

GPC2017



● ● ● The Polymer and Biomacromolecular
Applications and Characterization
Conference



July 19-20, 2017
W Atlanta – Buckhead
Atlanta,
Georgia



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Welcome to GPC2017:

The Polymer and Biomacromolecular Applications and Characterization Conference!

July 19, 2017

Dear Colleagues,

On behalf of the Scientific Committee and Tosoh Bioscience, it is our pleasure to welcome you to Atlanta, GA for the GPC2017 Conference. The program this year includes discussions around the characterization of biomacromolecules and natural polymers using Gel Permeation Chromatography (GPC) including case studies from leading chemical companies, as well as the latest in research and theory from academia.

This gathering is particularly special as we present Dr. Jimmy Mays with a Lifetime Achievement Award. Dr. May's lifetime dedication to the polymer field is evident in the numerous awards and honors he has received throughout his career, as well as the vast array of publications attributed to him. It is our honor to present this Lifetime Achievement Award to an esteemed scientist and a respected colleague. Please join us in congratulating Dr. Mays on his achievement.

We hope you get a chance to renew old friendships, to establish new contacts, and to exchange ideas with your colleagues and peers. Once again, we welcome you to the GPC2017 Conference and hope that you enjoy the venue and your stay in Atlanta!

Matthew Becker, Ph.D.
The University of Akron
Scientific Committee Co-Chair

John Reynolds, Ph.D.
Georgia Institute of Technology
Scientific Committee Co-Chair

Yoshiyuki Shindo
Tosoh Bioscience LLC
President

Scientific Committee

Committee Co-Chairs

Matthew Becker, Ph.D.

Associate Dean for Research; Professor, Department of Polymer Science, The University of Akron, Akron, OH

Dr. Becker received his Ph.D. in organic chemistry in 2003 at Washington University, and worked at NIST-Polymers Division from 2003-2009. Professor Becker joined the University of Akron in 2009 and is a W. Gerald Austen Professor of Polymer Science and Biomedical Engineering as well as the Associate Dean for Research in the College of Polymer Science and Polymer Engineering. Dr. Becker's research group has published more than 100 papers and has 25 patents pending.

John Reynolds, Ph.D.

Professor, Chemistry and Biochemistry, Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA

Dr. John R. Reynolds is a Professor of Chemistry and Biochemistry and Materials Science and Engineering at the Georgia Institute of Technology with expertise in polymer chemistry. He serves as a member of the Center for Organic Photonics and Electronics (COPE) and Director of the Georgia Tech Polymer Network (GTPN). His research interests have involved electrically conducting and electroactive conjugated polymers for over 35 years with work focused on the development of new polymers by manipulating their fundamental organic structure in order to control their optoelectronic and redox properties. His group has been heavily involved in developing new polyheterocycles for visible and infrared light electrochromism, along with light emission from polymer and composite LEDs (both visible and near-infrared) and light emitting electrochemical cells (LECs). Further work is directed to using organic polymers and oligomers in charge storing supercapacitors and photovoltaic cells.

Dr. Reynolds obtained his M.S. (1982) and Ph.D. (1984) degrees from the University of Massachusetts in Polymer Science and Engineering. He has published over 350 peerreviewed scientific papers, has 35 patents issued and ~10 patents pending, and served as co-editor of the "Handbook of Conducting Polymers" which was published in 2007. He serves on the editorial board for the journals ACS Applied Materials and Interfaces, ACS Central Science, Macromolecular Rapid Communications, Polymers for Advanced Technologies, and the Journal of Macromolecular Science, Chemistry. John has been married since October of 1986, has three children, and he and his wife make their home in Dunwoody GA. He can be reached by e-mail at reynolds@chemistry.gatech.edu or see <http://ww2.chemistry.gatech.edu/reynolds/>.

Honorary Chair

Jimmy W. Mays, Ph.D.

Distinguished Professor, University of Tennessee, Knoxville, Knoxville, TN

Professor Jimmy Mays received his B.S. degree in Polymer Science from the University of Southern Mississippi in 1979 and a Ph.D. in Polymer Science from the University of Akron in 1984 under the direction of Professor Lewis Fetters. After graduation he worked for several years at Hercules Research Center, prior to joining the faculty at the University of Alabama at Birmingham. In 2002 he moved to his current position as UT/ORNL Distinguished Scientist at the University of Tennessee, Knoxville and Oak Ridge National Laboratory. Professor Mays' research is centered on polymer synthesis and polymer characterization and solution properties. He is a Fellow of the American Chemical Society, Fellow of the Royal Society of Chemistry, and Fellow of the American Association for the Advancement of Science.

Committee Members

David Gillespie

Senior Research Chemist, The Dow Chemical Company, Freeport, TX

David Gillespie has been working in the area of GPC since 1986 and has a background in Chemical Engineering from Drexel University (Philadelphia, PA). Gillespie's initial industrial focus was on carbohydrate analysis (working with the USDA-ARS-ERRC) where he specialized in viscometry, multi-angle light scattering, and chromatographic deconvolution methods in both analytical and semi-preparative-scale GPC systems.

Gillespie joined Viscotek in 1990 and served as its Technical Services Manager, while he also headed their Applications Laboratory and Instrument Repair Services. Gillespie joined Chevron Chemical Corporation in 1997, where he focused on microstructure characterization of polyolefins, mainly involving the simultaneous interpretation of ATREF and GPC techniques to ascertain a more robust picture of these semi-crystalline polymers. Gillespie has been with the Dow Chemical Company since 2000, where he currently is in Performance Plastics Characterization, focused mainly on polyolefins. Besides his direct focus on interpreting GPC data, he is involved in chromatography simulations, deconvolution, and structure-property correlations. Additionally, Gillespie was involved in developing 2D cross fractionation (ATREF-GPC) technology for polyolefin technology and he works with semi-preparative and preparative scale systems involving molecular weight and crystallinity separations of polyolefins.

He has been awarded several patents on polymer resin compositions and polymer analysis technology. Above all, he appreciates others' time in lively discussions on solution properties vs. melt properties and how to extend the bounds of current polymer characterization technology. David Gillespie looks forward to meeting you and discussing how we together can continue to evolve, incorporate, and optimize GPC technology.

Scott Grayson, Ph.D.

Associate Professor, Tulane University, New Orleans, LA

Dr. Grayson completed his Ph.D. in Chemistry from the University of California, Berkeley (2002), studying the role of polymer architecture for drug delivery 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. As the Joseph H. Boyer Professor at Tulane, his present research 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 as well as their characterization and applications.

Emily Pentzer, Ph.D.

Assistant Professor, Case Western Reserve, Cleveland, OH

Dr. Pentzer 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 Case Western Reserve University in the Department of Chemistry and received a secondary appointment in Macromolecular Science and Engineering in 2015. Her research uses organic synthesis to access new materials and assemblies as a route to understand structure-property relationships and access electronic properties not possible with current state-of-the-art systems. Dr. Pentzer has received several awards including the NSF-CAREER award, and serves as an Associate Editor for the RSC journal *Polymer Chemistry* as well as the publicity co-chair for the Polymer Division (POLY) of the American Chemical Society. She was recently awarded a Glennan Fellowship from Case Western and was named a 2017 ACS PMSE young investigator.

Conference Agenda

Wednesday, July 19, 2017

- 07:00-08:30** **Registration/Breakfast Open**
- 08:30-08:45** **Opening Remarks**
- 08:45-12:00** **Session I: Biomacromolecules and Natural Polymers**
- 08:45-09:45** **Key Note Lecture:** *Post Printing Modification of Poly(propylene fumarate) Scaffolds for Enhancing Cellular Function*
Matthew Becker, The University of Akron
- 09:45-10:15 *Characterize Polymer Topology and Purity by GPC and MALDI-TOF MS*
Scott Grayson, Tulane University
- 10:15-10:30** **Break**
- 10:30-11:00 *Ultra-High Molecular Weights via Aqueous Reversible-Deactivation Radical Polymerization*
Brent Sumerlin, University of Florida
- 11:00-11:30 *Solvent-Free, Mussel-Inspired Polyester Adhesives with Impressive Underwater Adhesion*
Abraham Joy, The University of Akron
- 11:30-12:00 *Drag-Tagged Ethidium Bromides: Intercalating Dye-Tag Conjugates as Novel Mobility-Shifting Agents for Microchannel DNA Separations*
Annelise Barron, Stanford University
- 12:00-01:30** **Lunch**
- 01:30-04:00** **Session II: High Temperature GPC: Polyolefins**
- 01:30-01:40** **Lifetime Achievement Award Winner Announcement**
- 01:40-02:20 *Use of High-Temperature GPC to Characterize In Vivo Oxidative Degradation of Polypropylene*
Jimmy Mays, University of Tennessee, Knoxville
- 02:20-02:50 *An Assessment of Characterization Techniques for LDPE Microstructure*
David Gillespie, The Dow Chemical Company
- 02:50-03:00** **Break**
- 03:00-03:30 *Separation of Polyalphaolefins by Two-Dimensional HPLC-SEC Chromatography*
Youlu Yu, Chevron Phillips Chemical Company LP
- 03:30-04:00 *Utilizing Redox-Active Catalysts for the Synthesis of Tailored Polyolefins*
Brian Long, University of Tennessee, Knoxville
- 04:00-05:30** **Poster Award Winners Announcement and Poster Session**
- 06:00-08:00** **Group Dinner**

Thursday, July 20, 2017

- 07:00-08:30** **Breakfast Open**
- 08:30-12:15** **Session III: General Polymers**
- 08:30-09:30** **Key Note Lecture:** *Conjugated Polymers in Active Devices: Where is Molecular Weight Important?*
John Reynolds, Georgia Institute of Technology
- 09:30-10:00 *Highly Functionalized Polymer Backbones from Nontraditional Monomers*
Emily Pentzer, Case Western Reserve University
- 10:00-10:30 *Molecular Coplanarity of π -Conjugated Oligomers and Polymers: from Synthesis to Function*
Lei Fang, Texas A&M University
- 10:30-10:45** **Break**
- 10:45-11:15 *Functional Nanomaterials from Single Polymer Chains*
Erik Berda, University of New Hampshire
- 11:15-11:45 *GPC/MALS as a Tool to Optimize the Synthesis of the Strong Polyelectrolyte NaPSS under Aqueous ATRP Conditions*
Paul S. Russo, Georgia Institute of Technology
- 11:45-12:15 *Light Scattering Characterization of Nanostructured Materials*
Dan Savin, University of Florida
- 12:15-01:45** **Lunch**
- 01:45-04:00** **Session IV: Industrial Polymers**
- 01:45-02:15 *Generating Polythioaminals with Latent Crosslinks through the Stabilization of Reactive Intermediates*
Rudy J. Wojtecki, IBM - Almadan Research Center
- 02:15-02:45 *Robust Analytical Methods to Evaluate Bioresorbable Polymer Degradation Profiles In Vitro and In Vivo: A Case for Cardiovascular Stents and Scaffolds*
Eric Landry, PolyAnalytik Inc.
- 02:45-03:00** **Break**
- 03:00-03:30 *Study of the Effects of Sample Preparation on the Degradation of Polyolefin During High Temperature GPC (HT-GPC) Analysis*
Reza Farasat, Tosoh Bioscience LLC
- 03:30-03:40** **Closing Remarks**

Oral Presentation Abstracts

Post Printing Modification of Poly(propylene fumarate) Scaffolds for Enhancing Cellular Function

Matthew Becker, Ph.D., FRSC
The University of Akron, Akron, OH

Recent synthetic advances have enabled the synthesis of polymers designed to elicit specific cellular functions and to direct cell-cell interactions. Further advances in both synthetic methodology and scaffold fabrication are needed to drive these efforts forward. Newer materials are designed to stimulate specific cellular responses at the molecular level and degrade at the rate in which the tissue is repaired. The implants should mimic the dimensionality of the native tissue and degrade and defined rates with by-products that are benign and resorbable. Other significant limitations to bringing new materials to the clinic include the facts that fully synthetic materials lack cell specific receptors and have poorly defined serum adsorption properties, which can vary widely depending on the amount and nature of the adsorbed layer. Many potential solutions including doping with proteins or peptides or decorating the polymer with covalently tethered peptides that mimic the extracellular matrix or growth factors have been employed over the years. While these approaches have been demonstrated to aid the biochemical signaling and integration into host tissues, they generally reduce the mechanical properties of the material. We will demonstrate the use of several 3D printing technologies to print physiologically relevant structures from well-defined poly(propylene fumarate) and poly(ester urea) precursors. These scaffolds are functionalized post printing with highly active biologics and being applied to bone defect repair strategies.

Characterize Polymer Topology and Purity by GPC and MALDI-TOF MS

Scott Grayson
Joseph H. Boyer Professor of Chemistry
Tulane University, New Orleans, LA

The synthesis of high purity cyclic polymers remains challenging. Although a number of techniques have been reported for their synthesis, difficulties remain in confirming their topology and characterizing their architectural purity. However, MALDI-TOF MS provides an attractive complementary technique to GPC for confirming the presence of non-cyclic impurities. In addition, the precision of molecular weight calculations enabled by MALDI-TOF MS allows aspects of the architecture of these impurities to be elucidated, even when present in sub-microgram quantities.

Ultra-High Molecular Weights via Aqueous Reversible-Deactivation Radical Polymerization

Brent S. Sumerlin^{1,2,*}, R. Nicholas Carmean¹, Troy E. Becker¹, and Michael B. Sims¹

¹George & Josephine Butler Polymer Research Laboratory, Center for Macromolecular Science & Engineering, Department of Chemistry, University of Florida, Gainesville, FL

²Lead Contact

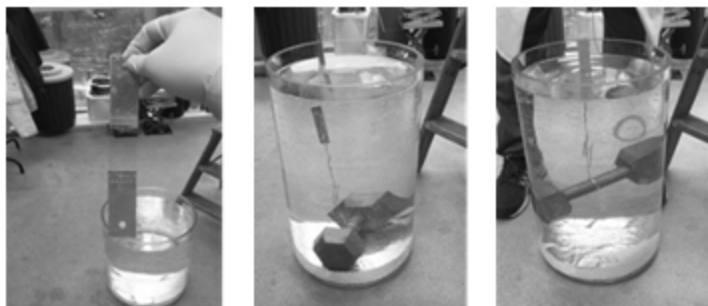
*Correspondence: sumerlin@chem.ufl.edu

Relying solely on mild ultraviolet irradiation of thiocarbonylthio compounds in the presence of vinyl monomers, a new avenue to well-defined ultrahigh molecular weight (UHMW) polymers has been developed. Through the use of aqueous conditions, well-controlled polymers with high molecular weights that are unprecedented for controlled radical polymerizations have been achieved. This photomediated polymerization approach reaches number-average molecular weights in excess of 8.00×10^6 g/mol with degrees of polymerization above 85,000, making these, to our knowledge, the highest molecular weight polymers ever achieved via reversible-deactivation radical polymerization. In many cases, well-defined UHMW polymers can be obtained in minutes. The utility of the technique is further demonstrated through (i) the synthesis of block copolymers, enabling access to a new field of well-defined UHMW materials; and (ii) photoinduced end group removal of thiocarbonylthio groups from polymers prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization

Solvent-Free, Mussel-Inspired Polyester Adhesives with Impressive Underwater Adhesion

Abraham Joy, Amal Narayanan, Ying Xu, Qianhui Liu, Sukhmanjot Kaur , and Ali Dhinojwala
Department of Polymer Science, The University of Akron, Akron, OH

Mussel adhesion has fascinated scientists for their ability to adhere to underwater substrates. They do this by the secretion of adhesive proteins underwater in a temporal fashion. The mixture of proteins secreted by mussels are tuned to provide both adhesive and cohesive interactions with the substrate. Synthetic adhesives in comparison are for the most part are compromised in an aqueous environment due to their inability to prevent water penetration into the adhesive interface. We will present our work on the design and evaluation of synthetic polyesters that demonstrate strong underwater adhesion. The polyester is designed to flow at room temperature, which enables application without any solvent. Catechol units of the polymer provide adhesive contacts with the substrate. The applied polymer is subsequently cured to a crosslinked polymer providing cohesive interactions. Lapshear measurements show strong adhesion even when the polymer is applied underwater and cured. Our current results indicate that the hydroxyl groups of catechol play a role in adhesion and that a hydrophobic environment is necessary for synthetic adhesives to show good performance in wet environments.



Drag-tagged Ethidium Bromides: Intercalating Dye-Drag-Tag Conjugates as Novel Mobility-Shifting Agents for Microchannel DNA Separations

Annelise E. Barron^{1,2,3,4}, Thomas P. Niedringhaus^{1,2,4}, Russell D. Haynes^{1,3}

¹Department of Bioengineering, Stanford University, Stanford, CA

²Department of Chemical Engineering, Stanford University, Stanford, CA

³School of Medicine, Stanford University, Stanford, CA

⁴School of Engineering, Stanford University, Stanford, CA

CE and chip electrophoresis are workhorse technologies to separate and analyze both ds and ss polynucleotides (PCR products, restriction fragments, RFLPs, siRNA, SSCPs, DNA homo- and heteroduplexes). Successful assays of DNA or RNA utilize optimized polymer matrix to provide high-resolution size-separations, as well as an optimized buffer, run temperature, and applied electric field. When very small DNA or RNA needs to be analyzed or if there are both ss/ds species to be resolved, achieving good selectivity can be difficult and the results hard to predict. Quite often, intercalating fluorescent dyes such as Ethidium Bromide (EtBr) or Yttrium Orange (YO) are used to allow detection of dsDNA analytes. While most studies have focused on altering electrophoretic conditions or the sieving polymer solution to increase separation efficiency, here we report a new strategy: unique chemical/structural modifications to the intercalating dye molecules. Widespread use and detailed (public) structural knowledge of ethidium bromide (EtBr) makes it an excellent basis upon which to study the effects of chemically modifying an intercalating dye on DNA separation. Two free amines on EtBr allow for facile chemical modification. With the goal of working with mono-modified Et (leaving one free amine to assist in DNA binding) we conjugated different water-soluble, uncharged, monodisperse oligomers onto ethidium. Terminally amino-reactive oligoethylene glycols (OEGs)—two different lengths—and amine-reactive oligo-N-methoxyethylglycines (oligoNMEGs)—three different lengths—were reacted with Et. Mono-conjugated products were isolated by HPLC and analyzed by LC-MS to confirm purity and correct conjugate mass. To evaluate the effect of these novel oligomer-modified intercalating fluorophores, a dsDNA restriction digest (Φ X174-HaeIII) as well as other nucleic acid samples were separated by electrophoresis in a lab-made sieving matrix, using a custom-built LIF point detection system for microchips. By comparison to dsDNA intercalated with standard Et, we find that dsDNA intercalated with OEG-Et and oligoNMEG-Et conjugates are separated in a much shorter time because of their higher electrophoretic mobilities. Given that we have added a “drag-tag” onto the Et dye, it is intriguing that substantially faster mobilities are observed. These sped-up separations either maintained or increased the resolution per base pair over Et alone. We will discuss the particular effects of the different uncharged drag-tag modifier structures on microchip electrophoresis separations, and propose possible mechanisms for these effects.

Use of High-Temperature GPC to Characterize In Vivo Oxidative Degradation of Polypropylene

Jimmy Mays

Department of Chemistry, University of Tennessee, Knoxville, TN

Polypropylene has been used as a biomaterial since the late 1950s, with applications including sutures, hernia mesh, and, more recently, pelvic meshes used to treat stress urinary incontinence and pelvic organ prolapse. Polypropylene, because of its lack of hydrolysable bonds, was initially (in the 1950s and 1960s) anticipated to be inert in biomedical applications. However, it has now been proven in numerous studies that polypropylene is not inert *in vivo*. Cracking and flaking of explanted polypropylene fibers has been observed by various researchers under SEM, along with increased stiffness of the mesh. These results have been interpreted by some researchers as due to oxidative degradation of polypropylene, while others have pointed to possible penetration of molecules of biological origin into the polypropylene accounting for cracking and changes in properties. We will show through use of high-temperature GPC that the weight-average and z-average molecular weights of polypropylene are greatly reduced after implantation in the human body. These results, supplemented by FTIR and SEM/EDS, show conclusively that polypropylene undergoes oxidative degradation *in vivo*.

An Assessment of Characterization Techniques for LDPE Microstructure

David Gillespie, Sydney Duckworth, Phillip Tyler, Harolyn Perkins, and Scott Foster
The Dow Chemical Company, Freeport, TX

High pressure low density polyethylene technology remains competitive as ever despite being commercialized approximately 80 years ago using a free-radical process. Today LDPE is used primarily in film and extrusion coating applications and is being manufactured by both autoclave and tubular processes. Often LDPE is referred to as a “treelike” structure for autoclave resins and more “comb-like” for their tubular varietiesⁱ. Although these descriptors “treelike” and “comb-like” are useful for understanding some of the relaxation phenomenon of these polymers, there is much controversy about what is happening at ultra-high molecular weight and chromatographers have concentrated on analyzing this portion of the distribution with on-line, batch, and very low shear modes of separation. By viewing these industrial polymers through the lens of processing, performance, and molecular structure assessment, we can begin to understand and unravel relationships in LDPE structure and properties; and we find proper chromatography conditions, proper assessment of LCB, and understanding of what chromatography tells us of the highest molecular weight structures is critical to our data interpretation.

ⁱKuhn, R. & Krömer, H., *Colloid & Polymer Sci*, **260** (12), 1083-1092 (1982)

Separation of Polyalphaolefins by Two-Dimensional HPLC-SEC Chromatography

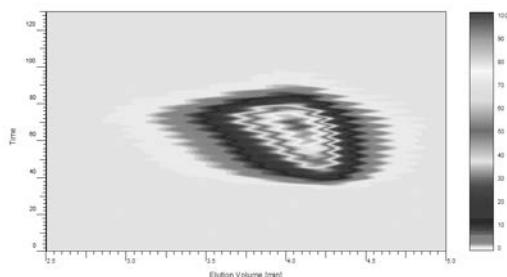
Y. Yu², R. Brüll¹, T. Macko¹, P.J. DesLauriers²

¹Fraunhofer Institute for Structural Durability and System Reliability, Plastics Division, Material Analytics Group, Darmstadt, Germany

²Chevron Phillips Chemical Company LP, Bartlesville Research & Technology Center, Bartlesville, OK, USA

Amorphous polyalphaolefins (PAOs) synthesized by polymerization of higher 1-olefins ranging from 1-hexene to 1-dodecene find a wide range of applications from lubricants, hydraulic fluids to heat-exchange media. PAOs may be selectively analyzed by gas chromatography (GC). However, the selectivity of the separation substantially decreases with increase of molar mass due to increasing poor volatility. The solubility of PAOs in a wide range of liquids at room temperature enables to apply liquid chromatography (LC) as an alternative way to their separation. Taking into account recent progress in liquid chromatographic separation of semicrystalline polyolefins at temperature as high as 160 °C [1-3], it was found that PAOs may be fully adsorbed on a column packed with porous graphite Hypercarb™ from several single solvents at room temperature and finally desorbed after addition of a thermodynamically good solvent into the mobile phase. The elution volumes are a function of the microstructure of the PAOs and may additionally be influenced by the molar mass of the samples when the molar mass of the macromolecules is low. Coupling the HPLC separation with SEC (HPLC-SEC) to two-dimensional liquid chromatography (2D-LC) yields information on the multivariate distribution of a PAO sample exemplified in Fig. 1 below.

Fig. 1 Contour plot of poly-1-octene obtained by coupling SEC (on x-axis) with HPLC (on y-axis).



[1] T. Macko, R. Brüll, Y. Zhu, Y. Wang, *J. Separ. Sci.* 2010, **33**, 3446.

[2] T. Macko, J. H. Arndt, R. Brüll, *Macromol. Symp.* 2015, **356**, 77.

[3] R. Chitta, T. Macko, R. Brüll, Ch. Boisson, E. Cossoul, O. Boyron, *Macromol. Chem. & Phys.* 2015, **216**, 721.

Utilizing Redox-Active Catalysts for the Synthesis of Tailored Polyolefins

Brian K. Long, Ph.D.

The University of Tennessee, Department of Chemistry, Knoxville, TN

The ability to provide ultimate control over catalytic activity, selectivity, and reactivity for transition-metal mediated polymerizations remains a prominent challenge within the fields of organic, organometallic, and polymer chemistry. To address this challenge head-on, our research group has chosen to examine how redox-active ligands may be used as an effective means by which enhanced polymerization control may be realized through simple *in situ* changes in a catalyst's oxidation-state. Toward this goal, we will provide ground-breaking results that show that redox-active olefin polymerization catalysts can be effectively used to modulate polyethylene branching and microstructure. Second, we will present recent results that demonstrate that ligand redox-state may alter polymerization rates for higher α -olefin monomers, and that this differentiation may be utilized to control comonomer incorporation levels in copolyolefins.

Conjugated Polymers in Active Devices: Where is Molecular Weight Important?

John R. Reynolds

School of Chemistry and Biochemistry, School of Materials Science and Engineering,
Center for Organic Photonics and Electronics, Georgia Tech Polymer Network,
Georgia Institute of Technology, Atlanta, GA

Conjugated polymers provide a unique encompassing set of structurally tunable optical, electronic transport, and redox properties that allows their present and potential use in a host of applications which span, field effect transistors, light emitting diodes, solar cells and photodetectors, electrochromism, along with batteries and supercapacitors. Processing of these materials is carried out using a variety of solution methods including spin-coating, spray-coating, blade-coating, slot die coating and ink jet printing. Each of these methods requires a polymer solution, in essence an electroactive polymer ink, with properties designed for that particular mode of processing. Considering electrochromic polymers, we find that our electrochemical and colorimetric properties are relatively insensitive to molecular weight, which is beneficial as color reproducibility is high and does not require a specific molecular weight to attain the desired color properties. At the same time, molecular weight is important for solubility and processing, which is also controlled through the use of various side-chains. On the other hand, in the area of solid-state organic electronic applications, such as field effect transistors and organic photovoltaics, molecular weight is highly important when it comes to the critical properties (charge mobility and power conversion efficiency). We will discuss what we call the "one atom change" approach where we synthesize a family of polymers under conditions as identical as possible, resulting in polymers of near identical molecular weight and dispersity. As minimal a structural change as possible is probed to understand its effect on properties. In this, we move beyond batch polymerization to flow chemistry to make polymerization as reproducible as possible, while at the same time being able to scale up under laboratory conditions.

Highly Functionalized Polymer Backbones from Nontraditional Monomers

Emily Pentzer

Department of Chemistry, Case Western Reserve University, Cleveland, OH

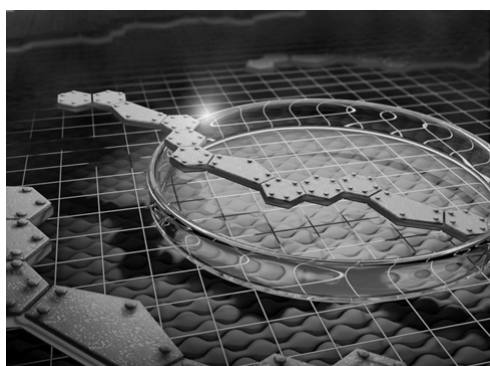
Synthetic chemistry is a powerful tool for developing new materials and dictating their properties in a bottom up approach. The Pentzer lab uses fundamental organic chemistry reactions to tune functionality and in turn the properties of small molecules, polymers, and nanoparticles with aims to improve the efficiency of the interconversion and storage of energy. This seminar will report the group's recent advances the development of highly functionalized polymers from silyl ketene monomers. While ketenes ($R_2C=C=O$) are highly reactive and difficult to isolate, silyl ketenes can be prepared on the large scale and isolated due to stability derived from the β -silicon effect. Silyl ketenes show distinct polymerization patterns compared to traditional monomers and yield polymers in which every backbone atom is functionalized. Moreover, silyl ketenes can produce different polymer backbone linkages, based on polymerization of $C=C$ or $C=O$. Ongoing efforts aim to understand the relationship between chemical functionality and mechanical, thermal, and electronic properties.

Molecular Coplanarity of π -Conjugated Oligomers and Polymers: from Synthesis to Function

Lei Fang

Texas A&M University, College Station, TX

Coplanar torsional conformation plays a key role in shaping the unique characteristics and functions of conjugated organic macromolecules. It is still an elusive task, however, to control the coplanar conformation of conjugated polymers for materials performance. We aim to establish general synthetic methodology and comprehensive structure-properties correlations of coplanar π -systems, through synergistic approaches combining chemical synthesis, process engineering, and materials characterization. In order to achieve this goal, we have designed and implemented multiple strategies, including the use of non-covalent bridging bonds, the employment of dynamic covalent reactions, and the use of highly efficient annulation reactions. Efforts were also made to solve the challenges associated with low solubility of this class of materials for characterization and processing. Unique optical, electronic and mechanical properties of these new materials are investigated and optimized for advanced applications.



Functional Nanomaterials from Single Polymer Chains

Erik Berda, Ashley Hanlon, Justin Cole

Department of Chemistry and Materials Science Program, University of New Hampshire, Durham, NH

Functional nanomaterials in nature depend largely on the primary, secondary and tertiary structure of proteins. While polymer synthesis has made strides in recent years with respect to control over structure across multiple length scales, effective synthetic mimics of protein tertiary structure remains an unmet research challenge. Work in our group focuses largely on this topic. Single-chain nanoparticles, formed through intramolecular cross-linking of individual polymer chains in dilute solution, represent a crude way to mimic the elegant folding process seen in proteins. This talk will highlight recent advances in our labs with respect to introducing functionality simultaneously with cross-linking using a variety of reaction conditions, along with recent insight into the design characteristics required for efficient intermolecular collapse, and a brief look at strategies to build reversible or responsive cross-links into these nanomaterials.

GPC/MALS as a Tool to Optimize the Synthesis of the Strong Polyelectrolyte NaPSS under Aqueous ATRP Conditions

Paul S. Russo, Paul Balding and Rafael Cueto
Georgia Institute of Technology, Atlanta, GA

Sodium poly(styrene sulfonate) or NaPSS is an important polyelectrolyte, both commercially and for fundamental physicochemical investigations. Usually NaPSS is prepared by harsh sulfonation of polystyrene. Often the sulfonation is incomplete, leaving behind hydrophobic styrene monomers that alter behavior. An alternative is to prepare NaPSS by aqueous polymerization of the styrene sulfonate monomer directly. Several such attempts have been made over the years, with varying degrees of success. It will be shown that atom transfer radical polymerization (ATRP) under aqueous conditions can yield polymers over a wide range of molecular weights and with low polydispersity. To optimize the ATRP synthesis, GPC with MALS detection was used to assess the variation of parameters such as catalyst concentration, solvent composition, pH, and added salts.

Light Scattering Characterization of Nanostructured Materials

Dan Savin

University of Florida, Gainesville, FL

This study involves the bottom-up design and tunability of responsive, peptide-based block copolymers. The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic triblock and star copolymers containing poly(lysine) (PK), poly(leucine) (PL) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. The peptide block in these structures can serve to introduce pH responsiveness (in the case of PK and PE), or can facilitate the formation of elongated, kinetically-trapped, or fractal structures (in the case of PL.) This talk will present some recent studies in solution morphology transitions that occur in these materials as a result of the helix-coil transition and associated charge-charge interactions. We exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH due to morphology transitions.

Generating Polythioaminals with Latent Crosslinks through the Stabilization of Reactive Intermediates

Rudy J. Wojtecki

IBM - Almaden Research Center, San Jose, CA

We've recently exploited the reactivity of 1,3,5-hexahydro-1,3,5-triazines towards sulfur containing compounds to generate polythioaminals, a unique class of dynamic covalent polymers that exhibit a chemically responsive behavior. The first generation polymers were produced from the reaction of HTs with dithiols where high molecular weight polymers could only be accessed through the removal of a small molecule amine generated during the reaction cycle. The need for the removal of this amine limits substrate diversity the reaction proceeds through a pathway that is inefficient atom economy. These challenges have motivated our more recent studies in broadening the substrate diversity of these polymers through the use of reactive intermediates. Molecular modeling and model reactions of the formation of HTs indicate the use of electron withdrawing groups slow the trimerization of aromatic amines with paraformaldehyde. In NMR studies an intermediate specie is stable enough to be observed and is subsequently consumed in the formation of HTs. If, however, a specie more reactive towards this intermediate is present, for instance a thiol, product formation can be driven towards the selective formation of thioaminals and HT formation completely suppressed. This method, of reacting stabilized intermediates, allowed us to prepare a number of fluorine containing polythioaminals without the need for the ring opening reaction of an HT. Furthermore, it was found that the resulting polythioaminals containing secondary amines act as a latent crosslinking sites at higher temperatures. These networks possess an attractive characteristic of easy to process fluorinated polymers with applications that range from hydrophobic coatings, adhesives and imprint lithography.

Robust Analytical Methods to Evaluate Bioresorbable Polymer Degradation Profiles In Vitro and In Vivo: A Case for Cardiovascular Stents and Scaffolds

Eric Landry¹, Ahmed Alassuity^{1,2}, Peng Xiang^{1,2}, Ahad Al-Hakim¹, and Joseph Paquette^{1,2}

¹PolyAnalytik, Inc., The University of Western Ontario Research Park, London, Ontario, Canada

²Department of Chemical & Biochemical Engineering, Western University Ontario, London, ON, Canada

This research focused on developing a reliable methodology that can be applied to in vitro and in vivo studies quantifying the degradation of polymers particularly related to drug eluting stents (DES) and bioresorbable scaffolds (BRS) used in the treatment of coronary artery disease. Early DES utilized permanent polymer coatings to control the release of their drugs and these durable coatings have been linked to chronic inflammation and late stage thrombosis, a potentially fatal complication. As a result, the next generation DES have incorporated bioabsorbable polymer technology, either as a replacement for the metal scaffold or as a coating on the metallic stent, in order to minimize the risk of complications in patients treated with these devices. A robust methodology to quantify polymer degradation is therefore critical for optimizing the design of polymer based fully bioresorbable and bioabsorbable polymer coated DES so that patients are implanted with safe and effective devices.

Our methodology utilizes size exclusion/gel permeation chromatography (SEC/GPC) equipped with a refractive index detector, an UV detector, and a light scattering detector using hexafluoroisopropanol as mobile phase. In brief, this new method can quantify accurately trace amount of polymers in a tissue sample. Unlike other reported methods in the literature, no interferences from tissue matrix or the drug complicate analysis of the polymer peak. By utilizing these methods to evaluate bioabsorbable DES, we can accurately assess polymer degradation profiles to ensure the optimal design for patient safety and device efficacy.

Study of the Effects of Sample Preparation on the Degradation of Polyolefins during High Temperature GPC (HT-GPC) Analysis

Reza Farasat, Ali Soleymannezhad and Toru Satoh
Tosoh Bioscience LLC, King of Prussia, PA

GPC analysis of polyolefins has proven to be a challenging task for scientists as the sample preparation and solution handling directly affects the reproducibility of molar mass moments and molar mass distribution values. Since the dissolution and the analysis require extreme temperatures (≥ 135 °C), employing the right conditions is critical to avoid precipitation or degradation of polymers in the mobile phase. In addition, historical hardware design limitations surrounding High Temperature GPC instruments such as lack of detector stability, precise solvent delivery mechanism, and/or accurate temperature control, have also posed additional challenges in reliable separation and molecular weight characterization of polyolefins. The right balance of dissolution temperature, dissolution time, antioxidant concentration, and applied shear or mechanical agitation is critical for obtaining consistency in stability at higher temperatures. The real challenge is to employ just enough heat to melt all of the crystalline structure and obtain/maintain total solubility without over exposure to avoid dissociation of polymer chains and degradation. Therefore, careful consideration to heat exposure history for each sample solution during the experiment is as important as employing the right chromatography conditions and parameters.

Here we report the analysis of polyethylene (PE) and polypropylene (PP) samples in a DOE (design of experiment) style as shown in the table below. The experiments were carried out at three dissolution time periods (1.5, 2 and 3 hours). Two sets of different sample dissolution temperatures were used; 135 °C and 150 °C for PE and 160 °C and 170 °C for PP. Samples were tested for each dissolution time period as a function of increasing concentration of BHT (250, 500 and 1000 ppm) at a specific temperature. One parameter was changed at a time; 12 consecutive injections were carried out at an interval of 1 injection per hour for each set of experiments. During the analysis, the solvent peak was used as a flow marker to avoid of any potential shift of elution time. Moments of molecular mass (M_n , M_w , and M_z), Polydispersity Index (PDI), and Peak Retention values were monitored to identify any signs of degradation for each set of experiment. Additionally, the system pressure (pump pressure) was also observed and recorded to identify possible signs of sample precipitation during each run. This study determines the optimum dissolution conditions and the required antioxidant concentrations for the samples of interest and proposes a basic baseline conditions for GPC analysis of polyolefins.

Poster Presentation Abstracts

Poster: High Performance Solar Polymers with Open Acceptor Units

Abigail A. Advincula
Georgia Institute of Technology, Atlanta, GA

An organic photovoltaic (OPV) is a type of solar cell that uses organic dyes, typically conjugated polymers, as the active component to produce electricity from sunlight. These devices have several potential advantages over silicon-based devices, such as – being lightweight, flexible, inexpensive, and easy to fabricate by roll-to-roll processing. Current OPV research focuses on tuning chemical structures and optimizing processing parameters to produce higher device power conversion efficiencies (PCE) (percentage of produced power to theoretical maximum).

A primary area of research is the design of donor-acceptor (DA) polymers. Recent work by Graham et al. indicates that higher PCEs can be achieved by molecular (steric) control of fullerene-polymer interactions. In this work, it was hypothesized that better fullerene “docking” on the acceptor units facilitated the more efficient charge transfer from donor unit to acceptor unit to fullerene. Based on this work, we hypothesize that placement of less bulky side chains on the acceptor can lead to improved OPV performance. To explore the concept of fullerene “docking” on the acceptor unit, we looked at state-of-the-art OPV polymers and found that the high-performing polymer PCE-11 fit our “minimally substituted acceptor” hypothesis. PCE-11 is a high performing solar polymer, but unlike other solar polymers, its acceptor unit lacks sidechains. To test our hypothesis, analogs of PCE-11 were proposed utilizing minimally substituted versions of various acceptor units (methylated forms of isoindigo, TPD, and DPP). The de-bulking of the acceptor units is hypothesized to promote fullerene-acceptor unit interactions leading to improved device performance.

Poster: Color Control in Wide Gap Cathodically Coloring Conjugated Electrochromic Polymers

Dylan T. Christiansen and John R. Reynolds
Georgia Institute of Technology, Atlanta, GA

Electrochromism is the change of a material's color upon the application of an electrochemical potential. These materials have prospective uses in full color passive displays, energy saving tinted windows, and dimmable visors for military and/or recreational use. Organic polymer electrochromes have the benefits of being solution processable, lightweight, and flexible. The absorbances of the neutral and oxidized states of these materials are synthetically straightforward to control through heterocycle choice, electron richness, steric strain, and copolymerization. This work compares and contrasts the methods of controlling absorption characteristics in cathodically coloring conjugated electrochromic polymers.

Among cathodically coloring materials, conjugated polymers have been synthesized that cover the visible spectrum. While thousands of switches have been demonstrated for colors such as magenta and blue, the challenge in this family of materials is creating stable wide band gap systems (yellows, oranges, and reds). Here, we show that using sterically bulky phenylenes as comonomers with dioxothiophenes (DOTs) give the ability to incorporate larger portions of electron rich DOTs while maintaining wide band gaps. We also show that reducing the electron density along the conjugated backbone by replacing the alkoxy substituents with an alkyl chain allows for widening the band gap. Both of these approaches have led to yellow, orange, and red electrochromic polymers that have significantly improved switching stabilities over the previous generations.

Poster: Conductive PEDOT: PSS Electrodes in Electrochromic Devices

Michel De Keersmaecker, Augustus Lang, Anna Österholm, and John R. Reynolds
School of Chemistry and Biochemistry, School of Materials Science and Engineering, Center for Organic Photonics and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, GA

We present new electrochemical device designs made entirely of electrically conducting polymer electrodes to reversibly switch a magenta colored poly(3,4-propylenedioxy-thiophene) (PProDOT) electrochromic polymer (ECP) film. Thin conductive poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) films have been incorporated as conductive transparent electrodes in solution processable absorptive/transmissive (window type) electrochromic devices making it available for high-throughput processing on a wide range of substrates. Different (in)organic acid and polar solvent post-treatments have been used to tune the conductivity of the blade coated PEDOT:PSS electrodes. We reached a conductivity up to 2000 S cm⁻¹ on different substrates, enough to reversibly switch our ECP film between -1 V and 1 V. We will demonstrate how the structural design, construction, charge-balancing, electrode conductivity and the electrochemical properties of the PProDOT have an influence on the device performance quantified by its contrast, switching speed and long-term stability. We combine our device design with a fundamental study of the electrochemical processes occurring at both electrodes. Using these new designs, we have developed an all-polymer solution processed electrochromic device approaching the characteristics of a device made using inorganic transparent conducting electrodes, e.g. indium tin oxide (ITO), with the added advantage of using flexible and rough substrates.

Poster: Synthesis of Polymer Bottle Brush Based on Poly(2-Isopropenyl-2-Oxazoline) Homopolymer and Block Copolymer

Hongbo Feng¹, Kunlun Hong², Nam-Goo Kang¹, and Jimmy Mays^{1,3}

¹Department of Chemistry, University of Tennessee, Knoxville, TN

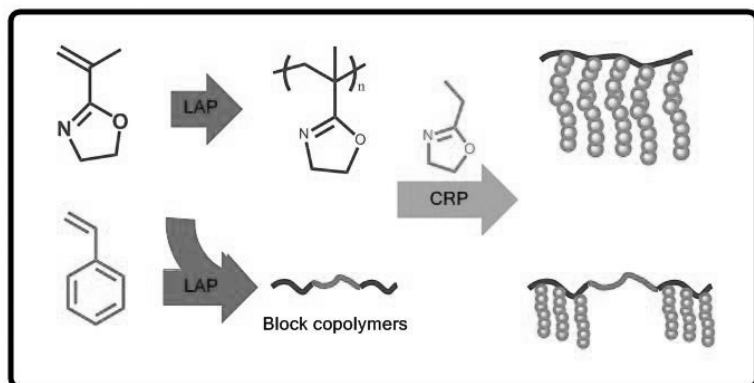
²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

³Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN

2-isopropenyl-2-oxazoline (IPOx) is a water-soluble dual functional monomer. IPOx has isopropenyl moiety, which can undergo reversible-addition-fragmentation chain transfer (RAFT) polymerization and living anionic polymerization (LAP). It also contains oxazoline moiety which is capable of polymerization under acid catalysis via ring-opening polymerization. On the other hand, polymer brushes with high grafting densities exhibit an interesting entropically unfavorable elongated shape and show applications as single molecule templates. In addition, incorporation of biocompatible oxazoline functionality in polymer brushes might provide intriguing platforms for applications of biomedical, polymer therapeutics, nanoscience, etc.

In this study, we reported the pioneering synthesis of polymer bottle brush based on PIPOx homopolymer and block copolymer through grafting-from approach. The polymer brush backbone was synthesized using living anionic polymerization of IPOx through high vacuum techniques. The obtained PIPOx was then quaternized using methyl triflate (PIPOx-MeOTf). The polymer brush was achieved via the subsequent cationic ring opening polymerization of biocompatible 2-ethyl-2-oxazoline (EtOx) using PIPOx-MeOTf as a macroinitiator. A series of polymer brushes with controlled molecular weight from 200,000g/mol to 5,200,000g/mol were successfully synthesized. Characterization using nuclear magnetic resonance spectroscopy (NMR), FT-IR and size exclusion chromatography (SEC) of the resulting polymer brushes revealed that a very high side chain grafting density and quantitative reactions were achieved. Furthermore, the bottle brush was visualized using atomic force microscopy (AFM).

Keywords: polymer bottle brush, 2-isopropenyl-2-oxazoline, biocompatible, anionic polymerization and cationic ring opening polymerization.



Poster: Monitoring the Synthesis and Purification of Cyclic Polyethers using Mass Spectrometry and Size Exclusion Chromatography

Farihah M. Haque, Ca'ra Schexnayder, Angel Alegría, Fabienne Barroso-Bujans, and Scott M. Grayson
Tulane University, New Orleans, LA

The zwitterionic ring-opening polymerization (ZROP) is a novel synthetic tool that allows for the synthesis of a family of polyethers using glycidyl based monomers with the catalyst B(C₆F₅)₃. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) MS, in addition to other analytical techniques, helped determine that samples have an inherent contamination of non-cyclic, OH-functionalized impurities. The end groups of the impurities proved useful in effecting their removal, as such contaminant species could be selectively functionalized and removed through a “click” scavenging protocol. Size exclusion chromatography (SEC) was used to quantify the removal of impurities, and also provided a means of fractionating both crude and purified samples. By means of fractionation, both a low mass and a high mass fraction of the initial molecular weight distribution could be analyzed by MALDI-TOF MS to understand the formation of impurities as a function of molecular weight. ZROP in combination with the scavenging protocol allows for a facile, efficient synthetic and purification route to generate polyethers in high yield. Continued work intends to help determine mechanistic reasons for the formation of impurities through precise detection and identification of all polymer constituents in samples before and after purification. Extensive analytical methods being employed to elucidate the mechanism include MALDI-TOF, quantitative Fourier transform infrared spectroscopy (FTIR), SEC and end-group functionalization of non-cyclic impurities. Other techniques like differential scanning calorimetry were employed to characterize physical properties as a function of purity.

Poster: Iterative Exponential Growth Synthesis and Assembly of Uniform Diblock Copolymers

Yivan Jiang, Matthew R Golder, Hung V-T Nguyen, Yufeng Wang, Mingjiang Zhong, Jonathan C Barnes, Deborah JC Ehrlich, and Jeremiah A Johnson
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA

Polymer chemists have long tried to replicate Nature's remarkable ability to make macromolecules of defined length, sequence, and chirality. Many new synthetic approaches have attempted to access precisely defined and diversely functionalized uniform macromolecules in useful quantities. Living statistical polymerization methods can yield polymers with precise nanoscale structures on kilogram scales, but these methods lack absolute mass control, sequence control, and stereocontrol. Solid-phase syntheses provide an extremely valuable tool for the synthesis of macromolecules with absolute structural control. However, these methods require large excesses of reagents in each step and are not yet amenable for the synthesis of polymers in a readily scalable way.

We are advancing a promising alternative synthetic strategy called Iterative Exponential Growth (IEG) wherein doubly protected molecules of length L undergo cycles of orthogonal activations and couplings to yield macromolecules with length $L \times (2^n)$ cycles. Though IEG is limited to repetitive or palindromic sequences, we have used it to make unimolecular, fully sequence-controlled and stereo-controlled polymers on multigram scales.

Through synthetic modification of our base monomers, we can install a variety of functionalities such as alcohols, electron donating and accepting aromatics, free amines, and primary alkenes. We have only just started exploring the vast sequences and topologies that can be made using our system. For instance, using sequential thiol-ene click chemistry, we have synthesized unimolecular block copolymers (BCPs) of up to 12.1 kDA on a gram scale in under a week. BCPs of decane-based side chains and either triethyleneglycol- or thioglycerol-based side chains phase-segregate into hexagonal cylinder morphologies. The assembly is not driven by side-chain crystallization, but is instead the result of amorphous BCP assembly. In addition, we have used similar BCPs as ligands for metal nanoparticles and for the synthesis of unimolecular macrocycles. It is our hope that by using our IEG system, we will elucidate the structure-property relationships that will guide the design of next-generation polymeric materials.

Poster: Solution Properties, Unperturbed Dimensions and Chain Flexibility of Poly(1-Adamantyl Acrylate)

Wei Lu¹, Panchao Yin², Masashi Osa³, Weiyu Wang⁴, Nam-Goo Kang¹, Kunlun Hong⁴, and Jimmy W. Mays¹

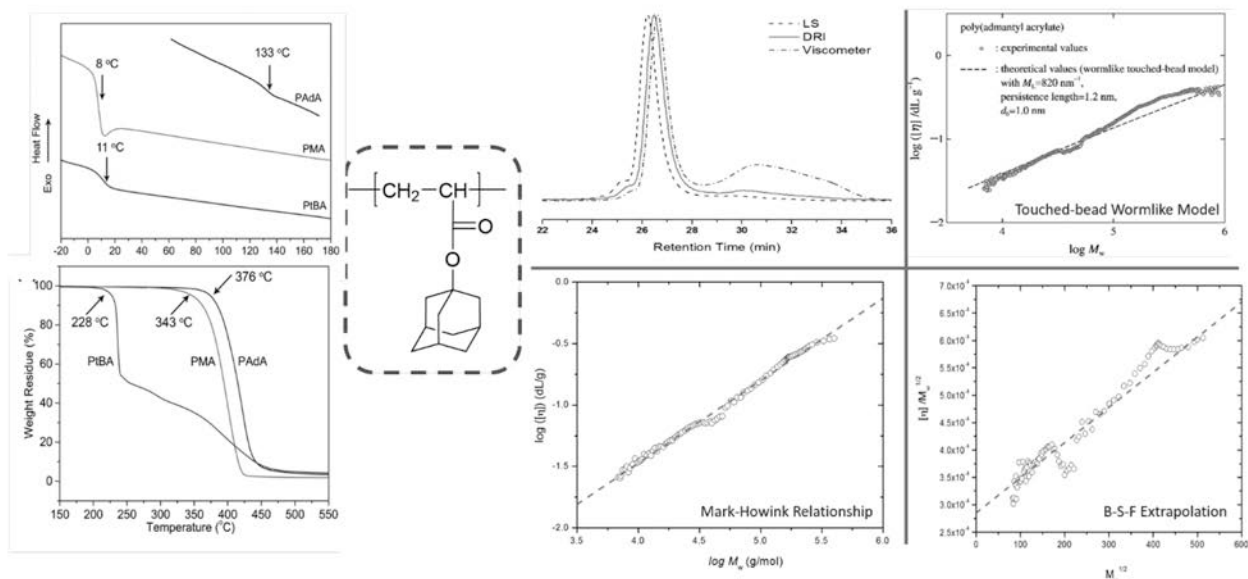
¹Department of Chemistry, University of Tennessee, Knoxville, TN

²Chemical and Engineering Materials Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN

³Department of Science Education, Aichi University of Education, Kariya, Aichi, Japan

⁴Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

The development of modern SEC instrumentation with size sensitive detectors provides a convenient approach for establishing the molecular weight dependence of intrinsic viscosity by using SEC with both light scattering and viscosity detectors, as compared to the traditional off-line measurements of molecular weights and intrinsic viscosities using narrowly dispersed polymer samples obtained by controlled synthesis or from solvent-nonsolvent fractionations. In this study, the dilute solution properties and conformational characteristics of poly(1-adamantyl acrylate) (PAdA) were evaluated. The polymer samples were synthesized via living anionic polymerization and showed low isotactic content. It exhibited much higher glass transition temperature and degradation temperature than values for other polyacrylates. However, the quantitative evaluation of the stiffness of this polymer chain has not been previously reported. Based on the molecular weights and corresponding intrinsic viscosities acquired from size exclusion chromatography equipped with both viscosity and multiple angle laser light scattering detectors, the unperturbed dimensions of this polymer were evaluated by using different theories, including Mark-Houwink relationship, Burchard-Stockmayer-Fixman (B-S-F) extrapolation and the touched-bead wormlike chain model. This polymer chain has a comparable persistence length, and diameter per bead to those of poly(methyl methacrylate) (PMMA) and polystyrene, and a characteristic ratio (C_∞) of 10.4, which is larger than that of PMMA. In addition, the second virial coefficient (A_2) of PAdA in different solvents was measured by static light scattering. Among the solvents investigated, tetrahydrofuran (THF) is a thermodynamically moderate solvent, with a Mark-Houwink coefficient of 0.67 at 40 °C and A_2 as $5 \times 10^{-5} \text{ cm}^3 \cdot \text{mol/g}^2$. All these results indicate that PAdA is less flexible than common polyacrylates.



Poster: Enhancing Thermal Stability and Minimizing Chain-Transfer in Co-Based Olefin Polymerization Catalysts

Nolan Mitchell, W. Curtis Anderson, Jr., and Brian K. Long
Department of Chemistry, University of Tennessee, Knoxville, TN

Olefin polymerization catalysts that employ late transition-metals hold tremendous promise for a variety of academic and industrial research interests. More specifically we are interested in the development of cobalt- and iron-based catalysts that are known to produce highly linear polyethylene, but that are susceptible to deleterious chain-transfer to aluminum events and that their thermal stability is poor. Herein, we will evaluate the time-resolved thermal stability and chain-transfer events for the catalyst, 2,6-bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)] pyridine cobalt(II)dibromide (1). This catalyst bears bulky 2,6-bis(biphenylmethyl)-4-methylaniline (iPr*) moieties that have been successfully used to enhance thermal stability in other related Ni- and Pd-based catalyst systems. Catalyst 1's polymerization activity, thermal stability, and chain-transfer events were evaluated using ethylene polymerizations at elevated temperatures. The polymers produced from these reactions were evaluated using detailed ¹H NMR spectroscopy, high temperature gel permeation chromatography equipped with refractive index, viscometer and two-angle light-scattering detectors, and differential scanning calorimetry.

To evaluate the temporal thermal stability of activated catalyst 1, time-resolved high temperature ethylene polymerizations were performed at 80, 90, and 100 °C and catalytic productivity (polyethylene yield) was monitored as a function of time. If catalyst 1 is stable at a given temperature, we expect to observe a linear increase in productivity versus time. As hypothesized, polymerizations using catalyst 1 at 80 °C showed a linear increase in productivity as a function of time, suggesting that catalyst 1 is indeed thermally stable at 80 °C for polymerizations times extending longer than 1 hour. In contrast, polymerizations conducted at 90 °C and 100 °C revealed that productivity deviated from linearity within the time period studied, presumably due to decomposition or deactivation of the active catalyst species. To evaluate the occurrence and extent of chain-transfer events, detailed ¹H NMR spectroscopy, high temperature gel permeation chromatography were used to monitor progression of molecular weight, molecular weight dispersity, and presence of olefinic end-groups that would signify chain transfer. After careful analysis, we confirmed that catalyst 1 exhibited no observable chain transfer events to aluminum and showed a steady progression of molecular weights as a function of time.

In conclusion, we evaluated the time-resolved thermal stability of Co-based catalyst 1, which shows near perfect thermal stability at 80 °C and greatly enhanced thermal stability at 90 °C. Furthermore, we have shown that the use of sterically demanding ligands has effectively eliminated chain-transfer to aluminum events that have plagued other Co-based catalysts. We attribute the observed enhanced thermal stability and mitigated chain-transfer to restricted N-aryl rotations brought about by ligand sterics, which minimizes catalyst decomposition and deactivation while also blocking the axial coordination sites of the active metal and associative displacement of the growing polymer.

Poster: Development of Adsorbable Light Harvesting Molecule Towards P-type Device Applications

Linda Nhon

Georgia Institute of Technology, Atlanta, GA

This work involves the design and synthesis of light harvesting compounds that will be applied in dye sensitized solar cells and dye sensitized photoelectrochemical fuel cell. Currently, the question that this work is attempting to address is: how can we design materials to efficiently inject holes into the p-type semiconductor? It was hypothesized that the energy level offset of these chromophores will affect charge injection kinetics in the p-type devices. To test this hypothesis, a set of donor-acceptor-donor (D-A-D) type molecules with different electron withdrawing acceptors units were synthesized. Electrochemistry, absorption and fluorescence spectroscopy were used to characterize these oligomers' electrochemical and optical properties. Based on the reduction potentials obtained through cyclic voltammetry and differential pulse voltammetry it was shown that by alternating the acceptor unit in the D-A-D trimer, the electron affinity values on these set of chromophore were affectively tuned, while their ionization potential (IP) were similar for all trimers. The difference between the valence band of the NiO semiconductor and the IP level for these chromophores was 1.1 eV, thus there should be a thermodynamic dynamic driving force for hole injection. These chromophores have been sent to the Schanze group at the University of Texas, San Antonio for device applications and photophysical studies. Moreover, by changing the acceptor unit, the optical energy gap of these oligomers was also changed. The UV-VIS absorption spectra demonstrate the ability to design chromophores to absorb in different regions of the visible spectrum. Although, it is important to note that these discrete molecules absorb in narrow regions. To continue the development of this chromophore family, the next set of materials will involve the synthesis of molecules exhibiting broad light absorption across the visible spectrum.

Poster: The Role of Cosolvent in Processing a Minimally Soluble Polymer for Organic Photovoltaics

Ian Pelse

Georgia Institute of Technology, Atlanta, GA

The use of cosolvents to improve the morphology of polymer:fullerene blends for use in organic photovoltaics is system dependent. Despite the ubiquity of 1,8-diiodooctane as a processing additive for bulk heterojunction OPVs, it may not be the best choice for all cases. In the case of poly(DPP-2T-TT), a polymer with a strong tendency to aggregate resulting in poor solubility, selective solubility for the fullerene (PC71BM) is not a mandatory property for a high performing the solvent additive. Rather, the solvent additive can balance solubility for the polymer and the fullerene. The photovoltaic and morphological properties of P(DPP-2T-TT):PC71BM blend films were studied as cast from different solvent systems containing chloroform and a select family of cosolvents, with variable solubility for the polymer vs. the fullerene. For a variety of additives with different relative solubilities for the two blend components, film morphologies and device characteristics are similarly improved, with emergence of nano fibers in the film and increased short circuit current density leading to higher power conversion efficiencies.

Poster: Utility of Baylis-Hillman Reaction for the Synthesis of Functionalized Polymers

Chao Peng and Abraham Joy
The University of Akron, Akron, OH

Currently, the assimilation of synthetic organic methodologies into the design of polymers has provided remarkable examples of precisely engineered polymers such as polyacrylates and polynorbornenes, polyesters, and polyurethanes with various functional groups, which have demonstrated many advantages over their nonfunctionalized counterparts. A novel method for the generation of functionalized polymers that has largely been under-explored is the use of monomers derived from Baylis-Hillman reaction. Baylis-Hillman reaction is a carbon-carbon bond forming reaction between an aldehyde and an activated alkene in the presence of a tertiary amine such as DABCO (1,4-diazabicyclo[2.2.2]octane), which provides densely functionalized molecules in a one-pot process. The work reported here describes the synthesis of Baylis-Hillman derived monomers and their uses in developing functionalized polymers.

Poster: Innovations and Applications of a Next-Generation Differential Viscometer for GPC

Mark Spears, Steven Trainoff, Michelle Chen, and Dan Some
Wyatt Technology Corp.

Online differential viscometers are commonly used as GPC detectors, either alone or in conjunction with multi-angle light scattering, to measure intrinsic viscosity and characterize size, shape, branching and aggregation of polymers and biomolecules. As a consequence of pump pulsation and thermal gradients, conventional differential viscometers are subject to a variety of limitations which produce tradeoffs between sensitivity, chromatographic resolution and solvent compatibility. We describe a next-generation differential viscometer that overcomes many of these limitations through multiple technological innovations:

- A new pressure transducer with short time constant and excellent resistance to corrosive mobile phase solvents
- A novel impedance-matching design for the capillary bridge that nearly eliminates pump-induced pressure fluctuations without loss of chromatographic resolution
- A proprietary algorithm that eliminates residual pump pulses
- A fast mechanism for automatically balancing the capillary bridge, readily readjusted as often as necessary
- Enhanced thermal design to eliminate thermal gradients in the instrument

The new sensor technology allows for greatly improved sensitivity and resolution with near immunity to pump pulses and an extended dynamic range of 135,000:1.

We present data highlighting the performance of the instrument, which include analyses of polymers in aqueous solution (PLGA and carboxymethyl cellulose) and in organic solvents (epoxy resin). Measurements of the hydrodynamic radius of IgG indicate a 10x increase in precision relative to the conventional means of measurement, online dynamic light scattering. Tests with various corrosive solvents, such as 1% acetic acid with 500 mM NaCl or DMF with 0.1% LiBr, indicate good resistance to corrosion.

Poster: Thermoresponsive Copolymer for Local Drug Delivery

Farrukh Vohidov, Qixian Chen, Lauren Milling, Darrell Irvine, and Jeremiah Johnson
Massachusetts Institute of Technology, Cambridge, MA

Efficacy of approved small molecule anticancer medicines and immunomodulators, as well as of the drug candidates currently in clinical development is often restricted by several important limitations. Because of their low water solubility and short circulation life-times, many chemotherapeutics are injected intravenously in repeated fashion, often in conjunction with an encapsulating agent to improve their solubility. The systemic administration and importantly narrow therapeutic window, are associated with severe side-effects. An alternative to systemic dosing is the use of drug-loaded delivery vehicles that can be directly injected at the tumor site allowing local drug release. We have developed a thermoresponsive delivery system that enables a single dose administration and maximizes concentration of drug molecules at tumor site for prolonged periods, at the same time minimizing unwanted exposure to healthy tissues, thereby reducing serious side-effects.

We describe a thermoresponsive three block copolymer made of polylactic acid (PLA), ethylene oxide (PEO), and poly(N-isopropylacrylamide) (PNIPAM) that can serve as a versatile platform for local delivery of anticancer medicines. The copolymer was extensively characterized. The copolymer is an amphiphile that self-assembles into micelles enabling solvation of hydrophobic drugs into water and at room temperature provides straightforward administration using a syringe for direct injection at the tumor site. We achieve efficient loading of three widely used chemotherapeutics: Paclitaxel, Gemcitabine, and SN-38. The drug-loaded micelles demonstrate rapid gelation when heated to 37 °C and in vitro experiments confirmed formation of a local reservoir for sustained release of medicines. We show that upon intratumor injection of combination drug-loaded hydrogel resulted in eradication of A549, human lung cancer cells, in mice. We further used the copolymer for immunochemotherapy, delivering Paclitaxel and Resiquimod, an important immunomodulator, intratumorally achieving significant inhibition in proliferation of aggressive colon cancer cells, CT-26. To best of our knowledge this is the first report of a platform that can be used for delivery of immunomodulator and along with a chemotherapeutic for combination therapy.

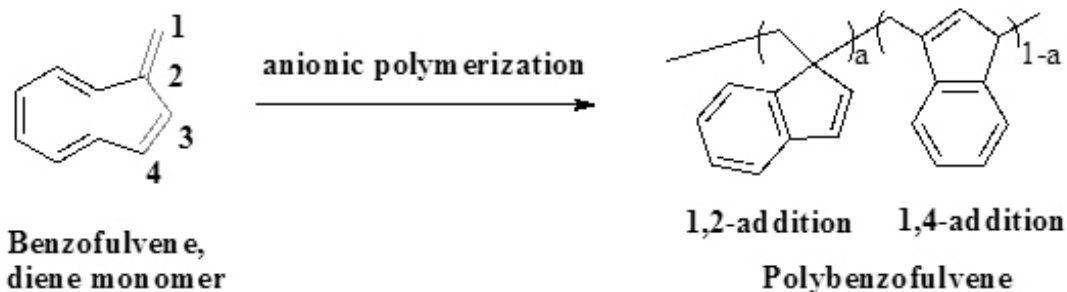
Poster: Effect of Microstructure on Chain Flexibility of Polybutadiene Derivative: Polybenzofulvene

Huigun Wang[†], Weiyu Wang[§], Wei Lu[†], Nam-Goo Kang[†], Kunlun Hong[§], and Jimmy Mays^{†,§}

[†]Department of Chemistry, University of Tennessee, Knoxville, TN

[§]Oak Ridge National Laboratory, Oak Ridge, TN

The microstructure of repeat unit and pendant group plays an important role in chain flexibility of polydienes. Benzofulvene, as a derivative of 1,3-butadiene, is recently found to produce only 1,2- and 1,4- repeat units in anionic polymerization. With a bulky pendant group, the polybenzofulvene(PBF) is readily predicted to be less flexible, which is evidenced by its higher glass transition temperature than polystyrene(PS). However, till now, detailed research on its chain flexibility have not been reported. Herein, microstructure-chain flexibility relationship of PBF is studied. Several PBFs were synthesized by anionic polymerization to ensure narrow molecular weight distribution, and their microstructures were tuned by polymerization solvent, the addition of additives, initiators and reaction temperatures. The chain flexibility of PBF, as defined by the characteristics ratio, was determined by combined measurements of intrinsic viscosity and weight-average molecular weight by using size exclusion chromatography equipped with multi-angle laser light scattering (MALLS) and online viscometer. It turns out that the characteristic ratio of PBF is indeed higher than PS, indicating a less flexible chain movement, and influenced by its microstructures.



Poster: Quantification of Secondary Loops in Polymer Gel Enabled by a Nondegradable Macromer Tracer

Junpeng Wang¹, Yuwei Gu¹, Rui Wang², Bradley D. Olsen², and Jeremiah A. Johnson¹

¹Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA

²Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA

Topological defects in polymer network significantly affect the mechanical properties of the materials, and it is therefore vital to directly quantify the amount of defects in a certain polymer network. Previous work from our group has successfully quantified the primary loop, but the method employed then cannot be used to measure the fraction of secondary loops, which also largely affects the mechanical properties of the network, despite its elastic effectiveness. Herein we demonstrate a method in which a nondegradable tracer enables the experimental quantification of both primary and secondary loops and the experimental results confirms previous theoretical work in this regard.

Poster: Effect of Minimal Structural Change in Conjugated Polymers on the Properties and Performance in Organic Photovoltaic Applications

Bing Xu¹, Xueping Yi², Chi Kin Lo¹, Iordania Constantinou², Zilong Zheng¹, Stefan D. Oosterhout³, Erik Klump², Amin Salehi², Rylan M.W. Wolfe¹, Michael F. Toney³, Jean-Luc Brédas¹, Veaceslav Coropceanu¹, Franky So², and John Reynolds¹

¹Georgia Institute of Technology, Atlanta, GA, United States

²North Carolina State University, Raleigh, NC, United States

³SLAC National Accelerator Laboratory, Stanford University, Menlo Park, CA, United States.

The design and synthesis of conjugated polymer donor materials are essential aspects in the development of organic photovoltaics (OPVs). In this presentation, we report our systematic studies on the structure-property-performance relationship of conjugated polymers enabled by introducing minimal structural changes.

On one hand, polar cyano groups (CN) were added to the side chains of dithienosilole-thienopyrrolodione (DTS-TPD) -based polymers, with the aim of modulating polymer dielectric constants. The synthesized CN-containing polymers exhibited increased dielectric constants, but the same band gaps and similar energy levels, compared to the analogues without CN groups. Surprisingly, despite the increase in dielectric constant, CN-containing polymers resulted in significantly inferior OPV performance than the parent polymers. Such behavior was attributed to the drastically lower hole mobility of CN-containing polymers, which was correlated to their higher energetic disorder induced by the CN permanent dipoles.

On the other hand, we changed the Group 14 atom (C, Si, Ge) at the center of a bithiophene fused ring, affording three “one-atom change” conjugated polymers, to elucidate the chemical structure impact of bond length difference (C-C: 1.56 Å; C-Si: 1.89 Å; C-Ge: 1.98 Å). Particularly, solution ¹H nuclear magnetic resonance (NMR) spectra and grazing incidence wide angle x-ray scattering (GIWAXS) results showed that poly(dithienocarbon-alt-thienopyrrolodione), P(DTC-TPD), exhibited different aggregation behavior in solution and different molecular packing orientation in solid state compared to poly(dithienosilole-alt-thienopyrrolodione), P(DTS-TPD), and poly(dithienogermole-alt-thienopyrrolodione), P(DTG-TPD). The differences in molecular structure and intermolecular packing ultimately affected device performance - the power conversion efficiencies (PCEs) of P(DTS-TPD) and P(DTG-TPD) were 7.0% and 7.7%, respectively, higher than PCE of 5.7% generated by P(DTC-TPD).

Our works reported here demonstrate the significant impact from only minimal changes in polymer structure. In each of the two projects, it is critical to have similar molecular weights and consistent material quality for the whole polymer family, in order to avoid influence from other factors besides the designed structural change. Therefore, the molecular weights of our synthesized polymers were carefully estimated by measuring in high-temperature GPC.



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TOSOH BIOSCIENCE LLC

3604 Horizon Drive, Suite 100
King of Prussia, PA 19406
Tel: 800-366-4875

email: gpc2017@tosoh.com
www.tosohbioscience.com