: Synthesis of polythiophene as a possible smart functional polymer

Mohammad N. Siddiqui, *mnaahid@kfupm.edu.sa*, Nisar Ullah, Abdurrahman Al-Betar, Abdulaziz Al-Saadi. Univ of King Fahd Petrol Min, Dhahran K S A, Saudi Arabia

Poly[1,5-naphthyridine-(3-hexylthiophene)], possible smart functional polymer, was synthesized, by both conventional as well as microwave techniques, through synthesizing a series of intermediates. FTIR analysis of spectrum shows prominent peaks of C=C and C-S bonds. Raman spectrum also have very distinct peaks for C-C, C=N and C-S bonds. The FESEM shows a uniform structure of the synthesized polymer. UV-Vis analysis was performed for the calculation optical band gap of semiconductor that was found about 2.26 eV with λ_{max} at 378 nm. TGA analysis showed that the synthesized polymer is stable until almost 200 °C and then start decomposing linearly. GPC analysis of the polymer showed the polydispersity index of 1.145 and Mw 892. The electrochemical and transport properties of the polymer were investigated both in the bulk as well as in thin film form. Cyclic voltammetry (CV) measurements of the polymer were conducted using a potentiostat coupled with an electrochemical cell. The CV results of polymer as a thin film exhibited two prominent single oxidation peaks. The aim of this work was to prepare the new quinoline based regioregular polythiophenes (RPTs) using microwave assisted synthesis via 2,6-Dibromo-1,5-naphthyridine as a key intermediate. The new semi-conducting materials will have several applications such as field-effect transistors, sensors, light-emitting diodes (LEDs), rechargeable batteries, smart cards, and non-linear optical materials.

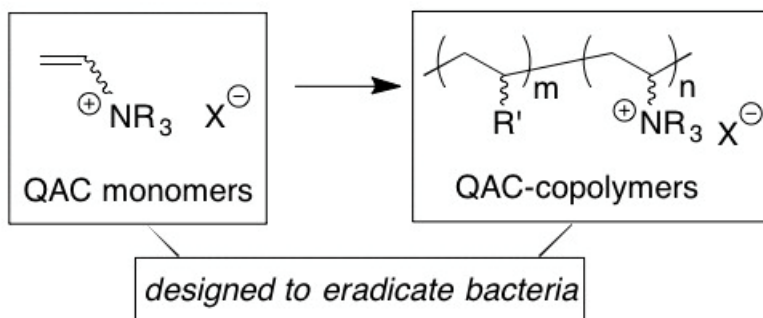


Scheme 1: Synthesis of polythiophene copolymer 9

POLY 406: Synthesis and characterization of multi-cationic quaternary ammonium containing polymers

Zachary D. Whitermore², zwhitem@villanova.edu, **Stephanie M. Duggan**², **Megan C. Jennings**⁴, **William M. Wuest**¹, **Kevin P. Minbiole**³, **Deanna L. Zubris**². (1) Chem Dept, Beury Hall 130, Temple Univ, Philadelphia, Pennsylvania, United States (2) Villanova University, Villanova, Pennsylvania, United States (3) Chemistry, Villanova University, Villanova, Pennsylvania, United States (4) Temple University, Philadelphia, Pennsylvania, United States

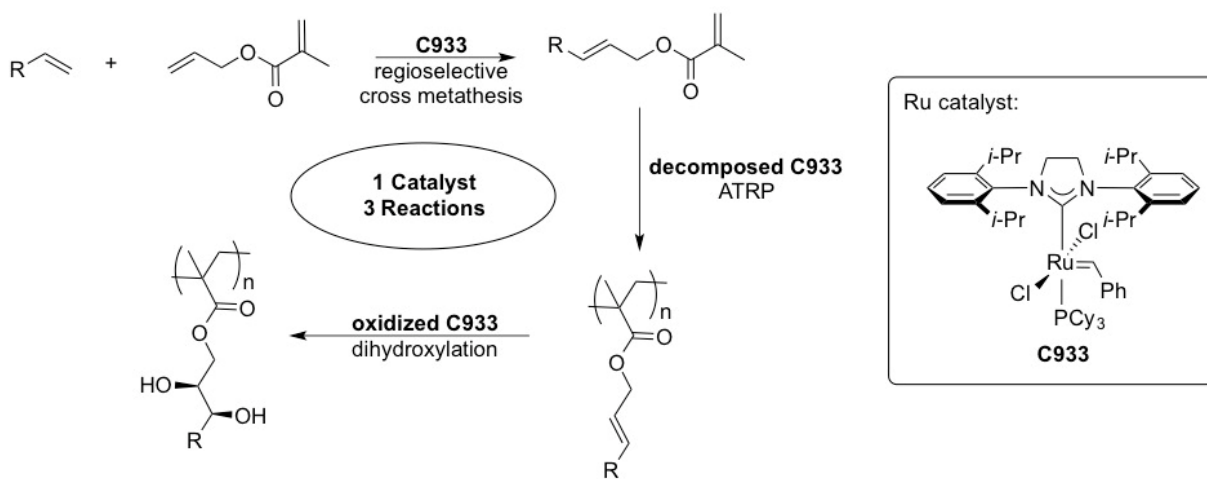
Our research team has described the synthesis of families of quaternary ammonium compounds including multiple cations (multi-QACs) for use as antimicrobial agents. The best in class for these multi-QACs can eradicate bacteria that have developed QAC resistance. Incorporation of multi-QAC functionality into monomers and corresponding polymers is a relatively unexplored area with the potential to provide antimicrobial surface coatings to inhibit biofilm formation. We have incorporated a methacrylate component into a monomer scaffold and have installed multi-QAC functionality. The incorporation of these multi-QAC containing monomers into methyl methacrylate containing copolymers will be described. Polymerization outcomes and biological activity of these materials will be discussed.



POLY 407: Polymer synthesis and post-polymerization modification by an assisted tandem cross metathesis/ATRP/dihydroxylation reaction

Shaoxiong Luo, *shaoxiongluo@caltech.edu*, Juneyoung Lee, Robert H. Grubbs.
Caltech, Pasadena, California, United States

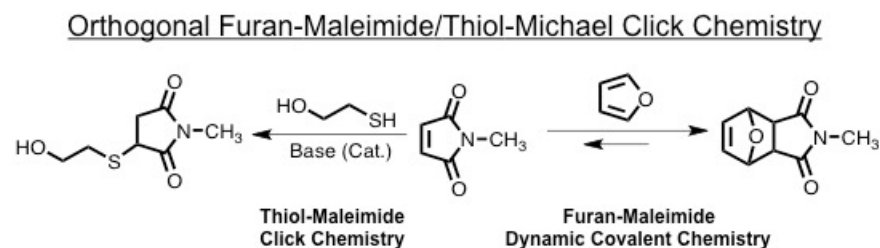
An assisted tandem cross metathesis/ATRP/dihydroxylation reaction is developed to harness the power of ruthenium metathesis catalyst to catalyze three distinct reactions sequentially, achieving the goal of constructing a polymer from simple small molecules and performing post-polymerization modification on its physical properties. The tandem process begins with a regioselective cross metathesis between a terminal olefin and allyl methacrylate (AMA), catalyzed by a modified second-generation Grubbs catalyst. After converting AMA to a methacrylate that contains internal olefin, the Grubbs catalyst is subjected to decomposition and becomes an ATRP-active catalyst. Polymer is formed in the presence of an ATRP initiator. Lastly, the catalyst is oxidized to enable the dihydroxylation reaction over the internal olefin groups on the polymer side-chains. This post-polymerization modification is expected to increase the hydrophilicity of the polymer and open up possibilities for crosslinking to access functional materials like hydrogel.



POLY 408: Computational and experimental investigations of the thiol-Michael click reaction and its applications in dendrimer synthesis

Stephen H. Frayne¹, sfrayne@wesleyan.edu, **Brian H. Northrop**². (1) Chemistry, Wesleyan University, Woodbury, Connecticut, United States (2) Department of Chemistry, Wesleyan University, Middletown, Connecticut, United States

Over the past 50 years the thiol-Michael addition reaction has become an increasingly popular tool for organic and materials scientists for synthesizing macromolecules with a high degree of control. The thiol-Michael reaction has been utilized in a myriad of applications ranging from bimolecular synthesis to surface modification to engineering adhesives and laminates to dendrimer synthesis and block polymer conjugation. Despite decades of fundamental investigations the thiol-Michael reaction remains not as well understood as is generally thought. In particular, it is unclear whether a variety of nucleophiles act as initiators or catalysts during thiol-Michael reactions. A more complete mechanistic understanding of the thiol-Michael reaction has implications in reaction efficiencies, propensity for side reactions and selectivity among reactants. We are currently studying the competing mechanisms of various nucleophiles along the thiol-Michael reaction pathway computationally and experimentally. Insight gained from a more detailed understanding of thiol-Michael reactions can be applied to more efficient macromolecule synthesis. For example, our computational efforts provide a platform from which to develop routes toward the highly efficient and selective growth of monodisperse dendrimers. Specifically, electron-poor maleimides react irreversibly with thiols in a kinetically driven 'click' reaction, and reversibly with furan in a thermodynamically driven process. The thiol-maleimide click reactions initiate dendrimer growth, and equally efficient furan-maleimide protection/deprotection reactions guarantee controlled and monodisperse growth with near quantitative yields. Combining the computationally idealized thiol-Michael conditions and orthogonal maleimide reactivity, we synthesized a new class of rationally designed dendrimers with precise control over the chemical composition of each generation, up to G4.



POLY 409: ^1H NMR study on polymer-peptide mixed micelles for adjuvant application

Oksana Zholobko¹, oksana.zholobko@ndsu.edu, Ananiy Kohut², Andriy S. Voronov¹.
(1) Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States (2) Organic Chemistry Department, Lviv Polytechnic National University, Lviv, Ukraine

AIPs were recently synthesized from either poly(ethylene glycol) (PEG) and aliphatic dicarboxylic acids or PEG and polytetrahydrofuran (PTHF). Macromolecules of amphiphilic polymers consisting of hydrophilic and hydrophobic constituents were shown to form micelles and to self-assemble in micellar nanostructures, changing conformation in response to changes in the polymer composition, concentration, and solvent polarity. Controlled self-assembly is targeted in our approach by having a precise number of short hydrophilic and hydrophobic fragments with a well-defined length in the amphiphilic macromolecules.

^1H NMR technique has been used for the systematic study of AIP micelles and micellar assemblies, as well as for the study of interactions between polymers and peptides. It has been shown that in an aqueous medium the macromolecules of AIPs form micellar structures with an interior consisting of the polar PEG fragments and an exterior made up of the lipophilic $-(\text{CH}_2)_n-$ moieties. Adding the peptide leads to a broadening of the signals attributed to the PEG protons indicating that the motions of the PEG fragments became limited, obviously, due to their interaction with peptide molecules. Also, a peak of protons of dodecanedioic acid moieties narrows slightly and moves upfield. It is concluded that hydrophobic fragments of the peptide are included into the hydrophobic interior of the micellar structures.

Microphase separation and further micellization of the AIP macromolecules in an aqueous solution lead to interactions between AIP and the peptide resulting in the formation of mixed micelles. The inner part of these micelles consists of the hydrophobic moieties of both AIP and the peptide whereas the hydrophilic fragments of AIP and the peptide build up a micellar exterior.

Hence, the “host–guest” interactions between peptides and self-assembled micellar nanostructures from AIPs by changing the polymer concentration and polymer/peptide ratio result in formation of stable AIP–peptide mixed micellar structures in aqueous solution. They can be considered as a potential material for localized delivery of peptides and release through a stimuli-responsive mechanism.

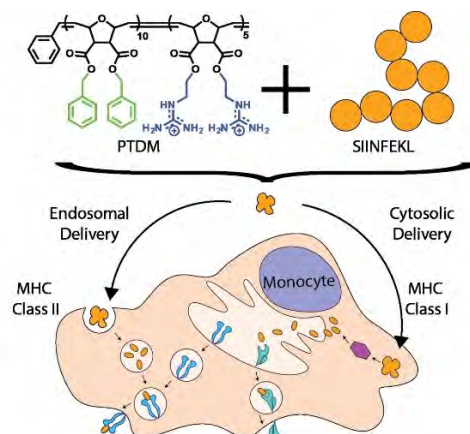


Figure. Mixed micelle formation from AIP and peptide

POLY 410: Delivering antigen to monocytes using protein transduction domain mimics

Coralie Backlund², backlund@umass.edu, Gregory N. Tew³, Thomas L. Andresen¹, Ladan Parhamifar¹. (1) DTU Nanotech, Technical University of Denmark, Lyngby, Denmark (2) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States (3) Polymer Science and Engineering, University of Massachusetts, Amherst, South Deerfield, Massachusetts, United States

Immune protection against most intracellular pathogens requires T cell stimulation by Major Histocompatibility Complex (MHC) class I molecules present on the surface of first antigen presenting cells and subsequently on the infected cells. However, because exogenous proteins do not ordinarily enter the cytosol and access the MHC class I processing pathway, protein based vaccines that induce class I restricted T cell responses have proven difficult to design. Thus, extended research has aimed at facilitating the intracellular delivery of exogenous proteins using protein transduction domains (PTDs), which allow transport bioactive molecules into cells. Synthetic polymers, inspired by PTDs, provide a well-controlled platform to vary molecular architecture for structure activity relationship studies. Here, we use ring-opening metathesis, a facile and efficient polymerization technique, through which we can vary structural parameters to optimize non-covalently encapsulated cargos such as proteins, peptides, and siRNA. In this study, we investigated the ability of these PTD mimics to deliver OVA₂₅₇₋₂₆₄ into whole blood along with their efficacy to stimulate a directed immune response toward the peptide sequence OVA₂₅₇₋₂₆₄. We have detected that over 90% of CD14⁺ monocytes in our sample take up the peptide in less than 15 minutes with nominal cytokine response and high cell viability. Further studies aim to investigate the co-delivery of agonists to promote a specific immune response against OVA₂₅₇₋₂₆₄ *in vitro*, allowing us to confirm that APCs process and present OVA₂₅₇₋₂₆₄ in association with MHC class I molecules and stimulate an antigen specific response. Understanding the efficacy of these PTD mimics provides an important foundation for future applications of PTD technology in the field of peptide-based vaccines towards intracellular pathogens and immunomodulation of cancer.

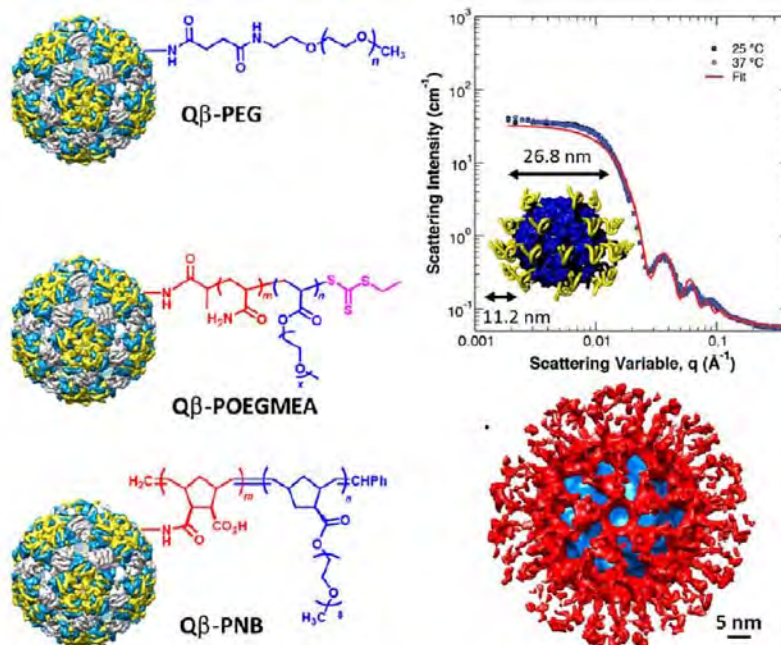


TDMs are non-covalently complexed with peptides and delivered into whole blood where they are taken up rapidly by monocytes.

POLY 411: Polymer structure and conformation alters immune recognition of viral nanoparticle-polymer conjugates

Parker Lee², *pwl19@case.edu*, **Sergey Isarov**², **Jaqueline D. Wallat**³, **Phoebe Stewart**⁴, **Nicole Steinmetz**^{5,1}, **Michael J. Hore**², **Jonathan K. Pokorski**². (1) Center for Imaging Research, Case Western Reserve University, Cleveland, Ohio, United States (2) Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, Ohio, United States (4) Pharmacology, Case Western Reserve University, Cleveland, Ohio, United States (5) Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio, United States

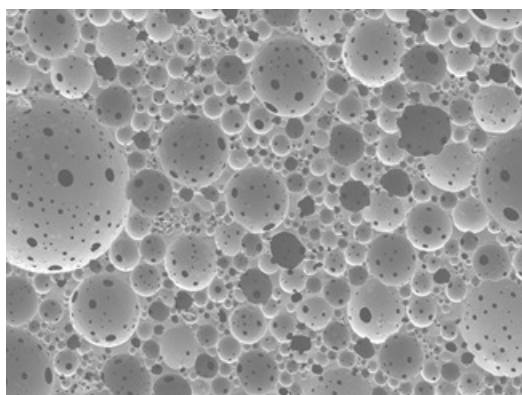
Covalent conjugation of water-soluble polymers to proteins is critical for evading the immune surveillance in the field of biopharmaceuticals. The most common and long-standing polymer modification is the attachment of polyethylene glycol (PEG), termed PEGylation, which has led to several clinically approved pharmaceuticals. Recent data indicates that brush-type polymers significantly enhance in vitro and in vivo properties. Herein, the polymer conformation of polyethylene glycol is detailed and compared to water-soluble polyacrylates and polynorbornenes when attached to icosahedral viral nanoparticles. Small-angle neutron scattering reveals vastly different polymer conformations between the multivalent conjugates. PEG shows an extended random coil conformation, exhibiting minimal interaction with the capsid. In contrast, acrylate and norbornene polymers strongly interact with the capsid, forming a raspberry like shell on the capsid surface. Cryo-electron microscopy reconstruction of polynorbornene conjugates showed that the polymer associates with the outer surface of the viral capsid and forms a heterogeneous halo extending ~15 nm from the viral surface. Finally, the immune recognition of conjugated particles was evaluated. These findings provide structural insight into the conformations of multivalent polymer conjugates and will likely impact the future design of new polymer conjugates in the pharmaceutical field.



POLY 412: Polymeric HIPE foams as multifunctional wound dressings designed for treatment of combat-related trauma

Christopher L. McGann, *christopher.mcgann.ctr@nrl.navy.mil*, Benjamin Streifel, Jeffrey Lundin, James H. Wynne. *Chemistry Division, Naval Research Laboratory, Washington, District of Columbia, United States*

The severity and lethality of combat-related trauma combined with limited access to hospital care has created a need for advanced wound-dressing materials with improved point-of-injury care. To this end, porous polymer foams, prepared via high internal phase emulsion (HIPE) templating, serve as a compelling method for the design of wound-contact materials that are highly absorptive, hemostatic and capable of delivering antimicrobial or analgesic drugs. Here, several polyHIPE chemistries are investigated including foams composed of poly(ethylene glycol)s, polyacrylates, norbornenes and chitosan. Compositions which successfully formed polyHIPE microstructure, confirmed via SEM, had their mechanical properties and absorptivity analyzed via tensile testing and swelling experiments, respectively. Initial studies into the performance of foams as wound-contact materials were conducted and include the analysis of hemostatic potential, cytotoxicity and controlled drug delivery. Polymeric foams with HIPE microstructure provide a promising path to the development of multifunctional, highly absorptive wound-dressing materials for traumatic injury.



PolyHIPE composed of PEG and polyacrylic acid.

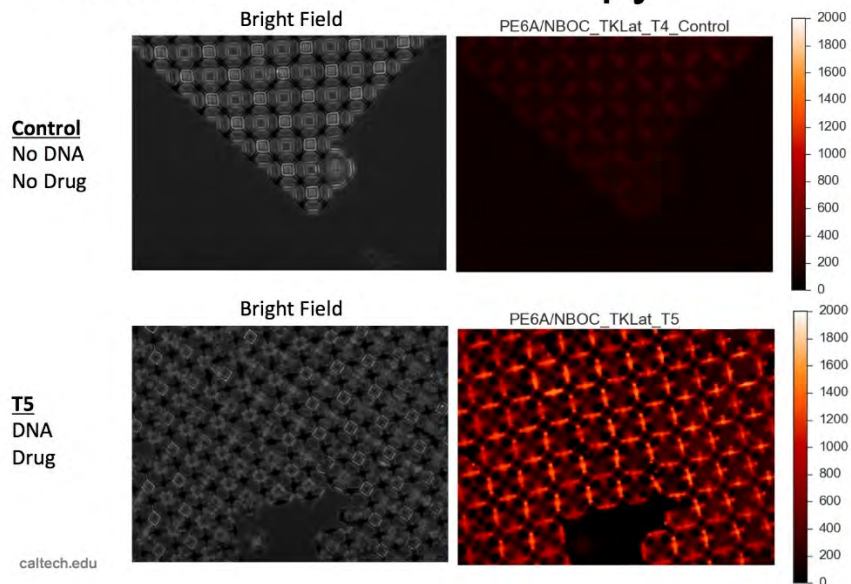
POLY 413: Genomic DNA functionalized architected materials fabricated via two-photon lithography for drug capture

Daryl Yee², daryl@caltech.edu, Michael D. Schulz⁴, Carl Blumenfeld⁴, Robert H. Grubbs^{4,1}, Julia R. Greer^{2,3}. (1) Cal Tech 164-30, Pasadena, California, United States (2) Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California, United States (3) MC 309-81, Caltech, Pasadena, California, United States (4) Chemistry and Chemical Engineering, California Institute of Technology, South Pasadena, California, United States

Two photon lithography has recently emerged as one of the most powerful tools for fabricating structures with virtually any geometry. This architectural versatility renders these 3D polymer structures useful for many technological applications, including drug delivery and tissue engineering. While significant headway has been made in understanding the physics of the two-photon process and the mechanical properties of these architected structures, making these structures have the right functional groups still remains a challenge. This is especially important if we want to utilize these structures for biomedical applications, as it is often necessary to have control over the chemical functionality on the surface and/or in the volume of these 3D materials.

In this talk, we describe a facile method of fabricating functional architected materials via the use of a functional acrylate monomer synthesized via the thiol -Michael addition. We then demonstrate the application of this by fabricating amine-functionalized structures which are then post-functionalized with genomic DNA for use as a drug capture device.

Fluorescence Microscopy



Bright field and fluorescence image of control structure and structure functionalized with genomic DNA. While both the control and functionalized structure were immersed in the drug solution, only the genomic DNA functionalized structure was able to capture the drug in question, as indicated by the significant difference in fluorescence intensity.

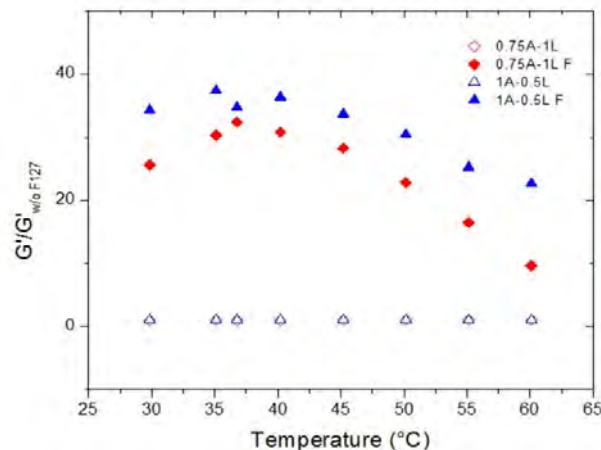
POLY 414: Rheological characterization of alginate-based hydrogels for biomedical applications

Wendy Hom, wendler@gmail.com, **Surita R. Bhatia**. Chemistry, SUNY Stony Brook, Stony Brook, New York, United States

Alginate-based hydrogels have emerged as a promising biomaterial for applications in tissue engineering because they are biocompatible, mucoadhesive, and non-immunogenic. The mechanical properties of a new type of nanocomposite gel, consisting of varying concentrations of the biopolymer alginate and the synthetic Laponite® clay, together with the temperature-sensitive copolymer, Pluronic®F127. Nanocomposite gels have been synthesized as one strategy to strengthen conventional hydrogels, which usually consist of a single polymer network. These alginate-Laponite®-Pluronic®F127 (ALP) gels were prepared using physical association and studied using rheology. The interaction between the components appear to be synergistic; that is, the resulting multicomponent hydrogels are much more elastic than the individual components. By comparison, the G' of one series of the nanocomposite gels containing F-127 Pluronic® is 85 times that of its respective control containing only alginate and Laponite®. 20-40x enhancement in G' is still observed at temperatures between 30°C and 55°C. This work shows that the nanocomposite ALP gels exhibit significantly higher storage and loss modulus (G' , G'') values than nanocomposite gels composed of only alginate and Laponite®, which encourages the synthesis of strong and 'smart' hydrogels.



Summary of Storage Modulus, G' , at Frequency = 1 Hz.



20-40x enhancement in modulus observed at temperatures between 30°C and 55°C.

POLY 415: Microcomputed tomography study of the wear behavior of porous PEEK for spine devices

David Safranski^{1,2}, david.safranski@medshape.com, Nathan Evans², Brennan Torstrick², Angela Lin², Ken Gall³, Robert E. Guldberg². (1) Vertera, Inc., Atlanta, Georgia, United States (2) Georgia Institute of Technology, Atlanta, Georgia, United States (3) Duke University, Durham, North Carolina, United States

Polyetheretherketone (PEEK) is widely used in medical implants because of its high strength, radiolucency, and favorable cytocompatibility. However, it is often linked to fibrous tissue formation instead of osseointegration. In order to overcome this limitation, porous polymers enable bone ingrowth, but inherently lack mechanical properties necessary for orthopaedic applications. Herein, we describe the wear behavior of porous PEEK and a porous PEEK spine device under multiple loading scenarios. Porous PEEK (pPEEK) was made by extruding Zeniva® PEEK (Solvay) through the spacing of NaCl crystals, followed by leaching. The resulting porous architecture is 60-70% porous with a pore size of approximately 350 μm . The abrasion resistance of pPEEK was characterized according to ASTM-F1978 to determine mass loss. pPEEK devices were impacted with a 1lb falling weight between two rigid polyurethane foam blocks, which represent vertebral bodies. The foam blocks were loaded in a custom fixture with an attached pneumatic cylinder at a preload of 200 N. μCT was used to quantify changes in the porosity, pore depth, and pore size of the structure before and after each test method. The measured mass loss after abrasion was $39 \pm 18 \text{mg}$ for the injection molded control and $27.6 \pm 12.3 \text{mg}$ for the pPEEK samples. Comparing the 3D pore structure before and after abrasion revealed a slight densification of the pore network and flattening of the top pore architecture. No change in porosity or pore depth was found between abraded and nonabraded pPEEK samples. μCT showed no significant difference before and after impaction for porosity volume fraction or porous depth. There was a significant difference in pore size (242 ± 3 vs $233 \pm 4 \mu\text{m}$), representing a 3.7% change. These results show that porous PEEK can withstand physiologically and clinically relevant loading conditions and still retain their porous architecture for bone ingrowth.

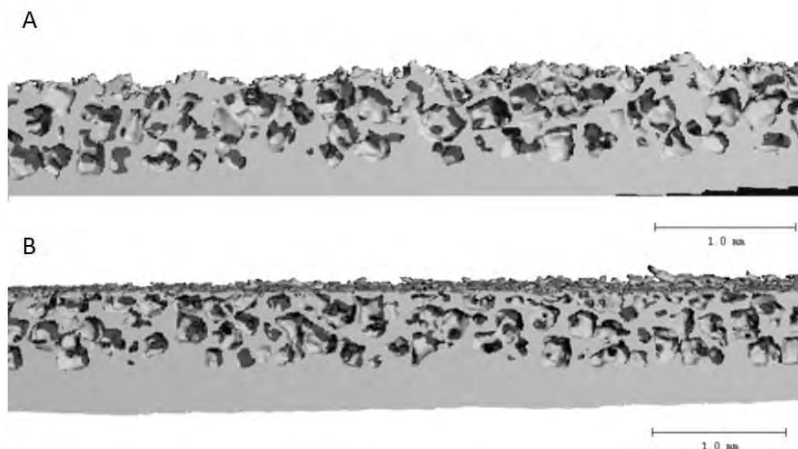


Figure 1. Representative μCT reconstructions of surfaces before and after abrasion. (A) Cross-section pre-abrasion. (B) Cross-section post-abrasion.

POLY 416: Adhesion-enhancing primer for high-performance bone adhesive

Viktor Granskog, vikgra@kth.se, Sandra García-Gallego, Yuning Zhang, Michael Malkoch. KTH Royal Institute of Technology, Stockholm, Sweden

The field of materials for osteosynthesis has evolved and innovative solutions have gained significant traction. Among these, bioresorbable fixators have matured and are taking market shares from conventional metal products. To continue the development of materials for bone repair, a natural step is to advance into the use of bone adhesives. Regardless of the desire from orthopedic surgeons to utilize adhesives, a clearly stated bone adhesive has not yet been presented in the same way as for the related field of dental restorations, where resin-based adhesives have been used with success for many years now. Adhesives could be used both as complementary fixation for multi-fragmented fractures or in non-load bearing reduction of fractures, holding the bone in place throughout the healing process. Many attempts have been made to produce bone adhesives with suitable performance, but the lack of high bond strength, biocompatibility or a viable fixation procedure have prevented further usage than of current use of bone cements. One promising adhesive methodology is the concept of the fiber reinforced adhesive patch (FRAP). FRAP consists of an adhesive system that is applied over the fracture and is reinforced with sheets of fibers to build up a fixating bridge to hold the bone pieces together without entering the cross-section of the fracture. However, the bond strength of FRAP to wet bone has been too low for it to be used in a realistic osteosynthesis setting. The use of adhesion-enhancing primers displayed promising increases in bond strength, which led us on the path of developing tailored primer solutions for the FRAP system.

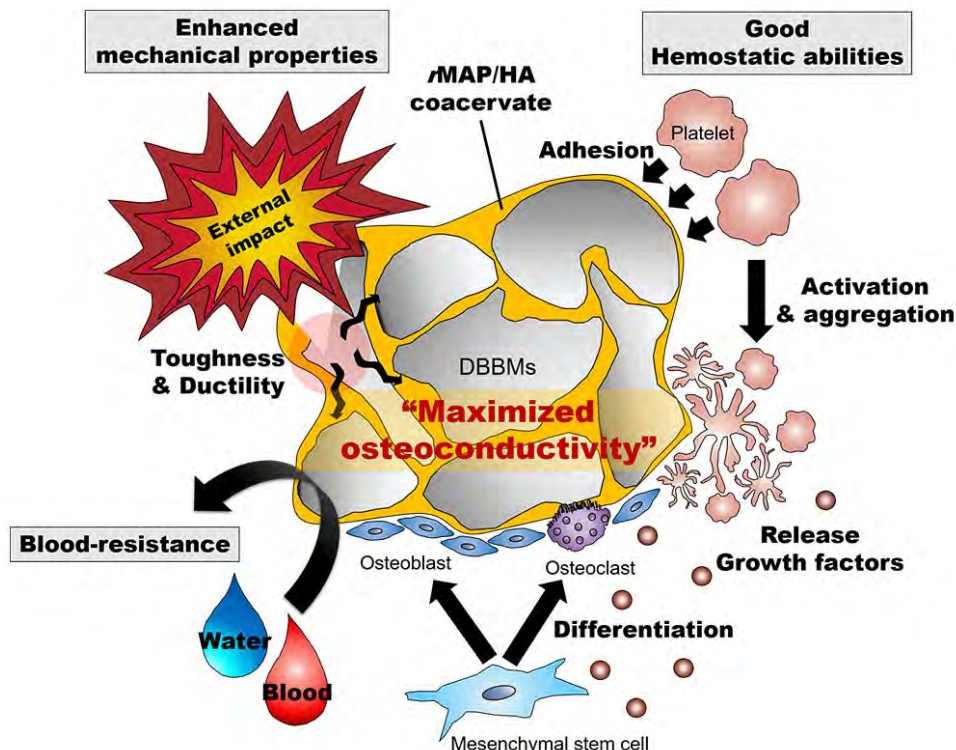
Here, we present a high-performance dual-functional primer concept that significantly enhance the adhesion to wet bone and make FRAP reach exceptional bond strength. The adhesive system relies on a light-initiated curing that immediately leads to high bond strength. In vitro results display good biocompatibility of the used constituents and the cured adhesive system did not dispense toxic leach-outs. This new primer solution opens the door to utilizing the FRAP concept in fracture repair.



POLY 417: Sandcastle worm-inspired blood-resistant bone graft binder using a sticky mussel protein for augmented *in vivo* bone regeneration

Hyo Jeong Kim², khjkye@postech.ac.kr, **Bong-Hyuk Choi**¹, **Hyung J. Cha**³, **Sang Ho Jun**⁴. (1) POSTECH, Pohang Kyungbuk, Korea (the Republic of) (2) Chemical Engineering, POSTECH, Pohang Gyeongbuk, Korea (the Republic of) (3) Chem Eng, Pohang University Sci and Tech, Pohang Gyeongbuk, Korea (the Republic of) (4) Dentistry, Division of Oral and Maxillofacial Surgery, Seoul, Korea (the Republic of)

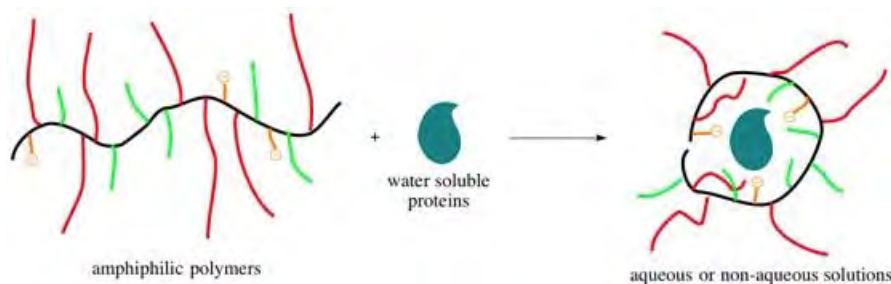
Xenogenic bone substitutes are commonly used during orthopedic reconstructive procedures to assist bone regeneration. However, huge amounts of blood accompanied with massive bone loss usually increase the difficulty of placing the xenograft into the bony defect. Additionally, the lack of an organic matrix leads to a decrease in the mechanical strength of the bone-grafted site. For effective bone grafting, this study aims at developing a mussel adhesion-employed bone graft binder with great blood-resistance and enhanced mechanical properties. The distinguishing water (or blood) resistance of the binder originates from sandcastle worm-inspired complex coacervation using negatively charged hyaluronic acid (HA) and a positively charged recombinant mussel adhesive protein (rMAP) containing tyrosine residues. The rMAP/HA coacervate stabilizes the agglomerated bone graft in the presence of blood. Moreover, the rMAP/HA composite binder enhances the mechanical and hemostatic properties of the bone graft agglomerate. These outstanding features improve the osteoconductivity of the agglomerate and subsequently, promote *in vivo* bone regeneration. Thus, the blood-resistant coacervated mussel protein glue is a promising binding material for effective bone grafting and can be successfully expanded to general bone tissue engineering.



POLY 418: Protein stabilization via Poly(Ethylene Glycol)-based (PEG) amphiphilic nanomicelles

Yu-Ling Lien, lienyu@chemistry.msu.edu, Milton R. Smith. Department of Chemistry, Michigan State University, East Lansing, Michigan, United States

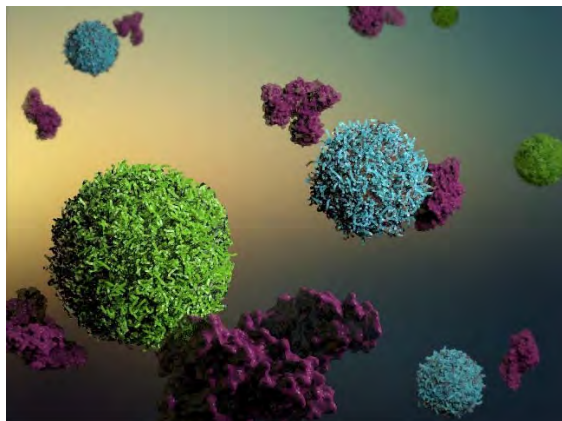
Enhancing protein stability is a significant challenge for many applications, ranging from protein therapeutics to *in vitro* enzymatic catalysis in aqueous and non-aqueous environments. Polymeric micelles have been used as a strategy for protein stabilization. In this regard, polyethylene glycol (PEG) functionalized polymers have been frequently employed in their design, owing to PEG's biocompatibility, water-solubility, and chemically robust nature. We have designed propargyl-substituted polymers as synthons for post-polymerization modification using Cu-catalyzed, "click" reactions of organic azides with the alkynes on the polymer to tailor the properties of the modified polymers. When hydrophobic and hydrophilic azides are combined in the click reaction, the amphiphilic polymers that result exist as unimolecular species over a range of concentrations. Their hydrodynamic radii vary according to the lengths of the backbone and side-chains, and some polymer properties are reminiscent of traditional micelles. This work will demonstrate the use of a series of "click" modified amphiphilic nanomicelles in stabilizing proteins in both aqueous and non-aqueous environments.



POLY 419: Brushed polymers as promising grafting agents against protein binding

Bo Wang¹, bwang4@g.clemson.edu, Thomas Blir², Aleksandr Käkinen², Xinwei Ge¹, Emily H. Pilkington², John Quinn², Michael Whittaker², Thomas Davis², Pu Chun Ke², Feng Ding¹. (1) Physics and Astronomy, Clemson University, Clemson, South Carolina, United States (2) Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria, Australia

The grafting of linear polyethylene glycol (PEG) is a common strategy in ascribing the stealth effect to nanostructure against protein adsorption for biomedical applications. However, PEG is not biodegradable and may still evoke side effects *in vivo* that compromises the circulation and efficacy of PEGylated drugs or nanocarrier. Recently, we demonstrated the synthesis of brushed phosphorylcholine (PC) as biomimetic alternative to linear PEG for the grafting of superparamagnetic iron oxide nanoparticles (IONP). Compared to brushed PEG (bPEG), brushed PC (bPC) rendered even better suspendability, stability, biocompatibility and cellular distribution. To further examine the structures of bPEG and bPC and directly test their antifouling properties against proteins, discrete molecular dynamics (DMD) simulations were performed. We found that brushed polymers were more rigid than the linear PEG while bPEG and bPC ligands displayed distinct globular and cylindrical morphologies. Grafting either bPEG or bPC onto IONPs led to different characteristics of the grafting layer, namely ligand coverage, height, and conformational strains both laterally and vertically. Upon mixing both bPEG and bPC onto the same IONP surface while maintaining the same grafting density, a conformational relaxation of the bPEG was observed in DMD simulations, as corroborated by fluorescence quenching of Cy5 attached to bPEGs in the experiment. Both bPEG- and bPC-grafted NPs displayed antifouling against human serum albumin (HSA), with an increased grafting density giving rise to enhanced protein avoidance. Our results suggest that, with a stronger repulsion to HSA and the capability to a higher grafting density due to its cylindrical shape, bPC is more advantage than both linear and brushed PEG for grafting NPs with minimal protein binding. These new structural and energetic insights offer a general guidance for NP synthesis and anti-fouling applications employing branched polymers.

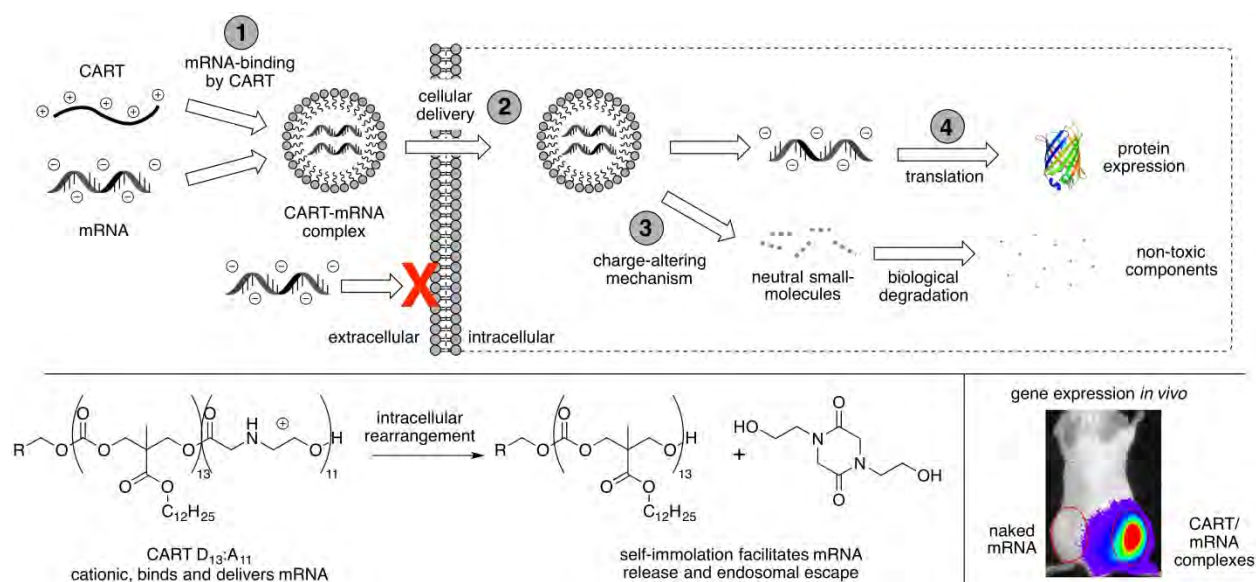


bPEG- and bPC- grafted NPs displayed nice antifouling against human serum albumin

POLY 420: Charge-Altering Releasable Transporters (CARTs) for the delivery and release of messenger RNA in living animals

Colin McKinlay¹, colinjm@stanford.edu, Jessica Vargas¹, Timothy Blake¹, Jonathan Hardy², Kanada Masamitsu², Christopher Contag^{2,3}, Paul A. Wender¹, Robert M. Waymouth¹. (1) Chemistry, Stanford University, Stanford, California, United States (2) Pediatrics, Stanford University, Stanford, California, United States (3) Microbiology and Immunology, Stanford University, Stanford, California, United States

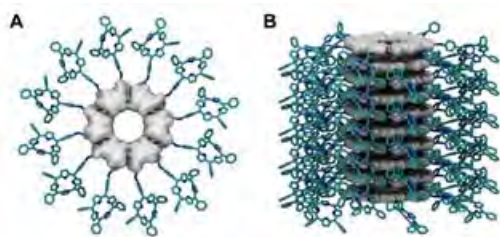
The delivery of messenger RNA (mRNA) to cells and tissues has the potential to fundamentally impact the detection and treatment of disease in areas of protein replacement therapy, vaccination, and genome editing by inducing the transient expression of exogenous proteins. However, the difficulty in delivering mRNA transcripts to cultured cells and *in vivo* targets requires new approaches to expand its clinical adoption. Here we report a new class of biodegradable delivery materials: charge-altering releasable transporters (CARTs), which are easily synthesized by the organocatalytic ring-opening polymerization of cyclic monomers. These CARTs are structurally unique and operate through an unprecedented mechanism, serving initially as oligo(α -amino ester) cations that complex, protect, and deliver mRNA, and then change physical properties through a degradative, charge-neutralizing intramolecular rearrangement, leading to intracellular release of functional mRNA and highly efficient protein translation. We demonstrate the utility of these materials for inducing mRNA expression in a wide range of cultured cell lines with >95% transfection efficiencies, and at high levels in animals through multiple routes of administration. We further show that the increased efficacy of these materials relative to non-rearranging oligomers is a direct consequence of their controlled immolation to neutral small molecules. The synthetic accessibility, and superior *in vitro* and *in vivo* efficacy of these CARTs should enable their broad adoption in numerous research and therapeutic applications.



POLY 421: Organic solar cell based on porphyrin functionalized Rosette nanotube

Ehsan Keyvani-Someh², *ehsan.keyvani@yahoo.com*, **Liang Shuai³**, **William Lee²**, **Hicham Fenniri¹**. (1) *Chemical Engineering, Northeastern University, Boston, Massachusetts, United States* (2) *Northeastern university, Boston, Massachusetts, United States* (3) *CNRL, Edmonton, Alberta, Canada*

Bio-inspired one-dimensional (1D) porphyrin arrays were obtained from the hierarchical self-assembly of DNA base analogs of guanine and cytosine nucleic acid motifs through hydrogen bonding and π - π stacking. Porphyrin-functionalized rosette nanotubes (RNTs) with lengths ranging from a few hundred nanometers to several micrometers were obtained and their tubular structure were characterized by SEM, AFM, and TEM. Narrow band gap, conductivity enhancement, and energy level alignment with common electron acceptor such as phenyl c_{61} butyric acid methyl ester (PCBM) indicate the high potential of these photo-active structures in the design of efficient organic photovoltaics (OPVs). Fluorescence study also showed a sufficient quenching of fluorescence emission of porphyrin groups in presence of PCBM. Solar cells with the architecture of ITO/PEDOT:PSS/RNT:PCBM/Ca/Al were fabricated and power conversion efficiency (PCE) of devices were measured under standard condition (1sun/1.5AM/25°C). PCE values for RNT-based OPVs was higher than unassembled porphyrin-based solar cells which is a result of nano-scale ordering. 1D arrays are boosting up the PCE by introducing order to the morphology of the photo-active layer and enhancing charge mobility. This work introduces a new strategy to build 1D structures with higher charge carrier mobility that displays unique optoelectronic properties to contribute to the repertoire of electron-donor materials in solution-processed OPVs.

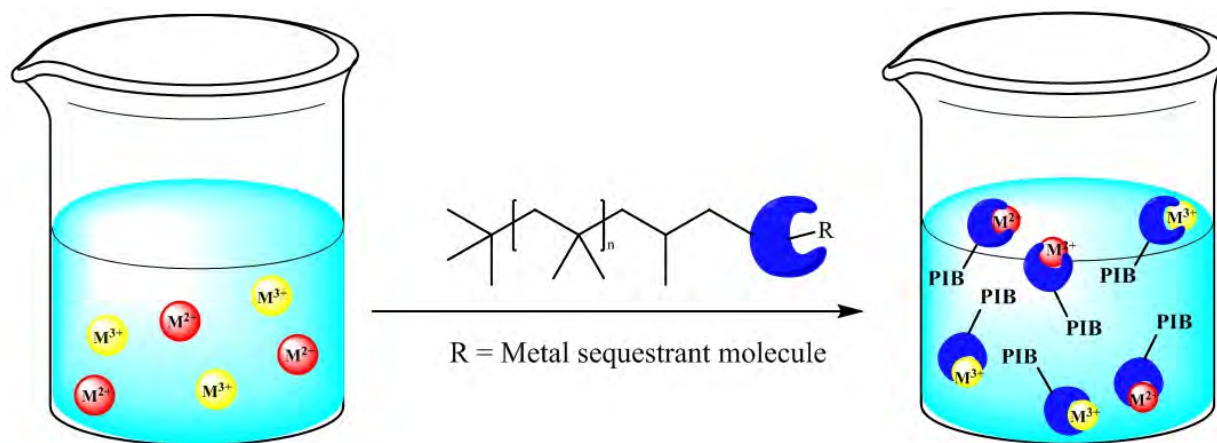


MD simulated RNT

POLY 422: Synthesis and applications of recyclable polymer-bound transition metals sequestrants

Dalila Chouikh², dalila.chouikhi@qatar.tamu.edu, **Thomas Malinski¹**, **Mohammed Al-Hashim²**, **David E. Bergbreiter¹**, **Hassan S. Bazz²**. (1) Texas A&M University, Bryan, Texas, United States (2) Science Program, Texas A&M University at Qatar, Doha, Qatar

Whether it is industry, agriculture, research experiments, or just ordinary activities, modern societies in the 21st century produce unwanted waste. In some cases, this waste is concentrated and can be easily dealt with. In other cases, such waste can be minimized, this has been demonstrated in the development of environmentally benign syntheses that have used polymer-bound metal catalysts to minimize chemical waste in homogeneous catalysis. However, waste most often cannot be completely eliminated. Even if it is minimized, unwanted by-products from industrial or agricultural endeavor or from a modern city often end up in organic or aqueous waste streams in a highly diluted form. Herein, we report the use of Polyisobutylene (PIB) as a polymeric support for metal sequestration in organic solutions. PIB is functionalized to convert its terminal C=C into metal sequestering groups (carboxylic acid, thiol or amine group). The use of a cleavable linker to regenerate the PIB-sequestrant is also studied.



POLY 423: Cross-linked films from star-shape poly(ϵ -caprolactone): Effects of branch number and chain length on elastic properties

Dr. Swapan Kumar K. Saha^{1,3}, *swapan@buft.edu.bd*, Mitsuhiro Ebara³, Takao Aoyagi^{2,3}. (1) Department of Natural Sciences, BGMEA University of Fashion & Technology, Dhaka, Bangladesh (2) Dept. of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Tokyo 101-8308, Japan (3) International Center for Materials Nanoarchitectonics, National Institute of Materials Science, Tsukuba, Ibaraki 305-0044, Japan

Among the biodegradable aliphatic polyesters, poly(ϵ -caprolactone) (PCL) has received significant attention due to their potential applications in a wide range of areas as biomedical materials and environment-friendly materials. PCL is well known to be a semi-crystalline polymer, however due to low thermal stability; new cross-linked PCL materials were developed to improve the mechanical properties. [1,2] However, the effects of branch number and chain length at each branch of the cross-linked PCL films on their elastic properties have not been investigated; in this presentation, authors will demonstrate the effects of branch number and chain length at each branch of cross-linked PCL films. Cross-linked PCL films were produced from branched PCL macromonomers with different branch numbers (2, 3 & 4) and chain lengths (20, 50 & 100 CL units) at each branch and characterized by DSC, and tensile testing. This investigation indicate that melting temperature (T_m) or softening temperature in the cross-linked materials (T_s) of each series slightly decrease with the increase of branch number. For the cross-linked PCL, the T_s decreased with the increase of branch number and the decrease of chain length at each branch. The strain-at-break increased with the increase of chain length at each branch of cross-linked materials at 25 °C. At 60 °C i.e. above the T_s , tensile strength, Young's modulus and strain-at-break of all the cross-linked films decreased significantly compare with those at 25 °C. It is interesting that strain-at-break of the films increased with the increase in chain length at each branch. The elasticity of the thermo responsive cross-linked PCL materials could be controlled by modulating the branched numbers and the chain length at each branch of the PCL macromonomer. The information obtained from the investigation would be useful for the selection, preparation, and application of cross-linked PCL materials in various applications.

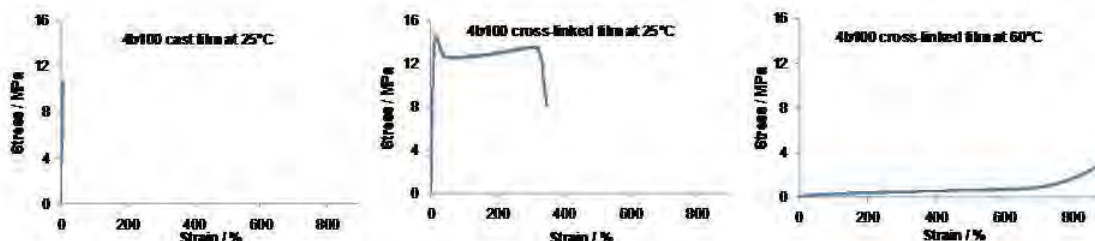
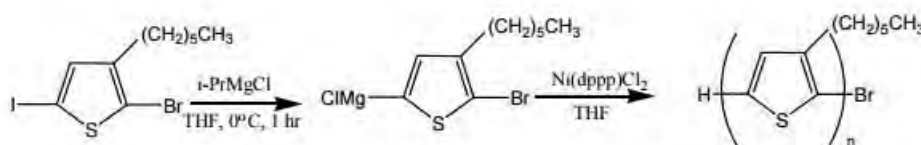


Figure: Stress-strain curve of cast 4 branch contain 100 ϵ -caprolactone unit at each branch (4b100) PCL film at 25° C (left), cross-linked PCL film from 4b100 macromonomer at 25° C (middle) and cross-linked PCL film from 4b100 macromonomer at 60° C (right)

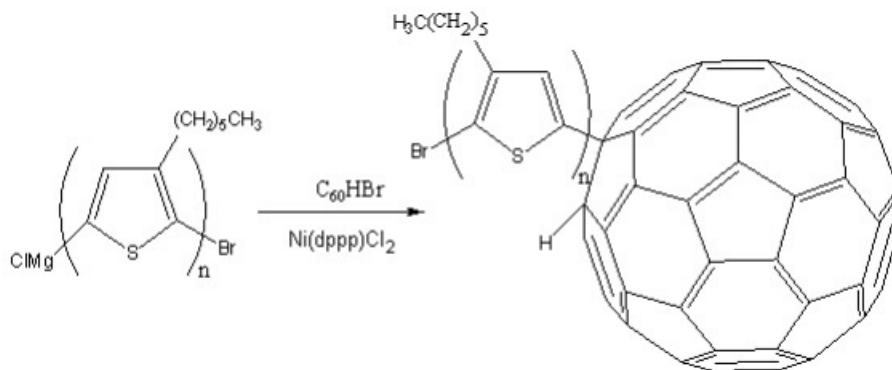
POLY 424: Effects of molecular weight on power conversion efficiency of an end-capped polythiophene

Phillip R. Pulley, *prp2p@mtmail.mtsu.edu*, **Dwight J. Patterson**, *Chemistry, Middle Tennessee State University, Chapmanboro, Tennessee, United States*

Organic solar cells have been thoroughly researched using Poly(3-hexylthiophene), P3HT, for many years due to its properties as a good electron donor. Studies have shown that molecular weight and regioregularity can be controlled via addition polymerization by varying the ratios of the catalyst to the monomer and time. Also, it has been seen that end capping polythiophene has an effect on the rate of degradation. The effect of molecular weight of polythiophene end capped with a Phenyl-C61-butyric acid methyl ester, PCBM, accepting species will be surveyed with respect to its power conversion efficiency and rate of degradation. Finally, the survey will be compared to the common P3HT/PCBM blend found in most organic solar cells.



Synthesis of P3HT

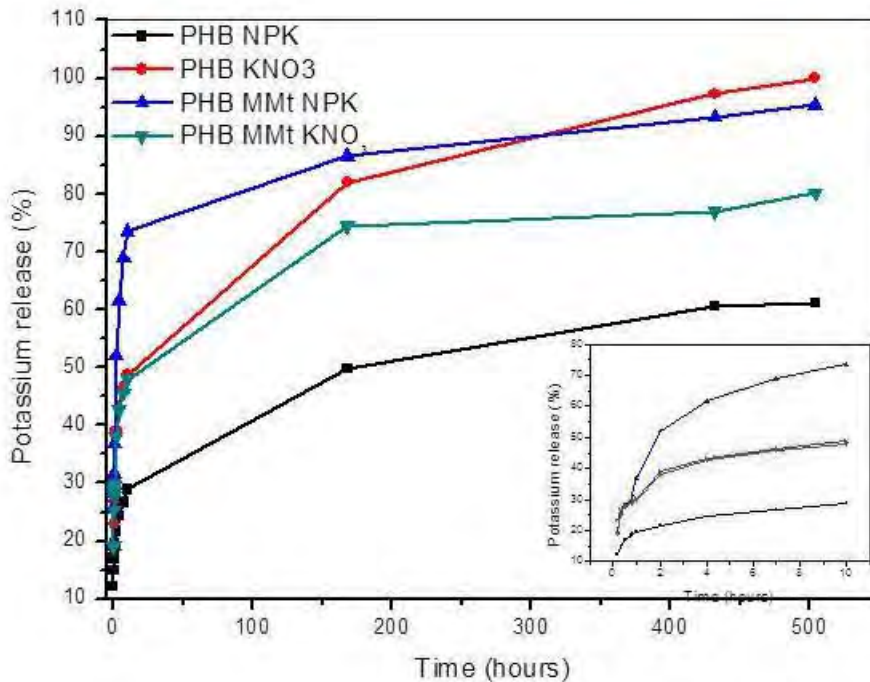


Coupling of P3HT and C₆₀ Fullerene

POLY 425: PHB and Montmorillonite Clay Composites as KNO₃ and NPK controlled release fertilizers

Josiane Souza, Adriana Campos, **Roselena Faez**, faez@cca.ufscar.br. Federal University of São Carlos, Araras, Brazil

Controlled release fertilizers (CRF) contributed for save fertilizer and reducing the environment pollution. CRF based on biodegradable polymers as poly (3-hydroxybutyrate) (PHB) and montmorillonite clay for KNO₃ and NPK fertilizers (Fert) were processed in an internal mixed chamber of a Haake torque rheometer with roller motors at 160°C, 50 rpm by 6 minutes in the ratios: PHB/Fert 90/10 and PHB/MMt/Fert 80/10/10. The composites were hot pressed at 150°C, 14 MPa for 3 minutes. The release analyses were performed in deionized water during 500 hours and the amount of potassium delivery was determined by flame photometry in 0.5 x 0.5 x 0.1 cm³ dimensions samples. A calibration curve of the fertilizers (KNO₃ and NPK) was used in order to quantify the potassium ion. The presence of MMt into PHB effects more the release profile for NPK content material. NPK impacts the interaction between MMt and PHB and two phases are observed. This behavior facilitates the diffusion of the salt from MMt phase. On the other hand, for KNO₃ content composite the PHB phase covers the clay-KNO₃ ones since the separation of the phases are not observed. The potassium release for NPK composites occurs mainly in the first hours (9 hours) while KNO₃ composites occurs in longer time.

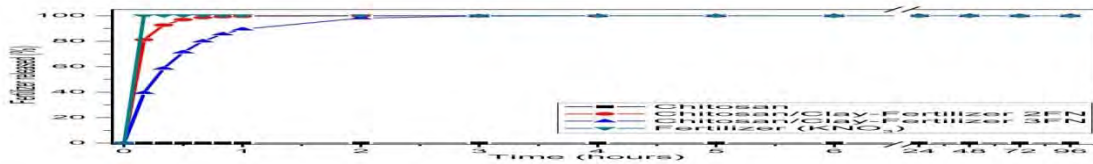


Release profile of KNO₃

POLY 426: Chitosan-montmorillonite spray dried microsphere and microcapsules for fertilizer encapsulation

Débora França^{2,1}, Ângela F. Medina¹, Claudinei F. Souza¹, **Roselena Faez¹**, faez@cca.ufscar.br. (1) Federal University of São Carlos, Araras, Brazil (2) Universidade de São Paulo, Pirassununga, São Paulo, Brazil

Slow/Controlled release fertilizer systems have been widely researched because of their advantages to agriculture, such as to release fertilizer at levels needed for plant nutrition, reduction of toxicity in soil and decrease the negative effects of overdosing. The purpose of this study was to develop a slow/controlled release material and compare their microsphere and microcapsule structure. The slow/controlled release fertilizers were based on chitosan matrix added with clay-nutrient (sodium montmorillonite and KNO_3) by spray drying technique (Mini Spray Dryer B-290-BUCHI, inlet temperature: 180°C , aspirator: 100%). Two-fluid (flowrate: 9ml/min) and three-fluid nozzle (inner flowrate: 0.5ml/min, outer flowrate: 5ml/min) were used to attain microsphere and microcapsule (core-shell) structure, respectively. The materials were characterized and compared by their structure (FTIR), morphology (SEM), thermal properties (TGA) and fertilizer release profile. The two- and three-fluid nozzles have formed different structure since three-fluid nozzle provided a delayed release of nutrients compared to sample from two-fluid nozzle. This can be attributed to additional layer of chitosan and the presence of fertilizer in the core structure, that may serve to trap the nutrient in order to its release be slower and dependent on water content. Core-shell structure may be interesting to produce materials for controlled release fertilizer.

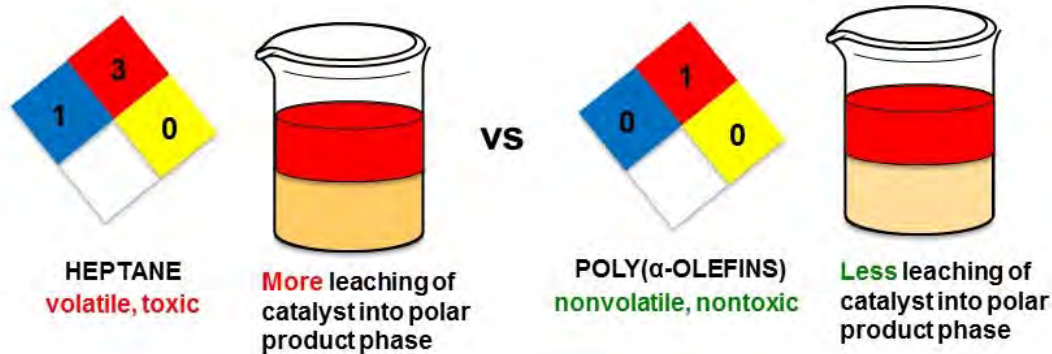


Nutrient release profile curve

POLY 427: Nontoxic and nonvolatile alternatives for hexane and heptane and their use in catalysis

Mary L. Harrell, *mary.layne.harrell@gmail.com*, Thomas Malinski, Coralys Torres-Lopez, Kimberly Gonzalez, David E. Bergbreiter. Chemistry, Texas A&M University, College Station, Texas, United States

The Bergbreiter group has focused for the last few years on the development of sustainable nonpolar polymer-supported catalysts that can be recycled by using thermomorphic solvent systems. These thermomorphic solvent systems are comprised of two solvents which are immiscible at room temperature but upon heating form a single phase. After cooling to ambient temperature, the catalyst can be isolated in a separate phase than the product. Recent work has shown that using nonpolar polymer solvents such as polyethylene or polyalphaolefins (PAOs) with polymer-supported azo dyes can reduce leaching of these polymer-supported azo dyes into a polar phase in comparison with traditionally used alkane solvents such as heptane. Since these dyes are surrogates of homogeneous catalysts, these “anti-leaching” solvents should be useful in catalytic reactions involving nonpolar phase selective Brønsted acid catalysts used to perform asymmetric catalysis. This work will involve the synthesis of such catalysts as well as their potential uses in catalytic reactions involving thermomorphic solvent systems.



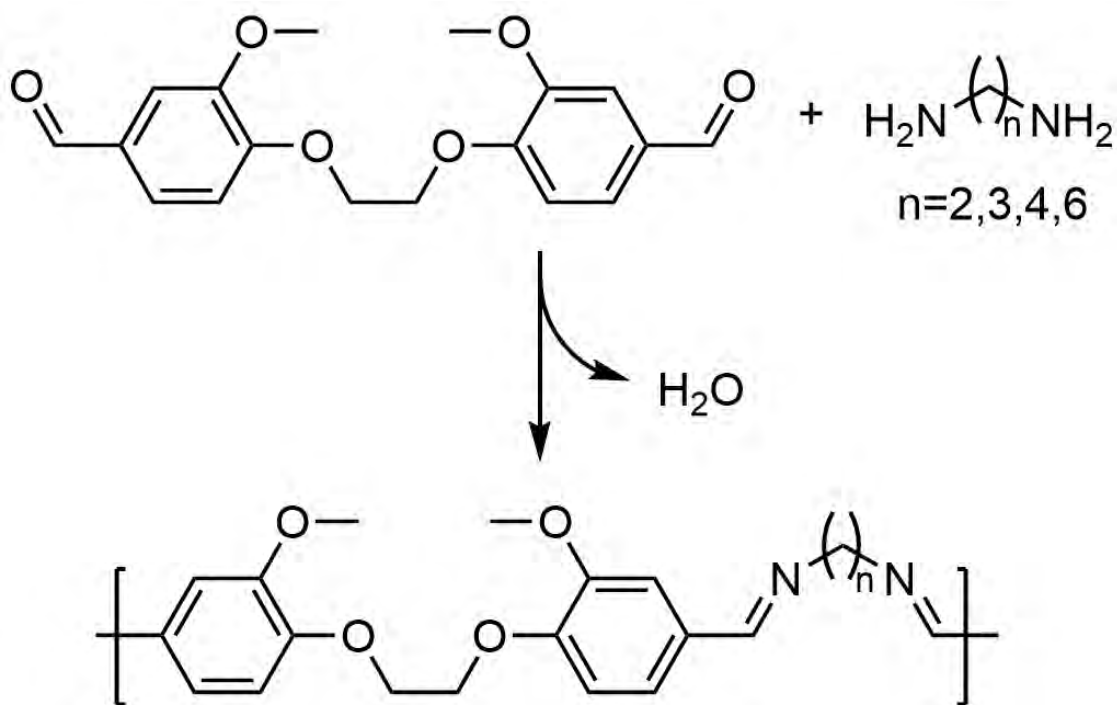
POLY 428: Sustainable polyaldimines from lignin-derived aromatic aldehydes and aliphatic diamines

Mayra Rostagno, *mayrus61@hotmail.com*, Stephen A. Miller. Department of Chemistry, University of Florida, Gainesville, Florida, United States

The current ocean trash crisis, added to non-guaranteed availability of oil and natural gas in the future, denotes the need for alternatives to current commodity plastics. The design of novel polymers should include the utilization of renewable resources for monomer preparation, as well as the installation of chemically cleavable groups to guarantee their degradation.

We have chosen polyaldimines as suitable polymer systems to fulfill those premises. The aldimine functionality is present in nature, and comes from the reaction of an aldehyde and an amine, releasing a molecule of water. We utilized aromatic aldehydes that can be obtained from the pyrolysis of lignin, of which vanillin is the best example. Aldehydes were linked via ethylene to yield dialdehydes, and then combined with commercially available diamines. The diamines were aliphatic with 2-6 methylene spacers. Although these diamines are not currently sustainable, they could be prepared from renewable α - ω diols and ammonia.

Obtained polymers had adequate thermal properties to compete with commodity plastics, with T_g ranging from 58 to 165 °C, and some of the samples were crystalline with T_m ranging from 143 to 297 °C. Preliminary degradation studies showed polymers start hydrolyzing immediately after exposure to acidic buffers in heterogeneous conditions.



POLY 429: High performance waterborne exterior coatings with improved durability, eco-footprint and cost through the use of self-assembled polymer pigment composites

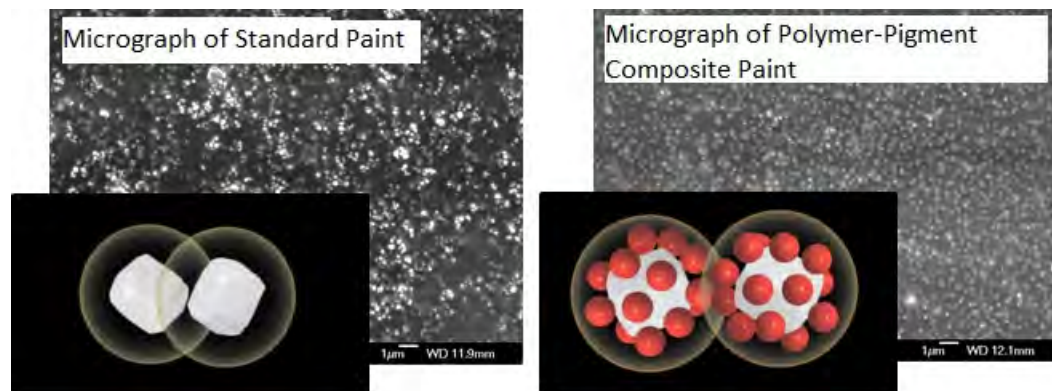
James Bohling, jbohling@dow.com, Pu Luo, Joseph Tanzer, Alvin M. Maurice, Meghan Koback, Matthew Belowich, Cory Valente, Wei Gao, John Reffner. The Dow Chemical Company, Lansdale, Pennsylvania, United States

Many important performance attributes of a coating film can be impacted by the dispersion quality of pigments and their interactions with polymeric binders. Improved pigment dispersion quality has been found to minimize photo degradation on latex paint films, which not only extends paint service life, but also can contribute to optimizing paint formulation costs.

Adsorbing latex technology facilitates the controlled formation of self-assembled polymer-pigment composites, which in turn, creates more ordered paint films. These smarter materials, with improved pigment efficiencies, are a step-change improvement of dispersion quality over conventional paint binders. The impact on eco-footprint has been validated by 3rd party validated life cycle assessment.

Poster topics will include: 1) Key factors facilitating the formation of stable polymer-pigment composites, 2) their impact on performance, as studied through analytical science, polymer chemistry, applications testing and 3) the mechanism and measurement of coatings degradation.

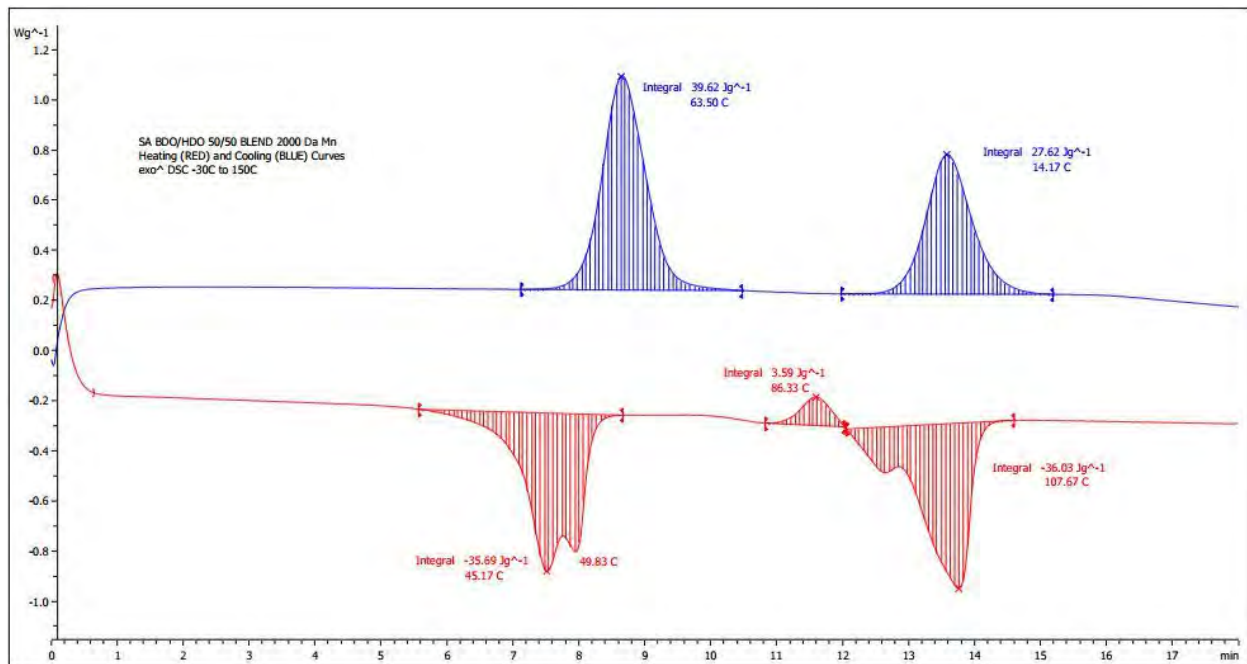
Considered both a commercial and technical success, this technology continues to enjoy broad market adoption and has been awarded the prestigious Presidential Green Chemistry Challenge Award by the United States Environmental Protection Agency.



POLY 430: Succinate polyester polyol copolymers and blends: Synthesis, compatibility, crystallization kinetics, and crystal morphologies

Heather S. Hamilton¹, hsc2@students.uwf.edu, **Amanda A. Seba**³, as139@students.uwf.edu, **Jacqueline E. Blue**⁴, jb129@students.uwf.edu, **William D. Coggio**², **Alan Schrock**¹. (1) Chemistry, University of West Florida, Pensacola, Florida, United States (2) BioAmber, Hudson, Minnesota, United States

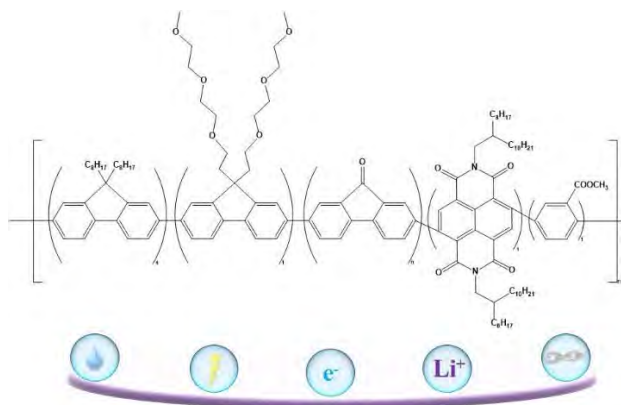
Succinic acid is a sustainable raw material growing in use for 2000 Da polyester polyols, although there is a lack of fundamental information about the compatibility and crystallization behavior in polyol blends and copolymers. To explore these issues, DSC characterization, crystallization kinetics, thermodynamics, and powder x-ray diffraction studies were performed on succinic acid-based polyols made with 1,4-butanediol, 1,6-hexanediol, their blends, and on copolyester polyols made at 20%, 50%, and 80% molar ratios of the diols. The polyol blends show incompatibility with separate crystallization dynamics from butanediol and hexanediol polyesters in the blends. The copolyester polyols show compatibility and new crystal morphologies. We will report the synthesis, Johnson-Mehl-Avrami-Kolmogorov crystallization kinetics, powder diffraction results, and thermodynamics for the crystallization processes of the polyol blends and copolymers.



POLY 431: Novel conjugated polymer binders and their processing for Si-based Li-ion battery anodes

Andrea L. Miranda¹, alm9@rice.edu, Xiaoyi Li⁵, Hyosung An⁴, Jodie L. Lutkenhaus³, Rafael Verduzco². (1) Chemistry, Rice University, Houston, Texas, United States (2) Dept of Chemical and Biomolecular Eng, Rice University, Houston, Texas, United States (3) Texas AM University, College Station, Texas, United States (4) Chemical Engineering, Texas AM University, College Station, Texas, United States (5) Chemical and Biomolecular Engineering, Rice University, Houston, Texas, United States

Li-ion batteries are used in countless portable electronics and are making their way to larger scale technologies like electric vehicles. To keep up with demand for a higher energy density battery, novel materials are being researched to optimize Li-ion battery performance. However, one often neglected component of Li-ion batteries, the polymer binder used in the electrodes, may hold the key to improved performance. Traditionally the role of the polymer binder has been limited to holding together the two other components of an electrode, the active material and conductive additive. But if beneficial electrical and mechanical properties can be combined into a multi-functional polymer binder, it is possible that the amount of conductive additive can be reduced or removed altogether, increasing the overall energy density of the electrode. In this work, we synthesize a series of conjugated polymer-based binder materials for silicon anodes. The polymers are synthesized through Suzuki-Miyaura polycondensation of a monomer mixture, and a variety of monomers are chosen to impart a specific functionality. Fluorene with di-octyl side-chains improve solubility and processibility, fluorene with oligo(ethylene glycol) side chains improve elasticity and electrolyte uptake, naphthalene diimide units provide redox activity, and methyl benzoate phenyl esters react with lithium to impart conductivity. We process electrodes through flow coating and compare their morphology, performance, mechanical properties, and electrochemical properties to electrodes fabricated with a PEDOT:PSS binder. Our work to date shows that the conductivity of the binder and battery performance is strongly dependent on doping and processing history. Current work is focused on systematic studies of battery performance with varying binder conductivity and investigation of electrode mechanical properties.

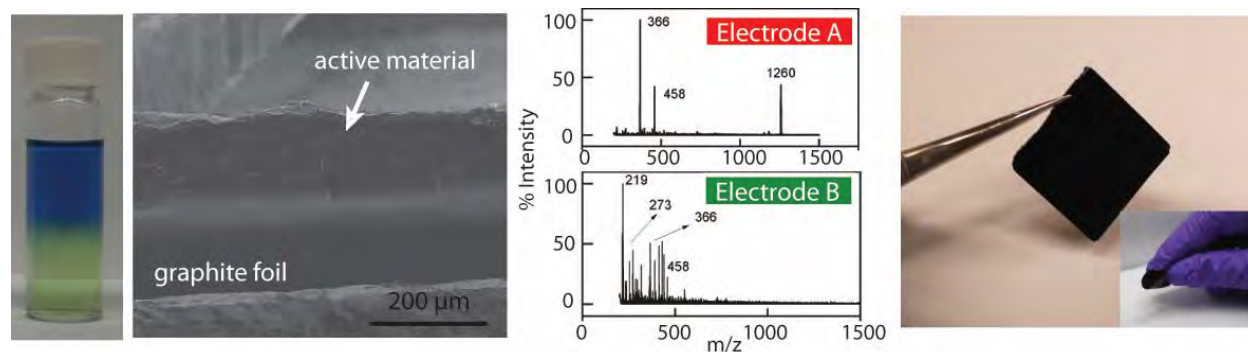


A variety of monomers are incorporated into a multi-functional polymer binder to enhance processibility, elasticity, electrolyte uptake, redox activity, and mechanical integrity of Si anodes for use in Li-ion batteries.

POLY 432: Aniline oligomers and polyaniline: Supercapacitors and freestanding films

Cheng-Wei Lin², chengweilin@g.ucla.edu, Rebecca L², Richard B. Kaner¹. (1) Dept of Chem Biochem, Box 951569, Univ of California, Los Angeles, California, United States (2) Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States

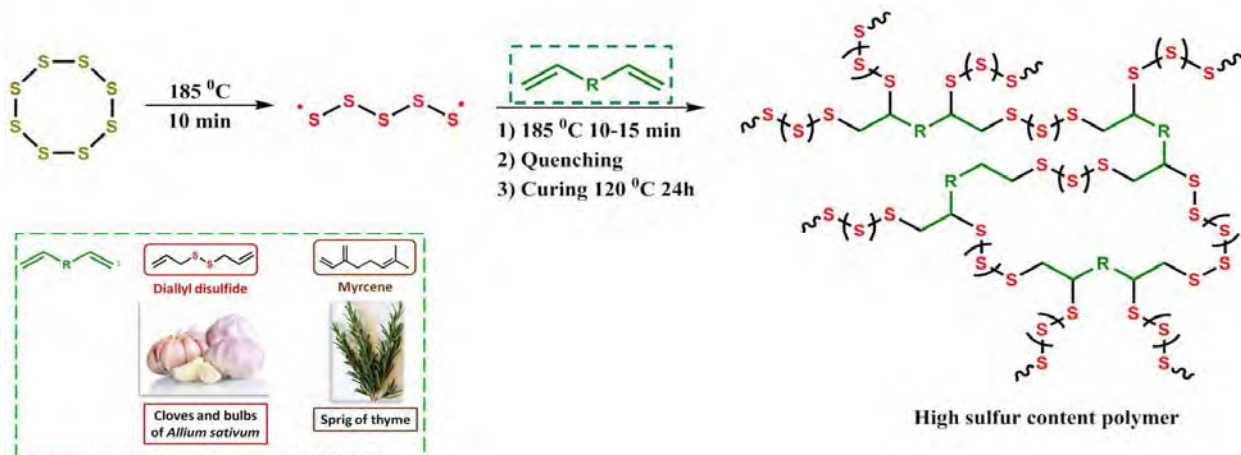
Aniline oligomers possess almost identical physical and chemical properties as the conducting polyaniline. Without the polymer natures and defined chain lengths, the initial order of doping is first examined by the aniline tetramer, providing insight into the doping chemistry under the condition of an insufficient amount of dopants. The electropolymerization of the aniline tetramer upon oxidative and reductive cycling under different potential windows is also studied by using direct mass spectrometry analysis. The cyclic voltammetry tests result in slightly polymerization and chain scission for the two electrodes, respectively. The results reach implications for energy storage devices, especially for designing future supercapacitors when using the conducting polymer family. Polyaniline, on the other hand, has many doping sites each string and forms robust freestanding films due to entanglements. The mechanical properties of the films doped with different dopants are reported. The results state how ions affect the strength of the films, and the idea might expand to other conducting polymers and composite materials.



POLY 433: Exploring inverse vulcanization of sulfur with natural source monomers as cathodic materials for long life lithium sulfur batteries

Iñaki Gomez¹, inaki.gomez@polymat.eu, Olatz Leonet³, Alberto Blazquez³, David Mecerreyes². (1) POLYMAT, Donostia - San Sebastian, Spain (2) POLYMAT, University of the Basque Country, Donostia-San Sebastian, Gipuzkoa, Spain (3) IK4-Cidetec, Donostia - San Sebastian, Spain

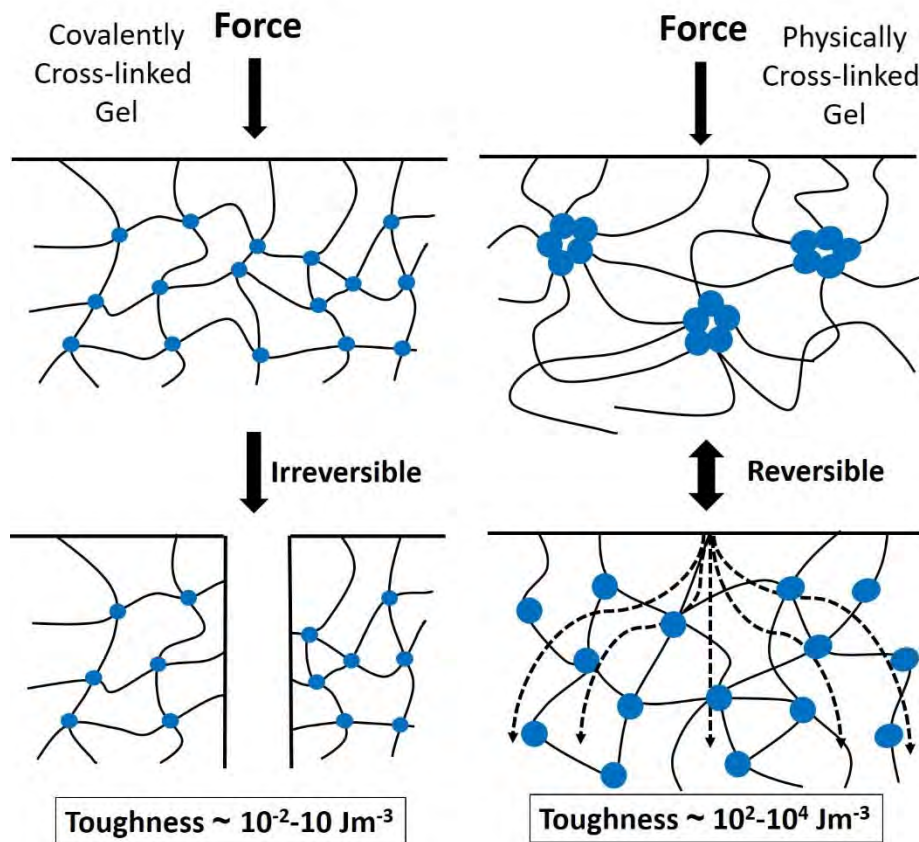
Lithium sulfur batteries are among the most promising next generation battery systems due to the high capacity properties of sulfur as cathodic material. Beyond its interesting intrinsic properties, sulfur possesses a very low conductivity and complex electrochemistry which involves the high solubility of the lithium sulfides in the electrolyte. These two characteristics trigger a series of limitations on its performance as active cathode material which leads to batteries with low cyclability. Recently, inverse vulcanized sulfur has shown to retain capacity far better than elemental sulfur leading to batteries with excellent cyclability. Nevertheless the diene comonomers used so far in the inverse vulcanization process are synthetic sourced molecules. Herein a tentative work on exploring inverse vulcanization with two natural sourced monomers, diallyl sulfide and myrcene is presented. The inverse vulcanization of sulfur was successfully completed and the resulting polymers were characterized by FTIR, NMR, DSC and TGA. Afterwards these polymers were tested as cathodic materials in lithium-sulfur cells. The sulfur-natural dienes materials exhibited high capacity at different C-rates and high lifetime over 200 cycles with very high capacity retention at a moderate C-rate of C/5. Altogether, these materials made by cheap and abundant chemicals are an excellent option of sustainable materials for electrochemical energy storage.



POLY 434: Synthesis and properties of physically cross-linked hydrogel obtained from amphiphilic copolymer

DIBYENDU DEBNATH¹, *dd68@zips.uakron.edu*, Robert A. Weiss², Coleen R. Pugh¹.
(1) Department of Polymer Science, The University of Akron, Akron, Ohio, United States
(2) Polymer Engineering, University of Akron, Akron, Ohio, United States

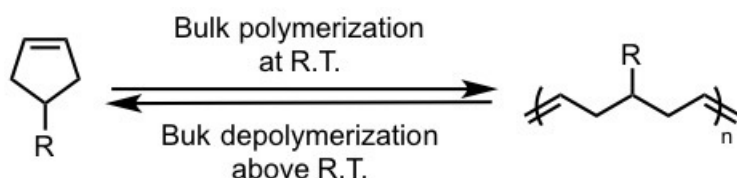
Covalently cross-linked gels typically have a low toughness because of inefficient energy dissipation. Increasing the amount of covalent crosslinks improves the stiffness of the gel but makes it brittle. Gels that are physically crosslinked are comparatively tougher due to better viscoelastic energy dissipation produced by non-covalent,¹ polar,² and ionic interactions³. In addition, they are processable and can be molded into desired shapes, unlike covalently cross-linked gels. We achieved hydrophobically modified hydrogels (HPMHs), in which the hydrophobic groups act as physical crosslinking sites. These HPMHs show a dramatic increase in the storage modulus (G') and the loss modulus (G'') compared to conventional physical hydrogels. The strength of HPMHs increases with increasing concentration of the hydrophobic species and decreases with increasing hydrophilic monomer content in the copolymer backbone. However, the swelling ratio increases with decreasing hydrophobic content.



POLY 435: Effects of substituents on the ceiling temperature of cyclopentene in ring-opening metathesis polymerization

Huiying Liu, hliu91@illinois.edu, Yi Ren. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Ring-opening metathesis polymerization (ROMP) is a powerful tool for the design and synthesis of polymeric materials with diverse applications such as self-healing and medical uses. While much efforts were made towards synthesis and applications of polymers with controlled length and composition by ROMP, less attention was paid on the depolymerizability and repolymerizability of the system. Since ROMP is driven by release of ring strain, we hypothesized that monomers with less ring strain such as cyclopentene are promising candidates for tunable polymerizability by incorporating different substituents. Herein, we investigated ceiling temperature (T_c) of a series of cyclopentene derivatives both in solution and bulk to quantify their polymerizability. Varying the substituents at the *b*-position of the cyclopentene ring dramatically affects both solution and bulk T_c . By judiciously selecting liquid monomers with bulk T_c values that are slightly above room temperature, the corresponding polypentenamers readily depolymerize in the neat state at elevated temperatures to generate liquid monomers. Upon cooling, these monomers repolymerize to yield solid polymers. This depolymerization-repolymerization cycle is solely triggered by mild environmental temperature changes, which opens up new opportunities towards development of functional materials with reversible polymerizability.



POLY 436: Periodical mesoporous polymers from H-bonding-modulated block copolymer supramolecules

Yong Wang, yongwang@njut.edu.cn, **Leiming Guo**, guoleiming@njtech.edu.cn.
Nanjing Tech University, Nanjing, China

Pore geometry and size uniformity dictate the performances and durability of porous materials in diverse applications. There is a constant demand for methodologies to design and realize tailor-made pores with sizes down to sub-100 nm with affordable expense. Block copolymers (BCPs) which undergo microphase separation allow the accessibility of a library of well-defined, periodical mesoscale structures. Controlled conversion of these structures which are the dispersed phases embedded in the matrix would yield porosity with the geometries coining the parent structures.

In this work, we fabricate ordered porous materials with different pore geometry by incorporating 3-*n*-pentadecylphenol (PDP) onto the P4VP moieties of cylinder-forming polystyrene-*b*-poly (4-vinylpyridine) (PS-*b*-P4VP) through hydrogen bonding, followed by ethanol treatment. Well-defined, periodical porous structures with the pore geometry of cylinders, lamellae, and gyroid are achieved by tuning the ratio of PDP and P4VP as well as the evaporation rate of the solvent in which the BCP and PDP are dissolved. Particularly, we obtain membranes with perpendicular through pores with length up to 65 microns, and prove their pore size can be adjusted in a larger scale by ethanol treatment at elevated temperatures. Ethanol treatment washes out the H-bonded PDP on one hand and swells the P4VP domains. Such membranes with adjustable thickness are obtained by controlling the evaporation of solvent, and the surface morphology transformations are investigated in this evaporation process for the first time.

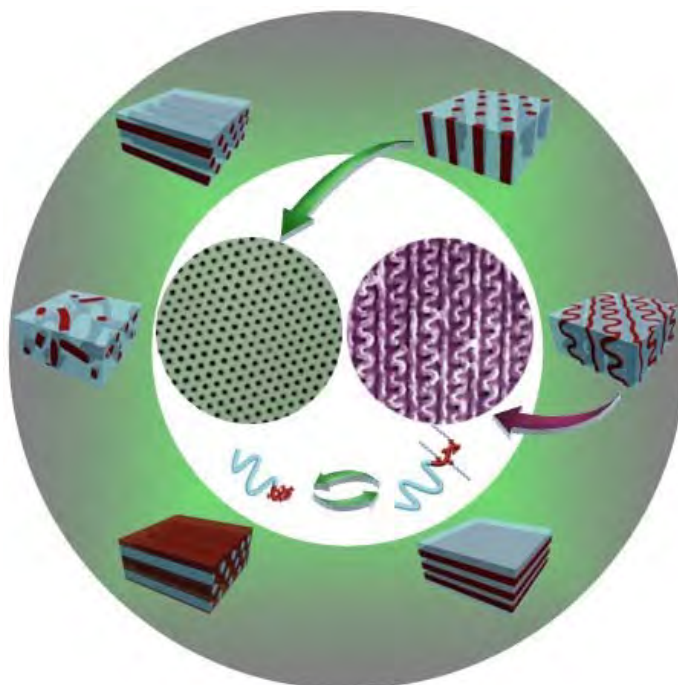
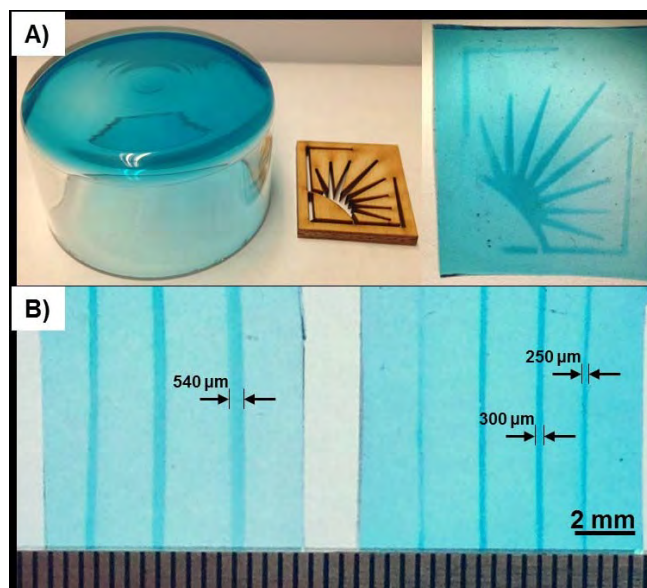


Figure 1. Periodical Mesoporous Polymers from H-Bonding-Modulated Block Copolymer Supramolecules

POLY 437: Photo-responsive solubility, color, and fluorescence of phthalocyanine dye in solution and polymer films

Bowen Li², *bxl316@case.edu*, **Peiran Wei**¹, **Al de Leon**¹, **Taylor Frey**³, **Emily Pentzer**¹.
(1) Chemistry, Case Western Reserve University, Cleveland, Ohio, United States (2) chemistry, Case Western Reserve University, Cleveland, Ohio, United States (3) chemical engineering, Case Western Reserve University, Cleveland, Ohio, United States

Phthalocyanine derivatives (Pcs) have been synthesized and used as dyes, catalysts, and optical limiting materials for decades. In recent years, such versatile conjugated macrocycles have attracted a great deal of interest as active components in modern organic electronic devices and photovoltaics. Solubilizing alkyl side chains on Pcs are ubiquitous because the parent core of Pc is insoluble and unprocessable without them. Unfortunately, such saturated alkyl chains are insulating and contribute to photochemical degradation, and thus can be detrimental to the desired electronic properties of the materials in bulk. The balance of processability and electronic properties leads to the introduction of solubilizing groups that can be removed without changing Pc structures. By taking advantage of photo-cleavable functional groups, we synthesized cobalt(II) phthalocyanine with solubilizing photolabile side chains via facile Yamaguchi reaction and demonstrated the cleavage in solution and in thin films. The molecules are characterized by FTIR, MALDI, etc. Irradiation of the Pc bearing the photolabile group in solution led to precipitation of the Pc core and turning on of fluorescence due to the small molecule byproduct. We also incorporate the tailored Pc into PMMA and PDMS films, and show that fluorescent as well as color patterns can be realized with resolution down to 0.3 mm. This work presents a fundamental method for tuning the solubility, color, and fluorescence of the conjugated small molecule phthalocyanine and will ultimately be used for sensing and data storage applications.



Permanent colored patterning of photolabile phthalocyanine in PDMS films

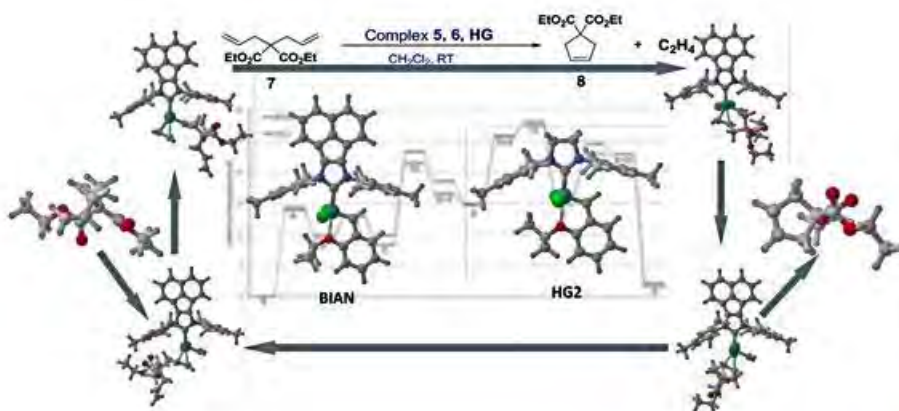
POLY 438: New achievement toward greener BIAN-NHC ruthenium complex

Antsar R. Hlil¹, antsar.hlil@qatar.tamu.edu, Janos Balogh¹, Robert Tuba^{1,2}, Mohammed Al-Hashimi¹, Hassan S. Bazzi¹. (1) Texas A&M University at Qatar, College Station, Texas, United States (2) Research Centre for Natural Sciences, Material & Environmental Chemistry, Budapest, Hungary

The progress of olefin metathesis since its discovery in the 1950's has proved to be a compelling tool in materials science, medicinal, polymer and organic chemistry. The development of easily separable ruthenium based complexes for ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP) with highly active, stable, and high functional group tolerance, remains attractive and of great interest.

Bis(arylimino)acenaphthene (Aryl-BIAN) ligands can easily be prepared via condensation reaction in acetic acid between acenaphthenequinone and amine. Moreover, such preparation is an efficient and reasonably inexpensive. The α -diimine ligands have an extended π -conjugated system, making them strong σ -donors and weak π -acceptors. These collective characteristics result in the stabilization of both the low and high oxidation states of the metal center, and therefore, improving the catalytic activity.

The BIAN Ru-complex exhibits promising excellent catalytic activity and tolerates wide range of substrates at low catalyst loadings. DFT calculations were also carried out on some selected key intermediates in the reaction mechanism to study the effect of having the conjugated aromatic moiety (BIAN ligand) in the backbone of the complex. The newly synthesized BIAN Ru-complex shows comparable catalytic activities to the commercially available second generation Hoveyda-Grubbs catalyst. Ru catalyst is successfully recycled and reused for several cycles for the RCM of *N,N*-diallyl tosylamine affording moderate to high isolated yield.

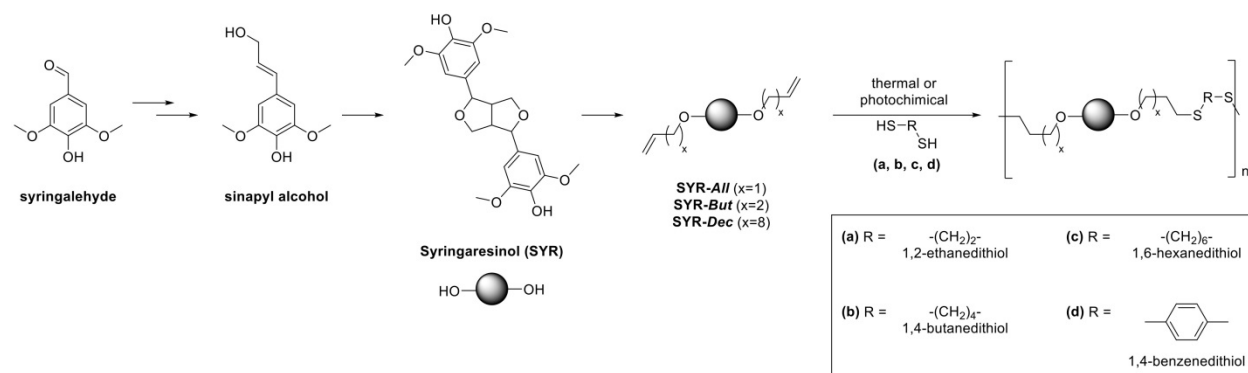


POLY 439: Thiol-ene polymerization of biobased monomers deriving from syringaresinol

Yixian Chen¹, Marine JANVIER¹, Samad Jaufurally¹, Paul-Henri Ducrot², **Florent Allais¹**, florent.allais@agroparistech.fr. (1) Chaire ABI - AgroParisTech, AgroParisTech, Reims, France (2) IJPB, INRA/AgroParisTech, Versailles, France

Industry and customers are increasingly demanding for eco-friendly and bio-based products. For instance, high concern has been recently raised towards the toxicity of bisphenol A (BPA), a widespread monomer in polymer industry. Dedicated to the valorization of lignocellulosic-derived phenolic compounds, our team developed a serie of biobased and non-toxic bisphenols. Recently, we explored the valorization of sinapyl alcohol through the synthesis of syringaresinol, a naturally occurring bisphenol, that proved to be a promising greener and safer alternative to BPA.

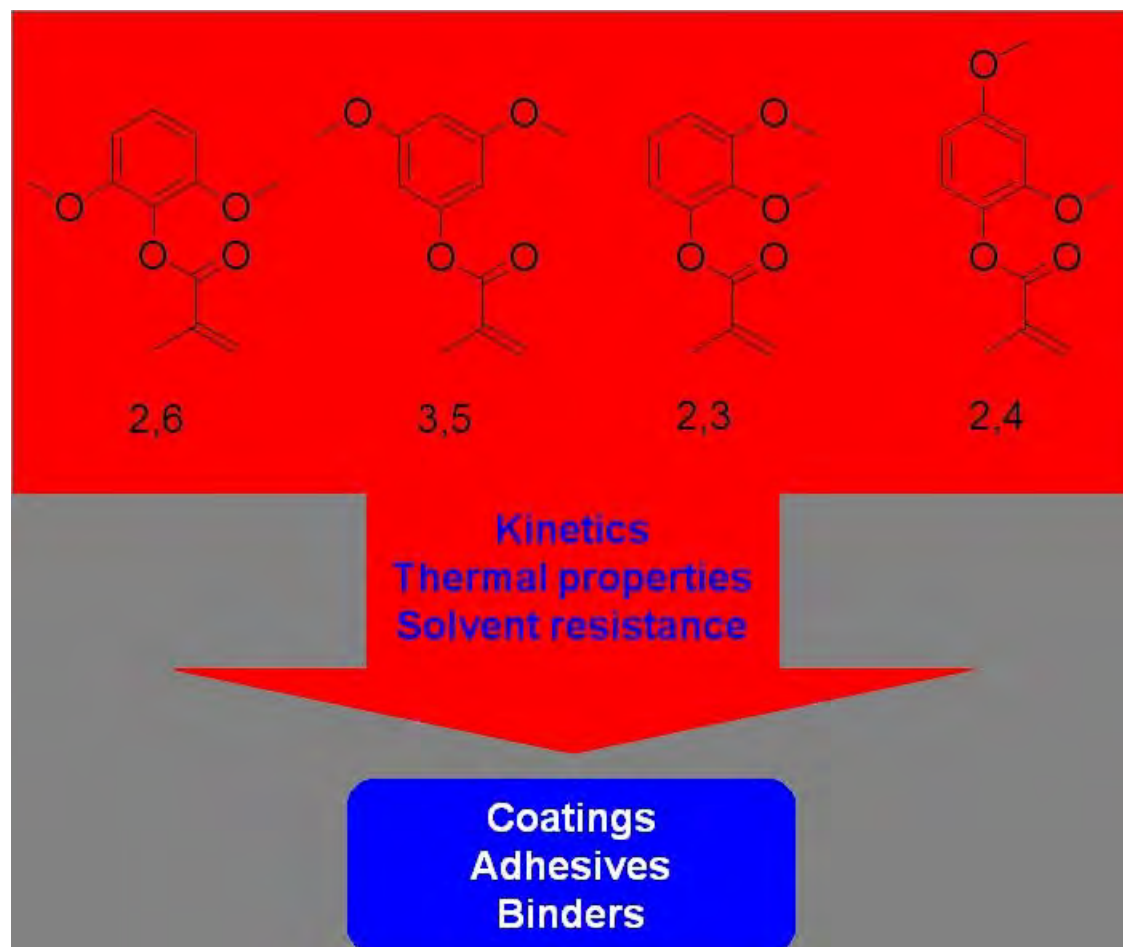
This poster presentation focuses on the synthesis of α,ω -diene monomers obtained from syringaresinol and their polymerization *via* thiol-ene coupling. This click-chemistry type polymerization aims at demonstrating the potentialities of syringaresinol-based polyolefins. Indeed, three renewable α,ω -dienes have been successfully synthesized from sinapyl alcohol, using a chemo-enzymatic synthetic pathway involving a laccase-mediated biocatalytic dimerization as key step, and then studied as monomers in thiol-ene coupling to provide a new class of aromatic “green” polyolefins. In order to optimize the polymerization, several parameters have been taken into account such as polymerization mode (thermal vs. photochemical), solvent, monomer concentration, initiator or wavelength. The scope of thiol-ene coupling was also studied with different dithiols (1,2-ethanedithiol, 1,4-butanedithiol, 1,6-hexanedithiol and 1,4-benzenedithiol) which led to polymers with molecular weight up to 8.1 KDa. The synthesis, functionalization, polymerization of the syringaresinol-based monomers, and the properties of the resulting materials (DSC, TGA, DMA, IR, HPLC-SEC) will be discussed.



POLY 440: Effect of methoxy substituent position on thermal properties and solvent resistance of lignin-inspired poly(dimethoxy phenyl methacrylate)

Shu Wang¹, shuwang@udel.edu, George Wieber¹, Thomas H. Epps^{1,2}. (1) Chemical Engineering, University of Delaware, Newark, Delaware, United States (2) Department of Materials Science & Engineering, University of Delaware, Newark, Delaware, United States

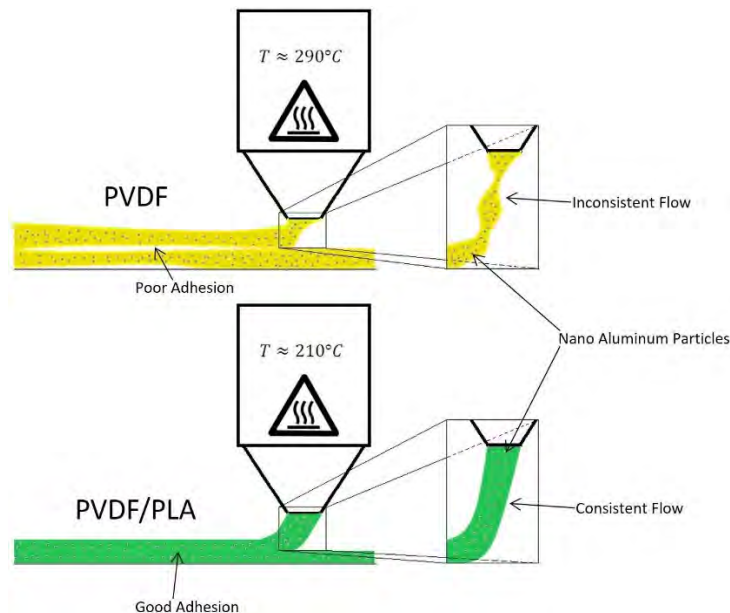
The macromolecular properties of lignin-inspired poly(dimethoxy phenyl methacrylate) are influenced by the position of the substituent. In this work, four dimethoxy phenyl methacrylate isomers with substituents in different positions (including 2,3-, 3,5-, 2,4- and 2,6-) were investigated. Reversible addition fragmentation chain transfer (RAFT) polymerization was employed for the polymer synthesis and kinetics studies. The glass transition temperatures of the resulting polymers differed significantly, spanning from below 100 °C to above 200 °C. The polymers also exhibited remarkably different solubility behavior in some common solvents. The understanding of the structure-properties relationships of poly(dimethoxy phenyl methacrylate) enables the rational design of polymers as a potential component in adhesives, coatings, and binders materials.



POLY 441: Improving the rheology and mechanical response in alumina-poly(vinylidene fluoride)-poly(lactic acid) composites

Jose Bencomo², jbencom2@uccs.edu, Jena M. McCollum², Scott T. Iacono¹. (1) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (2) Mechanical and Aerospace Engineering, University of Colorado Colorado Springs, Colorado Springs, Colorado, United States

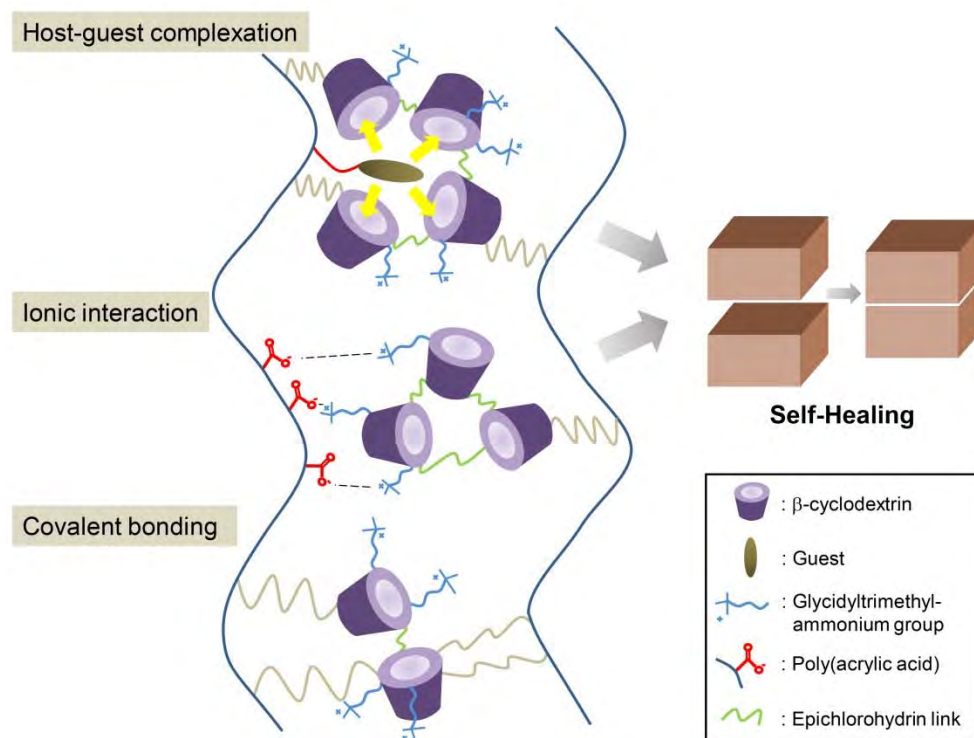
Modern developments in additive manufacturing have presented the opportunity to execute better control in polymer-composite design. When considering high-performance applications, polymer-based composites do not exhibit the adequate mechanical properties. A potential solution that is currently being studied is to infuse the polymer matrix with metal or ceramic particles to improve the mechanical properties. Due to the increased viscosity of the composite, processing becomes a challenge. In previous work, nanoscale aluminum (nAl) particles were added to poly(vinylidene fluoride) (PVDF) via melt blending and injection molding. This resulted in sharp viscosity increases and thermal instability which severely limits the composites. Increasing nAl concentration in the composites accelerated the thermal decomposition of PVDF. This limits the temperature range at which these composites can be processed. A resolution to this is to melt blend poly(lactic acid) (PLA) with PVDF and evaluate its potential as a metallized polymer matrix. Using fused deposition modeling (FDM), PVDF alone will deliver an inconsistent flow which results in poor layer adhesion. The composites were successfully printed at 75 wt. % concentrations of PVDF at 80 °C below typical processing temperatures. The viscosity of the PVDF and PLA composite increases slower which allows for better flow during printing. The purpose of this study is to examine the ability to process metal-oxide particle loading and the mechanical properties of these PLA-PVDF blends. Increasing concentrations of PVDF in PLA were used for determining mechanical and rheological loading limitations.



POLY 442: Self-healing hydrogels based on ionic interactions and host-guest complexation using both cationic β -cyclodextrin oligomers and anionic poly(acrylic acid) networks

Sang-Woo Joo, *sanchi900@gmail.com*, Daham Jeong, Seunho Jung. Department of Systems Biotechnology and Microbial Carbohydrate Resource Bank, Konkuk University, Seoul, Korea (the Republic of)

Self-healing hydrogels can be formed via ionic interactions and host-guest complexation. In this study, we developed self-healable supramolecular hydrogels using cationic β -cyclodextrin (β -CD) derivatives as a multifunctional cross-linker in anionic poly(acrylic acid) networks. The cationic β -CD derivatives were prepared as a monomer and an oligomer cross-linked by epichlorohydrin. They have allyl groups and quaternary ammonium groups. The cationic β -CD derivatives serve simultaneously as covalent and non-covalent cross-linkers. The electrostatic interactions between quaternary ammonium groups and poly(acrylic acid) networks as well as the complexability of cationic β -CD derivatives with guest chemicals including adamantane confer the hydrogel self-healing property. The structure and the mechanical performances of hydrogels were characterized by elemental analysis, FT-IR, NMR, SEM, and a rheometer.



The concept of the gelation and the self-healing.

POLY 443: Thermodynamic insights into the entropically driven self-assembly of rylene bisimide dyes in water

Pradeep Peethambaran Nair Syamala^{1,3}, pradeep.syamala@uni-wuerzburg.de, Daniel Goerl², Bartolome Soberats¹, Frank Wuerthner^{1,3}. (1) Center for Nanosystems Chemistry, University of Wuerzburg, Wuerzburg, Bayern, Germany (2) Laboratory of Macromolecular and Organic Materials, École polytechnique fédérale de Lausanne, Lausanne, Switzerland (3) Institute for Organic Chemistry, University of Wuerzburg, Wuerzburg, Germany

A fundamental understanding of the thermodynamic aspects of self-assembly is quintessential to develop supramolecular polymers with desired properties. This task is especially challenging in aqueous systems where supramolecular polymerization is principally determined by the intricate interplay between entropic contribution from solvation/dissolution of monomeric units and enthalpic contributions arising from the solvation of extended aggregates. We recently reported on the self-assembly behavior of bolaamphiphilic perylene bisimide dyes appended with oligoethylene glycol (OEG), which show an entropically driven aggregation process in water, while the process is enthalpically driven in the presence of THF as a co-solvent (Figure 1a). In the present study, a detailed thermodynamic profile of the self-assembly of various OEG based bolaamphiphilic rylene dyes is carried out in water at different temperatures, using isothermal titration calorimetry and UV/Vis studies (Figure 1b). Remarkably, we found that the entropic release of water from the OEG chains overcomes the enthalpic contribution from π - π stacking interactions (Figure 1c), which has a determining influence on the thermodynamics of the aggregation process. This fundamental study sheds light on thermodynamics aspects of self-assembly in water, providing new elements to control the aggregation processes.

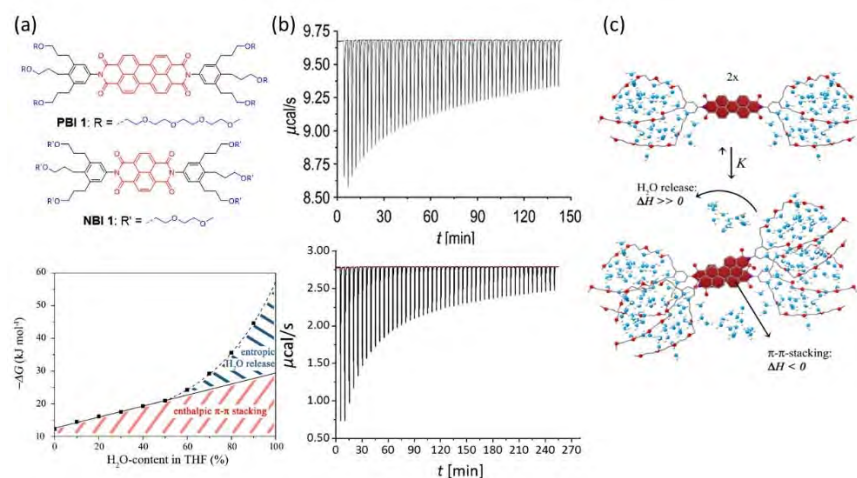


Figure 1. a) Chemical structures of **PBI 1** and **NBI 1** (top) and Gibbs free energy, ΔG of **PBI 1** self-assembly in H₂O/THF mixtures (bottom). b) Heat release per injection of an aqueous solution of **PBI 1** (top) and **NBI 1** (bottom) into pure water in an ITC dilution experiment showing enthalpic penalty associated with the self-assembly. c) Schematic representation of the proposed aggregation mechanism of **PBI 1** in water.

POLY 444: Kinetic control of supramolecular polymerization by ultrasonication

Marius Wehner^{1,2}, marius.wehner@uni-wuerzburg.de, Soichiro Ogi¹, Wolfgang J. Wagner^{1,2}, Vladimir Stepanenko^{1,2}, Frank Wuerthner^{1,2}. (1) Institute of Organic Chemistry, University of Würzburg, Würzburg, Germany (2) Center for Nanosystems Chemistry and Bavarian Polymer Institute, Würzburg, Germany

Supramolecular polymerization has recently attracted particular attention for the development of well-defined functional architectures. While the thermodynamics of supramolecular polymerizations were studied in detail by mathematical models, deep knowledge on the kinetics of aggregation processes is still lacking. The understanding of both, the thermodynamics and kinetics of supramolecular polymerizations, is important because it may enable the precise control of the structure and function of supramolecular polymers. Perylene bisimide (PBI) dyes are suitable to study these phenomena since they possess favorable aggregation behaviors and outstanding optical properties. Recently, the kinetics of self-assembly processes of PBI derivatives have been studied by seeded supramolecular polymerization. In the present work we achieved the kinetic control on the aggregation behavior of chiral (*S,S*)-PBI-C2* and studied the influence of external stimuli (e.g. ultrasonication) by IR, UV/Vis and CD spectroscopy as well as AFM (Figure 1).

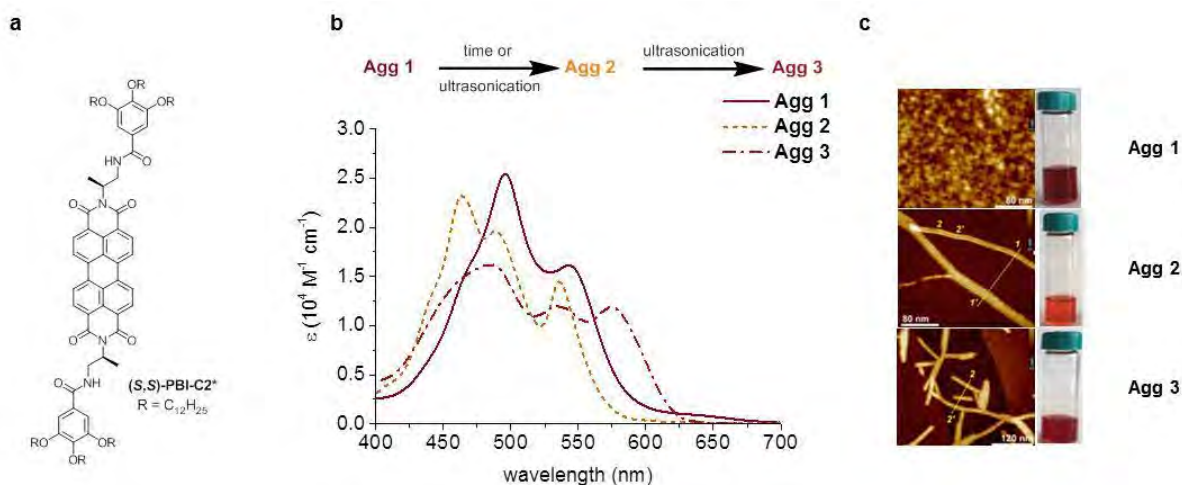


Figure 1. Chemical structure of (*S,S*)-PBI-C2* (a); absorption spectra (b) and AFM height images (c) of the different aggregates of (*S,S*)-PBI-C2* as well as photographs of their colored solutions in MCH/Tol 5:4 ($c_T = 400 \mu\text{M}$, 298 K).

POLY 445: Molecular weaving of flexible covalent organic frameworks

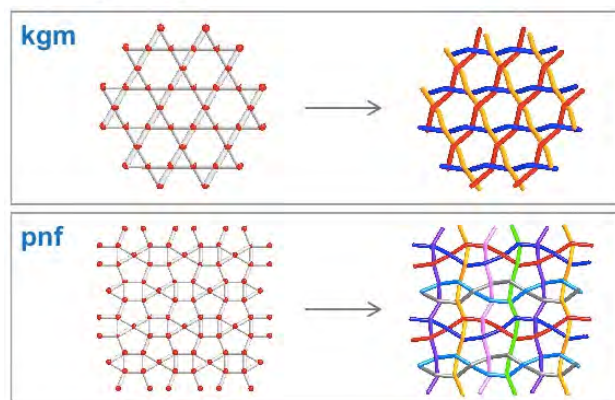
Yuzhong Liu¹, lyuzhong@berkeley.edu, Yanhang Ma², Osamu Terasaki², Omar M. Yaghi¹. (1) Chemistry, University of California Berkeley, Berkeley, California, United States (2) Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

Covalent organic frameworks (COFs) are a class of crystalline materials that can be made by linking organic building units with strong covalent bonds, and the building units themselves can be easily modified, resulting in materials with desired properties, such as high porosity and catalytic activity. By convention, these materials are constructed through directional bond formation between rigid molecular units, limiting their dynamic, mechanical and elastic properties.

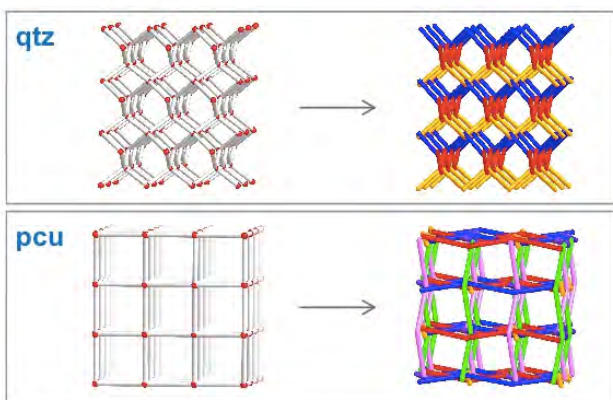
Weaving materials, made by the interlacing of long threads in fabric, are flexible enough to be worn, but also robust enough to not be torn apart easily. The chemical analogue of this important design concept was realized for the first time by COF-505 using copper(I) ions as templates upon coordination with functionalized phenanthroline ligands to direct the formation of a crystalline weaving structure with atomically accurate precision. The copper(I) ions can be reversibly removed and added while preserving the structural integrity, for which a tenfold increase in elasticity accompanies the demetalation.

The successful design and synthesis of COF-505 could be the first step in the development of a large area of synthetic chemistry for weaving structures with various topologies and connectivities. The dynamical robust nature of weaving materials renders them to be easily processed due to their structural flexibility. With their chemical stability to boiling water and ammonia gas, these materials could be potentially used towards toxic gas adsorption and conversion, assisted and catalyzed by the metal centers in the flexible reactive microenvironment. The pore size can also be tailored isoreticularly to include target gases of varied sizes. Upon demetalation, these weaving material can be applied as responsive metal sponges, where the open phenanthroline sites have high affinities for common metal ions and can sequester them efficiently, the uptake of which can be measured by mechanical properties, such as hardness.

2-D topologies



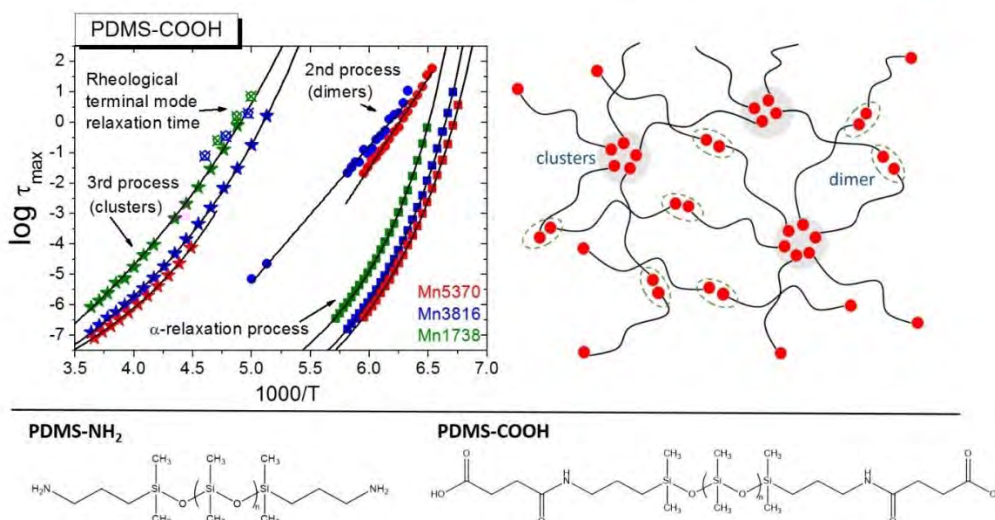
3-D topologies



POLY 446: Unique dynamics of poly(dimethyl siloxanes) with associating chain ends

Kunyue Xing², *kxing@vols.utk.edu*, Pengfei Cao¹, Martin Tress², Tomonori Saito¹, Vladimir Novikov², Shiwang Cheng¹, Alexei P. Sokolov^{2,1}. (1) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

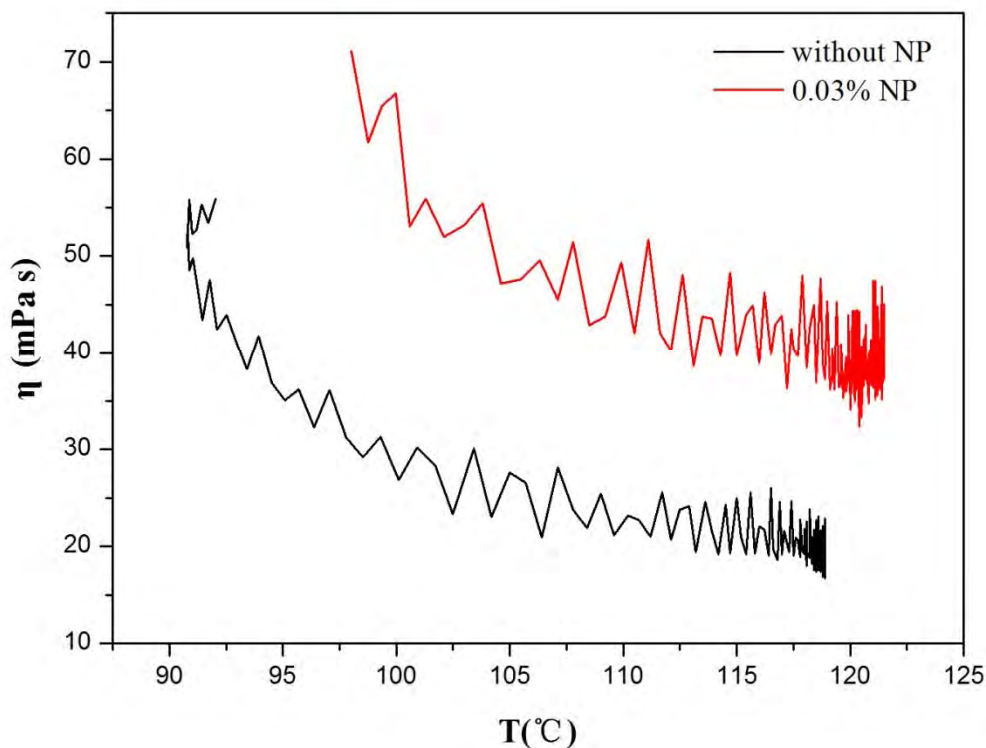
Associating polymers present a new class of materials with wide open tunability in macroscopic properties, for example, the viscoelastic properties. Here, we investigate the impact of associating strength of end groups on segmental relaxation and viscoelastic properties of end functionalized polydimethylsiloxanes (PDMS) with different molecular weight (MW). Specifically, we employed dielectric spectroscopy, rheology, and differential scanning calorimetry to study 3 low MW associating amine (NH₂-) and carboxylic acid (-COOH) terminated PDMS melts. We observed the glass transition temperature T_g in these polymers increases with decrease in MW due to chain end association. While the segmental relaxation and T_g have minor changes with variation in these end groups, the rheological response and viscosity show a remarkable mechanical reinforcement for the PDMS-COOH compared to the PDMS-NH₂. For both types of end groups we find indications for a dimerization of end groups, i.e. association of the low MW polymers to apparently long chains. Additionally, in the case of PDMS-COOH a second T_g is observed, about 45 K above the actual T_g . The corresponding slow relaxation process is observed in the dielectric spectra. This suggests collective association of multiple chain ends in clusters which resembles a phase separation and generates a crosslinked network. As a consequence, the viscoelastic properties can be tuned from the normal for short polymer chains at higher T , to properties of strongly entangled polymers at intermediate T , to reinforced rubber below the second T_g , while the material is still in the melt. This mechanism of unique tunability in viscoelastic properties demonstrates a promising route to novel functional materials.



POLY 447: Structure and Rheology of Hydrophobic Modified Polyacrylamide-Nanoparticle Mixture

Fangfang Peng, *smzl_2008@163.com*, Yangchuan Ke. College of Science, China University of Petroleum, Beijing, China

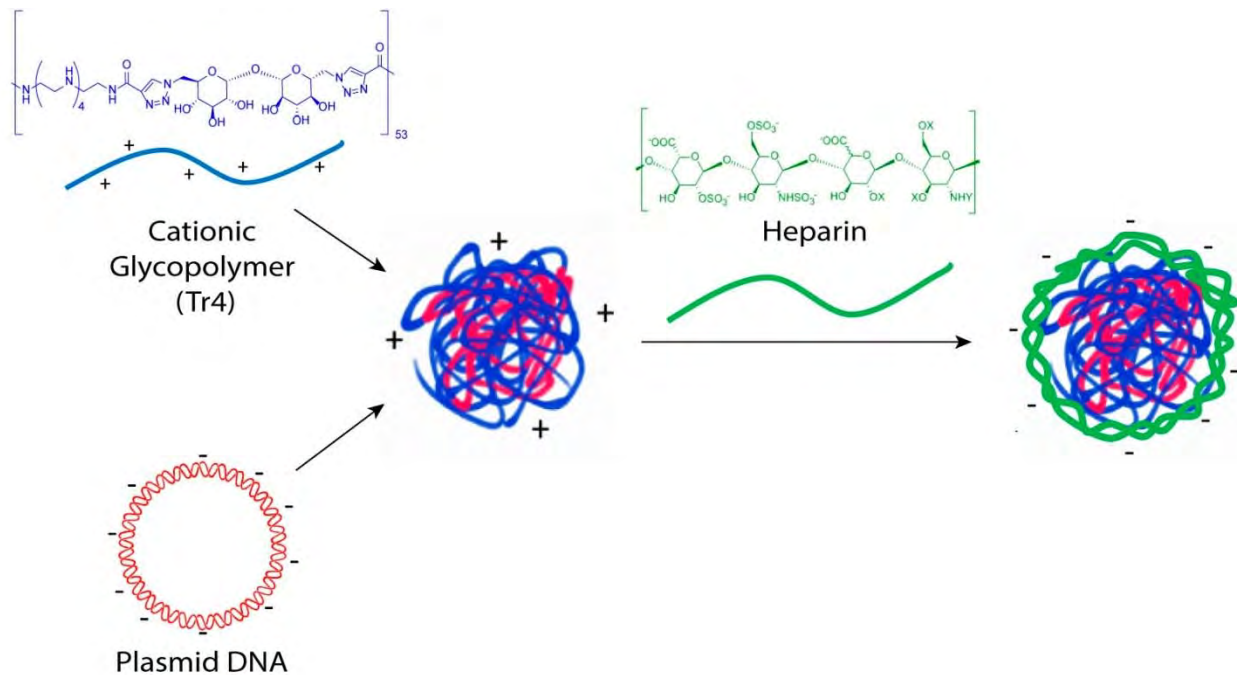
Hydrophobic modified polyacrylamide has received considerable attention over recent years and has been widely applied in oil field completion, stimulation, and production due to their unique rheological characteristics. However, the shortcoming of low thermal stability has limited their application in many occasions. It is therefore essential for finding an effective way to enhance their heat resistance. Adding inorganic nanoparticles into organic copolymers normally has a synergistic effect and the properties of the mixture system are superior to their individual composite, which provides an approach to resolve this problem. In this work, the interactions of hydrophobic silica nanoparticles and hydrophobic modified polyacrylamide was studied by dynamic laser light scattering (DLS), cryo-TEM and rheological measurements. DLS and cryo-TEM measurements were used to detect the morphological of the mixture in aqueous solution, which indicated that the aggregation of copolymer with silica nanoparticles exist a larger size than individual copolymer aggregations. The viscosity measurement showed that heat resistance of the mixture system significantly enhanced due to the introduction of the 0.03 wt% silica nanoparticles. In this presentation, the mechanism of the above phenomenon was discussed.



POLY 448: Heparin-Treated Trehalose-Based Polymers Exhibit Enhanced Transfection Efficiency in Challenging Cell Types

William Boyle, will121688@gmail.com, Theresa M. Reineke. Chemistry, University of Minnesota, SAINT PAUL, Minnesota, United States

Improving the delivery of nucleic acids such to diverse tissue types in culture is important for translating regenerative cell therapies. Herein, we report that the use of transfection media additives, particularly heparin, dramatically increases pDNA delivery efficiency and transgene expression in a wide variety of cell types. Low concentrations of heparin were added to polyplexes formed by combining pDNA and Tr4, a cationic glycopolymer containing repeated trehalose and pentaethylenetetramine groups, prior to *in vitro* transfection with plasmid DNA. Polyplex formulations were found to form ternary complexes upon heparin addition. Heparin-treated polyplexes offer significant increases (approximately 4-fold) in GFP expression compared to polyplexes prepared with Tr4 alone in primary fibroblasts, U87, and HepG2 cells. A linear relationship between heparin concentration and GFP expression was observed. Greater than 50% higher cellular internalization was found with the Tr4 polyplexes with HepG2 cells while showing minimal increases in U87 and primary fibroblasts. Endocytic pathway inhibition was used to further understand the internalization route taken during transfection with and without heparin. The heparin-treated polyplexes were found to be primarily endocytosed through macropinocytosis and clathrin-mediated pathways while Tr4 polyplexes in the absence of heparin were taken up by cells primarily via caveolae. The nuclear localization behavior of Tr4 polyplexes also appeared to be modified by heparin, which likely further increases efficiency and transgene expression.

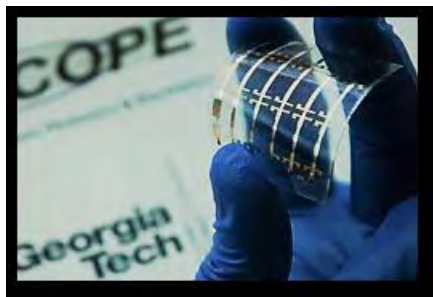


Heparin coats the surface of cationic polyplexes leading to increased transfection efficiency.

POLY 449: Design and synthesis of solution processable *n*-channel π -conjugated polymers and device applications

Amanda Tonnaer¹, amanda.tonnaer@gmail.com, Rrahul Topiwala², Neal Pate², Zhibo Yuan², Elsa Reichmanis². (1) Chemistry, University of West Florida, Pensacola, Florida, United States (2) Chemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

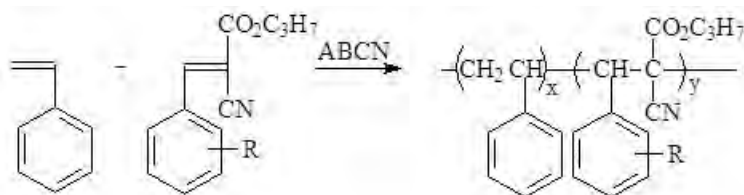
Compared to traditional inorganic materials, organic semiconductors have advantageous properties which allow for low cost, adaptability to low-temperature processing on flexible substrates, and tunable electronic properties. Organic semiconductors are essential for the evolution of flexible and stretchable electronic products and would allow for the development of low-power displays, and printable sensors among other applications. High-performance *n*-channel semiconductors are important for the development of plastic electronic devices such as organic field-effect transistors (OFETs) and complementary metal–oxide–semiconductor (CMOS)-like complementary circuits. *n*-Channel π -conjugated polymers were synthesized with a structurally engineered side chain to increase solution processability while maintaining close π - π stacking. The synthesized polymers were characterized by ¹H NMR.



POLY 450: Novel copolymers of styrene and some ring-disubstituted propyl 2-cyano-3-phenyl-2-propenoates

Gregory B. Kharas, GK HARAS@DEPAUL.EDU, Valeria A. Sloan-Lyon, Monika Cieszynski, John D. Manuel, Steve L. Mei, John B. Mubang, Paige E. Skorseth, Kaila E. Smith, Nicholas Tassone, Elizabeth Tolberd, David Z. Yan. Chemistry, DePaul University, Chicago, Illinois, United States

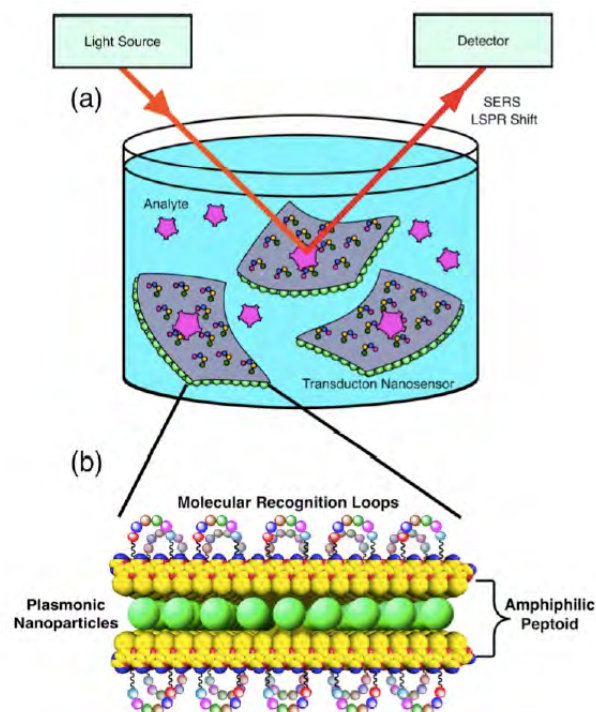
Novel trisubstituted ethylenes, ring-disubstituted propyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2C_3H_7$ (where R is 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-methoxy, 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 3-fluoro-4-methyl, 4-fluoro-3-phenoxy) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and propyl cyanoacetate and characterized by CHN elemental analysis, IR, 1H - and ^{13}C -NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, 1H and ^{13}C -NMR, GPC, DSC, and TGA. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500C range with residue (3-7% wt.), which then decomposed in the 500-800C range.



POLY 451: Fabricating novel optical sensors by embedding gold nanoparticles inside peptoid nanosheets

Kathleen Chen², *kathleenkchen16@gmail.com*, Ellen Robertson¹, Ronald N. Zuckermann¹. (1) Molecular Foundry, Lawrence Berkeley National Laboratory, El Cerrito, California, United States (2) Wellesley College, Wellesley, Massachusetts, United States

In the venture to improve the durability of chemical sensors, biomimetic materials research has received considerable attention because they have the potential to achieve selective molecular recognition even in harsh environments. Peptoids, or N-substituted glycines, are an enormously promising class of material because they are biomimetic, sequence-defined polymers that can be designed to fold into bilayer nanosheets that are structurally similar to proteins, yet they offer some advantages over proteins such as chemical diversity, environmental stability and ease of synthesis. Previously, functional loops have been displayed on the nanosheet surface for binding chemical and biological species. Here, we introduce a method to introduce gold nanoparticles into the nanosheet hydrophobic core to create an “all in one” sensor. By taking advantage of the nanosheet assembly mechanism via monolayer collapse at the oil-water interface, plasmonic nanoparticles can be embedded inside the sheets to provide an optical feedback system for analyte binding to the nanosheet surface. We have successfully fabricated temporally stable nanosheet/AuNP composites using methyl-substituted aromatic peptoids and dodecanethiol functionalized 5 nm AuNPs. Preliminary structural characterization by electron microscopy and ion binding studies indicate that the composites are efficacious in producing a response upon analyte binding.



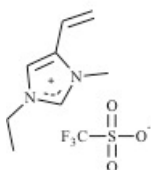
POLY 452: Exploration of the electron transfer reaction between 1-ethyl-3-methyl-4-vinyl imidazolium triflate and ethyl vinyl ether

Samual Lucisano¹, *sll5977@rit.edu*, Megan Detwiler¹, Thomas W. Smith². (1) Rochester Institute of Technology, Rochester, New York, United States (2) School of Chemistry and Materials Science, Rochester Institute of Technology, Webster, New York, United States

In the course of attempting to copolymerize 1-ethyl-3-methyl-4-vinyl imidazolium triflate with ethyl vinyl ether a violent reaction generating a highly colored reaction mixture was observed. Subsequent studies revealed that a similar reaction was observed between 1-methyl-5-vinyl imidazolium triflate with ethyl vinyl ether and 4-vinyl imidazolium triflate with ethyl vinyl ether.

1-methyl-5-vinyl imidazolium methyl sulfonate and 4-vinyl imidazolium methyl sulfonate however do not react violently and appear to form an alternating copolymer with methyl vinyl ether.

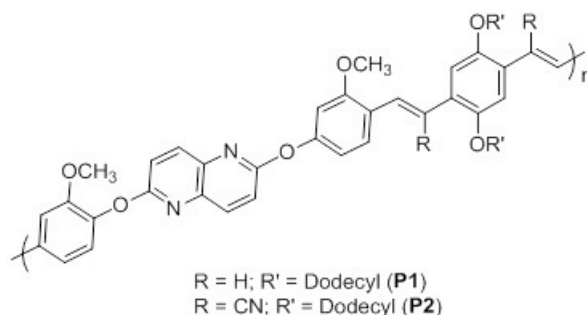
In this paper the reaction between 1-ethyl-3-methyl-4-vinyl imidazolium triflate and ethyl vinyl ether has been explored in greater depth. Specifically, the reaction was carried out at -40°C in CDCl₃. The results of NMR and UV-VIS spectra analysis will be reported.



POLY 453: Synthesis, characterization and photophysical properties of new 2-(2-methoxyphenoxy)-6-(3-methoxyphenoxy)-1,5-naphthyridine):phenylene vinylenes copolymers

Abdulmalik A. Boali¹, *abdulmalikboali@outlook.com*, **Muhammad Mansha**^{2,4}, **Nisar Ullah**³. (1) King Fahd University of petroleum and minerals, Riyadh, Saudi Arabia (2) King Fahd University of petroleum and minerals, Dhahran, Saudi Arabia (4) Centre Of Excellence in Nanotechnology, Dhahran, Saudi Arabia

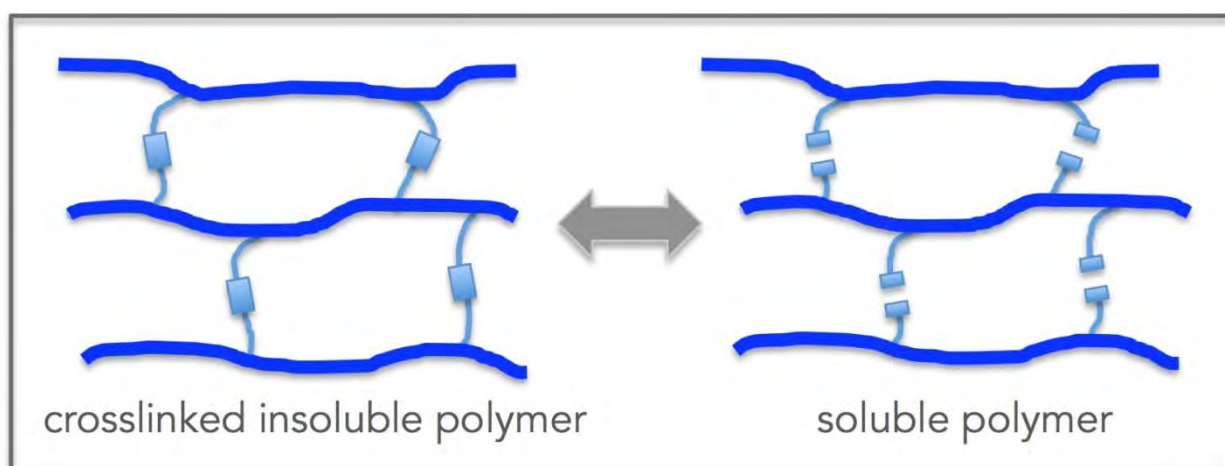
Two new conjugated copolymers poly(2-(2-methoxyphenoxy)-6-(3-methoxyphenoxy)-1,5-naphthyridine)-p-bisdodecyloxyphenylene vinylene) (**P1**) and poly(2-(2-methoxyphenoxy)-6-(3-methoxyphenoxy)-1,5-naphthyridine)-p-bisdodecyloxyphenylene cyanovinylene) (**P2**) have been prepared by the Horner-Emmons and Knoevenagel polymerization reactions. Polymers **P1** and **P2** were characterized by NMR, FTIR, cyclic voltammetry (CV), diffuse reflectance UV-vis spectroscopy (DR UV-vis) and thermal gravimetric analysis (TGA). In addition, the optical band gaps, derived from the onset absorption edge and CV measurement have been calculated. The polymers **P1** and **P2** constitute long alkoxy and alkyl side chains, bearing excellent solubility in most organic solvents which warrants their suitability for photovoltaic devices application. While screening iodide ion sensing ability of **P1** and **P2**, the addition of solution of iodide salts changed the initial colorless solution of polymer to deep yellow coupled with significant changes in the UV-vis spectra of the polymers. In addition, the color of polymers and UV-vis spectra remained unchanged when other common anions such as chloride, fluoride and bromide salts were added.



POLY 454: Synthesis and characterization of conducting polymers with degradable crosslinks

Randy Grant, grantr4@wwu.edu, Amanda Murphy. Chem Dept, MS9150, Western Washington Univ, Bellingham, Washington, United States

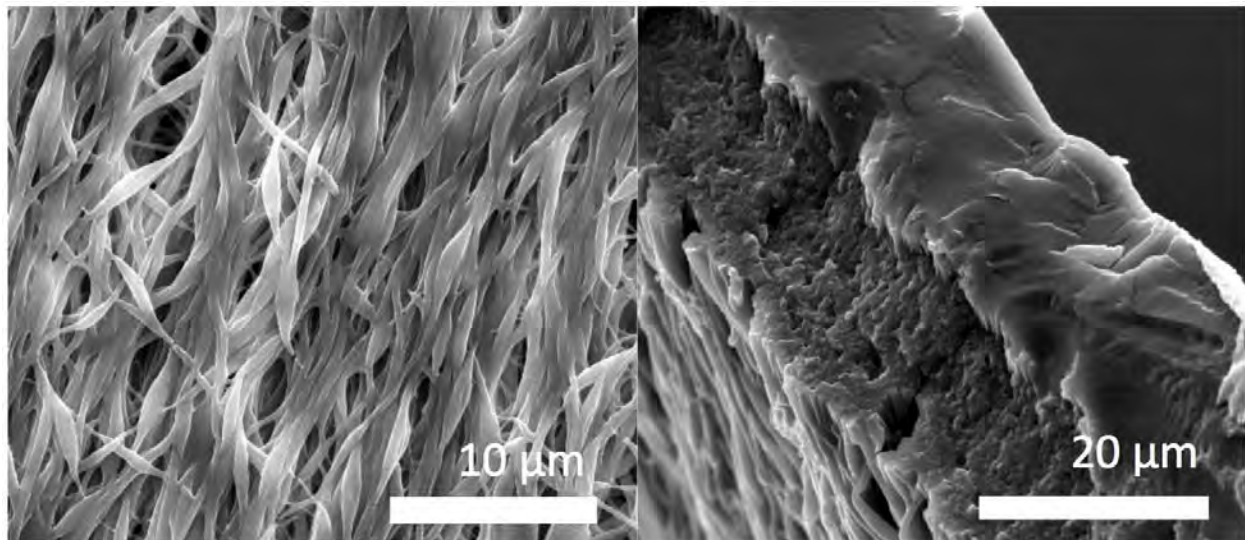
Conducting polymers have numerous features that are promising for use in biomedical applications, but their inability to biodegrade poses limitations. Here, we investigate the use of reversible crosslinks to control the degradation and dissolution of poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives. The synthesis and characterization of the monomers and polymers, as well as initial degradation studies will be presented.



POLY 455: Actuation of electrospun silk-conducting polymer composites

Jonathan Bontrager, jonsbontrager@gmail.com, Tatum Fuller, Stephanie Maxwell, Amanda Murphy. Chem Dept, MS9150, Western Washington Univ, Bellingham, Washington, United States

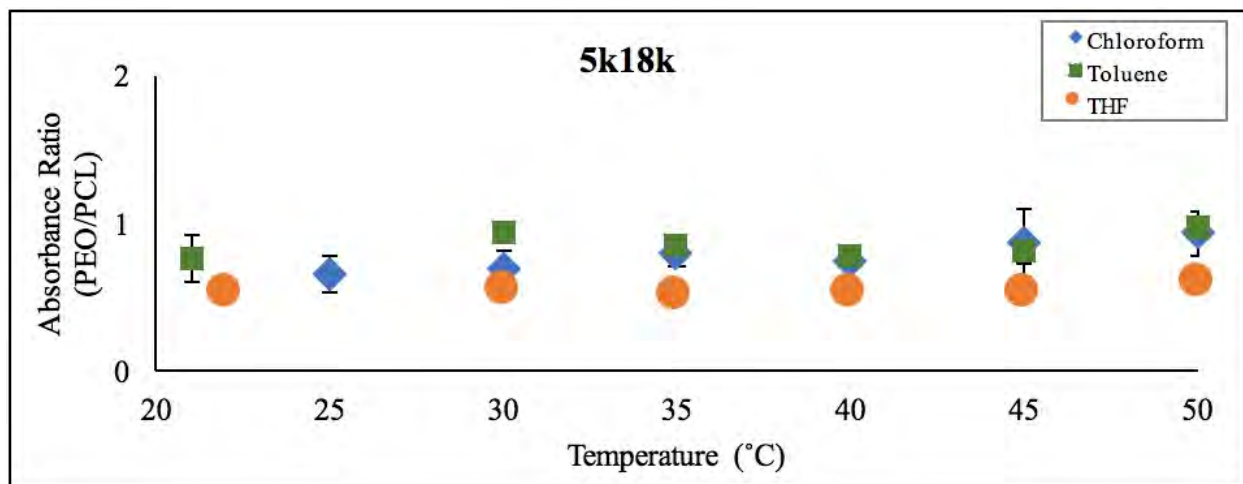
With heart disease being a leading cause of death in the United States, development of biocompatible materials that can mimic the structure and function of heart tissue is an important area of research. Electrospun silk mats have been shown to have a nanofibrous structure similar to cardiac tissue, and silk has been demonstrated to be highly compatible with biological tissues *in vivo*. Further incorporation of conducting polymers with the silk nanofibers allows the fiber mats to undergo electromechanical actuation. Here we present a method for fabricating devices that utilizes electrospun silk-conducting polymer composite mats to generate force during actuation, thus mimicking the structure and function of heart tissue.



POLY 456: Solvent effects and isothermal crystallization of poly(ethylene oxide)-block-poly(ϵ -caprolactone)

Cole Tower², coletower97@gmail.com, Ryan M. Van Horn^{2,1}, Kristi Allen^{2,1}, Allison Carandang^{2,1}. (1) Allegheny College, Meadville, Pennsylvania, United States (2) Chemistry, Allegheny College, Hilton, New York, United States

Crystallization of PEO-*b*-PCL films was shown to be affected by changing the drying (crystallization) temperature and/or which solvent was used to prepare the casting solution. To investigate the solvent effects on isothermal crystallization of the polymer, PEO-*b*-PCL films were created using three different solvents. Melt films were used as well for comparison. FTIR was used to measure differences in PEO and PCL relevant absorbances. Differing solubility of each block in the chosen solvent will affect the crystallization in these films. Isothermal crystallization temperature affects the crystallization of the copolymer in many ways including if and when one or both blocks crystallize. Using isothermal crystallization data as well as post isothermal cooling to 0 C, sequential block crystallization of PEO_{5k}-*b*-PCL_{16.3k} and PEO_{5k}-*b*-PCL_{18k} hypotheses have been supported.

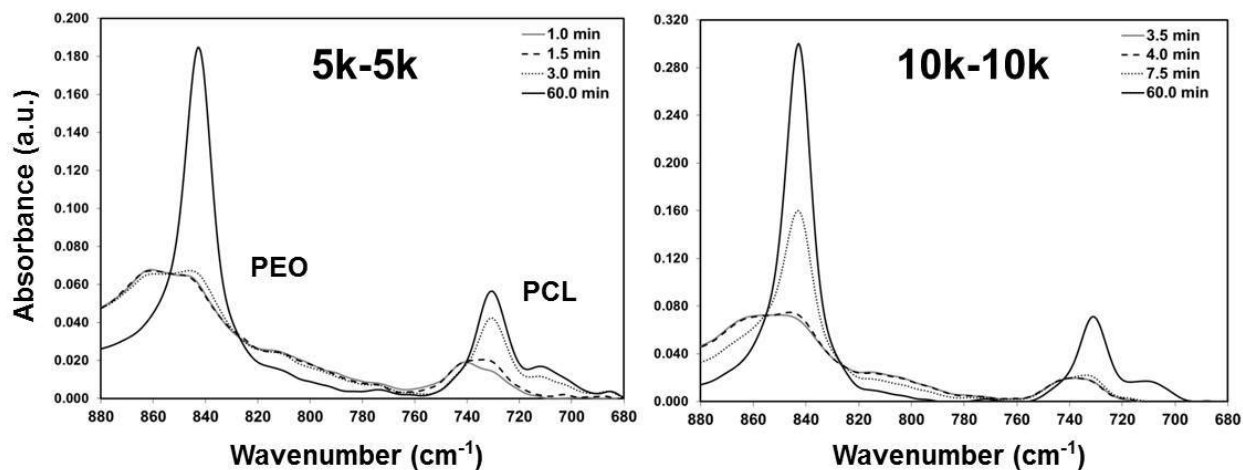


Absorbance ratio (PEO/PCL) versus temperature for 5k18k PEO-*b*-PCL.

POLY 457: Crystallization trends of equal molecular weight poly(ethylene oxide)-*b*-poly(caprolactone)

Natasha Brigham, brighamn@allegheny.edu. Chemistry, Allegheny College, Erie, Pennsylvania, United States

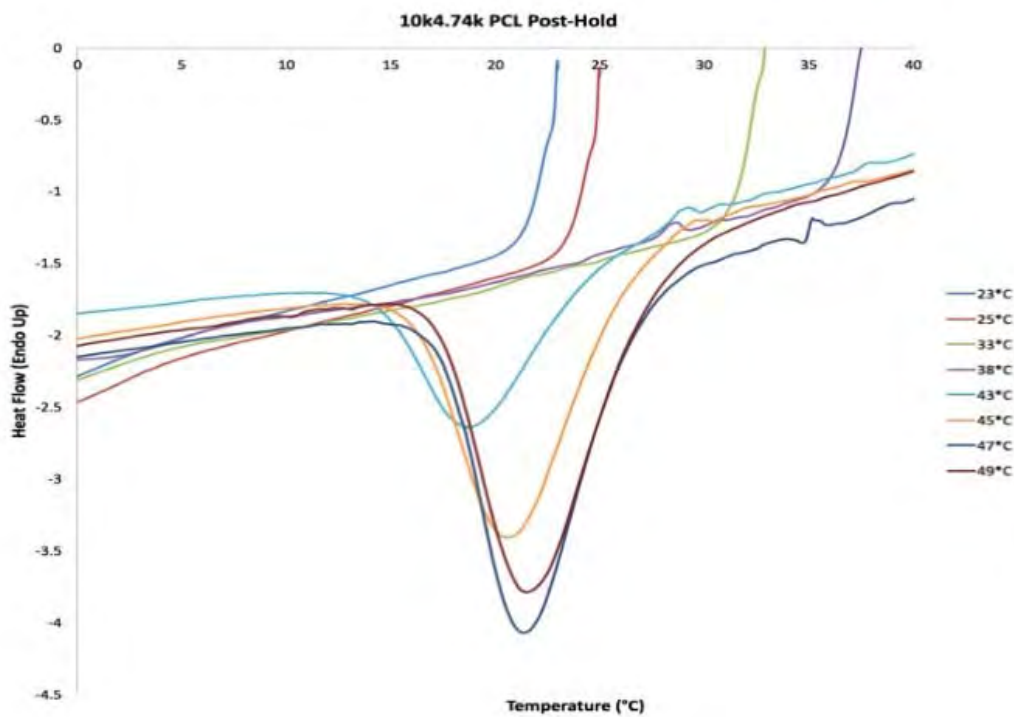
Temperature-Dependent Fourier Transform Infrared Spectroscopy (TD-FTIR) was used to observe the crystallization process and sequence of equal molecular weight poly(ethylene oxide)-*b*-poly(caprolactone) (PEO-*b*-PCL) samples. The copolymer was dissolved in chloroform and cast onto KBr salt plates to create films for analysis. Samples were melted after casting and crystallized isothermally at different temperatures. Differences in sequence of crystallization as well as the rate of crystallization were present in the process when temperature and molecular weight varied. These results have led to our present research on trying to control which block crystallizes first *via* solvent variation.



POLY 458: Isothermal crystallization analysis of poly(ethylene oxide)-block-poly(ϵ -caprolactone) with Larger w_{PEO} or w_{PCL}

Maxwell Steffen, *steffenm@allegheny.edu*, Ryan M. Van Horn. Chemistry, Allegheny College, Meadville, Pennsylvania, United States

Thermal history plays a key role in how polymers function. Poly(ethylene oxide)-*block*-poly(ϵ -caprolactone) (PEO-*b*-PCL) was explored after various isothermal crystallization procedures to show how crystallization of samples with larger w_{PCL} or w_{PEO} were affected. DSC provided evidence about how isothermal temperature affected the crystallization temperature (T_c) of the second block, the crystallinity, and whether sequential or coincident crystallization occurred. As the two blocks become further apart in M_n , the minority block crystallized after the majority block in a sequential manner. Overall, DSC showed that the thermal history of the minority block was altered using different T_c s for the majority block.

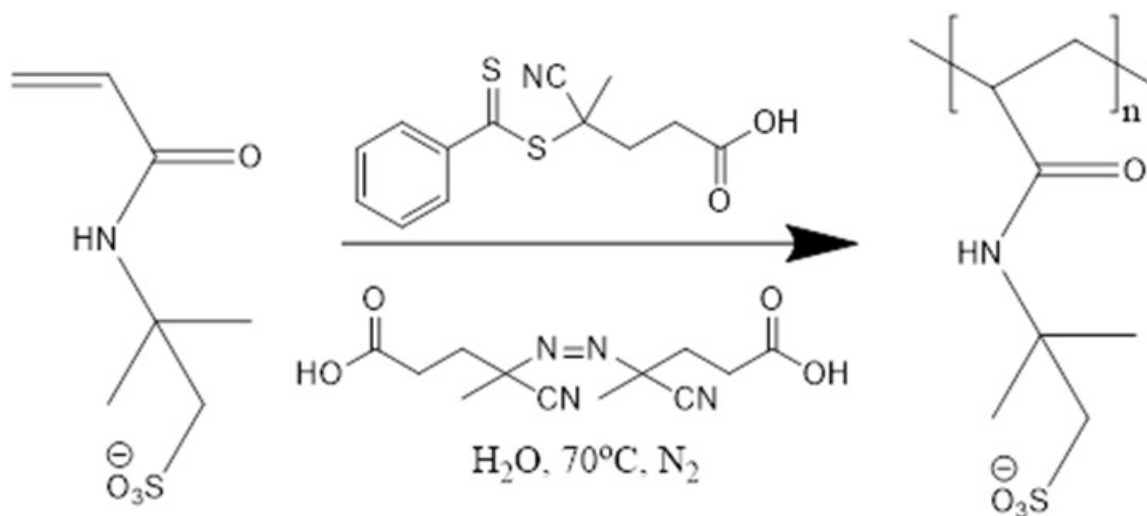


Isothermal DSC curve for a 10k4.74k sample of PEO-PCL that show heat flow (endo up) versus temperature.

POLY 459: Synthesis of low molecular weight anionic acrylamide-based polymers for determination of structure/binding interactions with α -gliadin

Hannah Kolell², hannah.kolell@valpo.edu, Ashleigh Bristol¹, Sarah E. Morgan¹. (1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Chemistry, Valparaiso University, Valparaiso, Indiana, United States

Experimental conditions for the synthesis of short, anionic acrylamide based polymers with controlled molecular weight and molecular weight distribution were determined for the preparation of materials that can be used as therapeutic agents for celiac disease. Aqueous reversible addition-fragmentation chain-transfer (aRAFT) polymerization was used to perform kinetic studies to elucidate polymerization conditions to obtain poly(2-acrylamido-2-methylpropane sulfonate) (polyAMPS) with target degrees of polymerization of 5, 15, and 25. Chain transfer agents (CTA) 4-cyano-4-(ethylsulfanylthiocarbonylsulfanyl) pentanoic acid (CEP) and 4-cyanopentanoic acid dithiobenzoate (CTP) were synthesized and their structures confirmed using ¹H-NMR. Kinetics studies showed CTP is a suitable CTA for target DP of 5 while CEP is preferred for DPs 15 and 25 for the polymerization of AMPS. The internal standard sodium benzenesulfonate was used as a reference to quantify monomer conversion, which allowed for M_n and DP calculations. From these calculations the time of polymerization for DP 15 has been determined.

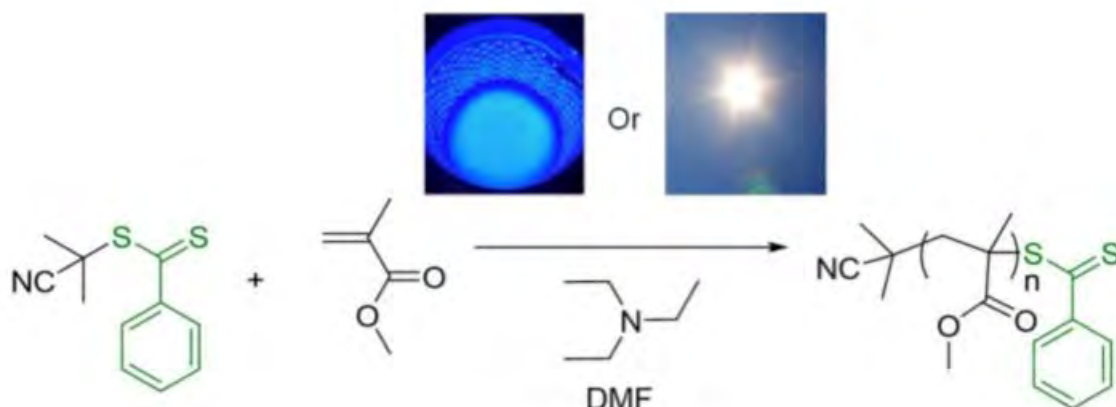


Polymerization scheme for polyAMPS with the RAFT agent CEP

POLY 460: Amine assisted photo-initiated RAFT polymerization using visible light: A kinetic and mechanistic study

Michael Allegrezza, Zach DeMartini, Alex Kloster, **Zachary Digby**,
digbyza@miamioh.edu, Dominik Konkolewicz. Miami University, Oxford, Ohio, United States

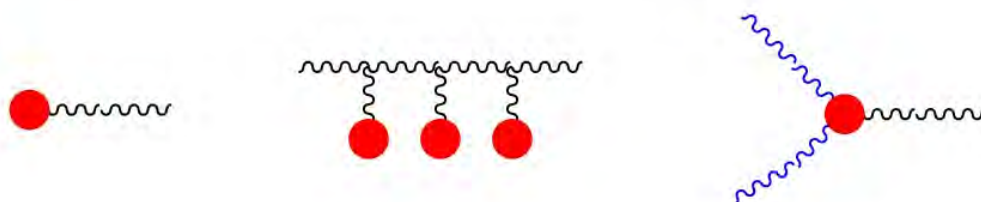
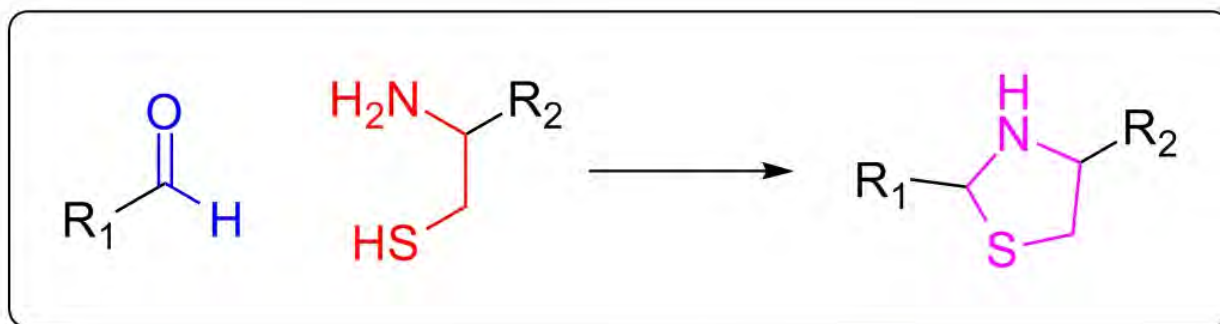
Photochemical polymerizations have become more and more popular recently as it is possible to selectively control the polymerization and perform it under mild conditions. In this study, the kinetics of photochemical dithiobenzoate-mediated RAFT polymerization in the presence of triethylamine is explored. The system uses no rare earth catalyst; it relies on triethylamine combined with RAFT polymerization reagents initiated via mild light sources such as visible light and sunlight. This is a multivariable study with variables such as effect of light source, RAFT chain transfer agent concentration, and amine concentration are investigated to better understand their role in the kinetics as well as the possible mechanism in which the polymerization proceeds. Data suggest that the major radical generation pathway is electron transfer from the amine to the excited RAFT end-group, however radicals are also generated directly from the excited RAFT end-group. This method allows the generation of living polymers as evidence by the synthesis of well-defined block copolymers.



POLY 461: Employment of thiazolidine chemistry for novel polymer composition and structure

Clement DeHoe, cdehoe@calpoly.edu, Catherine Sarantes, Karoline Eckhart, Lucas Souza, Philip J. Costanzo. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

Thiazolidine chemistry is a simple, efficient and under-utilized type of “click” chemistry. This work focuses upon using thiazolidine chemistry as a methodology for post-polymerization modification. Amino-mercapto functional groups were incorporated using simple organic chemistry reactions and installed at both chain-end and main-chain positions. Using aldehyde-containing monomers, materials such as gels and AB step-growth copolymers were synthesized and characterized.[figure1]

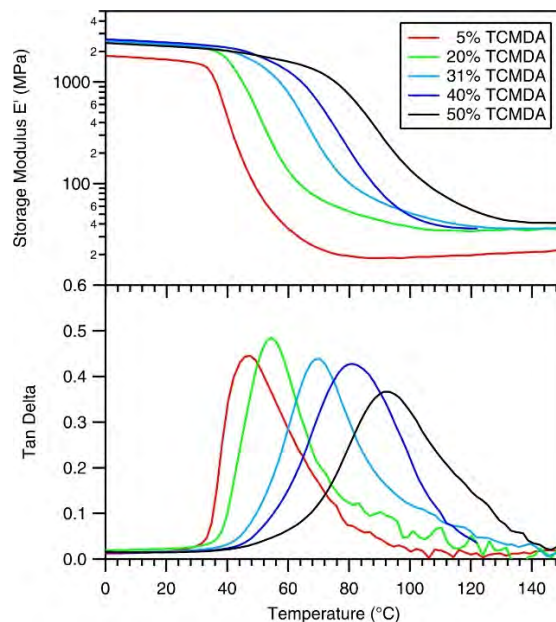


POLY 462: Characterization of a thiol-ene/acrylate-based polymer for neuroprosthetic implants

Dang-Huy Do¹, dang-huy.do@utdallas.edu, **Melanie Ecker**², **Walter Voit**². (1) The University of Texas at Dallas, Richardson, Texas, United States (2) Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States

Biotechnological advancements have created a field for flexible implants that help reduce the burden of damaged body systems. Previous technologies provide promising solutions but are limited by a biotic-abiotic mechanical mismatch and rigidity. Flexible shape memory polymer devices address this problem and are promising alternatives for application as neuroprosthetic implants in those who have sustained neurological injuries.

This study characterizes the thiol-ene/acrylate shape-memory polymer (SMP) system to determine their potential as implants. These smart polymers transition from a stiff state to an elastic state at specific temperatures, tuned by making small variations to the mole fractions of monomers used. By altering of stoichiometric ratios of 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO), trimethylolpropane tris(3-mercaptopropionate) (TMTMP), and tricyclodecane dimethanol diacrylate (TCMDA), different variations of the thiol-ene/acrylate polymer were studied. The obtained polymers were characterized by differences in monomer ratio and varied methods in for device synthesis. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), and swelling tests were performed to determine the thermomechanical behaviors of polymers. In addition, we investigated the softening behavior upon exposure to physiological conditions by means of immersion DMA. By carefully examining this combination of monomers, this work helps advance further research on the thiol-ene/acrylate system's potential as neuroprosthetic implants.

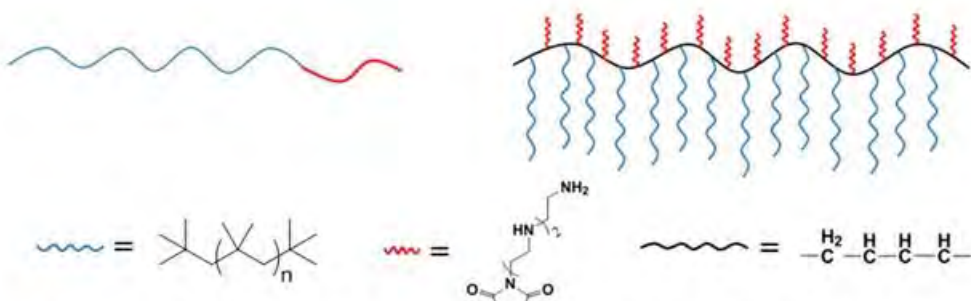


DMA Data for SMP with different ratios of TCMDA showing Storage Modulus on top and Tangent Delta on bottom

POLY 463: Synthesis and Dispersancy of Motor Oil Dispersants with Comb-Like Architecture

Joseph S. Murphy^{2,1}, *jsmurph2@go.olemiss.edu*, Travis Holbrook¹, Robson F. Storey¹.
(1) School of Polymers and High Perf Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Chemical Engineering, University of Mississippi, Oxford, Mississippi, United States

Lubricating motor oils intended for use in internal combustion engines are typically formulated with a variety of additives intended to aid in the reduction of corrosion, deposit formation, wear, etc. One type of additive is ashless dispersants, typically represented by polyisobutylene succinimide (PIBSI), whose role is to regulate viscosity increases due to the formation and presence of soot. Soot is produced by the incomplete combustion of fuel. Rather than the traditional linear diblock architecture of PIBSI, grafted PIBSI dispersants (PolyPIBSI) were prepared by the copolymerization of vinyl ether-terminated polyisobutylene (PIB) with maleic anhydride followed by imidization with tetraethylenepentamine and were characterized by proton nuclear magnetic resonance spectroscopy, gel permeation chromatography, and infrared spectroscopy. PolyPIBSI dispersants with PIB tails of 288, 1,250, and 2,620 g^{*}mol⁻¹ were prepared where it was found that increasing the PIB tail length increased solubility in non-polar media but limited the degree of polymerization of the dispersants. Characterization of the viscosity characteristics of PolyPIBSI dispersants with 2,650 g^{*}mol⁻¹ PIB tails was performed at various loadings in the presence of carbon black. It was found that the viscosity of the solution decreased until 2.5 wt% dispersant upon which increased loadings yielded higher viscosities.

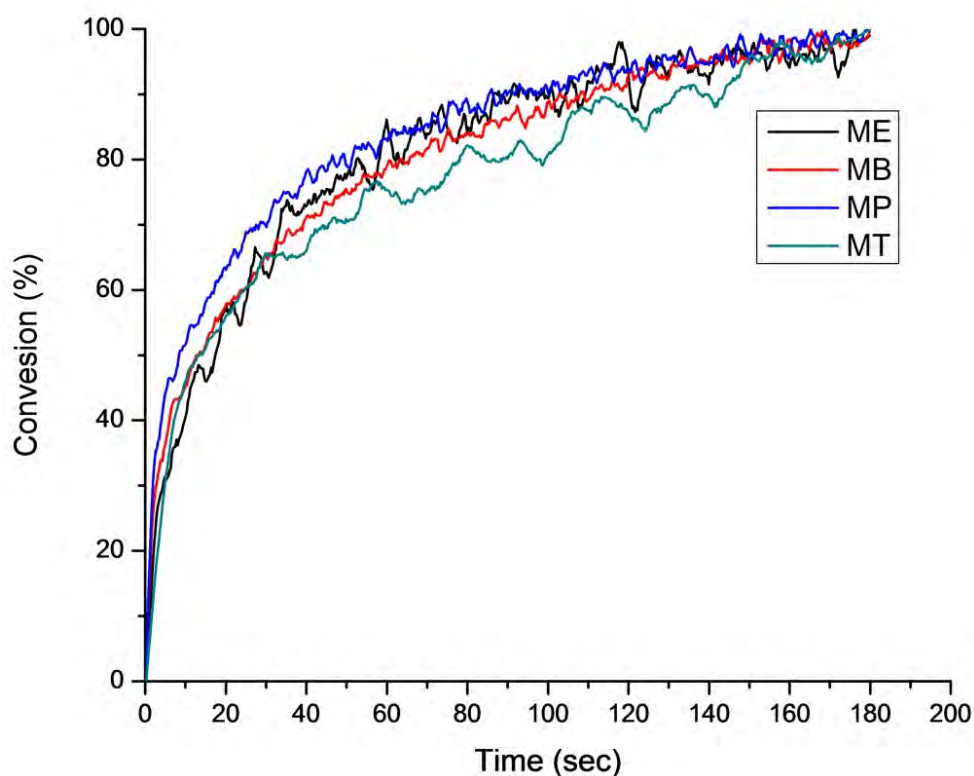


Comparison of traditional linear dispersants (left) and proposed comb-like dispersant (right)

POLY 464: Highly functional methacrylated bio-based resin system for UV/Vis-curable coatings

Jonas Sahouani¹, jsahouani@comcast.net, Arvin Z. Yu¹, Dean C. Webster². (1) Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States (2) Dept 2760, North Dakota State University, Fargo, North Dakota, United States

Highly methacrylated bio-based resins methacrylated epoxidized sucrose soyate (MESS) and dual methacrylated epoxidized sucrose soyate (DMESS) were synthesized from epoxidized sucrose soyate (ESS). These resins were formulated with styrene and thermally cured. Thermomechanical properties of the thermosets produced were investigated and measured. The versatility of these resins was explored and applied in UV/Visible light-cured coatings for dental composite applications. For UV light curing, the resins were combined with various multifunctional reactive diluents and cured under UV light using a photoinitiator (Irgacure 1173) at a 4:1:0.25 ratio, respectively. For visible light curing, camphorquinone was used as the initiator and a blue LED light was used as light source. Commercially available Bisphenol A glycerolate dimethacrylate (BisGMA) was used as the control. The extent of cure was determined using Fourier transform infrared spectroscopy (FTIR). Thermomechanical properties were determined by thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and atomic force microscopy (AFM). The curing kinetics was studied using real-time infrared spectroscopy equipped with a UV light. Coatings made from these formulations displayed good solvent resistance and hardness due to the high crosslinking.



POLY 465: Finding green alternatives to platinum catalysts for the hydrosilylation and hydrogenation of carboxylic acid derivatives

Joshua Arens¹, joshua.arens@coyotes.usd.edu, **Chen Cheng**². (1) Chemistry, University of South Dakota, Vermillion, South Dakota, United States (2) Chemistry, University of California-Berkeley, Berkeley, California, United States

Hydrogenation and hydrosilylation are two widely used reactions in industry for the preparation of many consumer products; however, both processes come with environmental costs. The industry standard for the reduction of esters is either an organic reaction using aluminum hydrides or the Bouveault-Blanc reduction using alkali metals in ethanol. Both produce excessive amounts of waste. While catalytic hydrosilylation reactions do not produce as much waste, they typically rely on platinum catalysts (e.g., Speier's and Karstedt's catalysts) which are costly and have large environmental footprints due to the terrestrial extraction of platinum. Consequently, green alternatives for these traditional methods are sought.

For hydrogenation reactions, an attractive alternative is the catalytic reduction of esters under H₂ (see figure 1 for reaction scheme). Specifically, ruthenium-based catalysts have received considerable attention (e.g. **1a-c** in figure 1). While catalysts **1b-c** are air-sensitive and have challenging synthetic procedures, they have been shown effective for the catalytic hydrogenation of esters. This project corroborated previous findings and specifically examined the effectiveness of these catalysts at reducing diesters.

For hydrosilylation reactions, catalysts based on Earth abundant metals—in lieu of platinum—have become a topic of interest to chemists; however, these newly discovered catalysts have not yet been shown to both tolerate esters or exhibit a broad silane scope. In particular, the Hu catalyst (**2a** in figure 2) tolerates esters, but has only a narrow silane scope. On the other hand, Chirik's catalyst (**2b** in figure 2) exhibits a broad silane scope, but it is unknown whether or not it tolerates ester groups. We sought to find a suitable catalyst for the hydrosilylation of internal double bonds of fatty acid derivatives (see figure 2).

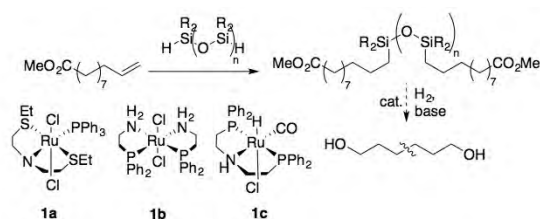


Figure 1. Ester hydrogenation reaction scheme and catalysts.

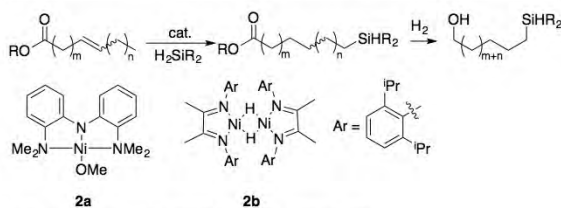
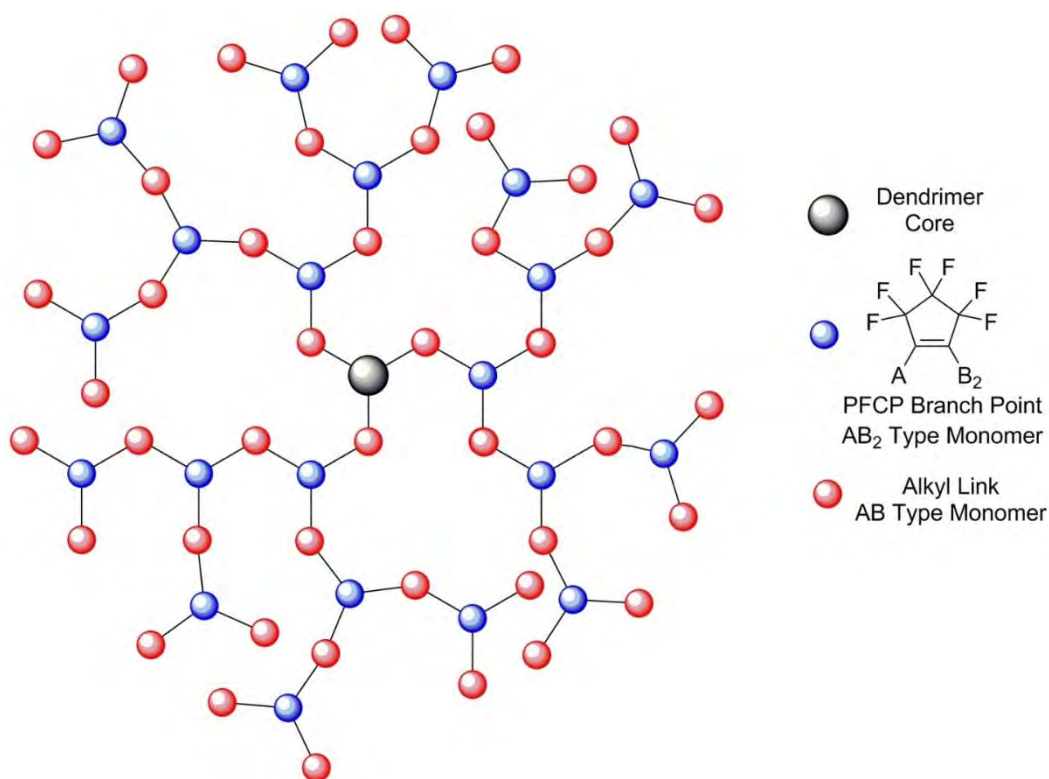


Figure 2. Hydrosilylation reaction scheme and catalysts.

POLY 466: Synthesis and characterization of highly fluorinated dendrimers utilizing orthogonal chemistry

averi richert¹, c17averi.richert@usafa.edu, Abby R. Jennings², Scott T. Iacono³. (1) Chemistry, United States Air Force Academy, USAF Academy, Colorado, United States (2) Chemistry Research Center, United States Air Force Academy, Colorado springs, Colorado, United States (3) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States

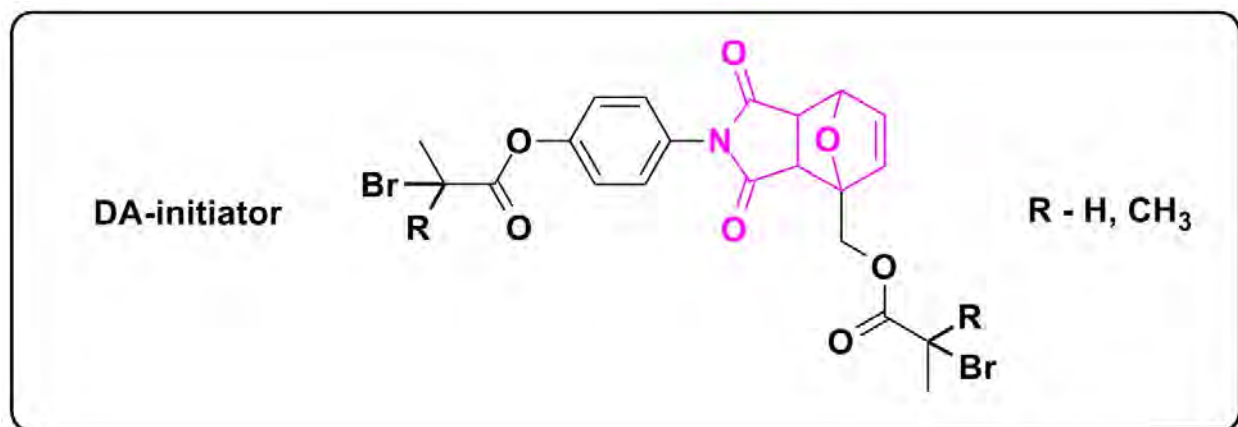
Dendrimers are unique multivalence materials that, by design, are uniform in size, have tailorable solubilities, contain internal cavities and surface functional groups. As a result, dendrimers provide an excellent platform for imaging and drug delivery applications. In order to obtain highly uniform dendrimers for such applications, one must employ chemical transformations that are known to be efficient and orthogonal. Recent work with perfluorocyclopentene (PFCP) has revealed that this moiety is selective towards nucleophilic addition. Taking advantage of this, highly fluorinated dendrimers were designed using a divergent method. Initial studies focused on the synthesis and characterization of a model compound that is used to investigate the chemical transformations proposed in the dendrimer synthesis. Preliminary model reactions show the successful growth of the dendrimer cores with a likelihood of further generational development. This work will focus on recent research efforts towards obtaining highly fluorinated dendrimers via PFCP.



POLY 467: Molecular weight changing polymers via Diels-Alder chemistry

Timothy Schoch, *tschoch@calpoly.edu*, Michael R. Martinez, Marianne Meyersohn, Miles Markmann, **Philip J. Costanzo**, *phil.costanzo@gmail.com*. Chemistry, California Polytechnic State University - San Luis Obispo, Valley Village, California, United States

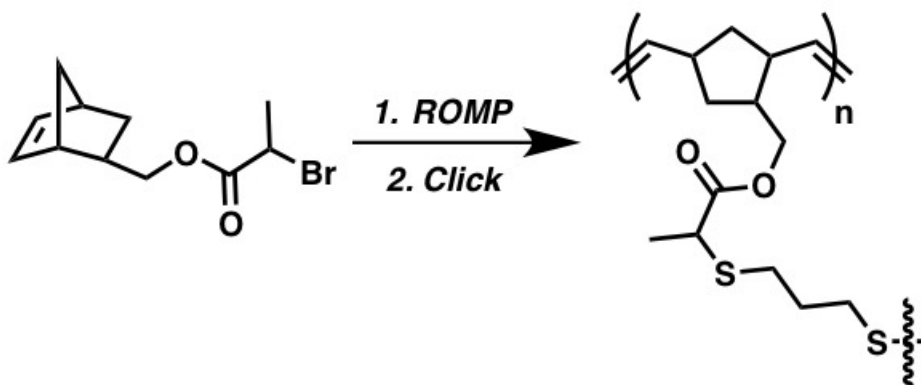
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to change the molecular weight for dynamic processing. Diels-Alder (DA) chemistry was incorporated within the main chain of the polymer backbone by using a DA-initiator and atom transfer radical polymerization. Next, polymer were utilized as macromonomers and coupled into high molecular species via atom transfer radical coupling. Upon the application of a thermal stimulus, the retro-DA was induced and molecular weight of the polymer was altered. [figure1]



POLY 468: Thio-bromo click approach for the preparation of a new class of cross-linked, ROMP-based gels

David Gutierrez, david.gutierrez@students.tamuk.edu, Christopher E. Hobbs. Texas A&M University Kingsville, Corpus Christi, Texas, United States

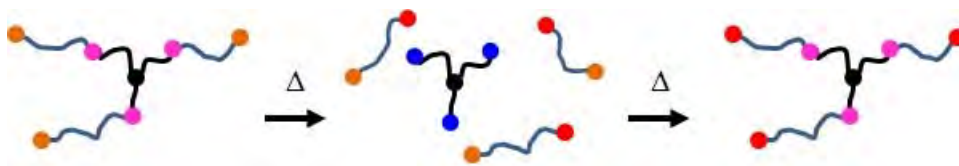
This poster describes our current efforts toward the use of a thio-bromo click reaction for the preparation of novel polymeric gels. Ring Opening Metathesis Polymerization (ROMP) can be utilized for the preparation of α -bromo ester-containing linear polymers that can undergo a post-polymerization cross-linking event through reaction with dithiols. These materials show excellent swellability in organic solvents and have potential applications as supports for developing recoverable catalysts.



POLY 469: Inversion of molecular topology and composition using Diels-Alder chemistry

Marianne Meyersohn, *meyersoh@calpoly.edu*, Miles Markmann, **Philip J. Costanzo**, *phil.costanzo@gmail.com*. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

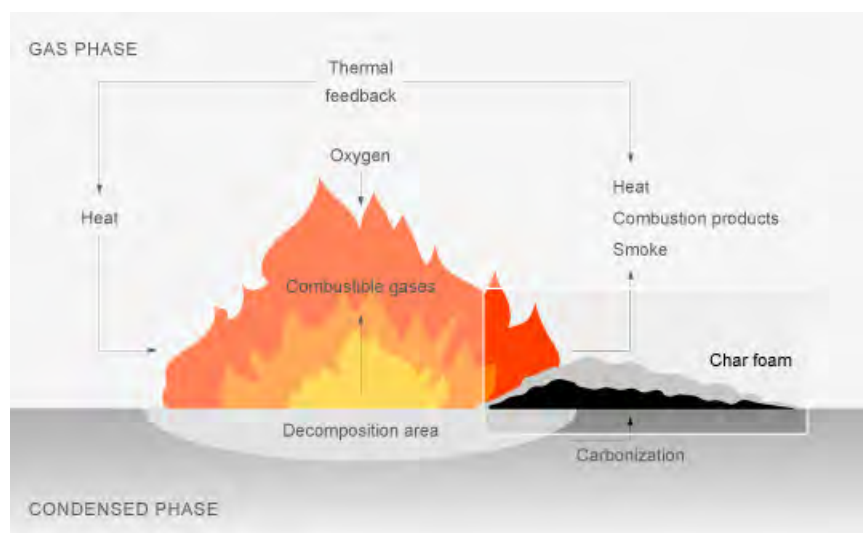
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and light-activated ATRP was utilized to incorporate DA linkages at a central core. By utilizing different DA linkages an inversion of polymer composition and topology was achieved upon the application of a thermal stimulus.[figure1]



POLY 470: Gallic acid esters with flame retarding properties

Kendahl L. Oberdorfer, oberd1kl@cmich.edu. Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, Michigan, United States

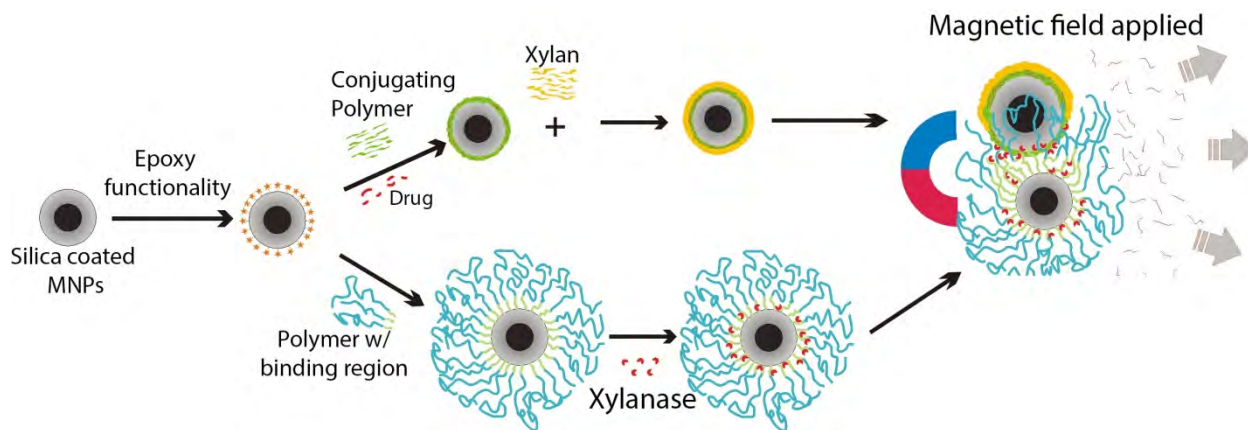
Gallic acid is a renewable biomaterial produced by a variety of plants. Structurally, it is benzoic acid containing three hydroxyl groups which offer the potential for conversion to a variety of phosphorous esters that may function as nontoxic flame retardants for polymeric materials. Treatment of the acid with thionyl chloride followed by aniline generates the corresponding amide. The hydroxyl groups may then be converted to phosphorous esters. For example, treatment of the amide with diethyl phosphite in the presence of carbon tetrachloride (Atherton-Todd reaction) may be used to generate the corresponding *tris*-phosphate. Other phosphorus esters may be generated in a similar fashion.



POLY 471: Magnetic field triggered degradation of xylan with a xylanase-copolymer conjugate for controlled drug delivery

Tyler Richardson, *tyler96@uga.edu. chemistry, University of GA, Athens, Georgia, United States*

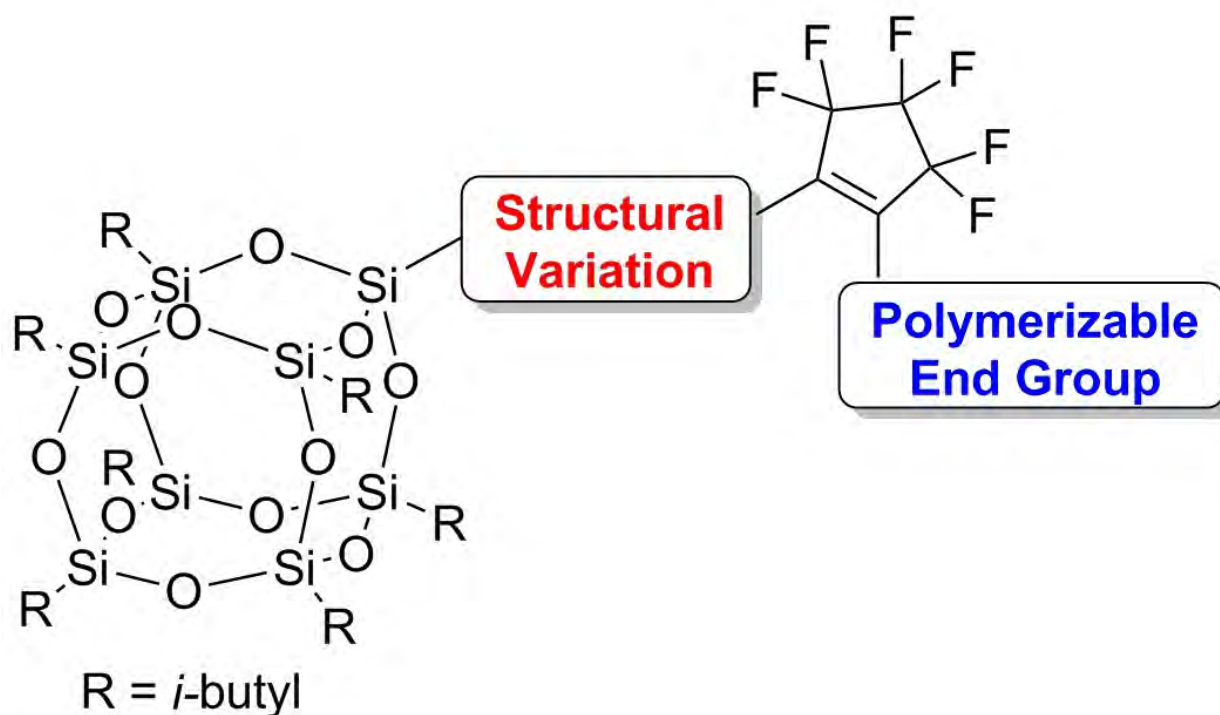
We have developed a concept of magnetic field-directed drug delivery system with two different populations of hybrid magnetic nanoparticles (MNPs). Each hybrid particle consists of an inorganic superparamagnetic core, however one is coated with the enzyme xylanase and the other with its substrate, a linear polysaccharide of xylan. These particles are responsive to an external magnetic field which when activated, aggregates the molecules together triggering the local biocatalysis of xylan degradation thus releasing the drug molecules at the site of interest. The set of hybrid particles consisting of a magnetic core coated with xylan is used to bind and protect the drug molecule while the second set of MNPs were coated with an amino functionalized silica layer which has the ability to immobilize a specially prepared xylanase-copolymer conjugate exhibiting improved biocatalytic efficiency as well as improved structural stability. The two sets of MNPs in colloidal suspensions were triggered with an external magnetic field to aggregate together and the biocatalysis of xylan degradation was monitored successfully using fluorescence spectroscopy.



POLY 472: Development of new fluorocyclic-polyhedral oligomeric silsesquioxane containing polymers of varying architectures

Emeline C. Lochmaier¹, c17emeline.lochmaier@usafa.edu, **Abby R. Jennings**², **Scott T. Iacono**³. (1) Chemistry, United States Air Force Academy, USAF Academy, Colorado, United States (2) Chemistry Research Center, United States Air Force Academy, Colorado springs, Colorado, United States (3) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States

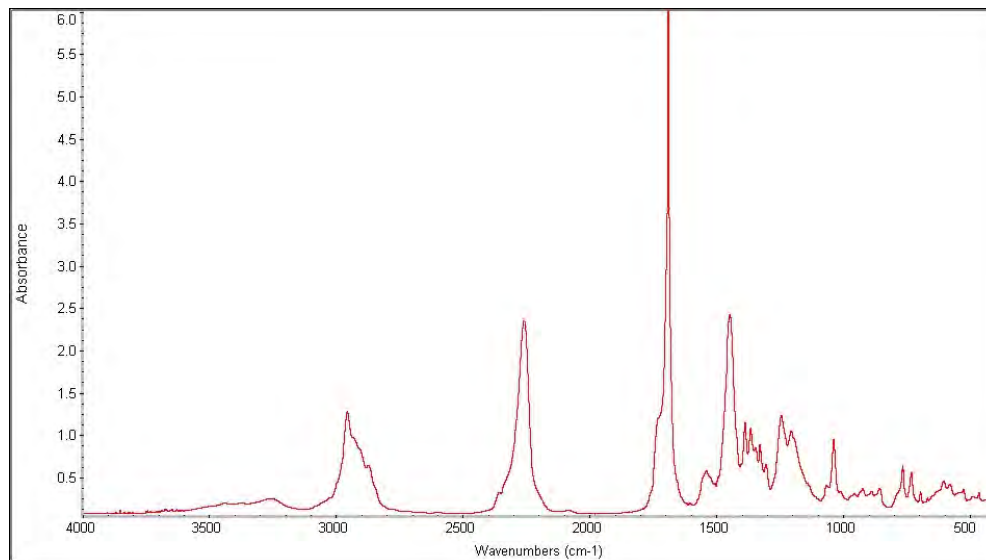
As polyhedral oligomeric silsesquioxane (POSS) structures become more prevalent in the literature, the demand for new compounds that utilize this unique nanometer-sized building block increases. Furthermore, by altering the composition of the POSS materials, one can tailor properties, allowing for a variety of applications. While the options for incorporation of POSS compounds into polymers and composites are endless, variations in fluorocyclic-POSS compounds with low surface energy are few and far between. This work will highlight the design of new fluorocyclic-POSS monomers that can easily be incorporated into polymeric materials. As a result of the structural variations of the fluorocyclic-POSS monomers, polymers of differing architectures are expected. To better understand this, model compounds were synthesized and used to evaluate the potential polymerization of the fluorocyclic-POSS building blocks. The results of these initial synthetic studies will be discussed.



POLY 473: Amphiphilic polyurethane coatings for fouling release applications

Ryan Burgett, *burgettryan@gmail.com*, Dean C. Webster, Teluka P. Galhenage. Dept 2760, North Dakota State University, Fargo, North Dakota, United States

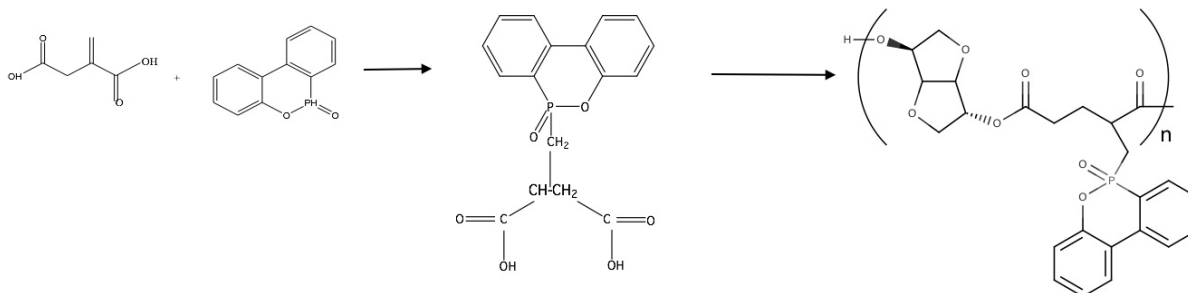
Biofouling is the buildup of organisms like algae and barnacles on submerged marine vessels. Biofouling increases frictional drag, fuel consumption and leads to migration of marine species into non-native environments. In the past, to combat BF, antifouling coatings containing tin or copper biocides were used. Toxicity of the coatings to non-target organisms has led to their replacement with elastomeric FR coatings. To overcome the lack of strength of the commercial FR coatings, self-stratified FR coatings, based on siloxane (PDMS) and polyurethane (PU), were developed in the Webster group. Further research showed that some organisms (Such as barnacles) attached strongly to hydrophilic surfaces while other organisms (Diatoms) preferred attachment to hydrophobic surfaces. Therefore, a combination of PEG and PDMS was required to understand an amphiphilic effect on the marine organisms. In one such attempt, Amphiphilic siloxane-polyurethane (AmSiPU) coatings were prepared using polyisocyanate modified with polyethylene glycol (PEG) and polydimethyl siloxane (PDMS) of varying molecular weights with, catalyst, solvent, acrylic polyol, and pot life extender. The pre-polymers of modified polyisocyanate with PDMS and PEG were characterized with Fourier Transformed Infrared Spectroscopy (FTIR) and isocyanate titrations. The pre-polymers were then integrated into coatings and characterized using mechanical testing. The resultant coatings showed high FR towards bacteria, diatoms, green algae, and barnacles. These AmSiPU compositions displayed similar or better FR performance to several of the latest commercial standards. These coatings also had the additional benefits of high mechanical strength and adhesion to primed substrates. Water contact angle was measured to reveal the coatings undergoing rearrangement at the surface with the introduction of water.



POLY 474: Oligomeric flame retardants for polymeric materials from itaconic acid

Victoria Hill, hill2vr@cmich.edu, Bob Howell, Yoseph Daniel. Chemistry & Biochemistry, Central Michigan University, Saranac, Michigan, United States

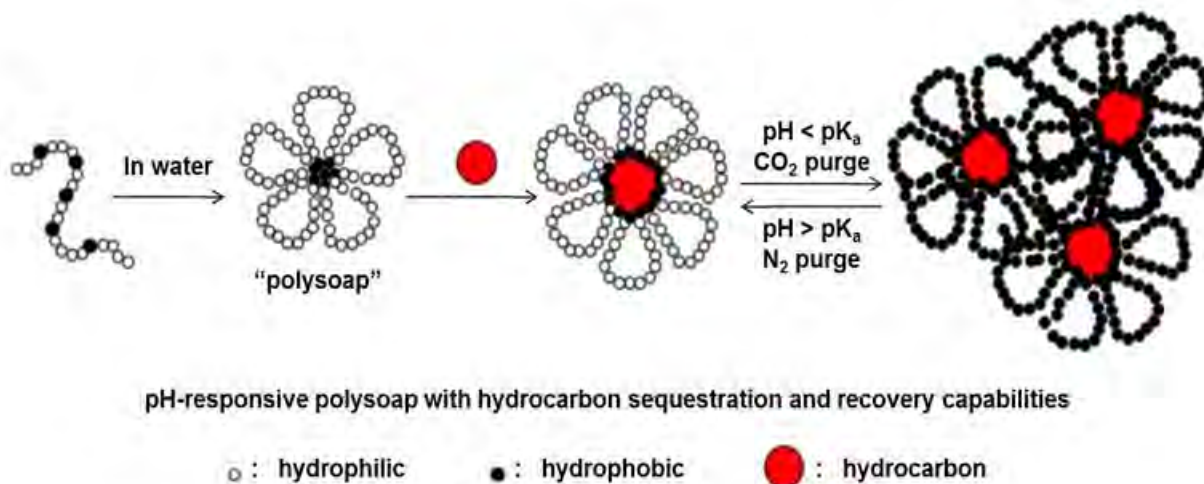
Itaconic acid is a four-carbon diacid containing a methylene group at the 2-position and is readily available from biosources. Michael addition of phosphites to the methylene group provides a route to a variety of phosphorus compounds. These compounds may be applied directly for flame-retarding of cellulosic fibers, principally cotton. Alternatively, they may be converted to oligomers with appropriate diols [isosorbide, 2,5-bis(hydroxymethyl)furan, substituted hydroquinones, etc.]. These oligomers should function as effective, non-migrating replacements for potentially toxic organohalogen flame retardants in a variety of polymeric materials.



POLY 475: Polysoaps to serve as stimuli-responsive micelles for environmental remediation applications

Christopher R. Kasprzak^{1,2}, chriskasprzak123@gmail.com, Phillip D. Pickett², Charles L. McCormick². (1) Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, San Luis Obispo, California, United States (2) Univ of Southern Mississippi, Hattiesburg, Mississippi, United States

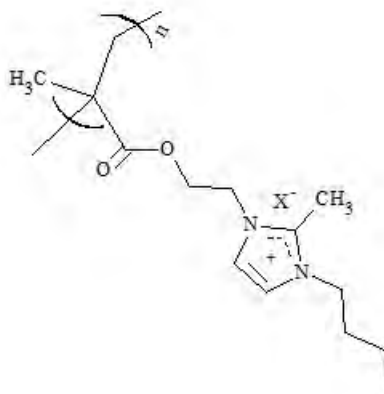
In this work, pH/CO₂-responsive polysoaps were prepared by incorporating functional sulfonamide monomers into a copolymer backbone. Upon lowering the pH or purging with CO₂, these copolymers become water insoluble, resulting in copolymer precipitation or phase separation from water. These responsive systems consist of methacryloyl sulfamethazine (mSMZ) as the hydrophilic monomer and 4-hexylphenyl methylacrylamide (4HPhMA) as the hydrophobic monomer. The sulfonamide polysoaps form micelles with well-defined hydrophobic domains capable of hydrocarbon uptake in water. All polysoap samples exhibited excellent CO₂-responsiveness with large decreases in % transmittance. The sPS10 sample demonstrated near complete reversible solubility upon purging with N₂. Additionally, hydrocarbon removal from water is possible as evidenced by decreases in pyrene absorbance after phase separation and centrifugation of all the polysoap samples. These materials appear to be good candidates for water treatment or other environmental remediation applications.



POLY 476: Counterion effects on the glass transition temperature of ionic liquid polymers

Ashley Mayers², axm2587@rit.edu, **Samual Lucisano**¹, **Thomas W. Smith**³. (1) Rochester Institute of Technology, Rochester, New York, United States (2) Rochester Institute of Technology, Rochester, New York, United States (3) School of Chemistry and Materials Science, Rochester Institute of Technology, Webster, New York, United States

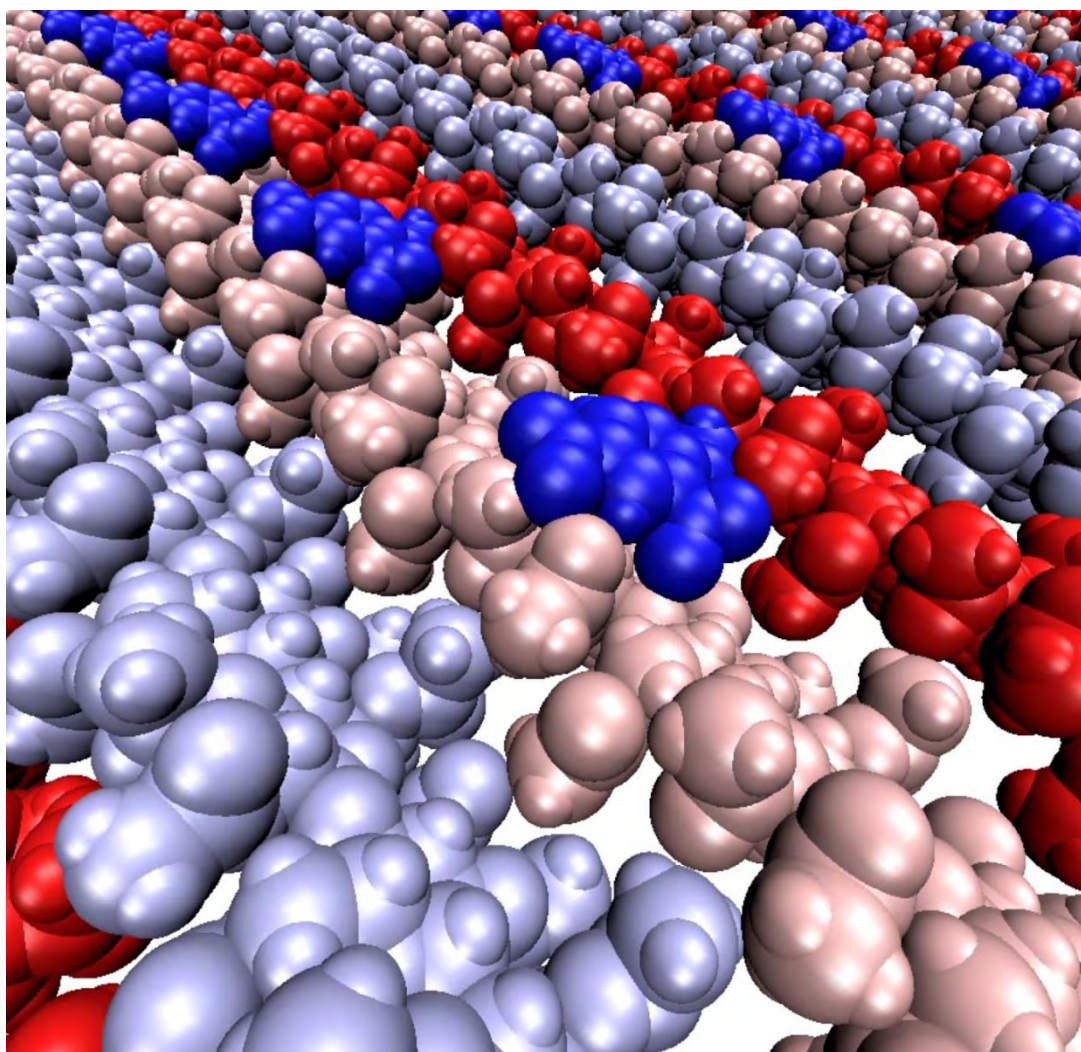
Poly(ionic liquids) (PILs), polymers synthesized by polymerizing ionic liquid monomers, have drawn considerable attention due to their potential utility as electrolyte membranes in capacitive electronic devices, (super capacitors, fuel cells, etc). Elabd at Drexel University studied acrylic imidazolium PIL's and observed that the conductivity and the glass transition temperatures of these polymers were dependent on the size of the counter anion. The glass transition temperature in these polymers decreased linearly with the increased size of the counter anion. Smith at RIT has also studied imidazolium-based PIL's and has observed that the glass transition temperatures of polymers derived from 2-substituted 4 -vinyl imidazolium salts may be substantially independent of the counter anion size. In order to further explore the impact of counterion size on the glass transition temperature of 2-substituted imidazolium polymers, 1-[(2-methacryloyloxy)ethyl]-3-butyl-2-methylimidazolium bromide was synthesized, polymerized, and ion-exchanged with bis(trifluoromethanesulfonyl) imide (TFSI), tetrafluoroborate (BF_4), trifluoromethanesulfonate (Tf), and hexafluorophosphate (PF_6). The effect of the counterion on the glass transition temperature will be reported.



POLY 477: Ab initio Monte Carlo simulations of military contaminants binding to cellulose and its derivatives

Tristan Truttmann¹, tristan.truttmann@gmail.com, **Michael Roth**², **Guido Todde**², **Manoj K. Shukla**³, **Gopinath Subramanian**². (1) Chemistry, Macalester College, St. Paul, Minnesota, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (3) Department of Plant and Environmental Sciences, New Mexico State University, Las Cruces, New Mexico, United States

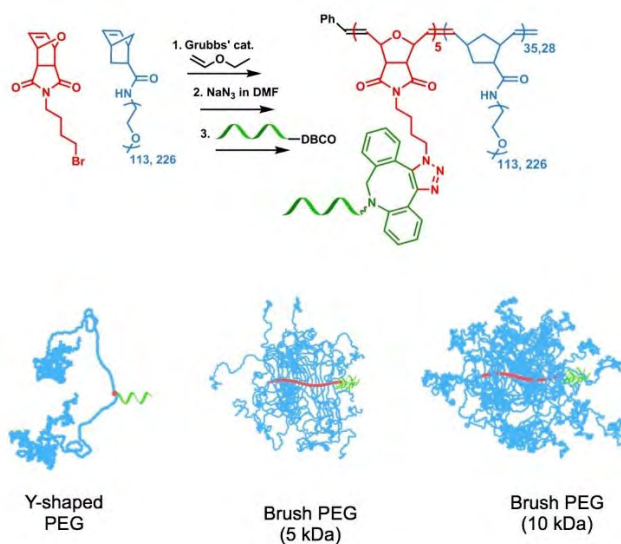
Monte Carlo simulations are typically carried out using molecular mechanics force fields due to their low computational cost. However, due to recent advances such as parallel computing, linear-scaling density functional theory, and metadynamics, it is now practical to do Monte Carlo simulations using quantum chemistry techniques, even on systems with hundreds of atoms. Here I present our work creating Monte Carlo software to screen for potential environmental remediation materials by calculating their binding energy to common explosives.



POLY 478: Reducing immune response of nucleic acids by brush polymer assisted compaction

Michelle Corley³, michellecorley72@gmail.com, Xueguang Lu², Xueyan Cao², Ke Zhang¹. (1) Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States (2) Ht102, Northeastern University, Boston, Massachusetts, United States (3) Winthrop University, Rock Hill, South Carolina, United States

Nucleic acids have been envisioned as therapeutics since 1970s. However, their applications as therapeutics are hindered by poor cell entry properties and an abundance of unfavorable side effects such as eliciting an immune response, enzyme-driven degradation, interference with the coagulation pathway, and clearance by the reticuloendothelial system. DNA sequences, which contain CpG motifs, can trigger severe immune response by interacting with Toll-like receptors. Recently, our lab has developed a non-cationic, polyethylene glycol brush polymer-DNA conjugate (pacDNA), which causes the DNA component to selectively bind to a complementary strand, and prevent interaction with proteins by steric hindrance. Previous studies have shown that pacDNA structure shows enhanced cellular uptake ability, enzymatic stability and biodistribution compared with molecular DNA. Herein, we demonstrate that pacDNA is able to reduce the immune response by protecting the oligonucleotides from interaction with Toll-like receptors. Three different brush-polymer-DNA conjugates with different degree of steric congestion were synthesized and incubated with macrophage RAW264.7 cells. The cytokines associated with immune response were quantitatively measured in both RNA and protein level by qPCR and ELISA assay. Our data imply that the better steric congestion of DNA leads to lower immune response. On the other hand, Lipofectamine 2K, which is a commercially available cationic transfection agent, triggers a significant higher production of certain cytokines compared with pacDNA.

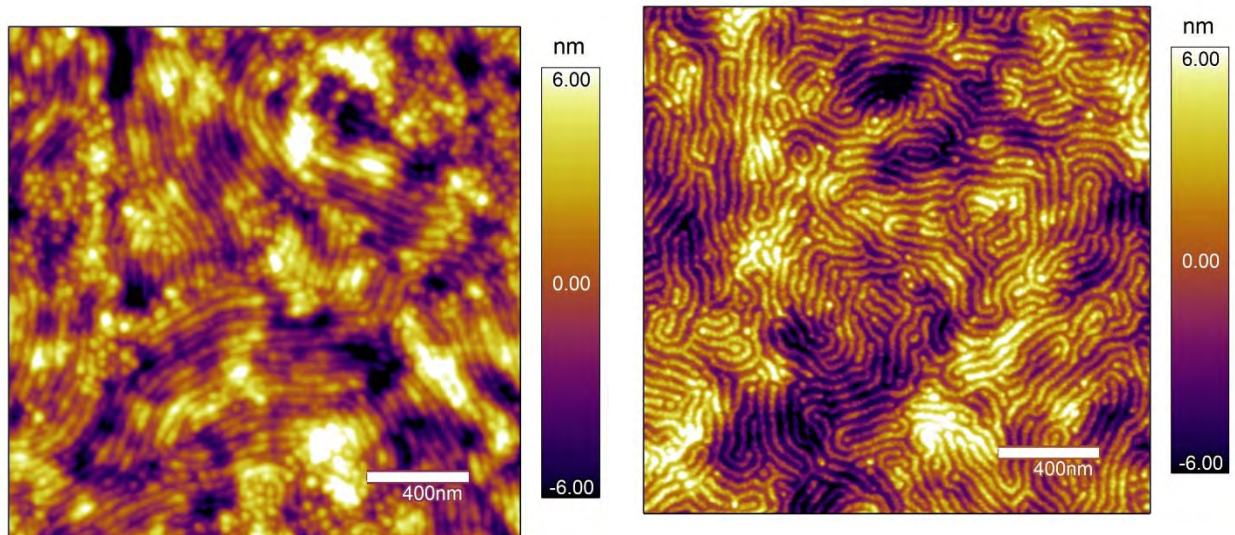


Synthesis of pacDNA.

POLY 479: Nanomorphology of novel synthesized diblock copolymers with and without lithium salt characterized by atomic force microscopy

Megan Longstaff, longstmr@plu.edu, Dean A. Waldow. Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States

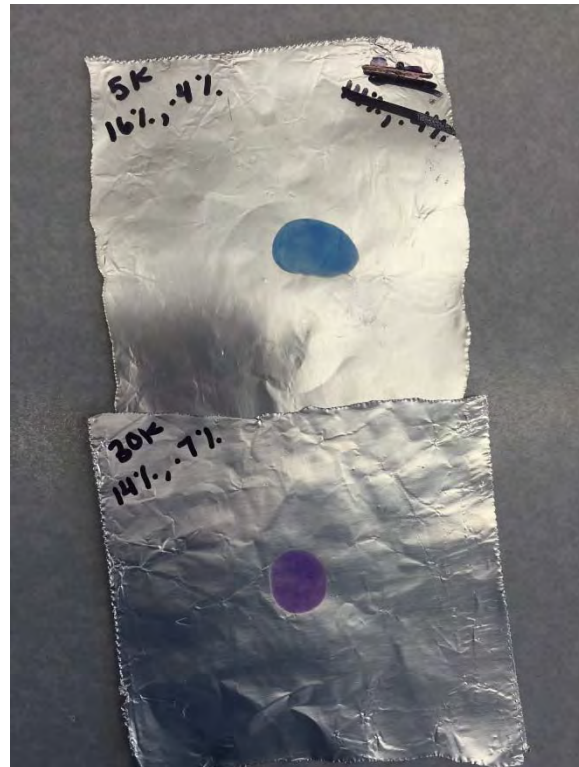
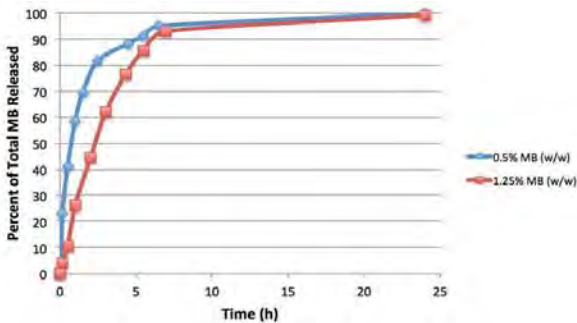
Novel diblock copolymers were synthesized by a ring-opening metathesis polymerization for use as solid polymer electrolytes in lithium ion batteries. The polymers were made to decouple the segmental motion from ionic conductivity with a bulky backbone to make safer batteries by also preventing dendrite formation in the electrolyte. These polymers have varying percent compositions and molecular weights of two blocks that share an identical backbone. One monomer has a phenyl group resulting in a block with a higher modulus and the other has an oligomeric ethylene oxide (EO) chain for ionic conductivity. Atomic force microscopy was used to study the nanomorphology of the neat diblocks and with added bis(trifluoromethane)sulfonimide lithium salt. The ordered morphology of the polymer with only spin coating was poor, but solvent vapor annealing induced and reinforced order throughout the sample. Salt improved the order and showed similar increased order as that from solvent vapor annealing. Samples with dissolved salt and solvent annealing were found to preserve order or induce longer range order. Each composition of polymer showed unique results and order. Grazing-incidence x-ray scattering was performed to compare to the surface topography. Testing the conductivity is the next step in determining the effectiveness of the polymers as solid polymer electrolytes.



POLY 480: Time-Dependent release of methylene blue from PEO-*b*-PCL films for the prevention of anaphylaxis

Hannah Fischer², fischerh@allegheny.edu, **Justin E. Jurczyk**², **Mark Seraly**², **Ryan M. Van Horn**¹. (1) Allegheny College, Meadville, Pennsylvania, United States (2) Chemistry, Allegheny College, Pittsburgh, Pennsylvania, United States

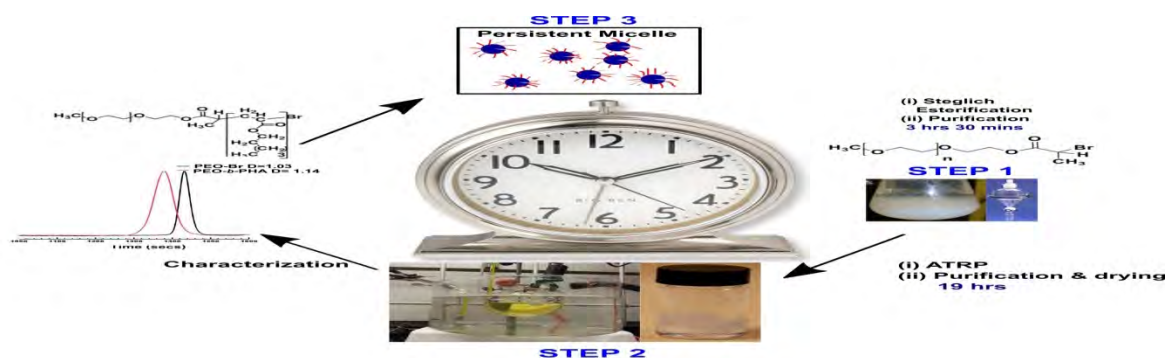
PEO-*b*-PCL diblock copolymer films of varying molecular weight were integrated with methylene blue (MB) dye and prepared under various conditions to determine their respective MB release rates. Prepared films were placed in DI H₂O, and UV-Vis spectroscopy was used to measure the solution's absorbance to determine MB concentration after diffusion into the water. Data was taken over time to determine the amount and rate of MB released. Release rates were influenced by the molecular weight ratio of the film and showed a fast release, a slow release, or a combination.



POLY 481: Synthesis and fabrication of Persistent Micelle Templates (PMT) in a single day

Amrita Sarkar¹, asarkar@email.sc.edu, **Morgan Stefik**². (1) Chemistry, University of South Carolina, Columbia, South Carolina, United States (2) Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States

Persistent micelle templates (PMT) enable a vast range of materials with independently tunable pore and wall dimensions. The use of a high- χ block copolymer such as poly(ethylenoxide-*block*-hexyl acrylate) (PEO-*b*-PHA) is needed, but are generally not commercially available. Furthermore, the need to synthesize custom block copolymers poses a significant barrier to entry. Here we present new strategies to enable the synthesis of PMT in less than 24 hrs and starting from low-cost commercially available reagents without the use of high-vacuum equipment. The steps include 1) synthesis and purification of Br-terminated poly(ethylene oxide) by Steglich Esterification and 2) ATRP chain extension followed by purification and 3) persistent micelle templating of metal oxides. Large batches of purified PEO-*b*-PHA were obtained with as little as 22.5 hrs. The persistent micelle conditions were determined from simple DLS experiments and validated by GISAXS and SEM. This facile and rapid pathway enables widespread development of PMT techniques to support broad nanomaterial investigations.



Synthesis and fabrication of Persistent Micelle Templates in a single day

POLY 482: Rapid free-electron initiated selective polymerization at room temperature

Boyce Chang, *boyce@iastate.edu*, *Stephanie Oyola-Reynoso*, *Jiahao Chen*, *MingChang Lu*, *Martin Thuo*. *Materials Science and Engineering, Iowa State University, Ames, Iowa, United States*

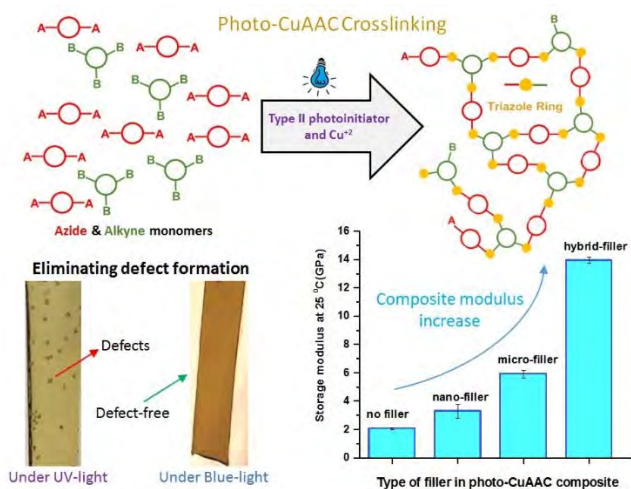
Solvated (free) electrons have intriguing properties and their complexity continues to bewilder us today. As part of the effort to expand our library of methods in polymer synthesis, we demonstrate the application of solvated electrons, which can be prepared at room temperature, in rapid and selective polymerization of commercially available monomers. The molecular weight distribution of the resulting polymer was found to be closely related to its solubility in the solvent used, whereby a departure from the expected normal distribution was observed in poor solutes. Furthermore, although monomers with negative inductive effects proved to be a requirement, our observations do not fully agree with purely anionic mechanism, leading to the proposal of a bi-mechanistic radical anion polymerization. This method is then further employed as a straightforward approach for producing block copolymers. Also, from using solvated electrons, we also exploit these high energy species to initiate polymerization of otherwise inactive monomers such as greenhouse gases (CO₂ etc).



POLY 483: Blue-light activated bulk photo-Cu(I)-catalyzed azide-alkyne cycloaddition (photo-CuAAC) click reaction-based networks: Properties and application

Abhishek Shete¹, ashete@udel.edu, **Bassil El-Zaatar**², **Christopher J. Kloxin**^{1,2}. (1) *Materials Science and Engineering, University of Delaware, Newark, Delaware, United States* (2) *Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States*

The photopolymerized bulk copper-catalyzed azide alkyne cycloaddition (photo-CuAAC) click reaction for crosslinked networks display unique features such as, spatial and temporal control over the reaction, and delayed gelation in the network. Hence, it is explored in diverse applications like wrinkle formation and photolithography. However, defects are observed during photo-CuAAC that compromises the sample integrity on polymerizing the network under UV light, which we hypothesize is due to the decomposition of azide functional group into a reactive nitrene and nitrogen gas. We show that a Norrish Type II photoinitiating system activated using blue-light prevents azide decomposition and accelerates the bulk photo-CuAAC polymerization (>75% conversion in 10 minutes), producing a glassy, transparent, and defect-free material. The photopolymerized networks are characterized using real-time Fourier transform infrared (FTIR) spectroscopy and dynamic mechanical analysis (DMA). The reaction exhibits dark polymerization after irradiation is ceased enabling higher conversion. Additionally, the step-growth nature of the CuAAC polymerization exhibits a characteristic narrow glass transition temperature (T_g). The incorporation of inorganic filler, such as silica, enhances the mechanical properties without compromising the positive kinetics and mechanical property attributes described for the unfilled resin. Moreover, the mechanical properties are readily tuned by using different filler size distributions. Specifically, the introduction of nano-sized and micro-sized fillers results in a 7-fold increase in modulus, from ≈ 2 GPa to ≈ 14 GPa, and a 15 °C increase in T_g , making this composite material a viable substitute for traditionally employed UV-curable methacrylate and epoxy composites.



POLY 484: Aza-Michael reaction applied to PDMS: Kinetic modelling, selectivity control and novel potentialities

Aymeric Genest^{1,3}, Sandra Binauld^{1,3}, Emmanuel POUGET², François Ganachaud^{1,3}, Etienne Fleury^{1,3}, **Daniel Portinha**^{1,3}, daniel.portinha@insa-lyon.fr. (1) IMP INSA de Lyon, Villeurbanne, France (2) Bluestar Silicones, , St-Fons, France (3) Université de Lyon, Lyon, France

The high chain flexibility, chemical robustness, low surface tension, high moisture resistance and low toxicity etc... are some of the reasons why poly(dimethylsiloxane) (PDMS) derivatives have been used for more than 60 years as high performance elastomers in numerous and various applications (e.g. in biomaterials, personal care products, semi-conductor devices and so on). However, to meet new requirements and broaden the domains of application of such polymers, it is important to develop synthetic strategies that allow the introduction of novel functionalities without, if possible, the use of metal-based catalysts. In this context, we have been interested in applying Aza-Michael addition reaction to PDMS-polymers: this reaction implies an amine as nucleophile and an electron-deficient alkene as acceptor, and may benefit from mild conditions (no metallic catalyst, no solvent, low T) and allows high yields with no by-product. Yet controlling perfectly the reaction remains an issue; indeed a primary amine can undergo two successive additions, such that a mixture of (1°, 2° and 3°) amines may result if the reaction is not well controlled (Figure 1). This communication deals with the understanding of the aza-Michael addition involving primary amine containing PDMS and various acceptors. For such purpose, the impact of operating conditions (such as T, organo-catalysts, type and amount of solvent) on the kinetics and the selectivity control on a model system will be presented. In particular, our attempts to obtain 100% mono-adduct (2° amine) or 100% di-adduct (3° amine) in a reasonable timescale will be discussed. The extension of the optimized conditions to various systems that differ in the donor molecular weight or structure (α,ω -telechelic or graft PDMS, amine content) or different acceptors demonstrates the robustness of such technology to synthesize polymers with controlled structures and novel properties.

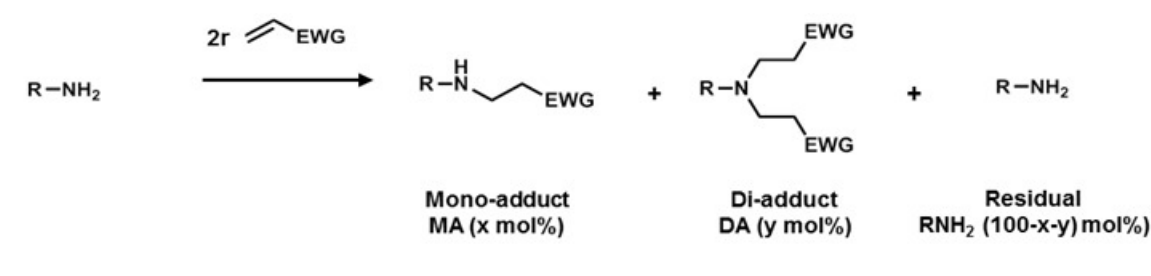
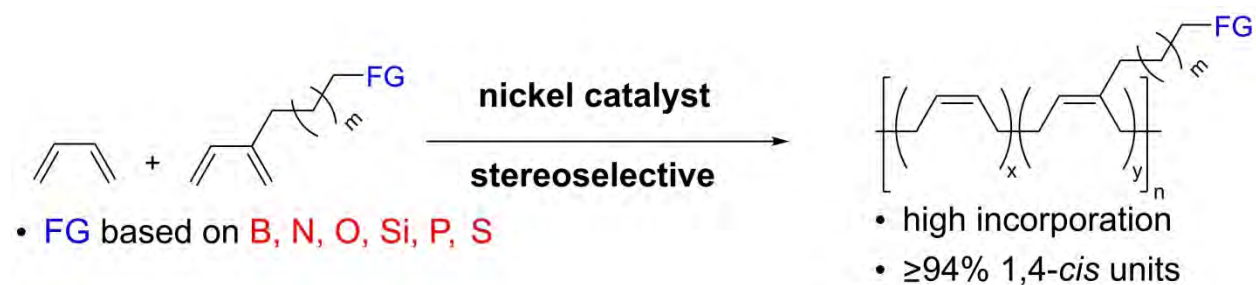


Fig 1: Aza-Michael addition of a primary amine to an electron-deficient alkene, and possible amine structures present at a given time

POLY 485: Stereoregular copolymerization of butadiene with heterofunctionalized diene monomers

Inigo Goettker Genannt, *inigo.goettker@uni-konstanz.de*, Hannes Leicht, Stefan Mecking. Department of Chemistry, University of Konstanz, Konstanz, Germany

Nickel catalyzed copolymerization of butadiene with silicon-, nitrogen-, sulfur-, oxygen-, boron-, and phosphorous-functionalized dienes exhibiting high regio- and stereocontrol, and a remarkably high comonomer incorporation into the formed copolymer will be reported. Decreasing overall polymerization rates in these copolymerizations are strongly correlated to increasing copolymerization parameters favoring functional comonomer- over butadiene incorporation. Steric modifications of the functionalized diene allow for the generation of gradient- or statistical copolymers by influencing copolymerization parameters. We will discuss a model rationalizing these observations.



POLY 486: Investigations on polystyrene – C60 nanocomposites

Elamin Ibrahim², *elamin.ibrahim@utrgv.edu*, **Sarahi Casas**², **Dorina Chipara**¹, **James Hinthorne**¹, **Mircea Chipara**¹. (1) Physics, University of Texas Rio Grande Valley, Edinburg, Texas, United States (2) Chemistry, University of Texas Rio Grande Valley, Edinburg, Texas, United States

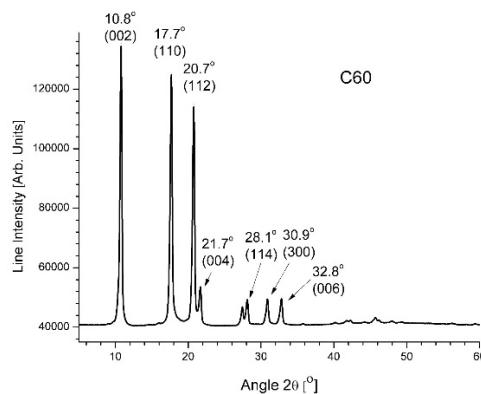
Atactic polystyrene is a very simple polymer, technically completely amorphous, characterized by a glass transition temperature at about 100 °C. The exact position of glass transition temperature depends on the average molecular mass of the polymer, experimental technique used to determine the glass transition, and the time scale of the experiment. The thickness of the polystyrene film and the presence of submicron fillers can modify the glass transition temperature.

C60 is a very small spherical molecule, with a diameter of about 1 nm, soluble in some organic solvents such as toluene. C60 crystallizes rapidly in a face-centered cubic configuration at room temperature and exhibits a transition towards a simple cubic structure at about 249 K.

Atactic polystyrene was purchased from Sigma Aldrich and C60 from Cheaptubes Inc. Various amounts of C60 have been dispersed within polystyrene by dissolving the polymer and the C60 in toluene followed by the mixing of the two solutions. In order to achieve a dispersion of C60 as good as possible, the mixture was stirred 1h at 500 rpm and then sonicated for 30 minutes at 50 W.

Polystyrene-C60 (PSC60) nanocomposites have been obtained by evaporating the solvent in an oven at 90 °C for 12 hours. TGA measurements confirmed the removal of the solvent. Differential Scanning Calorimetry was used to determine the crystalline transition of C60 at about 250 K and the glass transition temperature in PS-C60 nanocomposites. Several heating rates (1 °C/min, 4 °C/min, 8 °C/min, 12 °C/min, 16 °C/min, and 20 °C/min) have been used to determine the WLF parameters, glass transition temperature, C1g, and C2g.

Wide Angle X-Ray spectra have been used to further understand the crystallization of C60 in polystyrene, and to determine the effect of the polymeric matrix on the lattice parameters and on the size of C60 crystallites. The effect of C60 on the glass transition of polystyrene is investigated in details and analyzed within the free volume approximation.

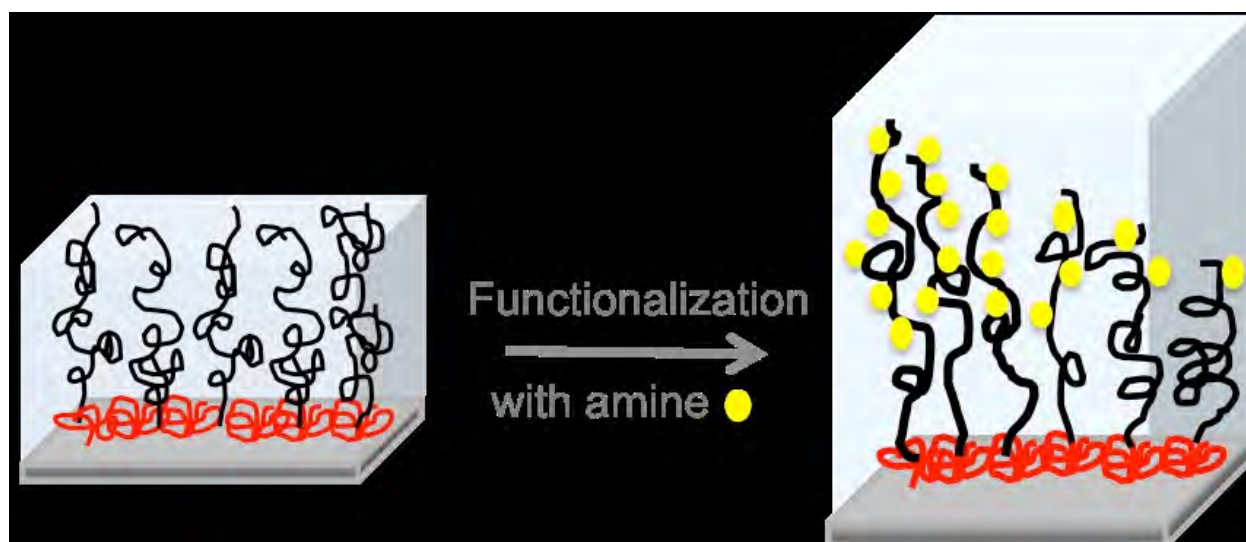


WAXS spectrum of as received C60

POLY 487: In situ gradient functionalization of azlactone-based block copolymer brushes

Bethany M. Aden¹, baden@vols.utk.edu, **Brad S. Lokitz**², **Michael Kilbey**¹. (1) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (2) Bldg 8610 MS 6494, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Reactive modification of polymer thin films provides a useful route to confer new properties to the underlying material, with the range, strength and type of interaction across the interface dictated by the display of functional groups decorating the surface. The design and development of gradient surfaces is an efficient technique to control and optimize the extent of chemical functionality for surface modifications that is useful for tuning properties. To address the links between design, *in situ* gradient functionalization and properties, layers of end-tethered polymer chains, or polymer brushes, were created by grafting chains of poly(glycidyl methacrylate)-block-(2-vinyl-4,4-dimethylazlactone) (PGMA-b-PVDMA) onto silicon substrates. The pendant azlactone rings of PVDMA readily react with nucleophiles, allowing *in situ* functionalization to be studied through the use of ellipsometry and neutron reflectivity measurements as a function of parameters that affect brush structure. The results indicate that the grafting density of chains and size of the functionalizing agent govern the extent of functionalization. In addition to an average view of the *in situ* functionalization process through ellipsometry, the sensitivity of neutron scattering methods to isotopic substitution (of D for H) provides insight into the location of functional groups installed within the PVDMA brush by reactive modification. These studies yield relationships between extent of reaction in the confined environment, the spatial display of functional motifs, and the swelling properties of the interfacial layer, as well as insight into general strategies that can be used to tailor frictional, adhesive, or biomimetic properties of polymer thin films.



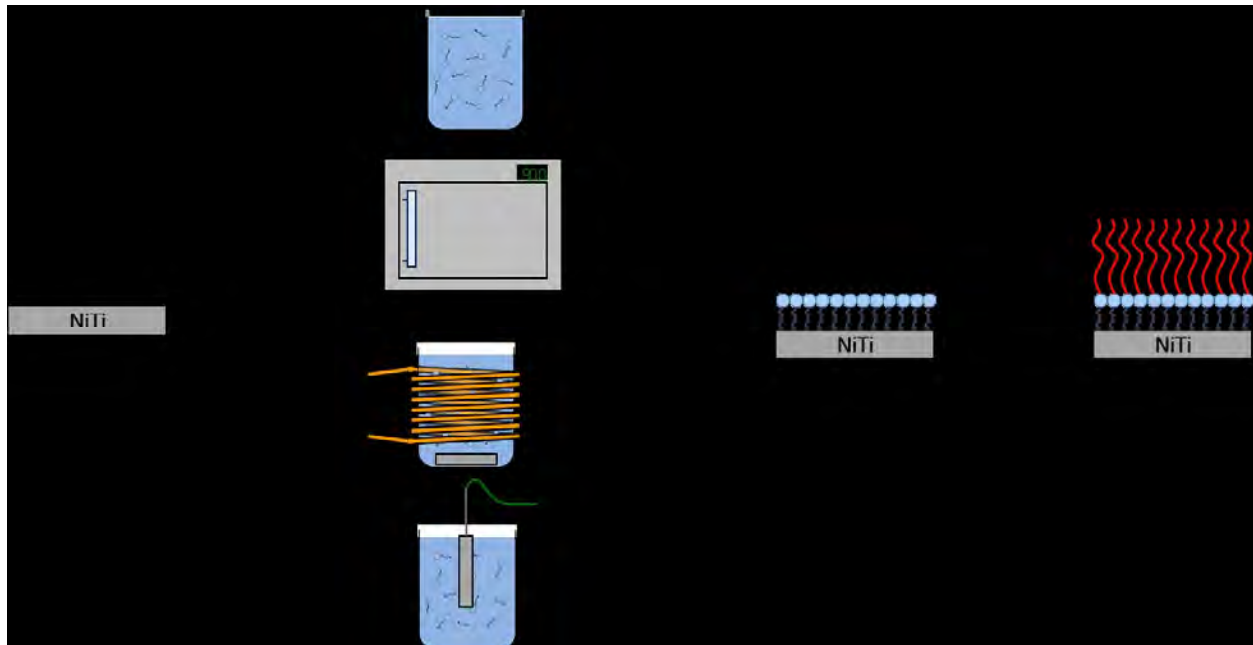
POLY 488: Improvement of nitinol corrosion resistance by SiATRP: The key role of electrografting process

Bastien Arrotin^{1,3}, Joseph Delhalle³, Philippe Dubois^{2,3}, Zineb Mekhalif³, Laetitia M. Mespouille¹, laetitia.mespouille@umons.ac.be. (1) University of Mons, Mons, Belgium (2) CIRMAP - SMPC, University of Mons UMONS, MONS, Belgium (3) Chemistry, University of Namur, Namur, Belgium

The coating of Nitinol (NiTi) surface by a polymer layer has become very appealing these last few years owing to its increased attractiveness in the biomedical field. While its intrinsic properties helped ensure its popularity [1,2], its worldwide implementation is still hampered by nickel inclusions, making it sensitive to pitting corrosion and lead therefore to the release of carcinogenic Ni²⁺ ions.

Among all the recent ways to modify Nitinol surfaces, the elaboration of self-assembled monolayers (SAM) that can kick off the initiation of a polymer layer is of great interest as their high order confer a reinforcement of the metal surface corrosion resistance, and allow to bring new functionalities to the metal for post-modification purposes.

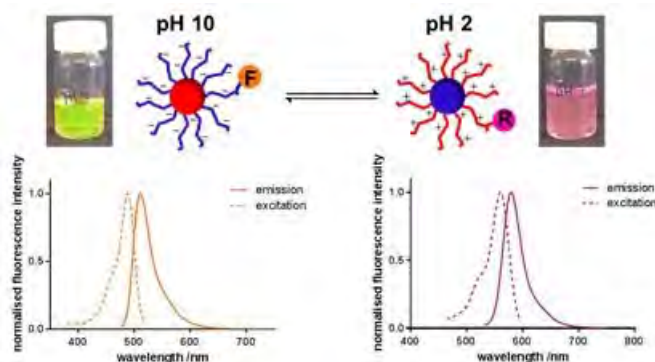
In this work, we emphasize the benefits of electro-grafting [3] assisted functional monolayer self-assembly onto nitinol alloy compared to the more traditional thermally-assisted ones by the preparation of functional monolayers that could initiate the SI-ATRP of a model monomer. More particularly it will be demonstrated how electro-grafting process allow fast SAM preparation in mild conditions while preventing degradation of ATRP initiating sites. The proof of concept is validated by initiation of poly 2-(dimethylamino)ethyl methacrylate (PDMAEMA) by ATRP and the characterization of properties of the resulting materials.



POLY 489: Zwitterionic diblock copolymer nanoparticles prepared by polymerization-induced self-assembly exhibit pH-responsive schizophrenic behavior

Sarah L. Canning, *s.canning@sheffield.ac.uk*, Steven P. Armes. Univ of Sheffield Dept of Chem, Sheffield, United Kingdom

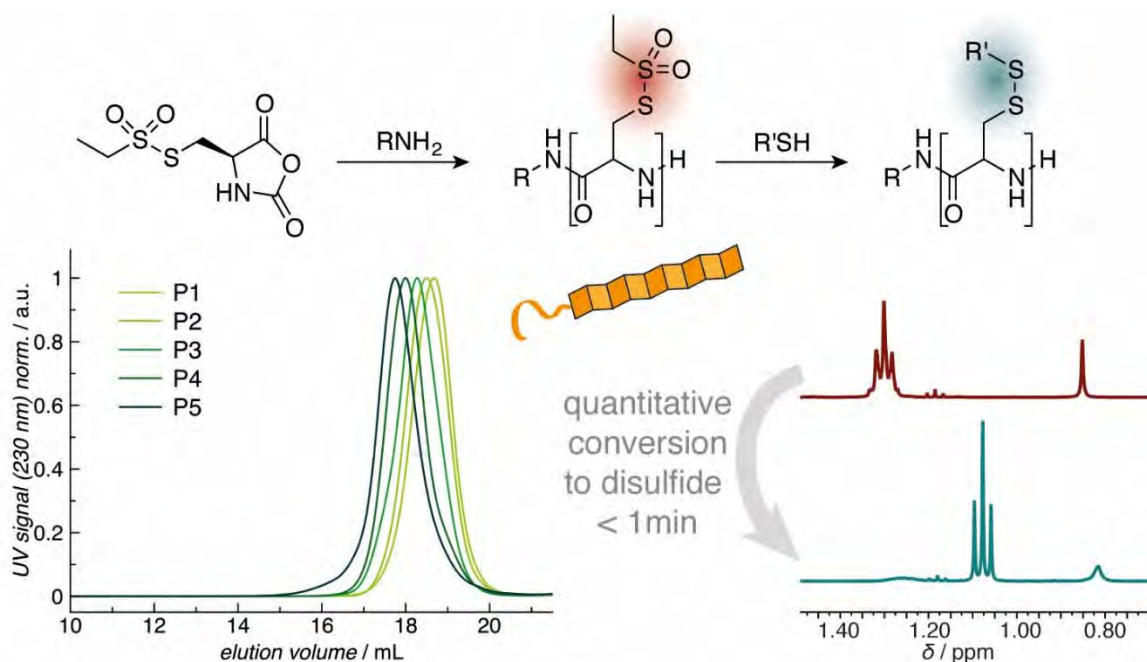
It is well-known that amphiphilic AB diblock copolymers self-assemble to form micelles in aqueous solution. However, certain AB diblock copolymers are able to form two types of micelles, with either the A block or the B block forming the micelle cores. In this case, both blocks are stimulus-responsive, so adjustment of the solution conditions can be used to tune their hydrophilic/hydrophobic character. Such copolymers have been termed 'schizophrenic'. Literature examples include both doubly pH-responsive and doubly thermo-responsive diblock copolymers. Polymerization-induced self-assembly (PISA) offers a robust strategy for the production of well-defined diblock copolymer nanoparticles in a wide range of solvents at high solids. In the present work, we have examined PISA for the highly convenient and efficient preparation of zwitterionic diblock copolymer nanoparticles directly in acidic aqueous solution. At pH 2, cationic nanoparticles are formed comprising a protonated polyamine stabilizer block and a hydrophobic polyacid core-forming block. At pH 10, micelle inversion produces anionic nanoparticles with an ionized polyacid stabilizer block and a hydrophobic polyamine core-forming block. Macroscopic precipitation occurs at around pH 6-7, which lies close to the isoelectric point of this zwitterionic diblock copolymer. Incorporation of fluorescein and rhodamine dye labels into the acid and amine blocks respectively leads to dual-color bifluorescent self-reporting pH-responsive nanoparticles.



POLY 490: Poly(S-alkylsulfonylcysteines): The first cysteine derivatives combining stability during polypeptide synthesis with fast chemoselective disulfide formation

Matthias Barz, barz@uni-mainz.de. Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

We present a novel class of thiol-protective groups for cysteines. The thiosulfonyl based protective group provides stability against hard nucleophiles, e.g. amines, while promoting reactivity towards thiols. (1) These properties lead to a protective group, which is stable during ring opening polymerization of N-carboxyanhydrides and peptide synthesis but can be selectively addressed by thiols to form asymmetric disulfides. Therefore, poly(S-alkylsulfonylcysteines) are the first reactive amino acid derivative in NCA polymerization, which can be employed in disulfide formation without additional activation steps. (2)



POLY 491: Bio-Based oligoethers from isosorbide and 1,3-propanediol: Synthesis and characterization

*Etienne Fleury*¹, *etienne.fleury@insa-lyon.fr*, *Jean-david Rodier*², *Alain Rousseau*¹. (1) INSA-Lyon, Villeurbanne, France (2) Gattefosse, Saint-Priest, France

The research in the field of bio-based polymers knows a growing interest over years with in parallel the development of chemical building blocks thanks to the biorefineries^{1,2}. Thus 1,3-propanediol and isosorbide are among the renewable monomers industrially available for producing polymers with low carbon foot-print. In particular, isosorbide, resulting from a double dehydration of sorbitol coming from the bioconversion of starch into glucose followed by a reduction³ is recognized as a monomer for future green polymers and is already valorized in commercial polymers like polycarbonate (Durabio™)⁴. The synthesis of polyethers from isosorbide and dihalogenated alkylene was already described but to our knowledge the direct and simple reaction of etherification between PDO and isosorbide was never described before⁵. The aim of this study was thus to copolymerize isosorbide and PDO according to two different melt processes without any solvent in presence of acid catalyst: co-etherification of PDO and isosorbide (Figure 1) and trans-etherification between polytrimethylene ether glycol and isosorbide. This led in both cases to oligomers having isosorbide units at each extremity and little inner isosorbide units. This is due to a mechanism involving etherification and trans-etherification reactions where isosorbide reacts decreasing the molar mass of polymers chains. These new telechelic oligoethers have higher compatibility to water and higher Tg level and thermal stability than oligomer of polytrimethylene ether glycol⁶. Therefore such oligomers can be considered as new intermediates for designing new surfactants and/or new copolymers.

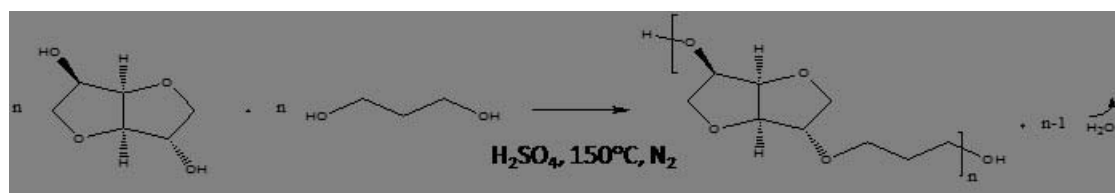


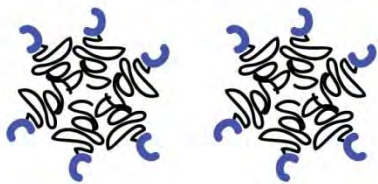
Figure 1: Etherification reaction between isosorbide and 1,3-propanediol, in acidic conditions

POLY 492: Bioinspired control of polymer self-assembly via ligand-metal ion interactions

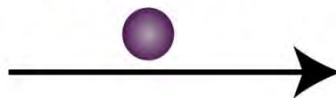
Abigail Knight², aknight@berkeley.edu, **Josefin Larsson**², **Craig J. Hawker**¹. (1) Univ of California, Santa Barbara, California, United States (2) UC-Santa Barbara, Santa Barbara, California, United States

Nature has created a vast array of responsive polymeric architectures for structural (i.e. collagen and microtubules) and functional applications (i.e. enzymes and DNA). Controlling the assembly of synthetic architectures is challenging, as we are currently limited to very few chemical strategies (change in pH, temperature, and oxidation state). Materials with responsive morphologies have significant potential as therapeutics in the dynamic biological environment. In order to design potent and efficient nanomaterial therapeutics, additional techniques that enable responses to a wide range of chemical and physical stimuli are required. Metal-ion interactions, which are critical to the structure and function of natural proteins, are currently underutilized for modulating the morphology of soft materials. We are developing a new class of nanomaterials using peptide-polymer amphiphiles that change their self-assembled morphology in response to coordinating metal ions. These smart materials open the door for developing a new class of therapeutics that interact with metal ions.

Polymeric Nanomaterial



Metal Ions



Induced
morphological
change

POLY 493: Let's get things in order: Sequence controlled anionic polymerization of aziridines

Elisabeth Rieger, *eli.rieger@gmail.com*, Tassilo Gleede, Angelika Manhart, Laura Thomi, Manfred Wagner, Frederik Wurm. Max Planck Institut für Polymerforschung, Mainz, Germany

The ugly cousin of the epoxide: *aziridines* are industrially polymerized by cationic polymerization with low control over molecular weight, structure and dispersity. The power of anionic polymerization is the preparation of well-defined macromolecules, control of microstructure and avoidance of heavy metal catalysts. No pathway *via* anionic ring opening polymerization (AROP) has been described before 2005. We recently started the investigation of the anionic polymerization of aziridines: the talk will summarize our efforts to establish sulfonamide-activated aziridines as a novel monomer family for the living anionic polymerization. The monomer family includes different pendant groups at the aziridine ring (aliphatic and aromatic) and various activating groups (such as tosyl and mesyl or ferrocenylsulfonate as a functional sulfonamide, Figure 1). A systematic investigation of the polymerization kinetics is represented and their in-situ monitoring by ^1H NMR-spectroscopy to determine the influence of different solvents, temperatures and counter ions. In particular the talk will illustrate the simultaneous azaanionic copolymerization of up to five competing monomers in an one-pot approach, also examined by real-time ^1H NMR-spectroscopy. The monomer sequence is gracefully adjusted by the monomer reactivity, related to the electron-withdrawing effect of the diversity of sulfonamide groups. This allows us for the first time to mix different monomers and control their incorporation in a multi-block copolymer with structures, ranging from random over gradient to block-like composed copolymers. Low molecular weight dispersities and living behavior was obtained in all cases. We believe that the AROP of aziridines will provide straightforward access to novel polyamides and –amines with interesting properties for a great number of applications. Furthermore it can be combined with other anionic polymerization setups with great success.

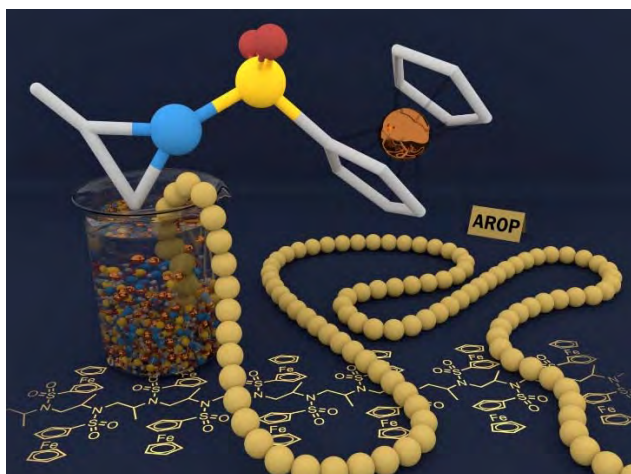


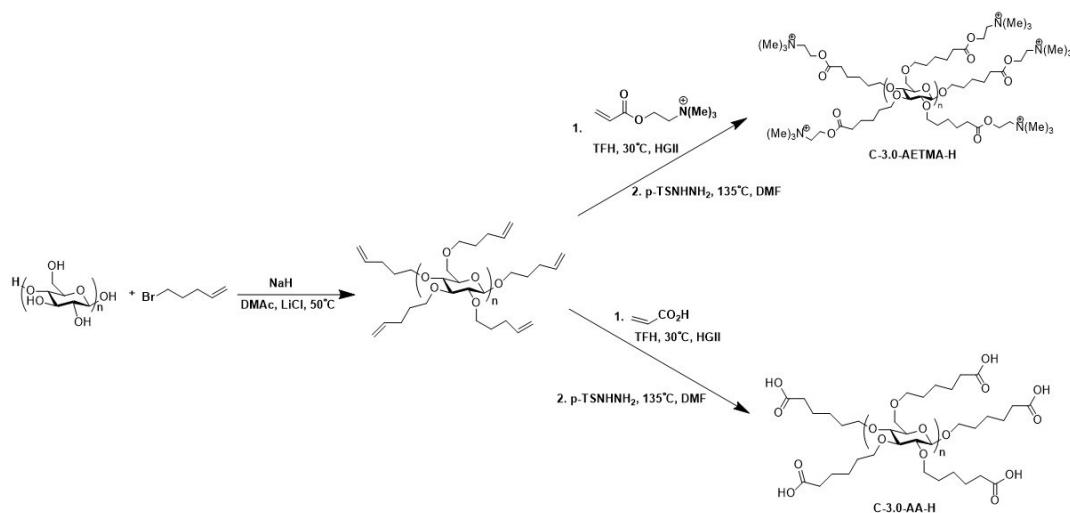
Figure 1: *N*-Ferrocenylsulfonyl-2-methylaziridine: the first ferrocene monomer for the AROP of aziridines.

POLY 494: Design and synthesis of cellulose based polyelectrolytes via olefin cross-metathesis

Brittany L. Nichols¹, brittan@vt.edu, **Kevin J. Edgar**². (1) Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Mail Code 0323, Virginia Tech, Blacksburg, Virginia, United States

Polyelectrolytes are of increasing interest in delivery applications involving charged and peptide drugs due to their ability to form polyelectrolyte complexes (PECs). Drug delivery systems composed of these complexes can avoid the need for chemical crosslinking while achieving desired physicochemical properties and maintaining high biocompatibility². Natural biomaterials such as cellulose are extremely attractive for this application due to renewability, biocompatibility and non-toxicity. Chemical modifications of cellulose to include ionic and pH sensitive groups is a promising route to novel delivery biopolymers. However, the introduction of highly charged groups to the cellulose backbone is challenging due to charge repulsion and basic reaction conditions.

We have utilized olefin cross metathesis as a synthetic strategy to overcome the challenges of charge repulsion in the synthesis of cellulose based polyelectrolytes. Olefin cross metathesis (CM) has proven to be a mild and efficient synthetic approach to impart a wide range of functionality to both cellulose esters^{3,4} and ethers¹. We have been able to utilize this strategy to fully modify cellulose with pH-responsive carboxyl groups that permit strong polymer-drug interactions. We expect these interactions to lead to the enhancement of drug solubility and bioavailability. The high functional group tolerance of CM has allowed us to reach the maximum charge content possible in both cationic (quaternary ammonium) and anionic (carboxylate) polyelectrolytes with promise for controlled release of charged and poorly soluble drugs through the formation of polyelectrolyte complexes. We report the synthesis, characterization and physical properties of these novel cellulose based hypercharged polymers and initial findings of their potential in PEC drug delivery systems.

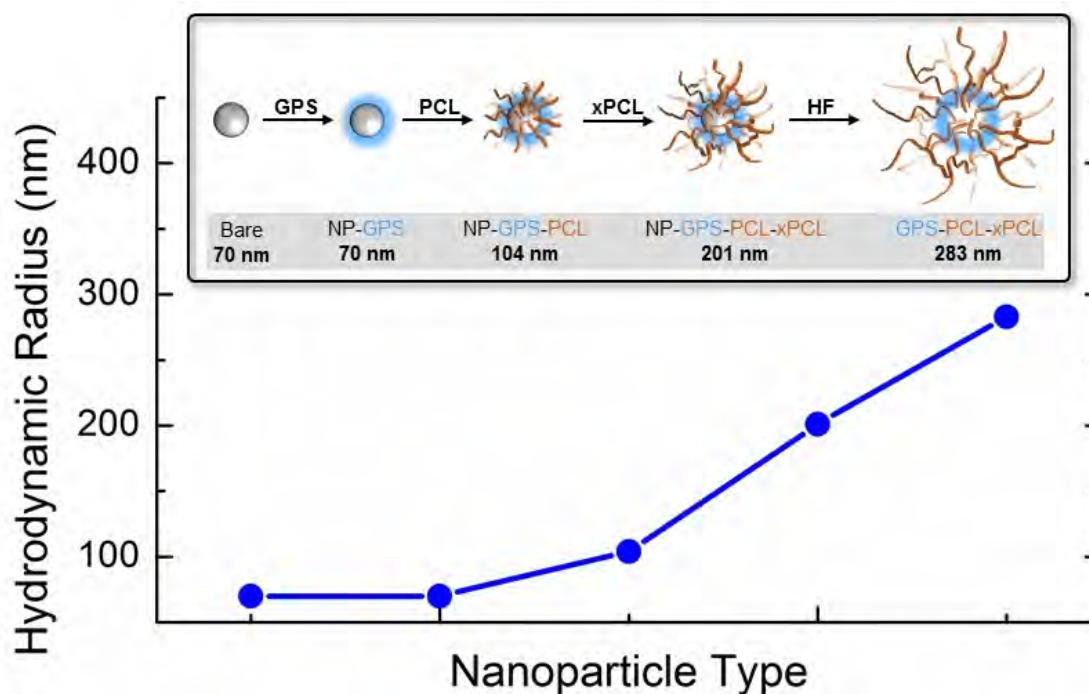


Synthesis of Cellulose Polyelectrolytes by Olefin Cross Metathesis

POLY 495: Hollow polycaprolactone nanocages from variable grafting-density polymer-grafted silica nanoparticles: Materials for next-generation oil dispersants

Kyle C. Bentz², kcbentz@chem.ufl.edu, Muhammad Ejaz¹, Scott M. Grayson¹, Daniel Savin². (1) Department of Chemistry, Tulane University, New Orleans, Louisiana, United States (2) Department of Chemistry, University of Florida, Gainesville, Florida, United States

The need for highly efficient and cost-effective remediation methods for marine oil spills is a major societal concern in an era of more extreme oil drilling methods. Hollow polycaprolactone (PCL) nanocages have been synthesized using silica nanoparticles (SiNPs) as a sacrificial scaffold. The use of a *bis*-caprolactone monomer in conjunction with ϵ -caprolactone monomer, allowed for the simultaneous crosslinking and grafting of PCL brushes from the surface of the SiNPs. Following removal of the SiNP core using hydrofluoric acid, PCL nanocages were obtained, which showed dynamic character in the presence of organic solvent. Specifically, the change in hydrodynamic volume from the SiNP core-intact particles to the free PCL nanocages showed nearly a 3-fold increase, changing from $3.4 \times 10^7 \text{ nm}^3$ to $9.5 \times 10^7 \text{ nm}^3$, demonstrating the remarkable capacity for payload in these materials. Additionally, due to the crosslinked nature of these systems, no dependence on concentration was observed. In the solid state, the core-intact material was able to uptake over 900 wt% solvent while still remaining mechanically robust. Furthermore, we have demonstrated the ability to finely tailor the brush length and grafting density in these materials. The ability to tune chain density, in combination with the formation of hollow PCL particles is expected to imbue these materials with a high level of tunability for the stability and high payload capacity as marine oil dispersants and potentially as highly efficient drug delivery systems.

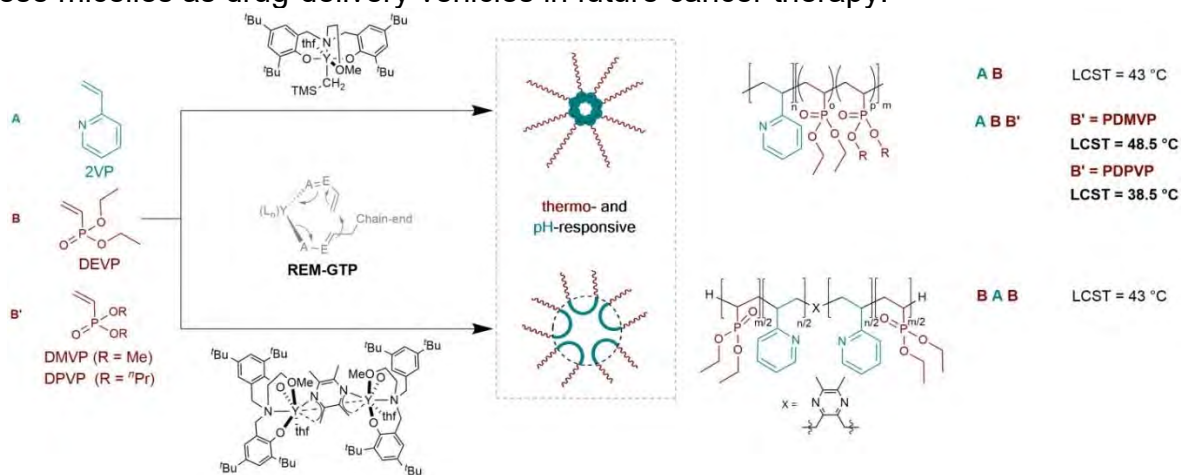


POLY 496: Group-Transfer-Polymerization: A highly versatile tool for tailor-made smart polymers

Friederike Adams, rike.adams@makro.ch.tum.de, **Peter T. Altenbuchner**, **Bernhard Rieger**. WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Munich, Germany

One of the main issues in polymer synthesis is the design of well-defined structures from simple precursors. To implement polymers for high-tech applications, it is necessary to accurately define the mechanical, thermal and stimuli-responsive properties *via* changes in microstructure and composition. The development of catalysts for precise synthesis of polymers with variable tacticity, controllable molecular-weights and narrow molar mass distributions is therefore an essential requirement in the field of polymerization catalysis.

The use of rare earth metal-mediated group-transfer-polymerization (REM-GTP) allows not only precise molecular-weights and narrow molecular-weight distributions, but also the synthesis of block copolymers in a living-type mechanism *via* simple sequential addition of different monomers. Our group developed highly active and stereospecific non-metallocene catalysts for the homo- and copolymerization of polar vinyl monomers such as diethylvinylphosphonate (DEVP), 2-vinylpyridine (2VP) and *N,N'*-dimethylacrylamide. C(sp³)-H-bond activation *via* σ -bond metathesis was performed with these catalysts to enhance activity and initiator efficiencies and on top of that to develop a new type of block copolymer-structure. The synthesized tailor-made and biocompatible AB-, ABB'- and BAB-block copolymers (A = 2VP; B = DEVP) self-assemble to micelles and show thermoresponsive behavior as well as pH-dependent solubility. In order to tune the lower critical solution temperature (LCST) to the physiologically relevant temperature range for applicability in release studies, the LCST can selectively be shifted through incorporation of small amounts of dialkylvinylphosphonates with variable hydrophilicity. The possibility to precisely diversify the micelle-structure *via* monomer feed opens a new field for the application of these micelles as drug-delivery vehicles in future cancer therapy.

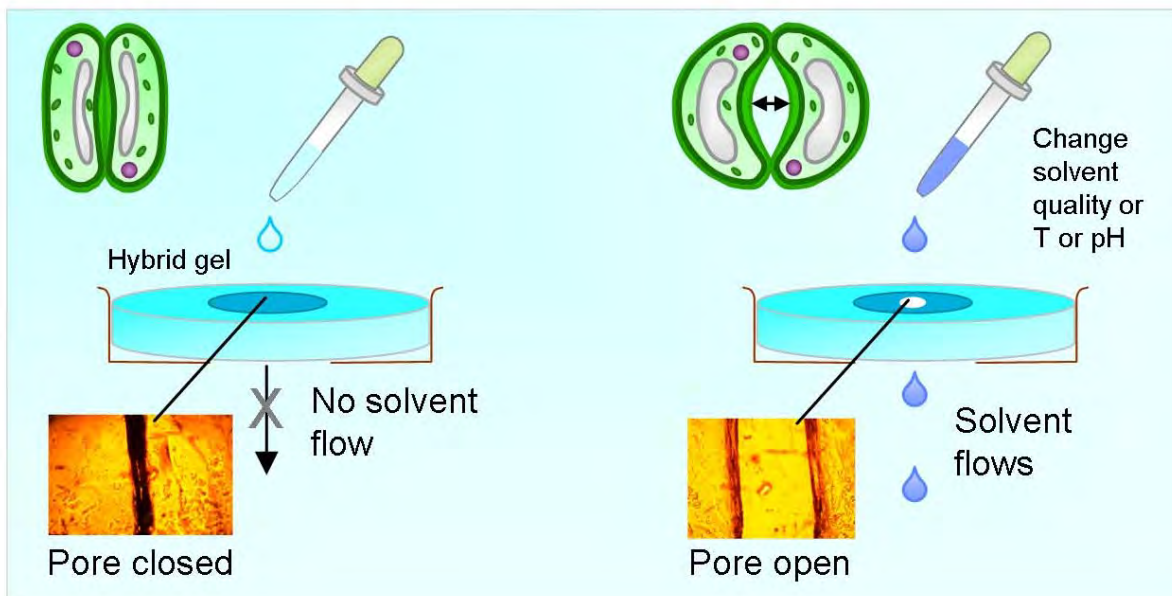


Sequential REM-GTP of 2VP and DAVP (DEVP, DMVP, DPVP) with non-metallocene catalysts to obtain AB-, ABB'- and BAB-block copolymers which self-assemble to micelle-structures.

POLY 497: Smart hydrogel-based valves inspired by the stomata in plants: Ability to regulate water flow based on temperature, pH, and light

Srinivasa R. Raghavan, *sraghava@umd.edu*, Ankit Gargava. *Chemical Biomolecular Engineering, University of Maryland, College Park, Maryland, United States*

We report the design of hydrogels that can act as “smart” valves or membranes. Each hydrogel is engineered with a pore (about 1 cm long and < 1 mm thick) that remains closed under ambient conditions but opens under specific conditions. Our design is inspired by the stomatal valves in plant leaves, which regulate the movement of water and gases in and out of the leaves. The design features two different gels, active and passive, which are attached concentrically to form a disc-shaped hybrid film. The pore is created in the central active gel, and the conditions for opening the pore can be tuned based on the chemistry of this gel. For example, if the active gel is made from N-isopropylacrylamide (NIPA), the actuation of the pore depends on the temperature of water relative to 32°C, which is the lower-critical solution temperature (LCST) of NIPA. The concentric design of our hybrid provides directionality to the volumetric transition of the active gel, i.e., it ensures that the pore opens as the active gel shrinks. In turn, contact with hot water ($T > 32^{\circ}\text{C}$) opens the pore and allows the water to pass through the gel. Conversely, the pore remains closed when the water is cold ($T < 32^{\circ}\text{C}$). The gel thereby acts as a “smart” valve that is able to regulate the flow of solvent depending on its properties. We have extended the concept to other stimuli that can cause gel-swelling transitions including solvent composition, pH, and light. Additionally, when two different gel-based valves are arranged in series, the assembly acts as a logical “AND” gate, i.e., water flows through the valve-combination only if it simultaneously satisfies two distinct conditions (such as its pH being below a critical value and its temperature being above a critical value).



POLY 498: Design and study of biodegradable and photodegradable thermoplastic elastomers

Kyle J. Arrington, *kjarring@vt.edu*, John Waugh, Scott Radzinski, John Matson.
Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia,
United States

The synthesis and study of a bio- and photodegradable ABA triblock copolymer that combines the high modulus of brittle polylactic acid (PLA) with a photodegradable elastomer is described. The B-block was prepared by ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene and an unsaturated cyclic ketone in the presence of cis-1,4-butenediol. This results in a hydroxyl-functionalized telechelic 1,4-polybutadiene (PBD) macroinitiator used to chain extend PLA by ring-opening polymerization of lactide. The resulting polymers are stretchy and tough. The modulus was tuned by controlling the weight fraction of PLA, allowing for a modulus as high as 1602 MPa to 182 MPa as measured by dynamic mechanical analysis. Additionally, the polymers are thermally stable up to 273 °C and exhibit two glass transition temperatures at -111 °C and 55 °C as measured by differential scanning calorimetry. Accelerated UV weathering was performed on polymer films with ranging concentrations of the photodegradable monomer. The degradation was tracked by IR, DMA, and SEC until complete mechanical loss. Further studies were performed using methylcellulose as the hard segment. These are the first examples of cellulose-based ABA triblock copolymers.



POLY 499: Stimuli-Responsive dendronized polymers for next generation biomaterials

Wen Li, *wli@i.shu.edu.cn*, Jiatao Yan, Kun Liu, Afang Zhang. Department of Polymer Materials, Shanghai University, Shanghai, China

Dendronized polymers are formed through densely attaching dendrons along a linear polymer main chain, which adopt cylindrical wormlike morphology with tunable thickness. Inspired from the smart properties of biomacromolecules in nature, an intriguing class of stimuli-responsive dendronized polymers were constructed through combination of dendritic oligoethylene glycols (OEG) with various kinds of polymer backbones. Due to the densely covered OEG pendants, these macromolecules show unprecedented thermoresponsiveness and excellent biocompatibility. This presentation will discuss our findings in developing versatile thermoresponsive worm-like dendronized polymethacrylates and polypeptides by decorating with dendritic OEG pendants through covalent linkages, dynamic covalent linkages or supramolecular interactions (Figure 1). Depending mainly on the molecular topology, amphiphilic structure in these dendronized polymers plays different roles on mediating their stimuli-responsive properties. Based on the thickness effects, dendronized polymers undergo heterogeneous dehydration and collapse on individual molecular level. Therefore, guest molecules can be encapsulated and released based on the phase transition temperature, heating rate and thickness of the polymers, resulting in interestingly the formation of molecular containers. This encapsulation property afford these thick polymers tunable shielding ability to protonation and metal coordination in aqueous solutions. In a word, combination of unique thermoresponsive behavior, reversible encapsulation and switchable shielding to guests, protonation as well as metal coordination from these OEGylated dendronized polymers may lead to their promising applications in biomaterials, including drug delivery and targeting, enzyme activity control and transportation.

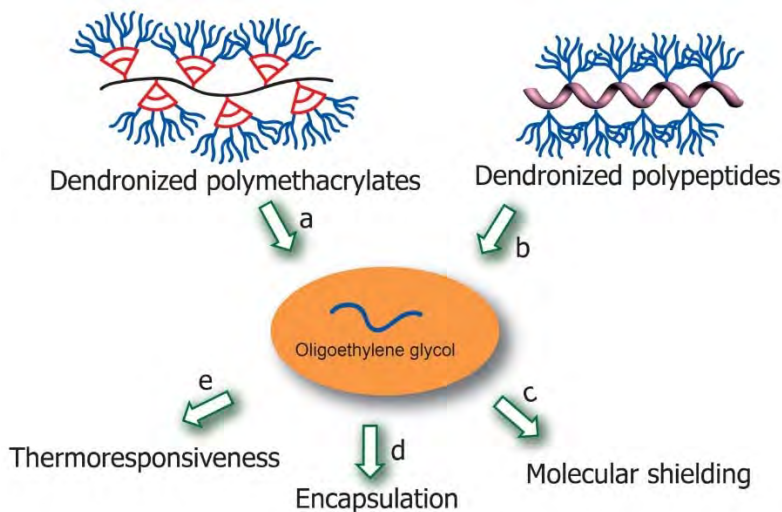
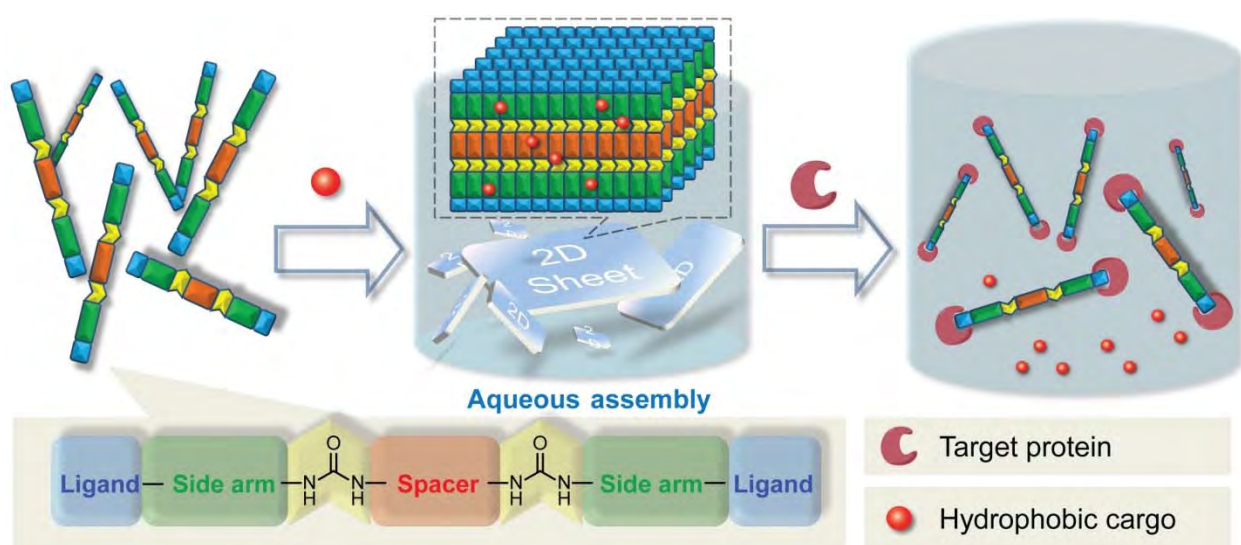


Figure 1. Cartoon presentation of OEGylated stimuli-responsive macromolecules: a) thermoresponsive dendronized polymethacrylates, b) thermoresponsive dendronized polypeptides, c) molecular shielding, d) encapsulation, e) thermoresponsiveness.

POLY 500: Smart organic two-dimensional materials based on a rational combination of non-covalent interactions

Jiang Ziwen, *jiangziwen@live.cn*, Wei Bai, Sankaran Thayumanavan. Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, United States

Rational design of organic 2D (O2D) materials has made some progress, but it is still in its infancy. A class of self-assembling small molecules is presented that form nano/microscale supramolecular 2D materials in aqueous media. A judicious combination of four different intermolecular interactions forms the basis for the robust formation of these ultrathin assemblies. These assemblies can be programmed to disassemble in response to a specific protein and release its non-covalently bound guest molecules.

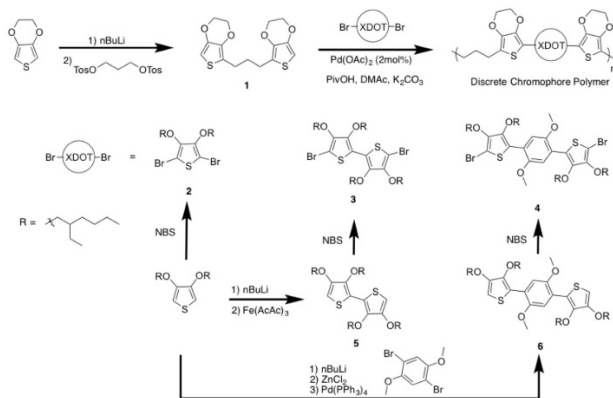


POLY 501: Discrete chromophores as a path towards high contrast anodically coloring electrochromic polymers

Dylan Christiansen¹, dylan.christiansen@gatech.edu, **Aimee L. Tomlinson**², **John R. Reynolds**¹. (1) School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (2) University of North Georgia, Dahlonega, Georgia, United States

Electrochromic materials have the ability to switch between two colored states, or transmissive states, upon the application of an electrochemical potential. They have prospective uses in full color passive displays, energy saving tinted windows, and dimmable visors for military and/or recreational use. Organic polymer electrochromes are solution processable, lightweight, and flexible. The current state of the art electrochromic materials are cathodically coloring, with broadly absorbing charged states that trail into the visible. In this project, a family of pi-conjugated chromophores was designed to be UV absorbing and switch to a vibrantly colored state upon electrochemical oxidation. Through collaboration, synthesis and theoretical calculations have worked in tandem to design materials to have electron rich, discrete chromophores with wide optical gaps absorbing in the UV in their neutral state and are anodically coloring.

We show that using a divergent synthetic approach allows for creating a series of polymers with discrete chromophores of various lengths with a consistent alkyl bridge. Increasing conjugation by increasing the number of dioxothiophenes in the chromophore has the hypothesized effect of red-shifting the neutral and radical cation absorptions; however, the introduction of a sterically demanding dimethoxybenzene unit has the effect of blue-shifting the neutral absorbance relative to a shorter and more electron rich chromophore. This steric effect is further extended to confining the radical cation absorption to an unusually high energy and sharp absorption focused inside the visible. This absorption confinement manifests itself in creating a very saturated chromophore in this oxidation state giving a broadly absorbing black colored state. Upon moving to wider gap systems we use a small molecule model to show that this method has the ability to make materials with contrasts exceeding what is possible in traditional cathodically coloring conjugated polymers.

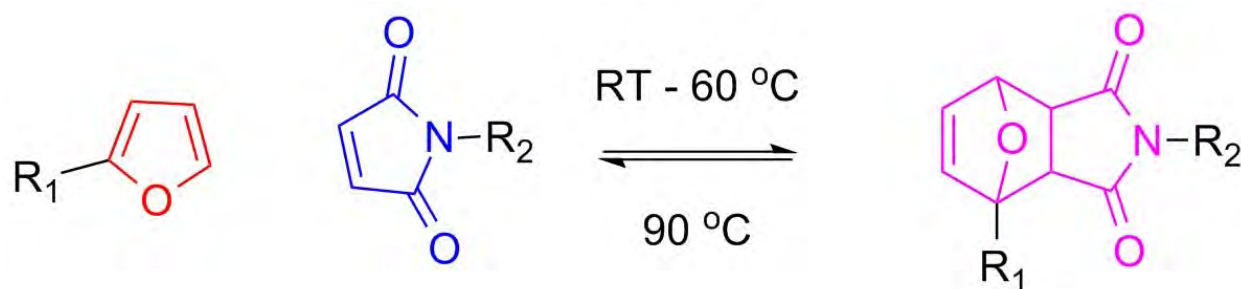


Synthetic scheme outlining the synthesis of the target polymers.

POLY 502: Synthesis and evaluation of thermally-responsive coatings based upon Diels-Alder chemistry and renewable materials

Dahlia Amato, Greg Strange, John P. Swanson, Kim Varney, Douglas Amato, Philip J. Costanzo, phil.costanzo@gmail.com. Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

A soybean based coating with thermally responsive Diels-Alder linkages has been prepared following an automotive 2-component formulation. The resulting coatings displayed the capability to be healed by a thermal stimulus after physical deformation. Various curing agents were employed, and resulted in variation of scratch resistance and re-healability. Different thermally responsive soybean resins were synthesized to have varying amounts reversible and nonreversible linkages when incorporated into the coating. It was found through the analysis of reheatability, hardness, gloss, and adhesion that the optimal combination was an acetylated resin (no irreversible crosslinks) with 54% reversible Diels Alder linkages at an NCO:OH ratio of 5:1 using isophorone diisocyanate. Materials were evaluated via differential scanning calorimetry (DSC), scratch resistance, Koenig hardness, gloss measurements, and topographical analysis. [figure1]



POLY 503: Superhydrophobic nanocomposite films based on polypentafluorostyrene-modified fumed silica

Quanyi YIN^{1,2}, yinquanyi@gmail.com, Emmanuel BEYOU¹, Aurelia Charlot², Daniel Portinha². (1) Ingénierie des Matériaux Polymères, UNIVERSITY LYON 1, Lyon, France (2) Ingénierie des Matériaux Polymères, INSA de LYON, LYON, France

Superhydrophobic nanocomposite films were simply obtained by spin coating polypentafluorostyrene (PPFS) modified fumed silica particles (SiO_2 -PPFS) embedded in PPFS-based polymer matrices. In this objective, PPFS chains were firstly anchored onto the surface of (acryloxypropyl)trimethoxysilane (APTMS)-modified fumed silica particles by nitroxide-mediated polymerization (NMP) in presence of PS-DEPN as macroinitiator and using a “grafting through” strategy. By tuning polymerization time and/or solvent polarity, the weight ratio of polymer chains to silica can be tuned from 5 to 32 wt. %. Secondly, free PPFS was chemically modified by 1H,1H,2H,2H-perfluorodecanethiol (PFDT) via a para-fluoro substitution reaction under basic conditions to give PPFS-PFDT derivatives with enhanced hydrophobicity. The resulting nanocomposite films (SiO_2 -PPFS/PPFS-PFDT), straightforwardly prepared in one step, exhibit superhydrophobic properties with a water contact angle (WCA) higher than 150° and hysteresis contact angle lower than 3° . This water repellent character results from the combination of the lower surface energy emanating from the perfluoroalkyl groups and from the micro/nano binary morphology arising to the presence of silica particles at the surface (and adjustable by the SiO_2 content). Many potential applications can be envisaged, especially in the field of self-cleaning and anti-fouling coating, for instance.

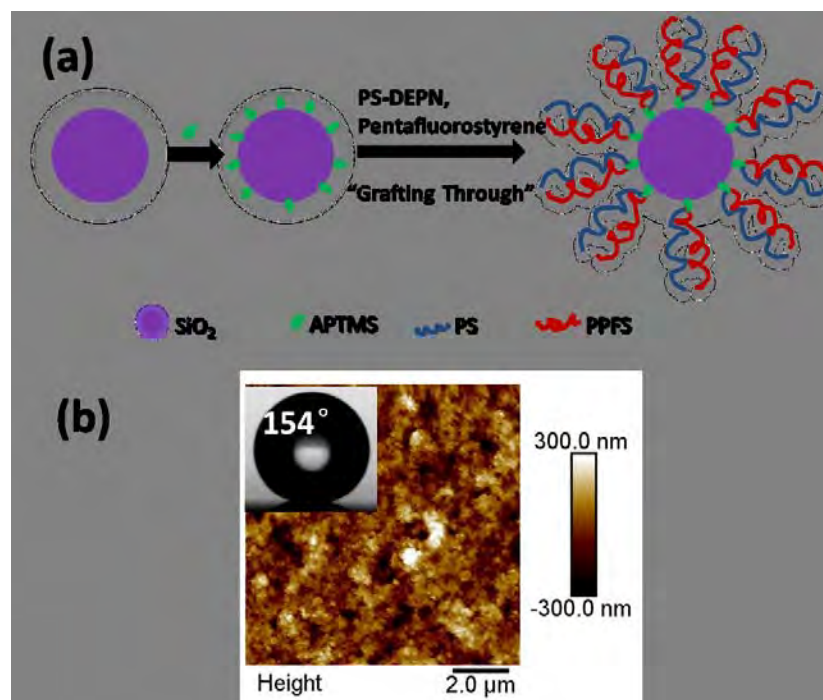
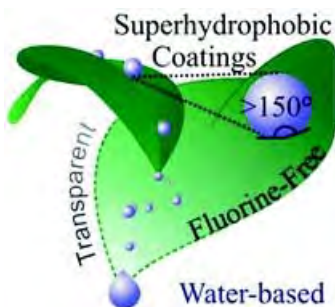


Fig (a) NMP of PFS initiated by PS-DEPN through the surface of APTMS functionalized fumed silica; (b) AFM and WCA images of superhydrophobic surface.

POLY 504: Environmentally-safe and transparent superhydrophobic coatings

Joseph Mates¹, *Joseph.Mates@gmail.com*, Ramsey Ibrahim², Alejandro Vera², Stephen Guggenheim², Jian Qin³, Debbie Calewarts³, Don Waldroup³, Constantine Megaridis². (1) Air Force Research Laboratory, Edwards AFB, California, United States (2) University of Illinois at Chicago, Chicago, Illinois, United States (3) Kimberly-Clark Corp., Neenah, Wisconsin, United States

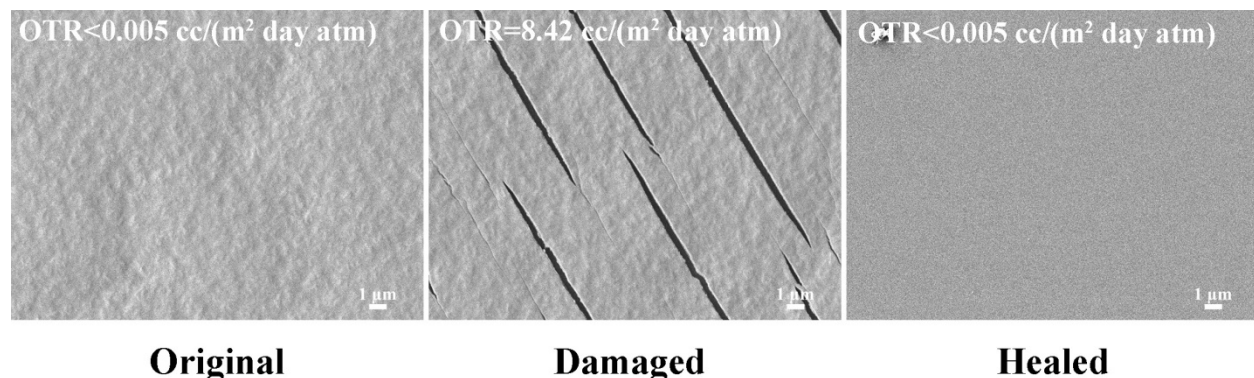
The bioinspired field of superhydrophobicity has almost universally deployed environmentally-detrimental approaches relying on organic solvents and fluorinated compounds to generate liquid-repellent surfaces, thus severely limiting application at industrial scales. Recent water-borne methods have reduced the use of volatile organic compounds, but these methods often rely on either fluorinated chemistries (to lower surface energy) or charge-stabilization (to suspend roughness-enhancing particle fillers). An entirely water-based and fluorine-free superhydrophobic formulation has been developed from hydrophilic titanium dioxide (TiO₂) nanoparticles and polyolefin copolymers, without additional surfactants or charge-stabilization. The commercially-available ingredients are combined in a single-step, substrate-independent, wet-process application to deliver an ultra-simple, semitransparent coating which is attractive for large-area, fluid-barrier surface treatments. The coating constituents are environmentally-safe and FDA-approved, overcoming a nontrivial hurdle in the scalable development of sustainable fluid management technologies.



POLY 505: Polyelectrolyte multilayer nanocoating exhibiting super oxygen gas barrier and 100% self-healing efficiency

Yixuan Song², *dorianxuan@tamu.edu*, Kevin Meyers⁴, RameshKrishnan Ramakrishnan⁴, Joseph Geringer⁵, Shuang Qin², Mohammad Humood¹, Sergei I. Nazarenko³, Jaime C. Grunlan¹. (1) Texas A M Univ, College Station, Texas, United States (2) Materials Science and Engineering, Texas A&M University, College Station, Texas, United States (3) Univ of Southern Mississippi, Hattiesburg, Mississippi, United States (4) University of Southern Mississippi Department, Hattiesburg, Mississippi, United States (5) Department of Chemistry, Texas A&M University, College Station, Texas, United States

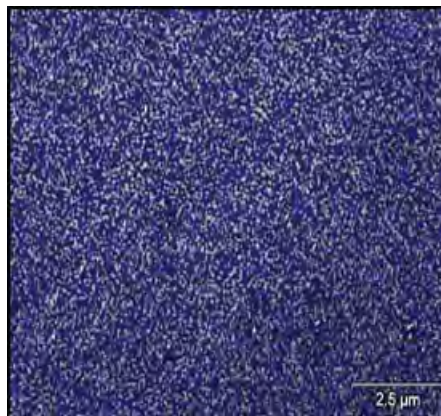
A self-healing gas barrier coating is demonstrated, which is fabricated by alternate deposition of polyethyleneimine (PEI) and poly(acrylic acid) (PAA) from water using the layer-by-layer deposition process. This nanocoating, with high elastic modulus, high glass transition temperature and small free volume, has been shown to be super oxygen gas barrier. An 8-bilayer PEI/PAA multilayer assembly (~700 nm thick) exhibits an undetectable oxygen transmission rate (OTR < 0.005 cc/(m² day atm)). This super barrier behavior is lost after moderate stretching due to its rigidity that leads to cracking. These cracks were completely healed after a 10 minute exposure to high humidity. The OTR of the multilayer nanocoating remained below detection after 10 stretching-healing cycles, which demonstrates the robustness of this behavior. This combination of high oxygen barrier and self-healing behavior could be very useful for a variety of packaging (food, electronics and pharmaceutical) and gas separation applications.



POLY 506: Polyphenylenesulfide and polyetheretherketone POSS nanocomposites: Improvements in rheological and crystallization behavior

Sarah E. Morgan², *sarah.morgan@usm.edu*, Katrina M. Knauer¹, Gregory Brust³, Michael Carr³, Rene Cardona¹, Joseph Lichtenhan³. (1) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (3) Hybrid Plastics, Hattiesburg, Mississippi, United States

Primary challenges in the processing of high temperature semi-crystalline thermoplastics are the high energy and temperature required to melt and form the materials. Processing aids designed to improve flow may detrimentally affect mechanical properties, thermal stability, and crystallization behavior. Polyhedral oligomeric silsesquioxane (POSS) nanostructured materials have been demonstrated to enhance flow in engineering thermoplastics. In this study POSS was incorporated in semi-crystalline polyphenylenesulfide (PPS) and polyetheretherketone (PEEK), and effects on melt rheology, crystallization kinetics, degradation behavior, morphology, and mechanical properties were evaluated. Significant reductions in melt viscosity were observed for both resins on the addition of POSS, with minimal changes in mechanical properties. The extent of rheological modification was found to depend on the structure and loading of POSS. Accelerated rates of crystallization were observed in POSS/PPS blends. The findings show the potential of tailoring POSS/polymer interactions to enhance performance in high temperature thermoplastic blends and composites.



TEM Si map for POSS/PPS nanocomposite

POLY 507: Carbon nanofiber and graphene nanoplatelet containing polycaprolactam nanocomposites: Improvements in mechanical performance in the context of unique interfacial interactions

J. Paige Buchanan, Paige.Buchanan@usace.army.mil, Erin R. Reed-Gore, Sarah L. Williams, Zackery B. McClelland, Robert D. Moser, Manoj K. Shukla. Engineer Research and Development Center, US Army Corps of Engineers, Vicksburg, Mississippi, United States

Owing to their unique aspect ratios, low density, and physical properties, graphene nanoplatelets (GNP) and carbon nanofibers (CNF) are considered excellent reinforcing fillers in high-performance polymer nanocomposites. Effecting homogeneous dispersions and promoting strong interfacial interactions between the carbon fillers and the polymer matrix continue to pose serious challenges in the development of nanocomposites. Using a high-shear method, a series of nanocomposites were prepared from 0.2 to 8 wt% loading of filler in polycaprolactam, which were solvent cast to produce uniform thin films. In this work a direct comparison between the two fillers, concerning the quality of the dispersion and the resulting effects on mechanical performance, was made. In general, the fillers were found to be well-dispersed, with little aggregation. Features common to both fillers were an increase in the glassy modulus, tensile strength, and percent elongation with increased loading. CNF containing samples yielded significantly enhanced relative performance, which was attributed to unique interfacial interactions and the disruption of polymer crystallinity. These findings provide insight into the specific molecular interactions between filler and matrix which drives mechanical performance in high temperature thermoplastic blends and composites.

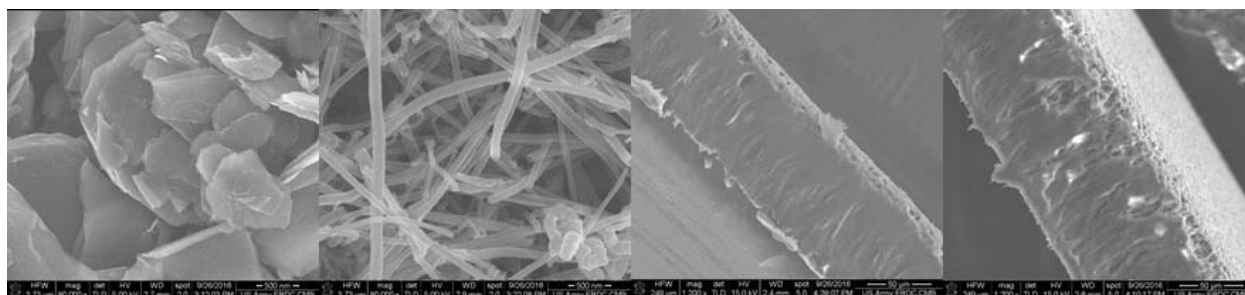
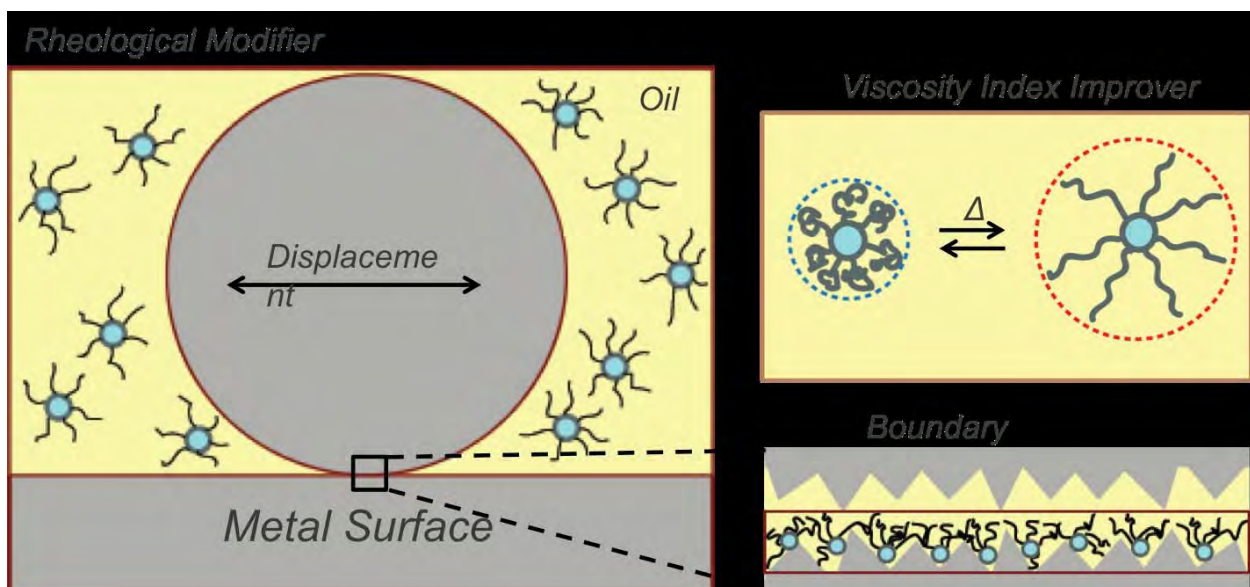


Figure 1: SEM images from left to right: GNP; CNF; 1 wt% polymer nanocomposites, GNP and CNF, in polycaprolactam

POLY 508: Robust and scalable macromolecular architectures as additives for lubrication oils

Raghida Bou Zerdan¹, rbouzerdan@chem.ufl.edu, Bas van Ravensteijn², Dongjin Seo¹, Nicholas Cadirov², Dong-Woog Lee², Jeffrey Gerbec³, Takumi Watanabi⁴, Craig J. Hawker^{1,5}, Matthew E. Helgeson², Jacob N. Israelachvili². (1) Materials research laboratory, University of California Santa Barbara, Santa Barbara, California, United States (2) Chemical Engineering, University of California Santa Barbara, Santa Barbara, California, United States (3) Mitsubishi Chemical Center for Advanced Materials, University of California Santa Barbara, Santa Barbara, California, United States (4) Mitsubishi Chemical Corporation, Tokyo, Japan (5) Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California, United States

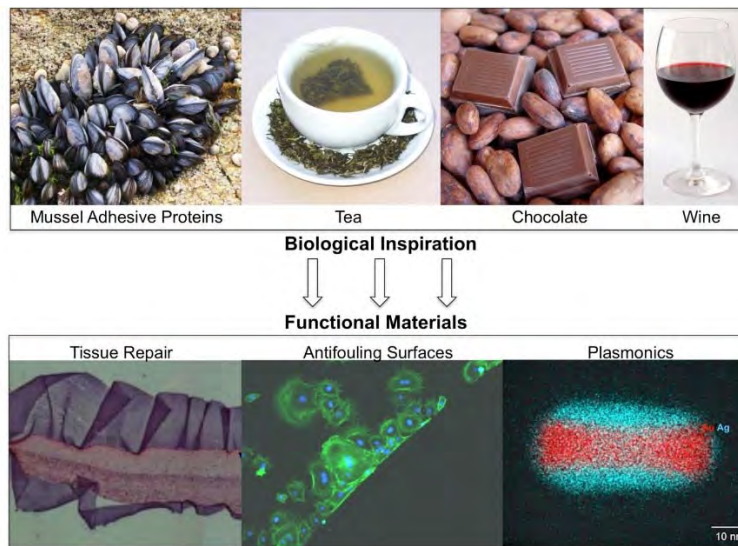
Worldwide energy consumption and concerns about the effect of fossil fuel emissions on the environment are increasing synergistically—instigating the necessity for improved energy efficiencies. To date, petroleum and other liquid fuels constitute the largest source of energy exploited due to their growing demand for the continuously evolving transportation and industrial sectors. Advanced petroleum lubricants reduce engine friction and therefore engine power loss, saving energy and decreasing emissions. These lubricants are typically rheological modifiers that improve performance of heavy equipment operation by allowing stable performance over a wide range of extreme temperatures (-50 to 200 °C). Herein, we report the synthesis and characterizations of macromolecular structures designed to be thermally robust and have long-term chemical/mechanical stability. We have demonstrated potential performance as wear protectant and/or viscosity index improver in selected commercially available conventional motor lubricant oils.



POLY 509: Natural and bioinspired polyphenols as multifunctional coatings

Phillip B. Messersmith, *philm@northwestern.edu*, **Patrick Burch**, **Willie Mae Reese**, **Kevin Healy**. *University of California, Berkeley, Berkeley, California, United States*

Polyphenols rich in catechol and gallol functional groups and are found in both plant and animal tissues, where they serve a variety of functions including mechanical adhesion, structural support, pigmentation, radiation protection, and chemical defense. The interfacial adhesion of polyphenols is exemplified by the adhesive proteins secreted by sessile marine organisms, which contain high levels of 3,4-dihydroxy-L-alanine (DOPA), an amino acid that is believed to be important in adhesion to substrates. In plants, polyphenolic compounds containing benzenediol (catechol) and/or benzenetriol (gallol) functional groups are widely distributed secondary metabolites with a variety of biochemical and physical functions. Included among these are anti-inflammatory and anti-oxidant properties. Consumption of foods and beverages rich in polyphenols, such as chocolate, tea and wine, are claimed to be beneficial to one's health. This talk will focus on selected catechol or gallol containing biological polyphenols used as building blocks for polymers and coatings. Exploiting their natural interfacial adhesion properties, we have engineered a method to form thin adherent polymerized films on substrates immersed in solutions of natural plant polyphenols. Deposition is facile from an aqueous polyphenol solution onto a variety of solid, porous and nanoparticulate metals, ceramics and polymers. In addition to possessing inherent antibacterial and antioxidant properties, the deposited polyphenol films serve as versatile 'primers' facilitating secondary modifications of the primer coating such as metallization and covalent grafting of biomolecules and synthetic polymers. These coatings can be exploited for a variety of practical applications, including antibacterial, antioxidant and fouling resistant coatings on medical devices, metal deposition, plasmonic tuning and surface functionalization of nanoparticles, and surface modification of organ-on-a-chip devices.



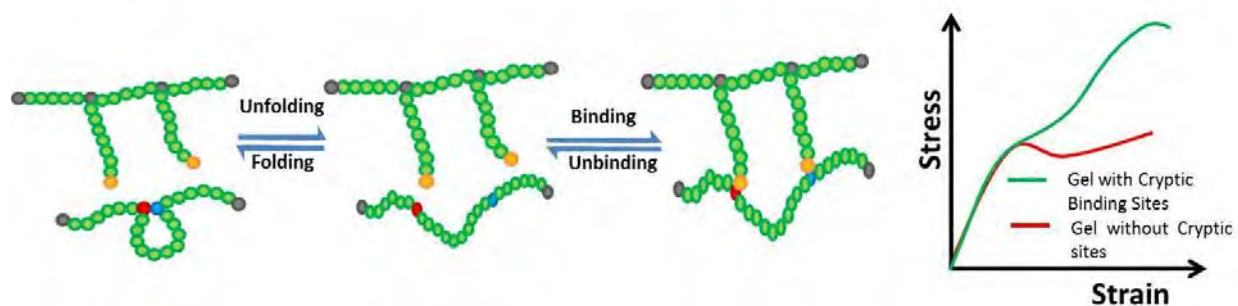
Inspiration for new materials and coatings from biological polyphenols found in plants and animals.

POLY 510: Designing mechano-responsive polymers that encompass biomimetic cryptic bonds

Santidan Biswas, Victor Yashin, **Anna Balazs**, *balazs@pitt.edu*. University of Pittsburgh, Pittsburgh, Pennsylvania, United States

Our aim is to design a new class of dynamic, bio-inspired polymeric materials that become *stronger* and *tougher* in response to mechanical deformation. Traditionally, mechanical deformation has been considered detrimental to the behavior of polymeric materials and is not commonly employed to improve the properties of such soft systems. Biological systems, on the other hand, have evolved a number of strategies for harnessing mechanical force as a beneficial stimulus—one that is vital to the functionality of the organism. Cryptic bonds are a prime example of an adaptive, biological component that is “switched on” by mechanical force and then serves to strengthen the biomaterial. Namely, “cryptic” binding sites lie buried and hidden within folded biopolymers (e.g., proteins), but become exposed under a mechanical deformation. The exposed cryptic sites then participate in bond formation, which in turn leads to more interconnected, and hence, stronger structures. Such cryptic binding sites play a crucial role in the structure formation of fibronectin (Fn), which is essential for wound healing, embryonic development, and the normal functioning of vertebrates. Based on their unique mechano-responsive behavior, cryptic bonds constitute a powerful design motif for creating synthetic polymeric materials that exhibit unprecedented mechanical behavior by becoming *responsively* strong and tough, and thus, address the pervasive need for materials that provide a beneficial response to mechanical stress.

We describe our results on developing new models for polymer networks that encompass the functionality of bio-inspired cryptic bonds and hence, design mechano-responsive and self-reinforcing materials.



Binding of exposed cryptic bonds to reactive ends on dangling chains leads to self-reinforcing networks

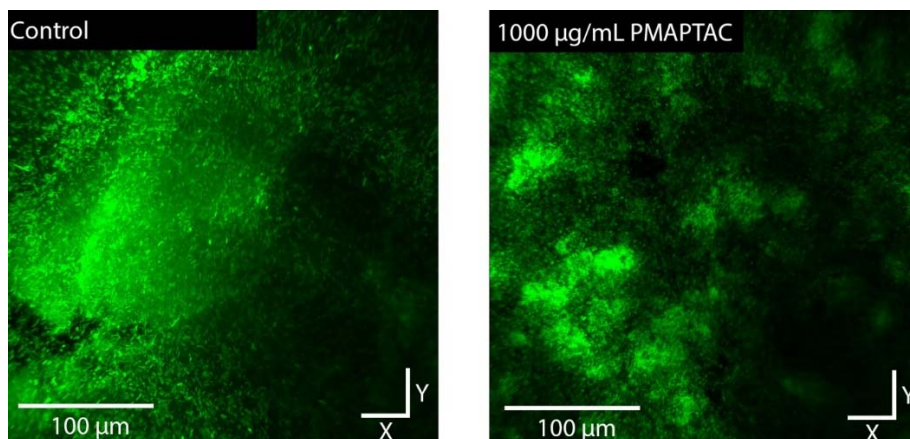
POLY 511: Host-defense peptide-mimetic polymers to target the solution state of bacteria for modulation of biofilm formation

Leanna Foster¹, lfoster@umich.edu, **Shin I. Yusa**³, **Kenichi Kuroda**^{1,2}. (1) *Macromolecular Science and Engineering, University of Michigan, Ypsilanti, Michigan, United States* (2) *School of Dentistry, University of Michigan, Saline, Michigan, United States* (3) *Department of Applied Chemistry, University of Hyogo, Himeji, Japan*

Antimicrobial polymers that mimic the mode of action of host-defense peptides (HDPs) have been previously explored in the field as a method to prevent bacterial infections. Host-defense peptides directly act by disrupting bacterial membranes. The cationic functionality of HDPs facilitates the binding of peptides to anionic bacterial membranes. Current work has further probed the role of cationic charge of HDP-mimetic polymers in polymer-bacteria interaction to control bacteria-bacteria interactions for the prevention of biofilm formation.

In general, biofilm formation begins by spontaneous attachment of bacteria to material surfaces or interface, and is not governed by bacteria behavior in solution. Traditionally, material surfaces have been chemically modified to prevent bacterial attachment and biofilm formation. However, it has been a scientific challenge to create synthetic material surfaces immune to bacterial attachment. In this study, we propose to modulate the properties of planktonic bacteria in solution by cationic polymers as HDP-mimetics for prevention of biofilm formation on material surfaces, while many studies have been centered on the direct killing function of HDPs and synthetic mimics.

The results indicated that the polymers prevented bacterial adhesion at the early stage of biofilm formation by sequestering bacterial aggregates in solution. Bacterial aggregation in solution has been reported to play a critical role in biofilm formation in diseases such as cystic fibrosis. Our study provides new insight into an anti-biofilm strategy targeting planktonic bacteria. Our approach will also fill the gap in our knowledge on the role of solution state of bacteria in the formation of biofilms.



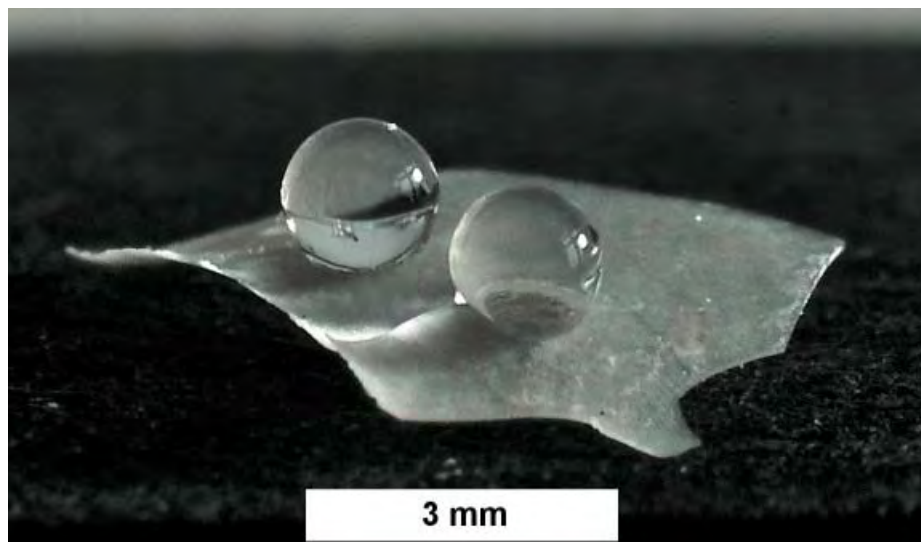
Structural differences in *Pseudomonas aeruginosa* PAO1 early biofilm formation (4 hours) observed by confocal microscopy.

POLY 512: Polymerization in micro channels of teeth towards artificial leaves

Joerg C. Tiller, joerg.tiller@tu-dortmund.de, *Christoph Fik. Bio and Chemical Engineering, TU Dortmund, Dortmund, Germany*

Plants and animals have often microstructured surfaces to control friction, adhesion, and water repellence and storage. Particularly hairy surfaces that mimic the surfaces of certain plant leaves and the feet of water striders have attracted attention because they may result in low friction and water storing surfaces. In order to create such surfaces several bottom up and top down methods have been developed. Using templates allows rather universal application of polymers, but templates with highly dense holes are hard to get.

Here, we present the synthesis of polymer hairs attached to a surface by using dentin as template, because it contains some 60.000 holes of 2-3 micrometer in diameter per square millimeter. Challenge of this method is the polymerization of various acrylates within the micropores of the dental material. After achieving this and removal of the dentin, hairy surfaces with near perfect structure that can mimic a leave of a plant such as corokia cotoneaster can be obtained. Post modification with hydrophobic particles allows controlling surfaces energy resulting in contact angles of more than 170° and complete adherence of the water drops. Changing the particles surfaces affords an additional implementation of contact-active antimicrobial properties and switching to water repelling behavior.



Water drops on artificial leaf surface

POLY 513: Effects of *Stenocara* beetle-inspired biphilic patterns on the rate of water collection from humid air

Jason J. Benkoski¹, jason.benkoski@jhuapl.edu, Konstantinos Gerasopoulos¹, Lloyd Luedeman¹, Matthew McCarthy², MD M. Rahman², Emre Ölçeroglu². (1) REDD, Johns Hopkins University APL, Laurel, Maryland, United States (2) Department of Mechanical Engineering, Drexel University, Laurel, Maryland, United States

Surface wettability plays an important role in water recovery, distillation, dehumidification, and heat transfer. The rate of water collection depends on the rate of droplet nucleation, droplet growth, the initiation of droplet rolling, and droplet velocity. Nucleation and growth theory predicts a large advantage for hydrophilic surfaces, while geometric considerations stemming from high contact angles favor droplet shedding from hydrophobic surfaces. Some plants and animals overcome this tradeoff through biphilic surfaces with patterned wettability. For example the *Stenocara* beetle uses hydrophilic patches on a superhydrophobic background to collect fog from air. Cribellate spiders similarly collect fog on their webs through periodic spindle-knot structures on their silk fibers. In this study, we investigate the effects of wettability patterns on the rate of water collection from humid air. The rate of water collection per unit area is measured as a function of undercooling, and angle of inclination. It is then compared for biphilic, hydrophilic, hydrophobic, and superhydrophobic surfaces. We then model each pattern by comparing the potential and kinetic energy of a droplet as it rolls downwards at a fixed angle. The results suggest that the rate-limiting step for condensate capture is the initiation of droplet rolling, and thus the fog-collecting strategies of the *Stenocara* beetle inhibit the rate of collection under these conditions.



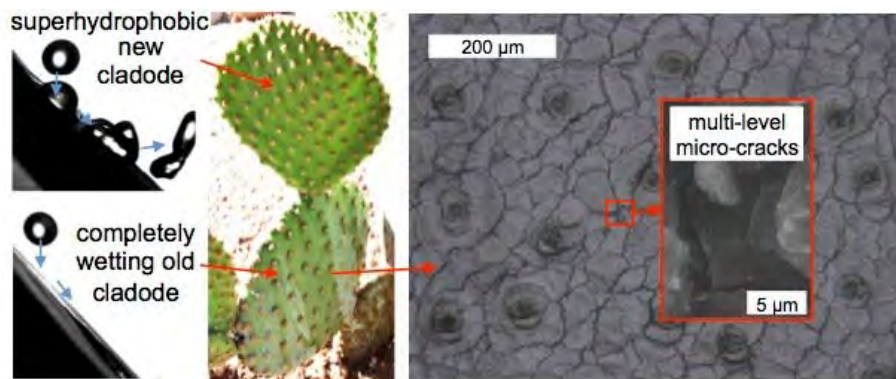
POLY 514: Effects of chemistry and dynamic three dimensional morphology of the epicuticular wax on water wettability and permeability of the prickly pear cacti cuticle

Konrad Rykaczewski¹, *konradr@asu.edu*, **Rubin Linder**¹, **Kenneth C. Manning**¹, **Lucas C. Majure**². (1) School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States (2) Desert Botanical Garden, Phoenix, Arizona, United States

To survive in xeric environments, the prickly pear cacti store water within succulent tissue in their stem and minimize its loss through production of a thick waxy exterior coating that acts as a water permeation barrier.¹ The cacti also reduce evapotranspiration through use of the Crassulacean acid metabolism, which means that the stomata open during the night to absorb carbon dioxide, but remain shut during the day. In this nearly closed state the water loss through the stomata is comparable to water diffusion rate through the outer hydrocarbon coating.²

Recently we showed that within a single growth season the surface properties of prickly pears switch from water-repelling to super-wetting under water drop impact.³ We used Nuclear Magnetic Resonance to demonstrate that only minor changes in the chemistry of the natural wax, which is mostly composed of alkanes, occur. In contrast, development of a network of deep 3D micro-cracks dramatically changes the morphology of this coating. Complete spreading of impinging water drops occurs because of pinning of the receding contact line on the highly hydrophilic inner cuticle layers exposed by these deep micro-cracks.

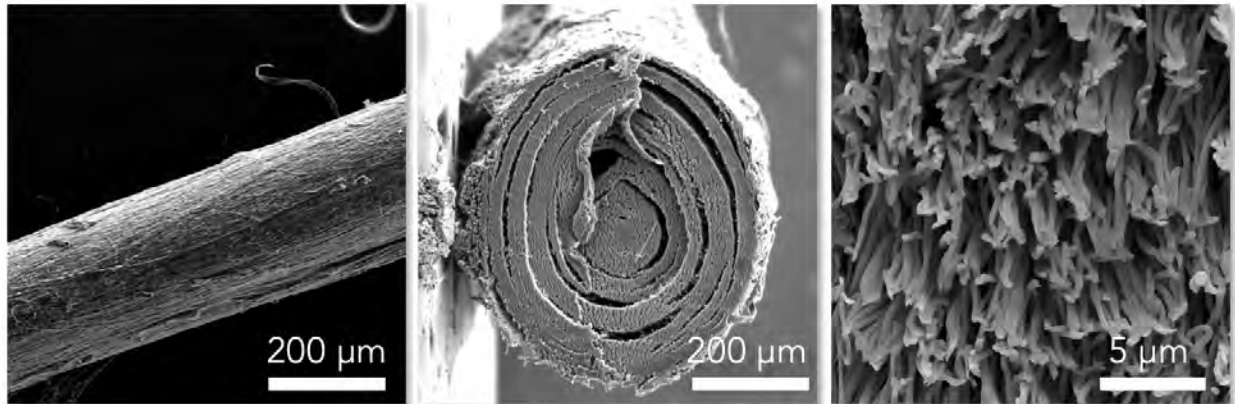
Here we describe how the 3D geometry of these fractures changes with the large seasonal volumetric shrinking and expansion of the plants. Specifically, we correlated the hydration state of the micro-fractured cladodes of Engelmann's prickly pear with topology of PDMS casts of the plant's surface. We also measured the water diffusion coefficient in the extracted wax using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy. In order to estimate how the hydration state of the plant changes permeation of water through its exterior via micro-fracture shape modulation, we substituted the measured value of the diffusion coefficient in un-cracked films and the geometry of the fractured films into Finite Element Method simulations. These results on the self-regulating cacti cuticle transport properties might provide new insight for desing of biomimetic smart membranes.



POLY 515: Mimicking muscle fiber structure and function through electromechanical actuation of nanofiber bundles

Sean Y. Severt¹, Stephanie Maxwell¹, Jonathan Bontrager¹, Tatum Fuller¹, Janelle Leger², **Amanda Murphy**¹, amanda.murphy@wwu.edu. (1) Chem Dept, MS9150, Western Washington Univ, Bellingham, Washington, United States (2) Physics and Astronomy, Western Washington University, Bellingham, Washington, United States

Biocompatible materials that mimic the structure and function of muscle tissues are highly desired for use as engineered tissues and next-generation medical devices. To this end, we have developed an artificial muscle made from composites of the natural biopolymer silk fibroin and conducting polymers. Using electrospinning, we are able to generate aligned nanofiber bundles of silk that mimic the structure of skeletal muscles. The silk fibers can then be infused with conducting polymers using a two-step chemical and electrochemical approach. The resulting bundles of individual, electroactive fibers undergo electromechanical actuation in biologically-relevant electrolyte solutions when low potentials were applied, thus mimicking the function of native muscles. The fabrication methods, stress and strain generation, and stability under repeated actuation for fiber bundles coated with different conducting polymer formulations will be presented.

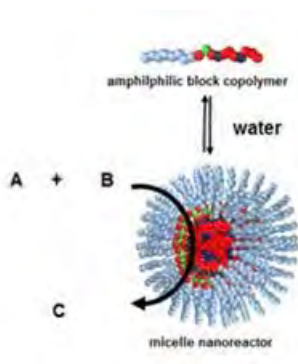


POLY 516: Advances in asymmetric heterogeneous catalysis: Synthesis of novel nanoreactors

elena lestini, *e.lestini@warwick.ac.uk*, *Lewis D. Blackman*, *Rachel K. O'Reilly*.
Chemistry, University of Warwick, London, United Kingdom

In the area of polymer-based heterogeneous catalysis, thermoresponsive polymeric core-shell nanoreactors are a relatively new class of biomimetic materials that allow both compartmentalisation of the catalytic sites in the hydrophobic inner pocket (core) of such nanoreactors and their use in aqueous media, owing to the polymer's stimuli-responsive dynamic nature and solubility in water, respectively. Catalysis in nanoreactors usually exceed performances of classical heterogeneous catalysts due to high reagent concentration and enhanced catalytic stability.[1]

In this work, we present the synthesis of novel chiral monomers, their RAFT copolymerisation and their application in asymmetric catalysis. As nanoreactors promise to have a great impact in sustainable chemistry because of their activity and recyclability properties in water, thermoresponsive amphiphilic polymers were also obtained by chain extension using RAFT polymerisation. Studies on their self-assembly into nanoreactors and their catalysis in water will also be discussed.



A micellar core-shell nanoreactor, highlighting the conversion of substrates A and B into desired product C within the catalytic core of the nanoparticle.

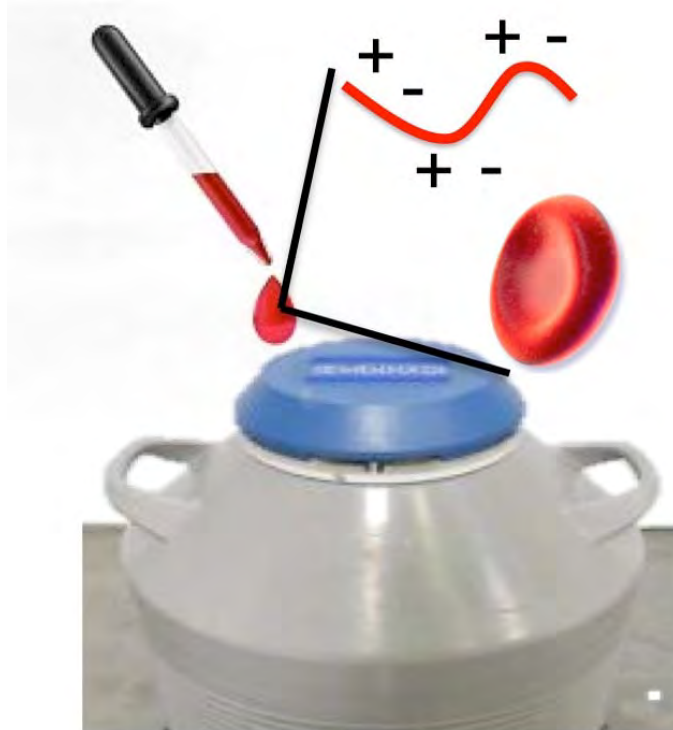
POLY 517: Rational design of antifreeze-protein mimetic materials to enable the cryopreservation of cells

Matthew I. Gibson, *m.i.gibson@warwick.ac.uk*. Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom

With an ever-ageing population in the Western world, the need for regenerative medicine, especially transplantation is increasing, but the methods to cryopreserve (and hence distribute) these cells and tissue still relies on addition of high concentrations of toxic organic solvents. We seek to create new macromolecular solutions to address this problem.

Antifreeze (glyco) proteins are found in many species adapted to live in the polar regions or at high altitudes, in sub-zero temperatures. These act to slow ice growth and also suppress the freezing point which are desirable properties for new cryoprotectants, but the proteins themselves may not be suitable for application. To address this challenge we have developed a range of synthetic polymer materials which can reproduce the properties of antifreeze proteins and ice nucleating proteins, but by using simplified structures, and scalable synthetic methods.

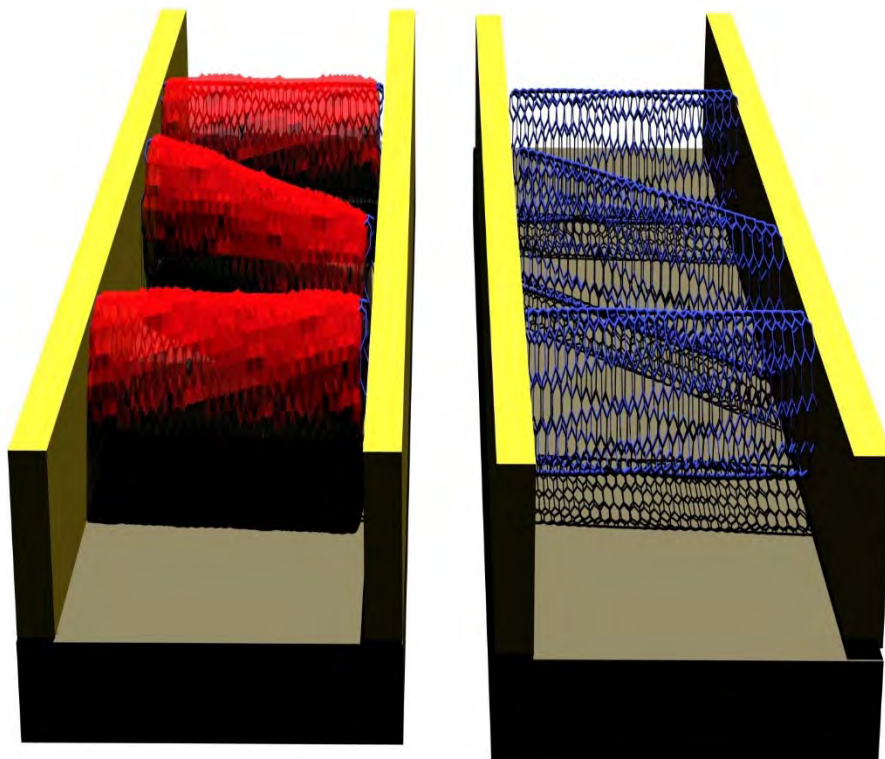
Using our new biomaterials we have been able to improve the cryopreservation and storage of several medically relevant cells including blood and primary hepatocytes, primarily by reducing the ice-induced damage during the thawing process. This contribution will discuss the progress in both understanding the mechanisms of action of these materials and their impact on cells for transfusion medicine.



POLY 518: Biomimetic polymer coated carbon nanotube gas sensor for real-time air quality sensor suite

*Yen H. Ngo², Grant Slusher², Kathy Fullerton², Carlos Suarez¹, Rajesh R. Naik², Jennifer A. Martin², Claude Grigsby², **Steve S. Kim²**, steve.kim.13@us.af.mil. (1) RX, AFRL, Dayton, Ohio, United States (2) 711HPW, AFRL, Dayton, Ohio, United States*

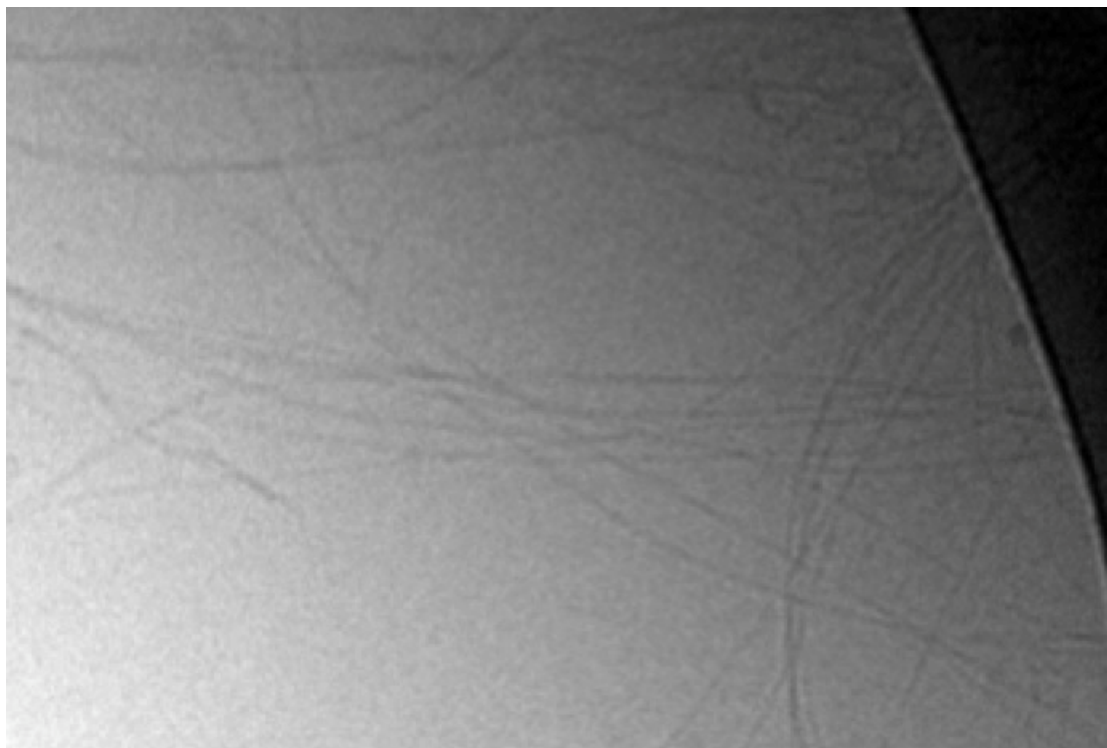
Volatile organic compounds (VOCs) existing in unexpectedly higher concentrations (high ppb to low ppm levels) than other potentially hazardous chemicals are great target of interest found from the previous studies on pilot air supplies in aircraft utilizing On-board Oxygen Generation Systems (OBOGS). While a variety of commercial means of detection are readily available for few VOCs of interests, there are currently no commercial off-the-shelf sensors (COTS) which can effectively discriminate low level VOCs from other molecules. Learned from nature's olfactory system, we show that a bioinspired capture element acting as the "sensing material" can selectively bind to a target VOC and may prove to be a good candidate to enhance the sensitivity and selectivity of a carbon nanotube based electronic sensor. The selectivity obtained from the sensor platform under this study is shown as well by performing parallel testing to a high sensitivity COTS device. The sensor performance will be tested in a custom-designed chemical exposure chamber with precise control of compound concentration, flow rate, and pressure to simulated flight conditions. Ultimately, this research will help to add a low-level VOC sensing capability for monitoring aircraft breathing air quality as part of a sensor suite designed to enhance aircrew health and safety.



POLY 519: Self-assembly and hydrogelation of a peptide derived from semenogelin I

Karin S. Akerfeldt, *kakerfel@haverford.edu. Chemistry, Haverford College, Rockland, Delaware, United States*

The aim of this research is to investigate the hydrogelation of a peptide segment derived from the natural protein Semenogelin I, the main proteinaceous constituent in seminal plasma. The oligopeptide under investigation self-assembles to form fibrils consisting of an extended β -sheet. We are currently studying a series of truncated versions of the original oligopeptide sequence employing CD and FT IR spectroscopy in order to compare the length requirement for hydrogel formation and the properties of the hydrogels formed. We are also developing a method using Raman spectroscopy for determining the pKa value of a His residue present in the sequence. The deprotonation of this residue, as the pH is changed from acidic to neutral, is postulated to be the trigger for hydrogelation. We are also in the process of incorporating isotopically labeled residues into the sequence in order to determine structural details of the hydrogel. In addition, the kinetics of fibril formation is under investigation, employing a thioflavine-based assay, which is also used as a tool to assess the effects of external variables, such as pH, on aggregation.

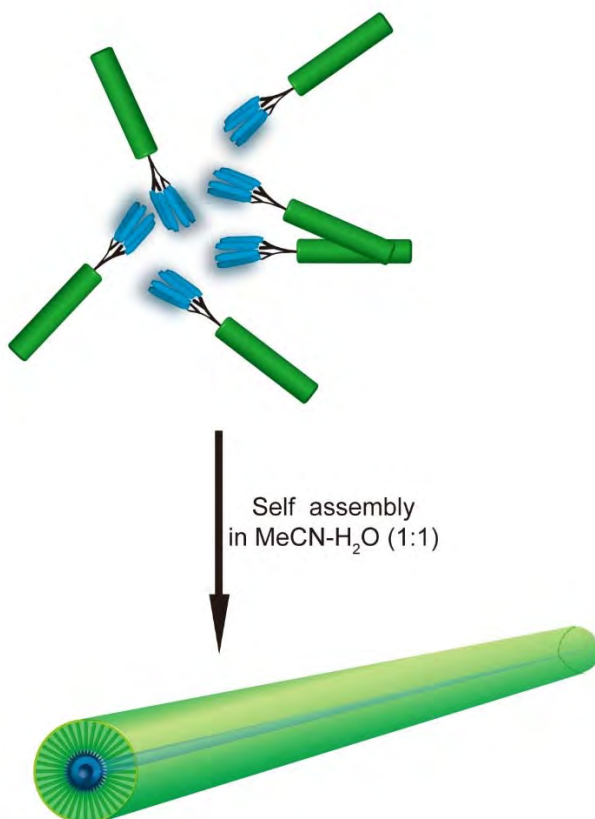


cryo-TEM image of fibrils generated by the semenogelin-derived peptide

POLY 520: Tubular supramolecular polymers

Honggang Cui, cuihonggang@gmail.com. 221 Maryland Hall, JHU Chemical and Biomolecular Engineering, Baltimore, Maryland, United States

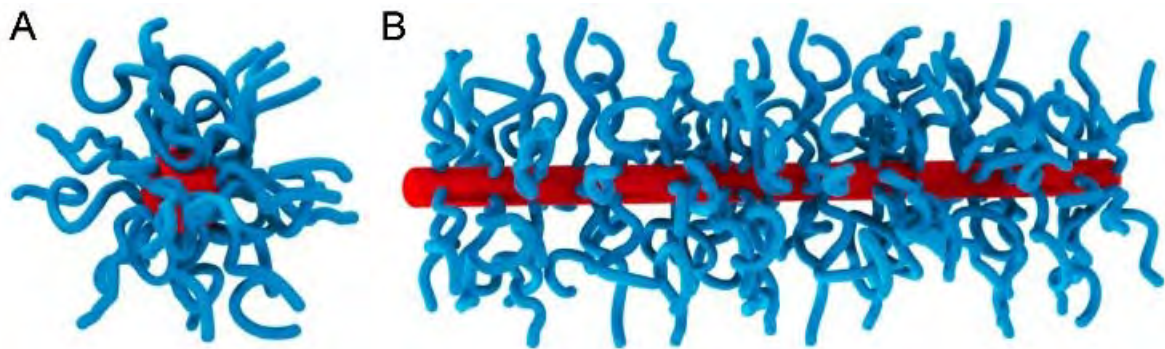
Supramolecular polymers are dynamic one-dimensional assemblies by rationally designed building units, possessing a high degree of internal order and well-defined surface chemistry. The reversible polymerization/depolymerization process is the key feature for their unique biomedical applications. We report here the distinct assembly and disassembly pathways of tubular supramolecular polymers formed by self-assembly of our drug amphiphiles (DAs). In the polymerization process, the DA monomers first assemble into filaments mediated by the π - π stacking among the drug moieties, followed by slow evolution into ribbons and nanotubes. Upon dilution or under mild sonication, these supramolecular nanotubes, however, would undergo fragmentation into short ones, instead of depolymerizing reversibly. In the presence of glutathione, a reducing agent to cleave the drug off the DA monomers, we found that these tubular supramolecular assemblies can be attacked at the defects of molecular packing, resulting in a cascade of nanostructures breakdown and reassembly.



POLY 521: Virus-Mimicking polymer molecular brushes as a novel family of highly potent antimicrobial agents

Wan Zheng, *bowlzheng@gmail.com*, Ankita Arora, Yunjiang Jiang, Hongjun Liang.
Texas Tech University Health Science Center, Lubbock, Texas, United States

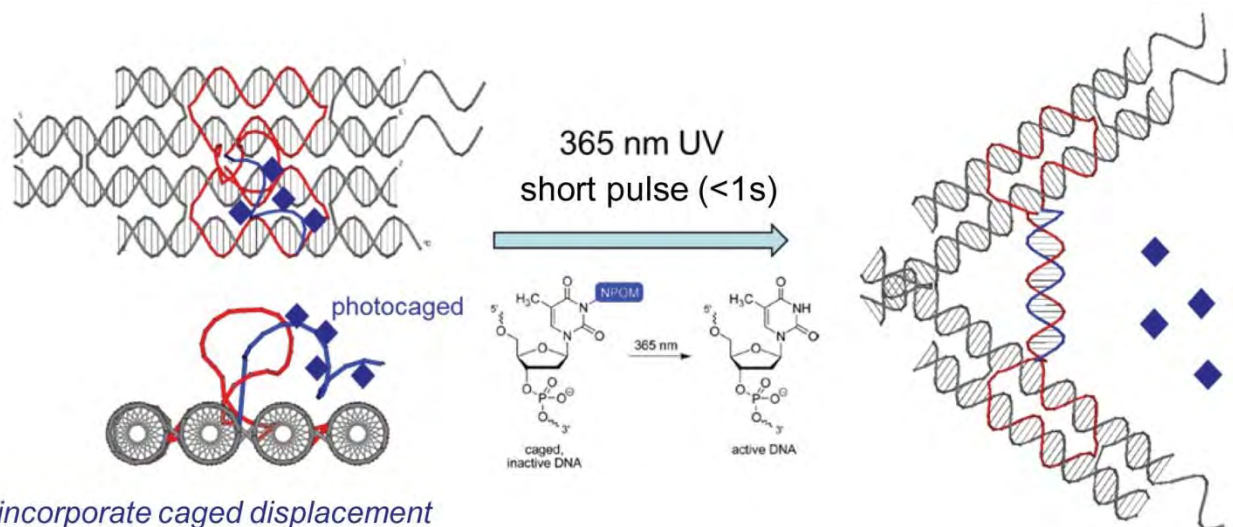
Viruses such as bacteriophages invade host cells efficiently and selectively with proteinaceous devices that are foremost recognized by their unique nanostructures. Synthetic mimics of these structures may bode well for the designs of new membrane active antimicrobials but have not been systematically examined yet. We study here well-defined spherical and rod-like polymer molecular brushes (PMBs) to mimic the two basic structural motifs of bacteriophages. We will discuss our preliminary data on the preparation of nanostructured natural-synthetic hybrid PMBs. We will reveal the structure-activity relationship and their favorable selectivity for different bacteria species and mammalian cells. Our results suggest that nanostructure is a critical determinant that induces topological changes of bacterial membranes, which in turn helps membrane-active antibiotics gain desirable activity and selectivity.



POLY 522: Light-triggered self-assembly and actuation of DNA nanostructures using photocaged nucleotides

Nicholas Stephanopoulos, *nikosteph@gmail.com*. Arizona State University, Scottsdale, Arizona, United States

DNA nanotechnology has emerged as one of the most powerful methods for constructing complex nanoscale devices with precise addressability. The ability to actuate these devices on-demand would provide a powerful method for creating dynamic nanomachines that can reconfigure nanostructures, apply precisely defined forces, or spatiotemporally control self-assembly. Typically, DNA nanostructures have been dynamically modulated by either incorporating photoswitchable azobenzene nucleotides that, while effective, often suffer from slow kinetics and undesired reversibility. Another approach involves adding displacement strands that can bind to toehold regions and out-compete other interactions to change the state of a nanostructure. However, this approach is limited by the need to add an exogenous strand, which is not feasible for many applications, especially in biology. To circumvent these limitations, we have developed a series of photo-cleavable oligonucleotides that block hybridization until illuminated with UV light. By incorporating caged displacement strands within an existing nanostructure, we can prevent their action until illuminated. These strands serve as effective "internal toeholds" that can be activated on-demand. We have designed three such switchable systems: (1) nanofibers that polymerize upon light exposure; (2) a nanomechanical tweezer that switches between the closed and open state, and (3) a DNA origami box that open when illuminated. These structures can reconfigure their internal state and/or apply a nanomechanical force within a few seconds of illumination, paving the way for dynamic nanomachines that can exert controlled motion. We will also describe the design principles for more complex nanostructures that can find applications in targeted drug delivery or reconfiguration inside cells to influence biological processes.

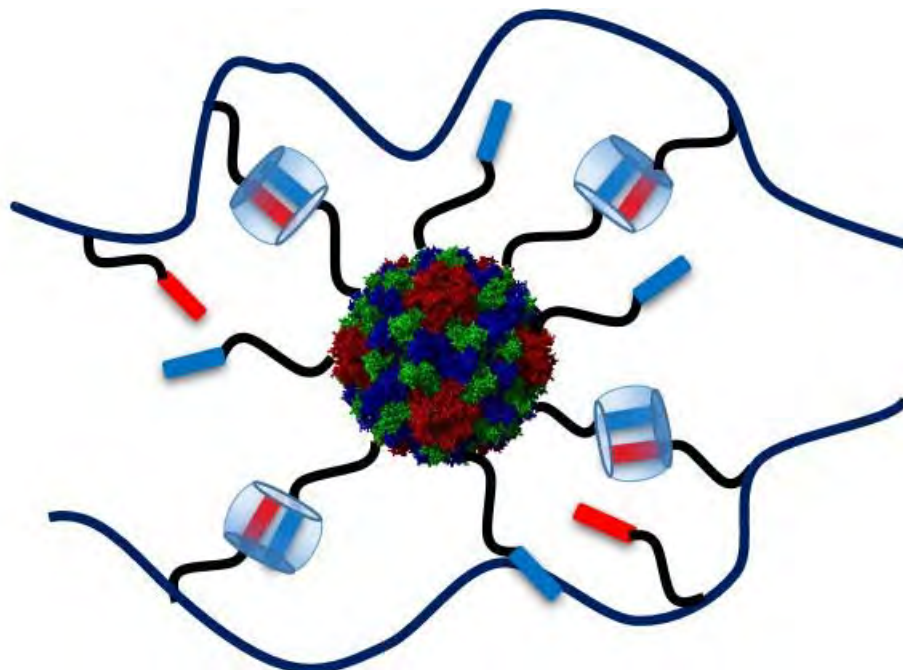


POLY 523: Supramolecular materials from virus-like particles as building blocks

Jeroen J. Cornelissen, *J.J.L.M.Cornelissen@tnw.utwente.nl. Laboratory for Biomolecular Nanotechnology, University of Twente, Enschede, Netherlands*

In recent years proteins and polymers have been combined in a variety of hybrid materials that have interesting properties, often incorporating characteristics of both building blocks in the same material. While much research in this field focuses on the use of single proteins, protein cages like viruses and virus-like particles (VLPs) offer extra possibilities. Viruses are well-defined supramolecular structures from protein building blocks that occur in different shapes and sizes depending on the virus species. They are monodisperse and highly symmetrical, often corresponding to Casper-Klug icosahedral symmetry in which the number of protein subunits per capsid is given by 60 times the triangulation number (T) of the virus. Furthermore, many viruses possess a natural self-assembly behavior which allows for the encapsulation a variety of materials. Finally, the proteins of these particles can be chemically and genetically modified giving them new, unique properties.

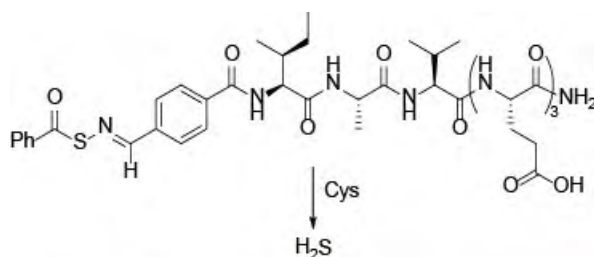
These latter properties have been employed by us to combine the self-assembly of the virus protein building blocks with other supermolecular handles that allow for the use of functional VLPs in the development of materials with a high level of nanoscale organization. In the present contribution examples will be given of the formation of hydrogels by linking the VLP with rigid macromolecules employing 2:1 complexes with cucurbiturils or their photo-reversible patterning on a surface employing a similar strategy.



POLY 524: Supramolecular gels for delivery of hydrogen sulfide

John B. Matson^{1,2}, jbmatson@gmail.com, Yun Qian², Kuljeet Kaur^{1,2}. (1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

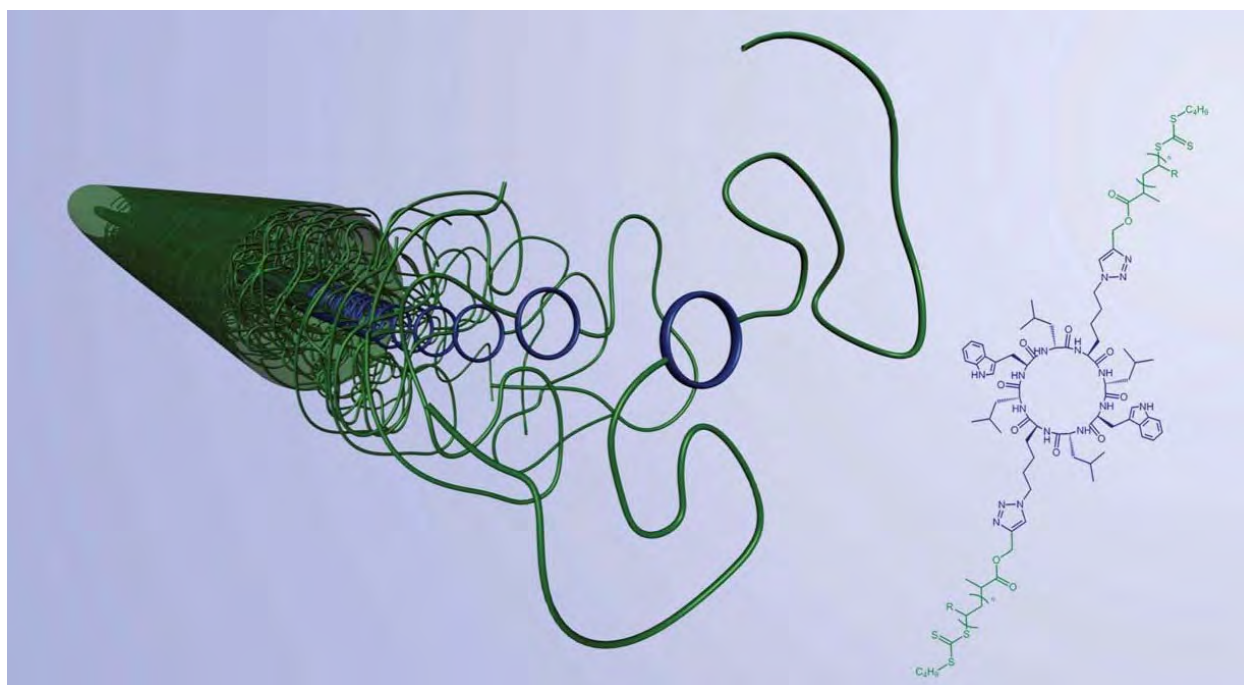
Peptide-based small molecule gelators have been studied widely for delivery of drugs and proteins. Here we present our efforts to deliver a biologically relevant signaling gas, H₂S, from physically crosslinked, peptide-based hydrogels. The gels are comprised of short peptides derivatized with *S*-aroylthiooximes—a functional group that releases H₂S in response to thiols. The functionalized peptides self-assemble in aqueous solution to form 1D nanostructures, and entanglement of these nanostructures leads to gelation in aqueous solution at <1 wt. %. Functionalization of the hydrophobic *S*-aroylthiooxime group allows for tuning of both the H₂S release rate and the observed assembly state. We present here the synthesis, mechanical properties, H₂S generation capacity, and biological evaluation of these unique gels.



POLY 525: Tubular supramolecular polymers

Sebastien Perrier, s.perrier@warwick.ac.uk. University of Warwick, Coventry, United Kingdom

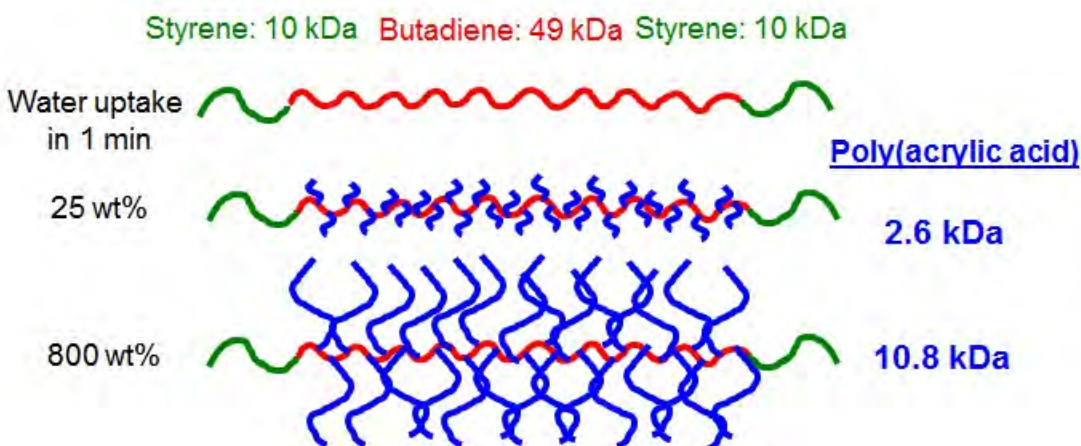
Cyclic peptides (CPs) of alternating D and L amino acids adopt a conformation that promotes stacking between CP units by the formation of cylindrical β -sheets. By tethering synthetic polymers to self-assembling cyclic peptides, we have formed conjugates that self-assemble into supramolecular polymeric brush structures with a central channel. These supramolecular polymers can be used as synthetic ion channels across lipid bilayers, drug delivery vectors, and functional nanoparticles.



POLY 526: Synthesis of a tough thermoplastic elastomer that rapidly absorb water for use in hemorrhage control applications

Tyler R. Long², Tyler.r.Long8.civ@mail.mil, **Erich Bain**², **Frederick L. Beyer**², **Randy Mrozek**², **Alice M. Savage**¹, **Joseph Lenhart**². (1) MSTB, U.S. Army Research Lab, Belcamp, Maryland, United States (2) U.S. Army Research Laboratory, Aberdeen, Maryland, United States

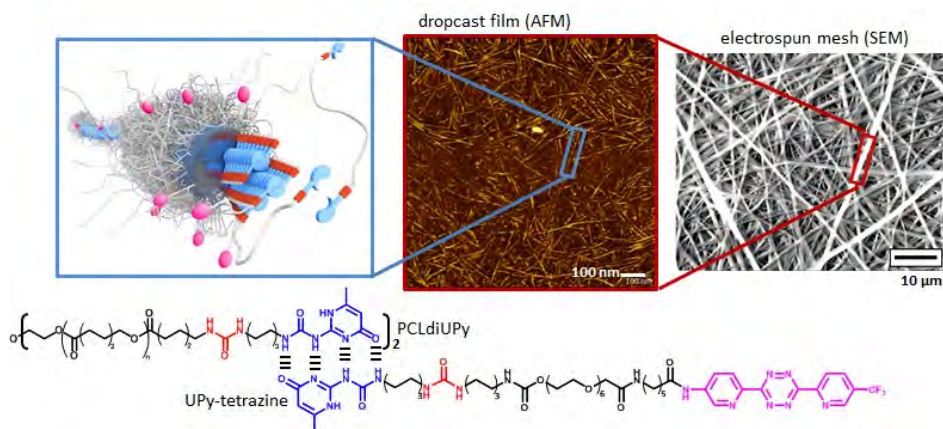
Uncontrolled hemorrhaging accounts for about 80% of the potentially survivable deaths of soldiers wounded on the battlefield. Of these deaths, approximately half are wounds to the torso that generally have complex, hard to treat wound geometries making a tourniquet ineffective. Other challenges unique to the battlefield include the time required to transport the injured soldiers and the fact that initial triage and treatment may be done by personnel without a medical background. The ideal hemorrhage control material must rapidly absorb water to concentrate clotting factors, expand to seal and exert pressure on the wound, and remain tough so it can be easily and safely removed. An additional goal would be to deliver therapeutic agents to accelerate hemostasis. We have developed a rapidly swelling polymeric material based on commodity thermoplastic elastomers that shows great potential to meet these goals. The swollen material has comparable toughness to current “tough” hydrogels, but can absorb up to 800 wt% water in just seconds. Rapid swelling and toughness are achieved by an ordered nanoscale structure with a continuous ionic phase supported by hydrophobically associated crosslinks. A material with optimized composition takes up 250 wt% water in < 1 minute under physiological conditions, and can be stretched up to double its length at 1 MPa stress without breaking while swollen. The ionic phase may also be used as a scaffold for delivery of therapeutics. The composition based on simple free-radical polymerization is easily tuneable, making this a low cost and versatile platform for a wide variety of hemorrhage control and other applications.



POLY 527: Functional, bio-inspired supramolecular polymeric materials – the interplay between covalent and non-covalent bonds

Olga Goor, Maxime Grillaud, Peter-Paul Fransen, **Patricia Y. Dankers**,
p.y.w.dankers@tue.nl. Institute for Complex Molecular Systems, Eindhoven University
of Technology, Helmond, Nederland, Netherlands

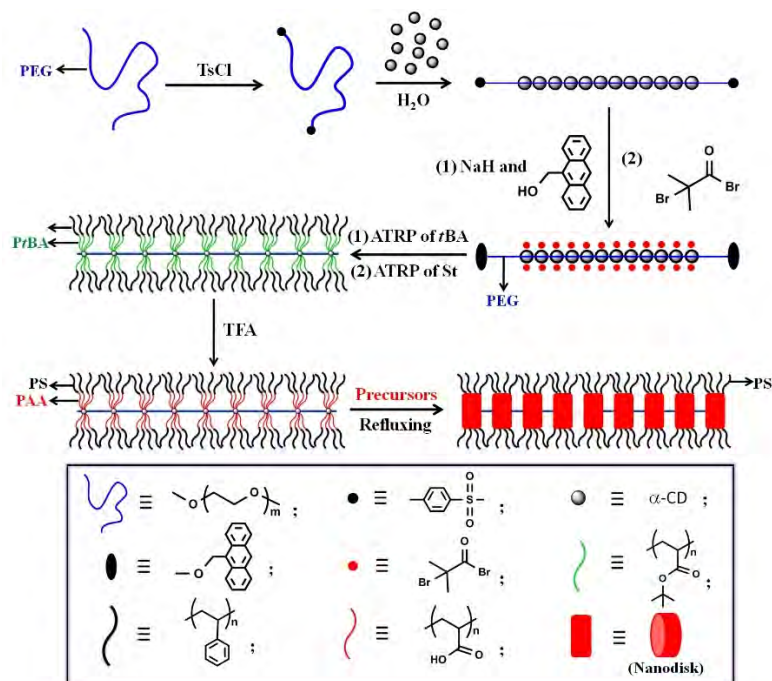
In regenerative medicine functional materials are developed to in-situ regenerate tissues. Full integration of synthetic materials into living tissues requires the interplay between synthetic and living materials in a spatiotemporal way. Bioinspired materials based on supramolecular units intrinsically show this dynamic behavior. However, the development of materials with stable bioactivity presentation and with good mechanical properties demands for the incorporation of covalent bonds. Inspired by nature we have combined supramolecular bonds based on hydrogen bonding, pi-pi stacking and hydrophobic interactions, with covalent bonds in order to incorporate (bio)functionality on supramolecular elastomers, and to introduce robustness in supramolecular hydrogels. The supramolecular motif employed, is the quadruple hydrogen bonding ureido-pyrimidinone (UPy) unit for both the elastomeric and hydrogel materials. Short prepolymers modified with UPy-units hierarchically self-assemble into nanofibers. Concomitant processing via electrospinning yielded micrometer-size fibers in which the self-assembled nanofibers are present (figure). Reactive supramolecular additives based on tetrazines were supramolecularly incorporated in supramolecular UPy-functionalized elastomers (e.g. based on short polycaprolactone prepolymers, i.e. PCLdiUPy). Post-modification via retro Diels Alder cyclo-addition was performed with reporter molecules, peptides, proteins and non-fouling molecules introducing specific functionality at the material's surface. Importantly we showed that the application of in depth 3D ToF-SIMS profiling resulted in elucidation of the bulk and surface composition of these supramolecular polymeric materials. Furthermore, the introduction of additional chemical crosslinks via 1,3-dipolar cyclo-addition in supramolecular UPy-hydrogel systems has shown to improve the mechanical properties while self-healing behavior is still displayed. In this way the control of both biological and mechanical properties in synthetic polymeric materials is regulated in a comparable way as natural polymers in the extracellular matrix control these properties; en route to synthetically meet nature's complexity.



POLY 528: From synthesis of nonlinear block copolymers based on cyclodextrins to functional nanoparticles and Shish-Kebabs

Zhiqun Lin, zhiqun.lin@mse.gatech.edu. School of Material Sci Engr, Georgia Institute of Technology, Atlanta, Georgia, United States

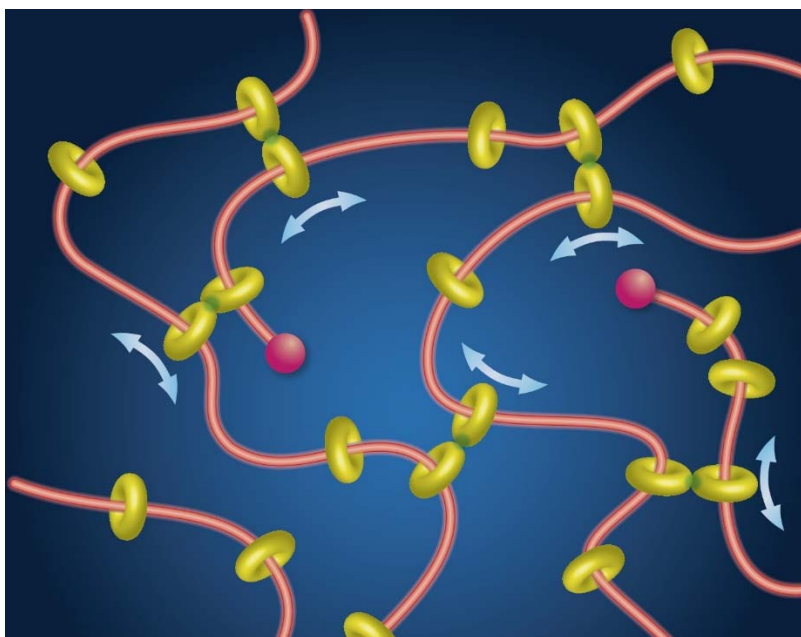
In this talk, I will demonstrate a general and robust strategy for the *in-situ* synthesis of a variety of 0D nanoparticles and 1D nanonecklaces composed of periodically assembled, uniform nanocrystals with precisely controlled size and composition using rationally designed amphiphilic unimolecular star-like and worm-like diblock copolymers poly(acrylic acid)-block-polystyrene (PAA-*b*-PS) as nanoreactors, respectively. As for nanonecklaces, first, nanoreactors are judiciously synthesized by sequential atom transfer radical polymerization (ATRP) of *tert*-butylacrylate (*t*BA) and styrene (St) from a polyrotaxane-based macroinitiator, yielding worm-like poly(*tert*-butylacrylate)-block-polystyrene (P*t*BA-*b*-PS), followed by the hydrolysis of P*t*BA into PAA (i.e., yielding PAA-*b*-PS). The polyrotaxane-based macroinitiator is virtually prepared by forming inclusion complex between α -cyclodextrin (α -CD) and linear polyethylene glycol (PEG). Subsequently, the preferential coordination interaction between metal moieties of precursors and functional groups of PAA in worm-like PAA-*b*-PS creates PS-capped inorganic nanonecklaces in which a wide range of regularly spaced disk-like nanocrystals (hereafter referred to as nanodisks), including semiconductor CdSe, magnetic Fe₃O₄ and ferroelectric BaTiO₃, are threaded by the flexible yet stretched PEG chain. These nanostructures can be regarded as organic-inorganic shish-kebabs, in which nanodisk kebabs periodically situated on a stretched polymer shish. Simulations based on self-consistent field theory reveal that the formation of organic-inorganic shish-kebabs is guided by the self-assembled elongated star-like diblock copolymer constituents constrained on the highly stretched polymer chain.



POLY 529: Slide-Ring materials: Tough polymers from cyclodextrin

Kohzo Ito, kohzo@k.u-tokyo.ac.jp. Department of Materials Sciences, The University of Tokyo, Kashiwa, Chiba, Japan

We have recently developed a novel type of polymer network called *slide-ring materials* by cross-linking polyrotaxane, the supramolecular architecture with topological characteristics. In the network, polymer chains are topologically interlocked by figure-of-eight cross-links. Hence, these cross-links can pass along the polymer chains freely to equalize the tension of the threading polymer chains similarly to pulleys. The structure and physical properties of the polymeric materials are drastically different from conventional cross-linked or noncross-linked materials. For instance, the slide-ring gel or elastomer shows quite small Young's modulus, which is not proportional to the cross-linking density and much lower than those of chemical gels with the same density. This arises from the difference in the molecular mechanism of the entropic elasticity: While the conformational entropy is mainly responsible for the elasticity in usual chemical gels or rubbers, the mechanical properties of the slide-ring gel should be inherently governed by the alignment entropy of free cyclic molecules in polyrotaxane as well as the conformational entropy of backbone polymer. This means that the softness in the slide-ring gel is due to the novel entropic elasticity, which is also expected to yield sliding state and sliding transition. Consequently, the slide-ring materials have the dynamic coupling between two kinds of entropy: the conformational entropy of strings and alignment entropy of rings. The concept of the slide-ring gel is not limited to cross-linked gels but also includes elastomer, cross-linked polymeric materials without solvent. Accordingly it can be applied to wide area such as soft contact lens, paints, rubbers, soft actuator and so on. As a typical example, the scratch-resist properties of the self-restoring slide-ring elastomer were adopted into the top coating on the mobile phone.



POLY 530: Supramolecular materials: Self-healing and stimuli-responsive polymeric materials through host-guest interactions

Akira Harada, *harada@chem.sci.osaka-u.ac.jp*. Graduate Sch of SCI Osaka Univ, Osaka, Japan

In recent years, much attention has been directed toward supramolecular chemistry. Although there have been a number of reports on supramolecular complexes and polymers, there are much less on supramolecular materials. More recently, we have found that supramolecular materials formed by host-guest interactions show unique properties, such as highly tough, flexible, and self-healing properties¹. When β -cyclodextrin(CD) monomer and guest monomer containing adamantane were copolymerized with acrylamide, we obtained a self-healable gel, because the gel is formed by host-guest interactions². We have also obtained a highly flexible gel by controlling a host-guest ratio. Recently, we found that [c2]daisy chains (doubly threaded host-guest dimers) can be used for stimuli-responsive materials³. When daisy chains composed by azobenzene as a guest and α -CD as a host are incorporated in the polymer network with tetra-armed polyethylene glycol, the network polymers show photo-responsive properties. When the gel was irradiated by UV light, the gel contracted, but when the contracted gel was irradiated by visible light, the gel stretched again to give an original state. Moreover, we found that freeze-dried gel (xero-gel) stretched 10,800 times faster than in water. Host-guest parts are incorporated in the gel only by mechanical bonds. Therefore, the system is the first example of artificial muscle moved through sliding between molecules, like sarcomere composed by actin and myosin filaments.

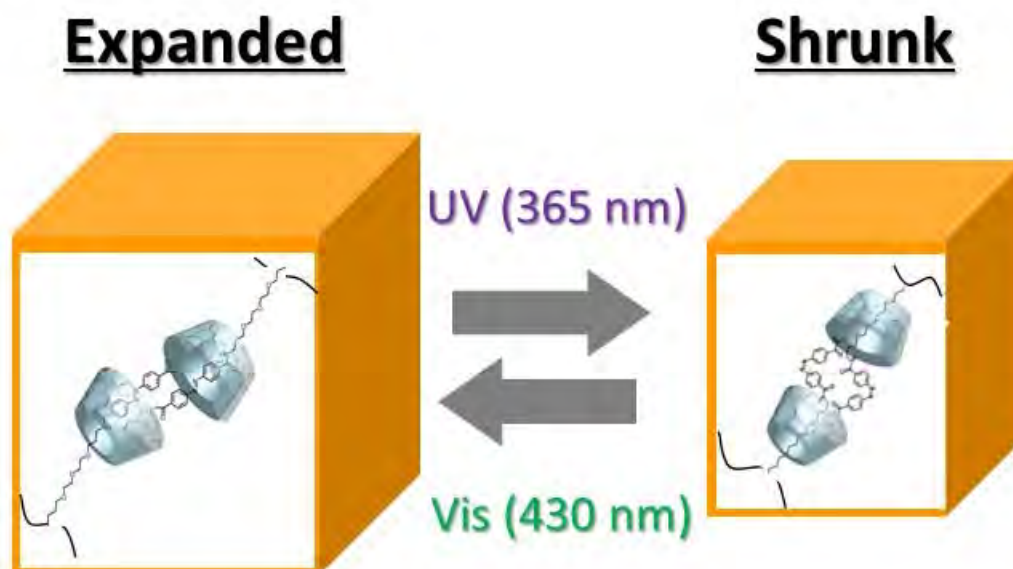
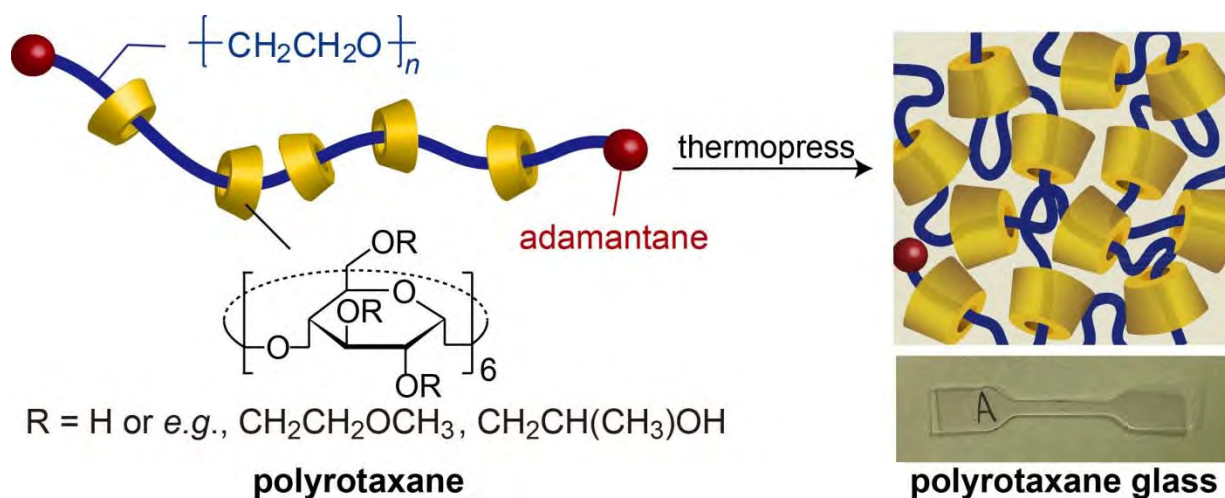


Photo-Induced Shape Change of Double-Threaded Dimer

POLY 531: Peculiar viscoelasticity and tensile behavior of polyrotaxane glass

Kazuaki Kato, *kato@molle.k.u-tokyo.ac.jp*, Kaito Nemoto, Koichi Mayumi, Hideaki Yokoyama, Kohzo Ito. Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, Chiba, Japan

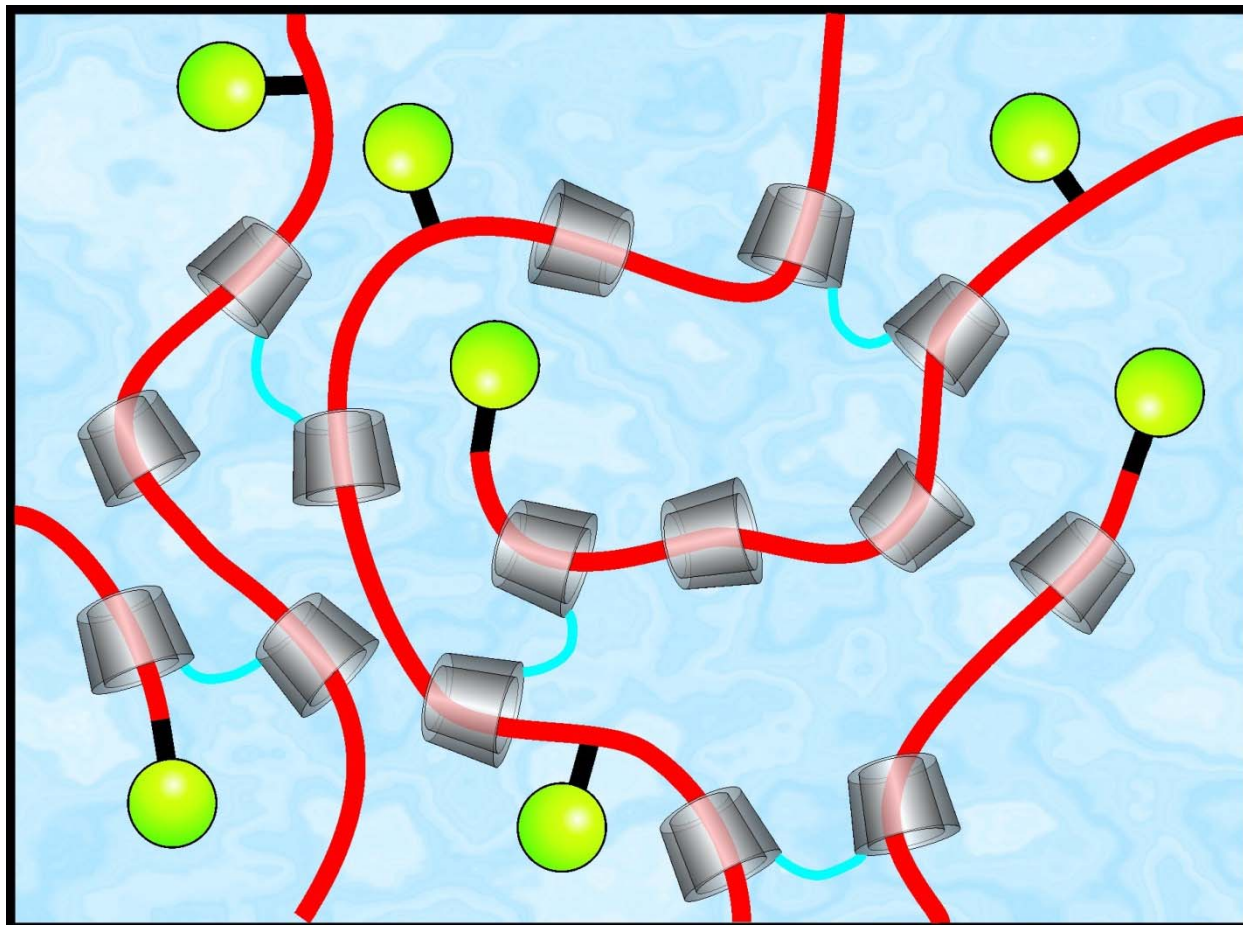
Control of the dynamics in polymer materials is crucial for the mechanical properties as well as the control of higher-order structures. From the aspect of unique molecular motions, mechanically interlocked polymers, such as polyrotaxanes, have been expected to show unique mechanical properties. We report here that a new class of glassy polyrotaxanes named “polyrotaxane glass” show unique viscoelasticity and tensile behaviors attributed to their intramolecular potential motions. Appropriate chemical modifications to the cyclodextrins (CDs) that are the cyclic components threaded with end-capped polyethylene glycol (PEG) yielded thermo-plastic polyrotaxanes. The polyrotaxanes were thermal press-molded to obtain glassy films. The polyrotaxane glass exhibited almost constant Young’s modulus of about 1 GPa at room temperature, and the glass transition temperature (T_g) is variable from 270 to 370 K depending on the substituents on CDs. The glass transition dynamics was almost Arrhenius-type, whereas the increase in apparent activation energy toward T_g was generally observed in conventional polymers. The sub-relaxation strength and the dynamics were constant as long as the backbone polymer and the coverage were the same. Notably, the unique viscoelasticity was not observed without the backbone. It indicates that large motions of the backbone PEG remain in the glassy frameworks formed by their cyclic components to generate the significant sub-relaxation. Under uniaxial tensile, the polyrotaxane glass showed crazing that accompanies the formation of nanoscale voids and fibrils and were extensible to >300% strain. In-situ X-ray scattering study under the tensile tests revealed that the microphase separation between CDs and naked PEG domains was induced by the deformation, as a result of the sliding of PEG through the cavity of CDs.



POLY 532: Self-healing car paints from cyclodextrin polyrotaxanes

Gerhard Wenz, g.wenz@mx.uni-saarland.de, *Gergely Kali*. Campus Saarbruecken, Saarland University, Saarbruecken, Germany

Fine scratches at a new car happen quite often and are always cumbersome. In an application oriented project we are going to develop a car paint with self-healing properties. Curing of our material is based on the elastic restoring force within a so-called slide ring gel (\rightarrow Scheme 1) obtainable after crosslinking of a polyrotaxane. For applications in car industry they have to be weather and uv resistant, robust, and finally producible at an acceptable price in large scale. We found a scaleable synthetic procedure for cyclodextrin polyrotaxanes which is performed in one pot in water resembling a standard emulsion polymerization. Smooth and transparent films are obtainable from it by coating or spraying techniques. These films can be toughened by conventional thermal crosslinkers being already in use for car paints. Relevant material properties (Vickers hardness, glass transition temperature, transmittance) are presently investigated and correlated with the molecular structure.



Scheme 1: Slide ring gel obtainable by crosslinking of cyclodextrin polyrotaxanes

POLY 533: Concurrent covalent and supramolecular polymerization

Xisen Hou^{2,3}, Chenfeng Ke^{1,2}, **J. F. Stoddart**², stoddart@northwestern.edu. (1) Department of Chemistry, Dartmouth College, Hanover, New Hampshire, United States (2) Department of Chemistry, Northwestern University, Evanston, Illinois, United States (3) Dow Chemical Co., Marlborough, Massachusetts, United States

Covalent and supramolecular polymerizations, both of which offer their own unique advantages, have emerged as popular strategies for making functional materials. In this presentation, we describe a concurrent covalent and supramolecular polymerization strategy by utilizing a rapid and efficient β -cyclodextrin(CD)-accelerated cucurbit[6]uril(CB)-templated azide–alkyne cycloaddition¹⁻³ with the supramolecular assembly of diazaperopyrenium dications, which are located periodically along the polymer backbone, by dint of π – π dimerization. We discovered that the orthogonal covalent and supramolecular polymerizations take place simultaneously in solution, resulting in an extended polymer network in an orthogonal dimension (Figure 1). We observed a two-dimensional polymer network in the form of monolayers with lateral sizes in the micron regime using TEM and AFM. This strategy⁴ benefits from both the robustness of covalent bond and the cooperative effect of noncovalent bonding interactions and could serve as a platform for the construction of a wide range of ordered materials.

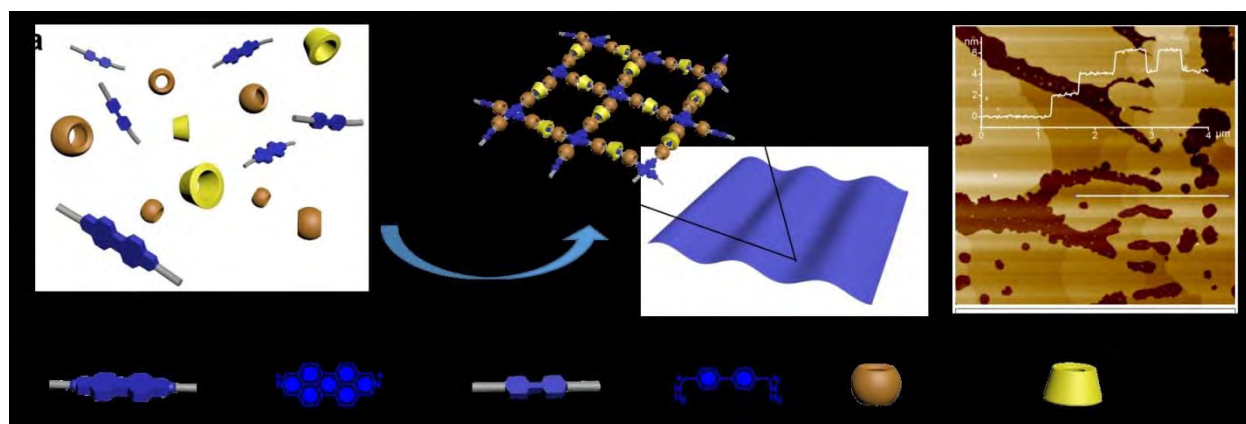
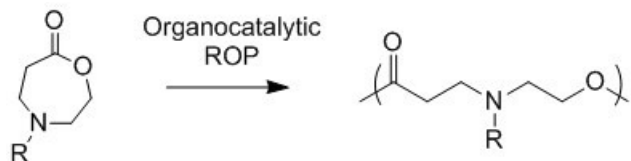


Figure 1. (a) Graphical illustration of the concurrent covalent and supramolecular polymerization. (b) Atomic force microscopic (AFM) image of the 2D polymer network revealing various stacks of monolayers.

POLY 534: Synthesis and Organocatalytic Polymerization of Azacaprolactones

Christopher Turlington¹, cturling@stanford.edu, Robert M. Waymouth². (1) Chemistry, Stanford University, Redwood City, California, United States (2) Dept of Chemistry, Stanford University, Stanford, California, United States

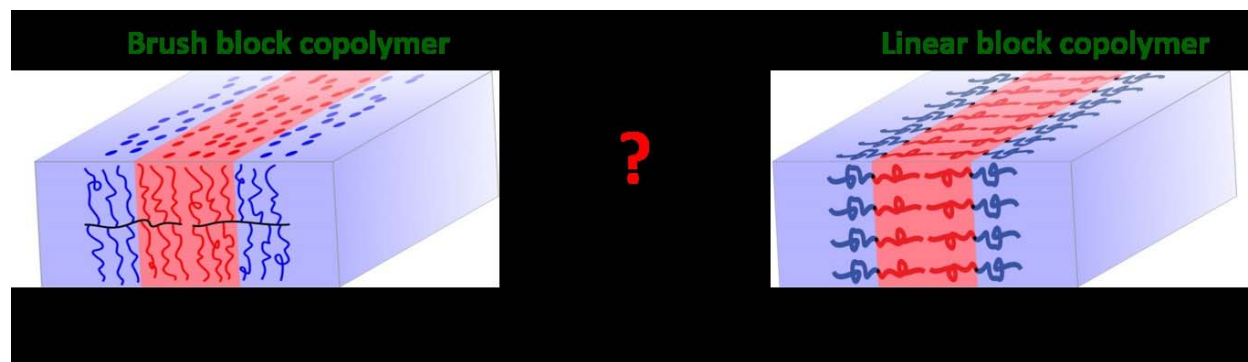
Synthesis of azacaprolactones with N-alkyl substituents is described. The substituted azacaprolactone products are strong bases when neutralized. Organocatalytic polymerization of the azacaprolactone monomers is explored using anionic thiourea catalysts. Attempts at homopolymerization and copolymerization are reported. The properties of the resulting polymers were explored and a self-immolative mechanism for a polymer was discovered following deprotection of an N-Boc group in the polymer backbone.



POLY 535: Synthesis and self-assembly of brush block copolymers with various grafting densities

Tzu-Pin Lin², tplin@caltech.edu, Alice Chang², Christopher Bates², Robert H. Grubbs¹.
(1) Cal Tech 164-30, Pasadena, California, United States (2) California Institute of Technology, Pasadena, California, United States

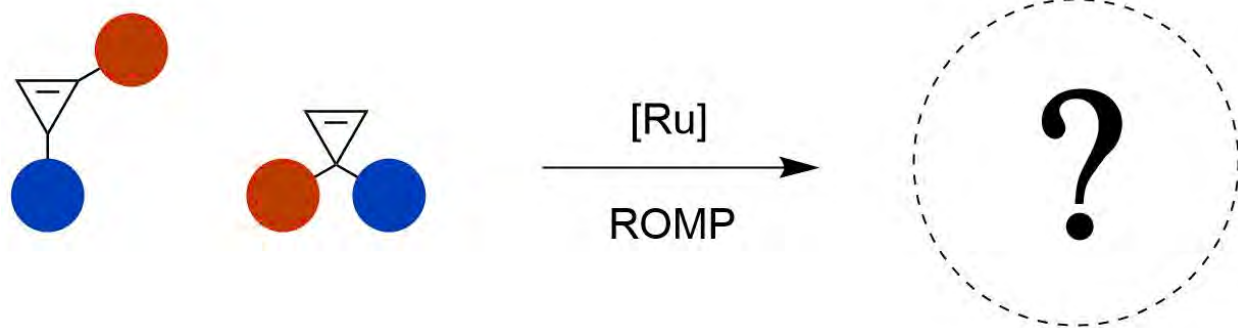
Brush block copolymers are of intensive interest due to their abilities to undergo rapid self-assembly, leading to potential applications in the field of nanoscience. The relatively low kinetic barrier to reach an ordered equilibrium structure can be, in part, attributed to the reduced chain entanglement engendered by the densely grafted polymeric side-chains. To better understand the effects of side-chains on the self-assembly and physical properties, we have prepared a series of di-block copolymers with various side-chain densities. These copolymers, synthesized by ring-opening metathesis polymerization (ROMP), are designed so that the side-chains are evenly spaced out across the entire backbone. The self-assembly of these copolymers have been investigated by SEM, TEM, and SAXS.



POLY 536: Surprising and diverse reactivities of cyclopropenes in ring-opening metathesis polymerization

Jessica Su, jksu@stanford.edu, Yan Xia. Chemistry, Stanford University, Stanford, California, United States

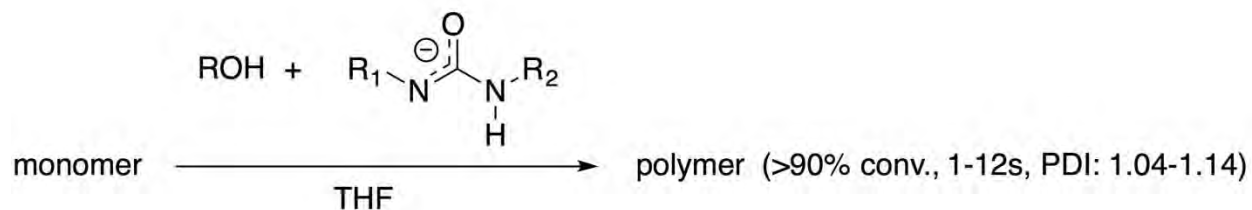
Cyclopropenes (CPs), the most strained cyclic olefins, surprisingly have been rarely explored as monomers for ring-opening metathesis polymerization (ROMP). We undertook the first systematic investigation of a library of functionalized 1,1- and 1,2-disubstituted CPs for ROMP, and discovered diverse and surprising reactivities depending on the substitutions on CPs. Some CPs undergo rapid and controlled homopolymerization to yield polymers with controlled MWs and low dispersities; some CPs do not homopolymerize but undergo alternating ROMP in a controlled fashion; some CPs however decompose the catalyst rapidly. We will present these reactivities of CPs, which can be fine-tuned via their substituents. Their ROMP adds to the repertoire of controlled polymerizations and creates a range of new, controlled, and functional polymer structures.



POLY 537: Deprotonated ureas as simple, ultra-fast and highly selective super catalysts for ring-opening polymerizations

Binhong Lin, binhong@stanford.edu. Department of Chemistry, Stanford University, Stanford, California, United States

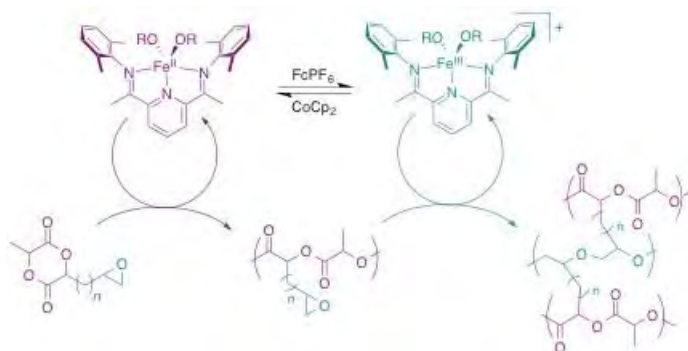
Polyesters and polycarbonates are ubiquitous polymers found in wide-ranging applications. Herein we have shown that the urea anions are a class of ultra-fast and highly selective ring-opening polymerization catalysts. With the appropriate anions, the living ring opening polymerizations of several common monomers (L-lactide, δ -valerolactone, ϵ -caprolactone, BnO-trimethylenecarbonate and iPr-phosphotriester) reached high conversions ($\geq 90\%$) to generate their respective polymers at room temperature within seconds (1-12s) and yielded polymers with narrow molecular weight distributions (PDI = 1.04-1.14).



POLY 538: Synthesis and characterization of crosslinked biodegradable polymers obtained using a redox-triggered crosslinking reaction

Kayla R. Delle Chiaie¹, krdc20@gmail.com, Ashley B. Biernesser¹, Lauren Yablon², Alexander W. Sudyn¹, Gregory R. Michalowski¹, Jeff A. Byers¹. (1) Chemistry, Boston College, Bonita Springs, Florida, United States (2) Chemistry, Columbia, New York, New York, United States

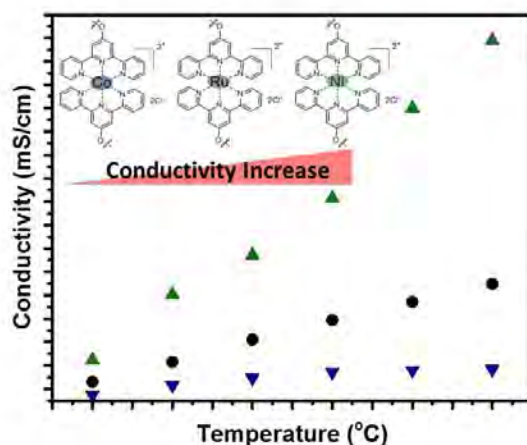
A catalyst system using the redox-active bis(imino)pyridine iron(II) bis(alkoxide) has been utilized to develop a new way to crosslink polymers that complements existing methodologies. The new method relies on the chemoselectivity of the catalyst, which is dependent on the oxidation state of the catalyst being active for cyclic diester polymerization in the iron(II) oxidation state and inactive when in the iron(III) oxidation state. Orthogonal reactivity was observed for reactions with epoxides (i.e. iron(III) is active for epoxide polymerization while iron(II) is inactive), which allowed for the application of the system for redox-triggered crosslinking when monomers that contain both a cyclic diester and epoxide functionality are employed. Investigation into the dependency that this reaction has on the identity of the crosslinking monomer will be discussed. Additionally, efforts to control the crosslinking density will be investigated including copolymerization reactions between the functionalized monomers and lactide, redox-switchable crosslinking reactions, and terpolymerization reactions between epoxide-functionalized cyclic diesters, lactide, and epoxides. The effect that these different cross-linked polymers has on the thermal, physical, and mechanical properties of the new cross-linked polymers will be revealed.



POLY 539: Going beyond ruthenium in metal-cation-based anion exchange membranes

Michael Kwasny¹, mkwasny476@gmail.com, Gregory N. Tew². (1) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Polymer Science and Engineering, University of Massachusetts, Amherst, South Deerfield, Massachusetts, United States

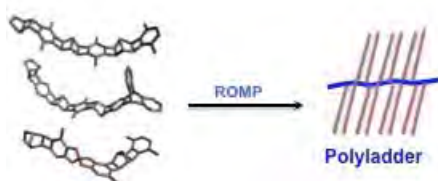
Here we explore the versatility of metal-cation-based anion exchange membranes (AEMs) to determine if metals other than just ruthenium can be implemented in this platform. Previously, our group synthesized a ring-opening-metathesis polymerization (ROMP)-based AEM featuring cationic ruthenium complexes to replace less stable organic cations. While these membranes demonstrated excellent chemical stability, mechanically robust properties and good conductivity, the choice of ruthenium, a rare earth metal, was not ideal for this type of application. Therefore, we synthesized AEMs containing more abundant metals, nickel and cobalt, in an effort to replace ruthenium. This was accomplished by synthesizing new monomers containing homoleptic metal complexes with norbornene functionalized terpyridine ligands. These monomers were then polymerized and crosslinked using ROMP to form AEMs which were tested for their water uptake, chemical and mechanical stability, and anion conductivity to elucidate whether nickel, cobalt, or both could be viable substitutes for ruthenium. The choice of metal effected neither water uptake nor mechanical properties and, despite more labile coordination bonds introduced through nickel and cobalt, all AEMs maintained excellent alkaline stability. However, changing the metal-cation in the AEM appeared to have an effect on the ability of the membrane to conduct anions, suggesting that the nature of the cation plays an important role in AEM performance. Results indicate that the nickel-containing AEM had the best conductivity of all three metals studied, demonstrating that other metals can be used in these types of AEMs, and in fact, there may be better options than ruthenium for overall performance.



POLY 540: Polyladders: A new polymer architecture via ROMP of rigid ladder motifs

Yew Chin Teo, yewchin@stanford.edu, Yan Xia. *Chemistry, Stanford University, Stanford, California, United States*

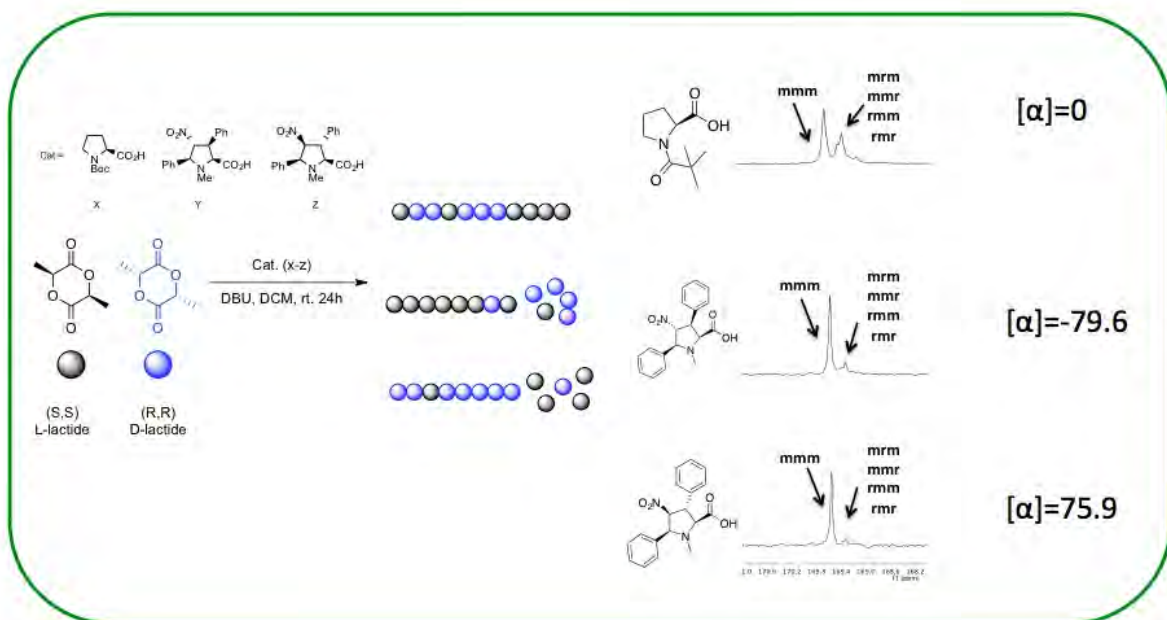
A range of norbornene functionalized rigid ladder-type monomers can be synthesized from facile catalytic arene-norbornene annulation (CANAL). Ladder structures with different conformations and functionalities were readily incorporated using the efficient CANAL chemistry. Ring-opening metathesis polymerization (ROMP) of these rigid ladder monomers proceeded to quantitative conversions to yield a series of polymers with ladder side chains, which we call polyladders. The synthesis and characterization of these new types of polymers will be presented.



POLY 541: Prolines as efficient catalyst for stereocontrolled polymerization of rac-lactide

haritz sardon¹, haritz.sardon@ehu.es, ana sanchez-sanchez¹, Ivan Rivilla², andere basterrechea¹, maddalen agirre², David Mecerreyes¹, fernando Cossio². (1) POLYMAT, University of the Basque Country, Donostia-San Sebastian, Gipuzkoa, Spain (2) Organic Chemistry I, University of the Basque Country, San sebastian, gipuzkoa, Spain

Stereoregular polymerizations have attracted great attention since the first report reported by Natta to prepare isotactic polypropylene. Given the almost limitless opportunities of ligand/metal combinations, it is not surprising that transition metal and organometallic catalysts have dominated the field. Nevertheless, their substantial toxicity and sensitivity is accelerating the development of organic catalysts to replace metal based catalysts in sensitive applications, such as biomedical or microelectronics. To date, some organic catalysts have shown the ability to promote stereocontrolled polymerization. However, none of them showed the ability to transfer the chirality from catalyst to polymer and promote different stereochemical outcomes by modifying the chirality of the catalyst. In this work we report for the first time the chirality transfer from a fully organic based catalyst to the polymer using proline based catalytic system.

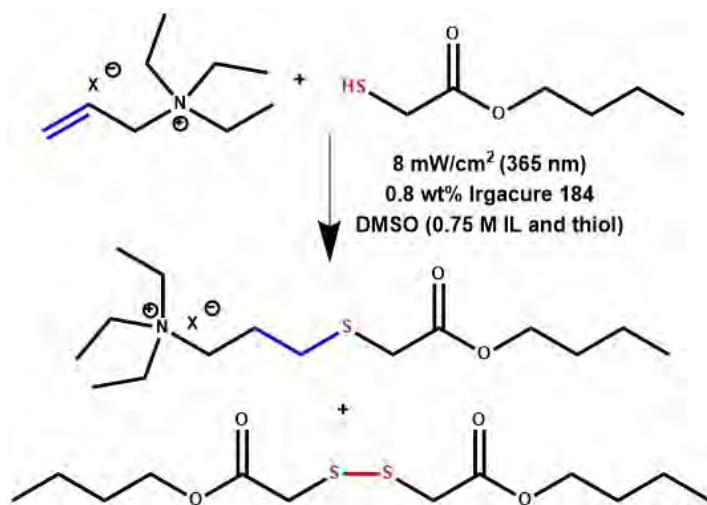


POLY 542: Taking charge of thiol-allylic ionic liquid photopolymerizations

Andrew Tibbits, *atibbits@udel.edu*, Laura Mumper, Yushan Yan, Christopher J. Kloxin.
Chemical Engineering, University of Delaware, Newark, Delaware, United States

Thiol-ene reactions are versatile organic reactions between a thiol (-SH group) and an 'ene' (an electron rich vinyl group, C=C) that proceed via an alternating step growth and chain transfer mechanism. Additionally, the photoinitiated reaction is observed to be rapid, selective, and high yielding in the fabrication of polymeric materials.¹ Covalent binding of low melting point salts, ionic liquids (ILs), directly onto polymers classifies them as polymeric ionic liquids (PILs) and imparts these materials with electrolytic properties such as ion conductivity.² The kinetics of the direct reaction between thiols and allylic ILs have not been studied in detail and would provide a framework for the selection of monomers for PILs with readily tailored properties.

Our studies show that the use of heterocyclic amine-based ILs, such as imidazolium and pyridinium, and thiols, such as mercaptopropionates, yield the fastest thiol-allylic IL rates for formation of ideal ionic thioether products as observed by NMR and FTIR spectroscopy. Furthermore, all of the thiol-allylic IL reactions studied are chain transfer limited by nature. Model spectroscopic studies show that the use of high polarity or chlorinated aprotic solvents promotes photoinitiated disulfide formation which competes with the thiol-ene reaction and shifts the overall reaction kinetics from first order to second order overall. These model studies demonstrate the scope and limitations of the thiol-allylic IL reaction and can be directly applied to the synthesis of both linear and crosslinked PILs with readily tuned physicochemical properties as will be showcased in the design of thiol-ene PIL networks as membranes for alkaline fuel cells³ or separations.

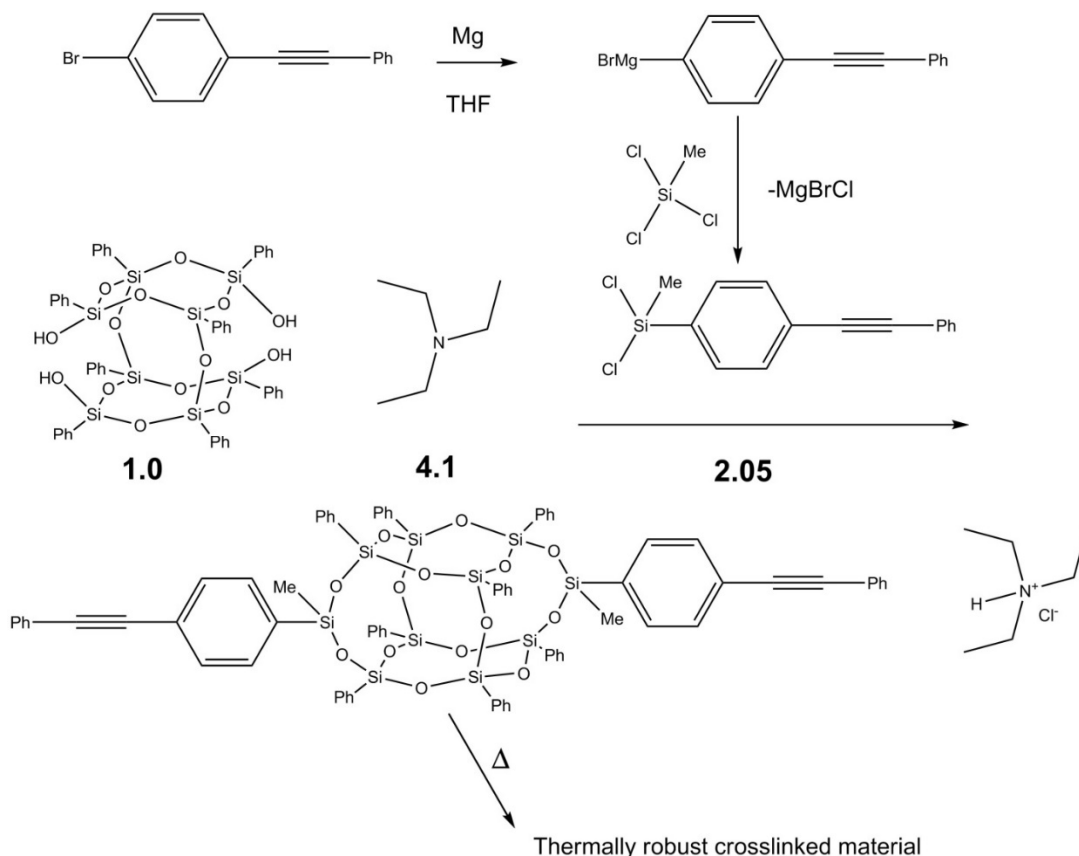


Representative schematic of allylic ionic liquid reaction with butyl thioglycolate to form ionic thioether product and disulfide side product.

POLY 543: Silsesquioxane-based thermosetting phenylethynyls: Synthesis, thermally induced crosslinking and thermophysical properties

Tim S. Haddad¹, *timothy.haddad.ctr@edwards.af.mil*, Gregory R. Yandek², jacob zavalala¹, jason lamb¹, Josiah Reams¹, Kamran Ghiass², Joseph M. Mabry², Andrew J. Guenther². (1) Aerospace Systems Directorate, ERC Inc., Air Force Research Lab, Lancaster, California, United States (2) Aerospace Systems Directorate, Air Force Research Laboratory, Lancaster, California, United States

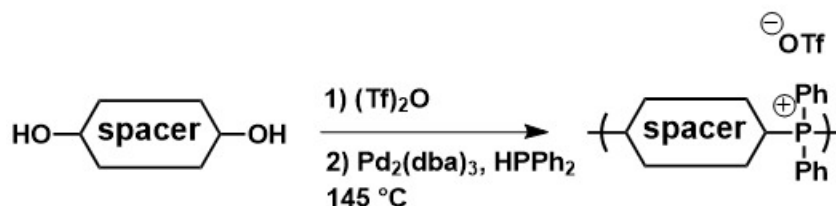
Polyhedral Oligomeric Silsesquioxanes (POSS) are inorganic/organic cages that are used as high-tech additives to enhance the thermal, mechanical and surface properties of many polymeric systems. A useful analogy is that a POSS is nano-sized particle of silica solubilized with organic modifiers ($\text{RSiO}_{1.5}$)_n; the organic periphery determines how well the POSS can interact with any host polymer, while the siliceous core adds thermoxidative stability. Beginning in 1993 and continuing today, there has been extensive research in understanding how POSS incorporation into various materials affects polymer properties. Herein is reported a synthesis strategy to produce POSS-containing, thermosetting phenylethynyls to yield high temperature materials with extreme thermo-oxidative stability, low moisture uptake and good mechanical properties.



POLY 544: New synthetic route to tetraarylphosphonium polyelectrolytes *via* Pd(0) catalyzed polycondensation from diols and diphenylphosphine

Wang Wan², wan2@g.clemson.edu, Xiaoyan Yang², Rhett Smith¹. (1) Clemson University, Clemson, South Carolina, United States (2) Chemistry, Clemson University, Central, South Carolina, United States

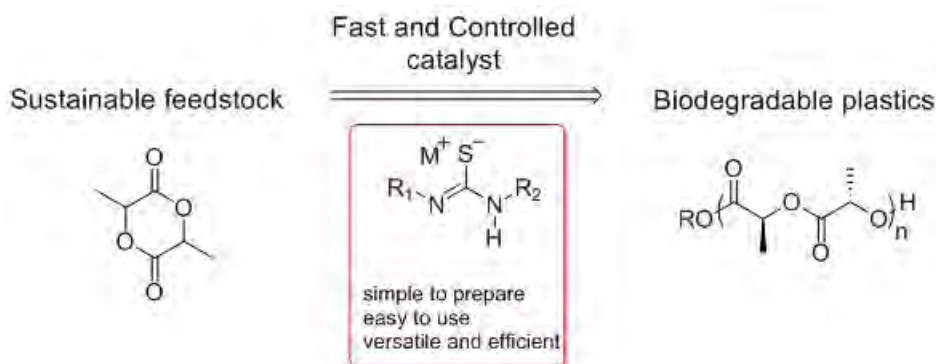
Based on former established P-C coupling reactions of small molecules and polymeric bromide, a new polymerization method involving triflate has been investigated, and a series of eight tetraarylphosphonium polyelectrolytes have been successfully synthesized starting from diols. The palladium catalyst is effective in polymerizing with high degree of polymerization up to 100 and outstanding yield. All triflates polymers have good thermal stability in the range of 350-450 celsius degree. The properties of tetraarylphosphonium polymers are investigated that strongly depend on the spacer between adjacent phosphonium sites as well as counterions. Success of this synthetic method provides a new way to tetraarylphosphonium polymer by using more commercial available precursors and it's not limited on dibromoarenes, so that more tetraarylphosphonium polymers can be prepared and their properties can be investigated systematically.



POLY 545: Thioimidates: Fast and selective catalysts for ring-opening polymerizations

Xiangyi Zhang¹, xiangyiz@stanford.edu, Robert M. Waymouth². (1) Chemistry, Stanford University, Stanford, California, United States (2) Dept of Chemistry, Stanford University, Stanford, California, United States

The development of new catalytic methods continues to drive innovation in polymer chemistry. Organocatalytic ring-opening polymerization (ROP) of cyclic esters and carbonates has proven particularly useful for the generation of biodegradable polymers. We discovered an operationally simple catalytic system combining alkoxides with thioureas that catalyze rapid and selective ROPs. Deprotonation of thioureas by sodium, potassium or imidazolium alkoxides generates a H-bonded alcohol adduct of the thiourea anion. The ROPs of L-lactide mediated by these alcohol-bonded thioimidates yields highly isotactic polylactide with fast kinetics and negligible transesterifications. Computational studies elucidate a bifunctional catalytic mechanism where thiourea simultaneously activates monomers and reversibly shuttles protons to alkoxide chain end to modulate its activity. The high selectivity of the catalyst towards monomer propagation over transesterification arises from a higher affinity of cyclic esters relative to open-chain esters to the H-bond catalyst. The catalyst motif is highly tunable through changing the counterions or the substituents on the thiourea scaffold. The strategy of using H-bond donors to modulate the reactivity of anionic chain ends could be useful for controlling other anionic polymerizations.

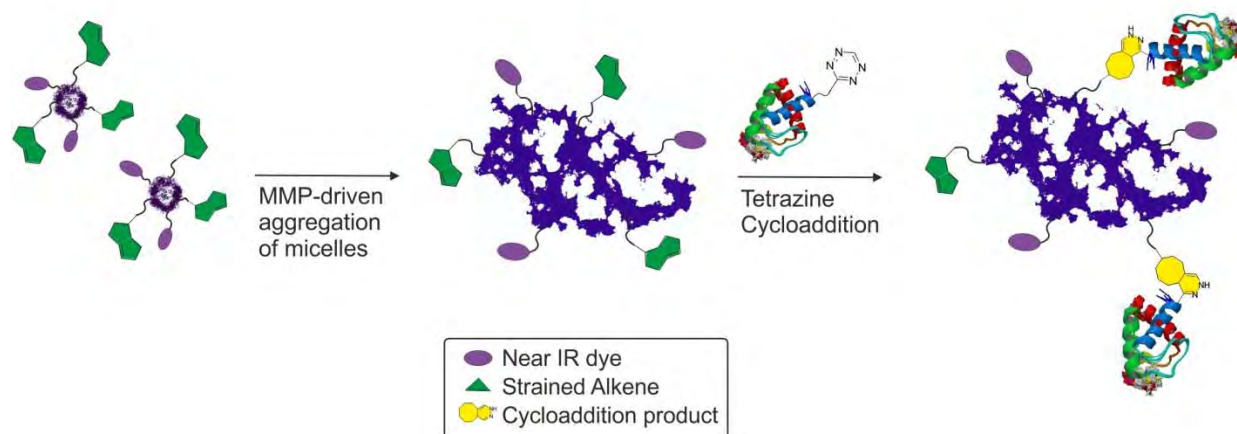


POLY 546: Enzyme-responsive nanoparticles for the targeted delivery of tetrazine-labeled proteins

Julia Michaelis³, ju.michaelis@gmx.de, Peter Tufar³, Michael D. Burkart², Nathan C. Gianneschi¹. (1) Chem M/C 0343, University of California, San Diego, La Jolla, California, United States (2) Mail Code 0358, University of California, San Diego, La Jolla, California, United States (3) Chemistry & Biochemistry, University of California, San Diego (UCSD), San Diego, California, United States

The use of nanomaterials in medical applications offers the promising possibility to deliver drugs through the selective accumulation of therapeutics in diseased tissue. In recent studies of the Gianneschi lab it has been demonstrated that enzyme-responsive micellar nanoparticles undergo a morphological transition from spherical-shaped materials into network-like assemblies when acted upon matrix metalloproteinases (MMPs). In xenograft mice this beneficial morphology switch leads to the accumulation and retention of these materials within tumor tissue in response to tumor-related overexpressed MMPs.

We present an approach in which we utilize these enzyme-responsive nanoparticles and their enzymatically formed assemblies as a scaffold to deliver a large biomolecule such as a protein by the means of a bioorthogonal cycloaddition reaction. We have synthesized MMP-responsive peptide polymer amphiphiles by ring-opening metathesis polymerization (ROMP) followed by the conjugation of a strained alkene. After assembling these into micellar nanoparticles we successfully conjugated a tetrazine-labeled membrane protein. The cycloaddition reaction with the protein was still efficient after the aggregation of our material into network-like assemblies. We envision that the in-tumor agglomerated nanoparticles may be labeled *in vivo* with any therapeutic biomolecule and as such facilitate a localized therapy at the tumor site.



POLY 547: Probing the causes of thermal hysteresis using tunable N_{agg} micelles with linear and brush-like thermoresponsive coronas

Lewis D. Blackman¹, lblackman1990@gmail.com, **Matthew I. Gibson**², **Rachel K. O'Reilly**¹. (1) Chemistry, University of Warwick, Coventry, United Kingdom (2) Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom

Thermoresponsive polymers are of great interest as switchable smart materials. poly(*N*-isopropylacrylamide) (pNIPAM), an important thermoresponsive polymer, has been widely studied but the question of its reversibility (hysteresis) may limit its potential. Herein, we aimed to utilize well-defined micelles with thermoresponsive coronas and tunable aggregation numbers (N_{agg}) to study the effects of altering micellar structure on hysteresis. To this end, initial efforts focused on micelles composed of a thermoresponsive pNIPAM corona and a non-responsive core block (poly(*n*-butyl acrylate-*co*-*N,N*-dimethylacrylamide)). The block copolymers were synthesized using RAFT polymerization to yield a series of micelles with varying core compositions, which led to tunable N_{agg} values. Thermoresponsive behavior at the molecular and macroscopic level was probed using complimentary analyses. Our results showed that the degree of hysteresis increased as a function of core hydrophobicity (Fig. 1, LHS), which was attributed to differences in core hydration. Similar micellar series were then used to investigate different thermoresponsive coronas in order to find structure-property relationships behind the origins of hysteresis. Using linear pNIPAM and poly(*N,N*-diethylacrylamide) (pDEAm) coronas, the effect of hydrogen bonding ability on hysteresis was studied (Fig. 1, LHS). By comparing these to brush-like poly(diethylene glycol monomethyl ether methacrylate) (pDEGMA) and poly(oligo(ethylene glycol) monomethyl ether methacrylate) (pOEGMA) coronas, which showed irreversible transitions at high chain density, the effects of chain architecture and T_g was elucidated (Fig. 1, RHS). These results highlight the need for consideration of the effect that self-assembly plays on the responsive behavior of particles when compared with free unimers in solution.

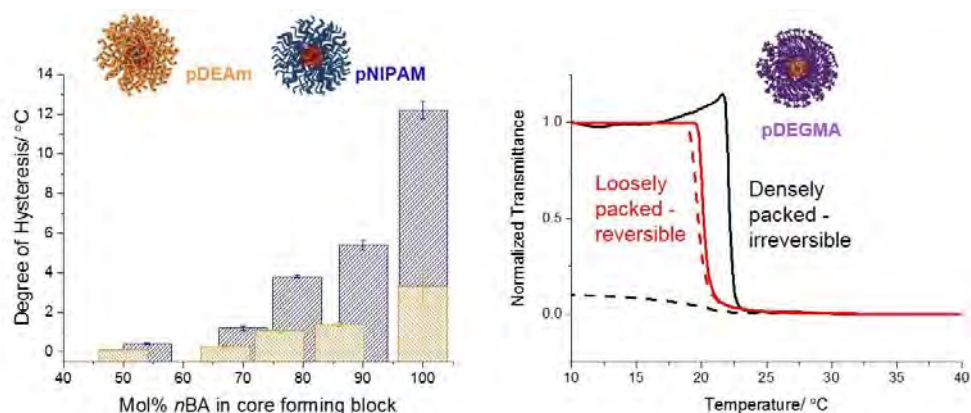
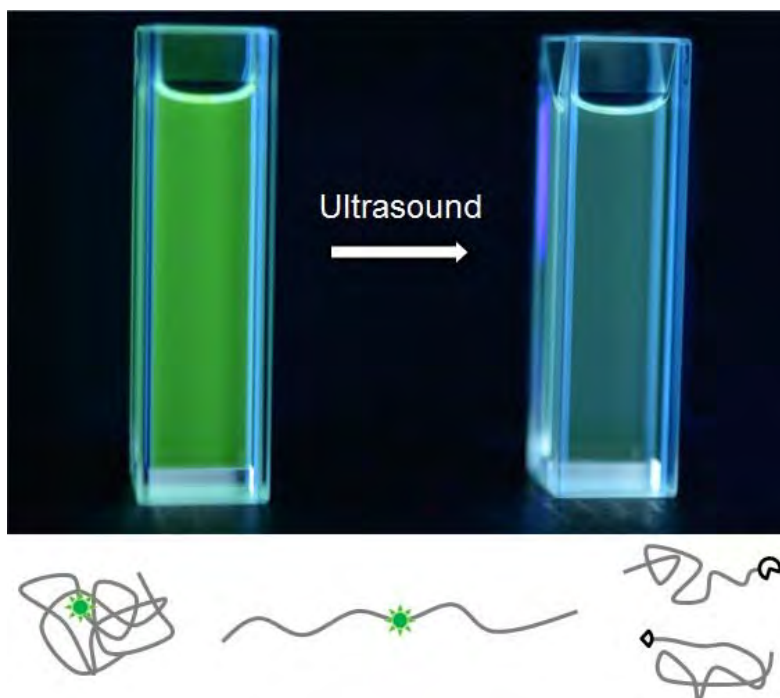


Fig. 1. LHS: Effect of hydrogen bonding ability and core composition on hysteresis of micelles with pNIPAM (blue) and pDEAm (orange) coronas. **RHS:** Reversible (red) and irreversible (black) phase transitions of micelles with pDEGMA coronas with loosely and densely packed chains, respectively.

POLY 548: Mechanochemical fluorescence switching in polymers containing dithiomaleimide moieties

Marc Karman¹, marc.karman@unifr.ch, Ester Verde-Sesto¹, Yoan C. Simon^{2,1}, Christoph Weder¹. (1) Adolphe Merkle Institute, University of Fribourg, Marly, Switzerland (2) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States

Despite many studies that have investigated mechanochemical effects in polymers, the number of polymers whose fluorescence characteristics change upon exposure to mechanical stress is still limited. We introduce here the fluorescent dithiomaleimide (DTM) motif as a mechanically responsive motif. This mechanophore was incorporated into poly(ϵ -caprolactone)s (PCL) of different molecular weights. Macromolecules featuring exactly one DTM moiety at their center (PCL-DTM) were prepared by the ring-opening polymerization of ϵ -caprolactone using a di-hydroxy functionalized DTM derivative (1-benzyl-3,4-bis(2-hydroxyethylthio)-1H-pyrrole-2,5-dione) as a difunctional initiator. Upon subjecting solutions of high-molecular-weight PCL-DTM to ultrasound, the fluorescence intensity and molecular weight decreased according to first-order kinetics with comparable rate constants. By contrast, the fluorescence characteristics of DTM-free high-molecular-weight PCL in the presence of unbound DTM and a PCL-DTM with a molecular weight below the critical limit required for sonochemical dissociation did not change when exposed to the same conditions. A substantial decrease of the fluorescence intensity was also observed when solid samples of the high-molecular-weight PCL-DTM were grinded. The data thus demonstrate the usefulness of the DTM motif as mechanophore that displays fluorescence turn-off upon mechanochemically induced scission.



POLY 549: Activation of a Maleimide-Anthracene Mechanophore Localized at a Silica-Polymer Interface

Jaeuk Sung², *jsung12@illinois.edu*, Maxwell Robb², Jeffrey S. Moore¹, Scott White¹, Nancy R. Sottos^{3,1}. (1) MC 251, Beckman Institute, Urbana, Illinois, United States (2) Material Science and Engineering, UIUC, Champaign, Illinois, United States (3) Materials Science and Engineering, University of Illinois, Urbana, Illinois, United States

Mechanophores, molecules that undergo chemical changes under mechanical stimuli, have been utilized in functional polymer material such as force probe, mechanically stimulated catalyst, and damage indicator. Although activation stress of mechanophores in homopolymer backbone chain have been readily studied, mechanophore activation at solid interface still requires further research. In this study, maleimide-anthracene mechanophores localized at a silica-polymer interface were fabricated to demonstrate mechanophore activation at solid interface and quantify its activation stress. Maleimide-anthracene cycloadduct mechanophore was functionalized and covalently bonded to a silica substrate suitable for laser spallation testing. When mechanical stress is applied, the mechanophore goes under [4+2] retro cycloaddition, leaving anthracene, a fluorescent molecule, on the silica surface. A polymer thin film was photo-patterned onto the surface and covalently bonded to the mechanophore. The mechanophore functionalized epoxy-silica specimen was loaded using laser induced stress waves. From the figure it is evident that beyond the critical threshold stress, 163 MPa, fluorescence signal from mechanophore activation is observed only on the surface where epoxy film spalled. In great contrast, control samples fabricated with non-covalent bonding between the mechanophore molecule and the polymer film did not exhibit any fluorescence, even after film failure. Further surface chemistry investigation was conducted through ToF-SIMS analysis. Elemental analysis confirmed that CNO⁻ ion, which originates from maleimide moiety of the mechanophore, was only present on the surface where epoxy film wasn't deposited. In summary, we demonstrated feasibility of mechanophore activation at solid-solid interface is feasible and quantified its critical activation stress using laser-induced stress wave loading. Quantified activation stress will serve as a key tool in designing functional polymer system such as self-sensing composite materials.

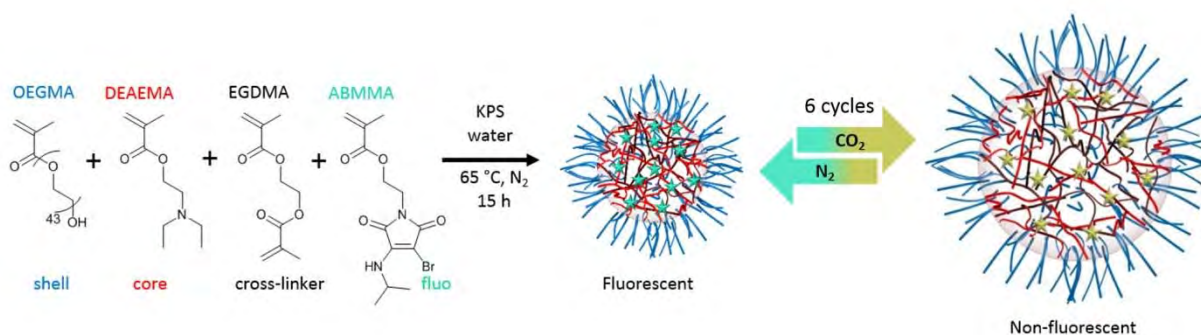


Micrographs of mechanophore-anchored polymer films on a silica substrate after laser impingement (a) 120 MPa. (b) 141 MPa. (c) 163 MPa, (d) 185 MPa. Scale bar 70 microns.

POLY 550: CO₂/pH-responsive polymeric particles with built-in fluorescence read-out

Anne B. Mabire¹, *a.b.m.mabire@warwick.ac.uk*, **Quentin Brouard**¹, **Anaïs Pitto-Barry**¹, **Rebecca J. Williams**¹, **Helen Willcock**^{1,2}, **Nigel Kirby**⁴, **Emma Chapman**³, **Rachel K. O'Reilly**¹. (1) Chemistry, University of Warwick, Coventry, United Kingdom (2) Loughborough University, Loughborough, United Kingdom (3) BP Exploration Operating Co Ltd., Sunbury-on-Thames, United Kingdom (4) Australian Synchrotron, Clayton, Victoria, Australia

Fluorescent dyes are widely commercialized for imaging and biological applications, however their large size coupled with the presence of several aromatic rings and their low solubility in aqueous media limits their use. To overcome these limitations, we firstly developed a dithiomaleimide functionality that we used to label proteins, polymers and nanoparticles. However, a thiol exchange reaction can occur in the presence of an excess of thiol: alkyl thiol substituents can be replaced by aromatic thiols, resulting in an ON-to-OFF emission switch. To overcome this switch, we further designed non-reversible emission systems by using amines instead of thiols on the maleimide unit, producing monoammonimaleimides and aminobromomaleimides (ABM). These compounds were developed for applications in materials science through the synthesis of a novel fluorescent monomer, which can be used to probe the state of CO₂-responsive cross-linked particles. The responsive cross-linked core-forming block of these particles was composed of poly(*N,N*-diethylaminoethyl methacrylate) (PDEAEMA), responsive to pH/CO₂ through the protonation of the tertiary amine, the cross-linker ethylene glycol dimethacrylate (EGDMA) and the novel aminobromomaleimide methacrylate (ABMMA), utilized to probe the particles' core state.



Synthesis of fluorescent responsive cross-linked particles and reversible response upon CO₂/N₂ purges

POLY 551: Preparing core-shell single molecules: Architecturally sound highly branched polymers with tuneable properties

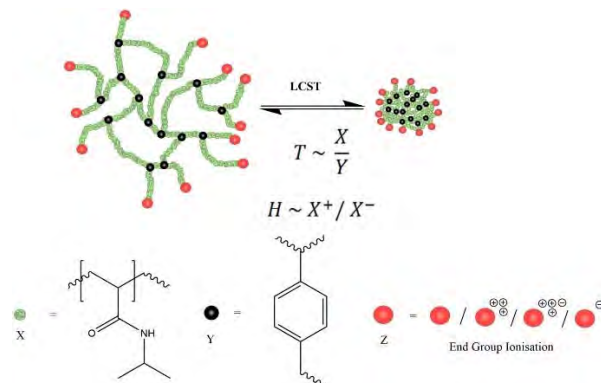
Thomas Swift, *t.swift@bradford.ac.uk*, Richard Hoskins, Stephen Rimmer. *Chemistry and Forensic Science, University of Bradford, Sheffield, United Kingdom*

Stimuli responsive (i.e. Lower / Upper Critical Solution Temperature) polymer materials have been shown to be effective trigger systems. However in order to be incorporated into devices polymers must be tuned to exactly match desired stimulating events. Part of the arsenal used to develop these systems are changing polymer architecture.

Branched polymers offer different solution, rheological and surface properties to their linear analogues. Highly branched materials, prepared via dual self-condensing vinyl (SCV) and reversible addition-fragmentation transfer (RAFT) polymerisation, have unique properties such as their single-molecule core-shell structures.

These materials exhibit core-shell properties due to their dendritic branching architectures. Consisting of a collapsed inner core and a swollen, solvated outer core. It has been shown that converting chain ends to binding ligands can trigger a collapse event across the polymer outer shell and desolvate the entire molecule. Previous demonstrated applications have included rheology modifiers, cell lifting systems and pathogen (bacterium) sensors. The strength of the desolvation has been shown to lift bacteria out of a biofilm and incorporation of drug molecules into chain ends can reduce their cytotoxicity to the host whilst improving their efficacy against pathogens. All these functions come from the unique core-shell structure exhibited by the branched polymer architecture.

We have investigated varying the degree of branching to change polymer properties as shown in F1. Control over branching density can alter the polymer globule, shifting the LCST temperature to higher and lower extremes. Conversely affecting the charge on the chain end can fundamentally affect the degree of desolvated collapse without greatly affecting the transition temperature. Control over polymer architecture, and these fundamental properties, are an important aspect of their use in next generation materials.

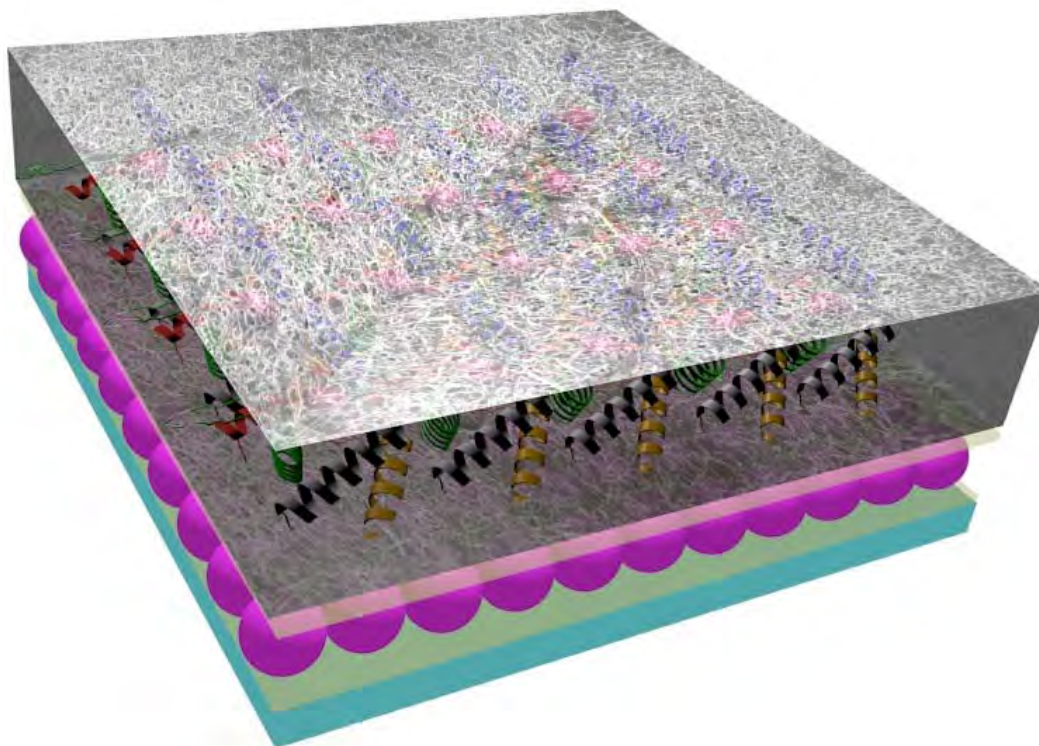


F1 - Desolvation Temperature (T) and Enthalpy (H) of highly branched polymers depends on ratio of monomer to branching unit and charge of chain ends.

POLY 552: Optical devices constructed from responsive microgels for polyphenols detection

Samuel M. Mugo¹, mugos@macewan.ca, Michael Serpe³, Qiang M. Zhang². (1) Physical Sciences, MacEwan University, Edmonton, Alberta, Canada (2) Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada (3) E3-44 Gunning Lemieux Chem Centre, University of Alberta, Edmonton, Alberta, Canada

Polyphenols are strong antioxidants existing in plant-derived foods including wine, tea, cacao or fruits, which were proved that it played an important role in human health. The catechol structures enable polyphenols scavenging free radicals and inhibiting lipoprotein oxidation, leading to reduction in the incidence of cardiovascular diseases, certain cancers and other diseases related to aging. Therefore, it is pretty important to detect such compounds in foods in the fields of food chemistry and healthy science. We developed a “block” concept for polyphenols determination using etalons. First, the surface of etalons was modified using tyrosine that could catalyze polyphenols oxidation generating polyphenol films on the etalon surface in presence of O₂. The thickness of polyphenol films depends on the concentration of polyphenols. When the device was soaked in ZnCl₂ solution, the polyphenol films blocked Zn²⁺ entering into etalon that caused optical properties changes of etalons. Therefore, the concentration of polyphenols can be deduced according to optical properties change of etalons. The complex polyphenol compositions were determined as a whole using the method, which did not get involved with complicated extraction and separation processes.



Schematic of the etalon based polyphenol detection sensor

POLY 553: Stimuli-Responsive helical dendronized polymers with switchable conformation

Wen Li, Kun Liu, **Afang Zhang**, azhang@i.shu.edu.cn. Department of Polymer Materials, Shanghai University, Shanghai, China

Helical polymers capable of responding to external stimuli will not only afford these polymers with novel functionalities but also pave a new avenue to broaden their promising applications. Here we report on OEGylation of chiral conjugated polymers with linear or dendritic oligoethylene glycols (OEGs) moieties, which offers these chiral polymers characteristic stimuli-responsive properties, and at the same time, affords them switchable helical structures (Figure 1). Covalent OEGylation of chiral polyisocyanides with linear OEGs leads to the first example of thermoresponsive helical polymers, whose thermoresponsive properties are dependent on OEG pendants, linkage between pendants and conjugated backbone, as well as polymer helicity. Alternatively, thermoresponsive OEGylated nonchiral polyisocyanides copolymers can be mediated with helical conformation through dynamic covalent chemistry with chiral components based on “sergeants-and-soldiers principle”. Similar strategy is applied to OEGylate polyphenylacetylenes (PPAs) with much bulky dendritic OEGs. These OEGylated PPAs can be mediated with tunable helicity and thermoresponsive properties, depending predominately on the linkages between chiral pendants and the main chains. Through covalent or dynamic covalent OEGylation, PPAs can be afforded thermoresponsive properties, and their helical conformations are varied accordingly during the thermally-induced aggregation. Metal coordination was found to prevent the helical conformation inversion of PPAs, which can be shielded reversibly by OEG dendrons.

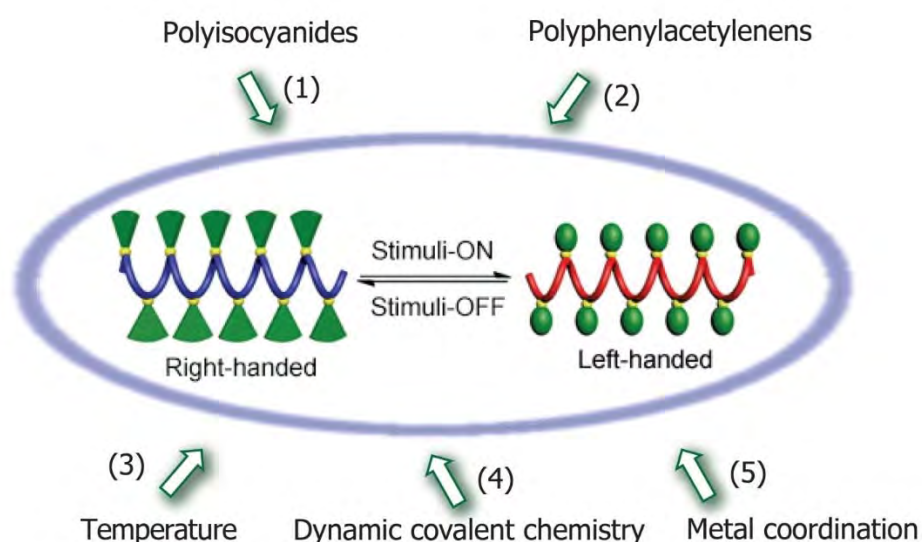
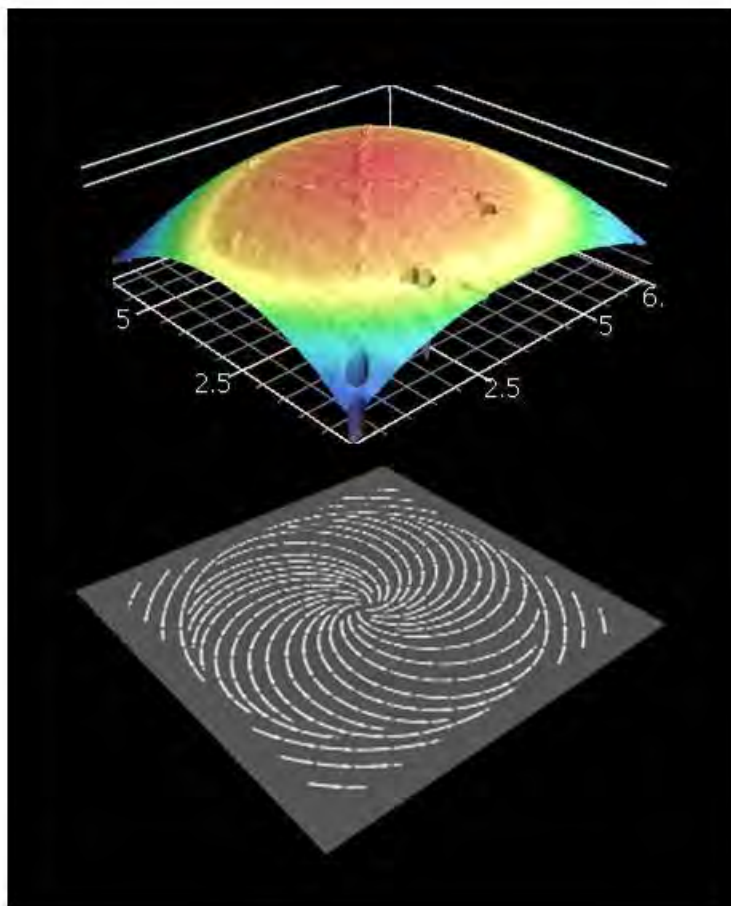


Figure 1. Cartoon presentation of helical conformation switching for dendronized polyisocyanides and polyphenylacetylenes mediated with temperature, dynamic covalent linkage or metal coordination.

POLY 554: Thermomechanical deformation of liquid crystalline elastomers: From flat to functional

Benjamin A. Kowalski¹, kowalski@colorado.edu, Cyrus Mostajeran², Mark Warner², Timothy J. White¹. (1) Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States (2) Dept of Engineering, University of Cambridge, Cambridge, United Kingdom

Liquid crystalline elastomers are inherently anisotropic materials. Recently, we have reported on the ability to arbitrarily imprint complex director profiles within these materials. Here, we report a detailed quantification of the thermally-induced 3-D shape deformations in these materials. Notably, we report on the deformation of a variety of director patterns with theoretical underpinnings predicted to form smooth curvatures. The deformations are quantified via real-time submicron-resolution optical 3-D scanning. This characterization shows good absolute agreement with theoretical predictions of curvature. This represents a significant step toward fully closed-loop design of complex actuating geometries.



Bottom: Director profile imprinted on liquid crystal elastomer film. Top: Thermally induced complex shape deformation, as measured via optical 3-D scanning.

POLY 555: Polymerizations with elemental sulfur: Sustainable fossil fuel chemistry

Yueyan Zhang³, Richard S. Glass², Kookheon Char¹, **Jeffrey Pyun**^{3,4},
jpyun@email.arizona.edu. (1) Seoul Natl Univ Sch Chem Eng, Seoul, Korea (the Republic of) (2) Chem Dept, Univ of Arizona, Tucson, Arizona, United States (3) University of Arizona, Tucson, Arizona, United States (4) School of Chemical & Biological Engineering, Seoul National University, Seoul, Korea (the Republic of)

The surfeit of elemental sulfur primarily derived from petroleum refining has driven recent efforts to develop new polymerization methods to use sulfur as an alternative feedstocks for polymeric materials. While the thermally initiated ring-opening homopolymerization of elemental sulfur has long been known, there remains a need for new synthetic approaches to prepare useful polymers from these chemical precursors. We will discuss our recent efforts on the polymerization of elemental sulfur to prepare chemically stable copolymers with a very high content of sulfur (50-90 wt% sulfur). We have recently developed a novel polymerization method, termed, *inverse vulcanization*, to form chemically stable and processable sulfur copolymers by the free radical copolymerization of elemental sulfur and 1,3-diisopropenylbenzene (DIB). The *inverse vulcanization* process is essentially a bulk copolymerization of sulfur and DIB that mechanistically is a thermally initiated thiol-ene reaction. We have also recently demonstrated the ability to copolymerize a broader wide range of vinylic styrenic and acrylate based comonomers which enables the design of new materials with improved properties. We will discuss these new synthetic advances as well as the applications of these materials in batteries and in optical imaging technologies. [figure1]

Sulfur Polymer Chemistry & Inverse Vulcanization

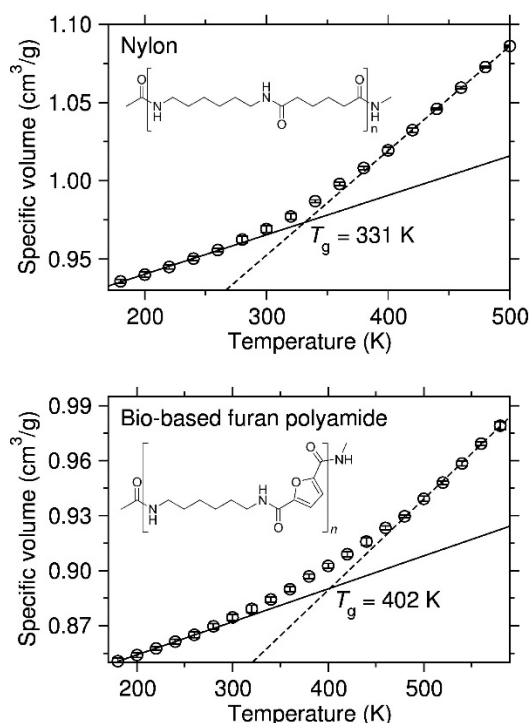


Pyun et al. *Angew. Chem. Int. Ed.* **2011**, 50, 11409; *Nature Chemistry* **2013**, 5, 518; *Polym. Chem.* **2014**, 5, 3617; *ACS Macro Lett.* **2015**, 4, 111; *Macromolecular Rapid Commun.* **2015**, 36, 1103; *Angew. Chem. Int. Ed.* **2015**, 54, 3249; *Prog. Polym. Sci.* **2016**, 58, 90; *Chem. Commun.* **2016**, 52(12), 2485

POLY 556: Computational modeling of bio-based furan polymers and bio-inspired polymer adhesives

In-Chul Yeh, inchulyeh@yahoo.com, Christopher B. Rinderspacher, John J. La Scala, Joshua A. Orlicki, Joseph Lenhart, Jan Andzelm. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States

To aid experimental efforts to develop environmentally-friendly polymeric materials, we performed atomistic simulations of bio-based furan polyamides and furfuryl alcohol polymers. Thermal and mechanical properties were characterized and compared with available experimental data. Bio-based furan polyamides showed higher glass transition temperatures and comparable mechanical properties despite having overall weaker hydrogen bonding than petroleum-based nylons. Glass transition temperatures of idealized furfuryl alcohol polymers without cross-linking and several analogous polymers were estimated and related with their underlying structural and dynamical properties. We also studied adsorption behaviors of catechol, which is a key functional group in marine adhesive proteins, several analogous phenolic compounds, and small block copolymers containing catechol functional group in an effort to develop biopolymer adhesives for extreme environments. In anhydrous conditions, without competing interactions from water molecules, catechol adsorbed readily to alumina surfaces. When comparing the phenolic moieties near the hydroxylated alumina surface in aqueous conditions, the catechol molecules displayed the strongest adsorptions mainly through cooperative hydrogen bonding interactions of two neighboring hydroxyl groups with the surface hydroxyl groups of alumina.

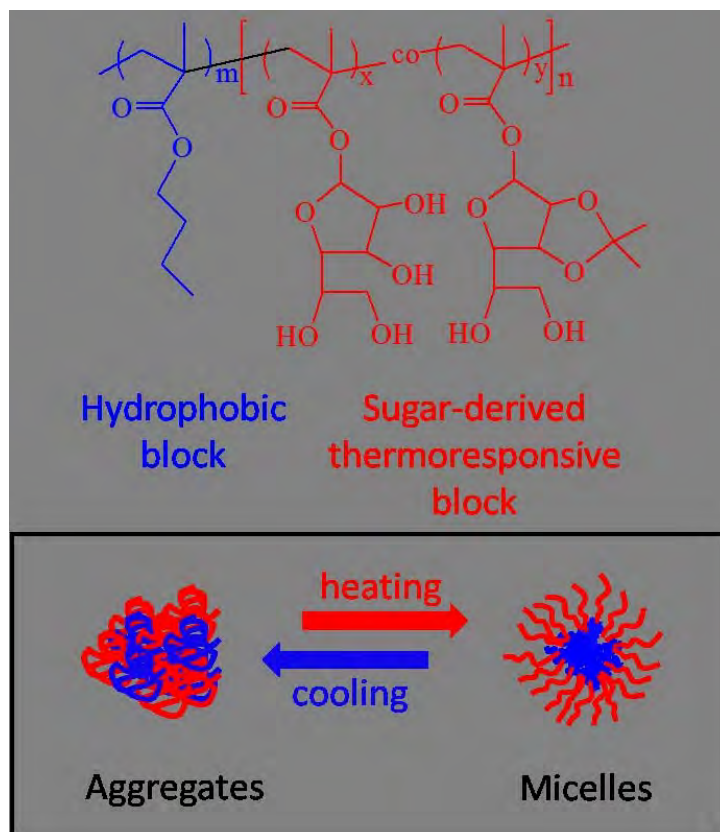


Glass transition temperatures of petroleum-based nylon and bio-based furan polyamide estimated by molecular dynamics simulations

POLY 557: Sugar-derived thermoresponsive block copolymers

Shu Wang¹, shuwang@udel.edu, Jian He², Marcus B. Foston², Thomas H. Epps^{1,3}. (1) Chemical Engineering, University of Delaware, Newark, Delaware, United States (2) Dept of Energy Enviro Chem Eng, 1050 Brauer, Washington Univ in St. Louis, Saint Louis, Missouri, United States (3) Department of Materials Science & Engineering, University of Delaware, Newark, Delaware, United States

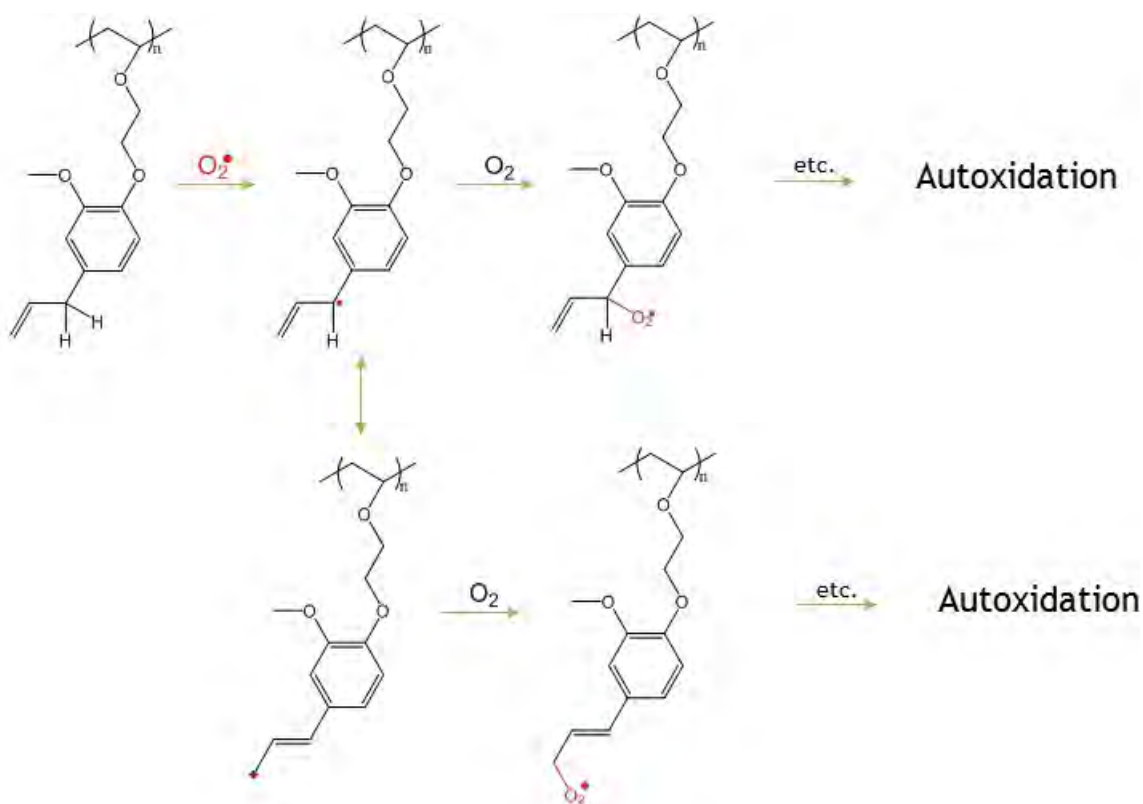
Thermoresponsive polymers are 'smart' materials that can undergo phase transition in solution in response to temperature changes. In particular, polymers derived from sustainable sources have attracted increasing attention in recent years; however, sustainable macromolecules exhibiting controlled thermoresponsiveness are scarce. In this work, we describe a sugar-derived polymer system that displayed an upper critical solution temperature (UCST) in water. The cloud point of the polymer was tunable by manipulating the fraction of protected vs. deprotected hydroxyl functionalities in the macromolecule. When copolymerized with a hydrophobic polymer [e.g. poly(butyl methacrylate)] to generate a block copolymer, micelles could be formed in aqueous solution at temperatures above the UCST of sugar block. Upon cooling to temperatures below the UCST, the copolymer aggregated and ultimately precipitated out of the solution. The transition was reversible, as micelles reformed upon heating. These thermoresponsive amphiphiles are an important addition to the library of sustainable polymers with potential applications in nanoscale catalysis, nanoseparations, and drug delivery.



POLY 558: Oxidatively-cured coatings from renewable-based poly(vinyl ether)s

Deep Kalita³, deep.kalita@ndsu.edu, **Bret J. Chisholm**², **Mukund P. Sibi**¹. (1) Chemistry Molec Biology, NDSU Dept 2735, Fargo, North Dakota, United States (2) North Dakota State University, Fargo, North Dakota, United States (3) Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States

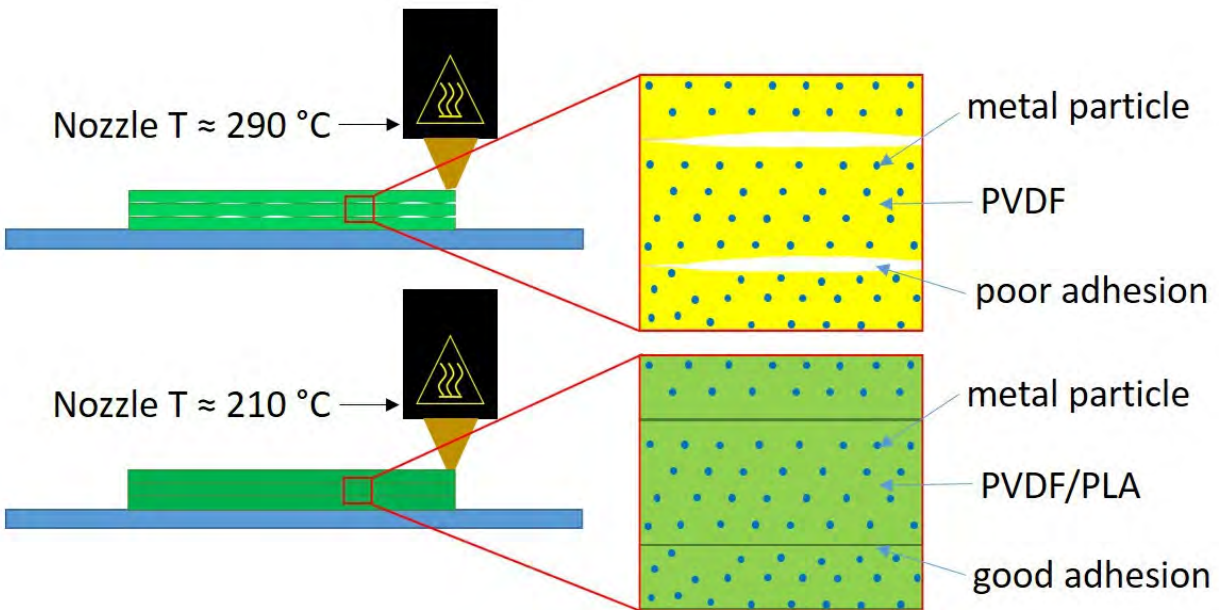
Recently, extensive research has been devoted to the development of coatings derived from renewable materials. For this study, vinyl ether monomers were prepared from soybean oil, eugenol, guaiacol, and syringol and a variety of homopolymers and copolymers produced using cationic polymerization. Since each polymer produced possessed pendant allylic and/or bis-allylic groups, they were utilized to produce thermoset coatings by oxidative curing. Structure-property relationships were determined and the results compared to coatings based on commercially available long oil alkyds. It was shown that the properties of the biobased poly(vinyl ether) coatings could be readily tailored by using copolymerization of the different biobased vinyl ether monomers. Coating properties varied over a wide range depending on the chemical composition of the biobased vinyl ether monomers as well as their relative concentration. In general, the biobased poly(vinyl ether)s showed far superior solvent resistance, film hardness, and hydrolytic stability than the commercial alkyds, while maintaining good flexibility and impact resistance.



POLY 559: Effects of metal oxide loading on mechanical and rheological response in poly(vinylidene fluoride)-poly(lactic acid) composites

Jena M. McCollum², jmccollu@uccs.edu, Jose Bencomo², Scott T. Iacono¹. (1) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (2) Mechanical and Aerospace Engineering, University of Colorado Colorado Springs, Colorado Springs, Colorado, United States

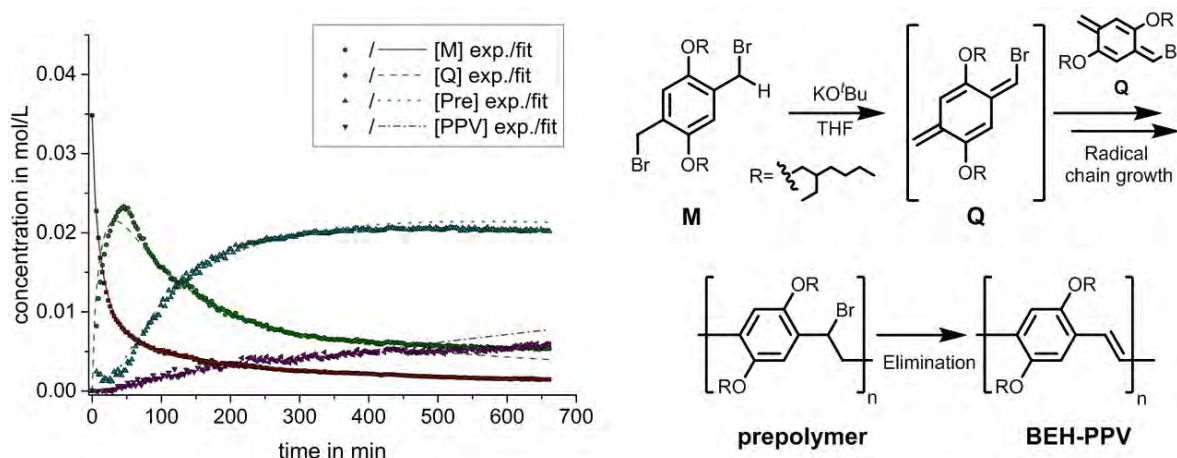
Recent advances in additive manufacturing technologies presents the potential to have better control in polymer-composite design. One limiting factor using polymer-based composites is insufficient mechanical toughness for high-performance applications. One solution is to infuse the polymer matrix with metal or ceramic particles to improve composite mechanical toughness. However, introducing hard materials to a polymer matrix results in an increase in composite viscosity which makes melt-processing a challenge. In previous work, nano-scale aluminum (nAl) was added to poly(vinylidene fluoride) PVDF via melt blending and injection molding. The composites viscosity increased with nAl concentration and PVDF decomposition was accelerated by almost 40 °C. In order to resolve this, poly(lactic acid) (PLA) was melt blended with poly(vinylidene fluoride) (PVDF) to assess its potential as a metallized polymer matrix. Composites were successfully printed 80 °C below typical PVDF processing temperatures for concentrations up to 75 wt% PVDF. This study examines the effect of metal and metal-oxide particle loading on the processability and mechanical toughness of PLA-PVDF blends. Mechanical and rheological loading limitations were determined for increasing concentrations of PVDF in PLA.



POLY 560: Mechanistic investigation and kinetic modeling of PPV polymerization via Gilch using time-resolved low temperature and *in situ* UV-irradiation NMR-spectroscopy

Ann-Kathrin Schönbein¹, *ak.schoenbein@gmx.de*, **Manfred Wagner**¹, **Jonas Kind**², **Paul W. Blom**¹, **Christina M. Thiele**², **Jasper J. Michels**¹. (1) Max Planck Institute for Polymer Research, Mainz, Germany (2) Clemens-Schöpf-Institut für Organische Chemie und Biochemie, TU Darmstadt, Darmstadt, Germany

The most efficient synthetic approach towards high molecular weight PPVs is the Gilch (precursor-) route. Treating α,α' -dibromo-p-xylenes with a strong base initiates a cascade of reactions leading to the conjugated PPVs. The complexity of this reaction network may well be the reason for the often encountered and undesired batch-to-batch variations in opto-electrical performance. Schwalm *et al.* studied the Gilch polymerization using ¹H-NMR spectroscopy and qualitatively indicated the species involved in the various reaction steps. Unfortunately, this study did not provide quantitative kinetic information.[1, 2] We investigated the reaction cascade of poly(2,5-bis-(2'-ethylhexyl)-1,4-phenylene-vinylene) (BEH-PPV) using time-resolved ¹H-NMR spectroscopy and developed an extended fitting model describing the kinetics of all individual reaction steps in the synthesis of BEH-PPV (see Figure 1). By fitting this model to our experimental data we not only derived rate constants for monomer consumption and polymerization, but also for the final elimination step towards the conjugated end product. We extended our study by investigating the influence of UV-light on the initiation process of the polymerization. Despite the fact that the Gilch polymerization has been known for some time, only limited and purely qualitative information is available concerning the influence of UV-irradiation.[3] For this reason, we investigated this system using *in situ* UV-irradiation NMR-spectroscopy to gain information at any time during illumination and to retrieve quantitative kinetic data.[4]

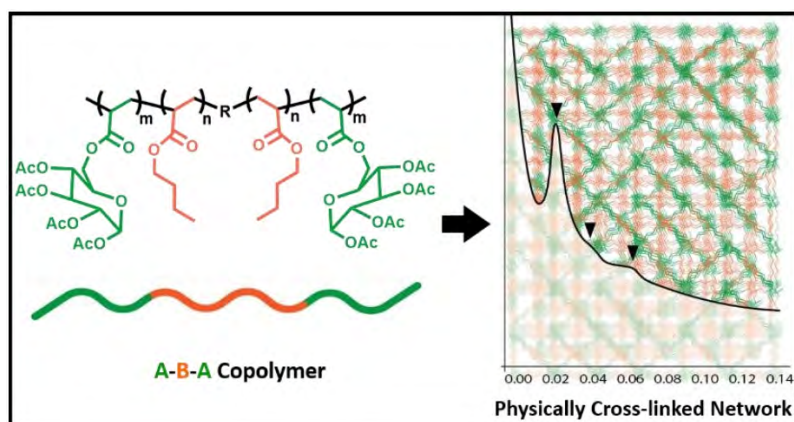


Left: Measured concentrations with corresponding fits: monomer M (square; solid line), quinodimethane Q (circle; dashed), prepolymer (triangle up; dot) and PPV (triangle down; dashed dot). Right: Reaction cascade from monomer M to BEH-PPV.

POLY 561: Incorporation of glucose in triblock copolymers to create sustainable adhesive and elastomeric materials

Mohammadreza Nasir², *mor.nasiri@gmail.com*, **Theresa M. Reineke¹**. (1) Chemistry, University of Minnesota, Vadnais Heights, Minnesota, United States (2) Chemistry Department, University of Minnesota, Minneapolis, Minnesota, United States

Thermoplastic elastomers (TPEs) are of high utility and interest for a wide variety of applications, ranging from adhesives and electronics to clothing and automotive parts. With the ability to fine-tune the chemical TPE architecture and properties, triblock copolymers with an ABA architecture can be designed to comprise of a soft middle segment (B) with two hard blocks at the ends (A). Self-assembly of the glassy endblocks into microstructures results in physical cross-links between the A segments, with the rubbery blocks bridging between the hard domains. The physically cross-linked network creates a superior resistance to flow, resulting in a material with elastomeric properties, and also allows for preparation of processable and recyclable materials. Here, we have directly functionalized glucose, as a sustainable component derived from an abundant and inexpensive feedstock, to create glucose-6-acrylate-1,2,3,4-tetraacetate (GATA). Poly(GATA) imparts a glassy segment into the block copolymers and was copolymerized with rubbery n-butyl acrylate (n-BA) via Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization, to create PGATA-*b*-PnBA-*b*-PGATA triblock copolymers. The triblock copolymers exhibited excellent thermomechanical characteristics, with decomposition temperatures higher than 279 degrees Celsius. Moreover, physically cross-linked networks were confirmed by small-angle X-ray scattering (SAXS). Pressure sensitive adhesives formulated from these copolymers exhibited adhesion properties comparable or superior to the commercial products. As one example, a 102 kDa triblock copolymer, containing 12 wt% GATA, showed peel adhesion of 5.07 N.cm⁻¹, when combined with 40 wt% of a rosin ester tackifier. The mechanical behavior of the polymers was investigated by tensile experiments and moderate elastomeric properties were observed. This work presents a new family of glucose-based ABA-type copolymers that demonstrate functionality of a glucose-based feedstock for developing green and practical polymeric materials.

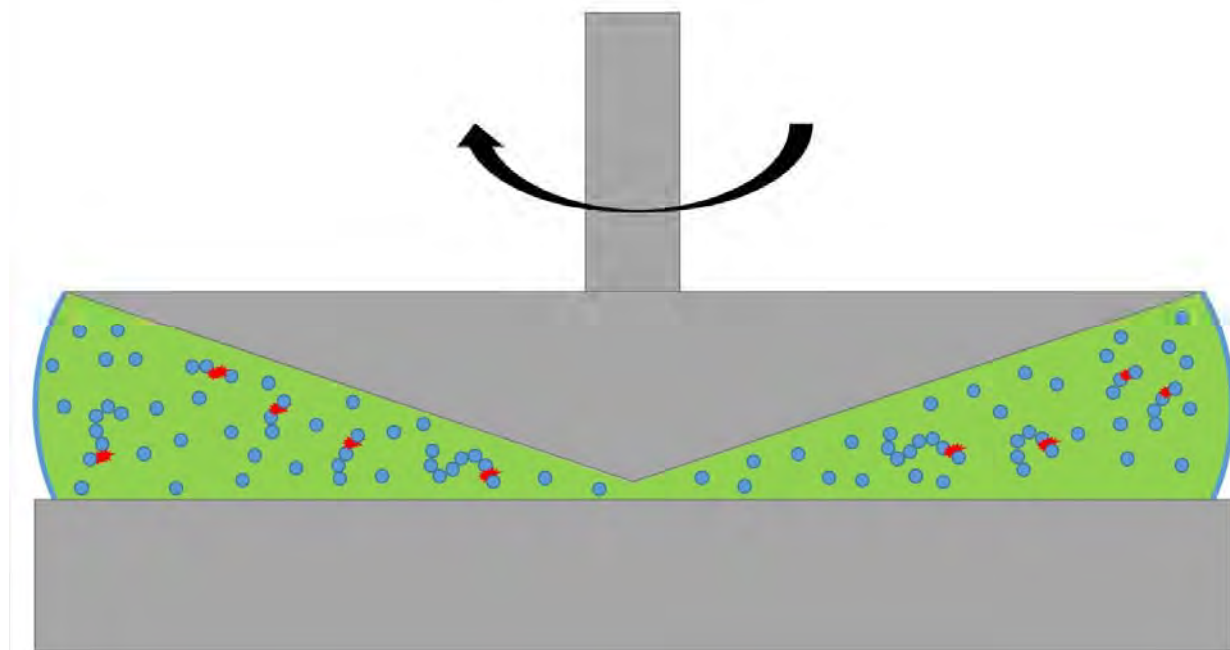


Physical cross-linking in PGATA-*b*-PnBA-*b*-PGATA triblock copolymers with a representative SAXS profile

POLY 562: Chemorheology of a methacrylate based thermoplastic resin

Dylan Cousins, *dcousins@mymail.mines.edu*, Yasuhito Suzuki, John R. Dorgan.
Colorado School of Mines, Golden, Colorado, United States

Thermoplastic composites represent a transformative, multifunctional technology which is applicable over a wide range of fields from wind energy, aircraft, ground transportation, and infrastructure. Composites incorporating a thermoplastic resin are more recyclable than their thermoset counterparts, thereby reducing the embedded energy of the material. Additionally, thermoplastic resins can potentially decrease cycle time for commercial fabrication which will further reduce costs and increase productivity. Fundamental characterization of thermoplastic resins is critical to make these materials viable for commercial application. The present work comprises two parts to characterize a methacrylate based resin system. First, a chemorheological study of Elium®, a commercial system from Arkema, is conducted to elucidate rheological properties as a function of reaction time and cure temperature. Second, a system of monodisperse poly(methyl methacrylate) (PMMA) dissolved in methyl methacrylate (MMA) is characterized under steady shear. Lastly, polydisperse solutions of PMMA in MMA are made from the different molecular weight PMMA and the viscosity is measured as a function of shear rate and temperature. The adjustable parameters of the isothermal, shear rate dependent Carreau-Yasuda viscosity model are fit to the data. This work is valuable for predictive models which will be used to simulate commercial processes for thermoplastic composite fabrication.



POLY 563: Mimicking mussel adhesive proteins: How close can we get to the real thing?

Jonathan J. Wilker, *wilker@purdue.edu*, Shannon Daily, Natalie Hamada, Samuel L. Huntington, Taylor A. Jones, Michael G. Mazzotta, Bradley McGill, Michael North, Amelia Putnam, Heather Siebert, Andres Tibabuzo. Department of Chemistry, Purdue University, West Lafayette, Indiana, United States

We continue to be captivated by biological materials. Although most such systems cannot usually be used, directly, for our needs, we can still benefit greatly by learning from nature. Biomimetic materials often incorporate various design aspects into synthetic systems. A prominent case is that of mussel adhesive proteins. In recent years, there has been a rapid expansion of research effort in which the key adhesive group 3,4-dihydroxyphenylalanine (DOPA) has been placed into several different synthetic polymers. Encouraging results continue to be forthcoming including development of new biomedical hydrogels, sensors, functionalized nanoparticles, and coatings. In terms of adhesion, how close are we to achieving all aspects of the mussel's bonding function? Some of the aspects unique to this biological adhesive, when contrasted with currently available commercial glues, include an ability to set underwater, creation of strong bonds in such an environment, degradability, modulus tailoring with regard to the substrates, and exhibiting specific protein features including charges. Here we will describe our recent efforts to create more faithful mimics of a fascinating biological underwater adhesive.



POLY 564: Adhesion under humid conditions: Lessons from Spider Silk

Saranshu Singla¹, ss321@zips.uakron.edu, **Gaurav Amarpuri**¹, **Nishad Dhopatkar**¹, **Todd A. Blackledge**², **Ali N. Dhinojwala**¹. (1) Polymer Science, The University of Akron, Akron, Ohio, United States (2) Biology, The University of Akron, Akron, Ohio, United States

Adhesion in humid conditions is a fundamental challenge to both natural and synthetic adhesives. Yet, glue from most spider species becomes stickier as humidity increases. Previous work has shown that spiders use a combination of proteins and hygroscopic salts as adhesive glue. Under humid conditions, the spider glue undergoes a cohesive failure; unlike synthetic adhesives, which fail interfacially. However, it is still unclear how these salts help in tuning the adhesion especially at high humidity. Here, we use a combination of two different spectroscopic techniques, infrared (IR) spectroscopy and surface sensitive sum frequency generation (SFG) spectroscopy to obtain a molecular level picture of the contact interface for spider capture glue as a function of varying humidity. Experiments are performed with both pristine and washed silk (devoid of hygroscopic salts) to understand the role of salts in these humidity responsive natural adhesives. Correlations between molecular structure and macroscopic mode of failure will be discussed. Understanding spider glue adhesion will help in designing synthetic adhesives that perform well under humid conditions.

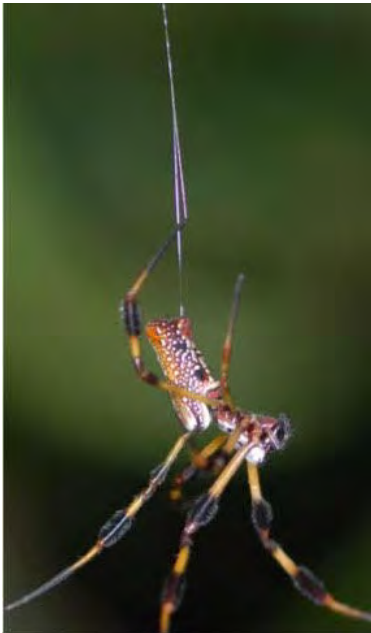
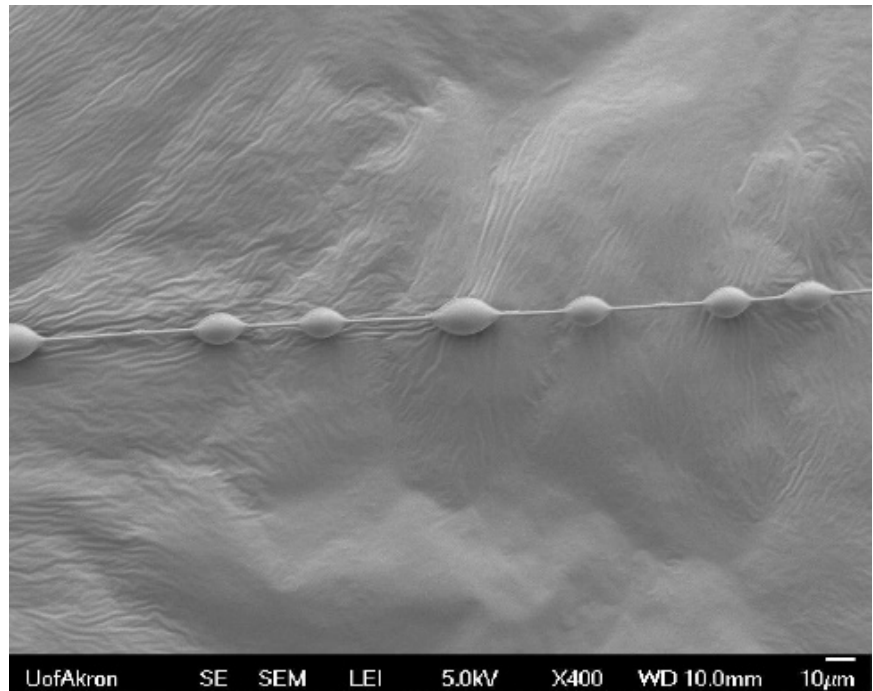


Image displaying a spider along with its silk.



The spider silk thread of an orb weaving spider exhibiting a bead on a string morphology.

POLY 565: Spiders tune glue viscoelasticity to maximize adhesion

Gaurav Amarpur², ga25@zips.uakron.edu, Nishad Dhopkatkar², Todd A. Blackledge³, Ali N. Dhinojwala¹. (1) Univ of Akron, Akron, Ohio, United States (2) Polymer Science, University of Akron, Cuyahoga Falls, Ohio, United States (3) Integrated Bioscience, The University of Akron, Akron, Ohio, United States

Adhesion in humid conditions is a fundamental challenge to both natural and synthetic adhesives. Yet, glue from most spider species becomes stickier as humidity increases. We find the adhesion of spider glue, from five diverse spider species, maximizes at very different humidities that matches their foraging habitats. By using high-speed imaging and spreading power law, we find that the glue viscosity varies over 5 orders of magnitude with humidity for each species, yet the viscosity at maximal adhesion for each species is nearly identical, 10^5 – 10^6 cP. Fourier transform infrared (FTIR) spectroscopy shows significant increase in protein hydration, specifically loosely bound water at high humidity. Further, we observe a reversible change in protein conformation such that the proteins become more flexible with an increase in humidity. However, after washing the low molecular weight molecules (LMM) from the glue, the protein became unresponsive to humidity. Many natural systems take advantage of viscoelasticity to improve functional response, but spider glue's humidity responsiveness is a novel adaptation that makes the glue stickiest in each species' preferred habitat. This tuning is achieved by a combination of proteins and hygroscopic LMM that determines water uptake in the glue. We therefore anticipate that manipulation of polymer–LMM interaction to control viscoelasticity can provide a simple mechanism to design humidity responsive smart adhesives.



Spiders use sticky glue droplets to capture and retain prey. The glue adhesion is humidity responsive such that it is maximum at the humidity of the spider habitat. We find macro and molecular scale evidence that spiders tune glue viscosity to tune adhesion.

POLY 566: Solvent-Free, Mussel-Inspired Polyester Adhesives with Impressive Underwater Adhesion

*Ying Xu¹, Amal Narayanan¹, Qianhui Liu¹, Sukhmanjot Kaur¹, Ali N. Dhinojwala¹, **Abraham Joy²**, abraham@uakron.edu. (1) Univ of Akron, Akron, Ohio, United States (2) Dept of Polymer Science, University of Akron, Akron, Ohio, United States*

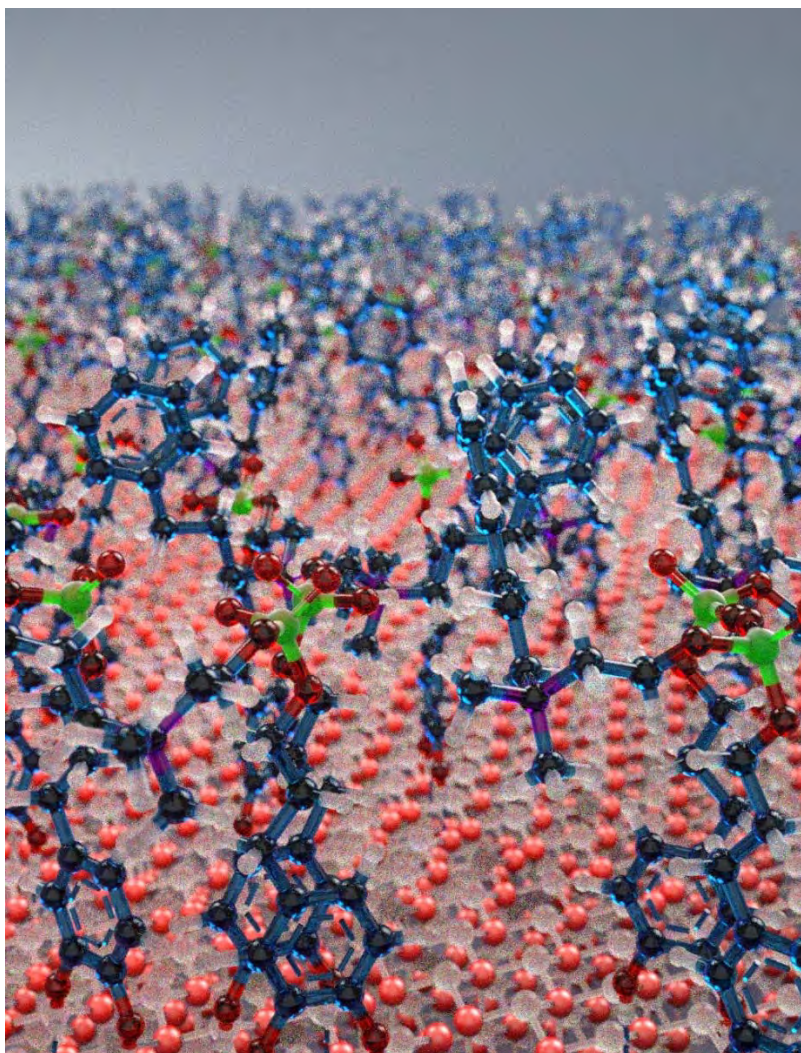
Mussel adhesion has fascinated scientists for their ability to adhere to underwater substrates. They do this by the secretion of adhesive proteins underwater in a temporal fashion. The mixture of proteins secreted by mussels are tuned to provide both adhesive and cohesive interactions with the substrate. Synthetic adhesives in comparison are for the most part are compromised in an aqueous environment due to their inability to prevent water penetration into the adhesive interface. We will present our work on the design and evaluation of synthetic polyesters that demonstrate strong underwater adhesion. The polyester is designed to flow at room temperature that enables application without any solvent. Catechol units of the polymer provide adhesive contacts with the substrate. The applied polymer is subsequently cured to a crosslinked polymer providing cohesive interactions. Lapshear measurements show strong adhesion even when the polymer is applied underwater and cured. Our current results indicate that the hydroxyl groups of catechol play a role in adhesion and that a hydrophobic environment is necessary for synthetic adhesives to show good performance in wet environments.



POLY 567: Paradigm shift in mussel-inspired adhesion

Kollbe Ahn, *kollbe.ahn@gmail.com*. University of California, Santa Barbara, Santa Barbara, California, United States

Biomimetics includes a sophisticated control of structural properties at multiple length scales, as nature employs, yet this has very often been missing in the field of bioinspired adhesion, in turn, the performance of those manmade adhesives is yet far lower than the bioadhesion, e.g., mussels. In this talk, we overview the major breakthroughs in this field, and highlight the recent advances reflecting the essential biomimetic design principle “systematic translation at the different length scales”. We will also discuss the widespread misconception that marine bioinspired wet adhesion depends on a single molecular entity (i.e., catechol or Dopa) and is instead bound to the choreographic coordination of key elements in the natural gluing system; that is essential for biomimetic wet adhesion become reality.

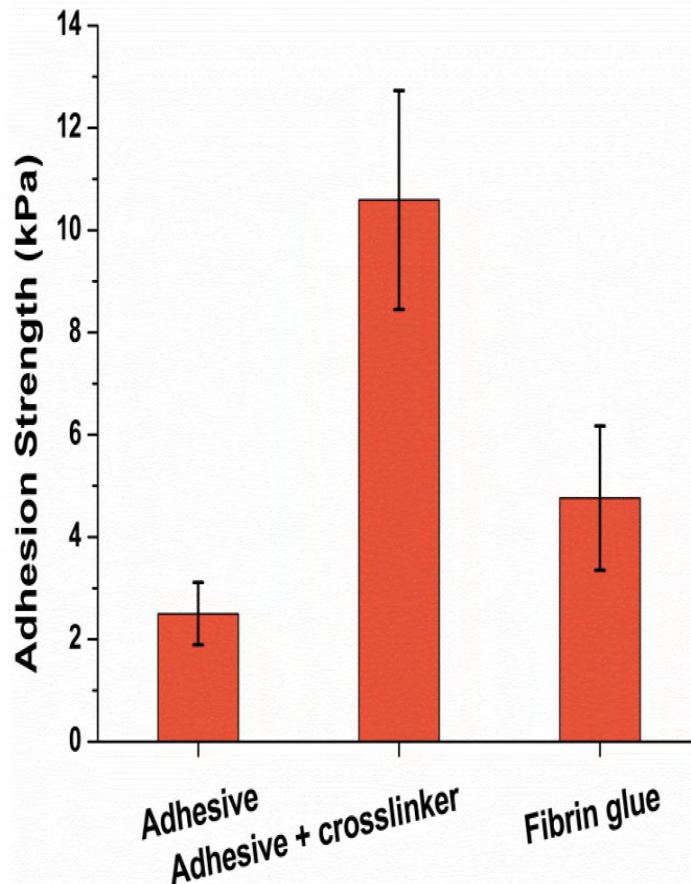


Mussel-inspired zwitterionic small molecules self-assembled on various mineral and metal surfaces underwater, and enhanced chemical and physical properties of materials.

POLY 568: Poly(ester urea) based adhesives: Improved deployment and adhesion by incorporating poly(propylene glycol) segments

Vrushali Bhagat, vdb6@zips.uakron.edu, Jinjun Zhou, Matthew Becker. University of Akron, Akron, Ohio, United States

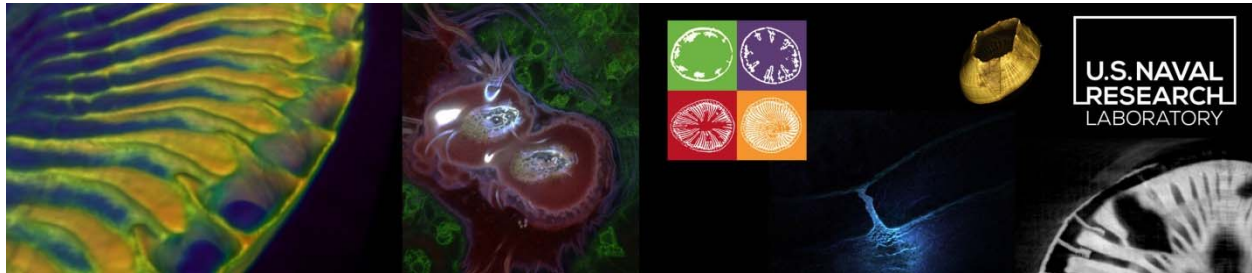
A number of studies have developed synthetic mimics of mussel glue for application in bone and tissue adhesives or sealants, however, these adhesives are delivered *via* biologically toxic solvents or water. Water soluble adhesives are difficult to be sequestered at the application site until they are completely crosslinked because they tend to dissolve in the surrounding body fluids. To overcome this complication, we synthesized an ethanol soluble but water insoluble tissue adhesive based on a poly(ester urea) copolymer. Ethanol being a clinically relevant solvent is a suitable delivery medium for tissue adhesives during surgeries. Incorporation of 20 mole% poly(propylene glycol) (PPG) groups in the polymer backbone resulted in ethanol soluble but water insoluble polymers. These polymers were further functionalized with catechol groups to mimic the mussel adhesive and their adhesion strengths on aluminum substrates and porcine skin were studied. By varying the catechol:crosslinker ratio and crosslinking time impressive adhesive strengths (10.6 ± 2.1 kPa) were obtained for these catechol functionalized poly(ester urea)s.



POLY 569: Constructing and deconstructing the barnacle adhesive interface

Christopher R. So, Kenan P. Fears, Daniel Barlow, Dagmar Leary, Christopher M. Spillmann, **Kathryn J. Wahl**, kathryn.wahl@nrl.navy.mil. US Naval Research Lab, Washington, District of Columbia, United States

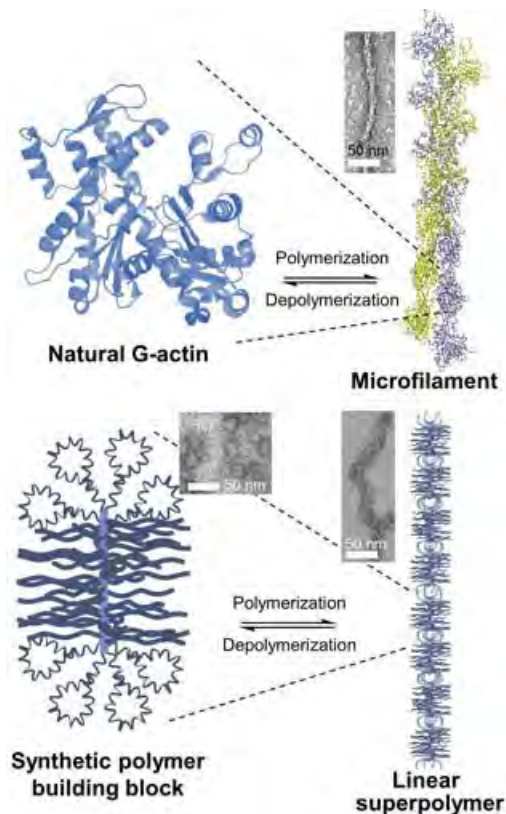
Barnacles are sessile marine arthropods that live and reproduce on nearly any available surface in the ocean. They adhere via a thin adhesive layer developed through a multistep secretory process synchronized with growth via molting. Unlike other arthropods, the combination of expansion, molting and protein secretion within the narrow adhesion interface leads to a nanofibrillar protein layer manipulated by shear stresses, protected by calcite, and containing a cocktail of chemically active molecules and proteins. Here we use *in vivo* imaging and spectroscopy of barnacle growth and development, coupled with mass spectrometry and proteomics to reveal much about the biophysics and biochemistry of barnacle adhesion. We will discuss the role of interfacial processes, self-assembly, amino acid composition, and chemical manipulation in the construction and function of the adhesive.



POLY 570: Programmable brush polymer self-assembly via DNA hybridization

Ke Zhang, *k.zhang@neu.edu*. Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States

Precision assembly of biological macromolecules is intimately associated with many vital phenomena of life, from cell motility and mitosis to viral capsids. We aim to mimic some of the precision assembly ability that natural proteins exhibit by extracting the requirements for such assembly, and recreating them in new forms accessible to modern polymer and organic chemistry. Towards this goal, we have designed conjugates of polymer brush and DNA, wherein the brush serves as a steric steer to guide DNA hybridization in a fixed dimension, while the DNA serves as a functional group equivalent to connect with desired partner brushes. With this approach, a new class of super-polymers with controlled architecture, macromonomer sequence, and end-group functionality is possible.



We aim to design synthetic polymers that mimic the proteins' directionality/specificity in assembly, to yield super-polymers with controlled primary sequence and architecture.

POLY 571: Self- and co-assemblies of BODIPY derivatives as drug nanocarriers

Alexander Rödle¹, Agata Ramos Torres¹, Vladimir Stepanenko², **Gustavo Fernandez¹**, gustavo.fernandez@uni-wuerzburg.de. (1) Organisch-Chemisches Institut, Universität Münster, Münster, Nordrhein-Westfalen, Germany (2) Universität Würzburg, Würzburg, Germany

BODIPY derivatives are one of the most deeply investigated chromophores in the fields of supramolecular chemistry and bioimaging due to their photochemical and physiological stability as well as strong absorption and narrow fluorescence bands with high quantum yields. In addition, the planar geometry of the BODIPY units enables a compact arrangement of the chromophores through stacking of the dipyrromethane core, which ultimately can lead to an H- or J-type excitonic coupling of the dye molecules. In this abstract, recent examples of self-aggregating hydrophobic and amphiphilic BODIPY dyes will be presented, with a particular focus on the supramolecular polymerization mechanism and packing modes. All reported molecules are specifically designed to self-assemble in polar or non-polar media through various non-covalent interactions. Some of the amphiphilic systems form spherical assemblies in aqueous media that are able to encapsulate and release small molecules reversibly. This capability has been recently exploited to deliver anticancer drugs such as doxorubicin and capsaicin to tumor tissues.

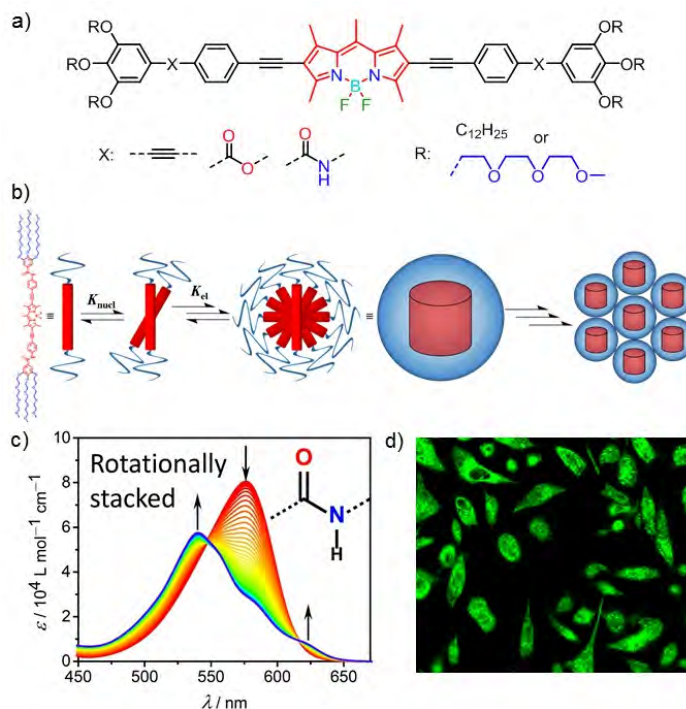
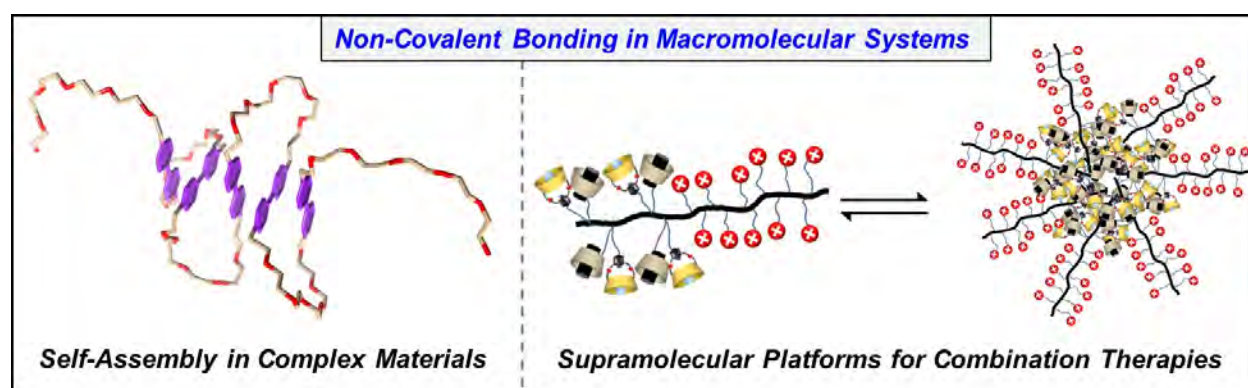


Figure 1. a) Chemical structures of various BODIPY derivatives investigated in our group. b) Hierarchical nanoparticle self-assembly of selected amphiphilic BODIPY. c) UV-Vis spectral changes of a hydrophobic BODIPY derivative upon aggregation. d) Confocal fluorescence microscopy images of the localization of BODIPY nanoparticles in prostate cancer cells.

POLY 572: Developing functional platforms for responsive materials and combination antimicrobials via non-covalent bonding in macromolecular systems

Jonathan C. Barnes, *jcbarnes@wustl.edu*, **Angelique F. Greene**, **Xuesong Li**,
Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States

Nature relies on non-covalent bonding to control important biological processes. Typically, these types of through-space bonding interactions are presented using a biomacromolecular platform that allows for greater complexity in structure and scale – albeit beginning from relatively simple and discrete monomer libraries. Chemists have long sought to emulate Nature’s ability to control hierarchical self-assembly by employing synthetic, non-natural building blocks, however, a comprehensive knowledge of how to translate individual recognition events to the bulk scale, and do so in a controllable manner, remains a formidable challenge. The Barnes research group at Washington University aims to explore redox-active units in the context of precise polymer networks in order to gain a greater fundamental understanding of self-assembly in complex materials. By capitalizing on the reversible redox chemistry of 4,4'-bipyridiniums (i.e., viologens), the degree of bulk actuation of a material can be investigated and correlated to the concentration of radical-radical pairing interactions that are present in the network, as well as to the degree of molecular motion during the formation of each radical domain. Other research interests of the Barnes group include designing and synthesizing functional supramolecular monomers for the purpose of developing copolymers and nanomaterials that possess precise ratios of antimicrobial agents in a truly plug-and-play platform. By investigating ratios of active agents that operate through disparate mechanisms of action in killing multi-drug resistant (MDR) bacteria, it is envisioned that “old” small-molecule antibiotics can be repurposed and a number of applications – such as wound healing and treating MDR infections – can be achieved.

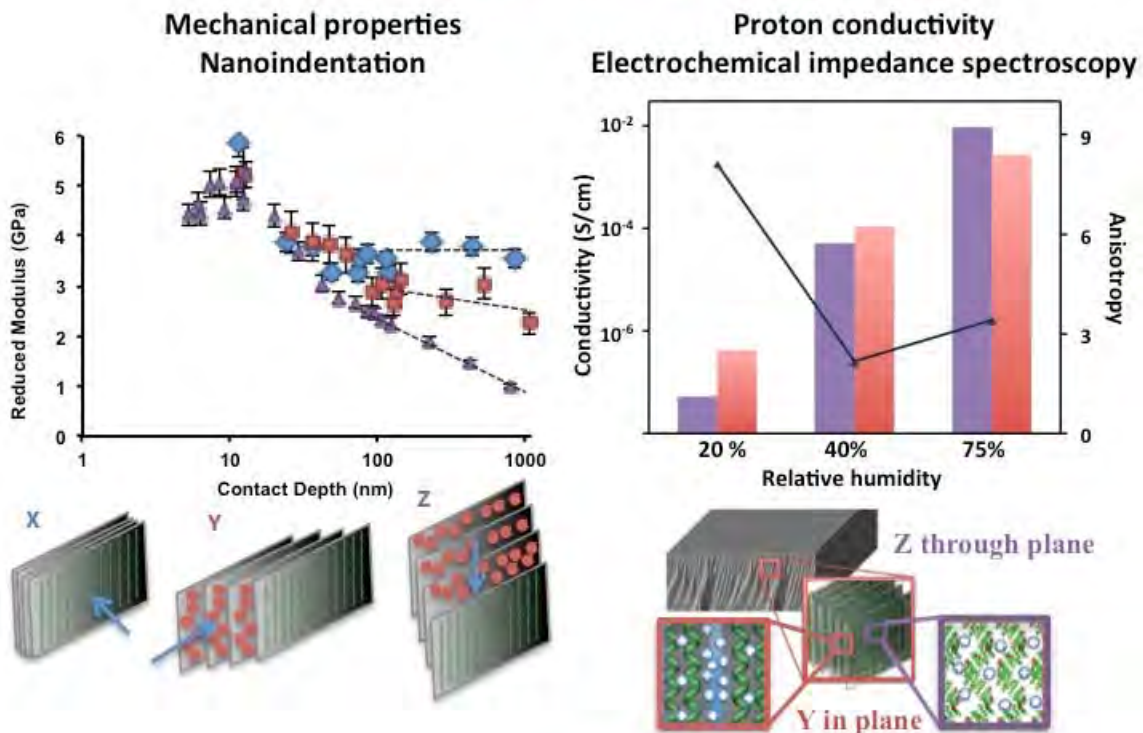


POLY 573: Molecular organization, mechanical properties, and ion transport in hierarchically structured repeat-protein materials

Tijana Zarkovic Grove, *tijana.grove@vt.edu*, Nathan Carter. Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Materials that can interface biological signaling with conventional technologies are crucial for the realization of new therapeutic and sensing platforms based on direct readout and responses to biological signals. However, one great challenge is lack of biocompatible ion and proton conducting materials that exhibit anisotropic properties at biologically relevant length-scales, nano to micro, and relevant time scales, milliseconds to seconds. In this talk I will present our work on the repeat-protein biomaterials that self-assemble through the combination of head-to-tail stacking and weak dipole-dipole interactions. I will further highlight the effect that this hierarchical structure has on the material's mechanical and proton and ion conduction properties.

Anisotropic emergent properties



POLY 574: Active materials by coupling self assembly to the consumption of fuel

Rienk Eelkema, *r.eelkema@tudelft.nl*, Jan H. van Esch, Ger Koper, Job Boekhoven, Wouter Hendriksen. Department of Chemical Engineering, Delft University of Technology, Delft, Netherlands

Biological tissue and the living cell arguably constitute the epitome of soft matter. Especially in terms of dynamic functions and processes such as transport, signalling/communication, self-healing, replication, transient assembly, and motion, biological systems go far beyond anything current artificial materials have to offer. In this presentation, I will show how we applied core concepts of biological self-assembly to the construction of dynamic, out-of-equilibrium soft molecular materials, in an attempt to bridge this gap. We can now start to control dynamic properties such as lifetime, self-healing, and spatial/temporal distribution by coupling the self-assembly process to chemical reactions.^[1,2]

In particular, I will show how a hydrogelator based fibrous network is grown far removed from thermodynamic equilibrium, using a chemical fuel as an energy source to drive the self-assembly. Reminiscent of GTP-driven growth of microtubules, the formation and collapse of the self-assembled structures is directly coupled to the consumption of the chemical fuel, allowing the formation of transient assemblies, and control over structure formation in time and space.^[3,4] I will show how such concepts may be used to control molecular scale forces and motion.

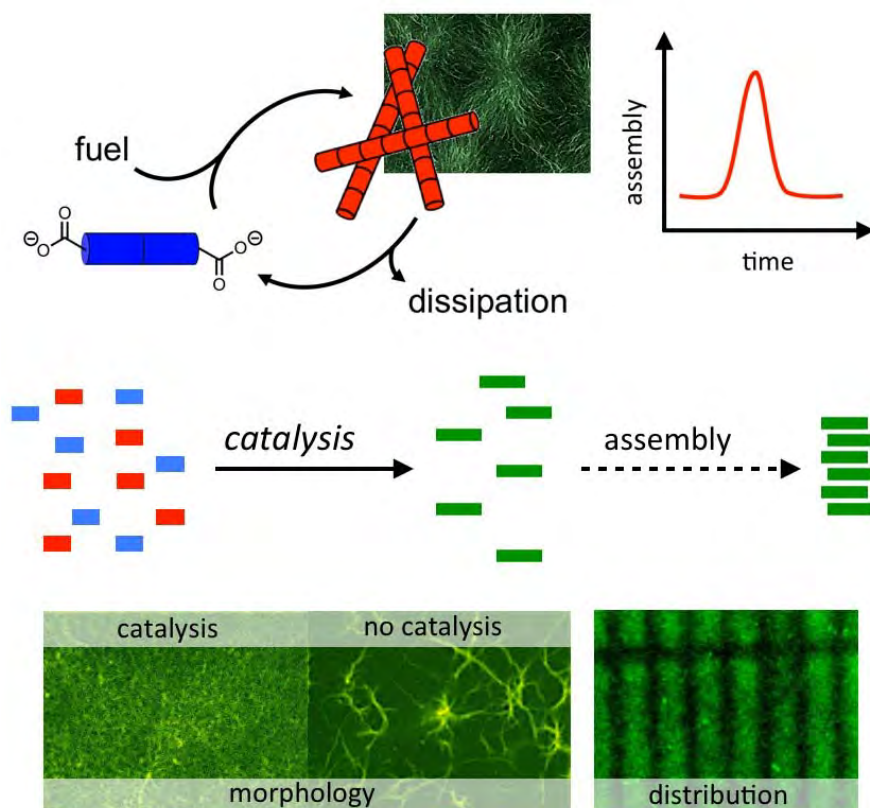


Figure 1. Transient fuel driven assembly of supramolecular fibrous materials.

POLY 575: Super resolution imaging of supramolecular materials

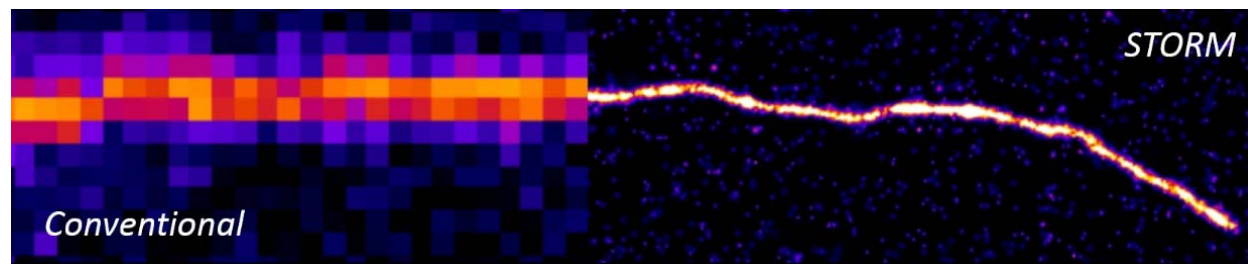
Lorenzo Albertazzi, lalbertazzi@ibebarcelona.eu. IBEC Barcelona, Barcelona, Spain

The use of nanocarriers for intracellular delivery of therapeutic moieties is a great challenge for synthetic chemistry and nanotechnology. In this framework, supramolecular materials such as micelles, liposomes, nanoparticles and supramolecular polymers play a pivotal role. A crucial factor limiting the design of effective architectures is the lack of understanding about supramolecular materials structures and dynamics in vitro and their cell interactions in the biological environment. Here we discuss the use of super resolution microscopy to image supramolecular materials in vitro and in mammalian cells. This novel technique, allowing to obtain a resolution down to 20nm, had a dramatic impact in the field of cell biology, however its use in the field of chemistry and nanotechnology is poorly explored. Super resolution microscopy offers nanometric resolution and multicolor ability, therefore it is an ideal tool to study nano-sized supramolecular assemblies of multiple components in vitro and in cells.

We employed Stochastic Optical Reconstruction Microscopy (STORM) to image biomaterials in vitro, with special emphasis on supramolecular polymers and nanoparticles, unveiling novel information on materials structure and dynamics, a key issue of supramolecular materials.

Moreover we propose a methodology to image nano-sized materials in cells, tracking them during their membrane targeting, cell uptake and intracellular targeting. We show how 2-color STORM can be used to perform nanometric-accurate colocalization unveiling at the molecular level materials-cell interactions.

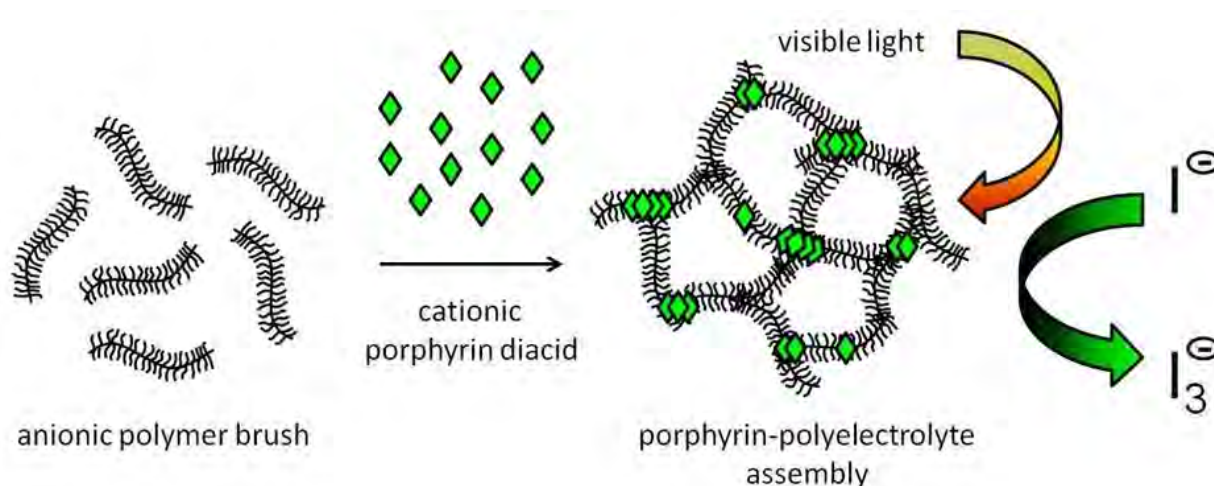
This allow to look at nanomaterials in action with new eyes and use the information obtained for the “STORM-guided” design of novel nanomaterials for drug delivery and other targeted therapies.



POLY 576: Tunable structure and function of electrostatically self-assembled polymer nano-objects in solution

Franziska Groehn¹, franziska.groehn@chemie.uni-erlangen.de, Anne Kutz¹, Maximilian Wagner¹, Anja Krieger¹, Sabine Frühbeißer¹, Giacomo Mariani^{1,2}, Ralf Schweins². (1) University Erlangen-Nuernberg, Erlangen, Germany (2) Institut Laue Langevin (ILL), Grenoble, France

With regard to the world's decreasing energy resources, developing strategies to exploit solar energy become more and more important. Inspired by natural systems such as assemblies performing photosynthesis, it is highly promising to self-assemble synthetic functional species to form more effective or tailored supramolecular photocatalysts. In this contribution, a new type of photocatalytically active supramolecular nanostructures in aqueous solution will be presented: supramolecular nano-objects obtained through self-assembly of polyelectrolytes and multivalent organic or inorganic counterions. For example, Polyelectrolyte-porphyrin nanoscale assemblies exhibit up to 20-fold higher photocatalytic activity than the corresponding porphyrins without polymeric template. Other supramolecular catalysts based on polyelectrolytes can exhibit expressed selectivity in a photocatalytic model reaction or even allow catalytic reactions in solution that are not possible with the building blocks only. Further, it is highly promising to extend the concept to include metal or semiconductor nanoparticles. Another approach is to transfer light energy into mechanical energy. While the effect of light on the nanoparticle size in electrostatic self-assembly has been recently established by us, the question of whether light can be used to trigger the nanoassembly shape will also be discussed. Shape responsivity is highly desirable for nanotechnology, sensors and in pharmacy, especially when realized in aqueous solution.

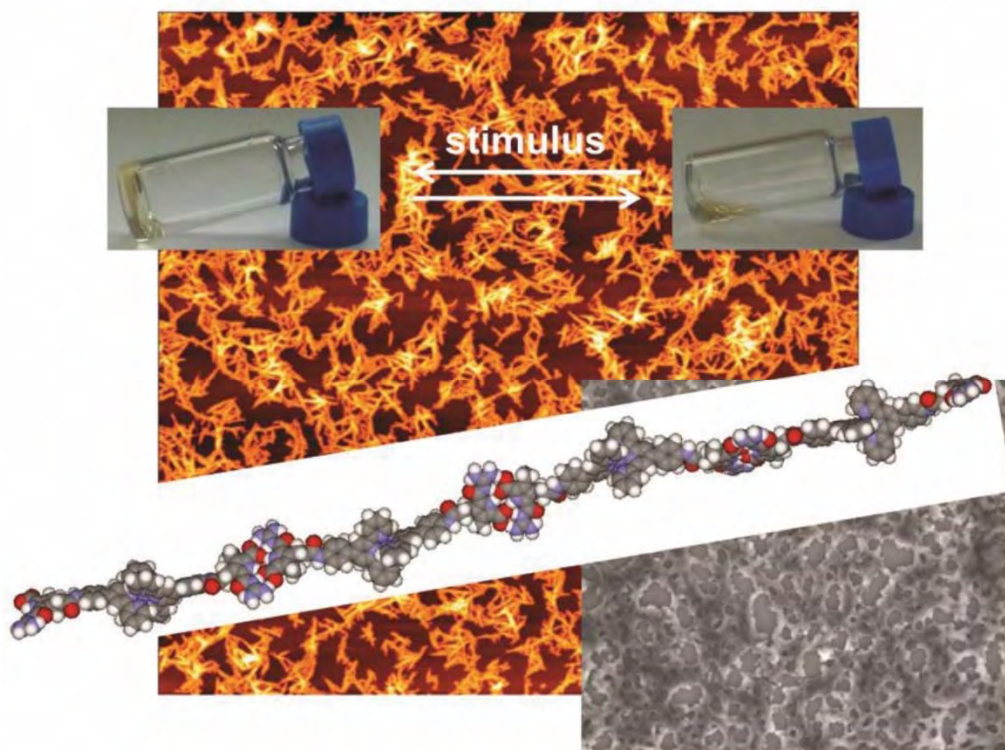


POLY 577: Self-assembling Zwitterions as building blocks for switchable gels and polymers

Carsten Schmuck, *carsten.schmuck@uni-due.de*. University of Duisburg-Essen, Essen, Germany

Our research focuses on the development, synthesis and evaluation of new supramolecular systems which function in polar solvents and thus might have prospect for applications. Currently our work mainly involves ionic interactions as a key non-covalent bond. We have introduced guanidiniocarbonyl pyrroles as one of the most efficient oxoanion binding motifs known so far relying on H-bond assisted ion pair formation.

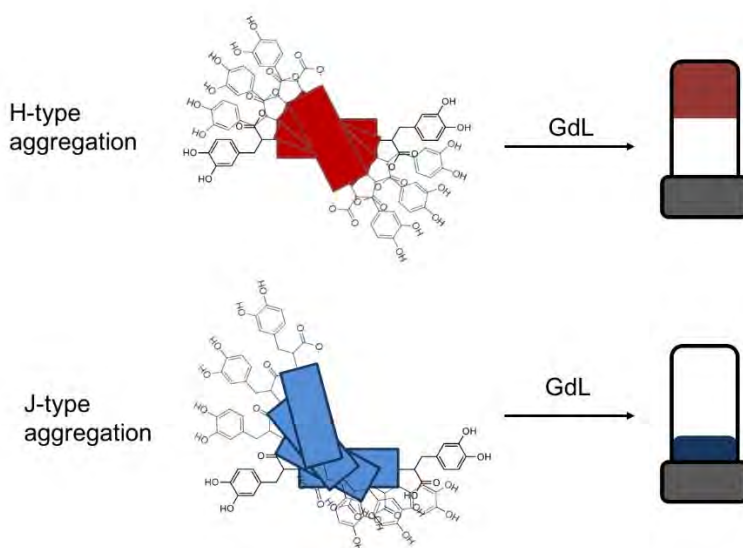
Combining a self-complementary zwitterion, that we developed in recent years, with metal-ligand binding sites (e.g. terpyridines, catechols, bipyridine) self-assembling molecules with two or more orthogonal interactions are obtained. Depending on the conditions (e.g. pH, presence/absence of metal ions, concentrations) different types of self-assembled aggregates are formed such as ion-paired dimers, metal-complexes, linear or three-dimensional polymers and gels. Such gels can be switched between gel state and solution by different stimuli such as pH, temperature or competing metal-binding ligands. Also conventional polymers such as polyethylene imine (PEI) can be functionalized with additional supramolecular binding sites to obtain hybrid materials which possess new and different properties relative to the original polymers. The lecture will focus on the design, the synthesis and the characterization of these new materials.



POLY 578: Reversible H- and J-type aggregation of a single perylene bisimide leading to different photoconductivity

Emily Rose Draper², Emily.Draper@glasgow.ac.uk, **Martijn A. Zwijnenburg**¹, **Dave J. Adams**². (1) University College London, London, United Kingdom (2) School of Chemistry, University of Glasgow, Glasgow, United Kingdom

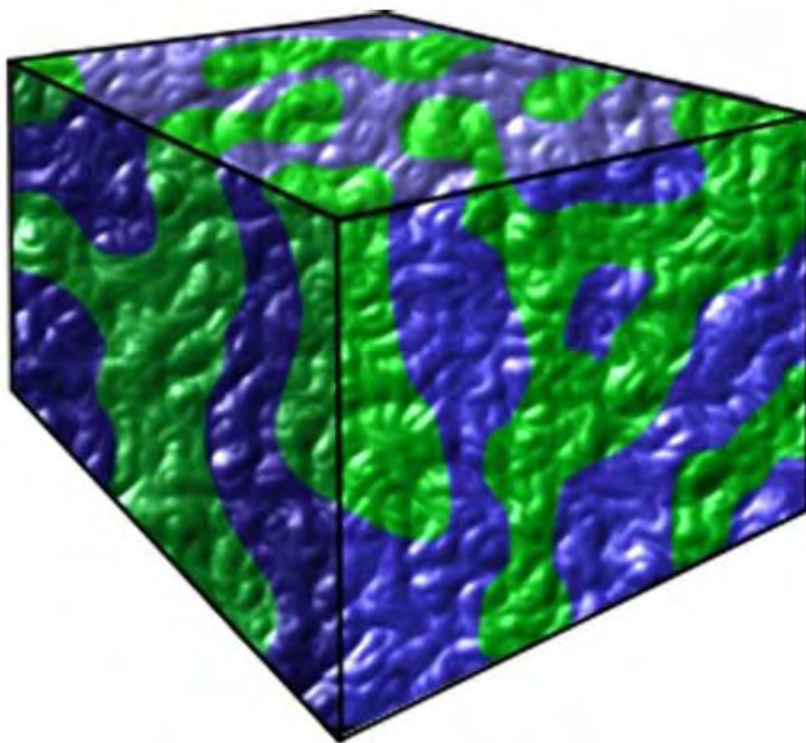
Perylene bisimides (PBIs) are really useful n-type materials. They are highly absorbent in the visible and are thermally stable. It is easy to modify the conjugated core with different functional groups. These different functional moieties can direct the self-assembly into different types aggregates, and strongly affect the solubility. This can lead to dramatically different properties. PBIs are suitable for such light driven processes as solar cells and H₂ evolution due to the formation of a radical anion upon irradiation with different wavelengths of light. By changing the aggregation type and the HOMO-LUMO level of the self-assembling molecules, one can tune the wavelength of light needed to drive these reactions. It is often difficult to control and predict the aggregation in advance and therefore the function of the material. Here, we will describe a levodopa-functionalised PBI that self-assembles into two different supramolecular aggregates depending on subtle changes in the pH of the solution, which show either H-type absorption properties or J-type absorption. We are able to switch between the two aggregation types by changing the pH. With the use of small angle neutron scattering, UV-vis absorption spectroscopy and imaging techniques, we are able to fully analyse these aggregates and post-rationalise the structures with computational modelling. Each of these aggregates exhibits different behaviour, with one being able to self-assemble into a gel upon lowering the pH and one not (Figure 1.). The aggregates interestingly also have different responses to light and we are therefore able to tune the photoconductivity of the materials by changing the aggregate type. This level of control from one molecule just by altering the pH shows great promise in applications such as OPVs and other optoelectronic materials.



POLY 579: Conductivity and mechanics in self-organized networks

Gregory N. Tew, tew@mail.pse.umass.edu. *Polymer Science and Engineering, University of Massachusetts, Amherst, South Deerfield, Massachusetts, United States*

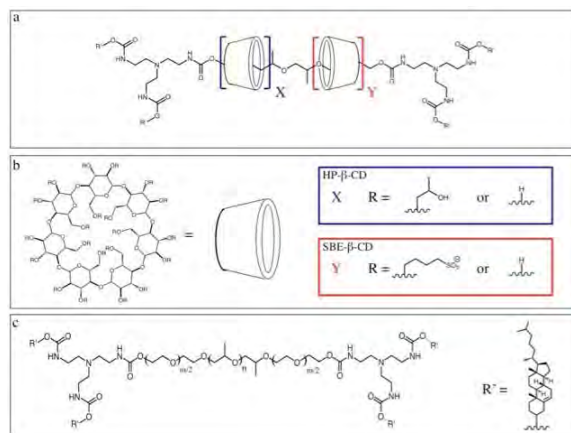
Phase-separated and self-assembled co-network materials offer a simple route to bicontinuous-like morphologies, which are expected to be highly beneficial for applications such as ion, charge, and oxygen transport. Despite these potential advantages, the systematic definition of co-network structures has not been achieved, largely due to the lack of well-controlled chemistries for their preparation. Here, a thiol-ene end-linking platform enables the systematic investigation of phase-separated poly(ethylene glycol) (PEG) and polystyrene (PS) networks in terms of the molecular weight and relative volume fractions of precursor polymers. The ion conductivity and storage modulus of these materials serve as probes to demonstrate that both phases percolate over a wide range of compositions, spanning PEG volume fractions from ~ 0.3 - 0.65. These findings demonstrate that this approach to thiol-ene co-networks is a versatile platform to create bicontinuous morphologies. Extending the chemistry concepts also enables novel multi-block copolymers to be prepared as well as new copolymers. These will also be discussed.



POLY 580: Structure-Activity relationships on the *in vivo* therapeutic efficacy of 2-hydroxypropyl- β -cyclodextrin:pluronic polyrotaxanes in Niemann-Pick type C disease

Christopher J. Collins¹, Bradley Loren¹, Yawo Mondjinou¹, Suhail Alam², Kasturi Haldar², **David H. Thompson¹**, davethom@purdue.edu. (1) Purdue Univ Dept of Chem, West Lafayette, Indiana, United States (2) University of Notre Dame, South Bend, Indiana, United States

Niemann-Pick Type C disease (NPC) is a panethnic, heterogeneous, and extremely rare metabolic disorder characterized by a disruption of normal cholesterol trafficking within the cells of the body. There are no FDA approved treatments currently available for NPC patients. Recently, 2-hydroxypropyl- β -cyclodextrin (HP- β -CD) has shown efficacy as an NPC therapeutic by increasing overall lifetime of NPC mice, delaying neurodegeneration, and decreasing the total cholesterol burden within a variety of organs. Although promising, HP- β -CD treatment is hampered by poor CD bioavailability and pharmacokinetic profile after systemic injection, with large percentages of the injected dose rapidly lost through renal filtration. To address these shortcomings, we sought to design a family of high molecular weight, HP- β -CD pro-drug polyrotaxane (PR) delivery vehicles, capable of increasing the efficacy of a given injected dose by improving residence time and bioavailability. PR can effectively diminish the cholesterol pool within the liver, spleen, and kidney at molar concentrations that are 10-to-100-fold lower than monomeric HP- β -CD. In addition to this proof-of-concept, use of PR scaffolds with differing physiochemical properties reveal structure-activity relationships in which PR characteristics were found to play both decisive and subtle roles in therapeutic efficacy toward unesterified cholesterol clearance. PR threading and polymer core characteristics appear to greatly influence therapeutic efficacy, with increased threading and hydrophobicity producing increased efficacy. Inclusion of negatively-charged β -CD derivatives increases solubility without impacting their cholesterol reduction capacity. In addition, PR scaffolds exhibit absorption, pharmacokinetics, and biodistribution patterns that are significantly altered from monomeric HP- β -CD. These findings suggest that PR scaffolds hold great promise as potential treatments for visceral disease in NPC patients.

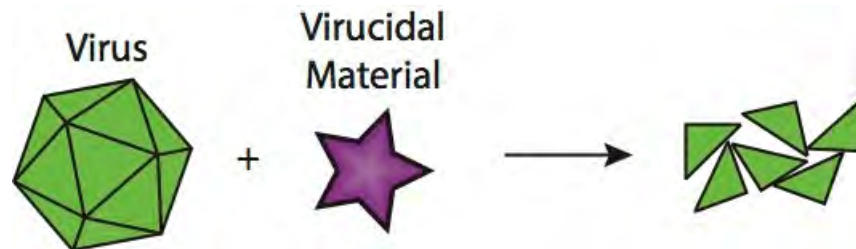


β -CD Pluronic PR Prepared as Potential NPC Therapeutics

POLY 581: Broad-spectrum anti-virals from cyclodextrins

Samuel Jones², samuel.jones@epfl.ch, **Francesco Stellacci**¹. (1) Institute of Materials, EPFL, Lausanne, Switzerland (2) Materials, Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland

Viral infections kill millions of people every year. Available antiviral drugs are virus-specific and active against a limited panel of human pathogens. They usually lose clinical effectiveness upon viral mutations, and interfere with the intracellular viral replication cycle. Arguably, to avoid all of these shortcomings the ideal antiviral drug should be broad-spectrum, non-toxic, and extracellular. Here, we show that it is possible to provide materials with an irreversible inhibition mechanism. By creating strong binders local forces (calculated to be ~130 pN) can be generated that eventually lead to irreversible viral deformation. Virucidal assays, electron microscopy images, and molecular dynamics simulations support the proposed mechanism. The particles achieved in this way show no cytotoxicity together with broad-spectrum efficacy i.e. *in vitro* irreversible activity against HSV, HPV, LentiV, RSV, Dengue virus, Zika Virus. Our materials proved also active in *ex-* and *in-vivo* assays. The supramolecular design rule presented here is a significant first step towards the achievement of an antiviral drug that would represent the medical equivalent of broad-spectrum antibiotics.



POLY 582: Development of HP-β-CD as a broad-spectrum antiviral therapy

Ihid Carneiro Leao², icleao@ucdavis.edu, **Caroline Spilere**^{1,5}, **Flavio Lemos Matassoli**^{1,6}, **James Hildreth**^{3,4}. (1) Molecular and Cell Biology, University of California Davis, Davis, California, United States (2) Molecular and Medical Microbiology, University of California Davis, Davis, California, United States (3) Meharry Medical College, Nashville, Tennessee, United States (4) Medical Microbiology and Immunology, University of California Davis, Davis, California, United States (5) Dermatology, USP, Sao Paulo, Sao Paulo, Brazil (6) Microbiology, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro, Brazil

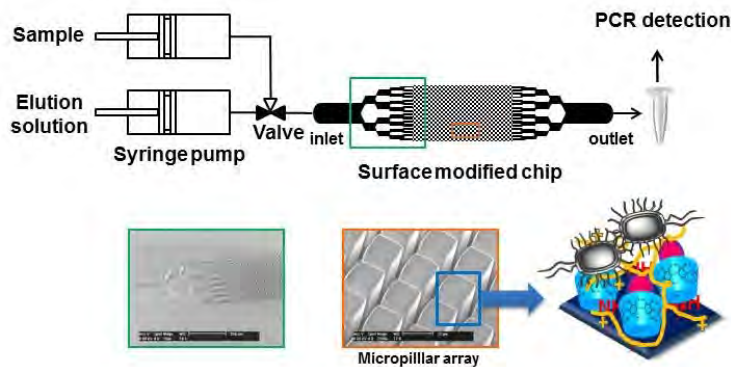
Broad-spectrum antivirals effective against emerging viruses are urgently needed. Most approved antiviral drugs (fewer than 10), target viral enzymes and are optimized to work against a single virus species. We are exploring the utility of 2-hydroxypropyl-beta-cyclodextrin (HP-β-CD) as a novel anti-HIV therapeutic. HP-β-CD, through its cholesterol depleting effects, has shown *in vitro* microbicidal properties against many families of enveloped viruses of medical relevance, including retroviridae, filoviridae and flaviviridae. Since HP-β-CD does not target a specific viral protein, HP-β-CD can be developed as a broad spectrum antiviral with a higher barrier for development of drug resistance. It also can be combined with other FDA-approved antivirals. We have developed data on the anti-HIV activities of combinations of HP-β-CD with currently available anti-HIV drugs (ARTs) using cell- based antiviral assays. HP-β-CD exerted the same anti-viral potency against wild-type and multi-drug resistant strains of HIV. The overall tendency of HP-β-CD was to have strong or moderate synergism with the nucleoside/nucleotide analogs tested but also additive effects with other ARTs (table 1). No evidence of drug-induced cellular toxicity was found in the dose range studied. Furthermore, HP- β-CD synergized with Tenofovir, one of the most frequently prescribed nucleotide analogues for prevention and treatment of HIV-1 infection, against ART resistant clinical isolates of HIV. HP-β-CD has also effects on the innate immune response that may explain its efficacy as antiviral compound. The clinical development of HP-β-CD as anti-HIV compound will open new opportunities for clinical studies repurposing it for use in other viral diseases lacking therapeutic options.

| ART class | Drug Names | Mean synergy volume (μM) ² ± SD | Mean antagonism volume (μM) ² ± SD | Interpretation of result |
|--------------------------|------------|--|---|--------------------------------|
| Nucleoside Analog | AZT | 36.08 ± 12.26 | -9.37 ± 2.69 | additive |
| | FTC | 110 ± 70 | -2 ± 3 | strong synergism |
| | 3TC | 1 ± 1 | -32 ± 15 | additive/minor antagonism |
| Nucleotide Analog | TDF | 97 ± 53 | -4 ± 7 | moderate synergism |
| Non-Nucleotide Inhibitor | NVP | 59 ± 32 | -19 ± 29 | moderate synergism |
| | EFV | 38 ± 27 | -26 ± 11 | minor synergism and antagonism |
| Integrase inhibitor | RAL | 3 ± 3 | -23 ± 15 | additivity |
| | DTG | 25 ± 12 | -51 ± 58 | additivity |
| Protease inhibitor | SAV | 17 ± 29 | -4 ± 2 | additivity |
| | | 1 ± 1 | -14 ± 13 | additivity |
| | DRV | | | |

POLY 583: Rapid enrichment of bacteria using a microfluidic device coupled with host-guest interactions

Alexandra Pérez-Anes^{2,1}, Anna Szarpak-Jankowska^{2,1}, Dorothee Jary^{2,3}, Guillaume Delapierre^{2,3}, **Rachel AUZELY-VELTY^{2,1}**, *rachel.auzely@cermav.cnrs.fr*. (1) CERMAV-CNRS, Grenoble, France (2) Grenoble Alpes University, Grenoble, France (3) CEA-Leti, Grenoble, France

Rapid and sensitive detection of pathogenic organisms at very low concentrations is crucial to safeguard public health from food- and water-borne pathogens as well as from infectious diseases. All the techniques currently used require a culture-based pre-enrichment step to reach enough bacteria to allow detection and identification. In recent years, many efforts have focused on the development of platforms allowing for rapid and efficient capture of bacteria from a sample to shorten this pre-enrichment step. In this regard, we recently developed a new and fast method for concomitant capture and detection of bacteria. Our method combines a micropillar-integrated microfluidic device and host-guest interactions for rapid enrichment of bacteria, and polymerase chain reaction (PCR) for bacterial detection. Interestingly, since the capture is mainly governed by reversible binding with cyclodextrin molecules, the microfluidic chip may be used for detection of different bacteria and re-used. This innovative platform thus exhibits great potential for use in various diagnostic areas like environmental or food processing controls.

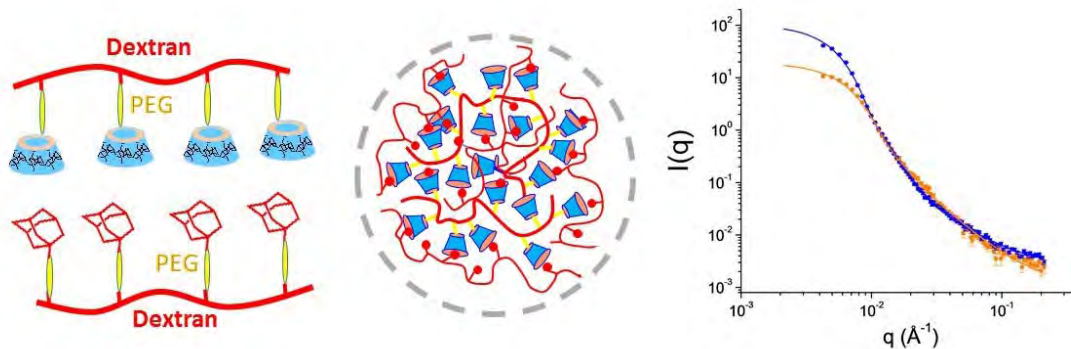


Experimental setup for real-time PCR detection of bacterial cells from aqueous samples

POLY 584: Host-guest macromolecular assemblies: Interplay between macromolecular design, interactions and structure

Catherine Amiel⁴, amiel@icmpe.cnrs.fr, **Iurii Antoniuk**⁴, **Beatrice Plazzotta**¹, **Daria Kaczmarek**², **Veronique Wintgens**³, **Gisele Volet**³, **Thorbjorn Nielsen**⁵, **Imre Varga**², **Jan Skov Pedersen**¹. (1) Aarhus University, Aarhus C, Denmark (2) Eötvös University, Budapest, Hungary (3) ICMPE - SPC, Thiais, France (4) University Paris Est Créteil, Thiais, France (5) Aalborg University, Aalborg, Denmark

Cyclodextrin polymers offer the possibility to tailor macromolecular assemblies in aqueous solutions due to their ability to form inclusion complexes with apolar guests. Indeed, the specific recognition between β -cyclodextrin units (β -CD) and hydrophobic derivatives such as adamantyl groups has been used to build three-dimensional structures spontaneously forming in aqueous solution. A guest polymer containing several β -cyclodextrin units (P β -CD) is mixed in water to a host polymer containing several lipophilic groups (hydrophobically modified dextran). The resulting multivalent interactions between the CD cavities and the lipophilic groups constitute the temporary crosslinks of a network of connected chains. The interplay between macromolecular design, structure and interactions in the nanoassemblies has been utilized to tailor different kinds of hierarchical nanostructures, such as host-guest self-assembled nanoparticles, core-shell nanoparticles constituted of a PLA core and a lbl P β -CD shell or core-shell PNIPAM microgels stabilized by a P β -CD and a dextran-adamantyl-PEG bilayer.¹⁻⁴ These systems are of great interest for drug delivery applications as they combine the low toxicity of the hydrophilic compounds, the easiness of preparation, the specific affinity for apolar drugs due to the presence of β -CD units and the ability to control the drug release.^{3,4}

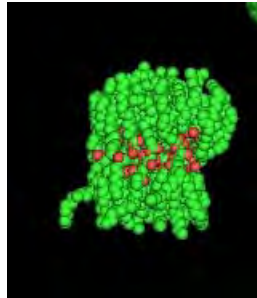


Host-guest macromolecular assemblies and SAXS analyses of the nanoassemblies

POLY 585: Novel emulsions from palmitoyl cyclic sugar

Artur Cavac-Paulo, arturmcpaulo@gmail.com. University of Minho, Guimaraes, Portugal

Beta (DP=7) and Gama (DP=8) cyclodextrines and cyclosapharose (DP~20) (annex figure) were fully couple with palmitoyl to prepare a serial of oils. Full reaction turnover is shown by NMR. The novel oils have a melting point ranging from 40 to 70 C and they can be used to prepare stable emulsions in water, with/without a protein shell under ultrasound mechanical stress. The novel emulsions are very stable for several weeks and they can be able to encapsulation of hydrophilic/hydrophobic compounds and promote control release of drug. A critical over is provided about the properties of those palmitoyl cyclic sugar oils.



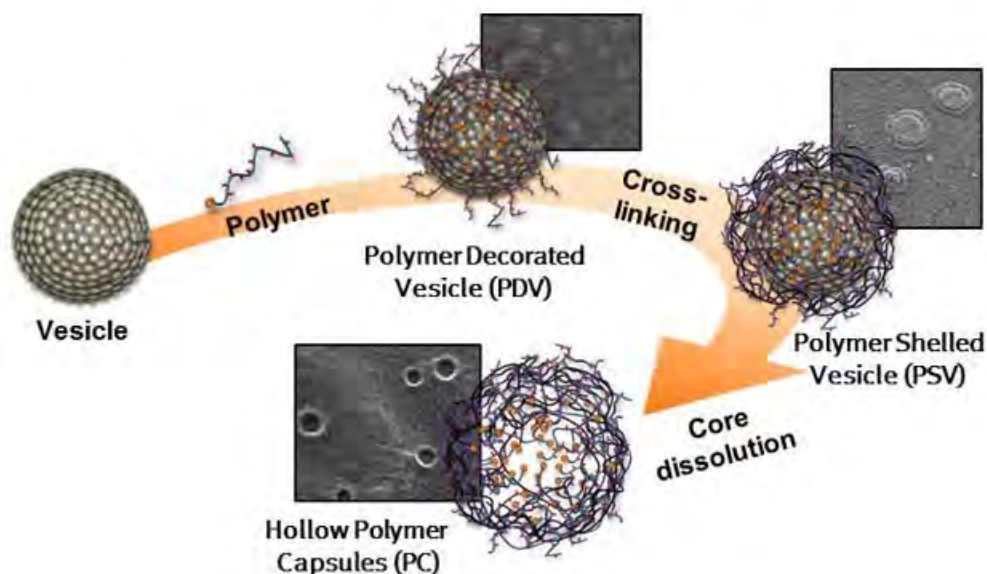
Palmitoyl cyclosapharose

POLY 586: Self-assembly of responsive nanocontainers based on cyclodextrins

Bart Jan Ravoo, *b.j.ravoo@uni-muenster.de*. Organic Chemistry Institute, WWU Muenster, Muenster, Germany

Self-assembly is emerging as a superior method to prepare adaptive and responsive nanomaterials. The structure and function of these materials is entirely determined by the dynamic and weak interactions of the constituent molecular “building blocks” of the material. Since the inherent interactions are weak, these versatile materials readily respond to even small changes and stimuli in their environment. Moreover, these materials are biomimetic and contain large amounts of water, so that application in biomedical technology can be foreseen.

This lecture will highlight self-assembled nanocontainers based on cyclodextrins that respond to various external stimuli. Amphiphilic cyclodextrins form bilayer vesicles in aqueous solution and the surface of these vesicles can be functionalized using host-guest chemistry. An artificial glycolix that selectively binds lectins is obtained if the cyclodextrin vesicles are functionalized with adamantane-tagged carbohydrates. Photoresponsive capture and release of lectins is possible if azobenzene-tagged carbohydrates are used. Shear-thinning hydrogels result if the cyclodextrin vesicles are mixed with adamantane-functionalized polymers, which act as supramolecular cross-linkers. Polymer-shelled vesicles and polymer nanocontainers are obtained if the cyclodextrin vesicles are decorated with adamantane-terminated poly(acrylic acid), which can be cross-linked with diamines. Recently, we have also shown that this polymer shell is redox-responsive if the cross-linker contains a disulfide unit. The resulting nanocontainer can deliver cargo into cells.



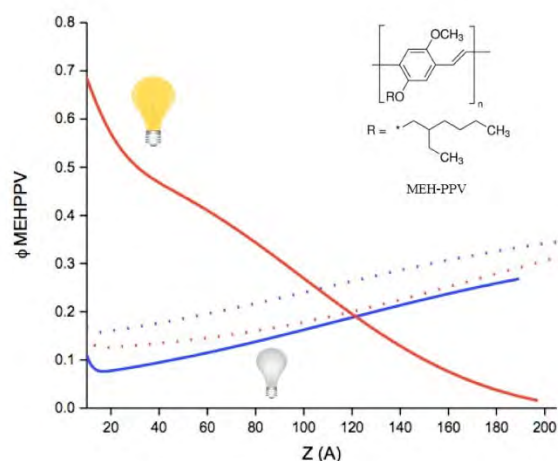
POLY 587: Illumination alters the conformation and thermodynamics of conjugated polymers

Brian Morgan¹, **Mark D. Dadmun**^{1,2}, dad@utk.edu. (1) Univ of Tennessee, Knoxville, Tennessee, United States (2) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Our recent studies have examined the effects that illumination has on the structure and conformation of conjugated polymers, both in solution and the bulk. Conjugated polymers are an important class of optoelectronic polymeric materials which make up the active layer of key organic electronic devices such as organic photovoltaics, transistors, and light emitting diodes. Considering the strong link between polymer chain structure and device efficiency in these materials, a comprehensive understanding of certain experimental conditions which may influence this conformation and thusly alter the functionality of the devices predicated upon them is of vital importance.

This presentation will outline our initial exploration of light induced effects on benchmark conjugated polymers in solution elucidated via the use of small angle neutron scattering and the impact of white light exposure on structural evolution of solution gels formed from conjugated polymers at multiple length scales. Our studies of the depth-profile of conjugated polymer composite thin films cast from a single solution through neutron reflectivity, including monitoring the effects of light exposure during the thermal annealing process upon the final film depth profile will also be discussed.

Ultimately, these works cumulatively provide strong evidence indicating that light exposure is an important parameter with far-reaching implications on the final structure of organic electronic materials. Overlooking illumination conditions and failing to provide a consistent ambient light environment throughout device fabrication will result in non-uniform chain conformations and layering architectures, inevitably impacting device performance.

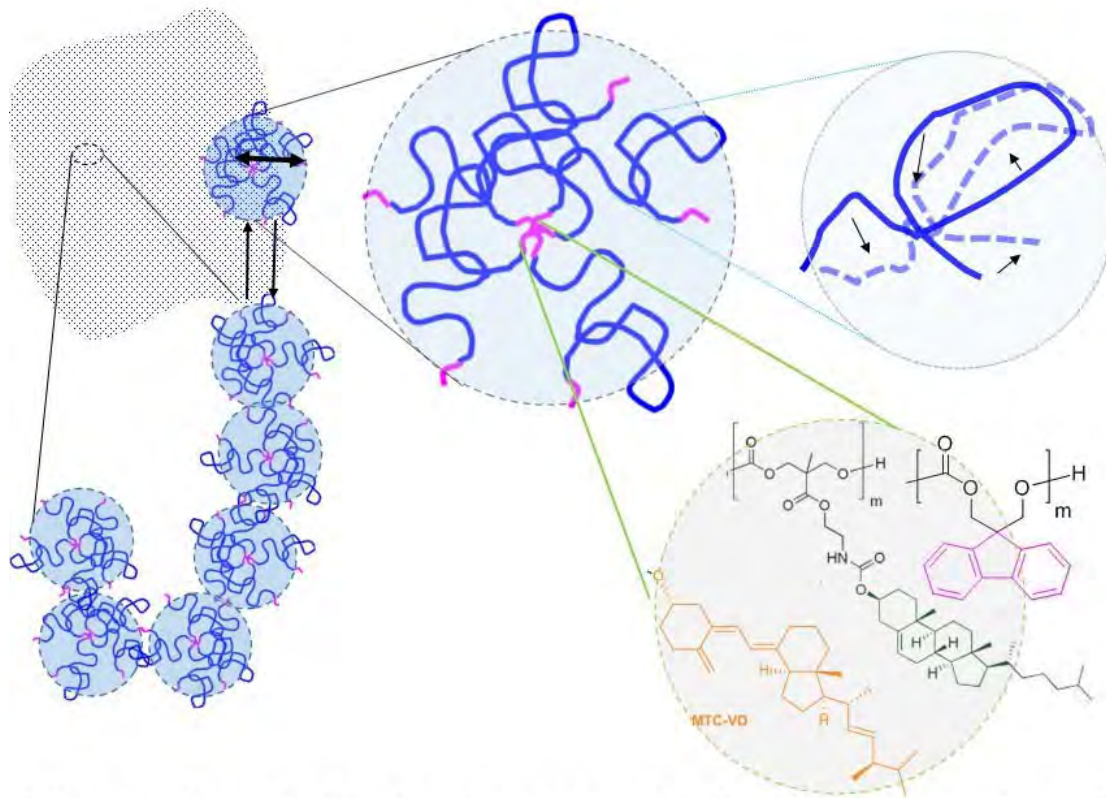


Volume fraction profile of MEH-PPV in a 10:90 MEH-PPV:dPS blend cast on HF stripped silicon. Broken traces indicate as-cast samples and solid traces indicate samples annealed for 15 minutes at 125°C (blue for dark, red for light).

POLY 588: Hierarchical structure and dynamics of oligocarbonate-functionalized PEG block copolymers

Vivek M. Prabhu, *vprabhu@nist.gov*. Materials Science and Engineering Division, NIST, Gaithersburg, Maryland, United States

Hierarchical, self-assembled block copolymers in aqueous solutions provide advanced materials for biomaterial applications. Recent advancements in the synthesis of aliphatic polycarbonates have shown nontraditional micellar and hierarchical structures driven by the supramolecular assembly of the carbonate block functionality that includes cholesterol, vitamin D, and fluorene. This presentation shall describe the supramolecular assembly structure and dynamics observed by static and dynamic light scattering, small-angle neutron scattering and neutron spin-echo spectroscopy.



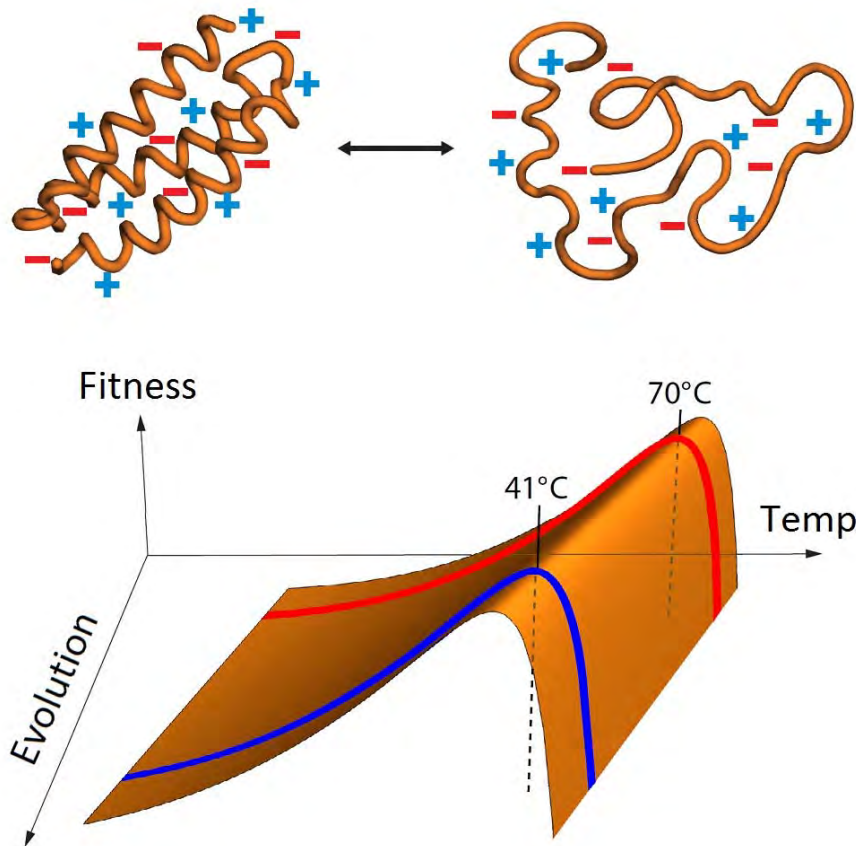
Hierarchy: Gel > Cluster > micelle > chain > junction

Supramolecular assembly driven by functionalized oligocarbonate-PEG polymers.

POLY 589: Polymer physics to understand protein evolution under extreme temperature

Kingshuk Ghosh, Kingshuk.Ghosh@du.edu. *Physics and Astronomy, University of Denver, Denver, Colorado, United States*

Thermophilic proteins -- extracted from organisms that live at high temperature -- can withstand temperatures much higher than their mesophilic counterparts, obtained from organisms that live near room temperature. This extreme thermal tolerance in thermophilic proteins is particularly intriguing given they share high structural and sequence similarity with their mesophilic homologues. We try to address this puzzle by tracing back to one of the early (almost thirty years ago) work of Muthukumar. Extension of this elegant theory reveals how evolution may have used subtle tricks with charge patterning in the protein sequence to gain such high temperature resilience. The theory also holds promise to another rapidly developing area of protein science, trying to model the Intrinsically Disordered Proteins (IDP).

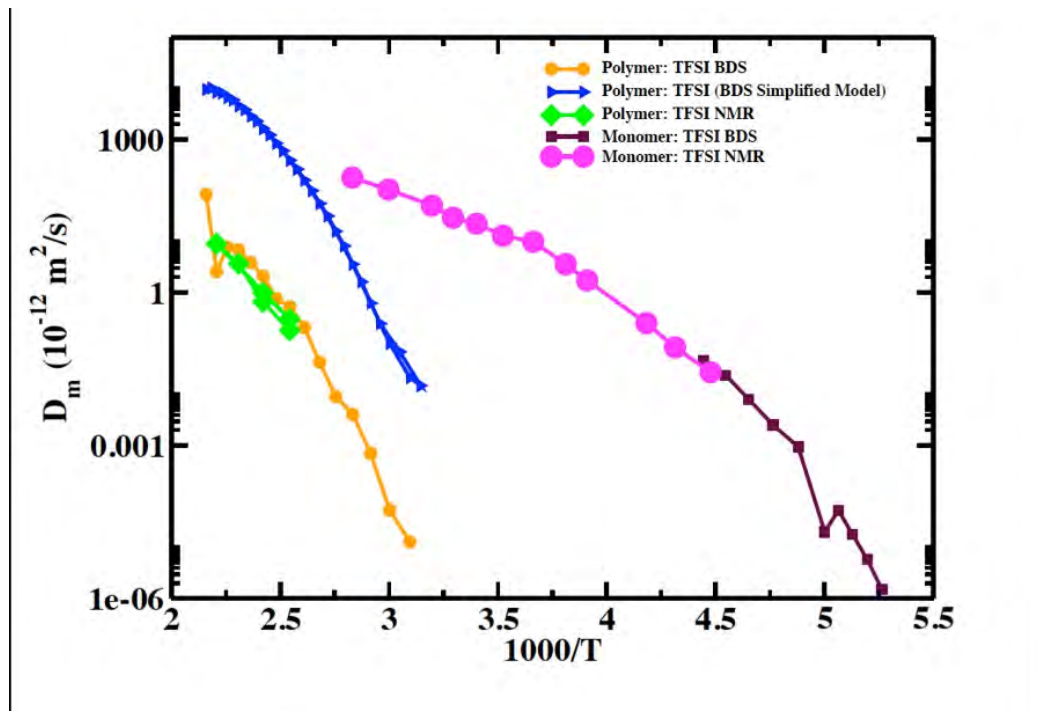


Fitness landscapes depend on proteome physical chemistry

POLY 590: Rayleighian approach for studying the kinetics of ionic transport in polymeric media

Rajeev Kumar, *kumarr@ornl.gov*. Oak Ridge National Lab, Oak Ridge, Tennessee, United States

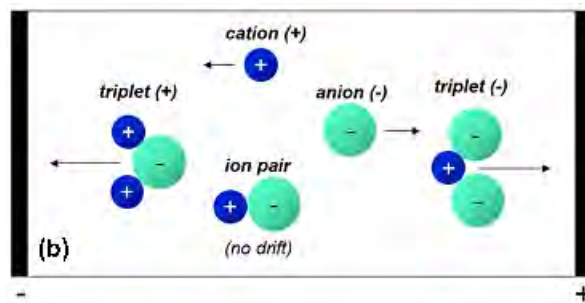
Understanding the kinetics of ionic transport in concentrated electrolytes such as ionic liquids and charged polymers is a topic of great fundamental interest and technological relevance. In this talk, I'll present our theoretical and experimental efforts in understanding the kinetics of ionic transport in ionic liquids and polymerized ionic liquids. In particular, Lord Rayleigh's dissipation function formalism (called the Rayleighian approach) is used for analyzing impedance of ionic liquids (ILs) and polymerized ionic liquids (PILs) within linear response. The approach provides a computational framework for a systematic study of various factors, including polymer dynamics in affecting the impedance. We have used the approach to extract mutual diffusion constants, the length scale of mutual diffusion, and thicknesses of a low dielectric layer on the electrodes from the broadband dielectric spectroscopy (BDS) measurements done for an IL and three PILs. Also, static dielectric permittivities of the IL and the PILs are determined. The extracted mutual diffusion constants are compared with the diffusion constants of ions measured using pulse-field gradient (PFG) fluorine nuclear magnetic resonance (NMR). For the first time, excellent agreements between the diffusivities extracted from the BDS spectra of IL/PILs and those measured using the PFG-NMR are found. The agreement allows the use of the BDS and the PFG-NMR techniques in a complimentary manner for understanding the ionic transport. Reasons behind failure of the models based on the linearized Poisson-Nernst-Planck (PNP) formalism in analyzing the concentrated ionic fluids will be discussed.



POLY 591: Ohm's law, polymer electrolytes and lithium batteries

Nitash P. Balsara, nbalsara@berkeley.edu, *Danielle M. Pesko*. Univ of California, Berkeley, California, United States

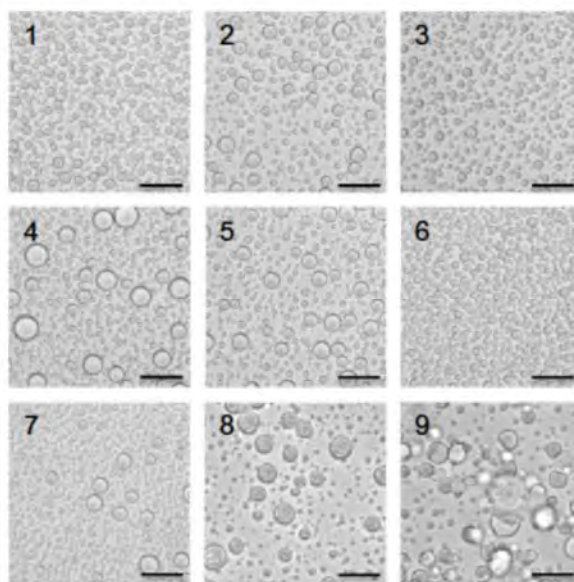
The need for creating safe electrolytes for lithium batteries is significant given the continued safety problems associated with current lithium-ion batteries. Nonflammable polymer electrolytes offer a possible solution but the rate of lithium ion transport is too low for practical applications. In this talk, I will discuss some of the fundamental factors that limit ion transport in polymers. Polymer electrolytes obey Ohm's Law, i.e. in the limit of small applied potentials, the current generated at steady state is proportional to the applied potential. Methods for using this measurement to determine the transference number of the electrolyte will be discussed. A surprising conclusion of our analysis is that the cation transference number of most polymer electrolytes is negative. In other words, in the absence of concentration gradients, both the cation and the anion are driven by the applied electric field to the same (positive) electrode. This reduces the efficacy of batteries with polymer electrolytes. Approaches for addressing this limitation will be discussed.



POLY 592: Directing the phase behavior of polyelectrolyte complexes using chiral patterned peptides

Naomi Pacalin, Lorraine Leon, **Matthew V. Tirrell**, mtirrell@uchicago.edu. IME, University of Chicago, Chicago, Illinois, United States

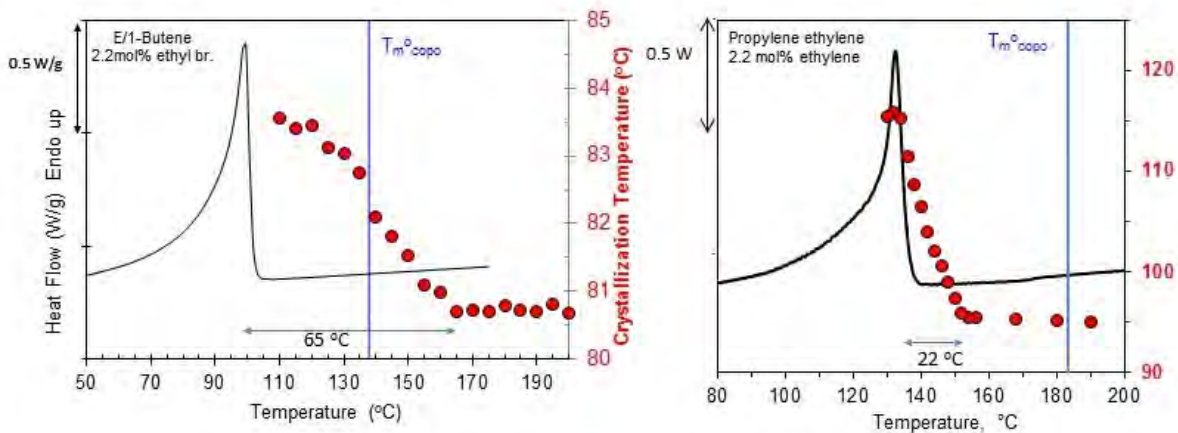
Polyelectrolyte complexes (PECs) have a range of promising applications as soft materials due to their self-assembly and diversity of structure and chemical composition. Peptide polymer PECs are biocompatible and biodegradable, making them useful for encapsulation of food additives and flavors, micellar drug delivery, medical and underwater adhesives and scaffolds for cell growth in tissue engineering. Parameters affecting PEC formation and stability in regard to charge effects are well researched, but little is known about the effects of van der Waals interactions, hydrogen bonding, and secondary structure in these materials. Chirality provides a unique opportunity to manipulate PEC phase to modulate the amount of solid-like or liquid-like character by influencing hydrogen bonding interactions among peptide chains. In previous work, we showed that chiral peptides form solid complexes, while complexes with even one racemic peptide were fluid. This raised the question of how long a homochiral sequence must be to result in solid phase formation. We have designed chiral patterned peptides of polyglutamic acid and polylysine ranging from 50 to 90% L-chiral residues with increasing numbers of sequential L-chiral residues. These polymers were mixed together to form PECs. We observed that 8 or more sequential L-chiral residues are necessary to achieve both the appearance of a solid phase and sustained β -sheets in the complex, as determined by optical imaging and FTIR Spectroscopy. Less homochiral content results in formation of a fluid phase. Thus, we show that chiral sequence can be used to control the phase transition of PECs. Understanding how to manipulate PEC phases using chiral sequence as presented here may enable tuning of the material properties to achieve the desired mechanical strength for coatings, or effective molecular release kinetics for drug delivery applications, for example.



POLY 593: Effect of melt viscosity on self-nucleation of ethylene- and propylene-1-alkene random copolymers

Rufina G. Alamo, alamo@eng.fsu.edu. Chemical and Biomedical Engineering, Florida State University, Tallahassee, Florida, United States

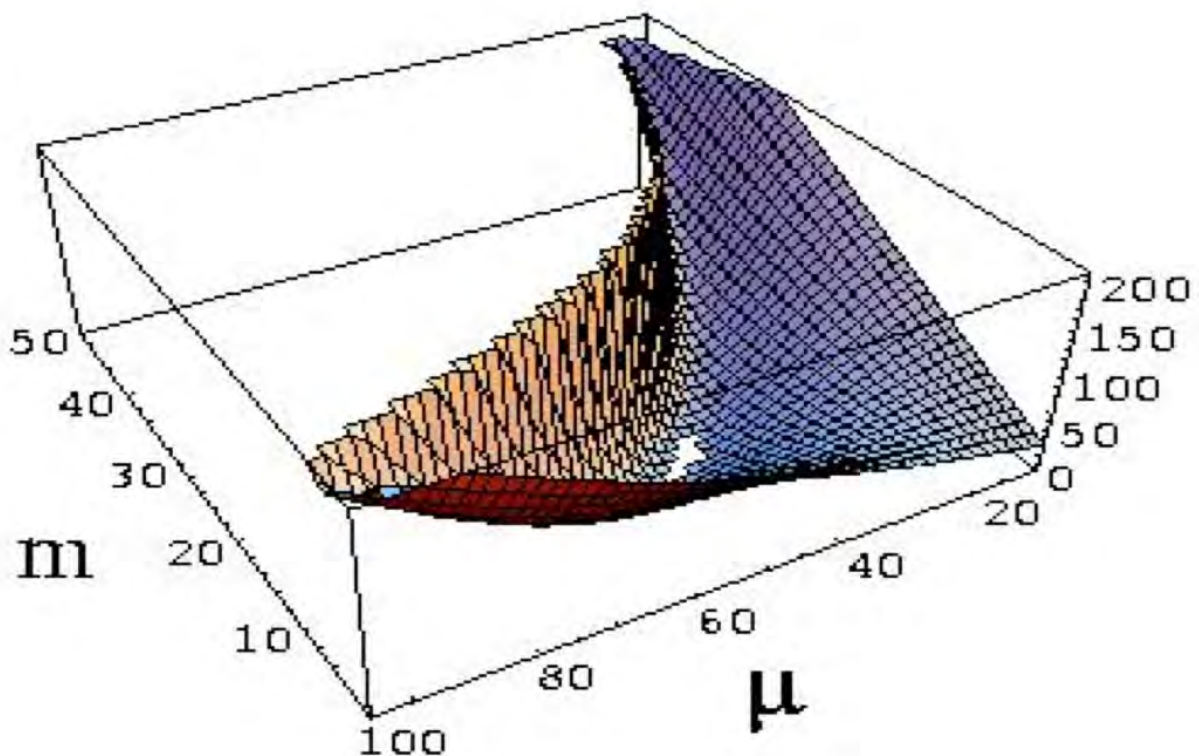
The strong memory of crystallization observed in melts of random ethylene copolymers has been attributed to self-seeds that remain in the melt as memory of the copolymer's ethylene sequence partitioning during crystallization. When cooled from seeded melts, the free energy barrier for nucleation of copolymer crystals decreases with a profound increase in crystallization rate. Cooling ethylene copolymers from their melts at a constant rate, the increase in crystallization temperature is observed even at temperatures 65 degrees above the observed melting point and at 30 degrees above the equilibrium melting temperature. This unusual strong melt memory is attributed to the topological constraints that build in the intercrystalline regions during crystallization. The effect of molar mass, long chain branching, and degree of crystallinity on increasing strength of melt memory support the correlation between melt memory and entanglements. As the entanglement molecular weight of isotactic polypropylene is about four times higher than for polyethylene, the number of entanglements per chain is much reduced; consequently, self-nucleation of random propylene copolymers is expected in a melt temperature range comparatively closer to the observed melting point. Self-nucleation data for metallocene-based isotactic polypropylene and a series of random propylene-ethylene copolymers give further evidence for the role of melt viscosity on melt-memory.



POLY 594: Award Address (ACS Award in Polymer Chemistry sponsored by ExxonMobil Chemical Company). Polymer crystallization: New concepts and implications

Murugappan Muthukumar, *muthu@polysci.umass.edu. Univ of Massachusetts, Amherst, Massachusetts, United States*

Crystallization of an entangled collection of interpenetrating polymer chains continues to be a challenging fundamental problem in polymer physics. Classical concepts on polymer crystallization are under revision, due to the demands made by a wealth of new information from experiments and computer simulations. New ideas based on the collective entropy will be presented and contrasted with the classical theories of polymer crystallization, which are based only on energy considerations. Issues related to the primordial stages of crystallization, selection of equilibrium lamellar thickness, sectorization, growth kinetics, melt-memory, and the origin of macroscopic chirality will be briefly described.

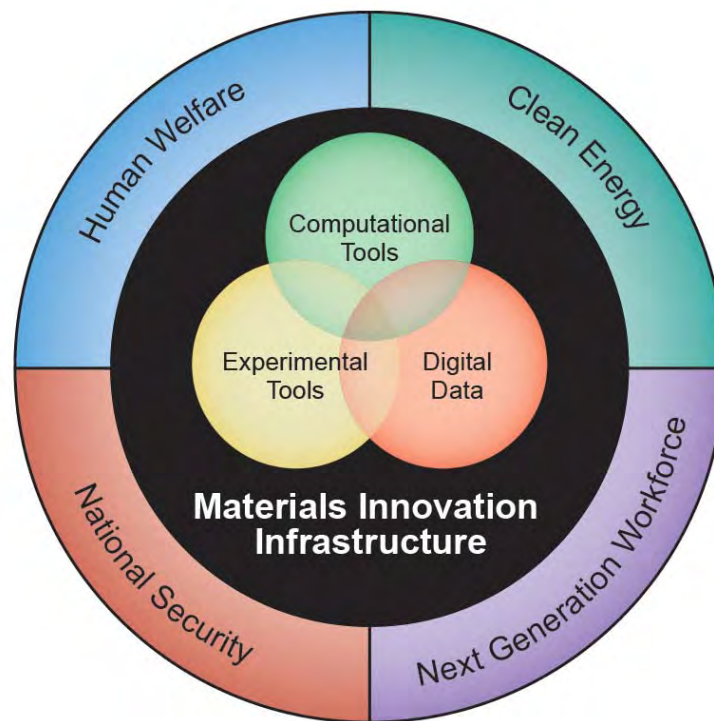


Equilibrium lamellar thickness is much smaller than the extended chain dimension.

POLY 595: Directed assembly of hierarchical polymeric materials

Juan J. De Pablo, depablo@uchicago.edu. Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Much of the richness of polymeric materials derives from their ability to adopt a seemingly infinite number of conformations. A grand challenge for polymers science and engineering is therefore that of controlling and manipulating such conformations in order to engineer innovative materials for emerging applications. Synthetic polymer chemistry continues to make advances in its ability to create new molecules with well-defined, specific sequences. There is therefore considerable interest in developing processes that rely on the application of external fields or constraints to direct the assembly of such molecules into desirable morphologies. In the longer term, there is a need to identify and develop design principles that might capitalize on synthetic advances to create assemblies with engineered structures and, importantly, function. Over the past decade, our research group has focused on development of theoretical and computational methods for prediction of the structure and properties of polymeric assemblies. That work has led to design of self-assembly strategies in which the morphology of block copolymer materials is manipulated by relying on patterned substrates. Building on that work, we are now aiming to understand how histone proteins can in fact direct the compaction of long strands of DNA to form functional, responsive chromatin structures. In this presentation I will discuss our recent work in the area of DNA-based polymeric materials, and describe some of the design principles that have started to emerge from such efforts.



Materials Innovation Infrastructure from Materials Genome Initiative (www.mgi.gov).

POLY 596: Chemical conversion of linkages in covalent organic frameworks

Peter Waller, wallerp@berkeley.edu, Steven J. Lyle, Thomas Osborn Popp, Christian S. Diercks, Jeffrey A. Reimer, Omar M. Yaghi. Chemistry, University of California, Berkeley, Oakland, California, United States

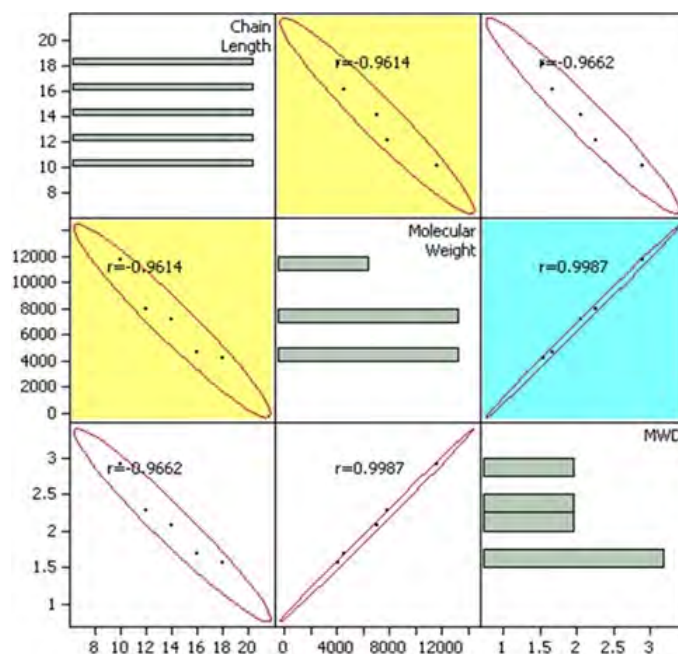
New linking reactions are highly sought-after in the formation of covalent organic frameworks (COFs), but this is often difficult to achieve since the linkage must be both stable and dynamic. This means that many possible linkage reactions remain unexplored. Instead of forming new linkages *de novo*, a better approach may be working to convert known linkages into novel ones. We discuss the transformation of imine-linked COFs into amide ones by direct oxidation with retention of crystallinity and permanent porosity. The amide COFs show improved chemical stability relative to their imine-linked progenitors.



POLY 597: Effects of α -olefin chain length and monomer concentration on molecular weights and molecular weight distributions of various α -olefin-maleic anhydride copolymers

Hoon Kim², *coboshin@yahoo.com*, **Colleen Tabasko**², **Nawel S. Khelfallah**¹, **Judy Arroyave**³, **Ramesh Sharma**³. (1) Innovation, Chemetall GmbH, Frankfurt, Germany (2) Innovation, Chemetall US, New Providence, New Jersey, United States (3) Molecular Analysis Group, Albemarle Corporation, Baton Rouge, Louisiana, United States

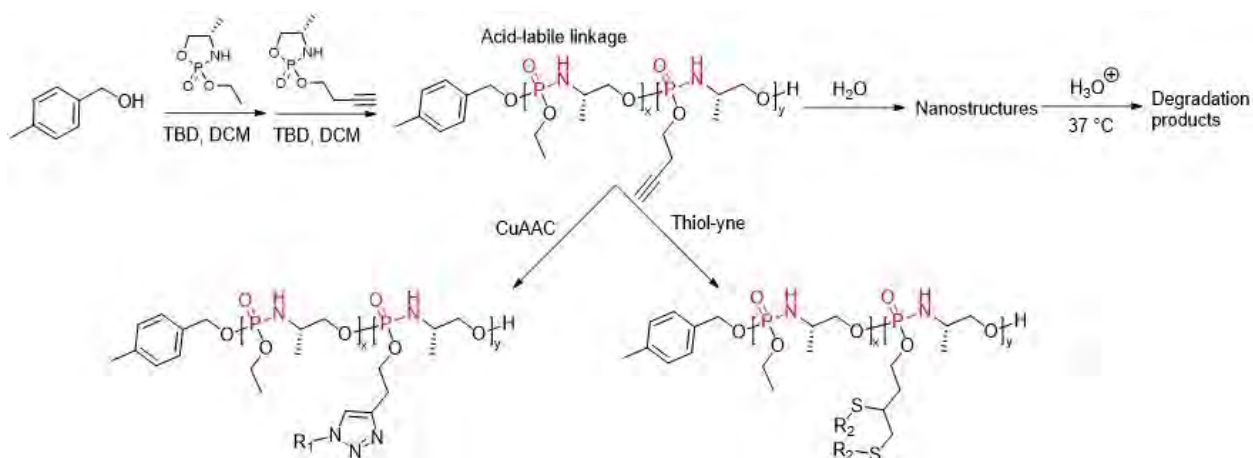
Amphiphilic α -olefin-maleic anhydride copolymers have served for many years as surface active functional materials such as lubricants, cosmetic compositions, wax dispersants, oil sorbents, pour point depressants and diverse surface modifiers throughout the industry. Although both α -olefin and maleic anhydride monomers are difficult to homopolymerize, copolymerization of these monomers readily proceeds via characteristic charge transfer complex formation resulting in unique alternating monomer sequences in the backbone. The succinic anhydride functional units of the copolymer backbone can then be easily modified or further functionalized by diverse post-polymerization functionalization methods including carboxylic acid salt formation, esterification, amidation, and imidation, etc. Along these lines, most of effort has been devoted to achieving high conversion in both polymerization and post-polymerization functionalization in research, and optimization of diverse properties of the final polymers in application. However there is little information available about molecular weight control of this unique copolymer system. Thus in this paper we report the effect of key experimental parameters including monomer concentration, solvent, and initiator addition mode. In addition, we especially focus on the effect of molecular parameter such as side chain length on the molecular weight build-up during the polymerization.



POLY 598: Functional polyphosphoramidates and nanostructures with acid-triggered backbone cleavage

Hai Wang³, wanghaihp@gmail.com, Lu Su², Richen Li³, Shiyi Zhang¹, Karen L. Wooley⁴. (1) MIT, Cambridge, Massachusetts, United States (2) Chemistry, Texas A & M University, College Station, Texas, United States (3) Chemistry, Texas A&M University, Bryan, Texas, United States (4) 3255 TAMU, Texas AM University, College Station, Texas, United States

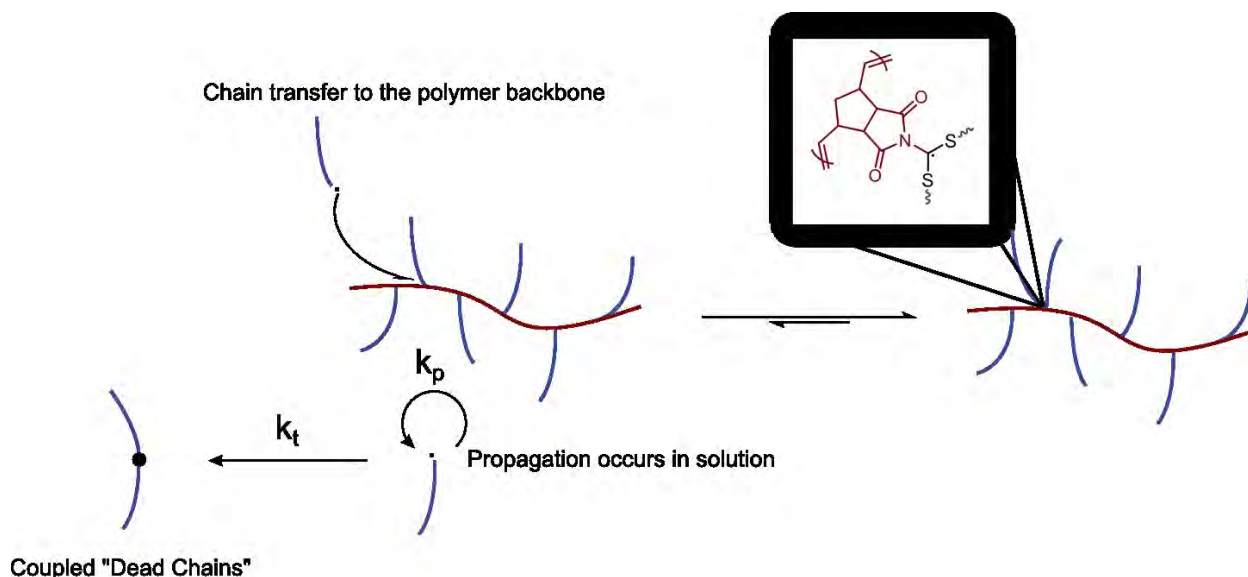
Unique diblock polyphosphoramidates (PPAs), with acid-labile phosphoramidate backbone linkages and alkyne side-chain functionalities, were developed as a versatile template for postpolymerization modifications, together with demonstration of their hydrolytic degradability as well as their aqueous assembly into functional nanoparticle morphologies. The introduction of acid-labile linkages along the polymer backbone led to rapid degradation of the polymer backbone dependent upon the environmental stimuli. Two oxazaphospholidine monomers, with one carrying alkyne functionality, were designed and synthesized to access well-defined diblock PPAs (PDI < 1.2) *via* sequential organobase-catalyzed ring-opening polymerizations (ROPs) with pendant alkyne groups for efficient functionalizations through click chemistry. Kinetic studies of the sequential ROPs showed a linear relationship between the monomer conversion and the polymer molecular weight, indicating the controlled fashion during each polymerization. The resulting PPAs with different block ratios, were further assembled into a family of nanostructures with different sizes, morphologies. In addition, two classic click reactions, copper-catalyzed azide-alkyne dipolar cycloaddition (CuAAC) and thiol-yne addition reactions, were employed to manipulate the alkyne-containing block and to provide a variety of diblock PPAs, which could be utilized for further biomedical and other applications. The hydrolytic degradation of the PPAs was studied, revealing breakdown of the polymer backbone through cleavage of the phosphoramidate linkages under acidic conditions.



POLY 599: Synthesis of bottlebrush polymers using the transfer-to approach

Scott Radzinski, *scr014@vt.edu*, Jeffrey Foster, John Matson. Virginia Tech, Blacksburg, Virginia, United States

Bottlebrush polymers are macromolecules with densely grafted polymeric pendent groups attached to a polymeric backbone. These polymers are traditionally prepared using one of three synthetic strategies: grafting-from, grafting-to, and grafting-through. We present here an alternative method of bottlebrush synthesis called transfer-to. The transfer-to method is a hybrid of the grafting-from and grafting-to approaches in which the growing polymer side chains detach from the backbone, propagate freely in solution, and then reattach to the backbone in a chain transfer step. This synthetic approach eliminates looping and bottlebrush coupling that grafting-from can suffer from. To prepare bottlebrush polymers using this method, we have developed a chain transfer agent for reversible addition fragmentation chain transfer (RAFT) polymerization with an orthogonally polymerizable Z-group (CTA1). CTA1 was first polymerized using ring-opening metathesis polymerization (ROMP) with Grubbs' catalyst to form poly(CTA1). This backbone polymer was then used in the transfer-to synthetic scheme to form large bottlebrush polymers ($M_n > 1$ MDa). By changing the R group, several different classes of monomers can be effectively polymerized. Lastly, the side chains can be cleaved by aminolysis at the dithiocarbamate linkage to further characterize the molecular weight and molecular weight distribution of the side chains.



POLY 600: Insight into the catalytic mechanism of metal-free ROMP – A DFT and experimental study

Joseph C. Johnson², j.casey.johnson@gmail.com, **Tori Kensy**⁴, **Christopher B. Rinderspacher**¹, **Andrew J. Boydston**³, **Daniel Knorr**². (1) Army Research Laboratory, Baltimore, Maryland, United States (2) U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States (3) Chemistry, University of Washington, Seattle, Washington, United States (4) Department of Chemistry, University of Washington, Seattle, Washington, United States

It has recently been reported that vinyl ether radical cations can function as ring-opening metathesis polymerization (ROMP) catalysts in norbornene based monomers.¹ Unfortunately, many monomers cannot be polymerized using the existing method. Therefore, it is imperative to understand the potential mechanistic pathways in order to expand the scope of this metal-free method. In this work, we present a hypothesized mechanism for the initiation of metal-free ROMP using high level DFT and wavefunction calculations while using experimental findings to test the hypothesized mechanism. Additional norbornene-containing monomers that do not work in metal-free ROMP are also investigated to identify possible propagation-inhibiting side reactions. Finally, we examine the thermodynamic effects of substituted vinyl ethers. Together, these results will allow for intelligent and strategically designed metal-free ROMP catalytic systems.

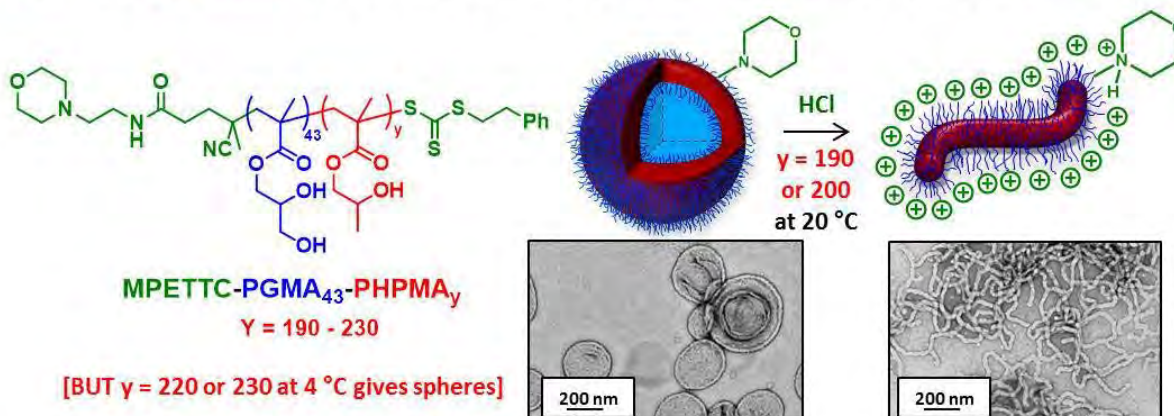


POLY 601: Stimulus-responsive non-ionic diblock copolymers: Protonation of a tertiary amine end-group induces vesicle-to-worm or vesicle-to-sphere transitions

Nicholas Penfold², njwpenfold1@sheffield.ac.uk, Joseph Lovett², Pierre Verstraete³, Johan Smets⁴, Steven P. Ames^{1,2}. (1) Univ of Sheffield Dept of Chem, Sheffield, United Kingdom (2) University of Sheffield, Sheffield, United Kingdom (3) Procter and Gamble, Brussels, Belgium (4) Procter & Gamble, Brussels, Belgium

A well-defined poly(glycerol monomethacrylate) (PGMA) macromolecular chain-transfer agent (macro-CTA) with a mean degree of polymerisation (DP) of 43 was prepared by reversible addition-fragmentation chain transfer (RAFT) polymerisation using a morpholine-functionalised trithiocarbonate-based chain transfer agent (MPETTC). Chain extension of this macro-CTA by RAFT aqueous dispersion polymerisation of 2-hydroxypropyl methacrylate (HPMA) at pH 7.0 – 7.5 produced a series of four MPETTC-PGMA₄₃-PHPMA_y vesicles (where y = 190, 200, 220 or 230). Protonation of the morpholine end-group increases the hydrophilic character of the PGMA stabiliser block, which leads to a reduction in the packing parameter for the diblock copolymer chains. However, such pH-responsive behaviour critically depends on the value of y. For y = 190 or 200, lowering the solution pH to pH 3 induces a vesicle-to-worm transition at 20 °C according to dynamic light scattering, aqueous electrophoresis, transmission electron microscopy and turbidimetry studies. This order-order transition is suppressed in the presence of added electrolyte, which screens the cationic end-groups. In addition, no change in copolymer morphology was observed on lowering the solution temperature at neutral pH, regardless of the y value. The diblock copolymer nano-objects obtained at pH 3 were also cooled to 4 °C to examine their dual stimulus-responsive behaviour to both pH and temperature triggers. In all four cases, a change in morphology from either worms or vesicles to afford spheres (or spheres plus relatively short worms) was observed. Temperature-dependent oscillatory rheology experiments performed on cationic worms at pH 3 indicated a worm-to-sphere transition on cooling from 20 °C to 4 °C, which leads to reversible degelation. In summary, spheres, worms or vesicles can be obtained for a *single* MPETTC-PGMA-HPMA diblock copolymer on first lowering the solution pH to pH 3, followed by cooling from 20 °C to 4 °C.

pH- and thermo-responsive non-ionic diblock copolymer vesicles

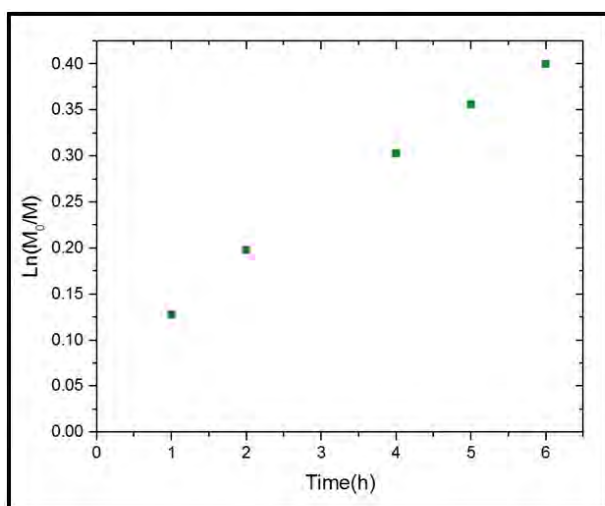


POLY 602: SI-RAFT Polymerization of chloroprene on silica nanoparticles for the application in rubber nanocomposites

Zaid M. Abbas⁴, zaidalmalki@yahoo.com, Yang Zheng³, Mohammad M. Mohammadkhani¹, Brian C. Benicewicz². (1) Chemistry and Biochemistry, Univ South Carolina, Columbia, South Carolina, United States (2) Dept of Chem Biochem, Univ of South Carolina, Columbia, South Carolina, United States (3) Chemistry, Univeristy of South Carolina, Columbia, South Carolina, United States (4) chem, university of South carolina, Columbia, South Carolina, United States

Properties of polymers have been an interesting topic in polymer science. Multi-functional polymers have been a central focus for many research groups in polymer science, due to their broad range of possible polymer properties and industrial applications. One of the most important class of monomers is dienes. Diene-based polymers have low glass transitions temperature (T_g), low degradability, and can be further modified by the latent polyvalent functionality presented by their double-bond-rich composition. One of the most important dienes is chloroprene, which the precursor of Neoprene, and has many attractive properties such as degradation resistance, water resistance, and mechanical durability.

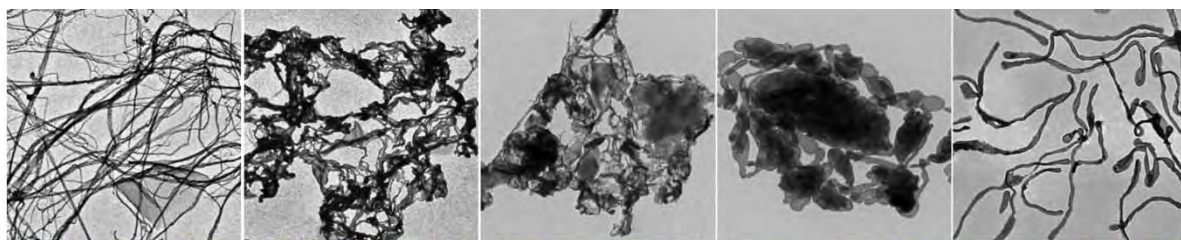
In this work we use surface initiated-reversible addition fragmentation chain transfer (SI-RAFT) polymerization technique to polymerize chloroprene on surface of silica nanoparticles. The RAFT technique is an attractive polymerization method due to the moderate polymerization temperatures, absence of metal catalysts, and ability to polymerize a wide range of monomers with a high degree of control. To our knowledge there are no reports on the surface polymerization of chloroprene and resulting properties of the nanocomposites. Therefore, we studied the effects of chain graft density, RAFT agent selection, and solvent on molecular weight, polydispersity and polymerization kinetics. Additionally, preliminary results were obtained on mixing the grafted nanoparticles in different matrices to investigate the mechanical properties and grafted particle dispersion.



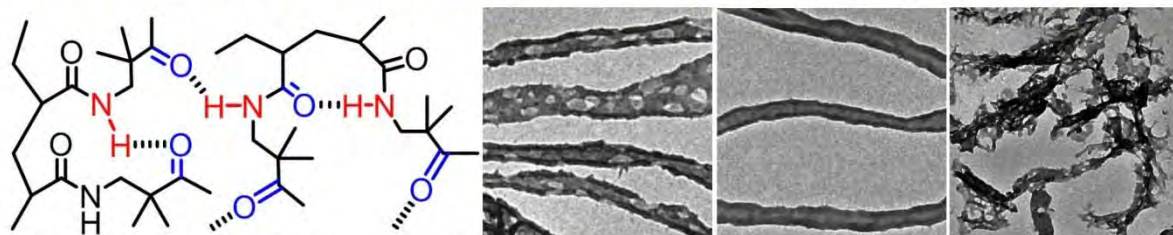
POLY 603: Hydrogen-bonded pore-switchable aqueous nanotubes via visible light-mediated room-temperature polymerization-induced self-assembly

Pan Gao, Yi Ding, Zhigang Cui, **Yuanli Cai**, ylcai@suda.edu.cn. College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu, China

Similar to cellulose, the polymers whose monomer units possess hydrogen-donors and acceptors are generally insoluble in ambient water because of hydrogen bonding (HB). Herein we present stimuli-responsive long cylindrical vesicles (nanotubes) synthesized directly using HB-driven polymerization-induced self-assembly (PISA) under visible-light-mediated RAFT aqueous dispersion polymerization at 25 °C. We show an unexpected film/silk-to-ribbon-to-vesicle transition, and films/silks/ribbons formed at rather short chain lengths (DP ~ 25-85) of the core-forming block in free-flowing solution. Pore-switchable nanotubes can be synthesized via perturbation of HB-association with repulsive force by inserting minor ionized monomer. These nanotubes are synthesized at >35% solids, and more sensitive than the corresponding spherical counterparts in response to aqueous surroundings. This approach thus highlights important implications in the scale-up production of advanced smart delivering nanomaterials for emerging biological applications.



PISA: Film/Silk-to-Ribbon-to-Tube in Water at 25°C



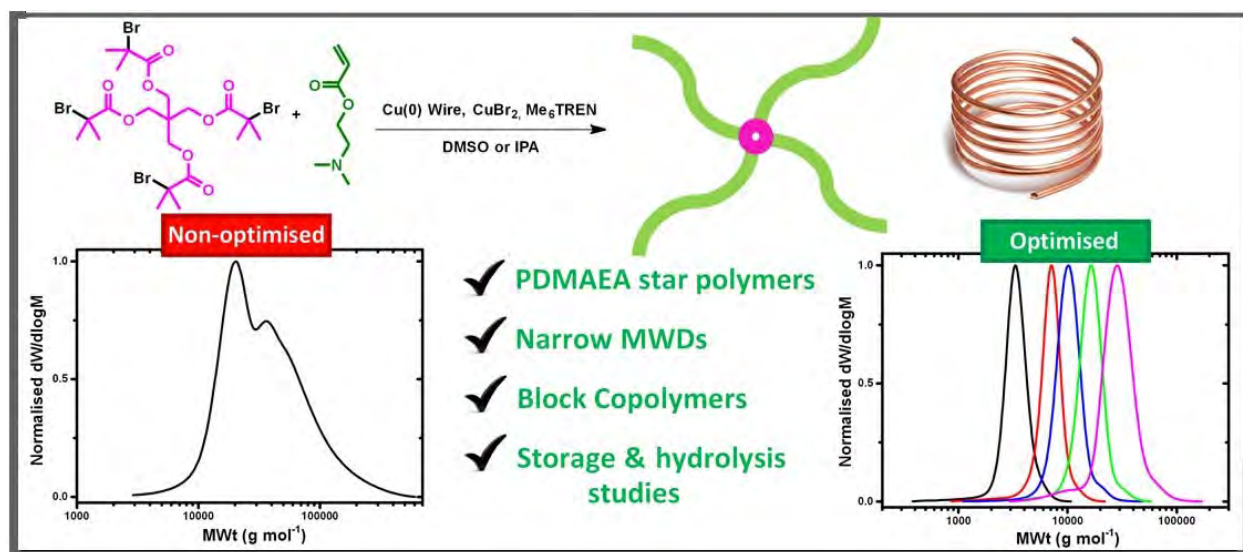
H-Bonded Pore-Switchable Long Cylindrical Vesicles

Hydrogen-Bonded Pore-Switchable Aqueous Long Cylindrical Vesicles Synthesized Directly via Visible Light-Mediated Polymerization-Induced Self-Assembly (PISA) in Water at 25 °C

POLY 604: Well-defined PDMAEA stars via Cu(0)-mediated reversible deactivation radical polymerisation

Richard Whitfield¹, *r.b.whitfield@warwick.ac.uk*, **Athina Anastasaki**¹, **Nghia Truong**², **Paul Wilson**¹, **Kristian Kempe**¹, **Thomas Davis**², **David M. Haddleton**¹. (1) University of Warwick, Coventry West Mids, United Kingdom (2) Monash University, Melbourne, Victoria, Australia

The Cu(0)-mediated reversible deactivation radical polymerisation of *N,N*-dimethylaminoethyl acrylate in DMSO and IPA at ambient temperature using Cu(0) wire is investigated. Tetra-functional and octa-functional initiators were utilised to facilitate the synthesis of well-defined PDMAEA star homo and block copolymers with a range of molecular weights ($M_n \sim 5000$ -41000 g mol⁻¹). Both solvents demonstrated to be excellent media for the controlled polymerisation of DMAEA yielding narrow molecular weight distributions (dispersity ~ 1.1) when the reactions were ceased at $\sim 40\%$ conversion. Interestingly, at high conversions (typically $> 55\%$) high and low molecular weight shoulders were evident by SEC when DMSO and IPA were used respectively, suggesting a large extent of termination and/or side reactions at prolonged reaction times. Nevertheless, high end group fidelity could be maintained when immediate precipitation of the polymers (at lower conversion) was performed yielding low dispersed P(DMAEA-*b*-MA) star block copolymers with molecular weights of around 20000 g mol⁻¹ (dispersity typically less than 1.20). Importantly, guidelines on how to prevent hydrolysis, termination and side reactions of PDMAEA as well as how to purify and store such materials are also provided and discussed.

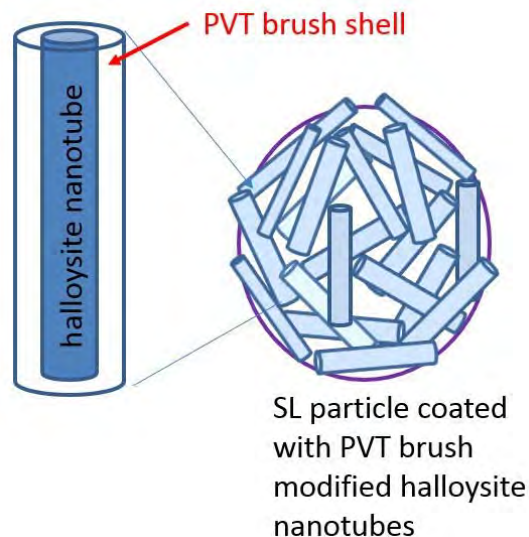


POLY 605: Hybrid nanoparticle-polymer brush composites for detection of radionuclides in water

Valery Bliznyuk², vblizny@clemson.edu, **Ayman Seliman**², **Scott M. Husson**¹, **Timothy A. Devo**². (1) Chemical Biomolecular Engineering, Clemson University, Clemson, South Carolina, United States (2) Environmental Engineering and Earth Science, Clemson University, Clemson, South Carolina, United States

Detection of radionuclides in water represents an important segment in environmental monitoring of pollutions, nuclear forensics and homeland security. Recently, this field of research has advanced due to development of new efficient organic ligands coupled with scintillators for selective sensing of radioactive elements of interest (e.g. U, Sr, and Cs). The research presented here is focused on combining the advantages of inorganic nanoparticles (durability, high surface area, broad range of possible surface modifications) with those of organic and polymer materials (chemical selectivity, efficient energy harvesting, and high quantum yield of photoluminescence). The above combination allows development of the next generation extractive scintillators for detection of trace amounts of radionuclides in water.

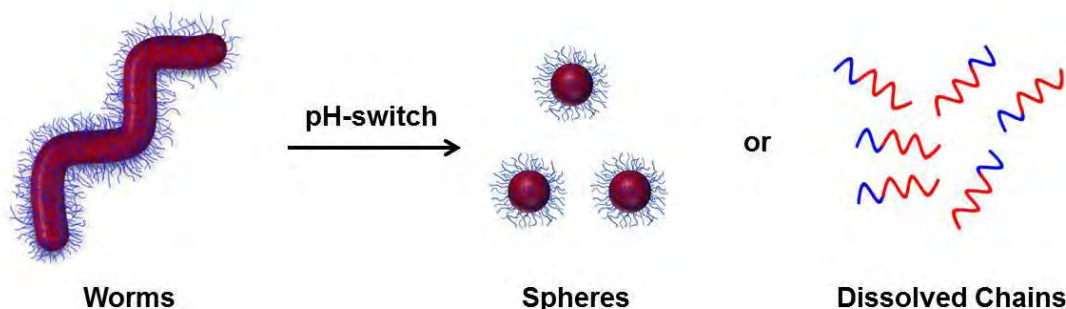
One example of these materials involves inorganic Superlig620 (SL) a commercially available material with high affinity to strontium. The surface of this silica-based material was modified with several different ways to introduce scintillating properties. The explored approaches include: a) “grafting from” scintillating polymer brush (polyvinyltoluene-fluorophore) of various architecture using atom transfer radical polymerization (ATRP); b) “grafting to” of pre-polymerized dendritic macromolecules containing fluors; and c) chemical or physical attachment of anisotropic nanoparticles (halloysite nanotubes, HS) coated with a fluorescent polymer shell. In the latter case, sorption and scintillating functions of the material can be optimized separately. The anisotropic shape of the nanotubes allows good analyte access to SL surface, while high luminosity function is achieved via surface initiated polymerization of a fluor containing polymer brush. Additional examples include modification of HS with polymerizable ligands for extraction/detection of uranium and/or plutonium in water.



POLY 606: pH-Responsive diblock copolymer nano-objects prepared by polymerization-induced self-assembly

Joseph Lovett¹, j.r.lovett@sheffield.ac.uk, **Nicholas Warren**⁵, **Nicholas Penfold**⁴, **Charlotte Mable**³, **Steven P. Armes**². (1) Dainton Bldg, Univ Sheffield, Sheffield, United Kingdom (2) Univ of Sheffield Dept of Chem, Sheffield, United Kingdom (3) Dept of Chemistry, Dainton Bldg, University of Sheffield, Sheffield, South Yorkshire, United Kingdom (4) Dept of Chemistry-F2, Dainton Bldg, University of Sheffield, Sheffield South Yorkshire, United Kingdom (5) School of Chemical and Process Engineering, University of Leeds, Leeds, United Kingdom

It is well known that AB diblock copolymers can undergo spontaneous self-assembly when placed in a solvent that is selective for just one block. Moreover, by changing the relative volume fractions of each block, various copolymer morphologies such as spheres, worms and vesicles can be obtained in dilute solution. Over the past decade or so, various research groups have demonstrated that polymerization-induced self-assembly (PISA) can be used to prepare the same diblock copolymer nano-objects in the form of concentrated dispersions. More specifically, a soluble homopolymer is chain-extended with a second monomer that polymerizes to form the insoluble block. For example, we have reported that such nano-objects can be prepared by chain-extending a poly(glycerol monomethacrylate) (PGMA) chain transfer agent (CTA) with 2-hydroxypropyl methacrylate (HPMA) by RAFT aqueous dispersion polymerization. Subsequently, we have shown that preparing the same PGMA-HPMA diblock copolymers using a carboxylic acid-functionalized PGMA CTA produces pH-responsive nano-objects. This is because ionization of the carboxylic acid end-group drives an order-order morphological transition by increasing the hydrophilic character of the PGMA stabilizer block. However, such pH-responsive behaviour is not observed in the presence of salt because this screens the charged end-groups. Herein we prepare new pH-responsive nano-objects via aqueous PISA by incorporating pH-sensitive monomers in either the stabilizer or the core-forming blocks. The latter approach enables the preparation of nano-objects that undergo order-disorder transitions. Furthermore, the preparation of PGMA-HPMA diblock copolymers using a dicarboxylic acid-functionalized CTA yields nano-objects that exhibit pH-responsive behaviour even in the presence of relatively high salt concentrations. Such nano-objects may prove to be useful for biomedical applications or as stimulus-responsive viscosity modifiers.



POLY 607: Innovative bionanocomposites based on polysaccharides and protein nanofibers

Nuno H. Silva^{1,2}, nhsilva@ua.pt, **Isabel Marrucho**³, **Carmen Freire**¹. (1) CICECO/ Department of Chemistry, University of Aveiro, Aveiro, Portugal (2) ITQB / New University of Lisbon, Oeiras, Portugal (3) Instituto Superior Técnico, University of Lisbon, Lisboa, Portugal

The production of chemicals, materials, fuels and energy is nowadays progressively moving in the direction of renewable resources, and there is a growing interest on the use of polysaccharides, such as cellulose, pullulan and chitosan for the development of new sustainable materials with distinct functionalities and applications. Proteins are also gaining increasing attention as singular components for multi-functional biomaterials. The assembly of proteins into long and insoluble ordered fibrillar structures (protein nanofibers) is a very recent and promising strategy for the development of nanosized reinforcing elements for bionanocomposites, with applications ranging from medicine to soft matter and nanotechnology.

In this work, proteins, such as insulin, β -lactoglobulin and hen egg white lysozyme, were fibrillated with alternative solvents as ionic liquids and deep eutectic solvents, which reveal to accelerate the fibrillation process and to reduce the time of conventional methods from 15h down to 2h. Furthermore, the nanofibrils produced were combined with different polysaccharides, namely chitosan, pullulan and cellulose (both vegetal and bacterial forms) to develop new functional biomaterials for application in the biomedical field. These new functional biomaterials were characterized in terms of morphology, mechanical properties and biocompatibility, as well as cell adhesion and proliferation and its potential to be used as scaffolds in the biomedical field.

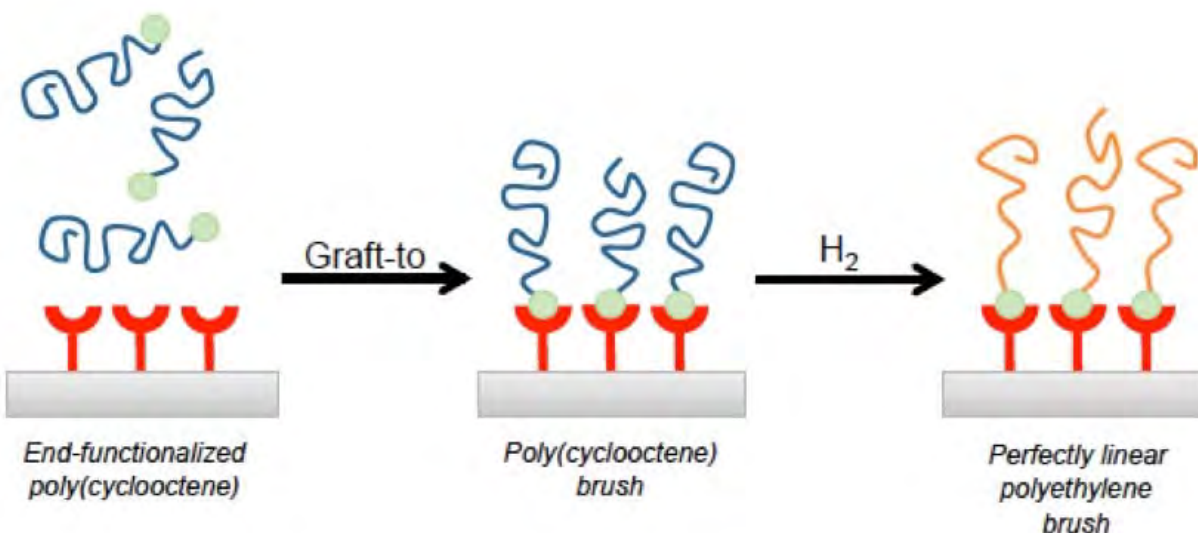


Hydrogel with lysozyme nanofibers.

POLY 608: Synthesis and characterization of polyethylene brushes on silicon surfaces

Wesley Farrell¹, wfarrell14@gmail.com, Sara V. Orskov², Kathryn Beers³. (1) Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States (2) Materials Science & Engineering, NIST, Montgomery Village, Maryland, United States (3) Materials Science and Engineering Division, NIST, Bethesda, Maryland, United States

Modification of a surface's properties through the covalent attachment of polymer brushes is an area which has been extensively studied for several decades. Despite the extensive work in this field and the ubiquity of polyethylene in society, reports of polyethylene brushes are surprisingly scarce. This can be attributed to the fact that the 'grafting-from' approach is limited due to the difficulty of tethering a transition metal catalyst to a surface in the proper orientation, and the 'grafting-to' approach is challenging given the insolubility of high molecular weight polyethylene, and the difficulty associated with producing polyethylene with suitable reactive end-groups. In this work, we have prepared narrow polydispersity polyethylene brushes by grafting end-group functionalized poly(cyclooctene) to silicon surfaces, followed by hydrogenation. Synthetic details, characterization, and potential applications of these surfaces will be discussed.



POLY 609: Self-healing polymers for electronic skin, energy storage and actuators

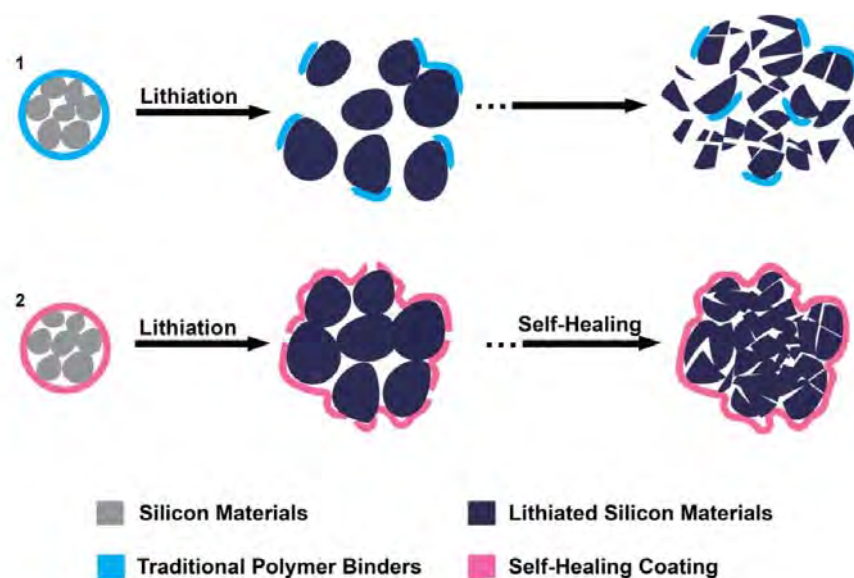
Chao Wang, *chaowang@ucr.edu*. Chemistry, University of California Riverside, Riverside, California, United States

Self-healing refers to the ability to repair itself spontaneously upon mechanical damages. The self-healing feature is highly desirable for electronics and energy storage devices, which suffer from mechanical failures and short lifetime. Here, we have successfully implanted self-healing capabilities into high-performance electronic skin, energy storage and actuators by using polymer material design.

By designing and synthesizing a supramolecular hydrogen bonding polymer composite, the first repeatable, room-temperature self-healing electronic sensor skin was demonstrated. A conductivity as high as 40 S/cm was measured for our composite. The composite material is mechanically flexible, and is capable of sensing tactile and flexion forces. ^[1]

The self-healing concept was further introduced into silicon microparticle based high-capacity lithium ion batteries to overcome their short cycling lifetime. Using the self-healing approach, anodes made from low-cost SiMPs (~3–8 microns), for which stable deep galvanostatic cycling was previously impossible, can now have an excellent cycle life when coated with a self-healing polymer. We attain a cycle life ten times longer than state-of-art anodes made from SiMPs and still retain a high capacity (up to ~3,000 mAh/g). ^[2]

Moreover, a self-healing artificial muscle was made successfully by designing and synthesizing an ultra-stretchable self-healing elastomers based on metal ligand coordination interactions. The actuator made from the new polymer has similar performance with conventional actuators. Upon mechanical damage such as a penetration, it can self-heal at room temperature. ^[3]



Self-healing polymer materials for high performance lithium ion batteries.

POLY 610: Synthesis of humidity-gradient responsive copolyamides via Retro-Michael reaction

David H. Wang^{1,2}, wanghuabin0903@yahoo.com, Ruel N. McKenzie¹, Philip R. Buskohl¹, Richard A. Vaia¹, Loon-Seng Tan¹. (1) Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States (2) UES, Inc., Dayton, Ohio, United States

Our previous research shows that monolithic polyimides containing ester-sulfonyl and carboxylic groups are humidity-gradient responsive and hygromorphic. As a complementary effort, a series of polyamides containing ester-sulfonyl (-CH₂CH₂SO₂Me) pendants, generically designated as PA-ES, were prepared from a diamine containing a polar ester-sulfonyl (ES) pendant and three aromatic diacid chlorides in N,N-dimethylacetamide (DMAc) at room temperature. Then thermally derived copolymers designated as PA-ES:A, which contains ES and carboxylic acid (A) pendants, were prepared from PA-ES via a retro-Michael reaction at 250 °C and 300 °C, in which A was formed from ES pendant with the concomitant expulsion of vinylmethylsulfone molecule. For various comparison purposes, a nonfunctional PA-N (i.e. without any stimuli-responders) homopolymer was also prepared from its respective diacid chloride and diamino monomer. In addition to physical/mechanical characterization by FTIR, thermal analysis, WAXD and DMA, the thin films have exhibited remarkable locomotion and beam-like oscillation under gradient (non-equilibrium) conditions created by humidity while the PA-N films have shown little response under the same conditions.

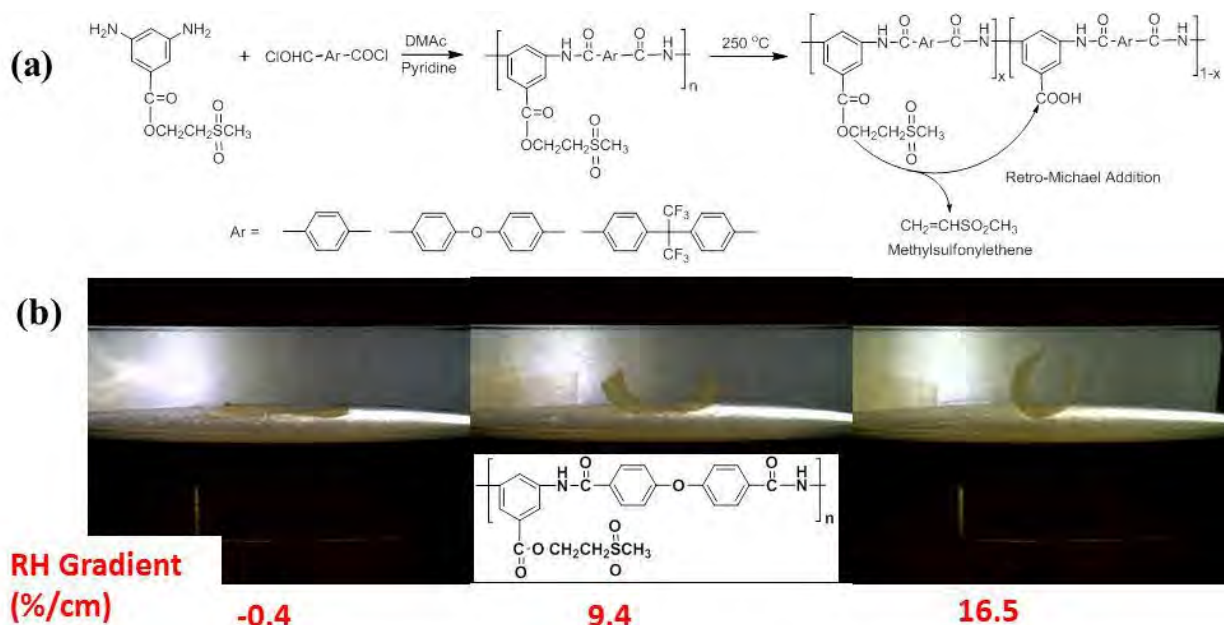


Fig 1. (a) Syntheses of Ester-Sulfonyl PAs (PA-ES's) and thermally converted copolymers (PA-ES:A's) via retro-Michael reaction of the methylsulfonylethyl ester pendant; (b) Bending of a PA-ES film in a humidity chamber.

POLY 611: Application of base amplification to extrinsic self-healing materials

Shuqi Lai, *laishuqi@gmail.com*, Thu Doan, Wenle Li, Nancy R. Sottos, Paul V. Braun.
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Extrinsic self-healing materials are smart materials that are capable of repairing damages autonomously, and are useful for the maintenance of structures that are currently impractical to repair. The majority of these materials, however, suffer from long healing time and low healing efficiency at low temperature, due to limited loading of sequestered healing agents and slow mass transport of healing agents in the solid materials. To solve these problems faced by current extrinsic self-healing systems, we incorporate base amplifiers, which decompose autocatalytically in response to even trace basic stimuli, into self-healable matrices containing base-encapsulated microcapsules or core-shell electrospun fibers. When damage occurs and results in the release of a small amount of alkaline healing agents, nonlinear decomposition of base amplifiers will be initiated to generate additional bases that can be delivered to the damage sites. Hopefully, the delivery of healing agents to damage sites can also be accelerated via a reaction-diffusion process. Thus, more efficient material recovery at low temperature is expected to be achieved compared to conventional extrinsic self-healing materials.

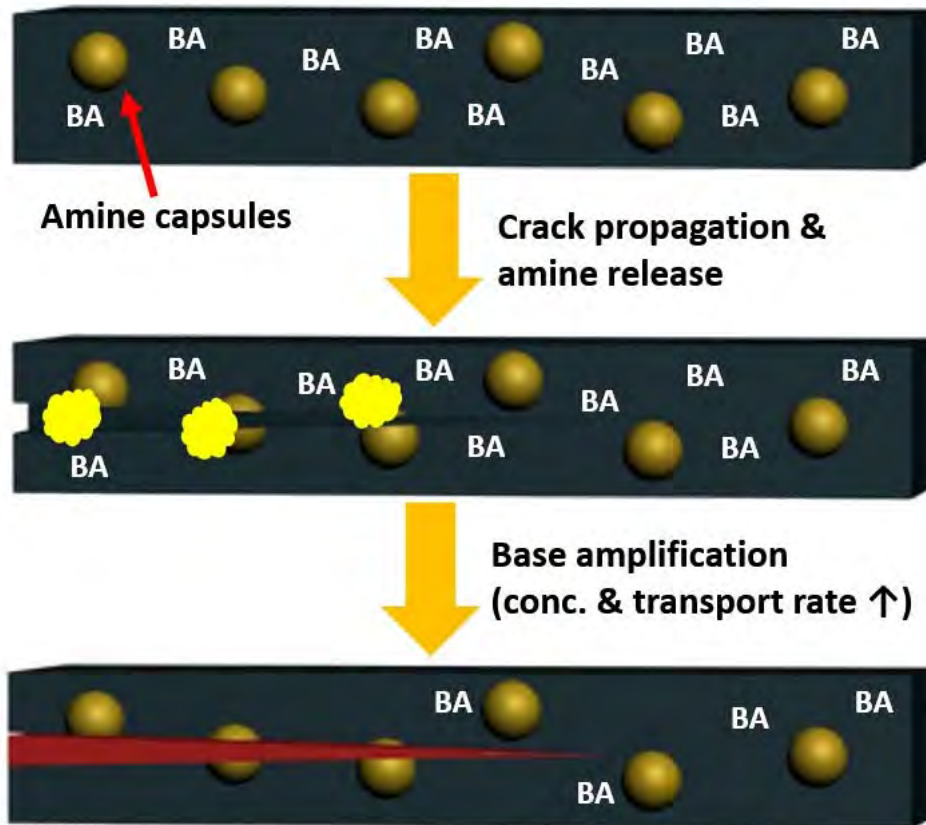
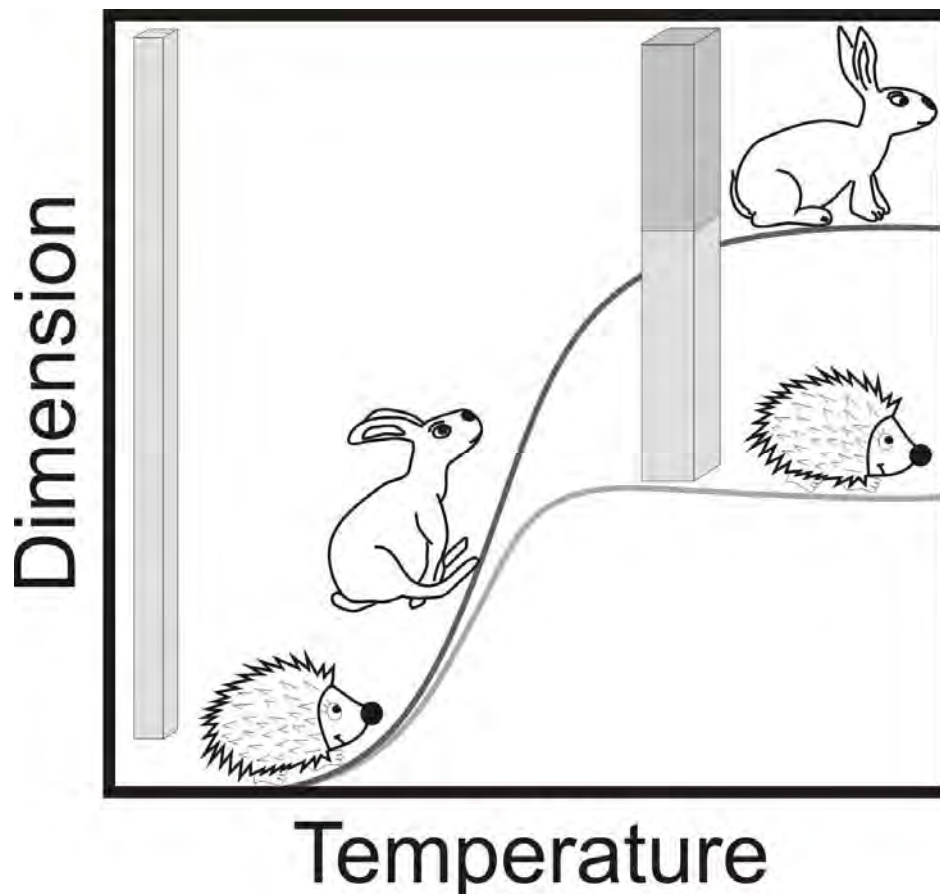


Illustration showing how a base amplifier (BA) works in an extrinsic self-healing system.

POLY 612: How to make a material predictive

Thomas Raidt, thomas.raidt@bci.tu-dortmund.de, Frank Katzenberg, Joerg C. Tiller.
Bio and Chemical Engineering, TU Dortmund, Dortmund, Germany

Overheating due to thermal inertia is a major problem and causes failure or even damage of numerous products. To protect products from overheating, processes must either be driven inefficiently at much lower temperature or have to be actively monitored and controlled by a complex sensor/ actuator system. Shape memory polymers (SMPs) may be suited to controlling such heat-sensitive processes but the response only contains information about exceeding a certain temperature. A material that can predict the maximal reachable temperature by sensing the heating-rate might act as an alternative control system, but no heating-rate-sensitive trigger is known so far. Here we report on a novel type of smart material that is capable of specifically responding to the changing rate of an environmental signal. This is shown on the example of lightly cross-linked syndiotactic polypropylene that reacts to a temperature increase by adapting its shape change according to the applied heating rate. In general, a material with such properties can be used to predict a system failure when used in a defined environment and is therefore called "predictive material".



POLY 613: Alkali-metal-ion accelerated on-demand release from cyclic poly(phthalaldehyde) microcapsules

Shijia Tang, *shijia1224@gmail.com*, Huiying Liu, Jeffrey Moore. University of Illinois, Urbana-Champaign, Urbana, Illinois, United States

On-demand payload release from microcapsules has been triggered by various stimuli, such as pH, UV, temperature and redox reactions, etc. Ion responsive microcapsules are a less well developed stimuli but one with interesting and important potential applications in areas such as batteries, fuel cells, sensors and electrochromics. The few studies that have reported on ion responsive microcapsules have mostly relied on crown ether grafted polymers. Here, we demonstrate an alkali-metal-ion accelerated release from cyclic poly(phthalaldehyde) (cPPA) microcapsules. Payload release rate assays indicated that in acidic solutions, the minimum required acid concentration for rapid payloads release (>80% in 20 h) was 10mM. Induced by alkali-metal-ions, especially lithium ions, the acid concentration threshold was lowered to 0.1mM. Also interestingly, different counter ions were found to have distinct co-activation effect. This co-activation effect can be potentially utilized for responsive systems such as auto-accelerating microcapsules.

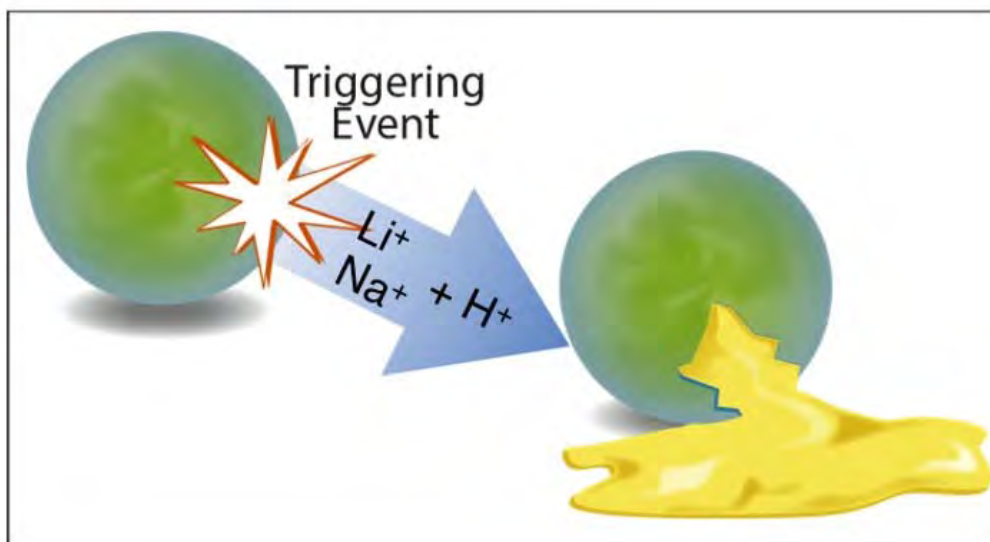
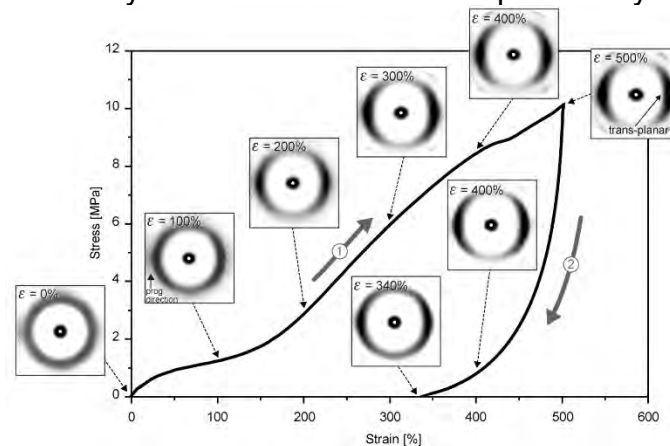


Figure 1. Co-activation effect of alkali-metal-ions and protons on release of cPPA microcapsules

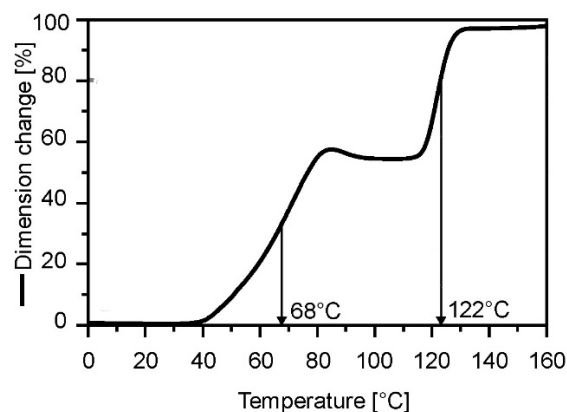
POLY 614: Shape memory polypropylene

Frank Katzenberg, frank.katzenberg@udo.edu, Thomas Raidt, Joerg C. Tiller. TU-Dortmund, Dortmund, Germany

Cross-linked polyethylene is the first shape memory polymer (SMP), established in the 1960s. Interestingly, polypropylene the other major mass polymer with excellent mechanical properties has not been rendered into an SMP. This may be explained by the fact that polypropylene cannot be easily cross-linked via radical recombination since radicals at tertiary C-atoms usually result in β -scission. Here we report on covalently cross-linked isotactic polypropylene (x-iPP), and covalently as well as ionically cross-linked syndiotactic polypropylene (x-sPP and ix-sPP, respectively). All networks exhibit recovery ratios of nearly 100% and large stored strains of up to 680%. While x-iPP has to be programmed classically by stretching above its trigger temperature and subsequent cooling, amorphously quenched x-sPP as well as ix-sPP offer the possibility of cold programming upon stretching at room temperature, which results in a distinctive triple shape memory effect. Due to the thermo-reversibility of the ionic netpoints, ionic cross-linking of sPP extends the properties of x-sPP by thermoplastic reprocessability and shape memory assisted self-healing (SMASH). Besides the described shape memory effect we found further that uniaxially stretched and constrained crystallized x-iPP is significantly multiaxially reinforced due to homoepitactic crystallization.



Stress vs. strain plot with respective WAXS patterns of the cold-programming procedure of amorphously quenched ix-sPP.



Thickness change during triggering of cold-programmed ix-sPP showing the triple shape memory effect.

POLY 615: Making wind power better – new polymer composites with improved sustainability metrics

John R. Dorgan, *jdorgan@mines.edu*. Colorado School of Mines, Golden, Colorado, United States

Wind generated electricity is the lowest cost renewable energy technology available today and as a result, rapid growth is occurring, Wind blades have become one of the world's largest markets for plastic composites. Glass fiber and thermoset resins (primarily epoxy and vinyl ester) are used to fabricate the vast majority of the total blade tonnage. At the end of service life, fiber-filled thermosets are difficult to economically recycle. Somewhere near 450,000 metric tons of composite blade structure will be produced this year and as the industry pushes to larger blade sizes, carbon fiber will be increasingly used. *The tonnage of composites used, the embedded energy of the materials, and the increasing use of more expensive carbon fibers are all strong incentives to recycle turbine blades in order to create a more sustainable wind-energy industry. Recycling also provides additional manufacturing jobs in the conversion of reclaimed materials.* Recent work performed under the Institute for Composite Manufacturing Innovation (IACMI) on making turbine materials from recyclable and renewable thermoplastics instead of petroleum based thermosets will be described and discussed. Biobased but infusible systems for both thermoplastic and thermosetting systems have been developed and demonstrated. These new systems will be discussed in terms of reaction chemistry, processing, recyclability, and life cycle costs.

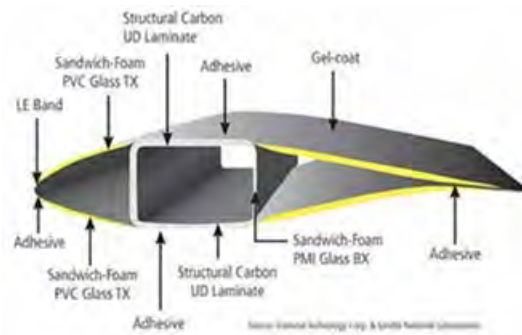
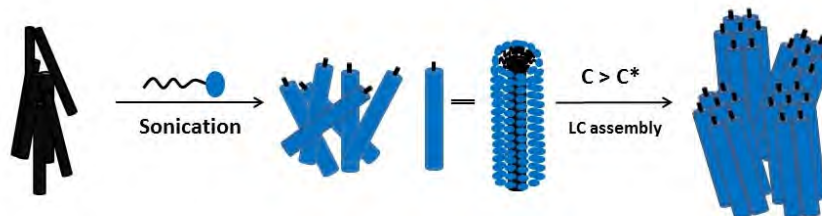


Figure 1. Present generation advanced wind turbine blade construction showing the use of many polymeric materials.

POLY 616: Hexagonal liquid crystal-carbon nanotube composites

Christopher R. Kasprzak, *chriskasprzak123@gmail.com*, Evan Scherzinger, Jacob Parkinson, Shanju Zhang. *Dept of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, California, United States*

Single-walled carbon nanotubes (SWCNTs) have demonstrated high water flux, when vertically aligned in a membrane, which could be formed by liquid crystalline (LC) materials. In this work, the effect of incorporating SWCNTs into the hexagonal LC phase was studied. The hexagonal phase was formed by both inert and polymerizable quaternary ammonium surfactants with variable alkyl tail lengths. The LC systems studied demonstrated an increase in thermal stability, without a significant effect on the hexagonal (ordered) to isotropic (disordered) phase transition (ODT) concentration, when SWCNTs were incorporated. Shear forces increased the alignment of the system, as shown by the development of a banded texture upon applying a shear force. No significant effect of incorporating SWCNTs, or applying a shear force on the LC system, was observed with respect to subsequent photopolymerization. Small angle x-ray scattering analysis demonstrated that the intermicellar distance increased with increasing alkyl chain length of the monomer. These materials appear to be good candidates for the development of novel reverse osmosis membranes that are more energy efficient.



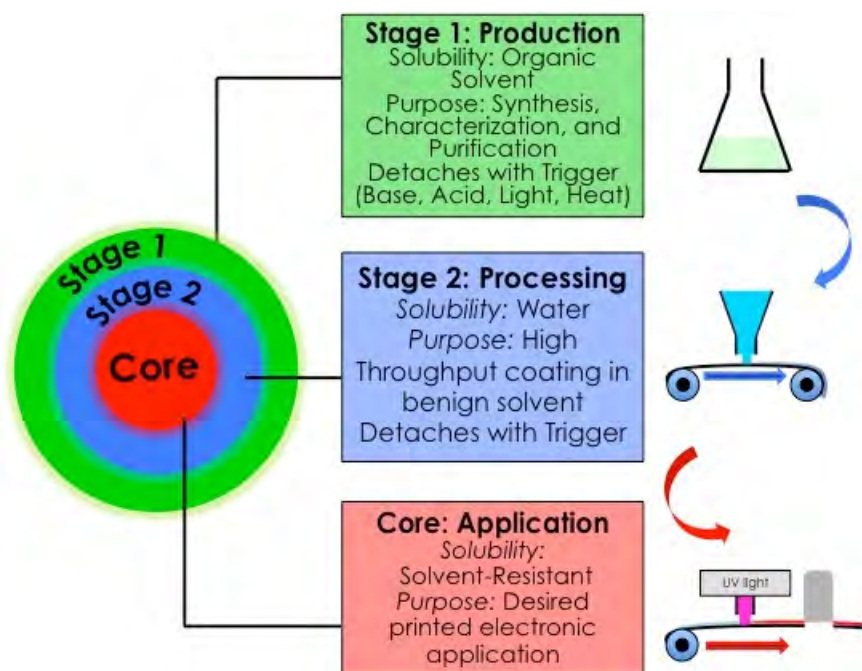
Formation of the composite material by increasing the concentration of the surfactant monomer in the presence of the dispersed carbon nanotubes.

POLY 617: Conjugated materials with multistage sidechains for water processable organic electronics

Brian Schmatz², bschmatz@gatech.edu, **Zhibo Yuan**⁴, **Augustus Lang**², **Jeff Hernandez**⁵, **Elsa Reichmanis**¹, **John R. Reynolds**³. (1) Georgia Institute of Technology, Atlanta, Georgia, United States (2) Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States (3) School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

The ability to process organic electronics via aqueous solution is highly advantageous for large scale roll-to-roll processing. However, maintaining competitive electronic properties while achieving aqueous solubility is difficult for several reasons. 1) Materials with polar functional groups that provide aqueous solubility can be difficult to purify and characterize. 2) Many traditional coupling and polymerization reactions cannot be performed in aqueous solution. 3) Ionic groups, though useful for obtaining aqueous solubility, can lead to a loss of solid-state order as well as a screening of any applied bias.

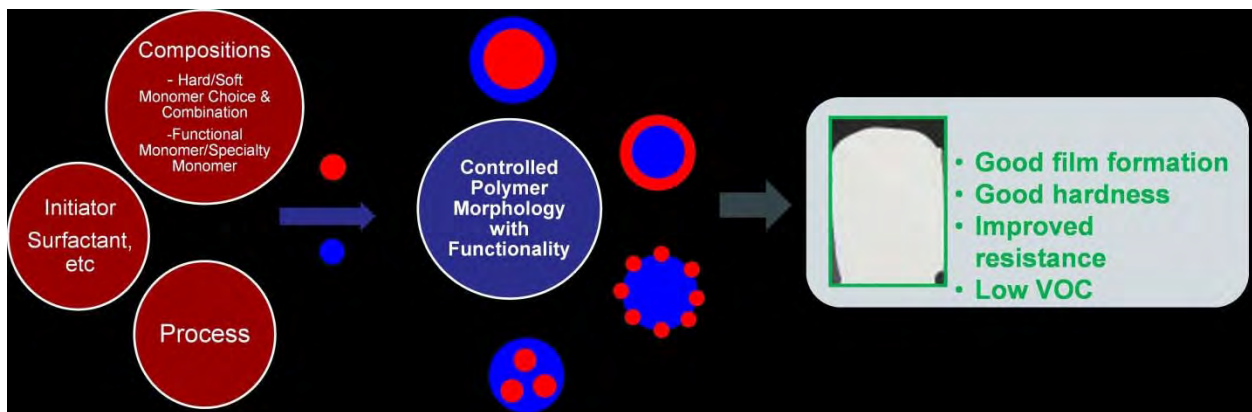
As an alternative, a multistage sidechain approach can be taken to obtain desirable processing attributes without sacrificing semiconducting capabilities. The idea behind multistage sidechains is to use a functional group for its intended purpose, then get rid of it once the functionality becomes unnecessary. Through the attachment of multistage sidechains, conjugated materials can be synthesized, characterized, and purified in organic solvent, converted to a water-soluble form for aqueous processing, and brought through a final treatment to leave behind the desired electronic material as a solvent-resistant film. Through this method we demonstrate aqueous processable materials for organic thin film transistors and electrochromics.



POLY 618: Driving performance in low VOC binder rich paints

Partha S. Majumdar¹, PSMajumdar@dow.com, David Conner⁴, Pu Luo², Sonya Eberly¹, Teresa A. Phillips¹, Paul Doll³, Gary W. Dombrowski¹. (1) Dow Coating Materials, Dow Chemical, Collegeville, Pennsylvania, United States (2) Advanced Materials, Dow Chemical Company, King of Prussia, Pennsylvania, United States (3) South3412, The Dow Chemical Co., Collegeville, Pennsylvania, United States (4) Dow Chemical, Collegeville, Pennsylvania, United States

Consumer demands and environmental regulations are currently driving volatile organic content (VOC) levels in architectural paints as low as possible. Properties such as hardness, block, and tack resistance which are associated with higher VOC paints are difficult to achieve with low VOC paints. This is more challenging in low pigment volume concentration (PVC) formulations, i.e. glossy deep tone paints, where the binder has been the main driver for film hardness development due to the absence of substantial amounts of inorganic extenders. Typical approaches to formulate lower VOC paints involve lower glass transition temperature (T_g) binders or alternatively higher T_g binders which are softened with a non-volatile coalescent. However, both approaches result in soft and tacky paint films. To overcome these challenges, post film formation crosslinking chemistries and latex particle morphology were investigated to drive hardness development along with low coalescent demand for film formation. Design of experiments was conducted to establish structure-property relationships between binder compositions and formulation variables. Predictive models from the experimental designs were used to optimize binder compositions. Optimized binders showed a significant improvement in hardness profile and maintained the balance of properties in low PVC formulations.



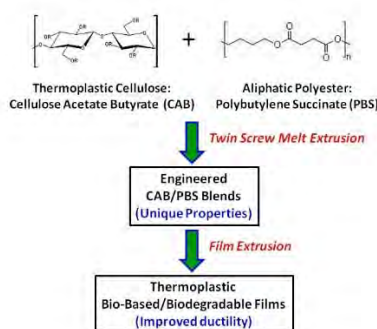
POLY 619: Bio-based/biodegradable materials from thermoplastic cellulose and aliphatic polyester

James H. Wang, jameswang.sshy@sinopec.com, Bing Zhou. Shanghai Research Institute of Petrochemical Technology, Sinopec, Shanghai, Pudong, China

Bio-based materials made from cellulose are of great technical importance due to availability and low-cost cellulose raw materials. Thermoplastic applications of cellulose represent a high-value utilization of cellulose resource. A cellulose co-ester, Cellulose Acetate Butyrate (CAB) was investigated in this study as an example of the thermoplastic cellulose. To obtain biodegradable/bio-based materials having balanced properties, a continuous melt extrusion process was used to prepare polymer blends of CAB with a biodegradable aliphatic polyester: Polybutylene Succinate (PBS).

A series of blends ranging from CAB/PBS 80/20 to 20/80 (mass ratio) were prepared and thoroughly characterized. It was found that the thermal properties of these binary blends were dependent on the blend compositions. Semi-crystalline materials were obtained when CAB content is 40% or less, while amorphous materials were resulted for the blends containing more than 40% CAB. The Tg of the blends decreased as PBS content increased, for the CAB/PBS 35/65 blend, and was as low as -24°C (i.e. 136°C lower than the Tg of CAB).

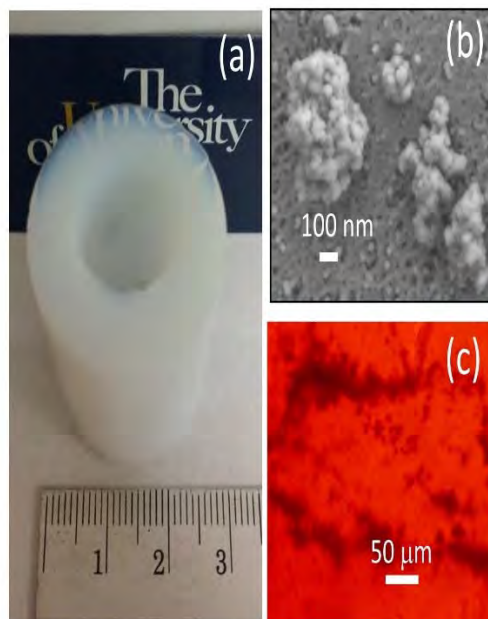
Unique and unexpected rheological properties of the CAB/PBS blends were discovered. All the CAB/PBS blends exhibited significantly lower shear viscosities than pure CAB or pure PBS. At a shear rate of 100 s^{-1} , the shear viscosities of the blends were 24.9% to 44.3% lower than the expected values calculated from the Additivity Rule, i.e. a “Viscosity Well” phenomenon was observed. These blends also showed significantly higher Melt Flow Rates (MFR) than CAB or PBS, a MFR increase up to 174% of expected value was achieved, resulting in a “Melt Flow Rate Peak” phenomenon. The CAB/PBS blend films showed significant improvement in ductility by introducing a miscible PBS component. The Elongation-at-Break of the blend films increased 12 times at 50% PBS over pure CAB film. The results have demonstrated the importance of developing innovative and effective polymer modification technology to significantly improve properties of thermoplastic cellulose materials.



POLY 620: Multifunctional materials based on nanofibers and open and closed cell aerogel foams for sustainability

Sadhan C. Jana², *janas@uakron.edu*, **Nicholas Teo**², **Sung J. Kim**², **Stuti Rajgarhia**², **Monoj Ghosh**¹. (1) Department of Polymer Engineering, The University of Akron, Akron, Ohio, United States (2) Univ of Akron, Akron, Ohio, United States

The paper will first present an overview of the field of multi-functional polymeric materials with special emphasis on sustainability followed by discussion of several case studies drawn from our work on bi-component polymer nanofibers, mesoporous aerogels, aerogel foams, and ceramic oxide nanofibers. In the first case study, nanofibers of interpenetrating network obtained from a hydrophilic and a hydrophobic polymer via gas jet method are used in efficient removal of water droplets from ultralow sulfur diesel fuel. In the second case study, strategies for manufacturing of open and closed cell aerogel foams from high internal phase emulsion methods are discussed. The resultant materials contain interconnected meso- and macroporosity and show fast absorption of hydrocarbon liquids, high permeability of air, and high efficiency of breaking water-in-oil emulsions as well as removal of airborne nanoparticles. In the third case study, the gas jet fiber method is used in the fabrication of 1-100 mm long nanofibers of semiconducting metal oxides of TiO₂, TiO₂/ITO, and TiO₂/V₂O₅ with side-by-side, core-shell, and nanorods-on-nanofiber arrangements. The heterojunctions with wide band gap in these nanofibers offer stronger photocatalytic degradation of ethanol and splitting of water molecules under ultra-violet and visible lights. The factors responsible for local nanostructures, surface energy, pore size distribution, and unique heterojunctions are discussed.

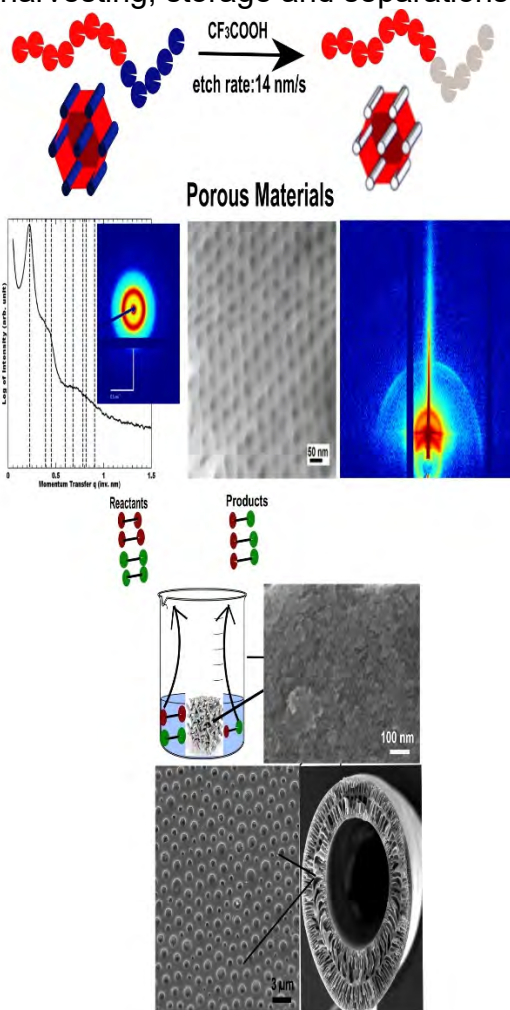


(a) Netshape aerogel sleeve filter. (b) Nanoparticles captured on the surface and (c) Nanoparticles captured inside the filter forming a fractal network.

POLY 621: Robust porous polymers enabled by rapid TFA-etch with improved selectivity for polylactide

Amrita Sarkar¹, asarkar@email.sc.edu, **Morgan Stefik**². (1) Chemistry, University of South Carolina, Columbia, South Carolina, United States (2) Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States

Porous materials derived from block copolymers are of significant interest for addressing environmental and sustainability challenges. Although numerous etching strategies for polylactide (PLA) have been developed, demonstrations to date are limited by slow etch rates that require as long as 7 to 10 days for etching of few-mm thick films. We have developed a significantly faster etching strategy that takes less than 1 day to fully etch 2 mm thick films. Specifically, aqueous trifluoroacetic acid (TFA) enables an etch rate of 14 nm/s. The technique has been applied to generate porous polymer templates with lamellar, gyroid and hexagonal morphologies as confirmed by SAXS, GISAXS, and SEM. These advances lower the cost to produce porous polymers at larger scales to enable the development of porous templates that are used in catalysis, sensing, energy harvesting, storage and separations.



Porous polymer templates obtained by rapid TFA-etch

POLY 622: Making silk without silkworms: Using industrial biotechnology to make performance protein-based fibers

David Breslauer, david@boltthreads.com. Bolt Threads, Emeryville, California, United States

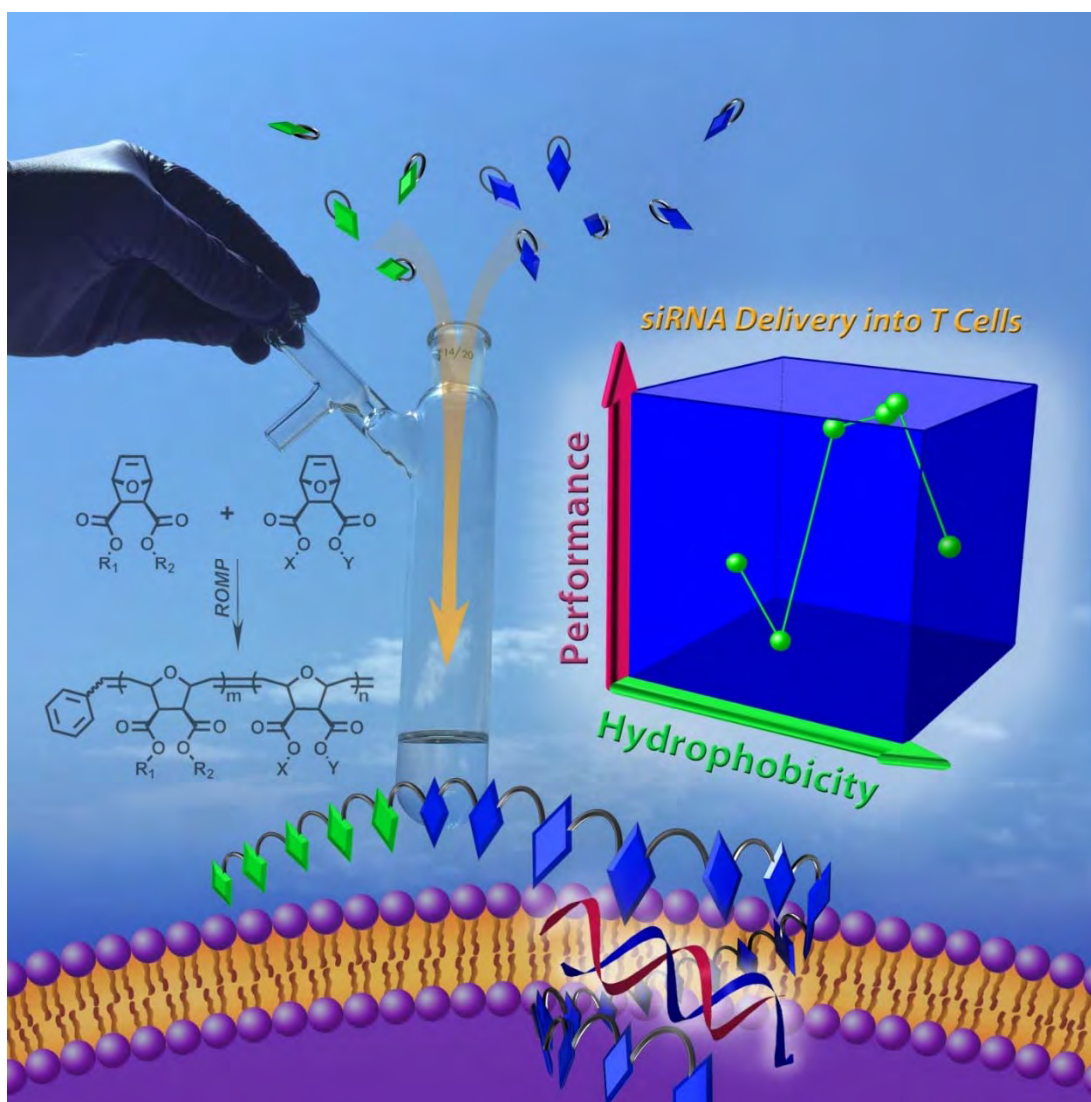
Bolt Threads is a Bay Area startup that believes that the combination of molecular biology and materials science can revolutionize how people think about and use natural materials. Bolt's materials can dramatically improve the performance and environmental impact of a broad range of consumer and industrial materials. Specifically, Bolt is developing the next generation of sustainable performance apparel by leveraging the latest advances in industrial biotechnology, automation, and materials science. Derived from our knowledge of spider silk protein, the company has developed a high-throughput platform to generate thousands of different silk proteins, all from a scalable microorganism host. Using industrial biotechnology processes and fiber spinning, Bolt is able to make commercial volumes of protein and fiber. Precision control from primary protein sequence through fiber extrusion allows the company to produce materials that combine the benefits of both natural and synthetic fibers, and to go beyond even what is currently available in nature and the marketplace. Leveraging the unique properties of its fibers, Bolt Threads will be delivering its own line of consumer apparel made with its Engineered Silk as well as working with partners across industry verticals.



POLY 623: Protein transduction domain mimics from simple polymer scaffolds

Gregory N. Tew, tew@mail.pse.umass.edu. Polymer Science and Engineering, University of Massachusetts, Amherst, South Deerfield, Massachusetts, United States

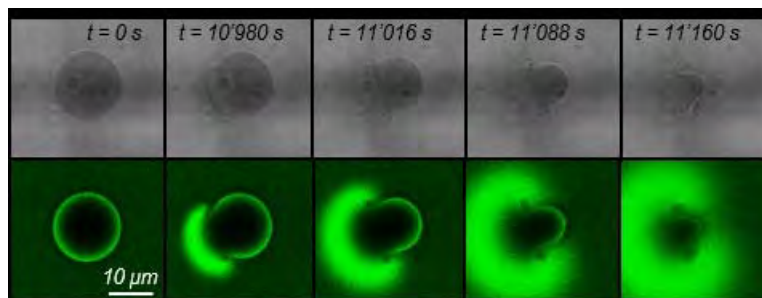
A new series of synthetic protein transduction domain mimics (PTDMs) was designed based on key parameters of Pep-1 and TAT. These novel PTDMs were significantly more active than either Pep-1 or TAT alone. To better understand the importance of guanidine and phenyl groups segregation along the backbone both membrane interactions and cellular internalization studies were conducted. The results showed that functional group segregation impacts activity. Their ability to deliver active peptides, proteins, and antibodies into primary T-cells was exploited. This study gives new design guidelines for the development of PTDMs.



POLY 624: Multi-compartmentalized polymersomes as structural analogues of eukaryotic cells

Ariane Peyret¹, ariane.peyret@enscbp.fr, Emmanuel Ibarboure¹, Arnaud Tron², Louis Beauté¹, Ruben Rust³, Olivier Sandre¹, Nathan McClenaghan³, Sebastien Lecommandoux¹. (1) LCPO-ENSCP, Université de Bordeaux, Pessac, France (2) University of Cambridge, Cambridge, United Kingdom (3) ISM, Université de Bordeaux, Bordeaux, France

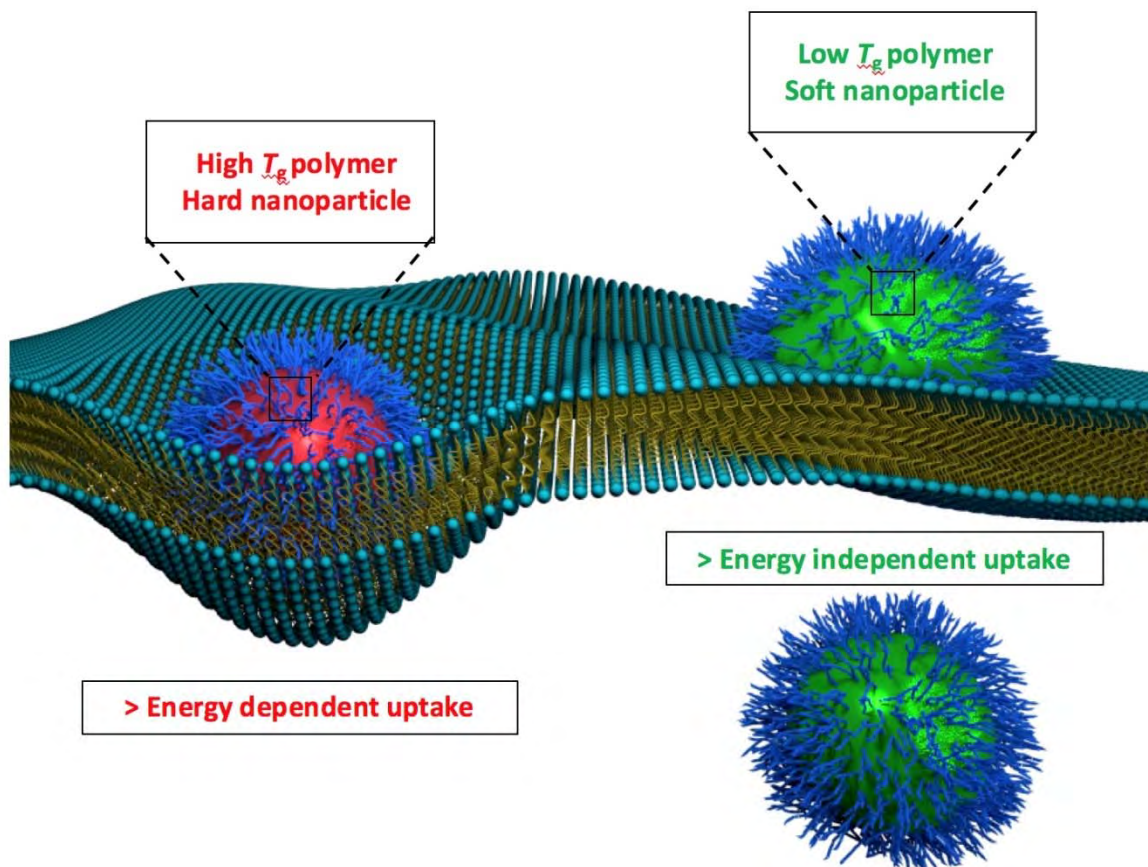
Polymersomes are robust self-assembled vesicular structures that are widely employed in a variety of domains from nanomedicine to artificial cell design. Control over their membrane diffusion properties and structural integrity is crucial for their future development, especially as artificial cell models. Compartmentalization in eukaryotic cells is a crucial feature that allows separation and protection of species as well as simultaneous different enzymatic reactions to take place independently in a confined space with high spatio-temporal control. A number of techniques have been developed to afford structural analogues of eukaryotic cells, namely multi-compartment systems, such as double-emulsion, layer-by-layer assembly, micro-fluidics or phase transfer of emulsion droplets over an interface. Liposomes in liposomes are the first compartmentalized systems that appeared in the literature. More recently, polymeric vesosomes (polymersomes in polymersomes) were developed and used as scaffolds for cascade enzymatic reactions. These complex systems both mimic the structural and functional characteristics of the eukaryotic cell and thus provide a simplified biomimetic model that can serve as a tool for the understanding and the study of the cell properties. The mixing of different biomaterials (i.e. lipids and polymers) is a new attractive orientation that widens the use of vesicular carrier platforms for cell mimicry. We focused our research on designing structural analogues of eukaryotic cells. Hence, we developed multi-compartment cell-like systems composed of nano-sized liposomes or polymersomes entrapped in the lumen of giant poly(butadiene)-*b*-poly(ethylene oxide) vesicles. We show that we can achieve controlled release of species in time and space by selectively bursting polymersomes with high specificity and temporal precision and consequently, deliver small encapsulated vesicles (polymersomes or liposomes).



POLY 625: Understanding the effect of nanoparticle rigidity on the mechanism of cellular uptake

Pratik Gurnani¹, pratik.gurnani@warwick.ac.uk, **Carlos Sanchez Cano**¹, **Sebastien Perrier**^{1,2}. (1) Department of Chemistry, University of Warwick, Coventry, United Kingdom (2) Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, Melbourne, Victoria, Australia

Polymeric nanoparticles have become increasingly relevant in biomedicine, with applications such as drug delivery and diagnostics. Our understanding of the mechanism by which these interact with biological systems has become less clear as nanoparticle design has become more complex. Here we show a systematic study of the effect of nanoparticle rigidity on the degree and mechanism of cellular uptake. We synthesised a library of PEGylated core-shell nanoparticles of 50 and 100 nm diameters, *via* RAFT emulsion polymerisation, with three different core polymer compositions of various T_g to modify nanoparticle rigidity. We observed that softer nanoparticles displayed greater cellular uptake than harder nanoparticles, and the mechanism of uptake shifted from being largely energy dependent for hard nanoparticles, to largely energy independent for softer nanoparticles. These findings may aid future developments of nanoparticles for biomedical applications.

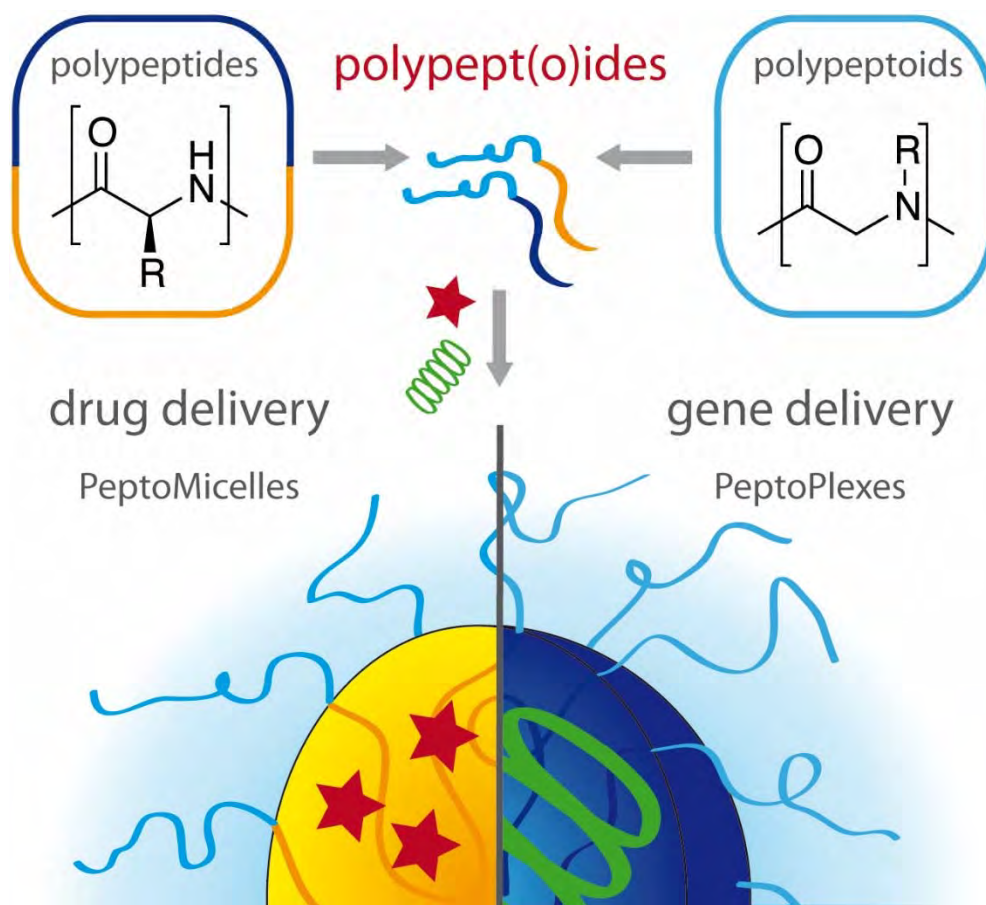


POLY 626: Polypept(o)ides: Combining the functionality of polypeptides with the stealth-like properties of polysarcosine

Matthias Barz, barz@uni-mainz.de. Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

Polypept(o)ides (polypeptide-block-polypeptoid copolymers) are a remarkable polymeric material because it combines the functionality of polypeptides with the proteinresistance and high water solubility of properties of polysarcosine.(1) The most versatile pathway to both classes of polymers is the polymerization of α -amino acid-*N*-carboxyanhydrides (NCAs). The ring opening polymerization allows to adjust polymer size, architecture, solubility, functionality and immunogenic properties and enables the incorporation of functionalities beyond nature's possibilities.

Polypept(o)ides can be synthesized by sequential ring opening polymerization using either mono or multivalent initiators, while functional end groups can be easily incorporated by either the initiator or end group modifications after the polymerization. We report on various polypept(o)ide architectures based on different natural and non-natural amino acids having molecular weights from 10 – 50 kDa and a dispersity index below 1.1 and focus on their application as functional surface coatings (macroscopic and nanoscopic surfaces), surfactants or drug delivery systems.

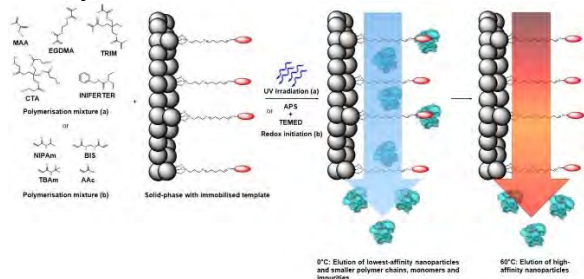


POLY 627: Synthetic antibodies

Alessandro Poma^{1,2}, a.poma@ucl.ac.uk, Antonio Guerreiro², Heli Brahmabhatt³, Hannah Pendergraff⁵, Jonathan Watts⁴, Giuseppe Battaglia¹, Nicholas W. Turner³, Sergey Piletsky⁶. (1) Chemistry, University College London, London, United Kingdom (2) Chemistry, University of Leicester, Leicester, United Kingdom (3) Life, Health and Chemical Science, Open University, Milton Keynes, United Kingdom (4) RNA Therapeutics Institute, University of Massachusetts Medical School, Worcester, Massachusetts, United States (5) Chemistry, University of Southampton, Southampton, United Kingdom

Molecular recognition processes are involved in almost every aspect of biological interactions, ranging from enzyme-substrate recognition up to DNA replication and translation. The very same recognition processes are exploited for *in vitro* diagnostics and therapeutic applications by using biologically-derived materials such as antibodies and natural receptors, which unfortunately are hindered by several drawbacks, not least their expensive production and poor stability. It is not surprising, then, that a considerable portion of nowadays research is directed towards the investigation and production of man-made materials capable of mimicking these molecular recognition processes. Amongst these materials, molecular imprinting polymers (MIPs) represent generic alternatives to antibodies and receptors in diagnostics and separation. MIPs, however, have always promised more than they could actually deliver, due to production issues and batch-to-batch performance variations. At least until recently. Indeed, the development of a new solid-phase synthesis technology for the production of MIP nanoparticles (MIP NPs) allows for the first time reliable manufacturing of water-dispersible “synthetic antibodies” with narrow size distributions. These MIP NPs exhibit many advantages in comparison to natural antibodies, since they can be imprinted for virtually any type of compound (ranging from small molecules to proteins). Moreover, the solid-phase synthesis process can be completely automated, thus minimising manual intervention, shortening processing times, and opening the technology to non-specialists as well as to potential full-scale industrial production whilst maintaining a competitive cost.

Thanks to the flexibility of the synthetic process, even “custom-made” monomers (i.e. nucleosides or DNA strands), have been used to produce the first “hybrid” DNA-MIP NPs. In all cases the affinity of MIP NPs is at the nanomolar or sub-nanomolar level. With this new development in MIP synthesis we foresee a time when the application of natural antibodies will be challenged by new assays, sensors or even therapies based on stable and inexpensive “synthetic antibodies”.



POLY 628: Permeable polymersomes as cascade nanoreactor protocells

Lewis D. Blackman¹, *lblackman1990@gmail.com*, **Matthew I. Gibson**², **Rachel K. O'Reilly**¹. (1) Chemistry, University of Warwick, Coventry, United Kingdom (2) Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom

The ability to mimic nature's constructs using artificial synthetic materials is of fundamental scientific interest with the potential to uncover countless new applications in bionanotechnology. Herein, we attempt to mimic rudimentary communication behaviors observed in living cells and organisms using synthetic polymer protocells and utilizing enzymatic cascade reactions. A biocompatible diblock copolymer was utilized as the inert protocell membrane-forming polymer to encapsulate reactive enzymes into their protected lumens using an organic solvent-free methodology. The permeability of the structures towards the reagents involved in the cascade was investigated as well as the protocells' ability to communicate across species by way of the enzymatic cascade reaction (Fig. 1). These results demonstrate a novel, facile, one-pot approach to enzymatic cascade nanoreactors that can be synthesized on a multi-gram scale. Investigation into gating the permeability of these protocells using external stimuli (e.g. chemical gradient, light, etc.) is also underway to further increase the complexity of this biomimetic system.

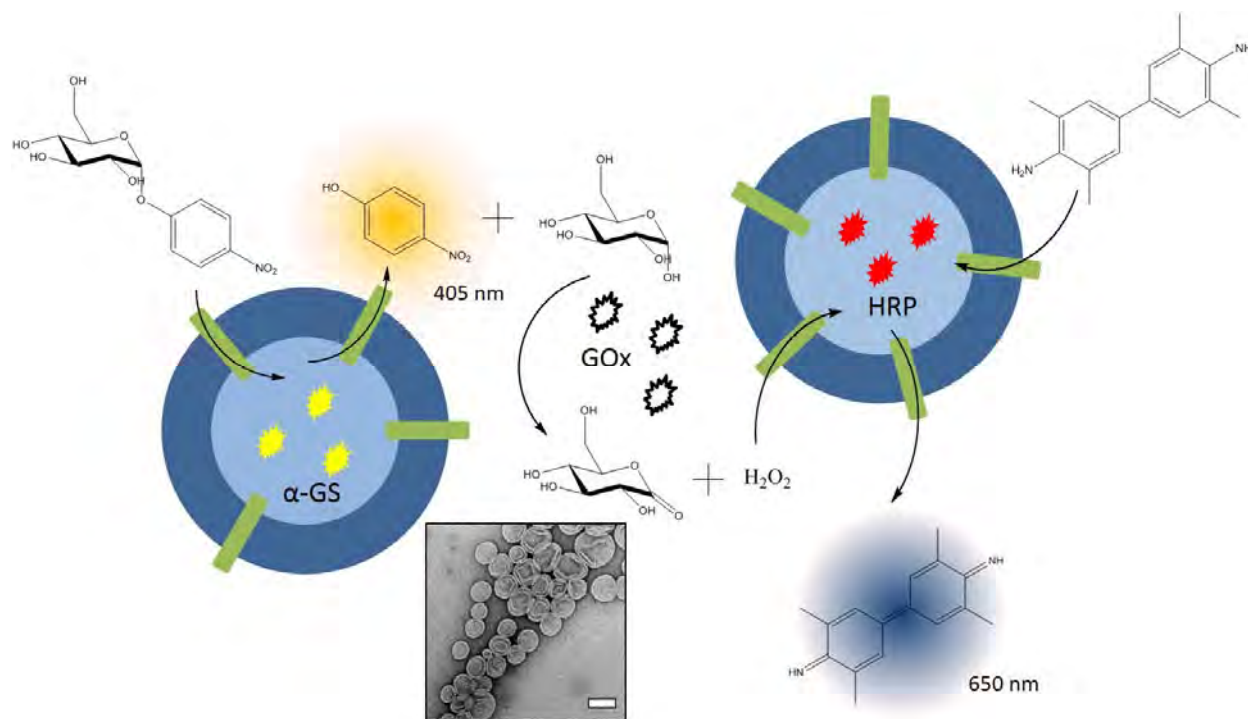


Fig. 1. Schematic of the enzymatic cascade. Inset: Uranyl acetate stained TEM image of enzyme-loaded protocells. The scale bar reads 0.5 μm .

POLY 629: Exploring principles of tissue morphogenesis and cancer progression using synthetic matrices

Xinqiao Jia, xjia@udel.edu. Univ Delaware , Newark, Delaware, United States

Synthetic matrices recapitulating key morphological features and presenting important signaling motifs found in the natural extracellular matrices have been developed for mechanistic investigations of morphogenesis and carcinogenesis. For example, synthetic scaffolds mimicking the mesh-like structure of the basement membrane with an average fiber diameter of 0.5 and 5 μm were used to test the significance of fiber diameter on epithelial-to-mesenchymal transition (EMT). Cell-adhesive peptide motifs were covalently conjugated to the fiber surface to facilitate cell attachment. Using Madin-Darby Canine Kidney (MDCK) cells, we discovered that the cell morphology and cell scattering are strongly dependent on the fiber diameter. The 0.5 μm fibers promote an epithelial phenotype and foster hepatocyte growth factor (HGF)-induced EMT. Contrarily, cells on 5 μm fibers remain fibroblastic, irrespective of the presence or the absence of HGF. Thus, the alteration of the fiber diameter of proteins found in the basement membrane may create enough disturbances in epithelial organization and scattering that might have important implications in disease progression. Separately, a biomimetic hydrogel was prepared using thiolated hyaluronic acid (HA-SH) and an acrylated copolymer with a multivalent presentation of cell adhesive peptide (PolyRGD-AC, Fig 1). LNCaP prostate cancer cells encapsulated in HA-PolyRGD gels formed multicellular tumoroids with close cell-cell contacts. Multivalent presentation of the RGD signal in the HA matrix increased cellular metabolism, promoted the development of larger tumoroids, and enhanced the expression of E-cadherin and integrins. Overall, hydrogels with multivalently immobilized RGD are a promising 3D culture platform for dissecting principles of tumorigenesis and for screening anticancer drugs.

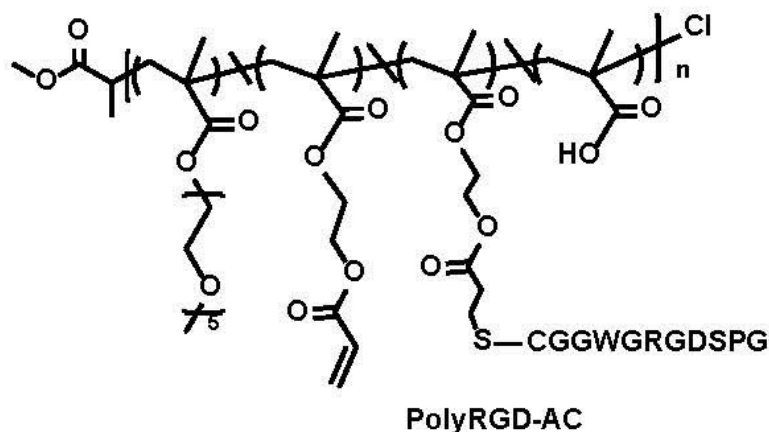
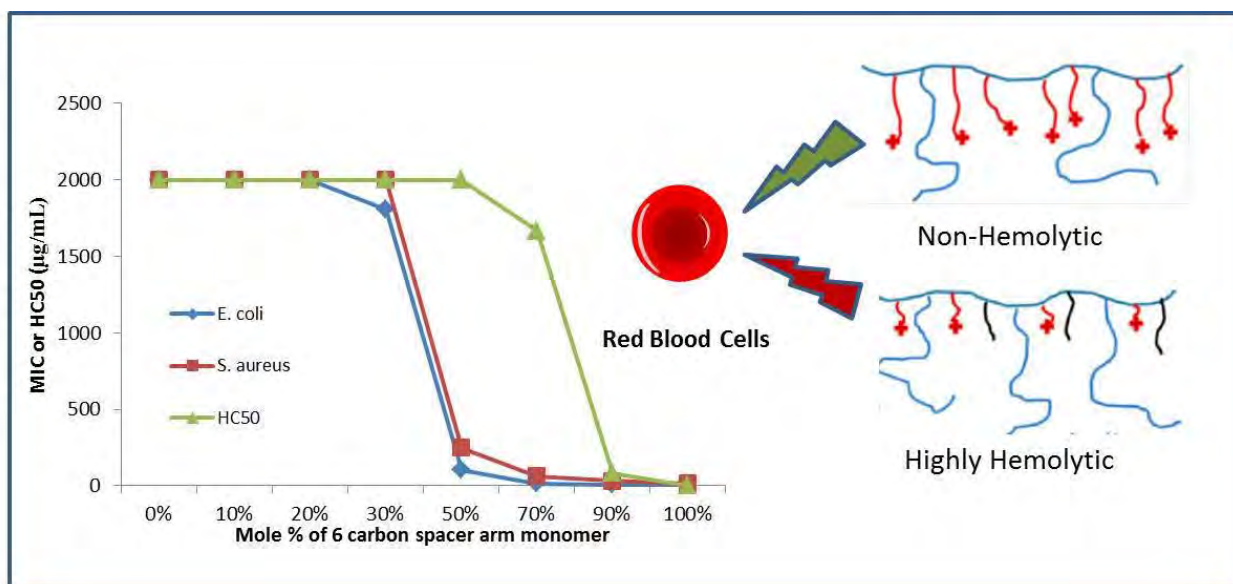


Figure 1: Chemical structure of PolyRGD-AC

POLY 630: Structural effects of relative side group locations on antibacterial and hemolytic activities of amphiphilic PEGylated macromolecules

Ashish Punia¹, *ashishpunia7@gmail.com*, Edward He², Kevin Lee³, Nan-Loh Yang¹.
(1) Ph.D. Program in Chemistry, The Graduate Center, the City University of New York, New York, New York, United States (2) Department of Chemistry, Macaulay Honors College, the City University of New York, New York, New York, United States

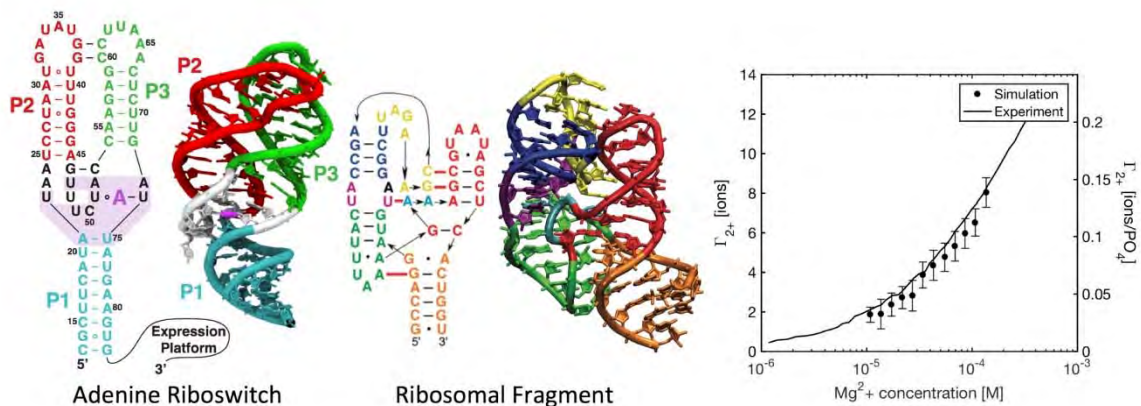
Peptide mimetic synthetic amphiphilic polymers have shown tremendous potential as antimicrobial agents to curb the global threat of antimicrobial resistance. Synthetic amphiphilic polymers act to rupture the cell surface of bacteria through non-specific lipophilic and electrostatic interactions leading to highly hindered bacterial resistance development, if any, as compared with conventional antibiotics. However, structure-activity relationships in synthetic amphiphilic polymers leading to selective activity against bacteria over mammalian cells are yet to be completely understood. We investigated the effects of relative topographical locations of non-ionic poly(ethylene glycol) (PEG) groups and hydrophobic and cationic moieties on the antibacterial and hemolytic activities of amphiphilic polyacrylates. Our investigations demonstrated the substantial effect of relative topographical placement of PEG groups along the backbone of amphiphilic polyacrylates. PEGylated copolymer with cationic group and hydrophobic hexyl spacer arm (distance from polymer backbone to cationic center) on the same repeating unit displayed high antimicrobial activity with concomitant low hemolytic activity. On the other hand, random PEGylated polyacrylate copolymer with lipophilic and cationic groups on separate centers demonstrated high antibacterial activity but also higher hemolytic activity. These results demonstrate the dramatically different effects of PEGylation on reduction of hemolytic activities in “same center” and “separate center” polymer architectures. Based on these findings, a new template for synthesizing the next generation of non-hemolytic polymers which can selectively attack bacteria over human cells is proposed: PEGylated polymer architecture with long hydrophobic spacer arms with pendant cationic groups.



POLY 631: Generalized Manning model captures excess ion atmosphere around highly charged polymers

Udayan Mohanty, *mohanty@bc.edu*. Department of Chemistry, Boston College, Chestnut Hill, Massachusetts, United States

RNA is a highly charged polymer. Folding of the polymer into stable tertiary structures is governed by its interactions with magnesium and other divalent and monovalent metal cations. The basis of how divalent and monovalent metal ions effect RNA stability, dynamics, and therefore function, are less well understood. We have developed a coarse-grained structure based model to investigate the excess ion atmosphere around an irregular RNA structure in aqueous solution containing MgCl_2 and KCl under physiological ionic strength. The structure based model captures the dynamics of outer sphere Mg^{2+} population. Condensation of K^+ and Cl^- is described implicitly, while Mg^{2+} ions are treated explicitly. The implicit model takes into account electrostatic heterogeneity of phosphates, electrostatic and mixing free energy of the screening ions, and enforces ion accessibility near the RNA. We couple the electrostatics to the structure based coarse-grained model and probe fluctuations by molecular dynamics simulations. KCl condensation dynamically responds to conformational fluctuations of the RNA. The RNAs investigated are 58-mer from the large subunit ribosomal RNA and a 26 nucleotide pseudoknot from Beet Western Yellow Virus RNA. We predict the excess ion atmosphere of the native and mimics of intermediate state conformations of the RNAs. We determine the effects of chelated ions (Mg^{2+} and K^+) on the excess ion atmosphere and the Mg^{2+} -RNA interaction free energy. We show that excess ion atmosphere is sensitive to small native basin fluctuations, i.e., RNA dynamics must be included for a quantitative description of the full conformational ensemble. For both RNAs, we compare our predictions against fluorescence titration data of Draper and coworkers.

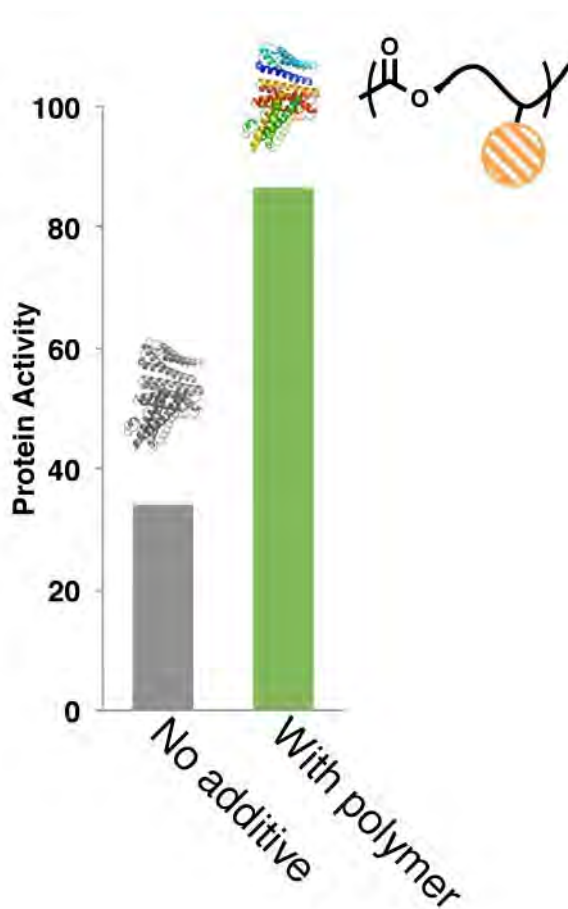


Excess ion atmosphere around RNA

POLY 632: Synthesis of a library of degradable and protein-stabilizing polyesters using thiol-ene post-polymerization modification

Emma Pelegri-O'Day, epelegrioday@gmail.com, Samantha Paluck, Heather D. Maynard. Chemistry and Biochemistry, UCLA, Los Angeles, California, United States

Proteins have wide applications in research and industry due to their substrate specificity and biological function. However, protein instability during transport, storage, and delivery increases costs for both patients and researchers. As a result, excipients such as small molecules, salts, or amino acids are often added as stabilizers. Herein we report a library of well-defined polyesters with bioinspired saccharide substituents that can be used to stabilize proteins. A common alkene-containing degradable backbone was synthesized using ring-opening polymerization (ROP) and multiple potential stabilizers were installed using highly efficient thiol-ene chemistry. This approach enabled the direct comparison of side chains without differences in degree of polymerization. The polymers were used to stabilize the therapeutic protein granulocyte-colony stimulating factor against activity loss from storage and thermal stress. Additionally, the molecular weight of the polyesters was varied and larger polymers demonstrated improved protein stabilization. This synthetic approach offers a new platform for biocompatible and degradable protein stabilizers that enables the rapid screening of novel excipients.

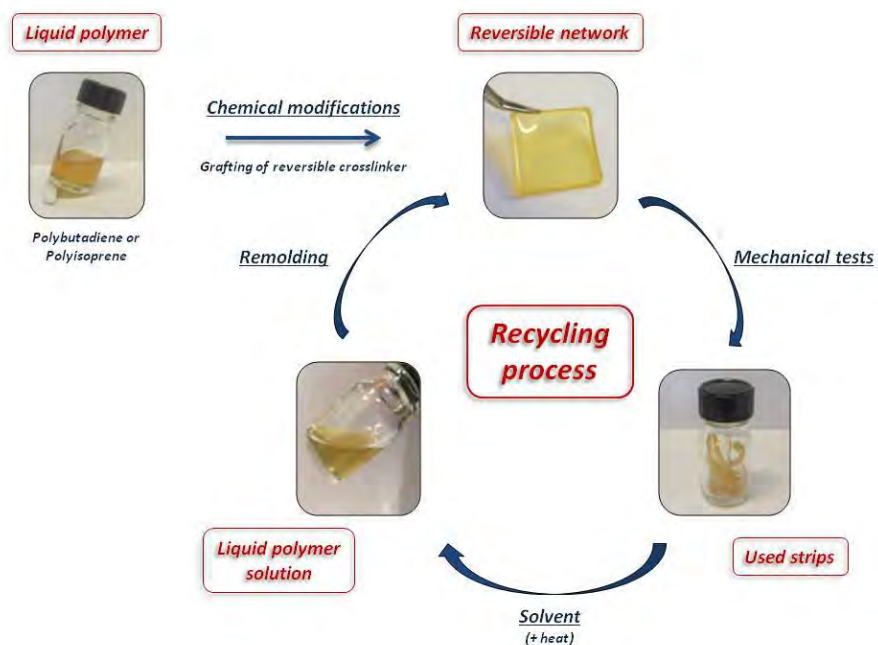


POLY 633: Recyclable elastomeric networks based on reversible cross-linking chemistry

Pierre Berto, pierre.berto@live.fr, Frédéric Peruch, Stéphane grelier. LCPO, Bordeaux, France

Rubbers can be found into various fields of applications like aerospace, sports equipments and tires. In the last decade, the rubber production has been increasing to overcome 26 million tons in 2015. Elasticity, solvent permeability and stress durability are the main characteristics targeted for elastomeric materials. In order to achieve these properties, polymer chains need to be cross-linked to form a polymer network. Sulfur vulcanization represents the main method industrially employed for tires. However, the irreversibility of this chemical reaction generates a large amount of rubber wastes. Additionally, there is not a viable method for recycling these irreversible networks. To tackle this issue, various dynamic linkages have been successfully used on different polymers to create reversible networks. Reversible linkages can be based on several reactions/interactions such as Diels-Alder reaction, π -stacking interaction, metal coordination or hydrogen-bonding.

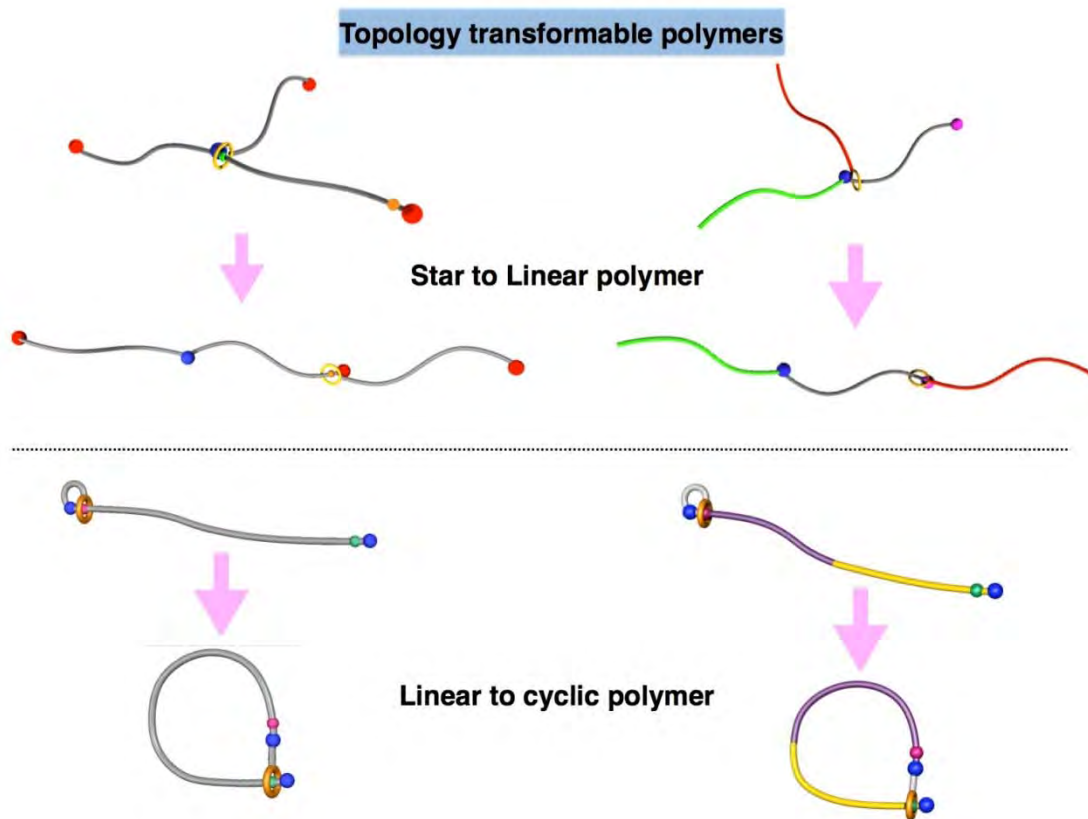
We report here a new method to synthesize a reversibly cross-linked polybutadiene/polyisoprene network based on covalent bonding or hydrogen bonding. High molar mass polymers were first chemically degraded into smaller chains, in order to obtain a liquid/viscous polymer. Then, polymeric chain were modified by furan or ureidopyrimidinone (UPy) moieties in order to develop reversible interactions. In both cases, a reversible network was obtained. Thermal stability of the material was then analyzed by Dynamic Mechanical Analysis (DMA) and elastic properties were studied by tensile tests. Impact of the chain length, cross-linking density and recyclability of the polydiene reversible networks will be particularly discussed.



POLY 634: Topology transformable polymers derived by mechanical linkage

Toshikazu Takata, *takata.t.ab@m.titech.ac.jp*. Tokyo institute of technology, Tokyo, Japan

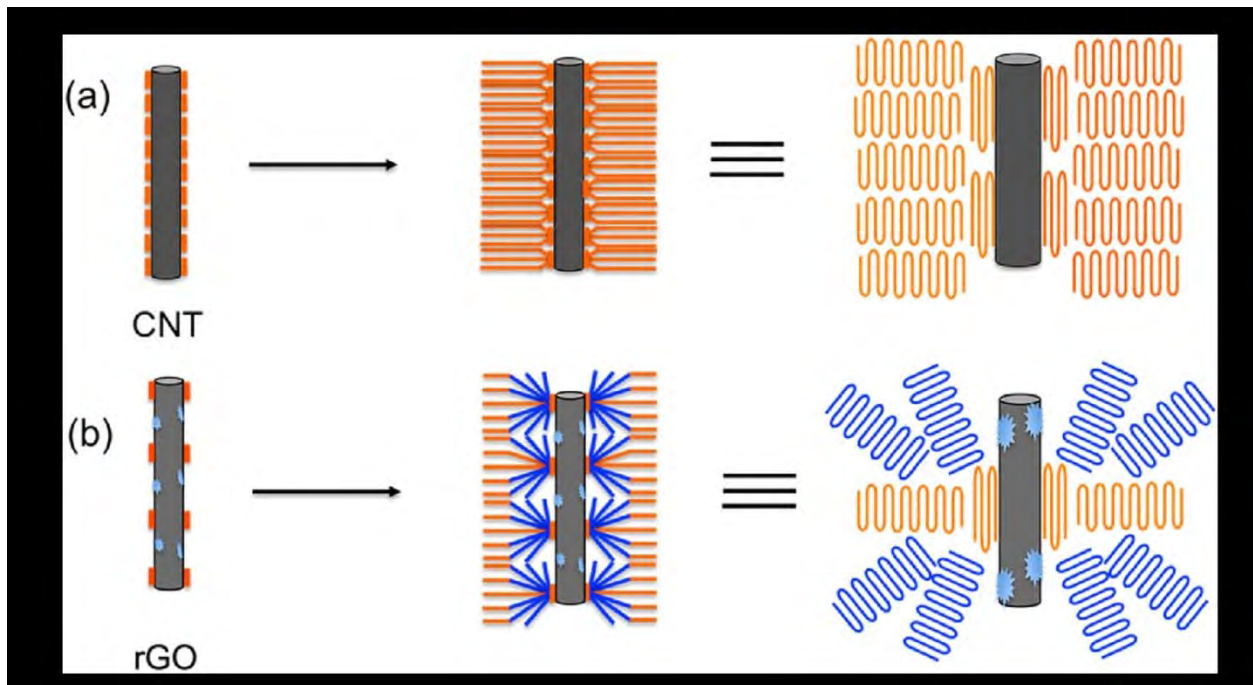
Differences in backbone structure of block copolymers have recently been recognized as an important factor for facilitating the formation of self-assembled structures and are also well known to affect their physical properties. Therefore, topology transformable block copolymers, which can transfigure the topology of their backbones, are of great potential for the development of polymer materials with desirable properties such as stimuli responsibility, self-mending aptitude, and shape-memory effects. In this paper, we report the synthesis and application of topology transformable polymers derived by mechanical linkage.



POLY 635: Supramolecular structures of polymers around nanocarbons

Shanju Zhang, *szhang05@calpoly.edu. Dept of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, California, United States*

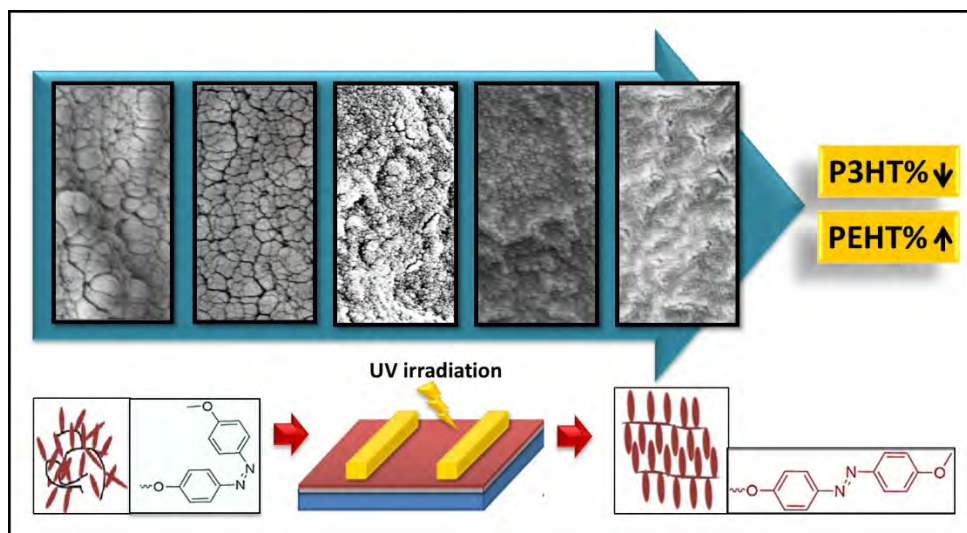
Assembly of polymers around nanomaterials plays an important role in controlling the polymer properties. Nanocarbon materials such as carbon nanotubes and graphene have shown promise as reinforcing agents for polymer nanocomposites. However, the assembly behaviors of polymers around nanotubes and graphene are little understood. Here we report supramolecular microstructures of various polymers around nanotubes and graphene at different length scales. At a molecular scale, we study kinetics and thermodynamics of assembly of conjugated polymers around individual nanotubes. Spectroscopic methodologies are applied to study the dynamic process of assembly. At a macroscopic scale, we investigate well-aligned supramolecular microstructures of various polymers around nanotube and graphene fibers including polythiophene, polyolefin, and biopolymers. We use the Hoffmann-Lauritzen theory to analyze thermodynamics of chain folding and alignment around the nanocarbon fibers. We propose a theoretical model to interpret the different assembly behaviors of polymers around nanotube and graphene fibers and the mechanism behind its influence on interfacial crystallization.



POLY 636: Tensile property enhancement and photo-actuation of supramolecular self-assembled copolymers of P3HT

Taniya M. Pathiranage², *txk121930@utdallas.edu*, Jennifer M. Boothby⁴, Michael C. Biewer³, Taylor H. Ware⁴, Mihaela C. Stefan¹. (1) Dept Chem UT Dallas, Richardson, Texas, United States (2) Chemistry, University of Texas at Dallas, Richardson, Texas, United States (3) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States (4) Bioengineering, University of Texas at Dallas, Richardson, Texas, United States

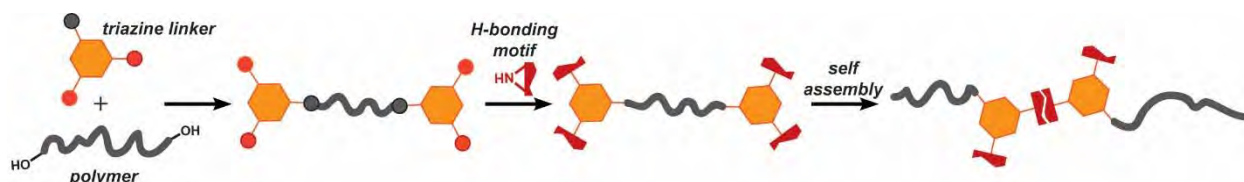
A set of block copolymers of regioregular poly(3-hexylthiophene) (P3HT) and liquid crystalline mesogens were synthesized with Grignard metathesis polymerization (GRIM) and atom transfer atom polymerization (ATRP). The azobenzene (nematic) and biphenyl (smectic) were the incorporated mesogens. Thermotropic liquid crystallinity of the block copolymers was investigated by polarizing optical microscope with heating stage and by differential scanning calorimetry (DSC). Photo-responsive properties of azobenzene with geometric isomerization were studied under UV for actuated topographical changes. The effect on hole mobility caused by photo-alignment of the block copolymers with azobenzene was measured in organic field effect transistors. Tensile modulus was calculated for all the copolymers using oscillation temperature ramping in Dynamic Mechanical Analysis (DMA). Observed Young moduli for copolymers fall in the same range with the reported values of P3HT homopolymer, yet the rigidity of the copolymers was slightly higher than in their P3HT precursors. The effect of poly(3-(2-ethylhexyl)thiophene) (PEHT) as an additive was studied by making blends of it with P3HT copolymers and their P3HT precursors. Surface morphology analysis of the films before and after the DMA was done with tapping mode atomic force microscopy (TMAFM) and the cross-sectional assembly was investigated with Scanning electron microscopy (SEM). The impact of the additives and alignment forces (UV, heat) on the lamellae packing and π - π stacking of P3HT segment was investigated by thin film XRD analysis. The field effect mobilities of the P3HT copolymers as high as 10^{-2} cm^2/Vs were measured with organic field effect transistors.



POLY 637: Hydrogen bonding supramolecular polymers with temperature controlled switchable mechanical properties reveal photoheable effects

Anton Razgoniaev, *arazgon@bgsu.edu*, Kirill Mikhailov, Filipp Obrezkov, Alexis Ostrowski. Department of Chemistry, Bowling Green State University, Bowling Green, Ohio, United States

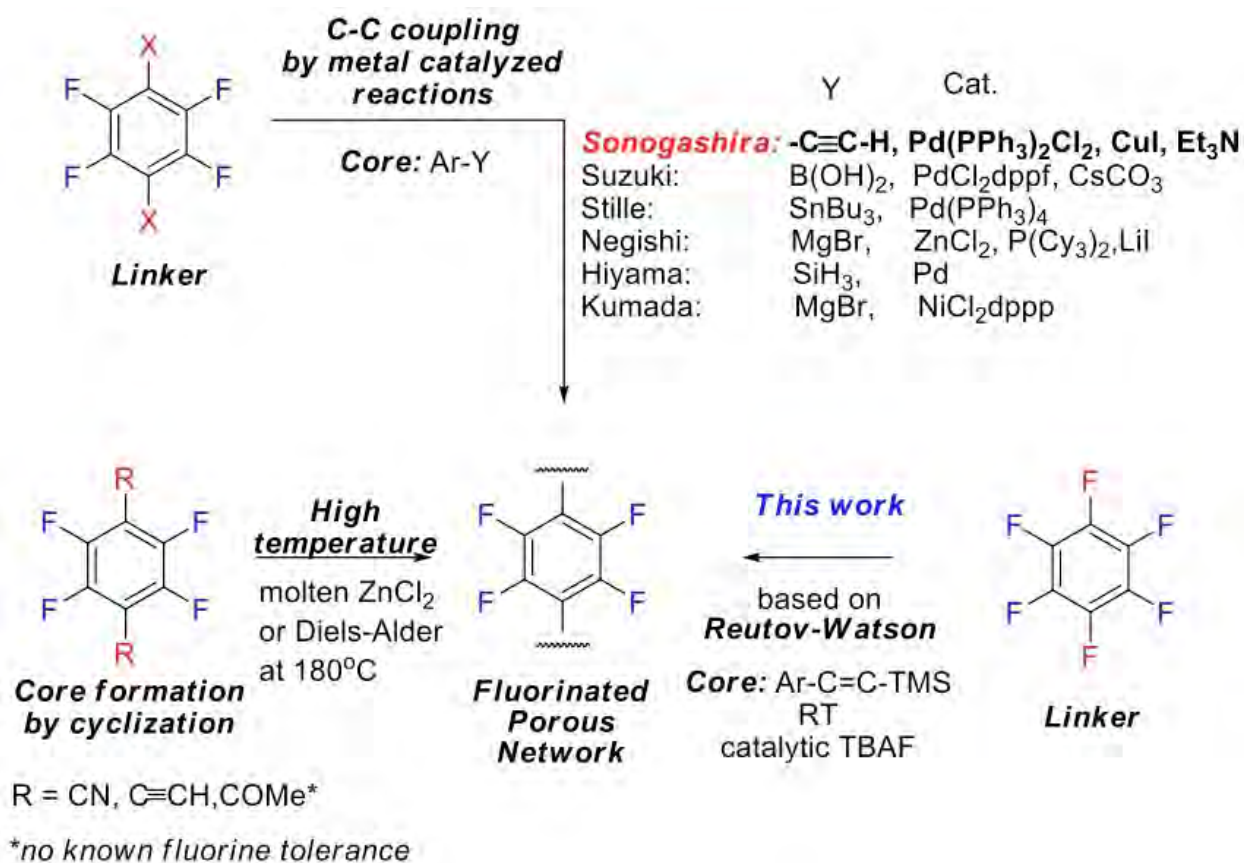
We have prepared hydrogen bonded supramolecular polymer melts via modification of soft non-polar hydrogenated poly(ethylene-co-butylene) polymer (HLBH-P 3000) termini groups with hydrogen bonding motifs. These interactions enhance the elastic properties of the material via supramolecular binding in the polymer matrix and result in a structurally dynamic supramolecular polymer network, whose properties could be temperature modulated. We have thoroughly studied the mechanical properties of the prepared material using oscillatory rheology. This supramolecular polymer exhibited interesting temperature-modulated behavior not seen in the previously reported systems. Namely, it had two switchable states with remarkably different mechanical properties that were achieved via reassembly of hydrogen bonding domains. To enhance the optical properties of these materials, we prepared a series of these supramolecular polymers with different organic and inorganic dyes incorporated into the polymer matrix. Introduction of the chromophores created materials that were capable of self-healing upon external light radiation. The healing rate was controlled by the light radiation power, time, and location as well as the nature of supramolecular interactions in the polymers.



POLY 638: Regioselective, metal free C-C coupling of hexafluorobenzene for stable porous polymer networks

Damien Thirion, Vepa Rozyyev, Aldiar Adishev, **Cafer T. Yavuz**, yavuz@kaist.ac.kr.
KAIST, Daejeon, Korea (the Republic of)

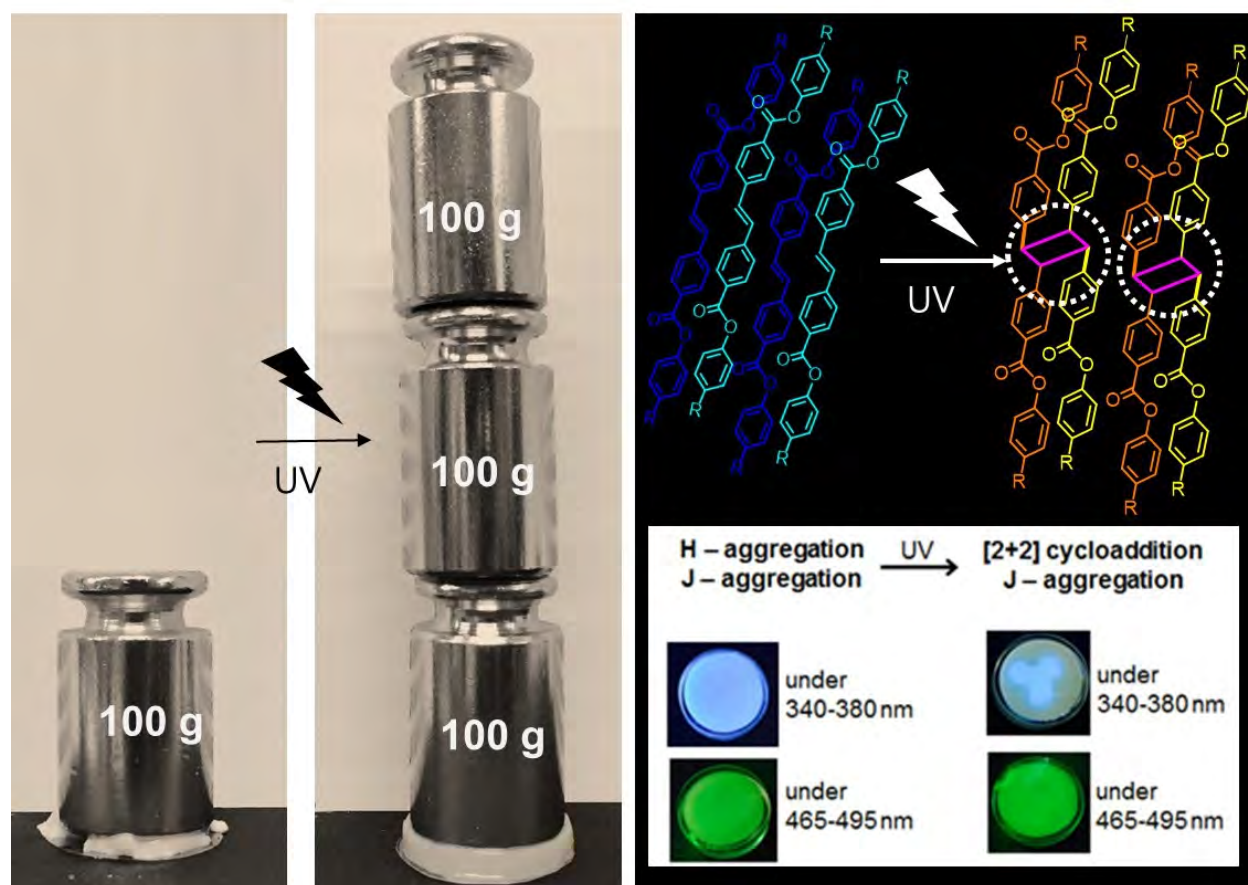
Porous materials as adsorbents with high affinities to target molecules have great potential to facilitate environmentally important separations and remediation. One key challenge is to keep a reactive functionality inert while building a super structure. Protection or post-modification methods are limited because of the incomplete activation, and often require harsh conditions that also compromise the framework integrity. We recently used (*Chem. Mater.* 28 (16), 5592–5595, 2016) a metal-free, one-pot, RT, deprotection-coupling, regioselective reaction for the first time to synthesize a porous network with high specific surface area (1035 m²/g) and easy post-functionalization. The obtained microporous polymer is a robust C-C bonded structure with alkyne and perfluorinated moieties. Aromatic fluorines readily undergo nucleophilic substitutions facilitating numerous post-modification possibilities, a particular feature that was not previously available.



POLY 639: UV Patterned calixarene-derived supramolecular gels with spatially resolved mechanical and fluorescent properties

Ji Ha Lee³, aprilgem@naver.com, **Jong H. Jung**¹, **Kazuo Sakura**². (1) Gyeongsang Natl Univ, Chinju, Korea (the Republic of) (2) U of Kitakyushu Dept of Chem, Kitakyushu Fukuoka, Japan (3) University of Kitakyushu, Fukuoka, Japan

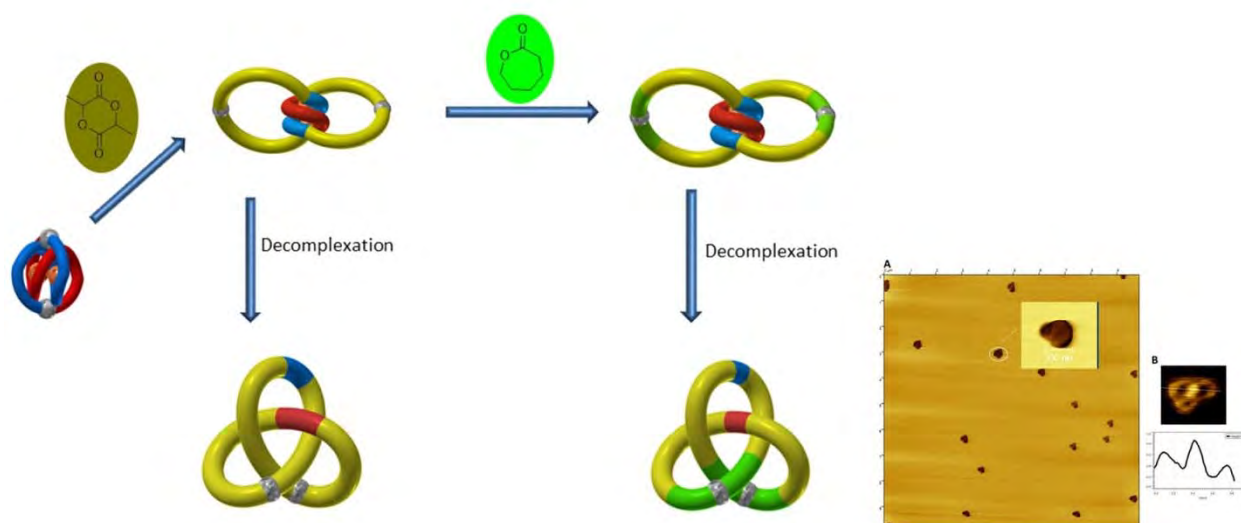
Supramolecular assemblies have largely been overlooked as prototyping or engineering material, as they are considered mechanically weak and in most cases are unable to withstand their own weight. Calixarene-derived networks can, however, provide robust supramolecular gels. Incorporating a photo-reactive stilbene moiety, we show that the aggregation state of the material can be tuned by heating and UV exposure in order to control the mechanical as well as the fluorescent properties. Regulating the extent of heating to control the proportion of H-aggregates and cross-linking H-aggregates by control of UV exposure allows for adjustable photo patterning of the fluorescence as well as the material stiffness in the range of tens to hundreds of kPa. We expect this straightforward supramolecular system will be suitable for advanced prototyping in applications where modulus and shape are important design criteria



POLY 640: Trefoil knotted block copolymer via ring-expansion strategy

Pengfei Cao^{2,1}, caopengfei686@gmail.com, Li-Han Rong¹, Joey Mangadlao¹, Rigoberto C. Advincula¹. (1) Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Knots are interesting structures not only in arts but also in mathematics. Beyond the aesthetic reason, the natural biomacromolecules include DNA, RNA and protein also extrude their fair share of knotty motif.^[1,2] The knotted structure in proteins appears to bury the active regions against the degradation for increased stability and enhanced functionality. The successful syntheses of molecular trefoil knots and pentafoil knots were demonstrated recently.^[3, 4] However, rational access to trefoil knotted polymer remains a formidable challenge although initial theoretical studies demonstrated the unique thermal, mechanical and dynamic properties of the knotted polymer. To achieve the experimental study of the “knot” effect on the polymer material, we demonstrated the first rational synthesis of trefoil knotted poly(e-caprolactone) and trefoil knotted block polymer poly(L-lactide)-*b*-poly(e-caprolactone) by ring-expansion strategy from a bis-copper(I) templated phenanthroline tin initiator.^[5,6] Compared with the linear analogue, the trefoil knotted polymer exhibited expected properties, such as reduced hydrodynamic radius and lower intrinsic viscosity. Moreover, the transformation of the C₂ symmetry of the templated trefoil knotted polymer to C₃ symmetry of the template-free trefoil knotted polymer was also firstly observed by atomic force microscopy imaging.



POLY 641: Perylene bisimide aggregation in water: Self-assembly features and development of stimuli responsive materials

Bartolome Soberats^{1,2}, bartolome.soberats_reus@uni-wuerzburg.de, Daniel Görl¹, Pradeep Syamala^{1,2}, Frank Wuerthner^{1,2}. (1) Institut für Organische Chemie, Universität Würzburg, Würzburg, Bayern, Germany (2) Center for Nanosystems Chemistry and Bavarian Polymer Institute, Universität Würzburg, Würzburg, Bayern, Germany

Self-assembly of dyes in aqueous media has attracted a great deal of attention for the development of biocompatible sensors and stimuli responsive photoactive materials. We recently focus on the elucidation of the self-assembly pathways in water of bolaamphiphilic perylene bisimide (PBIs) dyes bearing oligoethylene glycol (OEG) groups (Figure 1a). The self-assembly of these PBIs is not directed by enthalpic factors, but is driven by the entropic release of water molecules from the OEG units (Figure 1a). The entropic nature of self-assembly in water is characterized by an inverse temperature response which induces lower critical solution temperature (LCST) phenomena, where the solution phase separates at a particular temperature upon heating. In this work, we developed a supramolecular approach to adjust the LCST of PBI-water mixtures (Figure 1a). Furthermore, based on this concept, we prepared stimuli responsive hydrogels that undergo a color change triggered by the LCST phase transition between a hydrogel state and a lyotropic liquid crystalline state (Figure 1b).

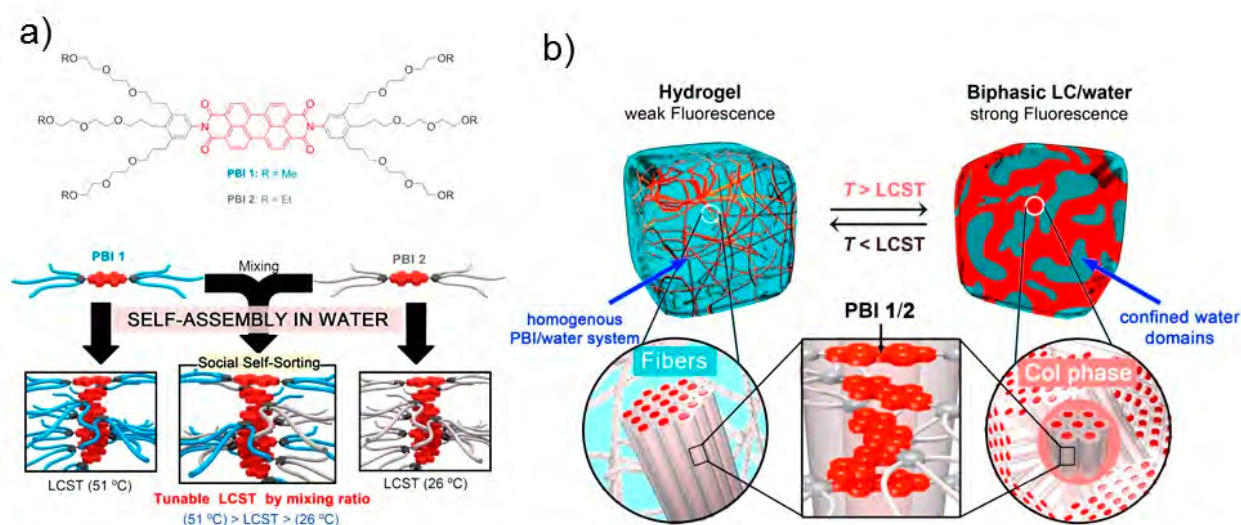


Figure 1. a) Schematic representation of the supramolecular approach applied to control the LCST phase transition in bolaamphiphilic **PBI 1** and **PBI 2** aggregates. b) Illustration of the LCST phase transition in **PBI1/PB2** hydrogels.

POLY 642: Developing cyclodextrin-based 3D printing materials

Qianming Lin, Hao-yi Wang, **Chenfeng Ke**, *Chenfeng.Ke@dartmouth.edu*. Chemistry, Dartmouth College, Hanover, New Hampshire, United States

The manufacture of self-contained, biocompatible micro-sensing devices is a major challenge in bioengineering and biotechnology. 3D printing,¹ an emerging technology capable of transferring computer-aided design (CAD) quickly into customized prototypes, has been shown to be able to create artificial tissues, bionic ears, Li-ion micro battery and chemical reactionwares in ordinary laboratories without other specialized equipment. Compared with other manufacturing technologies, 3D printing can (i) rapidly produce a prototype at low cost and (ii) print customized products designed by CAD software using a desktop printer. Among 3D printing methods, direct-write 3-D printing (or “direct writing”) has become the most widely recognized and adopted technique, because of its high resolution, less rigorous processing conditions (e.g., no high temperature or laser is required), and compatibility with a wide selection of printing materials, including soft materials such as hydrogels. Direct write technique requires that the printing materials should be rheologically tailored to possess shear thinning behavior. This requirement make cyclodextrin-based supramolecular materials² particularly adaptive – upon forming complexes with guest moieties, the non-covalent interactions can be disrupted during extrusion at a shear rate of 1–100 s⁻¹ and quickly re-established after the removal of the shear force. Herein, we report the design and synthesis of a supramolecular 3D printing material composed of cyclodextrin-based polyrotaxanes. We discovered that, after 3D printing and post-printing process, the printed monolith possesses solvent-dependent shape changing capabilities.

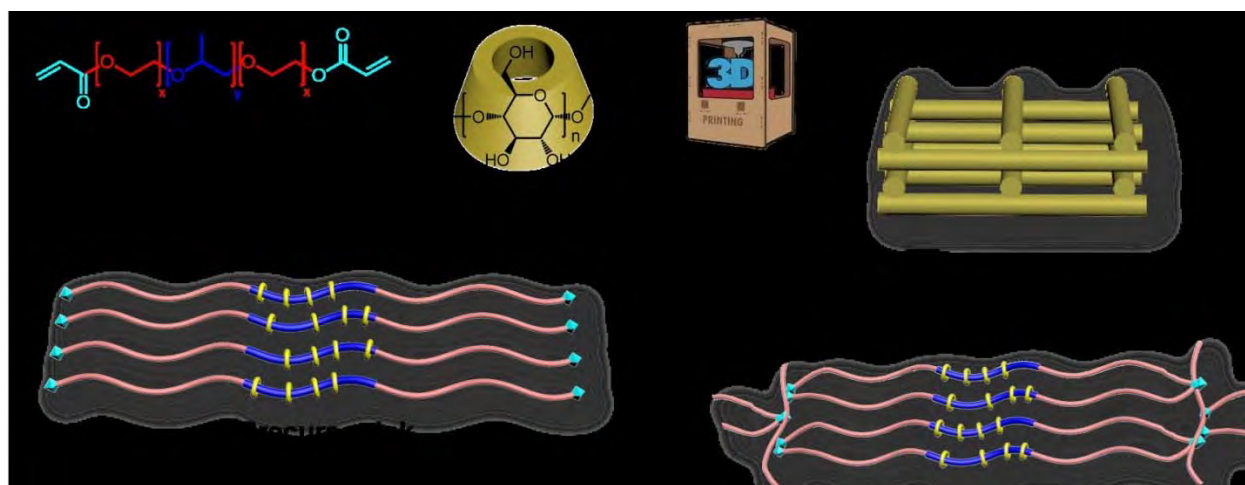


Figure 1. Design, synthesis and fabrication of a cyclodextrin-based polyrotaxane monolith.

POLY 643: Stimuli responsive nanoparticles from cyclodextrin polymers

Thorbjørn Terndrup Nielsen, *ttn@bio.aau.dk*. Department of Chemistry and Bioscience, Aalborg University, Aalborg, Denmark

Cyclodextrin polymers (CD-polymers) offer several advantages compared to native CDs with respect to the development of complex therapeutic drug delivery vehicles. Since CD-polymers contain several functional CDs units they can be used for macromolecular assemblies such as nanoparticles and hydrogels, enabling controlled release of drug compounds. In recent years CD-polymer based nanoparticles have found use as therapeutic vehicles in delivery of e.g. anticancer agents and siRNA. Here we present versatile and reliable synthetic approaches towards well-defined CD-polymers. The polymers have been prepared by means of RAFT-polymerization and Copper(I) catalyzed Azide-Alkyne Cycloaddition. Furthermore their formation of various stimuli-responsive nanoparticles will be presented.



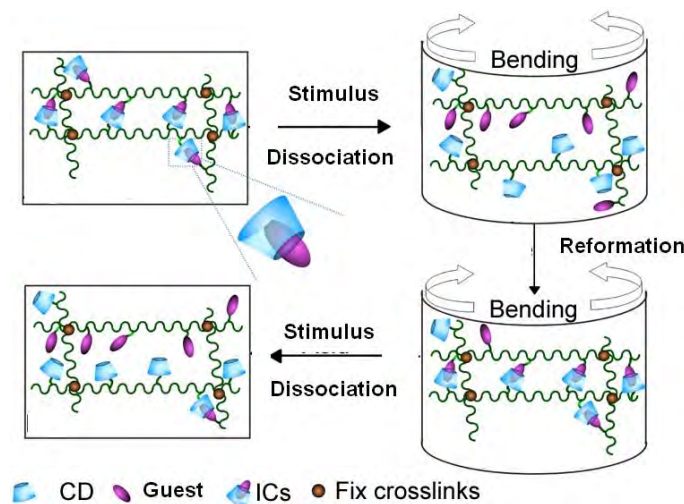
POLY 644: Preparation of shape memory polymers or self-healing composites based on cyclodextrin-based inclusion

Zhi-Chao Chao¹, Kun Guo², Yao-Yu Xiao¹, Bang-Jing Li³, **Sheng Zhang¹**, zslbj@163.com. (1) 1. State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu, China (2) Chengdu Institute of Biology, Chinese Academy of Science, Chengdu, China

Smart materials that exhibit special functions in response to external stimuli have been progressively developed. In recent years, utilize noncovalent interactions, such as cyclodextrin (CD)-based host-guest interactions, to construct smart materials has attracted more and more attentions from both academia and industries.

For shape memory polymers (SMPs), one of the most important smart materials, supramolecular interactions have been increasingly designed as molecular switches to construct novel SMPs. Firstly, we developed a series of supramolecular SMPs based on partial inclusion complex formation between CDs and polymer chains^[1]. The resulting materials contained two phase: fixing phase formed by stable CD-polymer crystallites for remembering the permanent shape, and reversible shape formed by non-complexed polymer segments for the temporary shape forming and recovering. It has been demonstrated that various polymers could be endowed shape memory properties by this approach. In addition, we also designed a series of SMP using the reversible interactions between CD and guest groups as molecular switches^[2]. As the CD-guest complexes formation/dissociation in response to an external stimulus such as light, redox and pH, the molecular mobility of the materials switch off/on correspondingly. As a result, the shape memory effect could be triggered by light, redox or pH respectively.

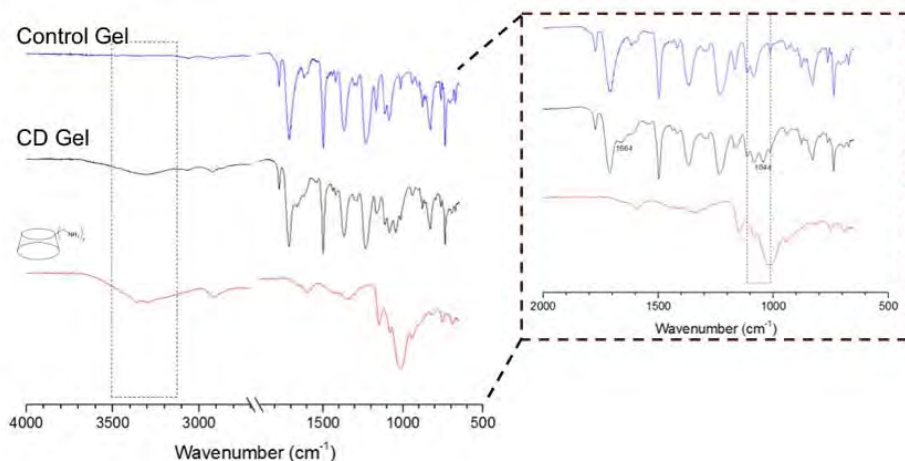
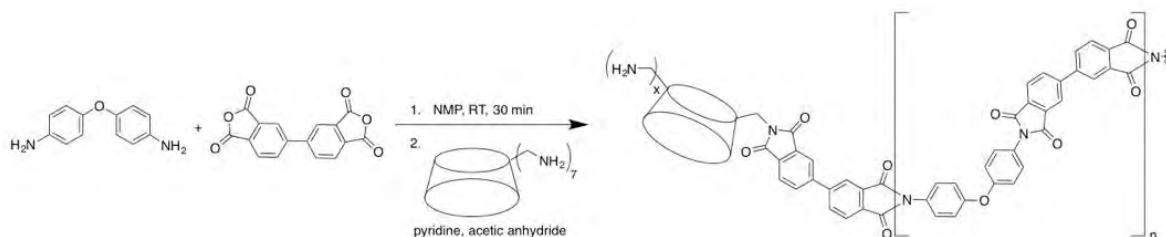
We also developed a new design strategy for self-healing functional materials by connecting functional inorganic particles (such as SWCNT) and a polymer network through CD-based interactions^[3]. The resulting materials not only combined the mechanical strength of the polymer network and the function of inorganic particles, but also showed self-healing ability owing to the host-guest interactions.



POLY 645: Highly porous, mechanically strong, cyclodextrin-rich polyimide gels designed for advanced applications: Synthesis, characterization, and applications

Eric Leonhardt², ericleonhardt@gmail.com, Tiffany Williams¹, Karen L. Wooley³. (1) 49-3, NASA Glenn Research Center, Cleveland, Ohio, United States (2) Chemistry, Texas A&M University, College Station, Texas, United States (3) 3255 TAMU, Texas AM University, College Station, Texas, United States

The preparation of polyimide gels with β -cyclodextrin contents exceeding 35% by weight is outlined. A large library of materials, designed for water purification and carbon dioxide sequestration applications, was prepared and characterized. These materials were prepared by cross-linking oligomers of common diamine 4,4'-oxydianiline (**ODA**) and dianhydride biphenyl-tetracarboxylic acid dianhydride (**BPDA**) with various cyclodextrins, followed by solvent exchange and drying, and exhibit large (>90%) porosities with thermal stabilities up to 500 °C and good mechanical strengths. The synthetic design, characterization, as well as performance for selected applications of two classes of gels will be discussed: Ester-cross-linked gels from β -cyclodextrin and imide cross-linked gels from heptakis(6-deoxy-6-amino)- β -cyclodextrin (**β -CD-NH₂**).



POLY 646: Monodisperse thermoresponsive cyclodextrins with switchable inclusion complexation

Jiatao Yan, Wen Li, Kun Liu, **Afang Zhang**, azhang@j.shu.edu.cn. Department of Polymer Materials, Shanghai University, Shanghai, China

Stimuli-responsive cyclodextrin (CD) materials have drawn much attention recently, and have shown promising applications in various areas, such as drug delivery, molecular devices or actuators. They are always constructed from the stimuli-controlled complexation of CDs with special guests such as azobenzene or ferrocene. Another often used strategy is to attach polydisperse stimuli-responsive polymers, such as poly(N-isopropylacrylamide)s to the rims of CDs. Herein, we report on monodisperse oligoethylene glycol (OEG)-modified CDs which show unprecedented thermoresponsive properties in aqueous solutions (Figure 1). They exhibit fast phase transition with negligible hystereses, and their phase transition temperatures (T_c) can be mediated in the range of 24-63 °C depending on the ring size of CDs and the structure of the OEG units. Importantly, these CD derivatives retained their inclusion ability for dye guests, and their inclusion can be reversibly switched on or off by varying the temperature below or above their T_c . Based on their unique thermoresponsiveness, conjugation of these OEG-modified CDs with solvatochromic dyes afford sensitive dual-sensors for both temperature and pH value. This characteristic feature is maintained when pending OEG-modified CD moieties onto polymer chains. Furthermore, reversible inclusion complexation of the OEG-modified CDs is proven to be extremely efficient in switching on or off the catalysis activity of carbonic enzyme by simply varying solution temperature below or above T_c .

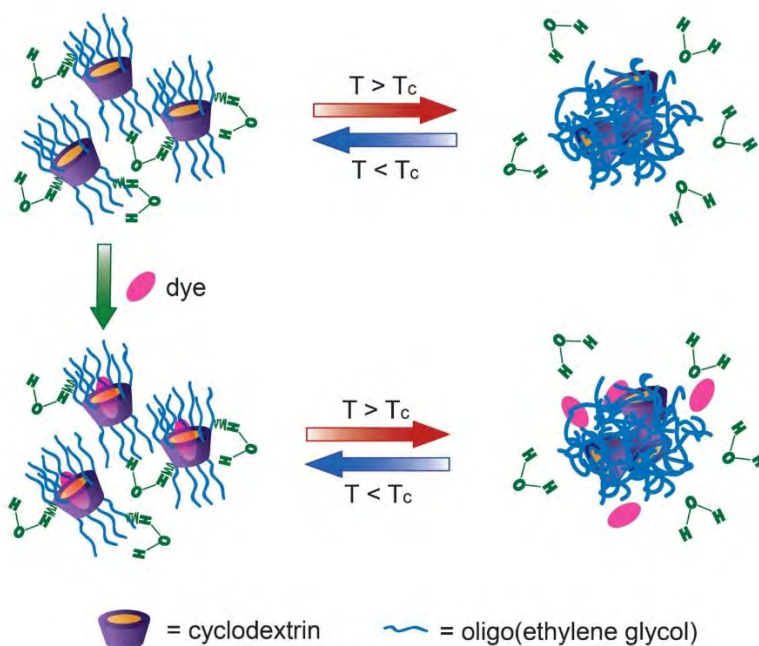
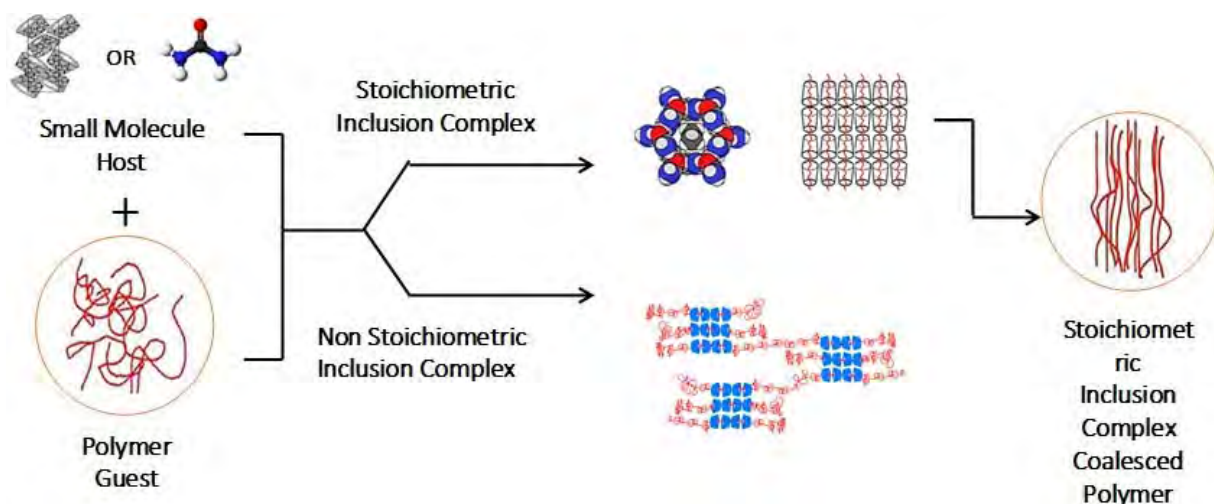


Figure 1. Schematic drawing of monodisperse thermoresponsive CDs and their switchable inclusion complexation with guest dyes.

POLY 647: Restructuring polymers *via* nano-confinement and subsequent release

Alan E. Tonelli, alan_tonelli@ncsu.edu. TECS, North Carolina State University, Cary, North Carolina, United States

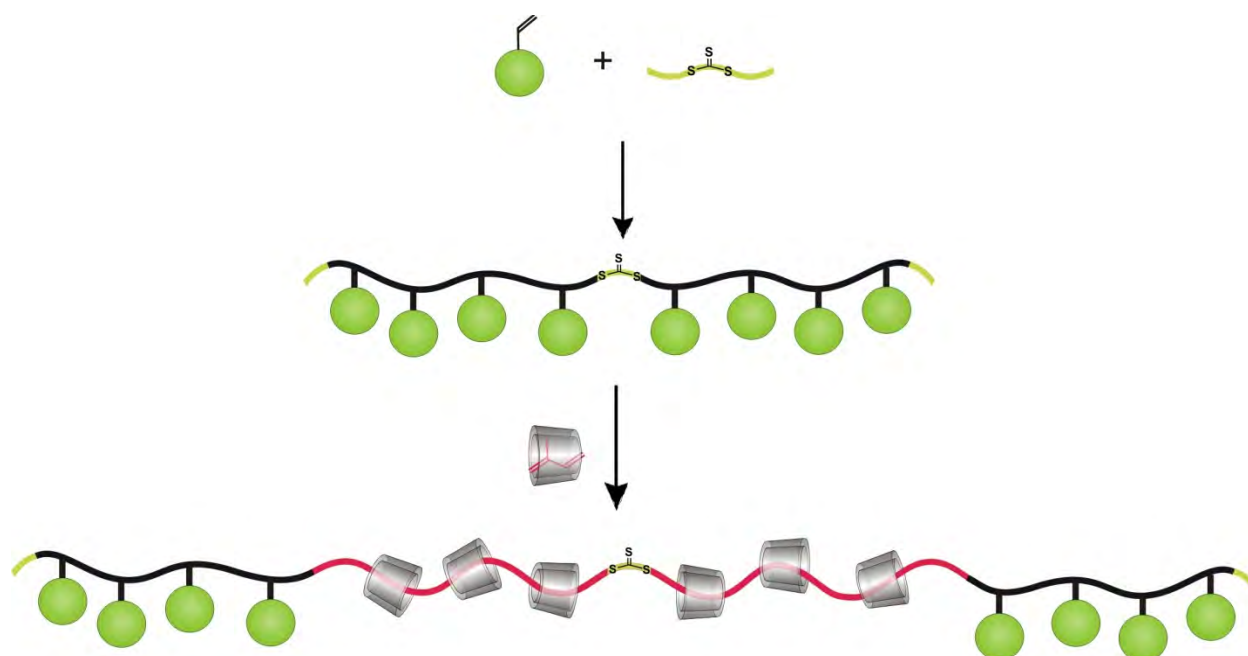
During the past several years my students and I have been utilizing small-molecule hosts [cyclodextrins and urea] to nanostructure polymers. This is accomplished by first forming non-covalently bonded inclusion complexes (ICs) between these small-molecule hosts and guest polymers, followed by the careful removal of the host molecule crystalline lattice to obtain a coalesced bulk polymer. We have repeatedly observed such coalesced polymer samples to behave distinctly from those produced from their solutions or melts. Coalesced amorphous homopolymers exhibit higher glass-transition temperatures, while crystallizable coalesced homopolymers evidence higher melting and crystallization temperatures, and sometimes different crystalline polymorphs. When ICs are formed with block copolymers or with two or more different homopolymers the resulting coalesced samples can evidence intimate mixing between the copolymer blocks or between entire homopolymer chains, respectively. All the distinct behaviors observed for polymers coalesced from their ICs is a consequence of the structural organization of polymer-host-ICs. Polymer chains in IC crystals are confined to occupy narrow diameter ($\sim 0.5 - 1.0\text{nm}$) channels formed by the crystallization of the small-molecule hosts around the guest polymers. This results in the high extension and separation of guest polymer chains, which leads to unique behaviors for bulk coalesced polymer samples. In addition, when excess polymer is used to form ICs with CD hosts, non-stoichiometric $[(n-s)]$ ICs, with partially un-included chains, are formed. We will describe several applications for polymers coalesced from their ICs and for $(n-s)$ -polymer-CD-ICs.



POLY 648: Controlled *rotaxa*-polymerization for well-defined polyrotaxanes

Gergely Kali, gergelykali@gmail.com, Jessica Hilschmann, Gerhard Wenz. Campus Saarbruecken, Saarland University, Saarbruecken, Germany

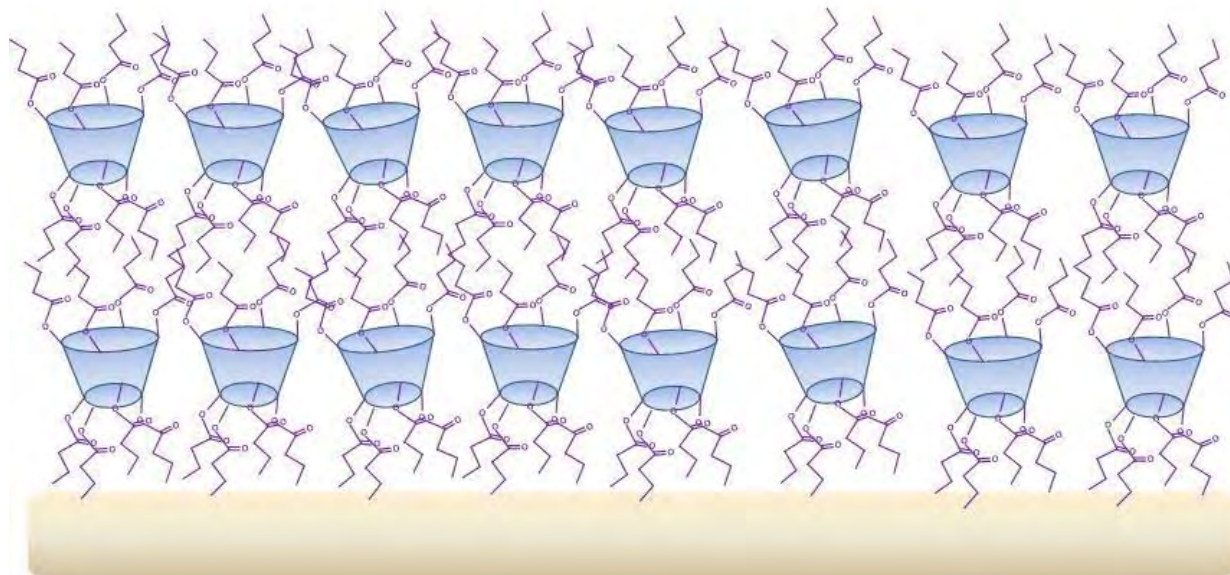
Controlled *rotaxa*-polymerization was used to prepare cyclodextrin-based polyisoprene polyrotaxanes with statistical- and block-copolymer axis. Aqueous reversible addition fragmentation chain-transfer polymerization was applied utilizing a symmetrical bifunctional trithiocarbonate chain transfer agent for the copolymerization of cyclodextrin complexed isoprene and bulky comonomers. The composition and architecture of the copolymer axis of the polyrotaxanes showing a huge effect on the cyclodextrin coverage, molar mass and the water solubility of the produced polyrotaxanes.



POLY 649: Amphiphilic cyclodextrin functionalized surfaces

Kim L. Larsen, *kll@bio.aau.dk*. Dept. of Chemistry and Biosciences, Aalborg University, Aalborg East, Denmark

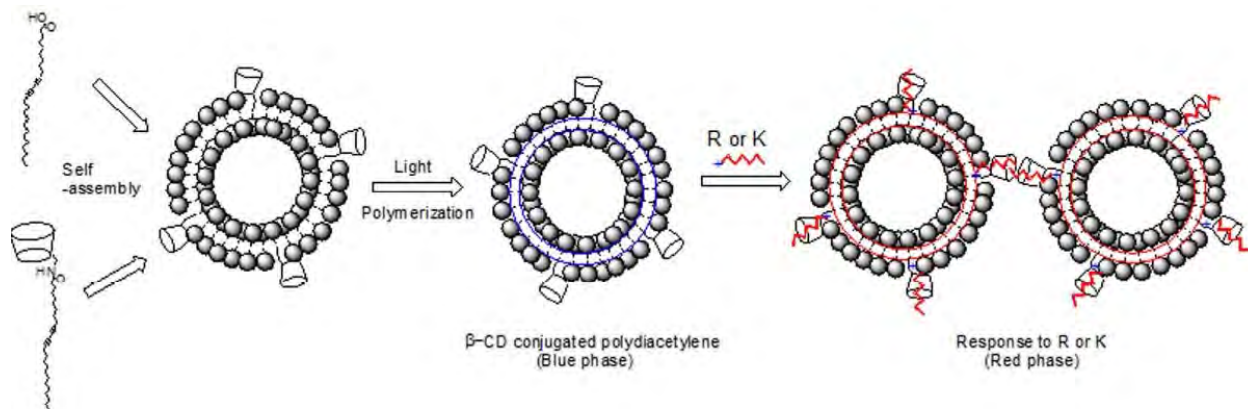
Modification of materials, e.g. textiles, with cyclodextrins (CDs) in order to obtain new functionalities, e.g. controlled release of fragrances or removal of malodours, has been the subject of many studies the past years ⁱ⁻ⁱⁱ. Traditionally, the grafting of CDs onto relatively inert materials such as polypropylene (PP) has required long reaction times, harsh organic solvents and/or advanced equipment^{iii-v}, thus impeding the overall production process of the final product as well as raising the production costs. Simple and fast functionalization with CDs, requiring only basic equipment (dip, spray or kiss-roll) and limited amounts of non-harmful organic solvent, can be achieved by exploiting the self-assembly of amphiphilic CDs (ACD) on the surface of the material. ACDs are CDs modified with hydrophobic hydrocarbon chains rendering the molecule amphiphilic and allowing them to form nanoparticles in solution, as well as, self-assembled layers on appropriate surfaces. This class of CDs can be produced by various synthetic routes and tailored for specific coating conditions. The self-assembly of the process has proven to yield permanent hydrophilic (in aqueous solution) multilayers retaining the inclusion complex forming properties of the CD and the mechanical properties of the material (e.g. PP nonwovens). This process enables the production of CD functionalized surfaces with minimal change to existing production lines. Due to the simple process the method can be applied to a wide range of materials without the need for advanced equipment and synthesis steps.



POLY 650: Polydiacetylenyl β -cyclodextrin based smart vesicles for colorimetric assay of arginine and lysine

Eunae Cho², Hwanhee Kim¹, Youngjin Cho⁴, Seung R. Paik³, **Seunho Jung**^{1,2}, shjung@konkuk.ac.kr. (1) Department of Systems Biotechnology and Microbial Carbohydrate Resource Bank, Konkuk University, Seoul, Korea (the Republic of) (2) Center for Biotechnology Research in UBITA (CBRU), Institute for Ubiquitous Information Technology and Applications (UBITA), Konkuk University, Seoul, Korea (the Republic of) (3) School of Chemical and Biological Engineering, Institute of Chemical Processes, College of Engineering, Seoul National University, Seoul, Korea (the Republic of) (4) Departments of Food Science and Technology, BioChip Research Center, Hoseo University, Seoul, Korea (the Republic of)

Selective visualization of arginine and lysine has been explored among 20 amino acids using the hybrid conjugate of β -cyclodextrin (β -CD) and polydiacetylene (PDA). The mono pentacosyl-10,12-diyne aminomethyl group was successfully coupled to either the primary or the secondary face of β -CD, where mono-6-amino-6-deoxy- β -CD or mono-3-amino-3-deoxy- β -CD reacted with the N-hydroxysuccinimide ester of 10,12-pentacosadiynoic acid. In this combinatorial system, the cylindrical β -cyclodextrin functions as a channel for the introduction of the cationic amino acids to the artificial membrane. The membrane perturbation and aggregation by the target amino acids could be exclusively visualized as a blue to red color change based on the responsive polydiacetylene domain. These interesting findings demonstrated that the developed β -CD conjugated PDA system may offer a new method of cell-penetrating mechanism, a promising vector system, as well as impact the production industry of arginine or lysine.



Co-assembly of PCDA with β -CD to form β -CD functionalized PDA and the schematic illustration of β -CD conjugated PDA for arginine- and lysine-response.