

# GPC2019



**The Polymer and Biomacromolecular  
Applications and Characterization  
Conference**



**July 10-11, 2019**  
**Le Méridien New Orleans**  
**New Orleans, Louisiana**



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**Welcome to GPC2019:**

***The Polymer and Biomacromolecular Applications and Characterization Conference!***

July 10, 2019

Dear Colleagues,

Welcome to GPC2019! On behalf of the Scientific Committee and Tosoh Bioscience, we are delighted to welcome you to New Orleans, LA for the GPC2019 Conference. This year's program highlights recent work from some of the top researchers in the field of polymer science, in both academia and industry, centering on the preparation and characterization of new macromolecular materials. This year also sees the introduction of "flash talks" from junior researchers from academia, where they give five minute highlights of their research interests. We expect many lively discussions will result from all presentations at this conference and are looking forward to the new collaborations and research directions that result.

We are also excited to take the opportunity to honor Dr. Kenneth B. Wagener with a Lifetime Achievement Award. Ken's life-long dedication to the field of polymer science is readily evident from numerous awards and honors already received: from various high impact publications, patents and presentations to the wide variety of top researchers he has trained. It is our honor to present the Lifetime Achievement Award to our esteemed colleague. Please join us in congratulating Ken.

GPC2019 offers the opportunity for you to establish new contacts, exchange ideas and renew established connections. One again, welcome! We hope you enjoy the conference and the beautiful city of New Orleans.

***Laissez les bon temps rouler!***

(Let the good times roll!)

Emily Pentzer, Ph.D.  
Texas A&M University  
Scientific Committee Co-Chair

Scott Grayson, Ph.D.  
Tulane University  
Scientific Committee Co-Chair

Yoshiyuki Shindo  
Tosoh Bioscience LLC  
President

# Scientific Committee

## *Committee Co-Chairs*

### **Scott Grayson, Ph.D.**

*Joseph H. Boyer Professor of Chemistry, Tulane University, Department of Chemistry, New Orleans, LA*

Scott Grayson completed his Ph.D. in Chemistry from the University of California, Berkeley (2002), studying the role of polymer architecture for dendritic drug carriers under Jean M. J. Fréchet. Following post-doctoral studies in the laboratories of C. Grant Willson at the University of Texas, he was appointed as a professor in the Department of Chemistry at Tulane University in New Orleans, Louisiana, USA.

He now holds the Joseph H. Boyer Professorship of Chemistry at Tulane, where he explores the synthesis and applications of well-defined, yet complex macromolecular structures. His research group has recently focused on the synthesis of amphiphilic and cyclic polymers for applications including transdermal drug delivery and gene therapies. He is presently the 2018-2019 Fulbright Fellow to Sweden, collaborating with the research group of Michael Malkoch at the Royal Institute of Technology in Stockholm.

### **Emily Pentzer, Ph.D.**

*Associate Professor, Department of Chemistry, Department of Materials Science and Engineering,  
Texas A&M University, College Station, TX*

Emily Pentzer is an Associate Professor in the department of chemistry and the department of materials science and engineering at Texas A&M University in College Station, TX. She received a BS in chemistry from Butler University (2005) and Ph.D. in organic chemistry from Northwestern University (2010), where her thesis work focused on metathesis routes for preparing and polymerizing unsaturated medium-sized lactones and lactams under the direction of Professor Sonbinh T. Nguyen. She then worked with Professor Todd Emrick in the Polymer Science and Engineering Department at UMass Amherst where she focused on the synthesis and assembly of electronically active materials for organic photovoltaics as part of a DOE EFRC on Polymer-Based Materials for Harvesting Solar Energy. In 2013, Dr. Pentzer joined the faculty at CWRU in Chemistry and received a secondary appointment in Macromolecular Science and Engineering in 2015.

Dr. Pentzer and her lab moved to Texas A&M University in the summer of 2019, as part of both the chemistry and materials science and engineering departments. Her research uses organic synthesis to access new materials and assemblies as a route to understand structure-property-application relationships and access functions not possible with current state-of-the-art systems. Dr. Pentzer regularly participates and organizes events aimed at the professional development of graduate students and facilitating the transition of graduate students and post-docs to successful and vibrant careers in academia. She has received several awards including the NSF-CAREER award (2016), the PMSE Young Investigator Award (2017), and the CWRU Faculty Diversity Excellence Award. She currently serves as an Associate Editor for the RSC journal *Polymer Chemistry* as well as the publicity chair for the Polymer Division (POLY) of the American Chemical Society.

## Committee Members

### **Matthew Becker, Ph.D.**

*W. Gerald Austen Endowed Chair in Polymer Science and Polymer Engineering, Associate Dean for Research in the College of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH*

Matthew Becker is the Associate Dean for Research in the College of Polymer Science and Polymer Engineering at The University of Akron. Professor Becker joined UA in 2009 where he is a Professor of Polymer Science and Biomedical Engineering. To date, his group has published more than 100 papers and has 20 patents pending. He is the founder of two start-up companies, 3D Bioresins & 3D Bioactives. In 2015, Professor Becker was one of two scientists worldwide under 40 named Macromolecules-Biomacromolecules Young Investigators. Professor Becker will move to the Department of Chemistry at Duke University on August 1, 2019.

Professor Becker completed his Ph.D. in organic chemistry in 2003 at Washington University in St. Louis under the direction of Professor Karen L Wooley as an NIH Chemistry-Biology Interface Training Fellow. In 2003, Dr. Becker moved to the Polymers Division of the National Institute of Standards and Technology for a NRC Postdoctoral Fellowship in biophysics. He joined the permanent staff in 2005 and led projects in bioimaging and combinatorial methods for tissue engineering working with the NIH, Industry and FDA to advance measurement methods for combination products. He received his BS in chemistry in 1998 from Northwest Missouri State University.

### **Eva Harth, Ph.D.**

*Director, Welch Center for Excellence in Polymer Chemistry, Professor, Department of Chemistry, University of Houston, Houston, TX*

Eva Harth studied chemistry at the University of Bonn, Germany and the University of Zurich, Switzerland. She obtained her Ph.D. in 1998 from the MPI for Polymer Research in Mainz. A postdoctoral fellowship with CPIMA (NSF-Center for Polymer Interfaces and Macromolecular Assemblies) brought her to the IBM Almaden Research Center, California, USA, focusing on the development of new living free polymerization techniques and approaches to nanoscopic materials. In 2001, she joined XenoPort, Inc. as a Staff Scientist and started in 2004 at Vanderbilt University as Assistant Professor with a primary appointment in the Department of Chemistry and a secondary appointment in the Department of Pharmacology, VUMC. In 2007, she was awarded with the NSF CAREER Award. In 2011, she was promoted to Associate Professor with tenure and served three years as the Director and DGS of the Interdisciplinary Materials Science Graduate Program (IMS). Starting in the Fall 2017, she moved to the University of Houston where she was appointed as Full Professor with tenure in the Department of Chemistry and serves as the Director of the Center of Excellence in Polymer Chemistry, funded by the Welch Foundation and the University of Houston. Since 2009 she serves as an Associate Editor for Polymer Chemistry, a journal of the RSC.

### **Stuart Rowan, Ph.D.**

*Barry L. MacLean Professor for Molecular Engineering Innovation and Enterprise, University of Chicago, Chicago, IL*

Stuart Rowan earned his B.Sc. (Hons.) and Ph.D. in Chemistry from the University of Glasgow. His post-doctoral work began in the Chemistry Department at the University of Cambridge, continued at Girton College, Cambridge, and culminated at the University of California, Los Angeles. Rowan was the Kent Hale Smith Professor in the Department of Macromolecular Science and Engineering at Case Western Reserve University before joining the faculty at the Institute for Molecular Engineering (IME) in 2016. Rowan won the American Chemical Society Mark Scholar Award, the Morley Medal, the National Science Foundation CAREER Award, and the CWRU School of Engineering Research Award. He is a Fellow of the Royal Society of Chemistry, Deputy Editor of Macro Letters, published by the American Chemical Society, and a member of the editorial advisory boards of the Journal of Polymer Science Part A: Polymer Chemistry, Chemical Science, the Journal of Macromolecular Science, and Pure & Applied Chemistry. Rowan has published more than 125 scientific papers and reviews.

**Brent Sumerlin, Ph.D.**

*George B. Butler Professor, University of Florida, Gainesville, FL*

Brent Sumerlin graduated with a B.S. from North Carolina State University in 1998 and received his Ph.D. in 2003 at the University of Southern Mississippi under the direction of Dr. Charles McCormick. He continued his work as a Visiting Assistant Professor/Postdoctoral Research Associate in the group of Krzysztof Matyjaszewski at Carnegie Mellon University from 2003–2005. In 2005 he joined the Department of Chemistry at Southern Methodist University as an Assistant Professor, and in 2009 he was promoted to Associate Professor with tenure. In the fall of 2012, Prof. Sumerlin joined the Butler Polymer Research Laboratory and the Center for Macromolecular Science & Engineering within the Department of Chemistry at the University of Florida, where he is currently the George Bergen Butler Professor of Polymer Chemistry.

Prof. Sumerlin is a Fellow of the Royal Society of Chemistry and was been named a Kavli Fellow (Frontiers of Science, National Academies of Sciences). He has won a number of awards, including the Alfred P. Sloan Research Fellow, NSF CAREER Award, ACS Leadership Development Award, Journal of Polymer Science Innovation Award, Biomacromolecules/Macromolecules Young Investigator Award, and the Hanwha-Total IUPAC Award. He is an associate editor of *ACS Macro Letters*.

**Karen Wooley, Ph.D.**

*W.T. Doherty-Welch Foundation Chair in Chemistry, Department of Chemistry,  
Texas A&M University, College Station, TX*

Karen L. Wooley is the W. T. Doherty-Welch Chair in Chemistry and a University Distinguished Professor at Texas A&M University, where she holds appointments in the Departments of Chemistry, Chemical Engineering and Materials Science & Engineering. She also serves as Director of the Laboratory for Synthetic-Biologic Interactions. Research interests include the synthesis and characterization of degradable polymers derived from natural products, unique macromolecular architectures and complex polymer assemblies, and the design and development of well-defined nanostructured materials. The development of novel synthetic strategies, fundamental study of physicochemical and mechanical properties, and investigation of the functional performance of her materials in the diagnosis and treatment of disease, as non-toxic anti-biofouling or anti-icing coatings for the marine environment, as materials for microelectronics device applications, and as pollutant remediation systems are particular foci of her research activities.

Her academic training included undergraduate study at Oregon State University (B.S., 1988) and graduate study under the direction of Professor Jean M. J. Fréchet at Cornell University (Ph.D., 1993). She began an academic career as an Assistant Professor of Chemistry at Washington University in St. Louis, Missouri, was promoted in 1999 to Full Professor with tenure, was installed as a James S. McDonnell Distinguished University Professor in Arts & Sciences in 2006, and in 2009, Karen relocated to Texas A&M University. Recent awards include the American Chemical Society Award in Polymer Chemistry (2014), Royal Society of Chemistry Centenary Prize (2014), Fellow of the Royal Society of Chemistry (2014), Honorary Fellow of the Chinese Chemical Society (2014), Oesper Award (2015), and Fellow of the American Academy of Arts and Sciences (2015). Karen currently serves as an Associate Editor for the Journal of the American Chemical Society, among many other advisory roles within the broader scientific community.

# Conference Agenda

Wednesday, July 10, 2019

**07:30-09:00**    **Registration/Breakfast Open**

**09:00-09:15**    **Opening Remarks**

**Scott Grayson**, Tulane University, **Emily Pentzer**, Texas A&M University

**09:15-10:30**    **Session I: Synthesis**

**09:15-09:40**    *Simple coupling strategies for construction of high molecular weight block copolymers*  
Craig Hawker, University of California Santa Barbara

09:40-10:05    *Designing polymers to degrade using thiol-ene polymerizations*  
Derek Patton, The University of Southern Mississippi

10:05-10:30    *Synthesis and properties of "Janus-type" linear-dendritic block copolymers (LDBC) for therapeutic applications*  
Davita Watkins, The University of Mississippi

**10:30-10:55**    **Break**

**10:55-11:45**    **Session II: Macromolecules**

10:55-11:20    *Synthesis of poly[n]catenanes*  
Stuart Rowan, University of Chicago

11:20-11:45    *Design block copolymer structures for porous carbon fibers*  
Greg Liu, Virginia Tech

**11:45-01:15**    **Lunch**

**Early Career Presentations by:**

Quentin Michaudel, Texas A&M University  
Kaitlyn Crawford, University of Central Florida  
Jimmy Lawrence, Louisiana State University  
Kristin Hutchins, Texas Tech University

**01:15-02:05**    **Session III: Analysis**

01:15-01:40    *Analyzing the sequence of semi-sequenced copolymers*  
Tara Meyer, University of Pittsburgh

01:40-02:05    *Three decades of examples illustrating the importance of rigorous characterization studies*  
Karen Wooley, Texas A&M University

**02:05-02:30**    **Break**

**02:30-03:45**    **Session IV: Responsive**

02:30-02:55    *Morphology transitions in responsive block copolymers: incorporating molecular probes and triggers*  
Daniel Savin, University of Florida

02:55-03:20    *Cationic polymerizations controlled by external stimuli*  
Brett Fors, Cornell University

03:20-03:45    *Externally-triggered heating of polymer-decorated nanoparticles for catalysis and drug release*  
Brent Sumerlin, University of Florida

- 04:00-06:00**    **Poster Session**
- 07:00-09:00**    **Group Dinner**  
*Napoleon House*, 500 Chartres Street, New Orleans, LA

## Thursday, July 11, 2019

- 07:30-08:45**    **Breakfast Open**
- 08:45-09:00**    **Presentation of Lifetime Achievement Award**
- 09:00-09:30    *You don't do anything by yourself*  
Kenneth Wagener, University of Florida
- 09:30-09:45**    **Presentation of Poster Awards**
- 09:45-10:15**    **Break**
- 10:15-11:30**    **Session V: Peptoid**
- 10:15-10:40    *Polymer research in an undergraduate laboratory course*  
Mark Watson, University of Kentucky
- 10:40-11:05    *Polypeptide, polypeptoid and beyond: synthesis, characterization and materials properties*  
Donghui Zhang, Louisiana State University
- 11:05-11:30    *The challenge of secondary structure formation: characterization of polypeptides in solution*  
Matthias Barz, Johannes Gutenberg University Mainz
- 11:30-01:00**    **Lunch**
- Early Career Presentations by:**
- Rachel Letteri, University of Virginia  
Abigail Knight, University of North Carolina, Chapel Hill  
Robert Comito, University of Houston  
Zachariah Page, University of Texas at Austin
- 01:00-01:50**    **Session VI: Radical Polymers**
- 01:00-01:25    *Insertion and radical polymerizations of metal-organic catalysts*  
Eva Harth, University of Houston
- 01:25-01:50    *A radical way to make nanomaterials*  
Erik Berda, University of New Hampshire
- 01:50-02:10**    **Break**
- 02:10-03:00**    **Session VII**
- 02:10-02:35    *Non-opioid, post-surgical pain management using degradable polymer meshes*  
Matt Becker, The University of Akron
- 02:35-03:00    *Macromolecular therapeutics - addressing multidrug resistant diseases*  
Jim Hedrick, IBM
- 03:00**            **Closing Remarks**

# Lifetime Achievement Award Recipient

## **Kenneth Wagener, University of Florida**

"Members of the Wagener research group focus on the chemistry associated with polymer science. We deal largely with mechanism as applied to the synthesis of new polymer structures. My contributions as a research advisor are to suggest opportunities for original research, and to maintain proper connections with external organizations that are interested in our work. Ultimately, I want to see all students in this group get what they want out of the degree, then enthusiastically proceed on to the next step in their career."

The common theme that defines our research relates to synthetic polymer chemistry and how it might be used in creating well defined polymer structures. A large part of our work is devoted to metathesis reactions, where the research has been mechanistic in nature. We immerse ourselves in the chemistry associated with creating new polymers, and we also find ourselves interested in modeling well known materials, like polyethylene, to better understand their behavior.

## PROFESSIONAL EXPERIENCE

University of Florida, Gainesville. George B. Butler Professor of Polymer Chemistry and Director, Center for Macromolecular Science and Engineering. Teaching, research, and administration related to organic and polymer chemistry. Research group pioneered acyclic diene metathesis (ADMET) polymerization, engaged in synthesis of precision model polymers for polyolefins, biologically directed polymers, morphological investigation of fuel cell membrane polymers, preparation of latent silicon elastomer structures. Joined faculty as Associate Professor of Chemistry in 1984. ADMET reaction now found in textbooks, internationally recognized as an integral part of polymer chemistry. 110 Students (undergrad, grad, and postdoc) have passed through research group to date.

Akzo Nobel nv, American Enka Research, Enka, NC. 1973 – 1984. Research Department Head and Technical Director. Directed activities related to polymerizations and structure/property determinations – research in medical membranes, nylon, polyester & cellulose fibers, biopolymers, polymerization catalysis, conductive polymers, polymer decomposition, and NMMO solvents for cellulose. Employed in various positions within this Dutch & German corporation. Continuous consulting in Europe with Akzo Nobel and sister companies the past 25 years.

Promoted four times during this eleven-year period (Research Department Head; Membrane Research Section Head; Research Scientist, Polymers; Senior Research Chemist) – served as Technical Director/Membrana, Inc. (an AKZO new venture in California), the last position held prior to entering academics.

University of North Carolina at Asheville, NC 1975 – 1984 Adjunct Professor of Chemistry. Evening teaching of organic and polymer courses (two courses each year) while working at Akzo Nobel during the day.



## Speaker Profiles

### **Craig Hawker, University of California Santa Barbara**

The Hawker Group is an interdisciplinary research group involved in a wide range of fundamental and applied materials chemistry and molecular engineering challenges. Current interests include design and synthesis of nanoscopically defined materials for applications ranging from next-generation microelectronic devices to polymer-based therapeutics. Major emphasis is on development of methods for facile synthesis of functionalized macromolecules with well-controlled architectures. This combination of fundamental advances in polymer synthesis with detailed understanding of physical properties have led to commercial success in the personal care, pharmaceutical and advanced material arenas.

### **Derek Patton, The University of Southern Mississippi**

Research in the Patton Lab is focused on the design and synthesis of functional polymeric materials. We are particularly interested in the use of surface engineering strategies that can enhance polymer materials' properties, such as surface reactivity, tailored wettability, or interfacial adhesion. Our lab environment is team-oriented and interdisciplinary bringing together scientists with expertise in polymer synthesis, surface chemistry, thin film fabrication, and surface analytical techniques for the design of functional polymer materials.

### **Davita Watkins, The University of Mississippi**

The Watkins Research Laboratory develops novel functional materials with tunable properties through molecular self-assembly. We design, synthesize, and study organic molecules that possess unique structural and functional properties. Our fundamental goals are the following: (1) identify unique building blocks for functional materials; (2) establish synthetic protocols for those building blocks; and (3) examine the behavior of the building blocks on a molecular and macromolecular level. The well-defined, programmable nanostructured materials produced in our laboratory are designed to be used in a variety of applications which range from therapeutics to electronic devices. In turn, our research allows us to use tools from all areas of science including analytical, computational, and materials chemistry.

### **Stuart Rowan, University of Chicago**

The Rowan Group focuses on the design, synthesis and study of new polymeric materials. Using a blend of organic chemistry, polymer synthesis and polymer characterization (both structural and mechanical) we are focused in 4 main classes of materials (1) Cellulose Nanomaterials, (2) Supramolecular Polymers, (3) Dynamic Covalent Polymers and (4) the design and synthesis of Interlocked macromolecules. We are specifically interested in the development of stimuli-responsive materials that have the ability to heal cracks, actuate, shape change and alter properties such as stiffness upon application of a specific stimulus. We are also interested in biomimetic materials and systems.

### **Greg Liu, Virginia Tech**

"Economical energy" has been listed as the number one challenge in the 14 Grand Challenges by the National Academy of Engineering. For several decades, researchers have made tremendous efforts toward finding a solution to this challenge, but no satisfactory answer has been reached. Admittedly, our knowledge of the materials that can potentially solve this challenge is ever growing, but the integration of these materials into practical applications has not yet met our requirements and is still far from our expectations. Organic polymers, composed of earth-abundant elements, are low-cost and easily-processible materials that can be manufactured into a wide range of macroscopic and microscopic structures. Inorganic nanoparticles, on the other hand, have tremendously rich optical, magnetic, catalytic, and plasmonic properties. Separately, neither has been utilized to the full potential for energy applications.

My group envisions that the two materials, if designed and engineered smartly, can be integrated together, resulting in unique collective emergent properties and impacting renewable energy and environmental science and technology at a tremendous level. The research in my laboratory is to integrate these two materials, bridge their respective properties, and find potential solutions to the grand challenge of energy. Specifically, we will design, synthesize, and utilize the two categories of materials (namely, polymers as structural matrices and inorganic nanoparticles as functional units) to create engineered nanocomposites and nanostructures for addressing challenges in the areas of energy, catalysis, and environmental science and engineering.

### **Tara Meyer, University of Pittsburgh**

Research in the Meyer Group is a collaborative effort that involves faculty, graduate students and undergraduates. We focus on two major areas: 1) the use of sequence to control the polymer properties and 2) the development of polymeric materials that respond to electrical signals. For sequence control, we target applications in drug delivery and optoelectronics while our work in electroresponsive polymers is directed at creating materials that would be moldable interfaces or be parts of soft robotic mechanisms.

### **Karen Wooley, Texas A&M University**

Our research interests are focused broadly upon the design, synthesis and characterization of unique polymers, with emphasis upon the development of synthetic methodologies that allow for the preparation of complex nanostructured materials. Just as typical synthetic chemists prepare molecules of specific stereochemistry and connectivity, using natural products as the targets to exercise their craft, we are identifying nanoscopic natural products, e.g. viral capsids, lipoproteins, and even dolphin skin, as synthetic targets. We do not attempt, however, to synthesize exactly these structures, but rather, to produce synthetic materials that capture the basic structural and functional elements.

### **Daniel Savin, University of Florida**

Research in the Savin group is largely associated with the applications of self-assembled polymers and block copolymers, with particular emphasis on solution characterization and property-structure relationships. Research projects can be broken into three broad categories: (1) Self-assembly and responsiveness in polypeptide and bioconjugate block copolymers, (2) Nanoparticle dispersants and organogels as novel remediation and delivery agents, and (3) Impact energy-absorbing polymer nanocomposites.

Although we invoke most polymer solution characterization techniques, the experimental workhorse in the laboratory is an ALV multi-angle light scattering goniometer for simultaneous static, dynamic and depolarized scattering measurements. We also rely heavily on microscopy (TEM, SEM, and AFM) for morphology characterization. Materials testing is done using rheology, DMA, Instron and Dynatup instruments. The PI has extensive experience in polymer characterization, in particular light scattering techniques for both solution and bulk/gel systems.

### **Brett Fors, Cornell University**

Research in the Fors group will focus on the development of new synthetic methods and catalyst systems to control polymer architecture, composition, and function. Under this general theme, three different areas of research will be pursued. First, new systems will be developed that will enable precise regulation over catalyst reactivity in situ with light. This general platform will allow control of a diverse array of polymerization processes (i.e., radical, cationic, ring-opening, insertion, etc.) with an external stimulus, which will facilitate a broad range of applications in polymer and materials science. Second, new strategies for the synthesis of conjugated polymers from the parent C–H based monomers will be investigated. These systems will provide more environmentally friendly processes, greatly simplify monomer synthesis, and provide access to novel structures. Lastly, new catalyst systems will be explored for photomediated radical polymerizations.

### **Brent Sumerlin, University of Florida**

The Sumerlin Research Group investigates well-defined polymeric materials with selected functionality, composition, and molecular architecture. Our particular focus is on polymers that are water-soluble and stimuli-responsive. Such "smart" polymers have the ability to self-assemble or dissociate in solution in response to changes in their surroundings. Potential target applications include controlled and targeted drug delivery, surface modification, and the synthesis of self-healing materials. Our interests are at the interface of bio-, organic, and polymer chemistry, with particular focus on fusing the fields to prepare materials with synergistic properties.

### **Mark Watson, University of Kentucky**

**Materials Chemistry** as defined by IUPAC committee is: *"The synthesis, processing, characterization and exploitation of substances that have useful, or potentially useful, properties and applications. The focus of the research is the creation, understanding and development of substances or systems with improved properties that will impact positively on business and personal life. To use chemistry to create substances that may lead to new technological opportunities or significant improvements in existing technology."*

Our materials chemistry research group mainly focuses on conceiving new organic materials, designing efficient (short) synthetic routes to prepare them, and then testing their properties. The types of materials we currently target include organic small molecules, oligomers, and polymers in the form of amorphous, crystalline, and liquid-crystalline materials. We select existing building blocks, or build new ones, and modify them chemically to rationally engineer their physical properties and processability. We employ more modern controlled radical polymerizations, as well as well-established "bread and butter" step polymerizations.

### **Donghui Zhang, Louisiana State University**

Research efforts in our group are focused on the design, synthesis and characterization of biomimetic, bioinspired and bio-related functional polymers (b3p). We are interested in developing synthetic tools to access well-defined polymers. In addition, synthetic efforts are also coupled with fundamental studies of the polymer structure and functions, providing understanding of how molecular structure and processing parameters impact macroscopic properties. Students participating in our research will receive training in polymer chemistry and various analytic methods for macromolecular characterization.

### **Matthias Barz, Johannes Gutenberg University Mainz**

In our research, we focus on the development of polypept(o)ides – a hybrid material based on polypeptides and polypeptoids, e.g., polysarcosine. Our aim is to meet the complex requirements of therapeutic materials with robust and clean chemistry to develop not only potent therapies but enable clinical translation. The reduction of synthetic efforts requires rethinking of existing concepts and developing new ones. With this in mind, we have developed protective groups for cysteines, which are stable against hard nucleophiles (ring-opening polymerization or solid phase synthesis), but reactive against soft ones (controlled disulfide formation), enabling post-polymerization of peptides by chemoselective disulfide formation. By applying these tools, we design nanoscopic or macroscopic materials based on polypept(o)ides either by chemical synthesis or by controlled self-assembly.

While we perform monomer, polymer and particle synthesis and characterization in-house (collaboration with Manfred Schmidt), we work in close cooperation with biologists, pharmacists and medical doctors to understand the biological behavior and to adjust our carrier systems to the biology of medical needs.

### **Eva Harth, University of Houston**

Our research is focused on the development of polymerization techniques to make specialized polymer materials with applications in industry and the biomedical field.

The discovery of the Metal-Organic Insertion/ Light Initiated Radical Polymerization (MILRad) allows us to design distinct block copolymer architectures with selected functionalities in a one-pot process guided by light irradiation. It is possible to polymerize for the first time olefines and acrylates together in a one-step process. It will be our goal to explore the MILRad polymerization with a variety of monomer combinations and catalytic systems to develop specialized thermoplastics.

A long standing interest in the area of biomaterials in our group has let us to explore hydrogel materials with unique mechanical properties which we develop with collaborators in Europe and the US.

We are active in the area of nanomaterials for drug delivery applications for the last 10 years and further develop our patented nanosponge technology to a second generation nanosponge material. Furthermore, photocatalytic processes allow us to probe deeper into functional expandable nanomaterials that are generated from one parent particle system. This technology affords nanomaterial size expansions, the integration of functional groups and other entities together with polymer linear and branched chains.

### **Erik Berda, University of New Hampshire**

The overarching theme for research in our laboratory is the synthesis of well-defined nanostructures with an emphasis on complex architectures with the ability to adapt based on external stimuli, similar to biological systems. While this research is fundamental in nature, it represents an important initial step towards advanced nanoarchitectures that are capable of mimicking the complexity found in natural systems.

Our laboratory specializes in synthesizing single-chain nanoparticles (SCNP), which are organic nanoparticles formed by the intramolecular reaction of single polymer chains in highly dilute solution. Currently, our lab is working on identifying synthetic methodologies that impart interesting functionality or structural features in SCNP.

## **Matt Becker, The University of Akron**

The Becker Laboratory for Functional Biomaterials seeks to develop new materials and methods which stimulate and direct specific cellular functions. The multidisciplinary group works at the interface of chemistry, organic materials and medicine and focuses on developing chemical methods to tether peptides, proteins and growth factors to translationally-relevant materials. These materials include peptide and carbohydrate derivatized materials, which incorporate bio-functional species in a controlled manner, with the goal of influencing cell response.

## **Jim Hedrick, IBM**

Our program approaches a set of clustered problems of fundamental and therapeutic interest. For example, the discovery and refinement of antibiotics was one of the crowning achievements in the 20th century that revolutionized healthcare treatment. If properly dosed, they could eradicate infection. Unfortunately, this therapeutic specificity of antibiotics also leads to their undoing as under-dosing (incomplete kill) allows for minor mutative changes that mitigate the effect of the antibiotic leading to resistance development. The pervasiveness of drug-resistant infections is a global health issue with significant healthcare, economic and societal burdens. A similar situation exists in cancer treatments, where multiple chemotherapeutics and chemosensitizers are required to mitigate resistance and loss of efficacy. We have developed numerous platform technologies based on rationally designed macromolecules that address key issues in multi-drug resistant diseases including cancer as well as bacterial, and viral infections. Supramolecular structures were developed for cancer therapy that target both cancer cells and cancer stem cells, mitigate drug resistance, and metastasis. Membrane-disruptive macromolecular antimicrobials for treatment of infections were demonstrated in vitro and in vivo, and shown to have efficacy and selectivity against multidrug-resistant *A. baumannii* and MRSA without inducing toxicity. We have demonstrated a general and broad-spectrum strategy to prevent viral infections using multi-functional macromolecules that inhibit viruses such as influenza, Zika, Ebola, and HBV. In each case, the dynamic nature of the non-covalent hydrogen bonding and ionic interactions allows these polymers to co-evolve concurrently with the disease, thereby preventing resistance without loss in effectiveness.

In a second example, living organisms have evolved a variety of interfaces and barriers to control the trafficking of small and large molecules in and out of cells, organs and tissues. Many diseases require the encapsulation, transport and release of foreign agents into healthy cells (viral and bacterial infections). An understanding of these processes is critical to the illumination of the molecular mechanism of disease, but also provides a guide to developing strategies to deliver therapeutic agents to specific cells and tissues. Nature's ability to assemble macromolecules into highly cooperative and functional assemblies provides an inspiration for our efforts to devise synthetic design criteria to interrogate and exploit the relationship between molecular structure, non-covalent interactions and processing conditions to create new functional macromolecular assemblies. The targeting and controlled release of therapeutic agents or probe molecules to specific organs and specific cells in the body is one of the major challenges in developing more effective therapies. Central to this goal are the many materials challenges associated with the encapsulation, transport and release of such agents at a specific time and place in the exceedingly complicated and dynamic environment of living organisms. We have developed modular self-assembly strategies to investigate the use of non-covalent interactions to assemble multifunctional assemblies that can encapsulate small molecules, genetic materials and probes, and reach its target through active and passive targeting. Using this approach, we have developed hydrogels that can encapsulate and release antibodies in a controlled manner to improve patient's compliance and increase treatment efficacy.

The foundation for this platform is based on an organocatalytic approach to the synthesis of biocompatible/degradable macromolecules with precisely defined molecular weights, end-group fidelity and backbone functionality.

## Early Career Presenter Profiles

### **Quentin Michaudel, Texas A&M University**

The focus of the Michaudel Lab lies at the interface of organic chemistry and polymer science. Polymers are truly shaping today's world and can be found everywhere, from commodity plastics to high-end technologies. As chemists, this raises many important questions: Can we make plastics more sustainable by replacing fossil fuel-based monomers with biorenewable resources? Can we develop biodegradable polymers with desirable physical properties? Finally, how do we maintain the rapid pace of advancements in solar cell construction, energy source systems, and biomedical technologies? These challenges in mind, our group is interested in the design of new polymerization methods and synthesis of unique monomers—all with the aim to prepare materials with unprecedented electronic and mechanical properties.

To this end, three areas of research are actively explored: (1) The design of sequence-controlled polymerizations to afford conjugated polymers with defined monomeric sequences. (2) The scalable synthesis of twisted/distorted conductive materials, including graphene nanoribbons, by employing "bottom-up" strategies. (3) The invention of a traceless click process to rapidly synthesize and functionalize both small molecules and polymers.

Through monomer, catalyst, and polymer preparation, researchers will receive extensive training in the fields of synthetic organic chemistry, as well as polymer synthesis and characterization.

### **Kaitlyn Crawford, University of Central Florida**

The Crawford Group, also known as the Soft Functional Materials and Sensors Lab, seeks to cultivate the synergy found in working across disciplines such as materials science, bioengineering, nanotechnology, chemistry and medicine, to address overarching human-health and environmental challenges relevant to our 21st Century society. Specifically, the Crawford group develops soft functional materials that are designed for dynamic use at the biological interface. Research interests related to these efforts include: block copolymers, nanomaterials, interfacial interactions, soft matter synthesis and characterization, self-assembly, wearable sensors, and bionic materials.

### **Jimmy Lawrence, Louisiana State University**

The Lawrence Lab focuses in the development of precision polymer- and nanomaterial-based building blocks to construct high performance materials. Such advanced materials having accurately tailorable properties and functions (e.g., stronger, safer, responsive) hold the solutions to our society's grand technological challenges.

We look forward to applying new insights from our research to spur interdisciplinary collaborations with other research groups and industries.

### **Kristin Hutchins, Texas Tech University**

Research in the Hutchins group is inspired by the way in which nature utilizes reversible, non-covalent interactions such as hydrogen bonding and metal coordination to create large, functional structures (e.g. DNA double helix, hemoglobin). Our group focuses on designing and synthesizing new functional materials that can be used in applications ranging from water purification and environmental remediation to molecular sensors and responsive crystals.

In our work, we study supramolecular (non-covalent) interactions and aim to develop a fundamental understanding of the solid-state (crystalline) behavior of small molecules such as pharmaceutical compounds and heavy metal complexes. We utilize a variety of techniques including X-ray diffraction, NMR spectroscopy, IR spectroscopy, and imaging characterization. The solid-state behavior of these small molecules inspires the development of new polymeric materials, which incorporate specific functional groups that are complementary to and can recognize the small molecule compounds in a specific, predesigned, and reversible manner. Our research in the design and synthesis of functional materials will address problems in materials science, environmental chemistry, and fields of industry and technology.

### **Rachel Letteri, University of Virginia**

The Letteri group will engineer materials that feature hierarchical structure and dynamic mechanical properties, and enable productive interactions with living systems. Intertwining the tunability and versatility of synthetic polymers with the sequence-dependent interactions and biological activity of peptides offers tremendous opportunities for the generation of materials well-suited to address central challenges in medicine and engineering.

### **Abigail Knight, University of North Carolina, Chapel Hill**

The Knight group focuses on designing novel macromolecular materials with functions inspired by biological systems. These materials will generate platforms of new biomimetic polymeric architectures addressing growing concerns in treating, diagnosing, and preventing human disease.

This research bridges the fields of chemical biology and polymer chemistry using characterization and synthetic tools including polymer and solid-phase synthesis and nanomaterial characterization. Specific project areas include: (1) developing a new class of peptide-polymer amphiphiles inspired by metalloproteins, (2) designing well-defined polymer bioconjugates for biosensing, and (3) evolving functional biomimetic polymers.

### **Robert Comito, University of Houston**

The fields of organic and polymer synthesis rely heavily on transition metal catalysis to achieve selectivity, without consuming impractical reagents. Thus, the development of improved catalysts, featuring broader substrate scope or higher selectivity, and new catalytic reactions are goals at the forefront of synthetic chemistry. Toward this end, main group elements offer a complementary platform of reactivity that could be a great asset to synthetic catalysis. In general, main group compounds are more coordinatively labile than transition metals, and thus as catalysts are less susceptible to coordinative inhibition. Thus, main group compounds feature improved compatibility with polar functional groups, valuable for the synthesis of medicinally relevant molecules and biodegradable polymers. Furthermore, alkyl-main group compounds are more stable to homolysis and  $\beta$ -hydride elimination than their transition metal counterparts. This property may enable living olefin polymerization with main group catalysts, useful for preparing olefin block copolymerization and end group functionalization. Yet main group catalysts are rarely used synthetically beyond simple Lewis acid or Lewis base catalysis. The Comito Laboratory aims to develop new methods for organic and polymer synthesis using organometallic catalysis. In particular, we will develop new main group catalysts to address longstanding challenges in transition metal catalysis.

### **Zachariah Page, University of Texas at Austin**

Current research in the Page Group at UT Austin is interdisciplinary in nature, including aspects of synthetic chemistry, materials science, and engineering. Tailored templating and photochemical approaches are being studied to generate well-defined soft materials and composites with interesting (opto)electronic and mechanical properties, with applications spanning bioelectronics, flexible electronics, and additive manufacturing.



## Poster Presentation Abstracts

### **Poster: Flow Enabled Control over Macromolecule Architecture**

Dylan Walsh, Sarit Dutta, Simon A. Rogers, Charles E. Sing and Damien Guironnet

Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana–Champaign

Shape, size and composition are nature's most fundamental design features, enabling highly complex functionalities. Despite recent advances, the independent control of shape, size and chemistry of macromolecules remains a synthetic challenge. We report a scalable methodology to produce large well-defined macromolecules with programmable shape, size and chemistry. Specifically, bottlebrush polymers (branched polymers with high branch density all originating from a linear backbone) are synthesized with variable brush length along the backbone. This enables the construction of any axisymmetric shape including: cone, sphere, hourglass, football, and bowtie shapes.

The synthesis is enabled by the combination of reactor engineering principles and controlled polymerizations. One controlled polymerization synthesizes the arms of the bottlebrush (ring opening polymerization or anionic polymerization) and the other polymerizes the backbone of the bottlebrush (ring opening metathesis polymerization). Theoretical derivations, in conjunction with a numerical model, are used to aid in the design and characterization of the shaped macromolecules. We have further characterized the materials through atomic force microscopy (AFM) as well as rheology. Rheological data is further correlated back to Brownian dynamics simulations. This methodology provides a unique opportunity to study the impact of macromolecules shapes.

**Poster: General Route for the Preparation of Olefin Based Block-Copolymers**

Dylan J. Walsh, Tianwei Yan and Damien Guironnet

Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana–Champaign

Block copolymers and their mesoscopic self-assembly remains a topic of intense research in polymer science. Potential applications of these materials include separation, nanolithography, catalysis, and plastics engineering. For the most part, block copolymers are produced by anionic or controlled radical polymerization, in which both polymerization techniques are not compatible with olefin monomers. Today, polyethylene and polypropylene account for more than 40% of the polymers produced worldwide. Therefore, developing an efficient synthesis route for the preparation of olefin-based block copolymers has high potential impact.

We will present a novel methodology that consists of converting any polyolefin made via catalytic polymerization into a macroinitiator compatible with anionic, ring opening polymerization and atom transfer radical polymerization. Our strategy yields olefin-based block copolymers with very precise architecture control. Finally, we also compare the productivity of our approach with previously reported synthetic strategies.

**Poster: Open-to-Air and Additive-Free Photocontrolled Radical Polymerization of Acrylates and Acrylamides**

Jessica R. Lamb and Jeremiah A. Johnson

Department of Chemistry, Massachusetts Institute of Technology

Overcoming oxygen sensitivity is a well-known challenge in the field of controlled radical polymerizations (CRP). Previous work on non-degassed CRP mainly relies on additives – such as enzymes, photocatalysts, or sacrificial reductants – to scrub the oxygen both in solution and in the headspace of a closed reaction vessel before polymerization can proceed. Limited examples in open vessels have been reported. We developed an additive-free iniferter polymerization utilizing high-intensity blue (450 nm) light to generate excess radicals to deplete the local oxygen concentration, allowing for the controlled polymerization of acrylates and acrylamides in completely open vials. Living behavior is demonstrated through control over molecular weight, narrow molecular weight distributions, chain extension, and block copolymer synthesis. The origin of oxygen tolerance and future applications will be discussed.

**Poster: Structured Macromolecular Materials for the Site Isolation of Iridium-Containing Catalysts**

Madalyn R. Radlauer, Jacob C. Hickey, Thaw Z. Myint, Dana Wong, Jessica C. Rodarte and Giovanna Bauer

Department of Chemistry, San Jose State University

Finding systems for tandem catalytic reactions is made especially difficult because of the numerous potential side reactions that can occur between the reagents, products, and catalytic species. Even if all of the species are compatible, accessing conditions under which both reactions will occur may prove tricky. Our research focuses on the design, synthesis, and use of structured macromolecular materials, which are intended to isolate a transition metal catalyst as well as alter the steric environment of this catalytic species. The distal position of the aromatic ring of a pincer ligand is substituted with an alkene to allow for direct polymerization. This procedure is paired with our work to optimize arm-first star polymer synthesis via reversible addition-fragmentation chain-transfer polymerization. The effectiveness of a small molecule iridium pincer complex for alkane dehydrogenation is compared with that of metallated macromolecular systems with linear or star structures. Modified small molecule catalysts have been successfully synthesized and catalytic work is ongoing.

**Poster: Building Degradable Materials via Ring-Opening Metathesis Polymerization**

Peyton Shieh and Jeremiah A. Johnson

Department of Chemistry, Massachusetts Institute of Technology

Ring-opening metathesis polymerization (ROMP) of norbornene-based monomers is a powerful approach to prepare complex polymer architectures. Nevertheless, a fundamental limitation of polymers prepared via this strategy is their lack of facile degradability, which may limit their utility in self-assembly and biomedical applications. Here, we describe a class of readily available monomers that copolymerize efficiently with norbornene-based monomers to provide copolymers with backbone degradability under mildly acidic aqueous conditions and degradation rates that can be tuned over several orders-of-magnitude depending on substituents. The application of these monomers to tuning the in vivo biodistribution and clearance rate of bottlebrush polymers, as well as to the synthesis of linear, bottlebrush, and brush-arm star copolymers with degradable segments, is described. This addresses one of the longstanding challenges for polymers prepared via ROMP, opening the door to responsive materials for biomedical applications and self-assembly.

Moreover, materials that demonstrate high mechanical robustness with full degradability may find use in myriad applications, but few examples exist. By combining our newly designed monomers with an in-depth understanding of network topology, we demonstrate a simple strategy to endow known mechanically-tough crosslinked materials with the ability to readily dissolve into soluble fragments on demand while preserving its mechanical properties, enabling in-depth characterization of network structure and opening the door to a variety of novel applications. Finally, we establish the generality of our approach by upgrading other types of commercially-relevant materials. Overall, this work demonstrates how an emphasis on molecular design can be an enabling strategy to improve known materials and endow them with novel properties.

**Poster: Impacts of Brush Density, Composition, and Identity on the Thermal Stability of Mixed Polymer Brushes**

Chester Simocko, Alexis Sarabia and Omar Munoz

Department of Chemistry, San Jose State University

Polymer self-assembly has been utilized to create nanoscale features which can then be controlled by micron sized templates, leading to well-defined and long-range ordered phases. This has potential applications such as nanoscale templating and electronics and smart surfaces. While block polymers are traditionally the systems studied when polymer self-assembly is being studied, mixed-polymer brushes have also been shown to self-assemble into distinct phase regimes. The phase behavior of both binary and ternary brushes has been studied, the thermal characteristics of these brushes have not been explored which can directly impact the potential applications of polymer brushes.

We have synthesized homo, binary, and ternary polymer brushes consisting of polystyrene (PS), poly (methyl methacrylate) (PMMA), poly (2-vinyl pyridine) and/or poly (4-vinyl pyridine) (P4VP). After thermal degradation, the polymer loss was found to depend on three factors; brush density, polymer identity, and brush composition. In particular, brushes brush density had the largest effect on that amount of polymer lost during degradation and brushes that contain P4VP demonstrated surprising stability compared to brushes that did not.

**Poster: Ambient Temperature Waterborne Polymer/Reduced Graphene Oxide Nanocomposite Films: Effect of Reduced Graphene Oxide Distribution on Electrical Conductivity**

Yasemin Fadil,<sup>1</sup> Le N.M. Dinh,<sup>1</sup> Monique O. Y. Yap,<sup>1</sup> Rhiannon P. Kuchel,<sup>2</sup> Yin Yao,<sup>2</sup> Taro Omura,<sup>3</sup> Florent Jasinski,<sup>1</sup> Stuart C. Thickett,<sup>4</sup> Hideto Minami,<sup>3</sup> Vipul Agarwal,<sup>1</sup> and Per B. Zetterlund<sup>1</sup>

<sup>1</sup> Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, University of New South Wales

<sup>2</sup> Mark Wainwright Analytical Centre, University of New South Wales

<sup>3</sup> Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University

<sup>4</sup> School of Natural Sciences (Chemistry), University of Tasmania

Graphene has enormous potential as an ideal filler in nanocomposite polymeric materials for a wide range of applications such as coatings, electronic devices, and electromagnetic shielding. We have prepared ambient temperature film-forming and electrically conductive polymer/reduced graphene oxide (rGO) nanocomposite films based on styrene and *n*-butyl acrylate by environmentally friendly aqueous latex based routes, namely miniemulsion polymerization using graphene oxide (GO) as surfactant and “physical mixing” approaches (i.e. mixing of aqueous polymer latex with aqueous GO), followed by heat treatment of the films to convert GO to rGO. The distribution of GO sheets and the electrical conductivity depend strongly on the preparation method, with electrical conductivities in the range  $9 \times 10^{-4}$  –  $3.4 \times 10^2$  S/m. Physical mixing approaches resulted in higher electrical conductivity than miniemulsion approaches, which is attributed to the former providing a higher level of self-alignment of rGO into larger linear domains. These results present substantial insight into how the distribution of GO sheets within hybrid nanocomposites can be controlled by preparation method, thus enabling nano-engineering design for specific potential applications.

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***Poster: Topological Design of a Hole Transporting Molecular Bottlebrush System for Highly Anisotropic Alignment in Solution-Processed Thin Films***

Nari Kang,<sup>3</sup> Eric E. Leonhardt,<sup>1</sup> Sangho Cho,<sup>1</sup> Stanislav V. Verkhoturov,<sup>1</sup> Michael J. Eller,<sup>1</sup> Fan Yang,<sup>1</sup> Yannick Borguet,<sup>1</sup> Yen-Hao Lin,<sup>1</sup> Tianyu Yuan,<sup>1</sup> Ashlee A. Jahnke,<sup>1</sup> Mariela Vazquez,<sup>1</sup> Lei Fang,<sup>1</sup> Emile A. Schweikert,<sup>1</sup> Guorong Sun,<sup>1</sup> and Karen L. Wooley<sup>1,2,3</sup>

Chun Liu,<sup>4</sup> Anatoliy N. Sokolov,<sup>4</sup> Travis McIntire,<sup>4</sup> Carl Reinhardt,<sup>4</sup> W. H. Hunter Woodward,<sup>4</sup> Liam Spencer,<sup>5</sup> and Peter Trefonas<sup>6</sup>

Departments of <sup>1</sup>Chemistry, <sup>2</sup>Chemical Engineering, and <sup>3</sup>Materials Science and Engineering, Texas A&M University  
The Dow Chemical Company, <sup>4</sup>Midland, MI, <sup>5</sup>Freeport, TX, <sup>6</sup>Marlborough, MA

In modern organic electronics and optoelectronics, anisotropic packing/alignment of charge transport functionalities has been recognized as a crucial factor for construction of high-performance devices. Depending upon the inherent charge transport direction within a device, molecular-scale “edge-on” orientation of charge-transporting hosts is favorable for organic field-effect transistors (OFETs), while the “face-on” orientational counterpart is preferential for organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).

Solution-cast polymer thin films for hole transport layer (HTL) devices in OLED display applications have been proposed in recent years. In this regime, a key requirement for the HTL device is high hole mobility and transport to the emission layer. We developed a novel solution-cast polymeric material that can achieve unprecedented high degrees of anisotropy, which we attribute to successful alignment of the charge carrying moieties. The structure-property relationship between obtained anisotropic data with polymer topology, monomer selection, and charge carrier group will be described in detail, as well as the effect of film processing. These results will be then correlated with measurement of charge transport using hole-only device and compared to control devices using the compositionally analogous polymer films but with little or no anisotropic molecular packing. While the films of this study were too thin to fully interpret the results in terms of measured hole mobility, the preliminary data indicate facile charge transport is commensurate with a high degree of anisotropic alignment. From these results, we propose the topological design strategy for anisotropic alignment of polymer, which is of potential usefulness for solution-processable HTL films with high charge mobilities.



**Poster: Bulk High Temperature Metathesis of Precision Polymers**

Julia Pribyl, Michael Bell, Grace Hester, Taylor Gaines and Ken Wagener

Department of Chemistry, University of Florida

Until recently, bulk synthesis of high melting point precision polymers via acyclic diene metathesis (ADMET) polymerization was impractical due to catalyst limitations. Advances in the synthesis of metathesis catalysts has enabled the performance of metathesis at unprecedented temperatures (>150 deg C)—a necessity for preparing high molecular weight ADMET polymers in a scalable fashion. Specifically, the bulk synthesis of precision polysulfones on a multi-gram scale has been accomplished. The bulk mechanical and chemical properties of these materials has been studied in detail; the results suggest these new materials may be suitable for forming fibers.

**Poster: Exploring the Polymerization-Induced Self-Assembly Process**

Taylor A. Jenkins, Cathryn M. Hierak, Brooke E. Barnes, Alban H. R. Charlier and Daniel A. Savin

Department of Chemistry, University of Florida

Block polymer assembly templates are often used to fabricate “smart” materials, but the methodology by which they are prepared often involves time-consuming steps like post-polymerization modification and solution processing. Polymerization induced self-assembly (PISA) is a facile, “one-pot” approach for preparation of well-defined block polymer nanostructures. Different morphologies can be obtained simply by varying the relative volume fraction of the hydrophobic block and the concentration of the polymerization (up to 50 w/w %). The novelty of our approach involves incorporating polypeptides into either the corona or the core of the assemblies, using reversible-addition fragmentation chain-transfer (RAFT)-mediated PISA and ring-opening polymerization (ROP)-mediated PISA, respectively. The corona polypeptides are pH-responsive, offering morphological control based on solution pH. The core polypeptides physically crosslink the nanostructures upon chain extension, leading to polymerization-induced gelation (PIG) in many cases. We are using light scattering (LS) and a specific spectroscopic technique, electron paramagnetic resonance (EPR), to probe the self-assembly event that occurs during PISA for both the polypeptide corona and core experiments. These types of structures offer bio-derived, pH-controllable materials for applications in biomimicry, nanoreactors, cargo delivery vehicles, and rheological modifiers.

**Poster: Determining Sequence Distributions in Random Terpolymers by Characterizing Cross-Metathesis Digestion Products**

Michael Cole, Jordan Fitch and Tara Meyer

Department of Chemistry, University of Pittsburgh

Block polymer assembly templates are often used to fabricate “smart” materials, but the methodology by which they are prepared often involves time-consuming steps like post-polymerization modification and solution processing. Polymerization induced self-assembly (PISA) is a facile, “one-pot” approach for preparation of well-defined block polymer nanostructures. Different morphologies can be obtained simply by varying the relative volume fraction of the hydrophobic block and the concentration of the polymerization (up to 50 w/w %). The novelty of our approach involves incorporating polypeptides into either the corona or the core of the assemblies, using reversible-addition fragmentation chain-transfer (RAFT)-mediated PISA and ring-opening polymerization (ROP)-mediated PISA, respectively. The corona polypeptides are pH-responsive, offering morphological control based on solution pH. The core polypeptides physically crosslink the nanostructures upon chain extension, leading to polymerization-induced gelation (PIG) in many cases. We are using light scattering (LS) and a specific spectroscopic technique, electron paramagnetic resonance (EPR), to probe the self-assembly event that occurs during PISA for both the polypeptide corona and core experiments. These types of structures offer bio-derived, pH-controllable materials for applications in biomimicry, nanoreactors, cargo delivery vehicles, and rheological modifiers.

**Poster: Evaluation of the Separation Effect on the Microstructure Characterization of PP and PE using Different Columns Manufacturers**

Laura Nyland, Luis Paulo Bernardi, Michael Schabowski and Renata dos Reis

Advanced Characterization/Polymer Science – Braskem

The evaluation of the molecular weight (Mw) and the molecular weight distribution (MWD) by Gel Permeation Chromatography (GPC) is an important information for the development of new polyolefins. These properties are directly related to the final properties of the material. Otherwise, the long chain branching distribution along the molar mass (LCBd) evaluation is another complex evaluation and this property strongly affects the rheology of the material. The short chain branching distribution (SCBd) is another important evaluation that strongly affects the mechanical properties. The determination of these properties will vary according to the set of columns used in the equipment. In order to understand the impact of the many columns technologies available on the Mw, MWD, LCBd and SCBd measurements it was evaluated two different types of mixed bed columns. The samples evaluated on this study were: homo polypropylene (PP), random PP, low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). The experiments were carried out in two Polymer Char GPCs differing only the set of columns. In the GPC1 it was used 4 TSKgel GMHHR-H(S)HT (mixed-bed) 13  $\mu\text{m}$  and in GPC2 it was used 3 PLgel Olexis 300 x 7.5 mm (mixed bed) 13  $\mu\text{m}$ . The experimental conditions for both GPCs were the same, 1 ml/min of flow rate and detectors temperature 160°C. The evaluation of the linear materials shows similar MWD's, since they are within the calibration range of the column. Samples with a broad MWD and high molecular weight fractions have evidenced the differences between the columns. These differences meet the information available by manufacturers that show a better separation in lower MW for Olexis column, in opposite, TSKgel has a better separation in higher molar mass fractions. As it is essential to characterize the high MW fractions of bimodal HDPE and LDPE samples, with this evaluation it was possible to have a better microstructure characterization in the TSKgel columns due the higher resolution in high MW. Therefore, it will also affect the LCBd evaluation, as the LCB appears in the higher MW fractions. At least, the SCBd did not show any significant difference between the columns. The columns have some differences in separation mechanisms and by the comparison of the results TSKgel column showed a better microstructure characterization for materials with a broader MWD.

**Poster: Characterization and Assessment of Cyclic Polyether Purity via Mass Spectrometry of Polymers Fractionated by Gel Permeation Chromatography**

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<sup>a</sup> Department of Chemistry, Tulane University

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<sup>e</sup> IKERBASQUE - Basque Foundation for Science

The research herein studies the electrophilic zwitterionic ring expansion polymerization (eZREP) of monosubstituted epoxides initiated by tris(pentafluorophenyl)borane [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] to generate cyclic polyethers. The work aims to understand the effect of substituents on the generation of functional macrocyclic polyethers and the formation of topological impurities for better control of architectural purity during polymerization. Monofunctional epoxides with varying chemical substituents and linkages were polymerized, fractionated by gel permeation chromatography (GPC), and analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Using GPC fractionation, the data revealed that side reactions coexist with the macrocyclization reaction, particularly in the higher molecular weight portion of the polyether samples. By performing GPC fractionation and MALDI-ToF MS analysis as a function of molecular weight, it was possible to elucidate impurities that do not ionize easily in the crude polymer sample. Moreover, it was possible to ascertain structural assignments of major and minor products and propose corresponding reaction mechanisms to describe their formation. Substituents effects were also studied to probe the functional group tolerance of this polymerization. Finally, computational studies were performed to examine the chemical interaction between the monomer and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst, which validated the experimental results by providing insight into the likelihood of generating non-cyclic byproducts. By using both analytical and computational tools, the polymerization could be optimized to generate macrocyclic polyethers with substantially increased purity.

***Poster: Investigation of Amphiphilic Polypeptoid-Functionalized Halloysite Nanotubes as Emulsion Stabilizers Towards Oil Spill Remediation***

Tianyi Yu,<sup>a</sup> Lauren T. Swientoniewski,<sup>b</sup> Marzhana Omarova,<sup>c</sup> Mei-Chun Li,<sup>d</sup> Ioan I. Negulescu,<sup>e</sup> Naisheng Jiang,<sup>a</sup> Omead A. Darvish,<sup>a</sup> Abhishek Panchal,<sup>f</sup> Diane A. Blake,<sup>b</sup> Qinglin Wu,<sup>d</sup> Yuri M. Lvov,<sup>f</sup> Vijay T. John,<sup>c</sup> and Donghui Zhang<sup>a</sup>

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<sup>f</sup>. Institute for Micromanufacturing, Louisiana Tech University

Large scale oil spills have devastating impacts on ecosystem. Bioremediation is a noninvasive and relatively cost-effective strategy for oil spill mitigation by using dispersants to break up the oil slick into droplets in the ocean and thus to facilitate the oil biodegradation by oil-degrading bacteria. Traditional dispersants are comprised of low molecular weight surfactants in organic solvents, which have raised environmental concerns due to their toxicity towards oil-degrading bacteria in the ocean. Thus, increasing efforts have been dedicated to the investigation of environmentally benign dispersant systems for oil spill remediation.

In this contribution, we investigated the functionalization of halloysite nanotubes (HNTs), a class of naturally abundant clay nanoparticles, with amphiphilic polypeptoids, an emerging class of biocompatible and biodegradable polymers, by surface-initiated ring-opening polymerization of N-substituted glycine-derived N-carboxyanhydride monomers (NCAs). The hydrophilic-lipophilic balance (HLB) characteristic of the grafted polymers can be systematically controlled by the ratio of the hydrophilic and hydrophobic NCA monomers used in the polymerization, thus allowing the surface wettability of the HNT particles to be systematically adjusted. We assessed the performance of polypeptoid-functionalized HNTs (g-HNTs) as stabilizers for oil-in-artificial sea water (ASW) emulsions and it was found that g-HNTs can stabilize the oil-in-ASW emulsion to varying extent, which is strongly dependent on the HLB characteristic of the grafted polypeptoids. Characterization of the emulsion index and the size of oil droplets in emulsion over time has revealed that the functionalized HNTs having relatively high hydrophobic content (HLB = 12.0-15.0) afforded the most stable oil-in-water emulsions containing the smallest oil droplet sizes. This has been attributed to the augmented interfacial activities of polypeptoid-functionalized HNTs, resulting in more effective reduction of interfacial tension, enhancement of thermodynamic propensity of the HNT particles to partition at the oil-water interface and increased emulsion viscosity relative to the pristine HNTs. In addition, cell culture studies have revealed the g-HNTs were non-cytotoxic towards *Alcanivorax Borkumensis*, a dominant alkane degrading bacterium found in the ocean after oil spill. The HLB characteristic of the grafted polypeptoids was found to affect the bacterial growth profile with notably more cell proliferation in the presence of HNTs having higher lipophilic contents (HLB= 12.0-14.3) than those that are less lipophilic or pristine HNTs. It was postulated that the functionalized HNTs with higher hydrophobic polypeptoid content may promote the bacterial proliferation by providing larger oil-water interfacial area and better anchoring of bacteria at the interface.

This study has highlighted the potential of polypeptoid-functionalized HNTs where the chemical composition and HLB characteristics can be systematically tuned as a class of environmentally benign stabilizers with enhanced emulsification performance that is desired for oil spill remediation.

**Poster: Photo-Liberated Amines for N-Carboxyanhydride Ring-Opening Polymerization**

Megan R. Hill, Sofia L. Goodrich, Rebecca A. Olson and Brent S. Sumerlin

Department of Chemistry, University of Florida

The polymerization of N-carboxyanhydrides (NCAs) affords access to a vast array of synthetic polypeptides with tunable molecular weights, functionalities, and architectures. The use of light to gain spatiotemporal control over these polymerizations expands the materials applications to include 3D printing and photolithography. In this research we utilized 2-(2-nitrophenyl)propyloxycarbonyl (NPPOC) as a photoprotecting group to cage a primary amine, creating a latent initiator that was activated upon UV irradiation for NCA polymerization. Full deprotection of the caged amine was achieved after 30 min of irradiation, and the addition of a small equivalence of base allowed for greater polymerization control with narrow dispersities. Overall this method advances photo-controlled polypeptide synthesis by demonstrating high chain end fidelity, efficient chain extension, and the capability to synthesize block copolymers.

***Poster: Probing the Local Environment of pH-Responsive Polypeptides with Electron Paramagnetic Resonance to Observe Secondary Structure Transitions***

Alban H. R. Charlier, Catherine Wu, Ian R. Smith, Brooke E. Barnes, Gail E. Fanucci and Daniel A. Savin

Department of Chemistry, University of Florida

Polypeptides are a promising alternative to other common synthetic polymers for in vivo cargo delivery vehicles due to their bioinspired characteristics, but there is still a need to fundamentally understand what governs the intra- and intermolecular interactions between polypeptide chains. Herein, we describe the inter- and intramolecular interactions between polypeptides that contribute to secondary structure formation using electron paramagnetic resonance (EPR) spectroscopy. EPR is a powerful technique that probes the local environment of a spin probe on the nanometer scale. A nitroxide radical was installed onto poly(glutamic acid) (PE) to probe local mobility and polarity changes via EPR spectroscopy. We utilized 4-amino-TEMPO as an initiator for the ring-opening polymerization of N-carboxyanhydrides, and we studied the polymerization kinetics using the covalently attached spin-probe. By exploiting the pH-responsive nature of PE, we were able to observe the helix-to-coil transition via mobility and polarity information obtained through the spin-labeled polypeptide.



**Poster: Three Stable-State Switchable Polymer Metal-Organic Cage Networks**

Nathan J. Oldenhuis, Peter K. Qin, Shu Wang, Hong-Zhou Ye, Eric A. Alt, Adam P. Willard, Troy Van Voorhis, Stephen L. Craig and Jeremiah A. Johnson

Department of Chemistry, Massachusetts Institute of Technology

Traditional synthetic polymer networks have a fixed composition and topology and thus a single set of properties under typical use conditions. Inspired by the diverse form, function, and multi-state behaviors of biological materials, we report a new class of supramolecular polymer metal-organic cage gels that can reversibly and stably switch between three states that each feature unique topology and mechanical, optical, and catalytic properties. This switching ability is controlled by a photo-redox process unique to the topology of coumarin functionalized cuboctahedral Cu<sub>24</sub>L<sub>24</sub> junctions, which allows facile access to three different oxidation states (Cu(II), Cu(I), and Cu(0)), each giving rise to the material properties in its respective state. The Cu(II) state is a robust supramolecular network with modular functionality and fast network dynamics, the Cu(I) state is a disassembled catalytically active fluid that allows the rapid formation of metal-organic cage interpenetrating networks (MINs), and the Cu(0) state generates a copper suspension that can deposit metallic films. Reversible switching between these states allows their individual properties to be combined in a spatiotemporally patterned multi-material. For example, extrusion of the Cu(II) material in the presence of polymeric azides and alkynes followed by switching to the Cu(I) state and re-oxidation provides 3D-printed MINs with >100-fold enhanced toughness in irradiated regions. Moreover, switching to the Cu(0) state enables patterning metallic copper onto soft materials. These complex functions, which cannot be accessed in traditional materials, arise from synergistic interactions between three independent and reversible material states, highlighting the power and possibilities of state-switching materials.

**Poster: Characterization of Amphiphilic Grafted Nanoparticles as Oil Dispersants**

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Recently, the synthesis of amphiphilic grafted nanoparticles (AGNs) has been reported illustrating the unimolecular micelle nature of these systems. Using a combination of surface-initiated ring opening polymerization (SI-ROP) and surface-initiated atom transfer radical polymerization (SI-ATRP), poly(caprolactone)-*b*-poly(oligo(ethylene glycol) monomethyl ether methacrylate), PCL-*b*-POEGMA, can be grafted from the nanoparticle surface with a high degree of control. SiO<sub>2</sub> nanoparticles are the primary focus of this study, but other more biodegradable cores have been investigated. After discovering that these systems could uptake oil from an aqueous environment, we began to experiment with the individual lengths of each polymer block. These studies will not only help us understand the process of oil uptake into the polymer bottlebrushes, but also allow the fine tuning of encapsulation of the oil. Chains can be cleaved from the surface of the nanoparticles or collected from polymer generated in situ from adventitious free initiator to be studied via traditional structural techniques: NMR, MALDI-ToF MS, GPC. The grafted NPs themselves can be studied via TGA and FTIR to illustrate the transitions of key functional groups, as well as the polymer's percent by weight relative to the NP cores. In comparison with the data collected from the free polymer generated, assumptions can be made about the relative size of the polymer backbones grafted from the nanoparticle surface. This combination of characterization approaches helps us understand the chemistries and kinetics necessary in order to achieve an ideal oil dispersant system.

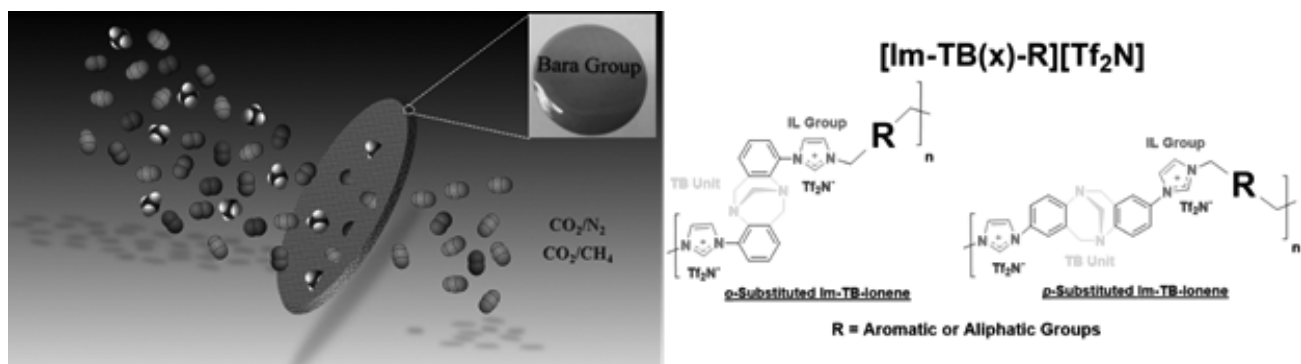
**Poster: Design and Synthesis of Imidazolium-Mediated Tröger's Base-containing Ionene Polymers for High-Performance CO<sub>2</sub> Separation Membranes**

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Herein, we are exclusively exploring a series of four novel imidazolium-mediated Tröger's base-containing ionene polymers for enhanced CO<sub>2</sub> separation. Two diimidazole-functionalized Tröger's base monomers synthesized from 'ortho' and 'para' substituted imidazole anilines were polymerized with equimolar amounts of two different aromatic and aliphatic co-monomers ( $\alpha,\alpha'$ -dichloro-*p*-xylene and 1,10-dibromodecane, respectively) via Menshutkin reactions to obtain four respective ionene-polymers ([Im-TB(*o&p*)-Xy][Cl] and [Im-TB(*o&p*)-C10][Br], respectively). The resulting ionene-polymers having halide anions were further exchanged by Tf<sub>2</sub>N anions, yielding a novel Tröger's base material [Im-TB(*x*)-R][Tf<sub>2</sub>N] or "Im-TB-Ionenes". The structural and physical properties, as well as the gas separation behaviors of the copolymers of aromatic and aliphatic Im-TB-Ionenes, have been extensively investigated with respect to the regiochemistry of imidazolium groups at 'ortho' and 'para' positions of TB unit. The results revealed that the newly designed ionenes yielded high molecular weight of polymers and displayed excellent thermal and mechanical properties. Most importantly, the imidazolium-mediated TB-Ionenes showed high CO<sub>2</sub> solubility and hence excellent CO<sub>2</sub>/CH<sub>4</sub> permselectivity of 82.5.



**Poster: Lewis Acid-Activated Reactions of Silyl Ketenes for the Preparation of  $\alpha$ -Silyl Carbonyls**

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The properties and applications of polymers are directly related to the backbone of the polymer and therefore the respective monomer. It is of interest to access new properties for materials, and in turn the need for new polymeric backbones. Silyl-substituted ketenes, for example, are attractive new monomers. These compounds are stable and easy to store relative to aryl and alkyl ketenes; as well as able to produce three unique polymeric backbones. Our group recently found that through anionic polymerization silyl ketenes can polymerize, however with little control over propagation. Under various conditions highly functionalized 2-pyranones and oligomers can also be obtained. To have a better understanding of silyl ketene reactivity and therefore the polymer system, methyl diphenyl silyl ketene (MDPhS) was reacted with various nucleophiles, including alcohols, thiols, and amines. To further examine ketene reactivity various silyl substituents were reacted with three nucleophiles to compare how the steric bulk and electronics of how the silyl substituent played a role in the reaction.

**Poster: Photonic Nanowires Arraying Masked Porphyrin Lanterns on G-Quadruplex Scaffold**

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Despite being renowned conventionally as a biopolymer of genetic importance, deoxyribonucleic acid (DNA) has drawn a lot of attention in recent years as a modular scaffold for potential applications in materials and devices. Owing to their high-fidelity self-assembly properties, DNA sequences can be programmed to dial in fluorophores to generate well-defined arrays of densely packed fluorescent dyes on 2D and 3D nanoscale architectures. To this end, we synthetically modified a short Guanine(G)-rich sequence ( $G_4T_2G_4$ ) with porphyrin fluors that self-assembled to form G-quadruplex structures which propagated further to offer long photonic wires. Our “tether and mask” strategy to protect very hydrophobic porphyrin dyes with per-*O*-methylated  $\beta$ -cyclodextrin (PM $\beta$ CD) caps to form a masked porphyrin lantern (PL) state precludes the generic pi-pi interaction of the dyes that could potentially lead to ill-defined aggregates and make the system non-fluorescent. As a result, we successfully arrayed numerous (in the hundreds) masked (with PM $\beta$ CD caps) PL units in close spacing (~2 nm) which displayed up to 180-fold enhanced brightness compared to the unmasked analogue. Such photonic constructs may find exciting applications in optical waveguides, solar energy funneling, signal enhanced fluorescent sensors, and super resolution imaging.

***Poster: How Low Can You Go: Tailoring the Dispersity and Chain Length of Polymeric Ligands to Engineer Nanoparticle Surfaces***

Jingya Xiao, Lucas Condes, Marie Claire DeKeyzer, Phihan P. Nguyen and Jimmy Lawrence

Department of Chemical Engineering, Louisiana State University

Innovations in sensing, medicine, energy harvesting, and catalysis are largely enabled by the implementation of functional nanoparticles. Due to homogeneous ligand coverage, traditional nanoparticles are isotropic materials, and the ability to impart surface anisotropy has been of great interest. Surface anisotropy can be achieved when immiscible ligands phase-separate and form microdomains on the nanoparticle surface, although controlling the ligand behavior by their structural parameters to curate nanoparticles having precise surface properties is a grand challenge. Nanoparticles with two distinct ligand shells (Janus NPs) have been shown to form when covered with small molecule- or high molecular weight polymer-based ligands. While polymers are synthetically versatile, they are inherently disperse and the impact of dispersity on ligand phase-separation behavior remains largely unexplored. Inspired by the self-assembly of discrete block co-oligomers, we hypothesized that decreasing the dispersity of polymeric ligands would promote their phase separation, even at low molecular weights. To test our hypothesis, a library of polystyrene and poly(tert-butyl acrylate) with varying degrees of polymerization and dispersities were prepared and characterized by nuclear magnetic resonance and gel permeation chromatography. Post-functionalization of the polymers allowed the polymer chain ends to be converted to thiol groups. This thiol moiety allows the polymeric ligands to phase separate while staying anchored to the surface of gold nanoparticles. Ligand phase separation behavior on the nanoparticle surface was studied using a combination of spectroscopic and microscopic techniques (UV-vis, NOESY NMR, TEM).

**Poster: Elucidating the Effect of Polymer Architecture on Metal Chelation**

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Department of Chemistry, Virginia Tech

With the continued expansion of the electronics, mining, paper manufacturing, and other industries, metal contamination of water is a growing problem. Additionally, many metal contaminants are valuable materials themselves, and metal recovery from industrial waste streams is potentially a highly sustainable process for metal production. Rare-earth elements (REEs), for example, are critical components in electronics, clean-energy technologies, catalysts, and other applications. Consequently, more effective technologies for extracting and purifying REEs are in ever increasing demand. Metal-chelating polymers have great potential in these applications due to their relatively low cost and high affinity for target elements. However, while much research has focused on specific chelating ligands attached to polymers, relatively little is known about the effect of the polymer architecture itself on metal binding.

To address this question, we have synthesized a series of polyethyleneimine derivatives with  $\alpha$ -amino phosphonate chelating groups. These materials were systematically varied with respect to molecular weight and polymer architecture (e.g., linear or branched). We then investigated the thermodynamics of binding between each material and a series of metal ions in solution using isothermal titration calorimetry (ITC) in order to gain insight into the specific structure-metal binding relationships of these materials. ITC directly measures the binding affinity ( $K_a$ ), enthalpy changes ( $\Delta H$ ), and stoichiometry of the interactions between macromolecules and metal ions in solution, which enables the elucidation of the complete thermodynamic profile of each polymer-metal interaction. We found that the stoichiometry of the polymer-metal interaction is molecular weight dependent, with smaller polymers binding more metal ions per polymer repeat unit than larger polymers with the same primary structure. ITC measurements also suggest a difference in the mode of binding between the linear and branched polymers. These results may lead to design principles for polymeric chelators to enable the development of more effective metal sequestration and separation materials.

**Poster: Multiphysics Modeling of the Separation of Polymeric Materials into Discrete Species**

Michael Dearman, Jingya Xiao, Lucas Condes, Krishnaswamy Nandakumar and Jimmy Lawrence

Department of Chemical Engineering, Louisiana State University

Synthetic oligomers and polymers with discrete structures have distinct properties that make them promising building blocks for designing future materials. Such precise building blocks are now accessible through separating disperse mixtures using automated column chromatography.<sup>[1]</sup> Thus, identifying optimal separation parameters is crucial for improving the yield and scope of this chromatography-based strategy. Traditional chromatography relies on extensive trial-and-error, which can be challenging for scalable isolation of discrete targets with minute structural differences.

To address this, we developed a finite element analysis model (COMSOL Multiphysics) with the goals of 1) understanding the elution of polymers subject to different separation conditions, 2) maximizing separation resolution, and ultimately, 3) improving the scalability and yield of discrete targets. In comparison with existing models that rely on dimensionless parameters,<sup>[2]</sup> we can incorporate solvent gradient, multiphysics (heat transfer), and other phenomena (size exclusion). To further improve the model, experimental data will be used to accurately account for the unique length-dependent properties of polymers (e.g., adsorption isotherm, glass transition temperature).

References:

<sup>(1)</sup> Lawrence, J. et al. *Journal of the American Chemical Society*, 2016, 138, 6306.

<sup>(2)</sup> Gu, T. et al. *Chemical Engineering Science*, 1992 47, 253.



## **Poster: Innovative Solutions in Gel Permeation Chromatography**

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Polymers are ubiquitous materials used in various disciplines of science, industry, and technology. They appear in countless commercial products including medical devices, pharmaceuticals, food products, and the automotive industry to name a few.

The applicability of a given polymeric product depends on its physical, chemical, and mechanical properties which must be considered when designing a product to ensure it can withstand application-specific strains and conditions. Many of these properties depend on the polymer's molecular characteristics including molecular weight, molecular weight distribution, and intrinsic viscosity. Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), has been the method of choice for determining the molecular characteristics. The accuracy of this solution-based method depends on the complete dissolution of the material. Many polymers pose unique challenges when dissolving, namely, cellulose and conductive polymers.

Cellulose is insoluble in most common solvents due to its crystallinity and strong hydrogen bonding networks. Historically derivatization or special solvent systems have been used for its solubilization which often require harsh conditions such as elevated temperatures and prolonged dissolution times. These methods are tedious and can cause undesirable reactivity including degradation, aggregation, or the association of cellulose fibers.

Conductive polymers known as "synthetic metals", such as polythiophenes and their derivatives, exhibit excellent conductivity, high mechanical strength, and good processability. These polymers have shown potential applications in biomedical engineering as neural probes and biosensors. Due to the presence of extended conjugation along the polymer backbone, the chains are rigid and possess strong interchain interactions resulting in poor solubility.

In this study, we address the dissolution challenges associated with these polymers and present the optimization of the GPC instrumentation, to create a robust, reliable, and reproducible method for GPC analysis. Our findings have led to a more in-depth understanding of the presented polymers molecular characteristics, which improves upon the efficacy and the end-use behavior of these materials.

***Poster: Investigating Solution Size Variations of Dendritic and Linear Polymer Analogues using Gel Permeation Chromatography, Diffusion Ordered Spectroscopy-Nuclear Magnetic Resonance, and Dynamic Light Scattering***

Oluwapelumi Kareem, Chris Keller, McKenna Redding and Scott M. Grayson

Department of Chemistry, Tulane University

Dendrimers are multi-functional, monodisperse, spherical molecules with high structure fidelity. They are made up of a series of branched polymeric arms that emanate from a central core leading to many end groups at the dendrimer's periphery. These peripheral end groups form what is referred to as the outer shell. This outer shell represents the primary interface between the dendrimer and solvent and changes in surface functionalization can have a significant impact on the solvent compatibility of these polymers. Though the impact of solvent quality on the solution size of various polymers has been explored in detail, solvent effects on dendritic molecules have not been explored to the same extent. Due to their "spherical" nature, it is assumed that the relative size of a dendrimer does not change greatly between solvents. This may be due to the inability of the branched arms to significantly expand or collapse relative to the core (comparative to analogous linear polymers) owing to steric barriers, especially at higher generations. It is expected that a linear polymer of an equivalent molecular weight would have a greater degree of size change relative to the quality of the solvent due to its innate flexibility and access to a wide range of conformations. To explore this concept, analogous dendritic and linear polymers will be analyzed using size measuring techniques including Gel Permeation Chromatography (GPC), Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance (DOSY-NMR), and Dynamic Light Scattering (DLS) in a range of solvents.

**Poster: Characterization of Narrowly Dispersed and Monodisperse Polyethylene Glycol using Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry**

Molly E. Payne, Oluwapelumi O. Kareem and Scott M. Grayson

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Polyethylene glycol (PEG) is an inexpensive, commercially available polymer that has many biomedical and material applications. Due to its water-solubility and biocompatibility, it has been used in drug conjugation, as a humectant, as an anti-foaming agent in food, and as a stabilizer for preservation of ancient wooden objects. PEG is typically synthesized to have hydroxyl end groups but can also be produced with specialized end groups depending on the application. Although there are many polymer characterization techniques available, few can provide as useful information about polymer end group analysis as matrix-assisted laser desorption time of flight mass spectrometry (MALDI-TOF MS). When sample preparation and data acquisition parameters are optimized, spectra should be obtained with sufficient resolution and mass accuracy to enable determination of overall molecular weight distribution, repeat unit mass, and subsequently, end groups of most homopolymers. Further evidence and confirmation of end groups can be confirmed via a selective functionalization. In this study of PEG, MALDI-TOF MS is used to identify end groups and is further confirmed by selective functionalization reactions. Furthermore, the oxidative degradation mechanism of PEG is described here by examining the degradative products through MALDI-TOF TOF MS and finally confirming the end groups by selective functionalization. These findings suggested consistent oxidative behavior for both narrowly dispersed and monodisperse PEG. However, monodisperse PEG helped to validate the results by providing much simpler spectra without the issue of overlapping signals, often found in dispersed samples. The results demonstrate that not only can end groups of PEG be identified by MALDI-TOF MS characterization, but also that this techniques can elucidate the mechanism of oxidation of PEG through analysis of the degradation products.

**Poster: Dispersion Emulsion Polymerization of Graphene Oxide and Cobalt Oxide Armored Particles**

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Emulsions are mixtures of two or more immiscible fluids that are stabilized by a chemical surfactant. The most common emulsions consist of oil droplets dispersed into a continuous water phase. In recent years' graphene oxide nanosheets have received much attention as 2D particle surfactants due to its amphiphilic properties. New particle surfactants are important for tuning the composition and properties of assemblies and enabling advanced applications, such as energy harvesting and management. The synthesis of a variety of graphene oxide-cobalt oxide (GO-CO) armored particles made from monomers with varying degrees of polarity. (i.e., hydrophobicity) was successfully carried out through dispersion emulsion polymerization. The particles were studied and characterized by optical microscopy, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA). Optical microscopy images that were taken post polymerization show spherical particle formation. Additionally, from the optical microscopy images, we can see that the particles vary in size depending on the monomer used. The SEM images reveal rough surfaces on the particles and XPS studies show traces of cobalt oxide. The thermal stability of the particles was also determined by TGA. Additional experiments were conducted using transmission electron microscopy (TEM) in order to determine the location of cobalt within the particle. The overall goal of this project is to evaluate the redox properties and coatings applications of the polymer -GO-CO composites.





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