

11th
National Graduate
Research Polymer
Conference



Baton
Rouge, LA

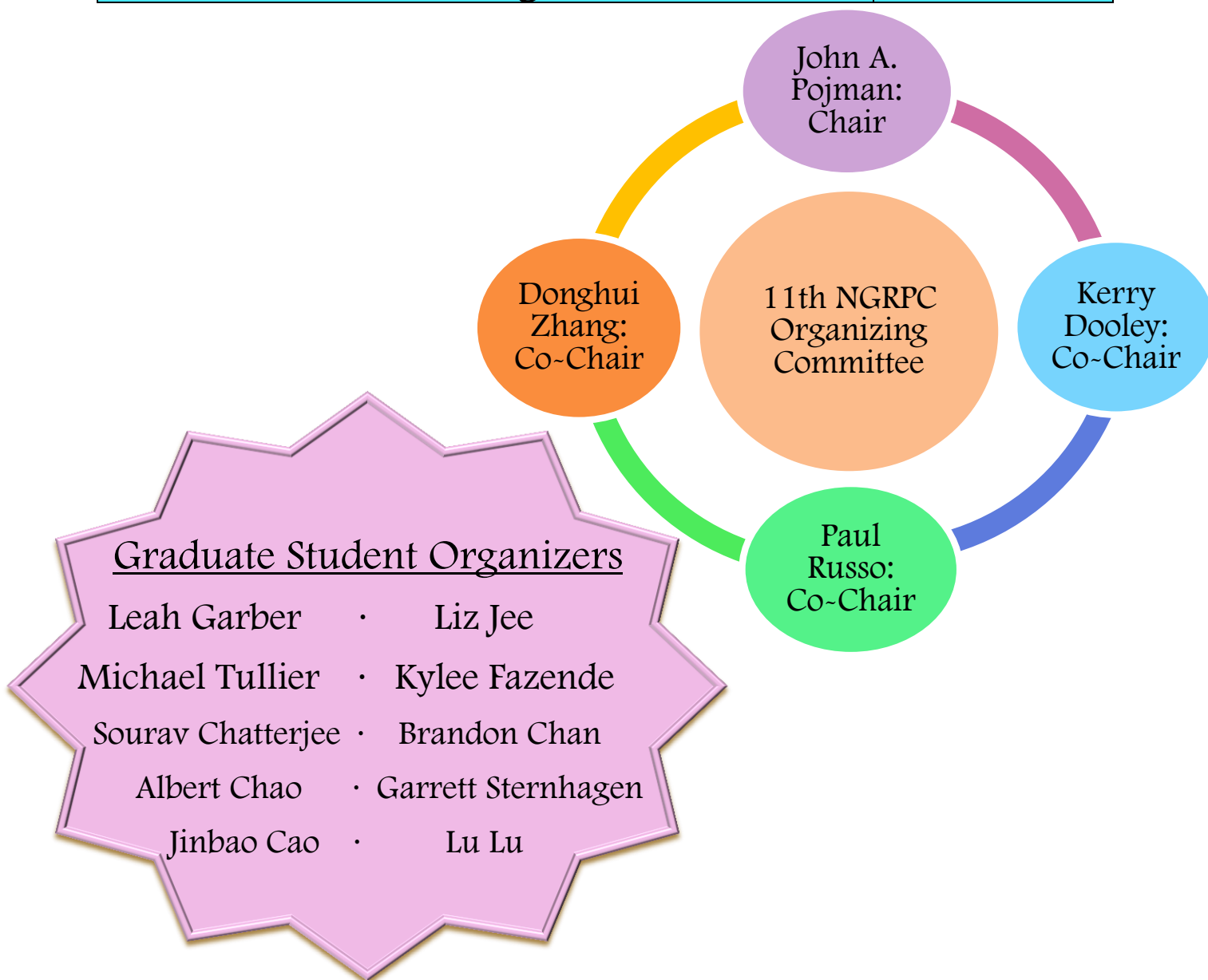


June 1-4
2014



Louisiana State University

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Welcome Letter from the Chair

Dear Conference Participants,

Letters such as this one are so often otiose that I hesitated to write one but I feel the need to welcome you, explain the philosophy of the meeting and thank those many people who have made this event possible.

Why have we gathered you at Louisiana State University in Baton Rouge, LA? We want you to do more than listen to many, many talks. We are inspired by Gordon Research Conferences where there are few talks, but much time for interaction. We want you to hear a few talks by top people in polymers but we want you to learn about career options in polymers. We mostly want you to meet your peers and make connections that can last a lifetime. The rise of rapid electronic communication has not reduced the need for face-to-face meetings but only increased it.

Of course, we also want you to see what a wonderful place LSU is for doing polymer research and what a delightful city Baton Rouge is.

We are fortunate to have financial support from LSU's Office of Research and Economic Development, the College of Science, the College of Engineering, the College of Agriculture and the Department of Chemistry.

Financial support and participation from industry has been essential to the organizing of this event. We want to thank all the representatives from industry but also offer special appreciation to Albemarle and the Applied Polymer Technology Extension Consortium.

This is a conference for students, organized by students. The Chemistry Graduate Students Association, the Student Affiliates of the American Chemical Society (SAACS), and the Macromolecular Studies Graduate Student Association (MSGSA) donated funds to support the conference. Students did most of the organizing and all of the logistical planning.

These four LSU Chemistry Graduate Students deserve our special thanks: Kylee Fazende, Leah Garber, Elizabeth Jee, and Michael Tullier. Jinbao Cao, Brandon Chan, Albert Chao, Sourav Chatterjee, Lu Lu, and Garrett Sternhagen also contributed significantly.

Sincerely,



John A. Pojman, Ph.D.

Professor

Important Notices from the Organizers

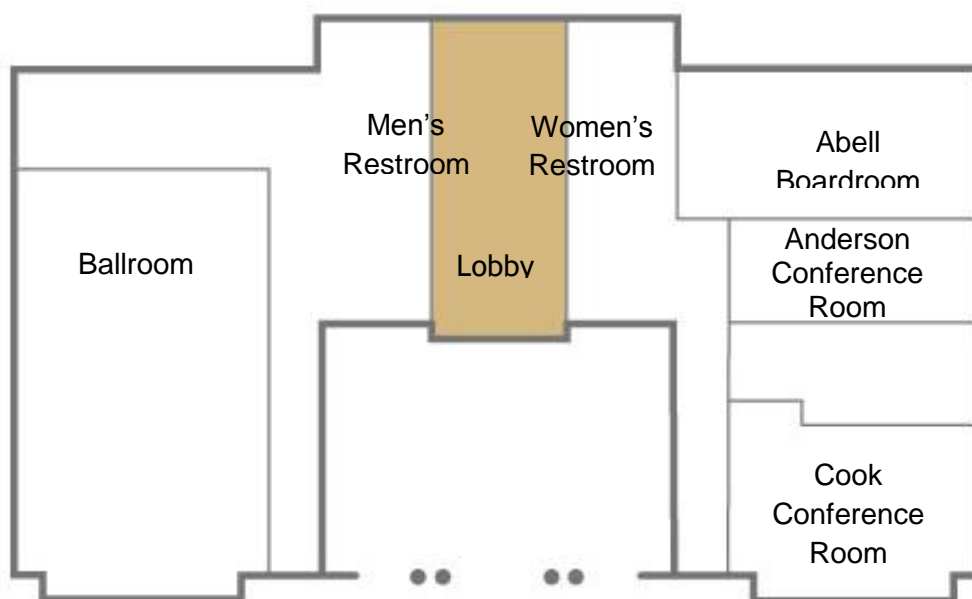
Hello, Participants! Thank you so much for attending the 11th National Graduate Research Polymer Conference on the beautiful LSU campus! We have a few important announcements we would like to bring to your attention.

- ❖ **Posters MUST be removed from the ballroom after lunch on Tuesday.** Any posters that are left after 2:45 PM will be discarded. Another group has rented the ballroom for Tuesday night and we must be cleared out of there by 3:00 PM.
- ❖ There will be a tour of LSU at 3:00 PM on Tuesday afternoon. **If you would like to participate please sign up** at the registration table or find a staff member to get your name on the list. We will meet in the lobby of the conference center and walk over there together.
- ❖ Dinner Tuesday night will be off campus at Mike Anderson's Seafood (1031 W. Lee Dr). **The bus will begin shuttling people there at 6:00 PM so please meet in the conference center lobby a few minutes before.** It will take two trips to get everyone there so we need to make sure 40 people get on each trip. We will **meet at the fountain** in front of the Lod Cook Conference Center.
- ❖ Interviews: If you submitted a résumé for industrial review, **they will contact you** to set up an interview time. Interviews will be held from 1:30 – 5:30 PM on Tuesday in the Anderson Conference Room.
- ❖ Please help yourself to coffee and drinks in the Cook Conference Room from 8:00 – 12:00 and 1:30 – 5:30 on both Monday and Tuesday. Snacks will be available at the times listed in the schedule.

We hope you enjoy the conference and please ask us if you have any questions or concerns. Now, make like a dendrimer and branch out!

-The 11th NGRPC Graduate Student Organizers

Floor Plan of Cook Conference Center



Sunday, June 1

Time	Event	Location
2:00 – 5:00 PM	Registration/ set up polymer art & posters	Lobby/ Ballroom
5:00 – 6:00 PM	Social Hour	
6:00 – 8:00 PM	Dinner – John A. Pojman (Welcome) & Sarah Morgan (Opening Session)	Ballroom
8:00 – 9:00 PM	Poster Session	

Monday, June 2

Time	Event	Location
8:30 – 9:15 AM	Scott Grayson (Tulane University) - Exploring the Effect of Polymer Architecture on Self-Assembly	Abell Boardroom
9:15 – 10:00 AM	John Droske (University Wisconsin – Stevens Point) - Sustainable Lifecycle Thermosetting Polyesters	
10:00 – 10:45 AM	Rafael Verduzco (Rice University) - Structure and Photovoltaic Performance of All-Conjugated Block Copolymers	
10:45 – 11:00 AM	Snack Break	Cook Conference Room
11:00 – 11:12 AM	Brandon A. Chan - 1,1,3,3-Tetramethylguanidine promoted ring-opening polymerization of <i>N</i> -carboxyanhydrides using an alcohol initiator	Abell Boardroom
11:12 – 11:24 AM	Ying Wang - Anisotropic Gel Electrolytes Composed of Ionic Liquids Distributed in Rigid Rod Polyelectrolytes	
11:24 – 11:36 AM	Emily A. Hoff - Thiol modification of air stable blocked isocyanate-functional polymers at room temperature	
11:36 – 11:48 AM	Caroline M. Grand - Tuning Polymer Solubility to Control Morphology in Organic Electronics	
11:48 – 12:00 PM	Mitchell L. Smith - New Synthetic Approaches to Poly(4-alkylthiazole)	
12:00 – 1:30 PM	Lunch	Ballroom
1:30 – 3:00 PM	How to get a job in academia and be successful – Julie Albert (Tulane), Sarah Morgan (USM), Evgueni Nesterov (LSU) John Droske (UWSP), Dave Norwood (SELU), & Donghui Zhang (LSU)	Abell Boardroom
3:00 – 3:30 PM	Snack Break	Cook Conference Room
3:30 – 4:30 PM	How to Get a Job in a Government Lab – Kathryn Beers (NIST) & H. N. Cheng (USDA)	Abell Boardroom
4:30 – 6:00 PM	Poster Session	Ballroom
6:00 – 7:30 PM	Dinner	
7:30 – 9:00 PM	Poster Session	

Tuesday, June 3

Time	Event	Location
8:30 – 9:15 AM	John Runnels - Introduction to Patent Law and Career Options	Abell Boardroom
9:15 – 10:00 AM	Dan S. Borné (Louisiana Chemical Association) - Renaissance: The Stunning Economic Impact of Louisiana's New Industrial Revolution	
10:00 – 10:10 AM	Snack Break	Cook Conference Room
10:10 – 10:22 AM	Brooks A. Abel - Versatile Molecular Brush Architectures for siRNA Delivery via Controlled Polymerization/Click Chemistry	Abell Boardroom
10:22 – 10:34 AM	An-Ting Chien - Multi-Functional Composite Fibers	
10:34 – 10:46 AM	Hailun Borjigin - Synthesis, Characterization and Gas Transport Properties of Isomeric Thermal Rearranged (TR) Polymer for Gas Separation Membranes	
10:46 – 10:58 AM	Sebla Onbulak - Synthesis of photo-cross-linkable core-shell bottlebrush copolymers and their transformation into well-defined organic nanotubes	
10:58 – 11:10 AM	Unique Luna - Assembly of Colloidal Clusters and Networks: A Dissipative Particle Dynamics Study	
11:10 – 11:22 AM	Kamlesh Bornani - Impact of microstructure on self-assembly of PCHD-based rod-coil diblock copolymers in solution and thin films	
11:22 – 11:34 AM	Jennifer N. Summerhill - Development and Testing of Intricate, Amphiphilic Crosslinked Hyperbranched Fluoropolymers as Anti-icing Coatings in Aerospace and Defense Applications	
11:34 – 11:46 AM	Achala Bhuwarka - Synthesis and characterization of new electron rich and electron deficient building blocks for organic photovoltaics	
11:46 – 11:58 AM	William K. Bell - Directly-Patternable Polyimide Dielectrics	
11:58 – 12:10 PM	Asem I. Abdulahad - Polyelectrolyte Complexes Based on Sodium Hyaluronate for <i>in vitro</i> Enhancement of Cellular Proliferation	
12:10 – 1:30 PM	Lunch	Ballroom
1:30 – 6:00 PM	Individual Interviews	Anderson Conference Room
1:30 – 2:45 PM	REMOVE POSTERS – All unclaimed posters will be discarded	Ballroom
1:30 – 2:50 PM	How to Get a Job in Industry – Sarah Morgan, Alex Norman (ExxonMobil), Andy Winesett (ExxonMobil), Chris Bounds (Albemarle), Scott A. Eastman (United Technologies Research Center), Claire Jalbert (3M), & Mark DeLong (SABIC)	Abell Boardroom
3:00 – 4:00 PM	Tour of LSU	Lobby
3:45 – 4:30 PM	Snack Break	Abell Boardroom
4:30 – 5:30 PM	How to Start a Polymer Student Group – Katrina Knauer & Brooks Abel	Abell Boardroom
6:00 – 6:30 PM	Take Bus to Mike Anderson's Restaurant for Dinner	Front Fountain
6:30 – 9:30 PM	Dinner	

Wednesday, June 4 – Depart

Oral Presentation Abstracts

Bio-inspired polymer materials design: surfaces and interfaces

Sarah E. Morgan, University of Southern Mississippi

It can be argued that most if not all polymer design is inspired by nature, and new discoveries in the mechanisms of biological systems continue to spawn technological advances. Protein assembly at surfaces and interfaces drives essential functions in biology, both those sustaining life and growth and those driving disease and infection. Hydrophobins, amphipathic fungal proteins with remarkable surface activity, play key role in the growth and reproduction of the species as well as in the surface recognition, attachment, and infection of hosts. These proteins self-assemble to form fibrillar, β -sheet structures, similar to the amyloid structures observed in neurodegenerative diseases such as Alzheimer's and Parkinson's, however, in the case of hydrophobin, the amyloid-like structures play a positive rather than a destructive role in the species. This talk will review our studies determining mechanisms of protein self-assembly at different interfaces and design of bio-inspired synthetic mimics of anti-microbial peptides (AMPs), which operate at the bacterial cell membrane. Hydrophobin protein self-assembly processes and their manipulation in the laboratory for potential biomedical applications will be explored. Self-assembly pathways for amyloid β (involved in Alzheimer's disease) and alpha-synuclein (involved in Parkinson's disease) as a function of different interfaces will be discussed. Synthesis and activity of AMPs mimics prepared via RAFT polymerization will be presented. Implications for high performance materials will be introduced.

Exploring the Effect of Polymer Architecture on Self-Assembly

Scott M. Grayson,* Boyu Zhang, Brittany K. Myers, Yi Wang, Dawanne E. Poree, Marco D. Giles

The self-assembly of linear block copolymers has been studied in detail and has demonstrated a range of practical applications, including drug delivery systems, surfactants, emulsifiers, etc. The effect of non-linear architectures on the self-assembly of amphiphilic polymers is less well understood. Research in our group has focused on the incorporation of cyclic or branched architectural motifs within the structure of amphiphilic polymers in order to clarify the role of macromolecular architecture in self-assembled systems.

Sustainable Lifecycle Thermosetting Polyesters

John P. Droske, University of Wisconsin-Stevens Point

Recent work in our group has focused on improving the mechanical and thermal properties of degradable aliphatic polyesters, such as PLA. This has been done by introducing thiol crosslinking sites in the main chain. The thiol pendant groups were incorporated by employing a solventless, “green” synthesis and afforded a series of bis(hydroxyalkyl)mercaptosuccinates. Thiols were utilized in an effort to affect crosslinking while maintaining the possibility of ready degradation, as the thiol groups form crosslinks via disulfide linkages, similar to cysteine moieties in proteins. The crosslink density in cured films was controlled by varying the mercaptosuccinic acid to succinic acid ratio in the uncured polyesters. Copolymers were characterized by DSC, GPC, FTIR, HNMR, and rheometry. In addition, cured resins were characterized for their ability to breakdown under hydrolytic and compost conditions.

Structure and Photovoltaic Performance of All-Conjugated Block Copolymers

Raphael Verduzco, Rice University

Organic electronic materials enable printable devices compatible with almost any surface. The success of organic light emitting diodes (OLEDs), used widely in smartphones and in development for large-area, transparent displays, represents a hallmark example. However, organic electronic materials have yet to make a substantial impact in areas such as energy storage, photovoltaics, and photocatalysis. These applications rely on efficient charge and energy transfer at an interface, which are poorly understood. In particular, organic photovoltaics (OPVs) rely on efficient charge separation of photoexcited states at the interface between two organic semiconductors. Here, we present the synthesis, characterization, and photovoltaic performance of all-conjugated block copolymers. All-conjugated block copolymers bring together distinct π -conjugated polymers, precluding large-scale phase separation and enabling improved control over the structure and properties at the interface of organic semiconductors. A series of all-conjugated block copolymers with a poly(3-hexylthiophene) (P3HT) polymer block are synthesized *via* a two-step route using Grignard Metathesis Polymerization with LiCl additive for the preparation of P3HT followed by Suzuki-Miyaura polycondensation. Film microstructure and crystallinity is analyzed using a combination of grazing-incidence X-ray scattering and differential scanning calorimetry. These measurements reveal a competitive crystallization process, and both polymer block ratio and processing conditions play an important role in determining thin film microstructure. All-conjugated block copolymers with P3HT as the p-type block and poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PFTBT) as the n-type block exhibit near 3 % power conversion efficiencies in solution-processed OPVs, without fullerene present. All-conjugated block copolymers thus have potential for use in solution-processible OPVs and for fundamental studies of interfacial charge and energy transfer processes.

1,1,3,3-Tetramethylguanidine promoted ring-opening polymerization of *N*-carboxyanhydrides using an alcohol initiator

Brandon A. Chan*, Sunting Xuan, and Donghui Zhang

N-butyl *N*-carboxyanhydride (Bu-NCA) was polymerized in THF to produce poly(*N*-butyl glycine) using benzyl alcohol initiator and 1,1,3,3-tetramethylguanidine organocatalyst. Poly(*N*-butyl glycine) (PNBG) with controlled polymer molecular weight ($M_n = 2.9 - 22.0$ kg/mol) and adequate size distribution (PDI = 1.04 - 1.23) can be obtained by controlling the initial monomer to initiator ratio. The reaction exhibits characteristics of a living polymerization, as evidenced by the linear increase of M_n with respect to conversion and successful chain extension experiments. MALDI-TOF MS and ^1H NMR analysis confirmed that the polymer chains were terminated with benzyl alcohol end groups. More sterically hindered alcohols appeared to initiate the polymerization less efficiently than less sterically hindered ones, resulting in more controlled M_n in the latter. The polymerization has been successfully extended towards the synthesis of block copolymers based on poly(ethylene glycol) and PNBG by using a PEG-OH initiator and TMG promoter.

Anisotropic Gel Electrolytes Composed of Ionic Liquids Distributed in Rigid Rod Polyelectrolytes

Ying Wang*, Jianwei Gao, Theo J. Dingemans, Louis A. Madsen

Anisotropic gels with high ion conductivity along a predetermined axis have been obtained by absorbing ionic liquids into aqueous rigid rod polyelectrolyte solutions of poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT). The anisotropy of the gels increases with the concentration of liquid crystalline polyelectrolyte solution, which is shown as faster ion diffusion and morphological alignment along the magnetic field as compared to the perpendicular directions. We will discuss the polymer matrix alignment, ion transport, and morphology of the anisotropic gel with varying composition (water content, IL content, and PBDT content) as measured by ^2H nuclear magnetic resonance (NMR) spectroscopy, pulsed-field-gradient NMR diffusometry, and single-crystal X-ray diffraction. By illustrating the formulation and the morphology of these gels, the polymer concentration and the IL content are considered as essential factors for flexible tailoring of the ion transport properties. These newly generated anisotropic ion gels show promise for applications in next generation batteries, fuel cell membranes, and optical sensors.

Thiol modification of air stable blocked isocyanate-functional polymers at room temperature

Emily A. Hoff*, Brooks A. Abel, Chase A. Tretbar, Charles L. McCormick, Derek L. Patton

Thiol-isocyanate “click” reactions have been used to synthesize complex polymer architectures, otherwise difficult or impossible to achieve, due to their high efficiency and versatility. Direct polymerization of isocyanate-functional monomers has been achieved with controlled radical polymerizations, both in solution and on surfaces, for precisely engineered modification platforms with highly reactive side chains. Despite the success of these strategies, the inherent reactivity of isocyanates still leads to adverse side reactions, such as hydrolysis, that are difficult to suppress thereby limiting the usefulness isocyanate functional polymers.

We report the polymerization and modification of blocked isocyanate methacrylate monomers. The isocyanate functional group allows facile modification of the side chains by thiol-isocyanate “click” reactions, while the blocking agent reduces detrimental side reactions. We investigate various blocking agents and the impact of the blocking agent’s structure on deblocking conditions such that stable polymers that can react efficiently with various thiols at room temperature are synthesized.

Tuning Polymer Solubility to Control Morphology in Organic Electronics

Caroline M. Grand*, Chi K. Lo, Wojciech Zajączkowski, Nabankur Deb, David G. Bucknall, Wojciech Pisula, Klaus Müllen, John R. Reynolds

Organic photovoltaics (OPVs) utilizing conjugated polymers are studied as light-weight alternatives to silicon devices. To achieve suitable efficiencies in OPVs, blends of polymer and fullerene are solution processed to form an interpenetrating network thin-film. In this contribution we discuss the hypothesis that tuning aggregation of polymers in solution via structure or processing additives leads to a predictable morphology in the thin-film. We have synthesized and characterized a family of poly(terthiophene-co-isoindigo) with varying side chains. Through this structural modification we are able to control the solution properties with preliminary results highlighting the importance of polymer solubility as a way to control domain size as characterized by GIWAXS, AFM, and TEM. The morphology can further be tuned by processing additives, which are shown to also have in effect on the polymer behavior in the casting solution. The changes in morphology are correlated to carrier transport in transistors and to OPV device parameters.

New Synthetic Approaches to Poly(4-alkylthiazole)

Mitchell L. Smith* and Anne J. McNeil

Conjugated polymers have numerous applications, including solar cells, light-emitting diodes, and field-effect transistors. Living, chain-growth polymerization methods afford polymers with well-defined chain lengths and monomer sequences, which influence their physical and electronic properties. However, there are few examples of chain-growth polymerizations with electron-deficient monomers. This presentation will describe our efforts to develop a living, chain-growth synthetic method for accessing poly(4-alkylthiazole). Our results indicate that thiazole presents challenges at the monomer activation, initiation, and propagation stages of the conventional Kumada catalyst-transfer polycondensation. By modifying reaction conditions and monomer structure, and with the use of a new class of nickel catalyst, high-molecular-weight polythiazole was obtained, albeit in a non-living fashion. This presentation will also highlight our efforts to prepare poly(4-alkylthiazole) using direct arylation polymerization. We show that this method readily affords oligomers in a step-growth fashion, but achieving high molecular weights remains a challenge. While thiazole polymerization presents difficulties not seen for analogous electron-rich monomers, we show that these difficulties can be systematically overcome.

Renaissance: The Stunning Economic Impact of Louisiana's New Industrial Revolution

Dane Borné, Louisiana Chemical Association

After decades of growth followed by years of shrinkage, Louisiana's petrochemical industry is on the leading edge of a tsunami of investment that will provide thousands of high-paying jobs for its citizens. The miracle of natural gas fracking turned a bleak future into a promising one and is energizing America's manufacturing engine. The result will be generational in nature.

Versatile Molecular Brush Architectures for siRNA Delivery via Controlled Polymerization/Click Chemistry

Brooks A. Abel* and Charles L. McCormick

Stimuli-responsive molecular brushes are being prepared to selectively disassemble in response to changes in redox potential. We report on the preparation of macromonomers via post-polymerization modification of polymers produced by reversible addition-fragmentation chain transfer (RAFT) polymerization with novel maleimide- and methanethiosulfonate-functional oxanorbornenes. Subsequent polymerization of oxanorbornene-functional macromonomers by ring opening metathesis polymerization (ROMP) affords the corresponding molecular brushes in a controlled fashion. This versatile route facilitates use of “off-the-shelf” styrenic-, acrylamido-, and acrylate-based RAFT polymers prepared under conditions specific to the monomer-type (e.g. polymerization in aqueous or organic media) for convenient synthesis of a variety of molecular brush polymers. Polymer brushes containing disulfide-linked side chains were shown to selectively and rapidly disassemble under intracellular conditions making them potentially useful as polymeric nanotherapeutics.

Multi-Functional Composite Fibers

An-Ting Chien* and Satish Kumar

Nano-fillers can exhibit various specific properties, such as mechanical, electrical, thermal, or magnetic properties. By introducing these properties into polymer with the original polymer characteristics, including flexibility, light-weight, and ease-of-use, these new nano-filler/polymer composite can be used for multi-functional fibers as the next generation textile or fabrics. In this research, polyacrylonitrile (PAN) is adopted as the main polymer incorporated with different nano-fillers, such as carbon nanotube (CNT), iron oxide nanoparticle (Fe_3O_4), and graphene nano ribbon (GNR). Using gel-spinning technology, PAN-based composite fibers are fabricated in single- or bi-component fibers with a fiber diameter as small as 15 μm and strong mechanical properties. With controllable electrical and thermal conductivity, composite fibers can be applied for wearable electronic, sensor, or active heating fibers. In addition, magnetic composite fiber with superparamagnetic properties can be applied for actuator, inductors, EMI shielding, or microwave absorption.

Synthesis, Characterization and Gas Transport Properties of Isomeric Thermal Rearranged (TR) Polymer for Gas Separation Membranes

¹Hailun Borjigin*, ²Qiang Liu, ¹Kyle Gaines, ²Benny D Freeman, ¹Sue J Mecham and ¹James E. McGrath*

Two Soluble Isomeric aromatic polyimides containing *ortho*-positioned functional groups (hydroxyl or acetate groups) were synthesized for thermal rearrangement (TR) processing to complex partially crosslinked polybenzoxazoles (PBOs). The latter have been shown to have great potential for highly selective CO₂/CH₄ separation membranes applications. Fully imidized film forming polyimides with high-molecular-weight were afforded via a 'one-pot' solution imidization technique utilizing the ester-acid (EA) method starting from 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) with two isomeric monomers, 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) and 3,3'-diamino-4,4'-dihydroxybiphenyl (AHB). The two isomeric polyimides were comprehensively characterized with respect to chemical structure, molecular weight, thermal and mechanical properties by NMR, DSC, and TGA. The synthesis, characterization, film casting, thermal treatment, gas transport properties of high molecular weight polyimides and the isomeric effect on the properties of the polymers will be discussed.

Synthesis of photo-cross-linkable core-shell bottlebrush copolymers and their transformation into well-defined organic nanotubes

Sebla Onbulak* and Javid Rzayev

Bottlebrush copolymers are comb-like macromolecules, which adopt cylindrical shape in solutions due to densely grafted polymeric side chains. Cylindrical bottlebrushes can be transformed into organic nanotubes via intramolecular cross-linking of the shell layer and degradation of the inner core. Organic nanotubes with controlled nanometer dimensions can be used in selective encapsulation and purification of nanomaterials. Herein, we report a new method for the preparation of organic nanotubes with controlled dimensions from photo-cross-linkable core-shell bottlebrush copolymers composed of an inner degradable polylactide block and an outer block containing photoactive coumarin functionalities. Upon UV irradiation at 365 nm, the peripheral coumarin functionalities undergo [2+2] cyclodimerization to form shell-cross-linked bottlebrushes. Subsequent degradation of the polylactide block provides hollow cylindrical nanoparticles held together by dimerized coumarin units in the shell layer. The length and the inner diameter of the nanotubes are determined by the length of the backbone and the polymeric side chains, respectively.

Assembly of Colloidal Clusters and Networks: A Dissipative Particle Dynamics Study

Unique Luna^{1*}, William Meyer², Brian Motil², Peter Koenig³, Matthew Lynch³, and Joao Maia¹

It is envisioned that stability in colloidal-structured products requires long-range connectivity of aggregate particulate strands that bare stress in the presence of gravity. The objective of this work is two-fold: 1) understand the factors that contribute to formation of initial strand structures, which spontaneously form after mixing particulate systems at different shear rates and 2) understand the factors that govern local- and long-range motions of the constitute particles in these strands that lead to weaken of strands when gravitational stress is applied. There is interest in bimodal spherical and asymmetric particulate systems where the inter-particle potential is governed by polymer-based (depletion) interactions. This work uses Core-Modified Dissipative Particles Dynamics (DPD) to simulate the colloidal gel network. The purpose of this paper is to show our progress with using Core-Modified DPD to simulate the characteristic structures assembled in the limit of strong interaction forces (non-reversible binding) for mono-dispersed mixtures of spheres.

Impact of microstructure on self-assembly of PCHD-based rod-coil diblock copolymers in solution and thin films.

Kamlesh Bornani^{1}, Xu Wang, Jesse Davis, Xiaojun Wang, Juan Pablo Hinestrosa, Jimmy W. Mays¹ and S. Michael Kilbey II^{1,2}*

Understanding the several parameters that control the micro phase separation of rod-coil block copolymers is interesting because, the interrelationship between morphology and properties of the formed micellar structures can be ascertained. The packing constraints imposed by the rigidity of the rod component influences the morphology of the formed micelles. With this assumption, we have studied the impact of tunable rigidity on the self-assembly of poly(styrene)-b-poly(1,3-cyclohexadiene) copolymers. Rigidity of PCHD was tuned by varying the ratio of 1,4/1,2 linkages (chain microstructure) between the cyclohexenyl rings in the backbone. Glass transition temperatures of three different microstructural ratios 90/10, 70/30 and 50/50 were measured by differential scanning calorimetry, which reflected differences in conformation and packing of PCHD chains. Light scattering analysis and imaging using electron microscopy and atomic force microscopy revealed the influence of changing persistence length of PCHD on the micelle structure of PS-b-PCHDs.

Development and Testing of Intricate, Amphiphilic Crosslinked Hyperbranched Fluoropolymers as Anti-icing Coatings in Aerospace and Defense Applications

Jennifer N. Summerhill,* Kevin A. Pollack, Jeffery E. Raymond, Karen L. Wooley

This work aims to develop robust, dynamic, anti-icing coatings for aerospace applications through the variation of two main material characteristics including hydrophobicity and thermo-responsive molecular ordering. We have previously synthesized crosslinked networks comprised of hyperbranched fluoropolymers (HBFP) and poly(ethylene glycol) (PEG), which demonstrated superb anti-biofouling capabilities credited to their amphiphilic morphology, nanoscopic surface topography and dynamic surface reorganization. By extension, this research seeks to expand the application of these materials by exploiting their characteristics for the purpose of inhibiting the crystalline organization of water molecules, and subsequently, preventing the formation of ice. Differential scanning calorimetry (DSC) data show that the materials presented here exhibit inhibition of ice formation, as determined from reductions in the water melting transition temperatures (T_m). The advances of these materials will be discussed in terms of formulation, the structure-function relationships driving the empirically-derived T_m and the final effect on the water phase at the surface.

Synthesis and characterization of new electron rich and electron deficient building blocks for organic photovoltaics

Achala Bhuwalka*, Monique D. Ewan, Jared Mike, Malika Jeffries-EL

Organic semiconductors have showed significant promise as alternatives to silicon based photovoltaic cells. One of the most effective strategies involves the use of small molecules and conjugated polymers that contain alternating electron-rich and electron-deficient units for use as donor materials in organic photovoltaic cells, organic light emitting diodes and organic field-effect transistors. Although tremendous progress has been made in the field, new electron-rich and electron-poor units are needed to further improve device efficiencies. Azoles have recently generated interest for use as electron-deficient building blocks. Incorporation of benzobisazoles and pyridalithiadiazoles as electron-deficient units for use in conjugated polymers and small molecules has shown much promise with PCE's exceeding 3% and 6% respectively. The synthesis and characterization of new electron rich building blocks and electron deficient azoles for use in organic photovoltaic cells will be presented.

Directly-Patternable Polyimide Dielectrics

William K. Bell*, Andrew R. Dick, Brendan L. Luke, C. Grant Willson

In integrated circuit manufacturing there is a need for polymers of low dielectric constant (low-k). Bridging the gap between the high-value silicon chip and circuit board is a substrate comprising alternating layers of metal and polymer dielectric. This integration of disparate materials requires matching of properties such as thermal expansivity. Due to cost concerns, direct photo-patternability is also desirable. To address this need, PMDA-TFMB, a low-k polyimide, was evaluated. This material demonstrates a dielectric constant below 3.0 and a thermal expansion coefficient of approximately 7 ppm/°C. Direct patternability is realized by leveraging the catalytic effect of amines on the imidization reaction. Addition of a photolabile amine to the PMDA-TFMB precursor allows for resolution of features below 10 microns. An ancillary benefit of this methodology is reduced cure temperature (<200 °C), a traditional drawback of polyimides. This combination of material and lithographic properties make PMDA-TFMB a strong candidate for this application.

Polyelectrolyte Complexes Based on Sodium Hyaluronate for *in vitro* Enhancement of Cellular Proliferation

Asem I. Abdulahad*, Heather Froggatt, Robert Cole Gage, and Timothy E. Long

Mucoadhesive nanoparticles are studied exhaustively for their potential as transmucosal carriers. A potential limitation of mucoadhesive nanoparticles is the possibility of irreversible binding to the mucus network, which can result in either expulsion of the particles by the mucus or degradation of the particles prior to reaching mucosal tissues. Employing non-mucoadhesive, or muco-inert, nanoparticles presents an alternative route to transmucosal delivery of nanoparticle carriers to protected mucosal tissues. In this work, the anionic character of sodium hyaluronate and PEGylated sodium hyaluronate was exploited to prepare a ternary polyelectrolyte complexes with protonated poly(2-dimethylaminoethyl methacrylate). PEGylation in polyelectrolyte complexes resulted in a significant increase in the colloidal stability of these nanoparticles, while providing enhanced cellular proliferation comparable to unbound low molecular weight hyaluronic acid. Improvements in particle stability in the presence of serum proteins suggest that this ternary polyelectrolyte complex formulation provides a viable candidate for regenerating mucus protected tissues.

Poster Presentation Abstracts

1. Synthesis and Characterization of UV-Crosslinkable Disulfonated Poly(arylene ether sulfone) Oligomers

Ali Nebipasagi*¹, Benjamin J. Sundell, Ozma R. Lane, Sue J. Mecham, and James E. McGrath

Disulfonated bisphenol-A based poly (arylene ether sulfone) random copolymers with controlled oligomeric molecular weights were synthesized via nucleophilic aromatic substitution reaction. meta-Aminophenol was selected as mono functional end-capper both to control the oligomer molecular weights and to achieve reactive amine endgroups. Subsequently meta-Aminophenol end-capped oligomers were reacted with 2- propenoyl chloride (acryloyl chloride) to obtain novel crosslinkable oligomers with acrylamide functionality. The oligomer structures were identified, and the degree of sulfonation and molecular weights (M_n) were calculated via endgroup analysis using ^1H NMR spectroscopy. The acrylamide terminated oligomers were crosslinked under UV radiation in the presence of multifunctional acrylates and UV initiators. Transparent ductile films were obtained with high gel fractions. Thin film composite membranes were prepared via photo-crosslinking of oligomers with high degree of sulfonation from aqueous or methanol-water solutions. Crosslinking of disulfonated poly (arylene ether sulfone) copolymers limited the water uptake and swelling of these hydrophilic materials, which is expected to enhance membrane properties. AFM micrograph showed thin film composites with a smooth membrane surface along with the hydrophilic surface were prepared which is expected to decrease fouling of the membrane. Synthesis of oligomers, membrane fabrication and transport properties will be discussed.

2. Alternating Stilbene-Containing Copolymers: Stimuli Responsive Semi-rigid Polyelectrolytes

Alice M. Savage,* Elizabeth Ulrich, Caitlyn Kost, Zach Kiernan, and S. Richard Turner

Due to the alternating sequences of stilbene-containing copolymers and their sterically crowded backbone, these semi-rigid copolymers demonstrate stimuli-responsive solution properties. Stilbene-containing polyampholytes and polyanions were synthesized from organic-soluble precursors by using conventional radical and reversible addition fragmentation chain transfer (RAFT) polymerization techniques. Solution shear rheology, and pH titrations were used to evaluate the physical solution behavior of the precisely defined stilbene-containing polyanions and to calculate the statistical segment lengths. Stilbene-containing, semi-rigid copolymers were also, incorporated into double hydrophilic block copolymers. These polyampholytes exhibited a "like-charge" attraction response in salt solutions where polymer aggregate size increased with an increase in $[\text{NaCl}]$. pH and salt responsiveness of these block copolymers were investigated with respect to charge density, molar mass, and polymer composition.

3. RAFT synthesis of pH responsive diblock copolymers for gene delivery

Annie K. McClellan*, Adam E. Smith

A wide range of gene delivery vehicles have been studied for their efficacy; however, the safe transport of nucleic acids remains a challenge for the further development of gene delivery as a clinical therapy. With advances in controlled radical polymerization techniques, reversible addition-fragmentation chain transfer (RAFT) polymerization in particular, the synthesis of precise polymeric architectures needed for gene delivery vehicles is now possible. In this work, a series of diblock copolymers were prepared utilizing an oligo(ethylene glycol) methyl ether methacrylate (OEGMA) stabilizing block and a cationic block derived from a family of pH-responsive, tertiary amine-containing methacrylates capable of complexing negatively charged nucleic acids. This series of AB diblock copolymers were investigated to determine the effect of polymer composition on nucleic acid binding and delivery, polymer-nucleic acid complex stability, cell toxicity, and gene silencing in vitro.

4. Printing Novel Polymeric Structures: From Bioinspired Pluronics to Conducting Poly(Ionic Liquids)

Alison R. Schultz*, Philip M. Lambert, Musan Zhang, Courtney P. Long, Niki Camateros-Mann, Christopher Williams, and Timothy E. Long

ask projection microstereolithography (MP μ SL) uses a dynamic mask and focusing optics to digitally pattern UV light and selectively cure tailored polymeric materials. This lecture will introduce the potential synergy between MP μ SL, 3D printed block copolymers, and 3D printed ionic liquid networks/gels wherein additional complex polymer morphologies configure structural performance of designed objects. Capable of creating 3D parts with features smaller than 10 μ m, MP μ SL is an ideal system for fabricating tissue engineering scaffolds and complex microelectromechanical objects. A novel diacrylate functionalized pluronic L-31 block copolymer was processed with MP μ SL, and the resulting 3D structures were analyzed for accuracy, mechanical strength, and biocompatibility to assess feasibility for use in tissue engineering scaffold fabrication. Preliminary scaffold parts are presented to validate experimental results. Additionally, a conducting phosphonium ionic liquid was also fabricated into 3D structures, revealing potential for enhanced thermal stability and ion conductivity in microelectromechanical objects.

5. Amorphous Poly(Arylene Ether Ketone)s as Materials for Higher Temperature Nano-Layered Capacitors Systems

Andrew T Shaver*, Matt Mackey, Yu Chen, Eric Baer, and James E. McGrath

Poly (vinylidene fluoride) (PVDF) has shown promise as a dielectric material in capacitors due to its good properties and high dielectric constant. In order to increase its breakdown strength, hysteresis performance and frequency stability Prof Baer and coworkers at Case Western(1) have developed nano-layered PVDF with other engineering thermoplastics such as polycarbonate and polysulfone. Our group is synthesizing both fluorinated and hydrocarbon based amorphous poly (arylene ether ketone) (PEAK) systems derived from 4,4'-difluorobenzophenone and either 6F bisphenol or bisphenol-A by nucleophilic step polymerization. These materials are amorphous, ductile, transparent polymeric materials which are capable of being nano-layered with PVDF. The PEAK system was prepared to a controlled Mn and was matched for processability with PVDF to have a comparable melt viscosity, which allowed processing into a 32 layered polymer films. The PAEK system showed enhanced breakdown strength, hysteresis, dielectric and Tan δ performance and this work is continuing.

6. Deep-eutectic solvents as support in the non-aqueous synthesis of macroporous polyHIPES

Arturo Carranza*, John A. Pojman, and Josué D. Mota-Morales

Emerging challenges in sustainable development and an increasing demand for functional materials have geared contemporary research to design bioinspired systems. Deep-eutectic solvents (DESs) are a new generation of green solvents comprised of a eutectic mixture with a drastically depressed freezing point than its original components. DES are amenable systems with many desirable features including low cost, biocompatibility, negligible vapor pressure, high thermal and chemical stabilities, and their ability to dissolve both ionic and organic solutes. High internal phase emulsions (HIPES) are highly viscous emulsions where the internal volume fraction accounts for more than 74% dispersed within a minor continuous phase. The introduction of a polymerizable continuous phase and subsequent removal of a DES affords the non-aqueous synthesis of highly porous materials with a wide range of applications.

7. Segmented Mesogen-containing Copolyesters for Electronic and Aerospace Applications

Ashley M. Nelson*, Gregory Fahs, Robert B. Moore, and Timothy E. Long

Thermotropic liquid crystalline polyesters possess many desirable properties such as a high modulus, high thermal and dimensional stability, and shear thinning due to the anisotropic morphology. In an effort to expand the range of potential applications and investigate structure-property-morphology relationships, segmented mesogen-containing copolyesters were synthesized using a one-pot melt transesterification strategy. A flexible oligomeric Pluronic® spacer was successfully incorporated at various weight percents with a known mesogen, dimethyl biphenyl-4,4'-dicarboxylate, and 1,6-hexanediol spacer. ¹H NMR confirmed the polymer structure and SAXS revealed a phase-separated morphology. Varying the amount of soft segment resulted in tunable thermal and thermomechanical properties with maximum melting temperatures increasing from 184 °C to 216 °C with 60 to 40 weight % soft segment incorporation. The morphology of these copolyesters, crystallization and ability to maintain a liquid crystalline morphology despite the presence of a flexible spacer, was also investigated with WAXD and POM respectively.

8. Synthesis, Oxidation and Crosslinking of Tetramethyl Bisphenol F (TMBPF)-Based Polymers for Oxygen/Nitrogen Gas Separations

Benjamin J. Sundell*, Andrew T. Shaver, Qiang Liu, Ali Nebipasagil, Priya Pisipati, Sue J. Mecham, Benny D. Freeman, James E. McGrath

Gas purification membranes were first commercialized in the late 1970s and are of particular interest in the 21st century due to growing energy costs, making them competitive against amine adsorption and cryogenic distillation. Novel, crosslinkable poly(arylene ether)s for gas purification membranes have been synthesized based on a tetramethyl bisphenol f (TMBPF) monomer. The polymers include a moiety capable of several oxidation reactions and UV crosslinking. Structural identification was confirmed by ¹H-NMR and IR spectroscopy and molecular weights were determined by SEC. Two oxidation reactions of the polymers were identified, one by chemical treatment using Oxone and KBr and one by elevated thermal treatment in air. DSC and TGA were used for thermal characterization, and TGA, ¹H-NMR and ATR-FTIR revealed the progress of the thermal oxidation reactions. Both polymers produced tough, ductile films and initial gas transport properties of an as synthesized and crosslinked polymer are provided.

9. Hydrophobically Modified Chitosan Coated PLGA Film for Liposome Capture; Promising Controlled Drug Release Technique

Benjawan Boonkaew*, Mary S. Osetinsky, Rubo Zheng, Jibao He, Vijay T. John

This research introduces a simple method to capture liposomes on a PLGA film. Hydrophobically modified chitosan (HMC), which acts as a linker between PLGA and liposomes, was casted on the PLGA film in order to capture liposomes. The proposed mechanism for liposome capture involves hydrophobic-hydrophobic interactions of the alkyl groups of HM-chitosan that insert themselves into the bilayer of liposomes. Liposomes capture was monitored by visualization on optical and cryo-SEM microscopy. Confocal Z-stack images showed labeled liposome captured on the fluorescent HM-chitosan layer. This film was proposed for use in controlling liposome release. As the polymer degrades over time, HM-chitosan should dissolve into solution, releasing drug containing liposomes. The liposomes should then disperse in solution and deliver drugs to cells. More studies on the mechanism of liposome release and the polymer degradation time course are required to support the new promising system for drug release.

10. Efficient Preparation of High Purity Homo-arm and Mikto-arm Poly(ethylene Glycol) Stars Using Stepwise Azide-Alkyne Click Chemistry

Boyu Zhang*, Hong Zhang, Ravinder Elupula, Alina M. Alb, and Scott M. Grayson

Multi-arms polymer, which consist of multiple linear chains connected to a central core, have a unique set of properties (e.g. crystalline, mechanical, and viscoelastic properties,) when compared with their linear analogs due to their multi-arm structure, compact shape and multiplicity of end groups. In this work, a stepwise “graft onto” approach to prepare high purity homo-arm and mikto-arm PEG stars by the combination of epoxide ring opening and azide-alkyne coupling reactions was reported. First, monohydroxy-PEG was modified via epoxide chemistry to bear one hydroxyl and one azide functionality at the same end. An alkyne functionalized PEG chain was then coupled to the azide. Subsequently, the remaining hydroxyl could be reactivated to an azide again and again to enable stepwise addition of alkyne functionalized polymer arms. This stepwise approach enables the preparation of star molecules with an exact number of arms and a specific degree of polymerization for each arm. Detailed characterization confirmed the high purity of multi-arm polyethylene glycol products.

11. Determination of Polyethylene Glycol End Group Functionalities and Confirmation of their Selective Modifications using Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

Boyu Zhang*, Hong Zhang, Brittany Myers, Ravinder Elupula, Janarthanan Jayawickramarajah and Scott M. Grayson

The end groups of linear macromolecules play a critical role in the resulting physical properties of the polymer and can be coupled to other macromolecules to construct more complex polymer architectures. However, traditional characterization techniques such as GPC, NMR, and infrared spectroscopy have severe limitations when determining the efficiency of end group transformations because any signal that originates from the end groups tends to be overwhelmed by the larger signal from the backbone. In this work, MALDI-TOF mass spectrometry was used to study end groups of linear polyethylene glycols. In particular, amine, hydroxyl and thiol end groups are investigated because these nucleophilic moieties are among the most common within biological and synthetic macromolecules. Through comparative characterization of alcohol, amine, and thiol end groups, the exact structures of various polymers were identification of these end groups could be confirmed by selective and quantitative modification.

12. Design and Synthesis of Highly Functionalized Benzobisoxazole Copolymers

Brian Tlach*, Aimeé Tomlinson, Ramiro Chavez, and Malika Jeffries-EL

Organic semiconducting materials have a distinct advantage over their inorganic counterparts in that their optoelectronic and physical properties can be tuned by chemical synthesis. A common class of organic semiconducting materials is copolymers consisting of alternating donor and accepting monomers. In our research group, we have extensively studied benzobisoxazoles as a versatile acceptor. Benzobisoxazoles are unique in that they have two axes that can be functionalized or used for polymerization to yield a large class of diverse benzobisoxazole copolymers. By simply switching the main conjugation axis, polymers with new properties are obtained. Furthermore, by functionalizing the non-polymerization axis, the polymer properties can be further be tuned allowing for their use in a wide-range of semiconducting devices.

13. MIP Hydrogel for DNA Detection

Britney Hebert*, Wei Bai, and David Spivak

Molecularly Imprinted Polymers (MIPs) are known to specifically bind to a template molecule that it was imprinted with through molecular interactions. A relatively new and growing area for MIPs involves hydrogels. The imprinting effect for hydrogels can be achieved by using an aptamer-based bioimprinting strategy. Polymerizable aptamers that specifically bind to a target molecule are incorporated with the target and copolymerized with additional monomers to create a multi-aptamer binding site that shrinks in the presence of the target. The MIP gels have been successfully applied to detecting proteins and a virus. A technique to make these gels involves grafting of a pattern by polymerizing in a lithographic mold. The mold gives the gel grooves that change distance upon addition or removal of the target caused by a shrinking/swelling effect. The molecular recognition is measured by observing the change in distance of the diffraction pattern when a laser is passed through the gel. To build upon past research, the MIP hydrogel will be applied to detecting a DNA mimic of mRNA-21. This mRNA-21 is a 22mer micro RNA and is known to be a cancer biomarker. The aptamers used for this system are two split complementary DNA strands that will hybridize to the DNA when it is added. The goal of this project is to have naked-eye detection of the mRNA-21 mimic at low concentrations.

14. Synthesis and Characterization of Amphiphilic Branched Polymers Based on Poly(ethylene glycol)

Brittany K. Myers*, Scott M. Grayson

Guest molecule encapsulation has garnered a lot of attention recently. Small molecule amphiphiles are known to yield micelles with limited stability and even amphiphilic linear polymers are susceptible to disaggregation at low concentrations. For this reason, branched, covalently-bound amphiphilic units are attractive. MALDI-ToF MS was used to characterize these well-defined amphiphiles which were prepared from a hydrophilic polyethylene glycol (PEG) segment, dendritic bis-MPA branching units, and a hydrophobic component such as lauric acid. These molecules are attractive both fundamentally and practically because they can be used to probe the structural parameters which define aggregation behavior and encapsulation. Furthermore, these molecules have potential to be used as drug delivery vehicles, sequestering agents, and surfactants. For biological applications, purity of the materials is paramount and MALDI-ToF MS represents a valuable technique for detailed monitoring of these dendronization and coupling reactions as well as characterization of the products.

15. Probing Lithium and Counterion Transport in a Crosslinked Polymer-Gel Electrolyte

Bryce E. Kidd*, Friedrich W. Steuber, Scott J. Forbey, Robert B. Moore, and Louis A. Madsen

Understanding small molecule and ion transport properties on the nm – μm lengthscale within polymer-based electrolytes is essential for designing next generation lithium-ion batteries. Nuclear magnetic resonance (NMR) techniques, such as spin-spin relaxometry (T_2) and pulsed-field-gradient (PFG) diffusometry, enable the comprehension of chemically specific transport and interactions in a family of electrospun and cross-linked polyethylene oxide (PEO) fiber mats swollen with $\text{Li}(\text{OTf})$ and $\text{Li}(\text{ClO}_4)$ salts. Bimodal T_2 relaxation times suggest that lithium exists in two environments, which are attributed to polymer-solvent-lithium and pure solvent-lithium interactions, respectively. Moreover, we use the Arrhenius activation energy to evaluate how local intermolecular interactions on ~ 1 nm lengthscales and ~ 1 ps timescales influence transport mechanisms. Increasing cross-link density does not influence ion transport, thus a mechanically stable matrix that dually serves as a battery separator and ion conduction medium is achieved.

16. Rheological and Mechanical Behavior of Highly Loaded Cellulose Nanocrystal/ Poly(vinyl alcohol) Composite Hydrogels

Caitlin Meree* and Meisha Shofner

The objective of this research is to characterize the viscoelastic and mechanical behavior of cellulose nanocrystal /poly(vinyl alcohol) (CNC/PVA) hydrogels to determine the effect of incorporating these renewable rigid fillers into a semicrystalline biodegradable matrix. Neat PVA aqueous solutions and CNC-loaded PVA aqueous gels were studied through dynamic rheological and mechanical experiments. Hydrogels with filler loadings up to 67% in 15 wt.% solution and films with up to 67% CNCs were produced. The results of these experiments indicated that the addition of CNCs increased the viscosity and shear thinning character of the polymer solution as well as mechanical performance. The measurements showed the CNC network formed in the hydrogel at sufficiently high filler due to a convergence of yield stress values was observed regardless of polymer molecular weight. The presented data allow for increased understanding of CNC/PVA nanocomposite interaction for future water-based processing applications.

17. Conditions for the Formation of P3HT Organogel During Spin-Coating: Tuning Electrical Properties of Thin Films

Cameron S. Lee*, Adam Holt, Wen Yin, Mark D. Dadmun

A thorough understanding of the structure of thin active layers used in organic photovoltaics (OPVs) and a related electronic device is nontrivial and difficult to acquire. We have developed a novel static light scattering instrument to monitor the onset of P3HT organogel formation in situ during spin coating. We demonstrate the ability to form aggregated networks on the micron scale directly from a dissolved solution of P3HT on spin-coated substrates. Using this novel apparatus, specific processing conditions, such as solvent choice and composition, are correlated to the formation of aggregates, aggregate size, and electronic properties of the final film.

18. Well-defined Imidazole-containing ABA Triblock Copolymers: Understanding the Synergy of Ether and Imidazolium Sites

Chainika Jangu*, Helen Wang, Dong Wang, Greg Fahs, Ralph H. Colby, James R. Heflin, Robert B. Moore, and Timothy E. Long

Controlled radical polymerization (CRP) facilitated the synthesis of a broad range of triblock copolymers with well-defined architecture and controlled molecular weights. The block copolymers offer immense potential as sensors and actuators, energy-harvesting devices, and biomimetic materials. Microphase-separated block copolymers synthesized using CRP techniques present a facile strategy to mimic morphology of Nafion[®] through the inclusion of hard domains for mechanical reinforcement and ion-rich soft phases that facilitate ion migration. Control over block composition enables tailored charge content, tune thermomechanical properties, and morphology. Dielectric relaxation spectroscopy (DRS) determined ion-transport properties of charged ABA triblock copolymers with different compositions. This presentation will introduce the efforts with imidazolium triblock copolymers that offer the opportunity to fine tune mechanical and ion-transport properties of electroactive device.

19. Crafting unimolecular nanocapsules from photo-crosslinkable core-shell star-like block copolymer

Chaowei Feng*, Xinchang Pang and Zhiqun Lin

Unimolecular nanocapsules with well-defined dimensions were crafted using spherical core-shell star-like diblock copolymers as templates. Monodisperse and structurally stable star-like diblock copolymers composed of inner degradable core blocks and outer photo-crosslinkable shell blocks were synthesized via a combination of two living polymerizations, namely, coordination-insertion ring opening polymerization (ROP) followed by reversible addition-fragmentation chain-transfer polymerization (RAFT). Subsequently, uniform core-shell nanocapsules were successfully produced by photo-crosslinking the shell blocks of star-like diblock copolymers. The core diameter and shell thickness of nanocapsules are determined by molecular weights of inner core block and outer shell block, respectively, thereby rendering nanocapsules with tunable structural characteristics. The crosslinking density of nanocapsules can be readily controlled by varying the exposure time of star-like diblock copolymer templates to UV illumination. The selective degradation of inner core blocks yielded hollow nanocapsules with well-retained structural integrity. The dye encapsulation and release studies revealed that nanocapsules may be exploited as a new class of nanocarriers and promising drug nano-vehicles.

20. During synthesis observation of onset of LCST of cationic copolymers of N-isopropylacrylamide.

Colin A McFaul*, Michael F Drenski, Wayne F Reed

We synthesize and characterize copolymers of N-isopropylacrylamide (NIPAM) and [2-(acryloyloxy)ethyl-trimethylammonium chloride (Q9)]. Using the ACOMP system, we are able to characterize the resulting polymers during synthesis. In addition, we demonstrate the 'Second-generation ACOMP' system, which allows us to measure the lower critical solution temperature (LCST) of the resulting polymers and track its evolution during the synthesis. By combining the second-generation ACOMP system with our simultaneous multiple static light scattering (SMSLS) system, we are able to correlate polymer parameters such as composition, charge, molecular weight, and solvent ionic strength with the LCST of the polymer system. Increasing charge from the Q9 content drastically raises the LCST, while increasing ionic strength of the solvent lowers the LCST. We are able to see these results in random copolymer chains produced by batch free-radical polymerization, and in gradient copolymer chains produced by semi-batch free-radical polymerization.

21. Thermoplastic Polymers from Lignin

Hinkens, D.* and Tapsak, M.

Lignin is a byproduct of the pulp and paper industry and an objective is to utilize lignin as building block to higher molecular weight polymers. Such polymers could be useful as plastics, particularly as thermoplastics. One method of treating lignin in order to make a potentially useful product involves forming lignin-based epoxides. For this project, polymers that were of high molecular weight, plastic-like in nature, white in color and soluble in THF were synthesized from epoxidized lignin.

22. Diblock Copolymer Stabilized Carbon Nanohorn Theranostic Nanocomplexes

David L. Inglefield Jr.*, Allison Pekkanen, Michael H. Allen, Marissa Nichole Rylander, and Timothy E. Long

Carbon nanomaterials represent popular scaffolds for nanocomposite materials due to their unique properties and graphene sidewalls that allow for extensive functionalization. Combination of carbon nanomaterials into nanocomposites with polymers and inorganic nanoparticles offers many possibilities in materials science and biomedical engineering. The size, shape, and lack of metal catalysts render carbon nanohorns, composed of spherical aggregates of conical single-walled carbon nanotubes, promising carbon nanomaterials for medical applications. Carbon nanohorns represent attractive candidates for photothermal cancer therapy, which utilizes laser induced heating of nanoparticles to thermally destroy cancer cells. Combining photothermal therapy with bioimaging capabilities increases the utility of photothermal agents in nanomedicine. Here, we report the formation of stable ternary theranostic nanocomplexes with average sizes < 100 nm, combining carbon nanohorns, quantum dots, and diblock copolymers. These nanocomplexes offer further possibilities including incorporation of targeting ligands and anticancer drugs into their multifunctional design, and represent promising candidates for photothermal therapy.

23. Imidazolium-containing ABA Triblock Copolymers for Electroactive Devices

Evan Margareta*, David L. Inglefield, Chainika Jangu, Dong Wang, Gregory Fahs, James R. Heflin, Robert B. Moore, Timothy E. Long

ABA triblock copolymers featuring polystyrene reinforcing outer blocks and imidazolium-neutralized acrylic acid central blocks were synthesized with low polydispersity through reverse addition fragmentation chain transfer (RAFT) polymerization. Copolymerization of t-butyl acrylate with n-butyl acrylate varied the central block composition. Acid-catalyzed cleavage of t-butyl esters afforded central blocks containing poly(acrylic acid-co-n-butyl acrylate). Subsequent neutralization with 1-methylimidazole yielded ion-containing ABA triblock copolymers. Thermogravimetric analysis, differential scanning calorimetry, and dynamic mechanical analysis determined the thermomechanical properties. Additionally, the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate was cast with films and the effect of the presence of ionic liquid was probed. Furthermore, atomic force microscopy and small angle X-ray scattering probed the morphology of the various triblock copolymers both with and without ionic liquid.

24. Synthesis and Characterization of Porphyrin/Poly(ethylene glycol)-b-Polycaprolactone Copolymer Nanoparticles

Hong Zhang*, Boyu Zhang, Scott M. Grayson, Janarthanan Jayawickramarajah

Poly(ethylene glycol)-b-polycaprolactone(PEG-b-PCL) conjugated porphyrin copolymer could be successfully prepared by the combination of ring-opening polymerization(ROP) and click reaction. Both PEG-c-porphyrin and PEG-PCL-porphyrin can self-assemble into micelles in aqueous environment. The diameters of nanoparticles are around 100nm which is confirmed by transmission electron microscopy (TEM) and Dynamic laser scattering (DLS) studies. Furthermore, these nanoparticles show increased fluorescence intensity by increasing PCL molecular weight of porphyrin copolymer. These improved photochemical properties could open a new way to enhance the porphyrin particles performance in vivo imaging and photodynamic studies.

25. Self-Assembly pH-Responsiveness of Polypeptide ABC Linear Triblock Copolymers through Molecular Design and Polymer Composition

Gregory A. Strange*, Ashley J Johnson, Christopher Keller, Abby L. Morris, Jacob G. Ray, and Daniel A. Savin

The use of polypeptide based block copolymer self-assemblies as drug delivery vehicles has been an area of intense research in recent years due to the biocompatibility and wide range of properties attainable with these materials. The additional hydrogen bonding, hydrophobic, and ionic interactions of these materials provide the basis from which new self-assembling structures may form in aqueous solutions that have not been typically observed in traditional random coil hydrophilic/hydrophobic block copolymer systems. A series of triblock terpolymers of poly(ethylene oxide)-b-poly(lysine)-b-poly(leucine) (PEO-PK-PL) as model hydrophilic-ionic-hydrophobic block copolymers have been synthesized from PEO macroinitiators and amino acid N-carboxyanhydrides (NCAs), the self-assembly properties of which will be determined between pH 3 and 10 using static and dynamic light scattering and TEM. Understanding the manner in which these additional interactions affect the self-assembly of polypeptide based block copolymers is a crucial step toward their application as drug delivery vehicles.

26. High Melting Temperature Copolyester Thermoplastics

H. Eliot Edling* and S. Richard Turner

The utilization of rigid, aromatic diesters to synthesize polyesters can yield thermoplastics with high melting temperatures. Current research involves using new as well as commercially available monomers to make copolyesters and studying how the different components affect the crystallinity, melting temperature and glass transition temperatures. Polyesters containing dimethyl biphenyl-4,4'-dicarboxylate (DMBP), dimethyl 2,6-naphthalenedicarboxylate (DMN), dimethyl p-terphenyl-4,4"-dicarboxylate (DMTP) and the diol 1,4-cyclohexanedimethanol (CHDM) have been synthesized. Differential scanning calorimetry (DSC) has revealed these copolyesters exhibit two adjacent melting transitions. Further investigation of the double melting peaks using DSC has shown the size of the peaks, relative to each other, to depend on the heating rate. This suggests melt-recrystallization-remelt characteristics.

27. Advances in biomimetic hydroxyapatite bioceramic composites

Jason Dyke, Huamin Hu *, Ching-Chang Ko, Wei You

Utilizing sol-gel chemistry, hydroxyapatite-gelatin modified siloxane (HAp-Gemosil) composites have been prepared, but flexural strength was insufficient. Incorporating a copolymer chain of L-Lactide (LLA) and an alkyne derivatized trimethylene carbonate, propargyl carbonate (PC) was shown to improve flexural strength by mimicking collagen and improving fiber bridging, without sacrificing biocompatibility. Though improvements were made, adhesion between inorganic and organic phases of the composite was poor, leading to a loss in compressive strength. In order to maximize interfacial adhesion, polydopamine (PD) was utilized. Inclusion of PD allowed us to maintain a polymeric component, previously responsible for improved mechanical properties, while also improving adhesion. We observed that the processing conditions and temperatures play an important role in the structure and performance of PD containing biomaterials. This work shows that a polymeric component helps improve mechanical properties of bioceramics, and how temperature plays a critical role in the formation of robust composite materials.

28. Catalysts for the Positional Isomerization of Long-Chain Olefins

James Bruno*, Kerry Dooley

Internal, long chain olefins (>C₁₂) are used in the production of paper sizing agents and as deep-sea drilling fluids. In this project, we studied the double-bond (positional) isomerization of C₁₆-C₁₈ olefins. Both solid acid and organometallic chain-walking catalysts were evaluated. Solid acids, such as sulfonated poly(styrene-co-divinylbenzene), perfluorinated ion exchange resins, and acidic zeolites were tested in packed bed reactors to determine catalyst lifetime and selectivity to internal olefins. The most promising catalysts had a high selectivity with slow deactivation. Iron pentacarbonyl, a chain-walking catalyst, was tested in a batch reactor to determine the optimal catalyst concentration, temperature, and residence time. We are currently studying the immobilization of Fe(CO)₅ on resin supports.

29. Approaching Soluble PEDOT Analogs: Dual Electrochromic and Charge Storage Applications

James F. Ponder Jr.* and John R. Reynolds

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly stable electroactive polymer used in a variety of applications from electrochromics, to charge storage, to biomedical coatings. However, PEDOT itself is insoluble and is normally processed from a dispersion prepared as the pre-doped material PEDOT:PSS. In order to obtain a material with the desirable properties of PEDOT and the solubility to allow for spray or blade coating, a family of soluble polymers has been prepared by copolymerizing various ratios of EDOT with a solubilizing monomer (a 3,4-propylenedioxythiophene derivative). The polymers were prepared by direct arylation polymerization in moderate to high yields and demonstrated high optical contrast (~70%) in the visible region, switching from a blue neutral state to a color neutral and transmissive oxidized state. Increasing the EDOT/ProDOT ratio increases the broadness of the electrochemical windows, approaching that of PEDOT. The results show the use of these materials in both electrochromic and charge storage applications.

30. Gas Transport Properties of a Crosslinked Poly(phenylene oxide) Copolymer

Jarrett R. Rowlett*, Qiang Liu, Hailun Borjigin, Andrew T. Shaver, Sue J. Mecham, Benny D. Freeman, James E. McGrath

A PPO-PAEK copolymer was prepared from a difunctional poly(phenylene oxide) oligomer and then chain extended with 4,4'-difluorobenzophenone to form a crosslinkable copolymer. The polymer films were crosslinked via UV light to a polymer network with high gel fractions. The crosslinked and uncrosslinked films were characterized in regards to their thermal stability, structure conformation, density and free volume, along with their gas transport data. The transport data was plotted against the upper bound for several different gas pairs and compared against several commercially available materials and other PPO derivatives. Synthesis, membrane characterization, crosslinking effects, and transport data will be discussed.

31. Vapor Pressure Effects on Organic Photovoltaics

Jeff Hernandez*, Elsa Reichmanis, John Reynolds

Semiconducting Conjugated polymers have drawn a great deal of attention over the past decade due to their solution processability and potential use in roll to roll fabrication of organic solar cells. Here we report the effect of solvent vapor pressure on poly(3-hexylthiophene):[6,6]-phenyl C₆₁-butyric acid methyl ester (P3HT:PCBM) blade coated inverted solar cells using ZnO as the electron transporting layer and MoO₃ as the hole transporting layer. The resultant morphology and device performance is investigated for both devices processed from a single solvent with varying vapor pressure and a mixed solvent. We report that the use of a mixed solvent system is advantageous for controlling the vapor pressure of the solution and thus controlling the phase separated morphology between P3HT and PCBM which impacts ultimate polymer:fullerene solar cell performance.

32. Multi-compartment Magnetic Nanoparticles for Sequestration of Pollutants from Marine and Fresh Water Environments

Jeniree A Flores,* Adriana Pavia-Sanders, Karen L. Wooley

Water contamination is a severe problem with ramifications affecting all levels of our ecosystem. There are several sources of contamination; however, one of the most devastating causes is associated with the production and extraction of crude oil. Recently, our laboratory has synthesized nanomaterials with an added magnetic component for ease of manipulation and recovery. However, a desire to have tailored materials for broader applications has led to the development of an enhanced, targeted system. To achieve this novel system, we have designed and synthesized multi-compartment magnetic nanoclusters composed of a magnetic core surrounded by shell crosslinked knedel-like (SCK) nanoparticles. The SCKs, composed of poly(acrylic acid)₉₀-block-polystyrene₁₄₀ (PAA₉₀-b-PS₁₄₀) block copolymers, exhibit hydrodynamic diameters of ca. 20 nm. Covalent linkage between the two components via amidation chemistry has resulted in multi-compartment nanoclusters, which are expected to absorb hydrophobic pollutants into the satellite SCKs, while being manipulated through the application of a magnetic field.

33. Self-Assembly of Architecturally Complex Block Copolymers in Solution and at Surfaces

Jesse Davis,* Xu Wang, Juan Pablo Hinestrosa, Jimmy W. Mays, and S. Michael Kilbey II

The self-assembly of binary mixtures of block copolymers based on polystyrene and poly(2-vinylpyridine) (PS and PVP), including linear diblock and triblock copolymers of varying block lengths and star block copolymers with different block sizes, PS/PVP ratios, and numbers of arms, was studied in selective (toluene) and non-selective (THF) solvents. While single component block copolymers remain as isolated, random coils in THF and simple spherical micellar aggregates in toluene, mixtures created by blending different architectures can lead to either spherical, worm-like, or large compound micellar aggregates. The aggregate shape and size depends on the constituent architectures and concentration, and novel structures such as intramicellar microphase-separated “brain coral-like” hierarchical structures are observed in a blend created from a mixture of a triblock and an 8-arm PS-PVP star copolymer. These structures inspire new ideas about how novel soft matter structures can be accessed, and deepen our understanding of self-assembly processes.

34. Synthesis and Characterization of Non-ionic Water-Soluble Helical Polypeptide with “Clickable” Side Chains for Conjugation

Jinbao Cao*, Donghui Zhang

Polypeptides consisting of poly(propargyl-L-glutamate) and poly{N ϵ -2-[2-(2-Methoxyethoxy)ethoxy]acetyl-L-lysine} were prepared by random ring-opening copolymerization (ROP) of the corresponding N-carboxyanhydrides using benzyl amine as initiators. Successful synthesis of the copolypeptides with different ratio of two segments was verified by size-exclusion chromatography (SEC) and ¹H NMR spectroscopy. These polymers with pendant clickable alkyne groups can be further modified with azide containing agents through copper-catalyzed alkyne-azide cycloaddition chemistry (CuAAC) with 100% efficiency. Cell adhesion pentapeptide GRGDS terminated with azido group was successfully attached to the copolypeptides in varying grafting density (2-9 mol%) in DMF using a copper wire catalyst. Circular dichroism (CD) analysis reveals that both the copolypeptides and their conjugates adopt α -helical conformations in aqueous solution. Cell adhesion assay indicates the conjugates are able to induce integrin-mediated cell adhesion.

35. Extruded Superparamagnetic Saloplastic Polyelectrolyte Nanocomposite

Jingcheng Fu*, Joseph B. Schlenoff

A simple 2-step mixing procedure has been performed to imbed Fe₃O₄ nanoparticles in polyelectrolyte complexes (PECs) to form a superparamagnetic composite. Three nano-PECs with different nanoparticle loading have been prepared. Nano-PECs made from poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium) (PDADMA) were extruded into fibers. TEM shows the average diameter of the nanoparticles is 11.6±2.7nm. Superconducting quantum interference device (SQUID) measurements show that the blocking temperature of the samples is 270K and the magnetic hysteresis loops reveal that all the samples have neglectable coercivities (less than 20 Oe) under 300K, indicating the composite possesses superparamagnetic behavior under room temperature. In addition, since composites with 4.5wt% nanoparticles loading can be heated up to 102 °C in an alternating current (AC) magnetic field, these composites have the potential to be applied to hyperthermia therapy. Tensile strength and toughness of nano-PEC fibers increases with the increase of nanoparticle loading.

36. Functional nanoporous polymers containing sterically congested comonomers

Jing Huang, Xu Zhou and S. Richard Turner

High surface area, functionalized nanoporous polymers have numerous potential applications in catalysis, gas sorption and chromatography separations. One major group of nanoporous polymers, hypercrosslinked polymers, is typically synthesized via the suspension polymerization and post-crosslinking reaction of divinylbenzene and vinylbenzyl chloride. We are pursuing several routes to prepare new nanoporous hypercrosslinked polymers. In our previous work, the sterically congested alternating copolymers containing substituted stilbene and maleimide or maleic anhydride were synthesized, and the resulting polymers possessed semirigid backbone. Now we are studying the effects of enhancing the rigidity of the backbone of the hypercrosslinked particles by inserting sterically congested stilbene/N-substituted maleimide comonomers. This also presents opportunities of incorporating various functional groups by using different substituted stilbene and maleimide comonomers. We are also crosslinking tert-butyl carboxylate or t-boc containing stilbene and N-phenyl maleimide monomers with divinylbenzene. The resulting copolymers were deprotected with either thermal deprotection or acid catalysis. With the leave of isobutylene or isobutylene and carbon dioxide, nanopores may be generated, and the sterically congested polymer backbone can prevent the nanoporous structure from collapse.

37. Improved Photopolymerization Kinetics of Acrylate and Amide Monomers in the Presence of LiTf₂N

John Whitley*, William J. Horne, Matthew S. Shannon, Kelsey Terrill, Spenser Hayward, Jason Bara

As radical reactions are increasingly used in the manufacture of polymers and polymer products, interest has increased in new methods of radical polymerization. Among these techniques is the process of photopolymerization in which the reaction proceeds through the production of radicals from a photoinitiator. Previously, ionic liquids have been found to increase the polymerization rate of multiple vinyl monomers including styrene and methacrylates. In our study, coordinated ionic liquids were synthesized containing the anion bis(trifluoromethylsulfonyl)imide (Tf₂N) and Li⁺ cations coordinated to the polar vinyl monomers methyl methacrylate, hydroxyethyl methacrylate, methyl acrylate, methacrylic acid, acrylic acid, and acrylamide. The resulting substances were photopolymerized and the monomer conversion measured using real-time Fourier transform infrared spectroscopy (FTIR). In addition, salt extraction tests were performed on the resulting polymers and the material properties were examined using differential scanning calorimetry (DSC).

38. Effect of Grafting Density on Chain Constrains and Resulting Brush Lengths in Polycaprolactone-Grafted Silica Nanoparticle Systems

Kyle C. Bentz*, Susan E. Walley, Daniel A. Savin

Using a grafting-from approach, polycaprolactone was grafted to silica nanoparticles (SNPs) at varying densities. Control of the grafting density was achieved by functionalization of the SNP surface using varying quantities of two molecules designed to impart different functionality to the SNP surface. The first molecule, trimethylethoxysilane, imparts an "inert" functionality which is unable to initiate polymerization. The second molecule, 3-(glycidoxypropyl)dimethylethoxysilane, imparts to the surface alcohol moieties which are able to initiate the ring opening polymerization of ϵ -caprolactone monomer. It was determined that SNPs that contained higher density of initiating species led to thicker brushes for polymers of the same molecular weight than SNPs with lower density of initiating species. The amount by which the brush length exceeds that of the radius of gyration of the free polymer in solution is due to the chain constraints as a result of grafting density.

39. Analysis of Oligomeric Copper β -Diketonate Molecular Complexes

Jonathan Casey* Paul Russo and Andrew Maverick

This research aims to determine the structure of Cu(II) complexes of silicon-based multidentate β -diketonate ligands. The ligands were designed to yield polyhedral complexes such as cubes Cu_{12}L_8 , decahedra $\text{Cu}_{24}\text{L}_{16}$, and dodecahedra $\text{Cu}_{30}\text{L}_{20}$ (L = coordinated ligand). These discrete molecules may have applications in drug delivery, fuel storage, and chemical retention. Analytical Ultracentrifugation was used to analyze the complexes. This technique was used to determine whether the samples contained a pure compound or a mixture of discrete molecules, and also to estimate their molecular weight. The AUC studies of the Cu(II) complexes indicate that the Cu complexes are polydisperse, with molecular weights in the 900-2300 range. This is considerably smaller than the values expected for cubes, decahedra, and dodecahedra (5000-15000). An alternate structural model for these supramolecular complexes will be presented.

40. Increased mass accuracy via enhanced dendritic calibrants

Joseph A. Giesen*, Brittany K. Myers, Scott M. Grayson

Mass spectrometers require constant calibration for highly accurate determination of analyte mass due to acquisition parameters affecting observed mass. Therefore, producing calibrants that are characterized by their low cost, low polydispersity and broad range of compatibility with solvents and matrices is essential for increasing mass accuracy determination. Dendrimers based on bis-MPA provide a synthetically straightforward way for producing calibrants that meet these needs as well as having a wide mass range, long shelf-life and other unique aspects. Through variation of the core of the dendrimers one can enhance counter-ion selectivity or apply a mass defect to the calibrant. Use of a tris-iodo core provides sufficient mass defect to unambiguously assign both analyte and calibrant signals, even with molecules of an identical nominal mass. Conversely, the presence of an amine-containing core ensures preferential ionization with a proton versus a metal counter-ion, which is useful for analysis of peptides and proteins.

41. Segmented Polymers via Step-Growth Polymerizations: From polyesters to polyoxamides

Joseph M. Dennis*, Musan N. Zhang, S. Richard Turner and Timothy E. Long

Segmented copolymers provide a wide array of applications beyond the physical constraints of their composing homopolymers. Recently, research has been primarily focused on the design of well-defined di- and triblock copolymers using anionic and controlled free radical polymerization methods. However, these techniques typically require the use of solvents during polymerization and purification. Utilizing bulk transesterification techniques to ascertain segmented block copolymers proves advantageous. Segmented polysulfones, polyesters, and polysiloxanes enable compositions with enhanced mechanical properties over their predecessors. Their properties will be discussed relative to the need for advanced membranes for emerging technologies.

42. Aliphatic iodinated polyesters as a versatile platform for radiopaque biomaterials and nanoparticles

Katelyn R. Houston*, Sarah M. Brosnan, Laurel M. Burk, Yueh Z. Lee, Valerie Sheares Ashby

Radiopaque polymeric biomaterials that maintain their thermal and mechanical properties are critical for the ever-expanding scope of implantable biomaterials. We have developed a platform of highly iodinated polyesters based on a stable iodinated, aliphatic monomer. These polyesters have high radiopacity, low cost and low cytotoxicity with tunable thermal and mechanical properties. Additionally, radiopaque nanoparticles have been formulated from the synthesized iodinated polyesters. These particles have the potential to overcome the limitations of traditional CT contrast agents, which include rapid excretion, unspecific biodistribution, and, most critically, renal toxicity. Also, they are unique in that they are much cheaper than currently developed gold or bismuth nanoparticles, and that they are completely nonaromatic.

43. Surface Control via Chain-End Chemistry in Rigid-Rod Polyethersulfone Films

Katrina Knauer* and Sarah Morgan

Polyethersulfone (PESU) is a widely used commercial thermoplastic that is known for its toughness and stability in extreme environments. This research provides a detailed study of the surface and interfacial chain-end localization in PESU films. PESU was fractionated and characterized using static and dynamic light scattering and gel permeation chromatography. Fractionated PESU films were prepared via solvent casting and removal of the solvent using a vacuum oven. Chain-ends were characterized by X-ray photoelectron spectroscopy and confocal laser microscopy. Surface properties of the PESU films with different chain-ends were analyzed using quantum nano-mechanical mapping and lateral force microscopy. Wettability of the surfaces was determined using water contact angle. Experimental results were correlated with molecular dynamics simulations to develop a model of chain-end localization in rigid rod systems. Chain-end localization to the PESU-air interface can be used to manipulate surface properties and further the development of PESU for membrane applications.

44. Altering charge density of hydrophilic-block-cationic copolymers for siRNA complexation and its effects on complex dissociation and gene suppression.

Keith H. Parsons,* Andrew C. Holley, Charles L. McCormick

Block ionomer complexes (BICs) formed from electrostatic association between hydrophilic-block-cationic copolymers and small interfering RNA (siRNA) are known to serve as superior vehicles for gene delivery. Such BICs stabilize and protect the siRNA while conferring hydrophilicity and reduced cytotoxicity, and incorporation of a targeting moiety deters nonspecific cellular uptake. Our group has previously demonstrated that BIC stability and siRNA delivery efficacy strongly depend upon cationic block length: increased block length greatly stabilizes the complexes and also increases the time required for gene knockdown. To explore this phenomenon, aqueous RAFT (aRAFT) polymerization was utilized to synthesize hydrophilic-block-cationic copolymers in which the cationic block contains a statistical incorporation of neutral, hydrophilic monomer such that the number of cationic groups remains unchanged but varies in distribution along the polymer backbone. Solution DSC experiments and in vitro gene knockdown studies were then performed to analyze the effect of increased cationic spacing on drug efficacy.

45. Formulation of Sodium Deoxycholate/TRIS Hydrogels for Various Types of Drug Delivery

Kelsey E. McNeel,* Susmita Das, Ioan Negulescu, and Isiah M. Warner

Sodium deoxycholate (NaDC)/TRIS-based hydrogels have been broadly modified by our group. Characterization of these hydrogels revealed a unique rheological property in several formulations that seems to provide unprecedented potential for use as injectable drug delivery vehicles. That is, upon shearing a rearrangement of internal gel structure occurs instead of breaking. In addition to this unique benefit, our hydrogels are injectable at room temperature in the gel phase, allowing greater facility in drug administration. Additional benefits include low cost, tunability, facile drug loading, and complete absence of organic solvents. The effect of shearing on drug release profiles has been investigated, and several systems have been designed with different release abilities. Drug size and drug concentration can also be used to control the release profiles from these hydrogels. Conclusively, our hydrogel systems can serve as distinctly beneficial, novel drug delivery systems that can be tuned for specific applications.

46. Synthesis and characterization of UV cross-linkable aromatic polyimide copolymers for gas separation membranes

Kyle Gaines, Hailun Borjigin, Kevin Stevens, Jaesung Park, Benny D. Freeman, Andy Shaver, Sue J Mecham and James E. McGrath

Aromatic polyimides are well known robust and thermally stable polymers that have shown excellent promise as gas separation membranes. Unfortunately, amorphous linear glassy polymers are susceptible to CO₂-induced plasticization, which significantly reduces membrane performance since the permeability of all components in the feed increases and the selectivity decreases dramatically. Chemically cross-linked aromatic polyimide networks have been reported to show good resistance to plasticization with improved chemical resistance and thermo-oxidative stability. VT and UT are investigating UV curable copolyimides based on methyl-substituted aryl diamines 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPDA), and 2,4,6-trimethyl-m-phenylenediamine (DAM) with commercial dianhydrides, via the ester-acid imidization route. Initially, 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) was chosen, since it has an aromatic ketone. UV excitation of aromatic ketones creates excited species that can abstract hydrogen from benzylic-methyl groups and ultimately form C-C crosslinks. Incorporation of bulky diamines into the polymer backbone disrupts chain packing and thus provides high gas permeability in the resultant film even in cross-linked systems. All copolymers were comprehensively characterized with respect to chemical structure, molecular weight, thermal and mechanical properties by SEC, NMR, DSC, DMA, TGA and stress-strain testing. The synthesis, characterization, film casting/curing, and initial gas transport properties of high molecular weight polyimide linear controls and random copolymers of varied dianhydride compositions will be discussed.

47. Biomedical Applications of Thiol-Ene Chemistry

Leah Garber*, Cong Chen, Mollie Smoak, Daniel Hayes, John A. Pojman

Biomedical applications of thiol acrylate in situ polymerizations were studied using different monomers and catalysts. The applications include bone defect repair, antimicrobial effects, and hydrogels. Polyethylene glycol diacrylate (PEGDA)-co-trimethylolpropane tri-3-mercaptopropionate (TMPTMP) was investigated as a potential bone defect repair material. It exhibited high elastic mechanical strength, which is an important characteristic in tissue engineering. The PEGDA monomer was also used to synthesize a transparent hydrogel for use as a carrier medium for UV-responsive micro-RNA. The hydrogel was synthesized by a thiol-acrylate mechanism containing PBS, PEGDA (575), and ethoxylated trimethylolpropane tri-3-mercaptopropionate (ETTMP-1300). However, the most evaluated application for bone defect repair included pentaerythritol triacrylate-co-trimethylolpropane tri-3-mercaptopropionate (PETA) blended with varying contents of hydroxyapatite (HA), cast as solids or gas foamed. It was evaluated for its potential as a biodegradable, biocompatible, and osteogenic material. Characterization using SEM and Micro-ct imaging analysis of the polymers showed the morphology and distribution of HA. A six week in vivo biocompatibility study validate that PETA:HA can be foamed in vivo without serious adverse effects. Antimicrobial scaffolds using the described PETA material were fabricated using silver nanoparticles. The scaffolds inhibited the proliferation of *Staphylococcus aureus* 31 99.5% and *Escherichia coli* by 99.9% within 24 hours.

48. Tri-(perylene bisimides) as an alternative to fullerenes in polymer organic photovoltaics

Levi Moore*, Mithun Bhattacharya, Qi Wu, Veena Choudhary, Sarah E. Morgan

Organic photovoltaics (OPVs), have the potential to be mass produced at much lower costs than conventional solar cells through facile methods like spin coating and inkjet printing, though they exhibit lower efficiencies than conventional cells. Present polymer OPV devices utilize fullerene derivatives as the electron accepting material, which give good performance but have many drawbacks, including high cost, narrow light absorption, environmental instability, and poor processability. This research focuses on the synthesis of novel electron acceptor materials, tri-(perylene bisimides) (tri-PBIs)--derivatives of inexpensive industrially available dyes--and have the potential to increase the efficiencies of polymer solar cells through increased light absorbance, morphology control, and greater photochemical stability. Tri-PBIs were synthesized according to established procedure, and characterized. They were then blended with poly(3-hexyl thiophene) and incorporated into OPV devices. Morphology and phase of the blends, as well as photovoltaic performance, were characterized.

49. Superamphiphobic inorganic-organic thiol-ene surfaces via spray-deposition and photopolymerization

Li Xiong, * Laken L. Kendrick, Hannele Heusser, Jamie C. Webb, Bradley J. Sparks, James T. Goetz, Wei Guo, Christopher M. Stafford, Michael D. Blanton, Sergei Nazarenko, and Derek L. Patton

Superamphiphobic surfaces, exhibiting high contact angles and low contact angle hysteresis to water and low surface tension liquids, have attracted a great deal attention in recent years due to the potential of these materials in practical applications such as liquid-resistant textiles, self-cleaning surfaces, and anti-fouling/anti-corrosion coatings. In this work, we present a simple strategy for fabrication of superamphiphobic coatings based on photopolymerization of hybrid thiol-ene resins. Spray-deposition and UV photopolymerization of thiol-ene resins containing hydrophobic silica nanoparticles and perfluorinated thiols provide a multi-scale topography and low-energy surface that endows the surface with superamphiphobicity. The wettability and chemical composition of the surfaces were characterized by contact-angle goniometry and x-ray photoelectron spectroscopy, respectively. The hierarchical roughness features of the thiol-ene surfaces were investigated with field-emission scanning electron microscopy. Droplet impact and sandpaper abrasion tests indicate the coatings respectively possess a robust anti-wetting behavior and good mechanical durability.

50. Investigating the heteroatom effect in new donor-acceptor polymers based on 2,1,3-benzochalcodiazoles and benzo[1,2-b:4,5-b']difuran for use in organic solar cells

Ewan, Monique D*.; Kobilka, Brandon M.; Muller, Evan.; Jeffries-EL, Malika

Synthesizing new donor-acceptor (D-A) polymers is of great importance for the development of materials with optimized energy levels. Among D-A polymers, 2,1,3-benzothiadiazole is a commonly used acceptor that can be found in polymers used for various high-efficiency solar cells. Far less common is its selenium counterpart, 2,1,3-benzoselenadiazole. Herein, we investigate the effect of the heteroatom substitution on solar cell performance in novel copolymers comprised of the aforementioned acceptors and our previously reported benzo[1,2-b:4,5-b']difuran donor.

51. Thermal and Mechanical Investigation of an Azide-Functional Modified Epoxy Resin System that Cures via Copper-Catalyzed Azide/Alkyne Cycloaddition

Mark R. Brei* and Robson F. Storey

We have developed an azide-functional, modified epoxy resin system that cures via copper-catalyzed azide/alkyne cycloaddition (CuAAC). The modified resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A, was synthesized by reaction of commercial diglycidyl ether of bisphenol-A with $\text{NaN}_3/\text{NH}_4\text{Cl}$ at reflux in a reaction medium of $\text{H}_2\text{O}/2$ -ethoxy ethanol. When this resin is crosslinked with an aliphatic polyalkyne, such as tripropargyl amine, the resulting thermoset has a T_g that is typically $\leq 130^\circ\text{C}$. To elevate the T_g , a number of tetra-functional aromatic propargyl amines were synthesized by reaction of the corresponding aromatic diamine with propargyl bromide/ K_2CO_3 at reflux in DMF. In this paper, we will report the thermal and mechanical properties of the cured thermosets obtained by reaction of the modified resin with the synthesized tetrapropargyl aromatic amines.

52. Surface investigation of the thermo-responsive polypeptoids using atomic force microscopy

Lu Lu,* Donghui Zhang and Jayne C. Garno

The phase transition of copolymer nanostructures was investigated using atomic force microscopy (AFM). Aqueous solutions of the random copolymer poly[(N-ethyl glycine)-ran-(N-butyl glycine)] P(NEG-r-NBG) become cloudy upon heating and clear upon cooling, which indicates reversible phase transitions. Changes in the composition of copolypeptoids can be used to adjust the cloud point temperature within the range of 20-60 C. Nanopores within a film of octadecyltrichlorosilane were prepared using particle lithography and solution immersion. A pre-synthesized copolymer P(NEG₃₂-r-NBG₁₇) was anchored to the sites of nanopores through "click chemistry". The morphology and surface arrangement of brush polymer nanostructures was characterized with AFM. Studies of thermo-responsive properties was accomplished using dynamic protocols and liquid imaging media. A temperature stage was used to heat the sample during time-lapse AFM imaging. Significant advantages are gained by localizing and patterning polymer brushes on surfaces for studies of thermo-responsive properties.

53. Urea-containing ABA Triblock Copolymers for Gold Nanoparticle Complexation

Mingtao Chen*, David L. Inglefield Jr., and Timothy E. Long

Urea-containing ABA triblock copolymers represent promising templates for gold nanoparticle self-assembly due to their efficient interaction with gold nanoparticles. Reversible addition-fragmentation chain-transfer polymerization of 2-ethylhexyl methacrylate afforded poly(2-ethylhexyl methacrylate) as macro chain transfer agents with narrow PDIs. Urea-containing methacrylate monomers from a facile and efficient reaction of amines with 2-isocyanatoethyl methacrylate permitted chain extension of the poly(2-ethylhexyl methacrylate) macro chain transfer agents to ABA triblock copolymers. This ABA triblocks copolymers exhibited good mechanical properties and efficient interaction with gold nanoparticles as a promising candidate for gold nanoparticles composites.

54. Monosulfonated poly(aryl ether sulfone) as an alternative material for reverse osmosis

Ozma Lane*, Eui-Seoung Jang, Ishan Mehta, Ben Sundell, Sue Mecham, and James E. McGrath

Disulfonated poly(arylene ether sulfone)s have been investigated as potential materials for reverse osmosis membranes. It is thought that their rejection properties might be improved upon by using a poly(aryl ether sulfone) as depicted below, where the hydroquinone units are monosulfonated using a post-polymerization reaction. While the investigations into post-sulfonated poly(arylene ether sulfone)s in the past was abandoned due to poor reproducibility and control of sulfonation, this reaction is easily tailored by the level of incorporated hydroquinone to have a reproducible degree of sulfonation, with a negligible impact on molecular weight. This presentation will discuss the post-sulfonation process and the transport properties of sulfonated poly(aryl ether sulfone)s with varying ion exchange capacities. Polymer structure/property relationships will be described using ¹H NMR, SEC, DMA, and tensile testing.

55. pH Clock Reactions that Trigger Crosslinking

Elizabeth Jee*, Annette F. Taylor, and John A. Pojman

A pH clock reaction is a reaction that has an abrupt change in pH at some point after the start of the reaction. In this work, we studied the bromate-sulfite-bisulfite pH clock reaction and the delay in clock time as a function of ammonium hydroxide. The unperturbed bromate-sulfite-bisulfite clock reaction proceeds within minutes when the initial at pH 7. When the initial pH is raised to 8.5 the clock can be delayed for several hours. However, it was found that the addition of ammonium hydroxide does not delay the clock indefinitely so storage of the clock is not possible. The second type of clock reaction studied was the urea-urease clock reaction. When sulfuric acid is added to the system a clock behavior is induced. The consumption of urea by urease produces ammonia. It is hoped that a crosslinking reaction between the ammonia and acrylated polymers can be achieved.

56. Auxetic behavior in paper and nonwovens

Prateek Verma*, Anselm Griffin, Meisha Shofner

Auxetic materials are a rare class of materials that exhibit negative Poisson's ratio. While most substances become thinner in lateral direction when stretched, auxetic materials grow thicker. We have found many types of paper to show an out-of-plane auxetic response (thickness increase on stretching). Additionally, we induced a similar response in needle-punched nonwovens. Thickness direction strain with respect to planar strain is measured for these materials and a series of microscopic and tomographic characterization is performed. From initial results, it is evident that the fiber network structure and the processing conditions play important role in defining the mechanism and magnitude of auxetic response. Ultimately, the fundamental understanding resulting from this research should lead to new product development opportunities for fiber-network materials as well as to the establishment of predictive processing-structure-property relations for auxetic materials.

57. An Investigation of Thermal Properties and Melt Processability of Polyacrylonitrile/ Methyl acrylate (PAN/MA) Statistical Copolymers and their Plasticized Blends

Priya Pisipati*, Sue Mecham, Susan Beck, Michael Bortner, Jianhua Huang, Donald Baird and James E. McGrath

Currently commercial PAN precursors for acrylic and carbon fibers are processed via wet or dry spinning. These solution spinning techniques are much less economically and environmentally friendly and operate at slower rates than melt spinning¹. Melt-spun fibers have been successfully generated when the copolymers were plasticized with water². The water plasticized systems however require high pressures for extrusion, since the boiling point of water is below the extrusion temperature. Glycerin, a high boiling non-toxic plasticizer was earlier discovered to have somewhat similar plasticizing effects to water³. Glycerin, ethylene glycol, glycerin/water combinations and high molecular weight ethylene-vinyl alcohol copolymers have been investigated as potential plasticizers for high molecular weight (~195,000 g/mol), high acrylonitrile(93-96 wt%) content poly(acrylonitrile-co-methylacrylate) random copolymers. Pure glycerin (25 wt %) induces an apparent crystallization followed by a reduced "T_m" of about 213 °C via DSC and ethylene glycol reduces the melting point of the copolymers well below 200 °C. Other high boiling alcohols such as propylene glycol, 1,4 butanediol and diethylene glycol have also been investigated as potential plasticizers.

58. The study of brominated flame retardants with their synergist, antimony oxide in High Impact Polystyrene, HIPS.

Mutairu B. Olatinwo, Kyungmin Ham, Marathe, Shashidhara, Jonathan McCarney, Lahsen Assoufid, Leslie G. Butler

Two-dimensional X-ray phase contrast movies have been acquired during the combustion of high-impact polystyrene blended with a brominated aromatic flame retardant and its synergist, antimony oxide. To interpret the movies, millimeter-sized sections from the burnt samples were also studied with scanning electron microscopy, variable energy X-ray absorption tomography, and phase contrast X-ray tomography. Seven blend samples were studied, a properly formulated blend and for comparison, blend with insufficient synergist or flame retardant. The sample passing the flammability test also exhibited a striking difference in a char layer as observed with absorption and phase contrast tomography. Key features of this apparently successful char layer are: a char layer thickness on the order of 200 microns; an absence of gas bubbles in the char layer but the presence of cracks some tens of microns wide; a striking structural homogeneity in both absorption and dark field images; and deposits of antimony bromide oxides on the surface. The surface of the burnt bar also showed evidence of occasional fluid flow that appeared to physically remove the protective char layer. In the interior, gas bubbles developed as the sample was heated with a gas bubble; the gas was attributed to the decomposition of the flame retardant and, when present, reaction with Sb₂O₃.

59. Development and characterization of a novel, antimicrobial, sterile hydrogel dressing for burn wounds: Single step production with gamma irradiation creates silver nanoparticles and radical polymerization

Benjawan Boonkaew, Philip M. Barber*, Margit Kempf, Vijay T. John, Leila Cuttle

This research introduces a novel burn wound dressing which contains silver nanoparticles (SNP) to treat infection in a 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS-Na⁺) hydrogel. Silver nitrate was dissolved in AMPS-Na⁺ solution and exposed to gamma irradiation to form SNP infused hydrogels. In one step gamma irradiation results in a cross-linked polymeric network of sterile hydrogel and a reduction of silver ions to form SNP infused in the hydrogel. All the hydrogels were found to be non-toxic to normal human dermal fibroblast (NHDF) cells. The silver loaded hydrogels had good inhibitory action against *Pseudomonas aeruginosa* and methicillin-resistant *Staphylococcus aureus* (MRSA). Results from a pilot study on a porcine burn model showed that the 5 mM silver hydrogel was efficient at preventing wounds from bacterial colonization and the results were comparable to the commercially available silver dressings (Acticoat™, PolyMem Silver®).

60. Liposomes tethered to a biopolymer film surface through the hydrophobic effect are effective lubricants

Rubo Zheng*, Jaspreet Arora, Benjawan Boonkaew, Srinivasa R. Raghavan, David Kaplan, Jibao He, Noshir Pesika and Vijay T John

Liposomes, which are composed of phospholipid bilayers, have been reported to be efficient boundary lubricants at physiologically relevant conditions. Here we report a novel concept of fabricating films of a specific biopolymer (hydrophobically modified chitosan) that interact with liposomes through the hydrophobic effect of hydrophobe insertion into liposome bilayers, to tether liposomes on the surface. Such tethered liposomal surfaces are robust and exhibit excellent lubrication properties reducing the coefficient of friction values between 10^{-2} and 10^{-3} , at pressures up to 500 MPa. The biocompatibility and antimicrobial properties of chitosan additionally make these systems potentially applicable for synovial joint lubrication.

61. Creating fairly monodisperse polyacrylamide free-radically

Preeti Datta*, K. Efimenko, J. Genzer

Bulk free radical polymerization reactions lead to highly polydisperse polymers (polydispersity index, PDI > 1.5). In the past, researchers have shown that polymerization in porous microreactors can lower polydispersity (PDI ~1.5-1.7) by promoting gelation. We employ free-radical thermal frontal polymerization reaction of acrylamide (AAm) in DMSO in highly confined reactors (height ~1mm) to produce high molecular weight (~300 kDa) PAAm of relatively low PDI (~ 1.2). In frontal polymerization systems, a localized reaction zone propagates in space along the direction of heat transfer, sustained by the interplay of heat diffusion and Arrhenius reaction kinetics. The directional heat transfer assists in maintaining the uniformity of the front temperature. While convection improves thermal transport, it causes inhomogeneity in the propagating front in horizontal reactors. In highly confined systems, convection is heavily suppressed, as manifested by the "flattening" of the reaction front and the absence of "fingering". Gelation lowers termination rate and increases the life time of the active reaction centers. Elimination of convection in confined geometries coupled with directional heat transfer and gelation results in polymers with high molecular weights and low PDIs.

62. Control of Nano-Morphology in Polymeric Thin Films

Qi Wu, Levi Moore, Mithun Bhattacharya, Sarah Morgan

The most widely studied photovoltaic system consisting of poly(3-hexylthiophene-2,5-diyl) (P3HT) as donor and [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) as acceptor is a nano-phase separated thin film. Precise control of nano-morphology in the P3HT:PCBM film plays a significant role in promoting power conversion efficiency of the photovoltaic devices to provide the maximum interface for charge separation. In this study, polyhedral oligomeric silsesquioxane (POSS) nanoparticles with precise chemical structures were introduced into the P3HT:PCBM film. The nano-morphology was controlled by the organic functionalities on the POSS to alter the interactions between P3HT and PCBM. Moreover, isopropanol solvent vapor annealing was used to form air stable photoactive thin films with favorable morphology towards charge separation. The surface morphology and composition were characterized by combined techniques involving c-AFM, nanomechanical mapping and Raman imaging. The performance of photoactive devices was measured to establish the relationship between morphology and efficiency.

63. Polymer processing using α -Cyclodextrin and its characterization.

R. Krishnaswamy*, B. R. Williamson, A. S. Krishnan, S. A. Khan, A. E. Tonelli

Host-Guest inclusion complex (IC) formation is a well known method to reorganize the polymer chains and improve their mechanical and rheological properties. Modifying polymers using cyclodextrins (CDs) is one such way of processing polymers. CDs, cyclic starches containing glucose repeat units, are often able to form non-covalently bonded ICs with guest polymers by threading them through their hydrophobic cavities. Cd-ICs with biopolymers like Poly(ϵ -caprolactone) ((PCL α -CD-IC) are bio-absorbable, bio-compatible and bio-Degradable and can be used for biomedical applications. PCL- α -CD-IC maybe coalesced by extensive washing with water and subsequently with HCL for a short time. On removal of the host α -CDs, the c-PCL that results is likely transformed into small domains ($\sim 1/10^{\text{th}}$ the size of the crystalline grains of the IC powder). In each domain the PCL chains are likely partially aligned and have largely un-entangled extended conformations, without, however, directional correlation among the different coalesced domains. In comparison to samples made from randomly-coiled and entangled as-received PCL (ar-PCL), the rheological and mechanical properties of c-PCL are distinct and improved. For example, c-PCL melt exhibits yield stress and shows a zero shear viscosity nearly 3 orders of magnitude below that of an ar-PCL melt, and frequency sweep behavior distinct from that observed in the viscoelastic melt of the ar-PCL. Also c-PCL films and undrawn and drawn fibers were observed to have significantly and greatly higher moduli, respectively, and greatly reduced extensibilities. The changes in the conformations of c-PCL chains and the resultant morphology induced by coalescence are stable to melt-annealing, without return to their original random-coiling entangled states, even when c-PCL stays in the melt for long periods of time. This may be attributed to the differences in the volumes influenced by each chain in c- and ar-PCL samples. A few weight percent of c-PCL was shown to act as an effective self-nucleating agent for the melt-crystallization of ar-PCL. As a result, the self-nucleated PCL (nuc-PCL) may potentially be melt-processed into products with enhanced properties for use as sutures, scaffolds etc.

64. Synthesis of Benzobisoxazole-Containing Small Molecules and Polymers for Organic Light Emitting Diodes

Ramiro Chavez*, Brian Tlach, Jeremy Intemann, Malika Jeffries-EL

Conjugated polymers have emerged as a promising class of materials for use in organic light emitting diodes (OLED)s. They offer several advantages to their inorganic counterparts such as tunable energy levels, solution processability and improved flexibility of the devices allowing for fabrication over large as well as curved surfaces. In spite of the remarkable progress, the performance of blue OLEDs have been limited due to the overwhelming problem of aggregation in both neat and host-guest systems. By implementing electron rich and electron deficient units in the backbone of the conjugated polymer, we have synthesized new wide bandgap materials that emit in the blue region. These materials are expected to mitigate aggregation and lead to improvement in device efficiencies.

65. Synthesis of novel polymer architectures and investigation of their physical characteristics

Ravinder Elupula*, Boyd A. Laurent and Scott M. Grayson

Recently Laurent and Grayson reported an efficient method for synthesizing cyclic macromolecules using “click” chemistry which has proven to be a versatile way for making macrocycles. Also Tezuka reported the synthesis of multicyclic polymers by cyclization via ionic pre-assembly followed by a covalent fixation. Further, the use of multicyclic “cryptands” demonstrated selective and strong interaction with potential guests. Inspired by these concepts, the synthesis of multicyclic “cage” polymers was explored. Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP), NMP and reversible addition fragmentation transfer polymerizations (RAFT) are powerful tools for preparing well defined polymeric architectures. ATRP is a particularly attractive approach for making star precursors because of the ability to modify the terminal end group in very high yields. The synthesis of polymer “cages” can be achieved by further clicking these end functionalized star polymers with a small molecule alkynylated caps consisting a complementary number of arms.

66. Solution processable conjugated polymers spanning the color palette as used in electrochromic devices

Rayford H. Bulloch*, Yinhua Zhou, Fengling Zhang, Aubrey L. Dyer, John R. Reynolds

Utilizing vibrantly colored electroactive polymers in conjunction with charge balancing polymers exhibiting minimal color change during redox switching, electrochromic devices can be created which exhibit high optical contrast and color purity. Devices incorporating these materials and their properties are increasingly important points of study. A wide color palette can be produced in devices with solution-processable polymers, via multi-layer devices or codeposition of mixtures. Color-mixing in electrochromic polymers can create a “CMY” color gamut, which is examined via spectroscopic and colorimetric measurements. Also examined is the powering of window-type electrochromic devices by a variety of power sources. Further, the photochemical stability of electrochromic polymers is examined, employing PProDOT-(CH₂OEtHx)₂ as a model system for study. The effects of prolonged irradiation to films of PProDOT-(CH₂OEtHx)₂ under a variety of atmospheric conditions is examined, via spectroscopic, colorimetric, and surface characterization measurements, to demonstrate the robustness of these materials to photodegradation.

67. Polymeric thermo-sensitive systems for cancer hyperthermia therapy

Rhythm R. Shah*, David E. Nikles, Christopher S. Brazel

To avoid patient discomfort and prevent serious side-effects associated with cancer therapy, nanoparticle-loaded temperature-sensitive polymeric gels and micelles were devised to deliver localized chemotherapy and hyperthermia in response to external stimuli. Polymeric systems were conceptualized to include hyperthermia therapy through the use of magnetic nanoparticles combined with localized chemotherapy triggered by magnetic heating. This system should efficiently generate heat inside human body, release the desired quantity of drug triggered by temperature rise, be completely non-toxic in vivo, and possess the ability to target cancer tumors. Here we investigate the design and performance of thermo-sensitive hydrogels and block co-polymer micelles with iron oxide nanoparticles. We also experimentally evaluate the heating efficiency, effect of viscosity on temperature rise, drug release efficiency, and toxicity of these drug delivery systems.

68. Synthesis and Characterization of Phosphonium Ionenenes from Step-Growth Polymerization

Ryan J. Mondschein*, Sean T. Hemp, Asem I. Abdulahad, and Timothy E. Long

Phosphonium ionenes are a distinct class of polyelectrolytes that incorporates the cationic phosphorous throughout the polymer backbone. Charge density, charge placement, macromolecular architecture and chemical composition all significantly influence the physical properties associated with these ionenes. Step-growth polymerizations of ditertiary phosphines with dibromoalkanes, dibromo-functionalized polyglycols, or a combination allowed for the synthesis of novel phosphonium ionenes. Size exclusion chromatography yielded absolute molecular weights and differential scanning calorimetry and thermogravimetric analysis determined thermal properties. Phosphonium ionenes exhibit better thermal stability compared to ammonium ionenes due to the cationic ammonium's tendency to undergo Hofmann elimination. Counterion exchange introduces bulkier anions creating more free volume influencing the thermal properties of the phosphonium ionenes. Possible applications for cationic polyelectrolyte phosphonium ionenes include flocculation, antimicrobials, nonviral nucleic acid delivery, and membranes.

69. Fluorescent multi-responsive nanostructures consisting of magnetite core and conjugated block copolymers

Sourav Chatterjee, Cornelia Rosu, Evgueni E. Nesterov and Paul S. Russo

Core-shell hybrid nanostructures have received an increased interest because of their many current and potential applications. Such nanostructures show combined properties of the core and shell which neither component can display alone. An increase in sensitivity of fluorescent chemo- and biodetection devices can be achieved as a response to external stimuli such as magnetic field. In this work, shells of fluorescent conjugated polymers and block copolymers (e.g. polythiophenes, poly-p-phenylenes) were prepared on magnetic (superparamagnetic) nanoparticles consisting of a magnetite core coated with a layer of silica by using surface-initiated living polymerization. The goal of this research was to investigate the change in fluorescent properties as a function of silica shell thickness, order of sublayers in the conjugated block copolymer shell, as well the effect of applied magnetic field, both in thin-film powder and in colloidal solution.

70. Effect of network structure from different processing conditions of blow molding on the mechanical property of semi-crystalline polymers

Xin Dong*, David McDowell and Karl Jacob

The blow molding process of thermoplastics involves multiple stages of melt extension, which will influence the crystallization behavior and consequently the mechanical property of the end product. To assist the design and choice of polymers and processing route, and predict their structure-property relationship, lamellar semi-crystalline structures from different thermodynamic crystallization conditions were investigated through multi-scale simulations and experiments. Uniaxial tensile tests were performed on the semi-crystalline samples sharing common morphological features such as in the crystallinity, crystal orientation, lamellae thickness and density distribution, etc. However, the results demonstrated significantly different stress-strain behavior. By combining the observations of morphologies during deformation tests and analysis of the stress-strain curves, conclusions were made that the effectiveness of the network had a strong influence on the mechanical property and strain hardening behavior. The oriented network from the constant stress crystallization, owing to the taut chains, gave rise to optimal mechanical response with substantial strain-hardening.

71. Free-standing Polyelectrolyte Multilayers of PDADMA/PSS

Yara E. Ghoussoub*, Joseph B. Schlenoff

Polyelectrolyte multilayer (PEM) thin films exhibit great potential for applications in areas such as the coating of biomaterials, drug delivery, wound healing and tissue engineering. To date, the majority of PEMs are firmly anchored to a substrate. Releasing these films would broaden their field of application and give the opportunity to elaborate new materials. Approaches used to make self-standing membranes include the disassembly of a sacrificial layer made of stimuli responsive materials. Biocompatible multilayers of poly(diallyldimethylammonium) (PDADMA) and poly(styrene sulfonate) (PSS) are released from an aluminum substrate by exposure to aqueous alkali (pH = 11). The morphology and viscoelasticity of the obtained PDADMA/PSS films have been explored with atomic force microscopy before and after the release. Surface and bulk composition were investigated by X-ray photoelectron spectroscopy.

72. Synthesis and properties of polyurethanes containing triptycene units

Zhengmian Chang*; S. Richard Turner

The properties of polyesters, polycarbonates and other polymer backbones containing triptycene units have been the topic of considerable recent research. With the unique paddle-shape structure, it is proposed that the triptycene structures can interlock with each other under strain and provide enhancement of mechanical properties. In our work, triptycene units were introduced into both hard and soft segments in polyurethanes to investigate the effect of bulky structure on the morphology and properties of polyurethanes. It was found that the bulky structure of triptycene, when used as chain extenders in hard segments, can disturb the hydrogen bonding interaction and phase separation. A flexible diisocyanate, such as 1,6-hexamethylene diisocyanate can be used to minimize such disturbance. When triptycene units were introduced into the soft segments, the bulky structures did not significantly affect the phase separation and crystallization can be controlled.

73. Controlling Polyelectrolyte Complex Formation for Adhesive and Drug Delivery Applications

Justin M. Serrine*, Asem I. Abdulahad, Chainika Jangu, and Timothy E. Long

Polyelectrolyte complexes were prepared in aqueous solution using a quaternary ammonium-containing methacrylate and sodium polystyrene sulfonate (PSSNa). Complex size was investigated via dynamic light scattering (DLS), and complexation occurred as a function of charge ratio (+/-), NaCl concentration, polycation molecular weight, and temperature. Complex size reached a maximum at a charge ratio of +/- = 1:1, and complex coacervate formation was observed at elevated salt concentrations and +/- = 1:1. Finally, evidence of kinetically trapped structures was found in DLS particle size experiments as a function of temperature. Polyelectrolytes and complex coacervates have applications in underwater adhesives, polymeric ionic liquids, glass-ionomer dental restorative cements, and drug delivery.

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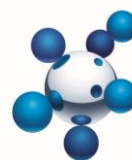


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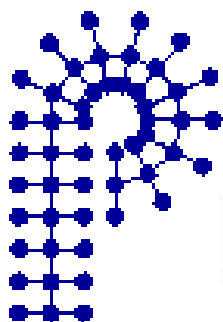


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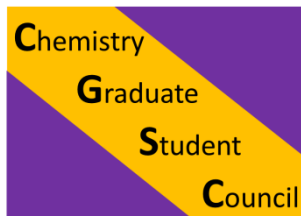
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