

2021 POLY PMSE Student Chapter Macromolecular Summer Seminar Series

10:15 – 11:45 AM EDT/ 9:15 – 10:45 AM CDT

May 06

Kevin J. Edgar, Virginia Tech

"Design of Functional Derivatives of Sustainable Polysaccharides"

Darryl A. Boyd, Science Made Simple LLC, US Naval Research Lab

"Slime, Polymers & The Future of Polymer Education"

May 11

Karen L. Wooley, Texas A&M University

"Synthetic Strategies by Which to Afford Natural Product-Based Polymer Materials: Impacts on Sustainability, Life, Health and the Environment"

Robson F. Storey, University of Southern Mississippi

"New Polyisobutylene-Based Polymers by Friedel-Crafts Alkylation"

May 18

John B. Matson, Virginia Tech

"Tapered Bottlebrush Polymers: Synthesis, Characterization, and Self-Assembly"

Tim P. Lodge, University of Minnesota

"Methylcellulose Fibril Formation and Gelation"

May 25

Quentin Michaudel, Texas A&M University

"Modern Organic Reactions as Tools to Access Dynamic Networks and Stimuli-Responsive Polymers"

Richard Laine, University of Michigan

"Finding Conjugation Where It Shouldn't Be"

MAY ABSTRACTS

May 06

Kevin J. Edgar, Virginia Tech

"Design of Functional Derivatives of Sustainable Polysaccharides"

Polysaccharides are one of the most abundant, structurally and functionally varied families of renewable natural polymers. The information content of certain natural polysaccharides is staggering, and immensely exceeds that of more familiar information carriers like DNA and proteins. High information content arises from complexity, which in turn means that precise synthesis of these complex polymers is a serious challenge. We will discuss approaches to regio- and chemoselective synthesis of polysaccharide and polysaccharide derivative synthesis, in every case producing novel materials with substantial potential for solving challenging problems. The presentation will include our work on synthesis of analogs of the biologically powerful and exquisitely complex glycosaminoglycans, as well as our approaches to controlled, brief, and efficient syntheses of polysaccharide-based block copolymers.

Darryl A. Boyd, Science Made Simple LLC, US Naval Research Lab

"Slime, Polymers & The Future of Polymer Education"

In 1907, the 1st synthetic polymer, Bakelite, was invented by Leo Baekeland. Since that time, synthetic polymers have become ubiquitous in the daily lives of billions of people around the globe due to their wide-ranging properties and utility. In recent years, the environmental and biological dangers of polymers have been increasingly made known to both the scientific community and the general public. Despite the awareness of these dangers, the common slime demonstration has remained a staple for those seeking to introduce polymers in educational settings. In this talk, Dr. Boyd will discuss the current state of environmental polymer contamination, and propose alternate ways in which polymers can be introduced into STEM education.

May 11

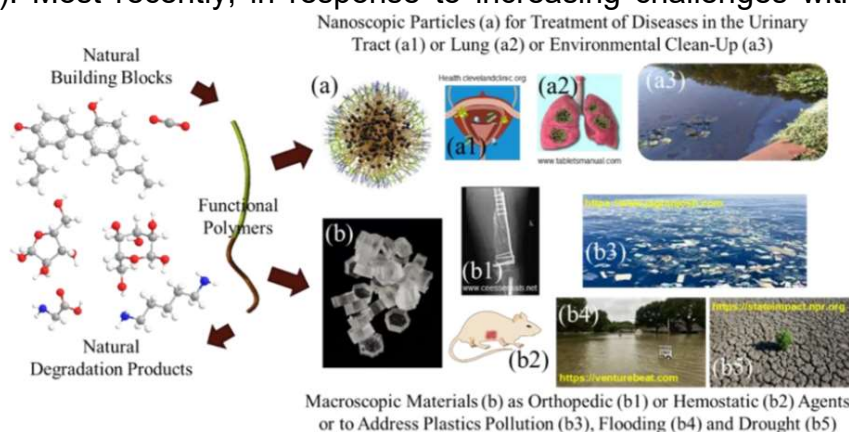
Karen L. Wooley, Texas A&M University

"Synthetic Strategies by Which to Afford Natural Product-Based Polymer Materials: Impacts on Sustainability, Life, Health and the Environment"

A primary interest in the Wooley laboratory is the production of functional polymers from renewable sources that are capable of reverting to those natural products once their purpose has been served. A long-standing focus has been the development of synthetic methodologies that transform sugars, amino acids and other natural products into polymer materials. This approach allows for the production of functional polymers from renewable sources that are capable of reverting to those natural products once their

purpose has been served (as is illustrated on the left side of the diagram below). This holistic life cycle approach is of importance from the perspectives of sustainable sourcing of materials feedstocks, while creating mechanisms for breakdown of the polymer materials after useful lifetime is complete, and providing for biological and environmental resorption of breakdown products. The overall process impacts the need to address the increasing accumulation and associated hazards of plastic pollution from the environmental persistence of nondegradable, petrochemically-sourced polymer systems. Moreover, inherent diversities of natural products provide opportunities to expand the scopes, complexities and properties of polymers, by utilizing fundamental organic chemistry approaches.

Target materials are designed for potential applications in diverse areas. For instance, we have produced amphiphilic block polymers that undergo supramolecular assembly in water to afford well-defined nanoscopic particles (diagram below, upper section (a)). By tuning the composition, structure and morphology, we are able to build functional nanoparticles that demonstrate efficacy as therapeutic nanomedicines for treatment of recurrent urinary tract infections (a1) and lung infections (a2), and we're working toward their use in the treatment of osteosarcoma lung metastases. When the amphiphilic block polymers are co-assembled with iron oxide nanoparticles, magnetically-responsive organic-inorganic composite nanosystems result, which are able to perform as environmental remediation agents that capture ten times their mass in crude oil from contaminated water (work that began following the Deep Water Horizon oil spill a decade ago). Macroscopic forms (diagram, lower section (b)) of our Sugar Plastics™ were initially studied with an aim toward their use in orthopedic applications (b1), when we identified that specific chemical compositions containing nanoscopic and microscopic porosities operate as bioresorbable hemostatic wound dressing materials (b2). We're currently working with Teysha Technologies, LTD to advance these polymer materials for commercial translation as naturally-degradable plastic packaging to address the growing plastics pollution crisis (b3). Most recently, in response to increasing challenges with climate change, we've designed analogs to exhibit properties that allow them to serve as superabsorbent degradable polymers to capture excessive liquid water, thereby preventing flooding, and later degrade to release the natural building blocks and water, thereby mediating drought and promoting crop growth (work that began from struggling through Hurricane Harvey in 2017).



This presentation will highlight synthetic strategies for the development of polymers, block polymers and crosslinked network materials, which can be produced by relatively simple approaches from glucose and can be made to exhibit a range of properties. Target materials are designed for potential applications in diverse areas, from

medicine, e.g., as nanotherapeutics or bioresorbable hemostatic agents, to the environment, e.g., as pollutant capture agents, climate resilient hydrogel materials or naturally-degradable plastics. Examples will highlight contributions that polymer chemistry can make toward bulk technological materials that are capable of impacting global needs, such as water-food-energy-health, and the grand challenges that must be solved in the coming decade.

Robson F. Storey, University of Southern Mississippi
"New Polyisobutylene-Based Polymers by Friedel-Crafts Alkylation"

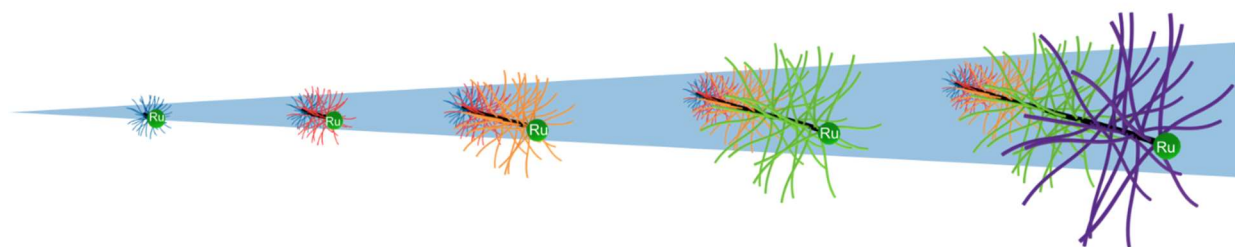
Polyisobutylene (PIB), an elastomer obtainable only through carbocationic addition polymerization, possesses a number of useful properties including superior impermeability to gases, high mechanical damping, excellent resistance to oxygen, ozone, and chemical attack, and biocompatibility. Isobutylene is copolymerized with 1-3 mol% isoprene to form the crosslinkable elastomer, butyl rubber. The major uses for butyl rubber/PIB include inner liners of automobile and truck tires, tire inner tubes, ball bladders, sealants, bubble gum base, protective clothing, and coatings for biomedical devices. This work describes two complimentary synthetic approaches to new functional polyisobutylenes. In the first approach, living carbocationic polymerization methods have been used to produce well-defined living PIB oligomers. The living ends are then end-quenched (trapped) by one of several types of nucleophiles, to produce useful terminal functionalities either through regiospecific elimination or addition to the chain end. In the second approach, butyl rubber is subjected to a reaction that cleaves the copolymer chain at the isoprene comonomer units, and simultaneously functionalizes the newly formed chain ends to form telechelic polyisobutylenes.

May 18

John B. Matson, Virginia Tech
"Tapered Bottlebrush Polymers: Synthesis, Characterization, and Self-Assembly"

Traditional bottlebrush polymers are comprised of a linear polymer backbone with densely grafted side chain polymers of a single molecular weight. In contrast, tapered bottlebrush polymers are comprised of side chain polymers of systematically varied molecular weights. For example, varying side chain molecular weights from 1 to 10 kg/mol from one end to the other end of the backbone chain creates a cone-shaped bottlebrush polymer. The synthetic method we use to produce these polymers is termed sequential addition of macromonomers ring-opening metathesis polymerization (SAM-ROMP) and is a combination of a reversible-deactivation radical polymerization reaction followed by a ROMP grafting-through polymerization. Successful synthesis requires careful design and preparation of each macromonomer and optimized conditions for the SAM-ROMP step. We have characterized a series of tapered bottlebrush polymers by small-angle neutron scattering (SANS), which has revealed differences in solution behavior between traditional and tapered bottlebrush polymers with similar molecular weights. Finally, we have begun to study the aqueous self-assembly of amphiphilic tapered bottlebrush block copolymers. Analysis of assemblies has been carried out using SANS and supplemented

by coarse-grained molecular dynamics simulations, CMC measurements, dynamic light scattering studies, and transmission electron microscopy.



Tim P. Lodge, University of Minnesota
"Methylcellulose Fibril Formation and Gelation"

Methylcellulose (MC) is a semiflexible cellulose ether derivative with a wide range of industrial applications, owing to its water solubility at low temperatures and thermoreversible gelation upon heating. The gelation mechanism of aqueous MC solutions has been debated for many years. However, in 2010, gelation was discovered to be concurrent with fibril formation upon heating, whereby the MC polymer chains self-assemble into fibrils with a remarkably consistent mean diameter, largely independent of polymer concentration, molecular weight, and temperature of gelation. This discovery has shed important light on the gelation mechanism, and initiated studies that lead to more intriguing questions about the fibrils themselves. This talk will emphasize various developments since the discovery of fibril formation, while highlighting unanswered questions that require further investigation.

May 25

Quentin Michaudel, Texas A&M University
"Modern Organic Reactions as Tools to Access Dynamic Networks and Stimuli-Responsive Polymers"

The synthesis of polymers with constantly increasing complexity is required in many fields to foster the discovery of new technologies. Since the specific function of polymers is dictated by their molecular structure (monomer composition, molecular weight distribution, self-assembly at the nanoscale, etc.), the invention of unique methods of polymerization for the precise design of macromolecules remains essential. This presentation will focus on 1) the development of a new click reaction to afford polysulfamides, an underexplored family of polymers with unique properties governed by hydrogen-bonding; 2) the synthesis of all-cis poly(p-phenylenevinylene)s via stereoselective catalysis and their application as light-responsive polymers. These new materials are currently constructed in the Michaudel lab with an eye toward applications in the fields of energy, medicine, and sustainability.

Richard Laine, University of Michigan

"Finding Conjugation Where It Shouldn't Be"

Multiple studies have explored using cage silsesquioxanes (SQs) as backbone elements in hybrid polymers motivated by their well-defined structures, physical and mechanical properties. As part of this general exploration, we reported unexpected photophysical properties of copolymers derived from divinyl double decker (DD) SQs, [vinyl(Me)Si(O0.5)2][PhSiO1.5]8[(O0.5)2Si(Me)vinyl] (vinylDDvinyl). These copolymers exhibit strong emission red-shifts from model compounds and implying unconventional conjugation, despite vinyl(Me)Si(O-)2 siloxane bridges. In an effort to identify minimum SQ structures that do/do not offer extended conjugation; we explored Heck catalyzed copolymerization of vinyl-ladder(LL)-vinyl compounds, vinyl(Me/Ph)Si(O0.5)2[PhSiO1.5]4(O0.5)2Si(Me/Ph)vinyl, with Br-Ar-Br where Br-Ar-Br = 1,4-dibromobenzene, 4,4'-dibromo 1,1'-biphenyl, 4,4''-dibromo-p-terphenyl, 4,4'-dibromo-trans-stilbene, 2,7-dibromo-9,9-dimethyl-9H-fluorene, 2,5-dibromothiophene, 5,5'- dibromo-2,2'-bithiophene and 2,5-dibromo-thieno[3,2-b]thiophene. Most surprising, the resulting oligomers show 30-60 nm emission red shifts beyond those seen with vinylDDvinyl analogs despite lacking a true cage. Further evidence for unconventional conjugation includes apparent integer charge transfer (ICT) between LL-co-thiophene, bithiophene and thienothiophene with 10 mol% F4TCNQ, suggesting potential as p-type doped organic/inorganic semiconductors. Brominating DD/LL-co-phenyl polymer vinyl groups eliminates emission red-shifts. Zn debromination thereafter restores vinyl groups and emission red-shifts but brominated phenyls remain providing potential access to families of "hairy" conjugated SQ polymers.