Division of Polymer Chemistry (POLY)

Graphical Abstracts

Submitted for the 246th ACS National Meeting & Exposition

Indianapolis, September 8-12, 2013
**Division of Polymer Chemistry (POLY)**

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**Primary organizer of Cosponsored symposium.**

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To create new functional materials for advanced technologies, control over their hierarchical structures and orders is vital for obtaining the desired properties. We utilized and functionalized fullerene (C60) and polyhedral oligomeric silsesquioxane (POSS), and assembled these particles with polymers to form those hierarchical structures. In order to achieve precisely defined molecular structures and functionalities, we have developed novel routes of functionalize C60 and POSS and attached them onto other organic materials in a highly efficient and controlled manner via “click” chemistry and other precise transformations. The structures of these assemblies along with the resulting ordered structures were analyzed to determine their structure-property relationships. One of the most illustrating examples is a series of novel giant surfactants and lipids possessing a well-defined amphiphilic head and polymeric tails. Various architectures of this class of materials have been constructed and their self-assembly processes in solution, in the condensed bulk and thin films have been investigated. Another set of examples are “nano-atoms”. These classes of molecules are designed to possess features of molecular Janus particles with various symmetry breakings. When specific interactions are introduced, these “nano-atoms” are functioned as building blocks to construct different amplified molecules and further to self-assemble into hierarchical ordered structures. Their thermodynamic phase diagrams and kinetic pathways are explored to understand this new class of materials and their potential applications in modern technologies.
2 - Isoindigo-based copolymers for field-effect transistors: The structure-property relationship

Ting Lei, Jian Pei, jianpei@pku.edu.cn. College of Chemistry and Molecular Engineering, Peking University, Beijing, China

Organic field-effect transistors (OFETs) are advancing rapidly in terms of their applications in low-cost large-area thin film transistors. However, PFETs with high carrier mobility and long-time stability are usually achieved in low-humidity and inert atmosphere. Therefore, to design new polymers for high-mobility PFETs with ambient-stability is still of great challenge. On the other hand, the structure-property relationship is important for designing new organic materials for optoelectronics. Although several design strategies and even computational methods have been proposed for small molecular OFETs, rational design strategy for PFETs are seldom reported.

Herein, we develop isoindigo-based copolymers for PFETs to investigate their structure-property relationship. Owing to the donor-acceptor interaction and the spatial steric hindrance caused by the branched alkyl chains, we envision that the small units dock into the cavity formed by the isoindigo cores and branched alkyl chains. We systematically compare FET device performances, polymer packings and film morphologies of the polymers, and find that this strategy is efficient to obtain high-performance FETs. Polymers with $C_{2h}$-symmetric donors exhibit systematically higher field-effect mobility than those with $C_{2v}$-symmetric ones.
3 - Synthesis of polypeptide brushes via catalysis and reactions on polypeptides

Timothy Deming, demingt@seas.ucla.edu, Department of Bioengineering, UCLA, Los Angeles, CA 90095, United States

Branched chain copolypeptides have intrigued scientists for many years. Recently, hyperbranched and dendritic polypeptides with their abundance of functional groups, and three-dimensional globule-like presentation of functionality, have been found valuable for multiple presentation of antigens in vaccines, as imaging agents, and for drug and oligonucleotide delivery. Although the properties of branched polypeptides show great promise, controlled synthesis of these materials remains challenging. High density cylindrical copolypeptide brushes are desirable synthetic targets since the potential to control their three-dimensional shape makes them intriguing as components in block copolymers, which can then be used for preparation of self-assembled materials with complex morphologies. Although there have been many successes in controlled synthesis of cylindrical hybrid-polypeptide copolymer brushes, the preparation of entirely polypeptide based cylindrical copolymer brushes has not been achieved. Here, we report new methods for synthesis of cylindrical copolypeptide brushes via NCA polymerization utilizing (i) a tandem catalysis approach that allows preparation of brushes with controlled segment lengths in a straightforward, one-pot procedure that requires no intermediate isolation or purification steps, and (ii) via development of reagents for chemoselective modification of functional polypeptides.

Sunday, September 8, 2013 09:20 AM
AkzoNobel Award for Outstanding Graduate Research in Polymer Chemistry: Symposium in Honor Hua Lu (08:30 AM - 11:50 AM)
Location: Hyatt Regency Indianapolis
Room: Regency B
4 - Cellular synthesis of non-linear proteins

Wen-Bin Zhang, Fei Sun, Frances H Arnold, David A Tirrell, tirrell@caltech.edu. Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

The spontaneous isopeptide bond formation between a peptide tag (SpyTag) and its protein partner (SpyCatcher) allows the synthesis of non-linear proteins in cellular hosts. Strategic placement of sequences encoding SpyTag and SpyCatcher within protein-coding genes programs the post-translational modification of the expressed proteins in situ, and enables the synthesis of a variety of unconventional protein topologies. For example, when SpyTag and SpyCatcher were placed at the N- and C-termini, respectively, of an elastin-like-protein (ELP), highly efficient cyclization of the ELP was observed. At low protein synthesis rates (e.g., at low temperature in relatively poor media), the product was almost exclusively monomeric circular ELP; at high protein synthesis rates (e.g., at high temperature in rich media), the major product was monomeric circular protein while significant amounts of chain-extended oligomers were also observed. The circular topology has been demonstrated by SDS-PAGE, MALDI-TOF mass spectrometry, proteolytic digestion, and single-site mutation.
5 - Multivalent polymer conjugates targeting amyloid oligomers

Yang Song\textsuperscript{1,3}, Pin-Nan Cheng\textsuperscript{3}, Lijuan Zhu\textsuperscript{3}, Edwin G Moore\textsuperscript{2}, Jeffrey S Moore\textsuperscript{1,3}, jsmoore@illinois.edu. (1) Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States, (2) Baxter Healthcare Corp., Round Lake, IL 60073, United States, (3) The Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Amyloid aggregation involves a complicated nucleation-dependent polymerization and many devastating human neurodegenerative diseases. While many strategies applied to prevent amyloid aggregation appear promising for potential therapeutics, it remains largely uncertain by which mechanism inhibition exactly occurs. To gain more mechanistic insights, we introduce multivalent polymer conjugates (mPCs) that may preferentially target and stabilize amyloid oligomers, and thus inhibit amyloid aggregation. To demonstrate this approach, we first conjugate polymers with multiple small molecule or peptide-based inhibitors to target amyloid β (A\textbeta) aggregation associated with Alzheimer's disease. Our studies show that mPCs can far more effectively inhibit A\textbeta aggregation than their monomeric counterparts. The inhibition of A\textbeta aggregation by mPCs may occur through stabilizing A\textbeta oligomers, which may also reduce toxicity from A\textbeta aggregation. We envision that the concept of mPCs can be generalized in different amyloid aggregation studies and provide a new avenue to develop polymer conjugate therapeutics for amyloid-related diseases and others.
Ring-opening polymerization mediated synthesis of drug-polymer conjugates and nanoconjugates

Rong Tong, Qian Yin, Hua Wang, Jianjun Cheng, jianjunc@illinois.edu. Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

Polymeric nanomedicine, an emerging field that involves the development of polymeric nanostructures for delivery and diagnostic applications, is expected to alter the landscape of oncology. In current formulation of anticancer polymeric nanostructures, drug molecules are either covalently linked to hydrophilic polymers through conventional coupling chemistry or non-covalently encapsulated into hydrophobic polymeric nanoparticles. In this proceeding we report a new nanoparticle formulation method through drug-initiated, chemo- and regioselective lactide ring-opening polymerization followed by nanoprecipitation. In vitro and in vivo studies will also be reported.
Polypeptides, mainly prepared by the ring-opening polymerization (ROP) of α-amino acid N-carboxyanhydrides (NCAs), are emerging biomaterials receiving increasing attentions for various biomedical applications. However, methods for controlled polymerization of NCAs are limited and suboptimal. In this abstract, I will discuss: a) controlled/living NCA polymerization technologies for the preparation of highly uniformed polypeptides and related mechanistic studies; b) chemical and biophysical properties of polypeptides; c) biomedical applications (such as gene and siRNA delivery) of those novel polypeptide materials.
8 - Sequence-controlled polymers: About the importance of chemical diversity

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

Synthetic polymers do not exhibit controlled sequences of monomers as biological macromolecules do. However, ordered comonomer sequences could open interesting technological avenues in synthetic polymer science. Very little research has been carried out during the last part of the 20th century for developing sequence-specific polymerization methods. Yet, for about five years, a renewed interest in the subject has emerged. This new trend will be described in my presentation. In particular, this lecture will emphasize the importance of chemical diversity in this emerging field of research. Indeed, synthetic sequence-defined polymer, specifically designed for targeted applications, could be a suitable alternative to currently used biopolymers such as DNA and proteins. This point-of-view will be illustrated by recent examples obtained in our laboratory. For instance, the preparation of complex macromolecular structures such as 1D macromolecular arrays or folded polymer origamis will be presented.
9 - Depolymerization-macrocyclization of arylene-ethynylene copolymers: Sequence matters

James H. Herbison, Jeffrey S. Moore, jsmoore@illinois.edu. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

Shape-persistent arylene-ethynylene macrocycles have drawn interest for their applications in supramolecular chemistry and electronics. Because it is reversible, the alkyne metathesis reaction has been shown to be an efficient tool for the synthesis of these macrocycles via dynamic covalent chemistry. Our group has recently developed a method for the synthesis of arylene-ethynylene macrocycles relying on the thermodynamic control of alkyne metathesis through depolymerization of arylene-ethynylene polymers. In this talk we will report the surprising observation that copolymers incorporating ortho-phenylene-ethynylene monomer units do not always produce product distributions that reflect thermodynamic control. For example, subjecting the alternating ortho-meta sequence to metathesis gave only the alternating macrocycle. Possible causes of this kinetic selectivity will be discussed.

Sunday, September 8, 2013 09:00 AM
Sequence-Controlled Polymers (08:30 AM - 12:15 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
10 - Precision sequence control in peptoid polymers

Jing Sun, Ronald Zuckermann, rmzuckermann@lbl.gov. Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

Peptoids are a versatile class of bio-inspired polymer whose length and monomer sequence can be precisely controlled. Peptoids are based on an N-substituted glycine backbone, and bridge a great materials gap between proteins and bulk polymers. Like proteins, peptoids are a sequence-specific heteropolymer, capable of folding into specific shapes and exhibiting potent biological activities; and like bulk polymers they are chemically and biologically stable and relatively cheap to make. Peptoids are efficiently assembled via automated solid-phase synthesis from hundreds of chemically diverse building blocks (primary amines) allowing the rapid generation of huge combinatorial libraries. Computational tools are also being developed which aid the prediction of chain folding. The precision synthetic control over the peptoid structure enables the rapid prototyping of new materials, as well as the testing of fundamental principles in polymer science and structural biology. Peptoids provide an ideal platform to discover nanostructured materials capable of protein-like structure and function.
11 - Sequence-controlled polyethylene possessing precisely placed acid groups

Kenneth Wagener¹, ken@wagener.org, Chet Simocko¹, Taylor Gaines¹, Karen Winey². (1) Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States, (2) Department of Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Precision Polyolefins. These are polymers made using metathesis polycondensation chemistry to regulate, without equivocation, branch identity and the exact location of the branch along a polyolefin backbone, including research involving very large branches.¹ The research has been extended beyond alkyl groups to precisely placed functional groups that can be highly interactive with each other, such as organic acid groups. Precision placement of acid groups (carboxylic, sulfonic, phosphonic, and boronic) along the backbone results in a dramatic change in morphology. Fig. 1 reveals a precision carboxylic acid polyethylene, where the morphology switches from clusters of ionic groups as in random, conventional ionomers to sheets interconnected via precision hydrogen bonding.² The phosphonic acid polymers are of special interest at the moment with comparative small angle X-ray data being particularly revealing.³ The difference in physical properties between these two types of polymers is significant.

The synthesis of new macro-RAFT agents \( \text{Z-C(S)=S-M}_1-M_2-M^n\text{R} \) by sequential insertion of monomers \( \text{M}_1, \text{M}_2, \text{etc.} \) 'one at a time' into an initial RAFT agent \( \text{Z-C(S)=S-R} \) will be described. The kinetics of the various process steps have been analysed. Critical factors for precision are a high transfer constant for the RAFT agent and a high rate of addition of synthesis he radical \( \text{R}^\cdot \) to monomer relative to further propagation. With these conditions satisfied, the rate of reaction is largely determined by the rate of \( \text{R}^\cdot \) adding to monomer. Initiator-derived by-products \( \text{Z-C(S)=S-(M)-I} \) are of particular importance when \( \text{R}^\cdot \) is different from the initiator-derived radical \( \text{I}^\cdot \).

The scope of the process will be illustrated with recent examples of optoelectronic polymers.


13 - Sequence-controlled vinyl polymers by chain growth control of radical species

Makoto Ouchi, ouchi@living.polym.kyoto-u.ac.jp, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Kyoto 615-8510, Japan

Radical polymerization, a representative chain-growth polymerization with vinyl monomers, is used for many industrial applications, and most of the products are related to copolymers rather than homopolymers. In such copolymers, the “averaged” composition ratio of co-monomers is statistically dependent on their monomer reactive ratios, and the sequence is ill-defined or totally random except alternating copolymerization of specific combinations. Now that control of simple primary structural factors (i.e., chain length, terminal, etc.) is achieved with living polymerization techniques, “sequence” is a next structural factor to be controlled.

Thus, we have designed “template” for molecules in metal-catalyzed living radical polymerization to control propagation-order independently of reactive ratios.1-5 In addition, our efforts were directed to how to control single monomer addition in living polymerization toward control of aperiodic sequences via the iterative cycle.

Monomer sequence control is one of the remaining Holy Grails in synthetic polymer chemistry. In this contribution, three techniques that introduce specific aspects of sequence control in RAFT-mediated polymerization will be discussed. The first technique is the smart use of the initialization process. It was shown previously that initialization can be very selective. Under certain conditions, this selectivity can be extended to more than one monomer unit. The second technique is the use of comonomer reactivities. The underlying mechanism of alternating copolymerization will be discussed and hypotheses will be formulated on extended possibilities for sequence control. The third and final technique is the application of two monomers that require different RAFT-agents for their homopolymerization. The implementation of all three techniques in one polymerization system has not been attempted yet, and may lead to serious practical problems. However, the addition of new techniques to the available toolbox will hopefully bring the Holy Grail a little closer.
This specific distribution/placement of monomer units along a synthetic polymer chain can confer remarkable structural and self-assembly properties. Here we report a novel strategy for the synthesis of high order multiblock copolymers: in high yield, narrow polydispersity and controlled structural complexity. To achieve this breakthrough we have applied recent advances in living free radical polymerization in the presence of zero valent copper to the iterative synthesis of block polymers. Unlike previous block polymer syntheses, this method involves no purification between the successive block formation steps, because each step is taken to full monomer conversion. This is only possible due to the high maintenance of “livingness” under high conversion/post-polymerization conditions. The approach is general, facile and offers the opportunity to synthesize new macromolecular materials with unprecedented control of block lengths (from small to large), providing materials that could find application in a diverse range of disciplines, from materials science to biotechnology. This approach is demonstrated for the synthesis of Poly(MA-b-nBuA-b-EA-b-2EHA-b-EA-b-nBuA) below.
16 - Reflections on my years of joint teaching and codirecting research and the VT polymer program with Jim McGrath

Garth L. Wilkes, gwilkes@vt.edu, Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061, United States

While having the good fortune of knowing Jim McGrath prior to his becoming a faculty member at Virginia Tech, this brief presentation will focus more on the interactions and joint adventures that occurred with Jim from 1978, the year that the presenter left the academic halls of Princeton University to join the Virginia Tech faculty, and to have the pleasure of working with Jim McGrath to the present day. Within the framework of seriousness and humor, I will try to accent the many positive qualities, capabilities and contributions of Jim McGrath…of which there are many.
17 - New monomers for legacy step-growth polymers: Insertion of 1,4-cyclohexylene monomers into poly(arylene ether sulfone) backbones

S. Richard Turner, srturner@vt.edu, Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061, United States

Significant alteration of the properties of legacy step-growth polymers, e.g. polyesters, polyamides, polycarbonates, and poly(arylene ether sulfones) generally requires the copolymerization of a new monomer into the backbone. Our recent research has focused on inserting new 1,4-cyclohexylene based monomers into PAESs. Among other approaches, a new bisphenol, 4,4’-[trans-1,4-cyclohexanebis(methylene)] bisphenol (CMB) was synthesized and copolymerized into the PAES backbone. Surprisingly enhanced elongation to break values were observed when CMB was copolymerized with 4,4’-dihydroxy- p-terphenol.
The upper bound relationship (both theory and empirical correlation) indicates that the permselectivity as a function of permeability is a consequence of the diffusivity based on gas diameter differences. The solubility selectivity is assumed to be invariant with permeability (and free volume). Several literature references note the solubility constant for specific polymeric classes exhibits a free volume variation. A large database of permeability, diffusivity and solubility data for glassy polymers was compiled to assess the above conclusion. A critical analysis of the data clearly demonstrates there is a modest solubility selectivity contribution to permselectivity as a function of permeability and free volume. The solubility selectivity ($S_i/S_j$) generally decreases with increasing permeability (and free volume) where the $j$ gas diameter is larger than the $i$ gas diameter. This is a consequence of the solubility of the larger gas being less accessible to polymer sorption sites as the polymer packing density increases and free volume decreases. The diffusion data allows for the determination of a diffusivity upper bound with modest differences versus expectations based on the permeability based upper bound relationship. The analysis of diffusion data allows for a determination of a new set of gas diameters more appropriate to gas diffusion in polymers than prior correlations.

The introduction to this presentation will discuss the upper bound analysis and permeability and permselectivity analysis previously published providing the background for this presentation. A brief review of relevance to the important technology involving membrane separation of gases will also be presented.
19 - PBI membranes for fuel cells and devices

Brian C Benicewicz, benice@sc.edu, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States

There have been major efforts for more than a decade to increase the operating temperature of polymer based membrane fuel cells above the traditional operating temperature of approximately 85°C. Polybenzimidazole (PBI) polymers are excellent candidates for PEM fuel cell membranes capable of operating at temperatures up to 200°C. One of the more important benefits of PBI polymers doped with phosphoric acid is the ability to operate efficiently without the need for external humidification and the related engineering hardware to monitor and control the hydration levels in the membrane. This feature has been widely explored for portable and stationary PEM fuel cell devices, and numerous companies are developing systems based on PBI MEA’s. Several years ago, a sol-gel process was developed to produce PBI membranes loaded with high levels of phosphoric acid. This process, termed the PPA process, uses polyphosphoric acid as the condensing agent for the polymerization and the membrane casting solvent. Membranes produced from this process showed the ability to maintain high levels of phosphoric acid (PA) and high proton conductivities while simultaneously exhibiting low levels of PA loss during standard operating conditions.

We have been exploring many chemical variants of the PBI chemistry to understand the effect of chemical structure on the basic membrane properties, as well as issues of stability and durability of the membranes produced by the PPA Process. In this presentation, we will review the recent development of PBI-acid complexes and recent results will be used to describe correlations between polymer structure and properties which provide valuable insights for designing membranes with extended durability tailored to devices and specific applications.
In order to create new materials having desired multiple functionalities for advanced technologies, control over their hierarchical structures and orders is vital for obtaining the desired properties. We utilized and functionalized fullerene (C\textsubscript{60}) and polyhedral oligomeric silsesquioxane (POSS), and assembled with polymers to form "nano-atoms" as building blocks to construct those hierarchical structures. Furthermore, novel routes of functionalize C\textsubscript{60} and POSS are designed and "click" them with other organic materials. The structures of these assemblies along with the resulting ordered structures are analyzed to exam their structure-property relationships. One of the most illustrating examples is a series of novel shape amphiphiles possessing a well-defined amphiphilic head and polymeric tails. Various architectures of this class of materials have been constructed and their self-assembly processes in solution, in the condensed bulk and thin films have been investigated. Another set of examples are giant Junas molecules and polyhedrons with various symmetry breakings. When specific interactions are introduced, these "nano-atoms: are functioned as building blocks to construct different amplified molecules and further to self-assemble into hierarchical ordered structures. Their thermodynamic phase diagrams and kinetic pathways are explored to understand this new class of materials and their potential applications in modern technologies.
21 - Influence of the molecular structure of core-corona nanoparticles on MRI relaxivities and images

Judy S. Riffle¹, jriffle@vt.edu, Nipon Pothayee¹, N Hu¹, S. Balasubramaniam¹, Richey M. Davis¹, A. Koretsky². (1) Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia 24061, United States, (2) Laboratory for Functional Imaging, National Institutes of Health, Bethesda, MD 20892, United States

Core-corona assemblies of block copolymers containing various cargo in their cores provide a flexible platform for biomaterials with potential as image enhancement agents in Magnetic Resonance Imaging. One block of the copolymer is designed to interact with the cargo and form the core, while the corona block(s) can be independently tailored to interact with physiological media or particular biological structures. We have prepared block and graft copolymers comprised of nonionic polyethers and polyanionic or functional segments. The ionic components bind to electropositive oxides and ions or cationic therapeutics to comprise the cores of these assemblies, while the nonionic polyethers form the coronas. This lecture will focus on the synthesis and properties of several examples of these materials containing magnetite or manganese cations complexed with carboxylates or phosphonates in light of their molecular and architectural parameters.

Sunday, September 8, 2013 10:55 AM
Charles Overberger Award (08:30 AM - 12:10 PM)
Location: Hyatt Regency Indianapolis
Room: Studio One
Polymer membranes are critically important in addressing urgent global needs in the 21st century for energy efficient gas separations as well as reliable, sustainable, efficient access to clean energy and clean water. In the gas separation field, polymer membranes are now well established for air separation, hydrogen purification, and, increasingly, natural gas processing. Polymer membranes have also emerged as a leading technology to desalination water (e.g., reverse osmosis) and are being explored for energy generation in applications such as reverse electrodialysis and pressure retarded osmosis. Furthermore, efforts are under way to develop additional applications of membranes for water purification, such as forward osmosis and membrane-assisted capacitive deionization. In each of these applications, control of small molecule transport (gases, water and ions) across polymer membranes is critically important for optimizing performance of such membranes. This presentation focuses on the fundamentals of small molecule transport in polymers obeying the solution/diffusion model. Structure/property correlations are shown for a variety of polymers, including uncharged and charged materials. The role of free volume in governing diffusion of solutes through polymers is explored. Consistent with the so-called upper bound relations in gas separation membrane materials, the existence of a water-salt permeability/selectivity tradeoff relation is observed for polymers being considered for water purification and energy generation applications. Areas where the physics of water and ion transport are both similar to and different from those of gas transport in polymers are highlighted.
23 - Prof. Overberger’s influence on my past and current career

James E. McGrath, jmcgrath@vt.edu, Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States

I had the pleasure of working with one of Prof. Overberger’s Ph.D.’s at Goodyear in the early 1960s and learned a great deal about organic and polymer chemistry during that time. This experience partially motivated me to pursue a Master’s and Ph.D. at the University of Akron with Alan Gent and Maurice Morton, respectively. After 8 years at Union Carbide in collaboration with Lloyd Robeson and other good colleagues, I joined the faculty at Virginia Tech. Working with Tom Ward and Garth Wilkes (and others), we developed the polymer program over the last several decades into a thriving, collaborative effort. Over the years our research has included a number of diverse areas, beginning perhaps with a focus on thermally stable polymers and polymer matrix composites. This background led naturally to our current research in membranes for water, gas, and fuel cell applications, where we have particularly enjoyed working with Prof. Benny Freeman at the University of Texas. This presentation will briefly review some highlights from these various experiences.

Sunday, September 8, 2013 11:45 AM
Charles Overberger Award (08:30 AM - 12:10 PM)
Location: Hyatt Regency Indianapolis
Room: Studio One
Light-induced polymerization is an industrially viable process that offers numerous economic and technical advantages over conventional thermal polymerization, particularly toward the fabrication of crosslinked thermoset thin films. These advantages include rapid through cure, low energy requirements, ambient temperature processing, solvent-free resin compositions, and spatial and temporal control over the polymerization process. Here, we report a simple and versatile method for the fabrication of superhydrophobic inorganic–organic thiol-ene coatings via sequential spray-deposition and photopolymerization under ambient conditions.

The coatings are obtained by spray-deposition of UV-curable hybrid inorganic–organic thiol-ene resins consisting of pentaerythritol tetra(3-mercaptopropionate) (PETMP), triallyl isocyanurate (TTT), 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMTVSi), and hydrophobic fumed silica nanoparticles. The spray-deposition process and nanoparticle agglomeration/dispersion provide surfaces with hierarchical morphologies exhibiting both micro- and nanoscale roughness. The wetting behavior, dependent on the concentration of TMTVSi and hydrophobic silica nanoparticles, can be varied over a broad range to ultimately provide coatings with high static water contact angles (>150°), low contact angle hysteresis, and low roll off angles (<5°). The cross-linked thiol-ene coatings are solvent resistant, stable at low and high pH, and maintain superhydrophobic wetting behavior after extended exposure to elevated temperatures. We demonstrate the versatility of the spray-deposition and UV-cure process on a variety of substrate surfaces including glass, paper, stone, and cotton fabric.
Symmetric and asymmetric H-shaped polybutadienes were synthesized by living anionic polymerization. While gel permeation chromatography (GPC) suggested such materials to be near-monodisperse, temperature gradient interaction chromatography (TGIC) and rheology experiments indicated the presence of impurities that significantly affected their rheological behavior. GPC is shown to be inadequate for characterizing the purity of such branched macromolecules. On the other hand, TGIC is shown to be an essential technique for both characterizing the purity of such materials and identifying and quantifying the impurities.
Polymer semiconductor materials are interesting alternatives to inorganic semiconductors in applications where low cost, flexible or transparent substrates, and large area format is required. Currently they have been incorporated into organic thin-film transistors, integrated display driver circuits, photovoltaics artificial electronic skin, and radio frequency identification tags. One of our fundamental interests is to understand how we can ultimately perform rational design of organic semiconductors. In this talk, I will present our efforts on understanding of molecular design rules for achieving efficient charge carrier transport and controlled growth of organic semiconductors. I will also present applications of these materials and devices for flexible and stretchable electronics applications.
27 - Creating complex interfaces using orthogonal click reactions

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Generating micro- and nanosized patterns on solid surfaces is an important area of research with relevance in many scientific and technological areas. In our recent approach to generate complex surfaces, we have developed a series of novel “click” reactions that can be used to selectively pattern different chemical functionality onto polymer brush supports using one pot, orthogonal chemical reactions. This talk will highlight post-polymerization modification of polymer brush supports as a means to generate spatially resolved patterns of complex functionality. The relative rates of each reaction are compared to that in free solution in order to determine how steric crowding, grafting density, size of reactant, and diffusion impact the rate of reaction.
28 - Radical polymers toward an organic-based rechargeable battery and photovoltaic cell

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We have focused on aliphatic polymers bearing organic robust radicals as pendant groups per repeating unit. The radical polymers are characterized by an ultimate population of unpaired electrons, which allows efficient redox-driven electron transport throughout the polymer layer. The high electron-transport reactivity provides very fast charge-propagation and reversible charge-storage in a rechargeable battery. A pair of two radical polymers with different redox potentials are used as a cathode- and an anode-active material in this organic battery. We are also fabricating dye-sensitized photovoltaic cells to replace the iodine-containing electrolyte and/or the titanium oxide semiconductor in Graetzel-type one with the radical polymer layers for charge-separation and -transport in the cell. The cells displayed significantly high open-circuit voltage of almost 1 V. Radical polymers are emerging as a new class of electroactive materials useful for various kinds of wet-type energy storage and conversion devices.

Sunday, September 8, 2013 03:35 PM
Mark Scholars Award: Symposium in Honor of Rigoberto Advincula (01:30 PM - 05:00 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen-based ligands is among most efficient controlled/living radical polymerization systems. ATRP has been successfully used to synthesize well defined organic-inorganic hybrids and also various bioconjugate materials. Some example of such new polymeric systems and their applications will be presented.
30 - Nanostructured polymer materials

Rigoberto Advincula C. Advincula, rca41@case.edu, Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States

The field of thin film polymer materials and nanoparticles converge in mastery of interfaces. Nanostructuring is not mere nanopatterning but understanding and controlling interfaces. This journey begins with that ability to do synthesis at the interface and the use of surface sensitive analytical techniques along the way. Interesting dimensions can be investigated as a function of composition, morphology, and field-effects. The Advincula Research Group for a while has focused in this area and our discovery driven paradigm has led to many interesting nanostructure and properties: controlled polymer brushes, electronanopatterning, hybrid dendrimers, and molecular imprinting. This would not have been possible without the hard work of all the students, post-docs, and collaborators who have been part of these project through the years.

Sunday, September 8, 2013 04:30 PM
Mark Scholars Award: Symposium in Honor of Rigoberto Advincula (01:30 PM - 05:00 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
Sequence control offers the potential to tune polymer properties while exploiting the unique properties of specific monomers.\textsuperscript{1} Poly(lactic-co-glycolic acid) (PLGA) is a polymer that is valued for originating from biorenewable resources and for exhibiting hydrolytic degradation to give biodegradable products. The ability to tune the properties of PLGAs has, until recently, been limited to control of molecular weight and the adjustment of the glycolic to lactic acid ratio. Using segmer assembly polymerization, a variety of sequenced PLGAs have been prepared.\textsuperscript{2} Sequence fidelity is demonstrated by examination of the MALDI-MS data and sequence specific bulk behavior by characterization of the thermal and mechanical properties of the polymers. Sequence specific hydrolysis behaviors can be seen in both the degradation profile\textsuperscript{3} and the penetration of water into the bulk.

\begin{align*}
\text{LG} & \quad [\text{O} = \text{C} - \text{O}]_n \\
\text{LLG} & \quad [\text{O} - \text{C} - \text{O} - \text{C} - \text{O}]_n \\
\text{GLG} & \quad [\text{O} - \text{C} - \text{O} - \text{C} - \text{O}]_n
\end{align*}

Ring-opening polymerization of heterocycles: A simple access to biodegradable polymers

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Given the growing need for inexpensive biodegradable plastics for use in various applications, the development of synthetic methods for the polymerization of a wide range of monomers with control over the stereochemistry and comonomer incorporation is of particular importance.

In this context aliphatic polyesters have emerged as biodegradable materials with huge potential. Recently we have reported new strategies to obtain biodegradable polyesters with controlled primary structures. For instance, this was achieved by tandem catalysis, which confers great interest to this approach. Commercially available complexes were used as efficient catalysts for cyclization of dicarboxylic acids followed by alternating copolymerization of the resulting anhydrides with epoxides. Given an operationally simple method, this tandem catalysis is an attractive strategy for the production of new renewable materials.

A series of glycomonomers have been prepared by reaction of 3-azidopropylacrylate (APA) and alkylated mannose, glucose and fucose, via Fischer-Helferich glycosylation. This was performed using CuSO$_4$ and sodium ascorbate in methanol/water mixture. SET-LRP of glucose monomer (GluA) was performed in dimethylsulfoxide (DMSO) using a Cu(0)/Cu(II) and Me$_6$TREN derived catalyst. Multi-block glycopolymers with a degree of monomer sequence controlled in various compositions from glycomonomers containing mannose, glucose and fucose moieties will be reported. Polymerizations were followed by $^1$H NMR, SEC and HR ESI-MS or MALDI-ToF MS to obtain information on the products. This technique gives a good degree of control over the monomer sequence along a polymer chain. The polymerization is performed in one pot by sequential addition of the subsequent monomers in a relatively a large scale. The obtained glycopolymers were examined for their binding behaviour to DC-SIGN. We observed higher affinity binding for the polymers with higher mannose content.
Controlled free radical polymerization has been used to synthesize binary and ternary gradient copolymers of various gradient strength. In these systems, the exact details of the sequence differ from chain to chain but on average are tuned in a sensitive manner based on the semi-batch nature of the polymerization. Like A-B block copolymers, gradient copolymers can undergo nanophase separation. However, because there are no pure A or pure B blocks within a gradient copolymer chain, the nanophase separation in copolymers with a linear gradient leads to a sinusoidal composition profile within bulk gradient copolymers. This unusual composition profile at the nanolevel results in behavior and properties that cannot be achieved with block or random copolymers, including glass transition breadth exceeding 100 K. In to glass transition behavior and its implications for damping applications, results of recent and ongoing research will be discussed related to unusual temperature dependent phase behavior rarely seen in block copolymers but more easily achieved because of the additional variable of gradient sequence. The superiority of gradient copolymers over block copolymers as interfacial agents will also be discussed. Examples will be provided in the field of blend compatibilization resulting, in some cases, in dispersed phase domains averaging ~100 nm in diameter.
35 - Synthesis of stimuli-responsive alternating or block copolymers via living cationic polymerization

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The recent considerable progress in the base-assisting living cationic polymerization made by our group allowed, for the first time, the controlled alternating cationic copolymerization of VEs with conjugated/aromatic aldehydes. This new technique combined with the findings of our systematic studies on precision synthesis of stimuli-responsive polymers such as thermo-, pH-, and photoresponsive poly[vinyl ethers (VEs)] encouraged us to develop a novel class of sequence-controlled copolymers such as stimuli-responsive alternating or block copolymers. This contribution focuses on the following challenging topics: (i) synthesis of chemically recyclable alternating copolymers of VEs and conjugated/aromatic aldehydes including biomass-based aldehydes, (ii) synthesis of thermo- or pH-responsive alternating copolymers with quantitative acid-degradability, and (iii) synthesis of amphiphilic or stimuli-responsive diblock copoly(VEs) with various functions such as thermoresponsive (LCST- or UCST-type) sol-gel transition, wettability control on the film surface, or micelle shuttling behavior between aqueous and organic phases; selective antibacterial activity; scaffolds for unique assemblies of silica nanospheres.
36 - WITHDRAWN
Radical chain polymerization has significant potential for the synthesis of polymers with a precisely controlled chain structure. In this paper, we report controlled radical copolymerization for the design of high-performance vinyl and diene polymers, such as thermo-resistant polymers, transparent and flexible materials, degradable polymers, and conducting polymers using non-vinyl monomers including oxygen, sulfur dioxide, and N-substituted maleimides as the comonomers. The radical reaction mechanism for the regio- and sequence-controlled copolymerization is discussed based on the experimental polymerization and the DFT calculation results. The solvent effects on the control of the radical reactions are also mentioned. The alternating and 2:1 sequence-controlled maleimide copolymers exhibit excellent thermal, mechanical, and optical properties, while the regiospecific alternating copolymers of 1,3-diene monomers with oxygen and sulfur dioxide were readily degradable upon heating.
Our group uses computationally-driven rational design of conjugated oligomers and copolymers for optoelectronic applications. Control of monomer sequence offers a new dimension in conjugated materials. For example, DFT-computed HOMO-LUMO gaps in sequence-controlled oligophenylene vinylene hexamers, illustrate that sequence control can tune band gap by 1 eV.

We will discuss the connection between computational exploration and experimental characterization in these conjugated, sequence-controlled oligomers, as well as the use of statistical methods and computational exploration to determine expected sequence effects averages across many monomer combinations. The combination of accurate, reliable computational exploration of sequences with targeted synthesis offers a route to rapidly study sequence-determined variation of polymer properties.
Hybridization of organic materials with inorganic nano-structures has been approved to be one the best approach to enhance the thermal performance of polymers and small molecules, and POSS has been proven to be excellent platform for developing new hybrid materials with enhanced mechanical and thermal performance. Here we showed that the coupling of POSS with azobenzene can significantly enhance the thermal and chemical stability azobenzene dyes without obvious change its photophysical properties. Confirming this, we have successfully designed and synthesized a new hybrid copolymer containing POSS and oligofluorene. This new hybrid polymer exhibits high thermal stability as well as retaining oligofluorene photoluminescent property both in solution and solid state.

Its application in OLED device was also demonstrated in the present report. Furthermore, we also explore the Benzothiadiazole/POSS/Fluorene hybrid system to study the FRET both intra-chain and inter-chain and several color tunable polymers were achieved.
40 - Multifunctional block copolypeptide vesicles for therapeutic delivery

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We have designed new vesicle forming, amphiphilic diblock copolypeptides that contain multiple levels of functionality within their hydrophilic domains. Aside from providing water solubility, hydrophilic segments have been developed to assist in cell binding, cell uptake, and to promote intracellular vesicle disruption for cargo release. By employing new synthetic methods, unprecedented levels of functionality can be programmed into these materials. We report on the self-assembly of these vesicles and analysis of their cell uptake, minimal cytotoxicity, and intracellular disruption. We will describe how polypeptide design can be used to control interactions between the polypeptide assemblies and the cells and tissues relevant for therapeutic delivery applications.
41 - Phage panning, peptides, and polymers: From ligand identification to in vivo applications for drug delivery

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We have recently synthesized brush-shaped, peptide-based copolymers by RAFT polymerization of peptide monomers with HPMA. These materials possess the biological functions contributed by their peptide components with the scalable synthesis of synthetic polymers. In this presentation, I will summarize our work in bioactive peptide identification, synthesis of peptide-based polymers, and applications of these materials for drug delivery. In one example, we use a cell-based phage screening method to identify a peptide that preferentially binds to "anti-inflammatory" (M2) macrophage. We further demonstrate that this peptide recognizes tumor-associated, M2-like macrophage, and that the peptide can be used for drug delivery to these cells. In a second example, we synthesize multifunctional materials for neuron-targeted delivery of nucleic acids. These peptide-based copolymers contain motifs for nucleic acid packaging, neuron targeting, and endosomal release. We also synthesized enzymatically-cleavable polymers using peptide monomers containing cathepsin B-cleavable sequences. The polymers were tested in vitro by reporter gene delivery to neuron-like, differentiated PC-12 cells and by direct, intraventricular injection in mice.
Polymeric stimuli-responsive nanocarriers are discussed as promising drug delivery systems. They can also be used as containers for active compounds in other biomedical applications, such as wound dressings. In this context, we work on the implementation of in situ infection diagnostics in wound dressings that may also treat bacterial infection. Dressings for burn wounds are not only essential for proper healing and the prevention of scarring, but may contribute to reduce the spread of antibiotic resistance from prophylactic administration of broadband antibiotics. In particular, we synthesized and investigated vesicles of amphiphilic block copolymers (polymersomes). Various PEG-b-PCL, PEG-b-PLA and novel hyaluronic acid-block-polycaprolactone and hyaluronic acid-block-poly(lactic acid) copolymers were obtained and assembled into vesicles. Since hyaluronic acid is digested by the enzyme hyaluronidase that is excreted by the bacterium *staphylococcus aureus*, the polymersomes are opened by the bacterial enzymes in infected wounds. The response of dye-loaded polymersomes to bacterial enzymes was investigated showing a pronounced lightup effect. In addition, the stability of the vesicles in different media and storage conditions was tested, as well as the sterilization and cytotoxicity. Finally, using confocal fluorescence lifetime microscopy the characteristic time constants for drying and rehydration and their dependence on the vesicle sizes were unraveled. The hyaluronic acid containing polymersomes show all the required properties for potential application in advanced infection signaling, responsive wound dressings.
43 - WITHDRAWN
44 - Novel dendritic nanocarriers: Dendron micelles and dendrimer-polymer hybrid nanoparticles

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Despite the ongoing fight against cancer, the debilitating disease remains the second most cause of death in the US. This presentation will highlight our current research in an effort to intervene cancer progress through developing novel nanocarriers for targeted drug delivery. As a delivery platform, dendrons have been utilized as a component of a delivery system to impart highly localized peripheral functional groups enabling virus-mimicking multivalent binding and distinct reactivity of core and surface groups allowing preparation of various amphiphilic block copolymers. By engineering the amphiphilic dendron copolymers, we have prepared a novel micellar system that demonstrates enhanced thermodynamic stability, high surface coverage by the PEG layer, modular surface chemistries, and high drug payload. Another nanocarrier design is focused on integrating advantages of highly flexible poly(amideamine) (PAMAM) dendrimers (5 nm in diameter) and larger polymeric nanoparticles (100 nm in diameter), while minimizing the drawbacks of each. Through hybridization of targeted dendrimers and PLA-PEG nanoparticles, we have achieved long circulation in plasma, efficient penetration through solid tumors, and high targeting efficacy, all validated in cultured cells, spheroids, and a tumor-bearing mouse model. These two novel nanocarrier platforms hold great promise to be widely used for highly specific delivery of a variety of anti-cancer drug molecules.
45 - Translational nanomedicine from self-assembling prodrugs

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Nanocarriers achieving high therapeutic index must be capable of simultaneously satisfying two pairs of opposite requirements at the right places, that is, “drug Retention in blood circulation vs. Release in tumor cells (2R)” and “Stealthy in blood vs. Sticky in tumor (2S)”. Besides the 2R2S capability, the feasibility of the nanocarrier materials to be proved for use as excipients (material excipientability) and the ability to establish scaling up production processes for good manufacture processes (GMP) for the nanocarrier and its formulation with drug (process scale-up ability) are other two elements indispensable for a truly translatable nanomedicine. Herein, I will present our self-assembling prodrugs approach aimed at translatable nanomedicine for cancer drug delivery. By employing drugs themselves as components of nanocarriers, we obtained prodrugs self-assembling into nanoparticles or nanovesicles with tailored sizes, high and fixed drug loading contents, and inhibited premature burst drug release. Very importantly, the nanocarriers are also characteristic by 100% loading efficiency and easy reproducible fabrication process, making it easier to establish GMP processes. Furthermore, by using intracellular responsive linkers, we can further make the nanovesicles responsive to intracellular stimuli for fast drug release.
46 - Anticancer drug-poly(o-carboxyhydride) nanoconjugates

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We report a novel synthetic strategy of polymer-drug conjugates for nanoparticulate drug delivery: hydroxyl-containing drug (e.g., camptothecin, paclitaxel, doxorubicin and docetaxel) can initiate controlled polymerization of phenyl O-carboxyhydride (Phe-OCA) to afford drug-poly(Phe-OCA) conjugated nanoparticles, termed drug-PheLA nanoconjugates (NCs). Our new NCs have well-controlled physicochemical properties, including high drug loading, quantitative drug loading efficiency, controlled particle size with narrow particle size distribution, and sustained drug release profile over days without “burst” release effect as observed in conventional polymer/drug encapsulates. Compared with polylactide NCs, the PheLA NCs have increased noncovalent hydrophobic interchain interactions and thereby result in remarkable stability in human serum with negligible particle aggregation. Such distinctive properties can reduce the premature disassembly of NCs upon dilution in bloodstream, prolong NCs’ in vivo circulation with the enhancement of intratumoral accumulation of NCs, which has a bearing on therapeutic effectiveness.

Drug-Initiated Controlled Ring-Opening Polymerization
Alginates and dextrans are naturally occurring polysaccharides and have been investigated for controlled drug delivery. The success of alginates in hydrogel form in controlled drug delivery is limited by high water solubility and premature drug release. Hydrophobically modified alginate hydrogels offer slightly better, yet still poor bioavailability. In our lab, we have taken on a different approach to the utilization of alginates by engineering novel amphiphilic material capable of self-assembly in aqueous solution. Synthetic route consisted of reduction in molecular weight, solubility modification and functionalization, and finally grafting synthetic polymers (pMA, pMMA, pMEGMEMA) from or onto alginates using living radical polymerization (LRP) in aqueous environment to produce amphiphilic structures. Low molecular weight dextran was also used in order to study the effect of alginate’s carboxylic groups on the synthetic route and stability of final product. Chemical structure and molecular weight of the material was analysed by H-NMR and aqueous-gel permeation chromatography (aq-GPC), respectively. Micelle size and morphology were studied by dynamic light scattering (DLS) and Transmission Electron Microscopy (TEM). We are currently working on better controlling the molecular size of a polymer graft, size distribution of micelles, reducing undesired side reactions such premature micelle formation. The longer term objective is to incorporate small molecule, and larger peptide based, pharmaceuticals into self-assembling nanoparticulate structures for \textit{in vitro} and \textit{in vivo} drug release studies.
48 - Screening for specific interactions: Precisely tailored drug transporters for small molecule solubilization and release

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Novel small molecule compounds in pharmaceutical research can be identified by high-throughput screening or structure based design. Frequently those lead structures suffer from restrictions in applicability and ease of approval due to unfavorable properties e.g. water insolubility. Therefore, much effort is spend, including cost-intensive structure optimization cycles, to overcome these drawbacks.

Polymer-block-peptides are especially suited to render insoluble drugs water-soluble, without the need to structurally adapt the small molecule entity.[1]

A generic approach is presented for advanced tailoring of polymer drug carriers based on polymer-block-peptides to develop specific drug formulation agents.[2] Combinatorial means are used to select suitable peptide segments to specifically complex small molecule drugs. Precise adjustment of drug-release profiles can be programmed in the peptide segment, which can be considered as an improvement over established block-copolymer carriers.

Proof of principle is shown on the photosensitizer m-tetra(hydroxyphenyl)chlorine (m-THPC) as a partially approved drug for photodynamic cancer therapy. To assist the design of peptide-block-poly(ethylene oxide) copolymers, a fluorescence-based screening method was established. Solubilization capacity and release kinetics from the transport system proved to depend strongly on the peptide sequence of the peptide-PEO conjugates.


Sunday, September 8, 2013 05:10 PM
Biomacromolecules for Therapeutics and Diagnostics Delivery (01:30 PM - 05:50 PM)
Location: Hyatt Regency Indianapolis
Room: Studio One
Photodegradable gene delivery system for enhanced nuclear transport

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Polycation-based gene carriers, though promising as safer alternatives to viral gene carriers, have yet been limited in large part due to their poor transfection performance. Future design and development of better polycation gene carriers will be greatly facilitated by an improved understanding of the relationship between the polycation chemistry and performance mechanism. In particular, there exists a significant gap in our understanding of how the size and compactness of polycation carriers influence their delivery performances in overcoming the most important cellular-level transport barrier, i.e., nuclear entry. In order to study this problem, we developed a photo-degradable polymer DNA carrier that is degradable upon exposure to mild UV irradiation; this carrier allows us to control the precise location of the disintegration of the PEI/DNA polyplex particles within the intracellular environment. By using this photolytic DNA carrier, we found that the exact (timing and) location of the photo degradation (i.e., cytosol, nucleus or no degradation) significantly influence the nuclear localization and the gene transfection efficiencies of the polymer/DNA complexes; the degradation of the carrier molecules impacts not only the size characteristics of the associated polyplexes which directly influence their nuclear import properties, but also the capabilities of the polyplexes to protect (against endonucleases) and release (for polymerase transcription) DNA which both impact the final gene expression levels.
50 - Tempering radicals behavior in controlled radical polymerization

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Many advanced nanostructured functional materials have been recently designed and prepared by controlled/ living radical polymerization (CRP). More than 100 million tons of polymers are produced annually world-wide by conventional radical polymerization (i.e., ~ 20 kg per capita!). However, macromolecular engineering is impossible in this process, because radicals are very reactive intermediates and their lifetime is less than a second. In order to tame or temper this uncontrolled radical behavior, was introduced a new concept of extending life of propagating chains from ca. 1 second to more than 1 day, by inserting a dormant period of ~ 1 minute after each ~ 1 ms activity. Thus, the 1 second of radical activity is expanded, as in an accordion, to several hours with thousands intermediate dormancy periods. This would be like extending person's life from 70 years to 2000 years, if after each 1 day of activity one could be dormant for 1 month. Various synthetic methods as well as materials prepared using this concept will be presented.
Elemental sulfur is currently produced as a major byproduct from hydrodesulfurization processes in petroleum refining. However, due to the limited usages of sulfur, an enormous excess of sulfur is generated annually (over 6 million tons) and simply stored as outdoor, exposed deposits in either brick, or powder form. Because newer fossil fuels reservoirs, such as, the tar sand regions in Alberta, Canada, contain a high content of sulfurous substances, elemental sulfur will likely be continually generated via hydrodesulfurization processes, ensuring sustainable access to this material as a novel feedstock for chemicals and materials. We will present our recent work on the direct polymerization of sulfur with conventional vinylic monomers via free radical processes to prepare a novel class of sulfur-rich copolymer materials. The synthesis and characterization of these polymers will be discussed.
52 - Using structurally dynamic polymers to access stimuli-responsive materials

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Structurally dynamic polymers have dynamic (reversible/equilibrium) bonds, which can be either covalent or non-covalent in nature, incorporated within their architecture and as such exhibit the ability to reorganize their components in response to a stimulus. Thus these materials are inherently responsive to any stimulus that disrupts the dynamic bond and allows one to control the nature of stimulus the material will respond to through judicious choice of the dynamic bond incorporated into the polymer structure. We have been interested in the potential of such systems to access new material platforms and have developed a range of new mechanically stable, structurally dynamic polymer films that exhibit properties that range from chemical sensing to shape memory and photo-healing. Our latest results in this area will be discussed.
Soft materials, such as polymers, colloids, surfactants, and liquid crystals, are a technologically important class of matter employed in a variety of applications. One sub-class of soft material, block copolymers, provides the opportunity to design materials with attractive chemical and mechanical properties based on the ability to assemble into periodic structures with nanoscale domain spacings. Several applications for block copolymers currently under investigation in my group include battery and fuel cell membranes, analytical separations membranes, nano-tool templates, precursors to electronic arrays, and drug delivery vehicles. One area of recent progress in the group focuses on the behavior of conventional block copolymer and tapered block copolymer systems for separation membrane and lithium battery membrane applications. We find that we can tune poly(styrene-b-ethylene oxide) diblock copolymer nanostructures by adjusting the lithium counterion and lithium salt concentration, as well as the taper volume fraction and composition. Additionally, we can estimate the effective interaction parameters ($c_{eff}$) for the salt-doped copolymers to determine the overall influence of tapering on the energetics of copolymer assembly. These tapered materials allow us to design nanostructured membrane systems, possibly containing nanoscale networks, with increased conductivity and improved mechanical properties for ion transport and separation devices.

Examples of possible nanoscale networks in ion-conducting systems generated from tapered block copolymers. Transmission electron microscopy (TEM) images are stained to improve contrast.
Andrew P Dove, a.p.dove@warwick.ac.uk, Department of Chemistry, University of Warwick, Coventry, United Kingdom

Aliphatic poly(carbonate)s and poly(ester)s are excellent candidates for biomedical applications as a consequence of their low toxicity, biocompatibility and biodegradability. Tailoring of the polymer structure by manipulation of pendant functionality on the polymer backbone enables precise control over the physical properties of the polymer or the addition of biologically active molecules. Recent advances in the synthesis and ring-opening polymerization (ROP) of cyclic carbonate and ester monomers has enabled a wide range of materials to be accessed and consequently provides an attractive and versatile methodology for the synthesis of functionalized degradable polymers that can be studied for applications in a wide range of areas.
Polymerized ionic liquids (PILs) are unique polyelectrolytes with cationic and anionic groups included in the repeating unit. They are extremely attractive in the field of materials science as they combine the properties of ionic liquids (high ionic conductivity, thermal and chemical stabilities) with those of polymers (mechanical stability, processing and tunable macromolecular design). Many examples have demonstrated their potential in applications such as dye sensitized solar cells, fuel cells, batteries, permselective membranes for CO₂ recovery or catalysis. In all these applications, imidazolium-based PILs are by far the most widespread and investigated materials. Since the striking development of the copper-catalyzed azide-alkyne cycloaddition (CuAAC) modular ligation, a large variety of materials containing 1,2,3-triazole groups have been reported. However, applications of 1,2,3-triazoliums as anion recognition structures, organocatalysts, metal ligands and precursors of N-heterocyclic carbenes has only been explored lately. We have recently pioneered the synthesis of 1,2,3-triazolium-based PILs. The tuning of structural parameters has a tremendous effect on ionic conductivity and thermal stability, crucial properties in most applications of PILs. The first generation TPILs not only demonstrates ionic conduction similar to that of PILs with comparable structure, pendant substituent and anion, but their synthesis also benefits from the robust and orthogonal nature of CuAAC. This oral communication is an attempt to demonstrate the potential of 1,2,3-triazolium chemistry to tackle new synthetic challenges using unexplored approaches competent to broaden the current structural variety of PILs.
56 - Hierarchical assembly with functional block copolymers

Ian Manners, ian.manners@bristol.ac.uk, Chemistry, University of Bristol, Bristol, United Kingdom

This talk will focus on recent work in our group and with collaborators on the self-assembly of functional metal-containing and pi-conjugated organic block copolymers in thin films or in solution to yield hierarchical structures.

Monday, September 9, 2013 11:30 AM
Mark Scholars Young Award: Symposium in Honor of Rachel O'Reilly (08:10 AM - 12:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
57 - New methods for polymer and nanostructure functionalization and labeling

Rachel K O'Reilly, R.K.O-REILLY@WARWICK.AC.UK, University of Warwick, Coventry, United Kingdom

There has been much recent interest in the use of core-shell polymeric nanoparticles as contrast agents and in-cell delivery platforms in nanomedicine. Common issues with conventionally labeled systems, in application, include the inability to readily observe how incubated molecules interact with the host and often no conclusive way to track particle degradation in vitro as it occurs. Another problem arising from encapsulation is decreased emission from loaded contrast agents, either through probe-polymer interactions or probe-probe self-quenching events. Furthermore, it is known that incorporation of an emissive handle, often a large hydrophobic molecule, can lead to changes in scaffold size, stability and even encapsulation potential due to surface modification effects. One solution to these particular difficulties is the formation of a reporter group system which can be readily incorporated into the polymeric scaffold and used as an emissive reporter with a non-ambiguous location in the nanostructure.

To address this challenge we report the development of a thiol-maleimide functional group as a highly emissive functionality which can readily be incorporated into polymeric scaffolds in a facile manner. A key advantage of this new reporter group is its versatile chemistry and its notably small size, which allows for ready incorporation without affecting or disrupting the self-assembly process critical to the formation of core-shell polymeric contrast and drug delivery agents. We demonstrate the potential of this functionality through incorporation into a diblock system which has been shown to be appropriate for micellization and, when in the micellar state, does not self-quench.

[Figure 1]
Sequence-specific co-, ter-, and block polymers by ROMP

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Ring-opening metathesis polymerization (ROMP) is a powerful method for the preparation of polymers with controlled structure and functionality. In the case of cyclooctene, many substituted variants have been prepared and subjected to ROMP conditions to give the corresponding functionalized polyalkenamers with substituents placed along the backbone every eighth carbon on average. In nearly all the examples reported to date, relatively low degrees of stereo- and regioselectivity have been observed. We recently discovered that ROMP of 3-substituted cyclooctenes gives rise to polymer structures that exhibit very high degrees uniformity with respect to the geometry of the olefin in the backbone and the placement of substituent along the backbone. For example, the ROMP 3-phenyl cyclooctene using a ruthenium-based metathesis catalyst gives greater than 98% trans double bonds and greater than 99% head-to-tail regiochemistry. In this presentation, the utility of the ROMP of 3-substituted cyclooctenes for the preparation of such sequence specific co-, ter-, and block polymers will be presented. One ultimate goal of the work is to prepare sequence specific quarterpolymers by the ROMP of tetrasubstituted cyclooctenes as shown below.
Control of position and numbers of reactive functional groups in a structurally well-defined polymer has been a significant challenge, because such polymers would be useful for the fabrication of functional polymer materials with enhanced or new properties. We report here a synthesis of mid-chain functionalized polymers with controlled number average molecular weight and low molecular weight distribution by the photo-induced radical coupling reaction of polymers prepared by organotellurium-mediated living radical polymerization (TERP) in the presence of dienes.\textsuperscript{1} Since the number of the diene unit inserted in between two polymer chains was controlled, the number of functional groups at the mid-chain was also controlled by using functional dienes.

60 - Controlling monomer sequence distribution in living anionic (co)polymerization

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Natural polymers such as nucleic acids and proteins are the blueprint of the living world with repeat unit sequences perfectly reproduced from molecule to molecule. It is this absolute control over the specificity of monomer sub-units that directs the secondary and tertiary structure and, in turn, form and function. However, sequence control in synthetic polymers is a subject that has until recently been almost totally neglected. Some progress has been made in the synthesis of short copolymer sequences prepared via complex and time consuming processes involving protection/condensation/deprotection chemistry but little research has been carried out in the field of sequence-controlled chain growth polymerization. One method of controlling monomer sequence distribution is through kinetic control arising from differential monomer reactivity. We present herein a series of anionic copolymerisations using diphenylethylene (DPE) and its derivatives which enable the synthesis of perfect alternating copolymers (see MALDI analysis), sequence controlled terpolymers and telechelic polymers.
The alternating copolymerization of two monomers can be attained either by the same mechanism for each monomer with an alternating preference or by the alternating repetition of two mechanistically distinct transformations.

. Here in this presentation, we present our latest achievements operated by each mechanism; namely, (i) the Pd-catalyzed alternating copolymerization of polar vinyl monomers with carbon monoxide and (ii) the ping-pong polymerization by allylation and hydroformylation.
Recently, we have found a new class of step-growth radical polymerization of the designed monomer bearing a reactive carbon–halogen bond and an unconjugated carbon–carbon double bond in a single molecule, which is based on atom transfer radical addition similarly to controlled/living radical polymerization.

In this paper, the step-growth radical polymerization was evolved into the systems for sequence-regulated vinyl polymer synthesis or simultaneous chain- and step-growth radical polymerization. The former is a novel strategy for preparing sequence-regulated vinyl copolymers by step-growth polymerization of sequence-regulated vinyl oligomers prepared from common vinyl monomers as building blocks, such as styrene, acrylate, acrylamide, acrylonitrile, and vinyl chloride. In the later part, the simultaneous chain- and step-growth polymerization was investigated via the copolymerization of step-growth monomers with conjugated vinyl monomers, i.e., the step-polymerization was simultaneously compatibilized with the metal-catalyzed atom transfer radical polymerization. The combined polymerization resulted in the polymers with periodic functional moieties.
The synthesis and characterization of alternating copolymers from co-monomer complexes of styrene (St) and 2, 3, 4, 5, 6-pentafluorostyrene (FSt) is described. Proton NMR experiments demonstrate the formation of complexes in bulk St/FSt mixtures even at relatively high molar ratios ($K_{\text{complex}}=0.2 \pm 0.1$). Reactivity ratio studies indicate that these complexes contribute to the 1:1 consumption of monomers and ultimate alternating structure as shown by kinetics and hetero-nuclear multiple bond correlation (HMBC) NMR spectroscopy respectively. The addition of solvent can disrupt these complexes; providing a variable by which the polymer structure can be fine-tuned to include gradient polymer structures. This approach to sequence controlled polymerization is extended to include functional monomers (eg. 4-azidomethyl styrene), which allow for post-polymerization orthogonal modification. Previous work in our group has focused on the “click” functionalization of hyperbranched polymers. The current study adopts this approach as an important access point to a library of well-defined and versatile linear polymer-supported organo-catalysts.
64 - Sequence-regulated polymers by multicomponent polymerization based on Passerini reaction

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Inspired by the unique structure and functions of biomacromolecules like proteins and nucleic acids, polymer chemists have long been dreaming in developing simple synthetic methods to create polymers with controlled microstructures. One direction is to synthesize copolymers with ordered backbone or side group sequences. Passerini reaction, a three component reaction first described in 1921, has been proved to be a powerful synthetic method that can yield an ester-amide linkage from a carboxylic acid, an aldehyde and an isocyanide.

Based on this reaction, we developed a facile multicomponent polymerization method to synthesize copolymers with both main chain sequence and ordered side group sequence.

Monday, September 9, 2013 11:25 AM
Sequence-Controlled Polymers (08:30 AM - 11:50 AM)
Location: Hyatt Regency Indianapolis
Room: Regency F
65 - Rational design of macromolecular therapeutics

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The design principles of water-soluble polymer - drug conjugates based on a solid biological rationale will be discussed. Two new approaches will be presented – the design of backbone degradable N-(2-hydroxypropyl)methacrylamide (HPMA) copolymers and the design of drug-free macromolecular therapeutics.

To endow biodegradability to polyHPMA, a RAFT chain transfer agent containing an enzyme cleavable GFLG spacer was utilized to produce homo- and hetero- telechelic copolymers via RAFT polymerization. Multiblock copolymers were generated by connecting synthetic polymer chains via tetrapeptide bridges through “click” reactions. Conjugates of anticancer drugs with multiblock copolymers possess enhanced therapeutic efficacy.

Two biorecognition motifs, complementary peptides and complementary morpholino oligonucleotides were designed. The unique biorecognition of these motifs at the cellular surface was able to control apoptosis. Exposure of Raji B cells to anti-CD20 Fab'-CCE or Fab'-MORF1 conjugate decorated the cell surface with CCE or MORF1 (CD20 is a non-internalizing receptor) through antigen-antibody fragment recognition. Further exposure of the decorated cells to P-(CCK)x (P is the copolymer backbone grafted with multiple copies of CCK) or P-(MORF2)x resulted in the formation of CCE/CCK or MORF1/MORF2 heterodimers at the cell surface. This second biorecognition induced the crosslinking of CD20 receptors and triggered the apoptosis of Raji B cells in vitro and in a Non-Hodgkin lymphoma animal model in vivo. This is a new concept, where the biological activity of drug-free macromolecular therapeutics is based on the biorecognition of complementary motifs.
Polymer based conjugation of therapeutics, both small molecule and biologics, is a well-established concept with many products on the market. In these products, the polymer delivery vehicle of choice is predominantly PEG (polyethylene glycol) and its structural derivatives.

A number of recent reports suggest that PEG is demonstrating clinical limitations (immunogenic response, degradation, tissue accumulation) and some commercial limitations (most notably a crowded IP space).

This talk will demonstrate the use of RAFT polymer based therapeutic delivery as a viable alternative to the use of PEG. The use of RAFT to generate new polymer systems with structural, functional and compositional variations will be demonstrated and the influence of polymer structure and composition on biological performance will be evaluated.
67 - Polypeptide and polysaccharide based polymersomes for therapy and diagnosis

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We report an overview on the self-assembly in water of amphiphilic block copolymers into polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules. We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles that we have studied these recent years in our group. These newly developed copolymers that mimic the structure and function of glycoproteins represent an example of the effectiveness of a biomimetic strategy in implementing materials design. In addition, magnetic polymersomes, including iron oxide γ-Fe₂O₃ nanoparticles are currently investigated, together with their potential applications as contrast agent for imaging and as therapeutic nanoparticles using hyperthermia. Exciting and very promising results about their therapeutic evaluation for tumor targeting and in vivo tumor regression studies will be presented.
68 - Boronic acid block copolymers: Sugar-responsive materials for drug delivery

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Block copolymers of a hydrophilic monomer with either 3-acrylamidophenylboronic acid or 4-vinylphenylboronic acid) were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization. The resulting well-defined block copolymers demonstrated interesting solution behavior in water and were capable of forming aggregates that could be induced to dissociate in the presence of high concentrations of sugars. Replacing the hydrophilic block with a block of poly(N-isopropylacrylamide) led to triply-responsive block copolymers with the ability to form micelles or reverse micelles depending on the environmental conditions. The kinetics and concentration of glucose needed for disassembly have been investigated by a combination of turbidity measurements, light scattering experiments, and fluorescence spectroscopy.
69 - WITHDRAWN
70 - Polysaccharide-based nanogels: Facile synthesis and potential applications as versatile biomedical nanocarriers

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In this study, various of polysaccharide-based nanogels were synthesized facilely from several polysaccharides and different monomers by using a self-assembly assisted approach. Cytotoxicity study confirmed the low cytotoxicity of these nanogels to various of cells, which indicated their promising applications in cell imaging and drug delivery. Our study disclosed potential applications of the nanogels in these biomedical fields. For example, in order to utilize these nanogels in cell imaging, several kinds of fluorescence dyes were conjugated to one typical polysaccharide-based nanogel, dextran-based nanogel, to produce fluorescent nanogels. Through adjusting the ratio of reactants, the fluorescent nanogels with various sizes ranged from 60 to 500 nm were fabricated. Furthermore, surface modification of the nanogels were realized to prepare polysaccharide-based fluorescent nanogels with different surface charges. Fluorescent nanogels with various sizes and different surface charges were then co-incubated with phagocytic cells and non-phagocytic cells. Our study confirmed the feasibility of the fluorescent nanogels working as cell imaging probes. In addition, the size and surface charge of nanogels affected greatly the labeling efficiency. Besides working as cell imaging nanoprobe, the polysaccharide-based nanogels were confirmed excellent carriers for anti-cancer drug. A typical example is the successful conjugation of Doxorubicin (DOX) to dextran-based nanogels through pH-labile hydrazone bond. After capping Folic acid (FA) onto the DOX carried nanogels, the resultant composite nanogels exhibited capability of delivering DOX into the nucleus of HeLa cells.

Figure1. Synthesis, modification and applications of polysaccharide-based nanogels
71 - Preparation and characterization of fluorescent hyperbranched poly(amido acid)s-encapsulated iron-oxide nanoparticle hybrids

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In this study we used self-condensation of an AB\textsubscript{2} monomer to prepare fluorescent hyperbranched poly(amido acid)s (HBPAAs) featuring wholly aliphatic backbones, multiple terminal CO\textsubscript{2}H units, and many internal tertiary amino and amido moieties. We prepared the AB\textsubscript{2} monomer through an efficient synthetic scheme, involving blocking and deblocking processes, in 81\% yield. Subsequently, we synthesized a series of water-soluble HBPAAs with molecular weights ranging from 2400 to 10,100 g mol\textsuperscript{-1}. The strong blue fluorescence emissions (at 395 nm) of the CO\textsubscript{2}H-terminated HBPAAs in aqueous media were influenced by the pH of the solution. The fluorescence quantum yields reached as high as 23\% when the branching tertiary amino moieties were confined within a self-polymerized globular environment. Moreover, magnetic Fe\textsubscript{3}O\textsubscript{4} nanoparticles incorporated into the globular HBPAAs were synthesized by \textit{in situ} Fe\textsuperscript{2+}/Fe\textsuperscript{3+} coprecipitation process. These blue fluorescent emission from water-soluble HBPAAs, through pH-induced behavior, provides the way toward tracking nanocarriers and molecular-level containers, might opening up opportunities for globular macromolecules in probing intercellular interactions.
Reliability of aerospace structures is among the key metrics of their performance. It is usually based on probabilistic understanding with very tight requirements, e.g., failure probability in many applications is well below one in a million. In aerospace structures, polymers are primarily used as components of polymer-matrix matrix composites (PMC), and therefore, their statistical variability can play significant role in reliability. Thus, the objective of this work is to summarize major issues controlling correlations between statistical variability of polymers and PMC structural reliability, explain their physical rational, and provide algorithms for corresponding quantitative assessments. In addition to material variability, inevitable imperfections of PMC structural designs are considered. Representative cases from recent and current work are discussed to illustrate the effect of polymeric variability and imperfections. An example of random imperfections and voids in thick composite component is shown in the figure. Finally, opportunities to optimize reliability through more focused development of polymers are discussed as well.
Use of lightweight advanced composites in place of conventional composites and other aerospace materials can enable significant reductions in vehicle weight. These weight reductions can translate into reduced fuel consumption and emissions for aircraft and increased payload and reduced launch costs for spacecraft. Recent advances in the development of carbon nanotube structural materials, such as sheets, yarns and fibers, suggest that it is possible to develop advanced composites from these reinforcements that have aerial densities as much as 40% lower than conventional carbon fiber reinforced composites. NASA researchers are currently working on the development of high strength reinforcements from carbon nanotubes and their application in advanced, lightweight composites. This presentation will provide an overview of this project and discuss recent results.
74 - Investigation of functionalized carbon nanofillers and polymer matrix interfacial interactions on thermal conductivity

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Criteria for aerospace materials are extremely demanding and typically require high strength, low weight and additional functionality such as thermal conductivity, electrical conductivity, electromagnetic interference (EMI) shielding, and/or high operating temperature capability. For polymeric materials, these criteria can only be met in the form of composites. The work presented in this talk will investigate several fundamental parameters that dictate thermal conductivity for polymer nanocomposite systems. Multi-wall carbon nanotubes (MWCNTs) were chosen as a model filler based on availability of various surface functionalities and aspect ratios. The fillers were also chosen for their potential EMI shielding and electrical conductivity properties which will be addressed in future work. While these systems are under thorough examination currently by many investigators, our specific interest is to understand the interfacial interactions between the filler particle and matrix to enable optimization of thermal conductivity and other properties through manipulation of that interface. The goal is to understand how to design a particle/matrix interface with minimal interfacial and contact resistance via changes in surface chemistry and particle/matrix interactions. Once the interfacial interactions are established, processing techniques can be implemented to optimize dispersion, orientation and interparticle spacing. Our study of the particle matrix interfacial thermal resistance and composite morphology design will be driven by molecular dynamics simulations and scrutinized by empirical characterization of MWCNT filled polymeric systems.
In this presentation, an overview will be presented of recent research into sustainable composites, with specific focus given to the automotive sector. Cellulose Nanocrystals (CNCs) and Cellulose Nanofibrils (CNF) are attractive materials for possible applications in nanocomposites reinforcement, nanomaterials and biomedicine as they have high strength and stiffness, yet are renewable, biodegradable, non-toxic, cheap, and optically transparent. Here, we will detail efforts to utilize these materials in composites, both as nanoreinforcements and as a neat material for both structural materials and consumer applications with discussion of the resultant mechanical and thermal properties. Thus, we provide new elements to understand the interconnection among preparation variables towards an optimal CNC or CNF materials design. Additionally, the overview will detail recent efforts at sustainable resins for structural composites in an effort to “green” high embodied carbon composite materials that are necessary for lightweighting efforts in vehicles.
76 - Carbon nanotube nanocomposites with POSS dispersants for enhanced performance

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Covalent attachment of Polyhedral Oligomeric Silsesquioxane (POSS) to the surface of multi-walled carbon nanotubes (CNT) can increase CNT dispersion in solution and in polymer matrices. While covalently attached dispersants generally provide a greater degree of dispersion than physically adsorbed dispersants, they degrade the CNT properties. The effects of POSS structure, functionality and the length of the tether to the CNT surface on CNT dispersion were evaluated, and compared to the dispersion achieved with non-covalently attached POSS dispersants. Mechanical, thermal and electrical properties of the nanocomposites will be discussed.
Covalent crosslinking of carbon nanotube materials for improved tensile strength

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Carbon nanotubes have attracted much interest in recent years due to their exceptional mechanical properties. The tensile properties of the currently available bulk carbon nanotube-based materials (yarns, sheets, etc.) fall far short of those of the individual nanotubes due to inter-tube sliding.

Our group is examining covalent crosslinking between the nanotubes as a means to increase the tensile properties of carbon nanotube materials. We are working with multi-walled carbon nanotube (MWCNT) sheet and yarn materials obtained from commercial sources. Several routes to functionalize and crosslink the nanotubes have been examined including nitrene, aryl diazonium, and epoxide chemistries. Electron beam irradiation induced crosslinking of the non-functional and functional nanotube materials was also conducted.

For example, a nanotube sheet material containing approximately 3.5 mol % amine functional groups exhibited a tensile strength of 75 MPa and a tensile modulus of 1.16 GPa, compared to 49 MPa and 0.57 GPa, respectively, for the as-received material. Electron beam irradiation (2.2x 10^{17} e/cm^2) of the same amine-functional sheet material further increased the tensile strength to 120 MPa and the modulus to 2.61 GPa. This represents approximately a 150% increase in tensile strength and a 360% increase in tensile modulus over the as-received material with only a 25% increase in material mass.
Cellulose nanocrystals (CNCs) have attracted attention in recent years as potential green reinforcing fillers for polymer nanocomposites. A key aspect of these materials are the interactions between the CNC and matrix polymer and as well as between the CNCs themselves. We have recently shown that sulfonated CNCs (from a range of different biosources such as tunicates, cotton and microcrystalline cellulose) embedded within a variety of polymer matrices (including poly(vinyl acetate), polyacrylates, poly(ethylene oxide-co-epichlorohydrin), polybutadiene, styrene-butadiene rubber and polyurethane) show mechanical switching upon exposure to water. It is proposed that in the dry state hydrogen bonding interactions between adjacent CNCs play a role in this reinforcing network, transferring mechanical stresses across the sample, and resulting in stiff materials (see figure).

Once the water diffuses into the nanocomposite, it competitively hydrogen bonds to the CNC surfaces disrupting the stress-bearing CNC scaffold and softening the nanocomposite (Figure). We are currently investigating these mechanically-adaptable nanocomposites as the basis of biocompatible intracortical electrodes, which are stiff to allow facile insertion into the brain and soften after implantation to minimize the bioresponse. This presentation will focus on our latest results on the systems.
Ultra dense perfectly ordered structures with nanometric periodicity are of crucial importance for applications such as microelectronics or data storage media. Herein we demonstrate the use of a polymeric guiding pattern to control the self-assembly of block copolymers into highly-ordered 2D arrays. For this, a sinusoidal surface-relief grating was interferometrically inscribed onto an azobenzene containing copolymer sub-layer (1). A poly(styrene-b-ethylene oxide), PS-b-PEO, film was cast on top, resulting in cylinders with a 6-fold coordination. When film thickness reaches a critical value where the PS-b-PEO free-surface is smooth and no hint of the underlying sinusoidal pattern is apparent, a defect-free 2D-array of PS-b-PEO cylinders is observed over a large surface. Our results show that the surface deformation induced by the topological pattern controls the diffusion of defects and consequently their annihilation.

80 - Vitrimers: A new class of polymer materials

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Solid at low temperatures and malleable when heated yet insoluble whatever the temperature, vitrimers constitute the third – new - class of polymers along with thermoplastics and thermosets (elastomers).\(^1\) Vitrimers are polymer networks that are able to change their topology without changing the total number of bonds through thermo-activated catalytically controlled exchange reactions such as trans-esterification.\(^1,2\) They exhibit two glass transitions: the usual one, at lower temperature, \(T_g\), by quenching of segmental motions, and the vitrimer transition, at \(T_v\), due to network topology quenching. In striking contrast to all organic and polymer glass forming liquids that increase their viscosity and rigidify abruptly when cooled and are soluble during cooling, vitrimers increase their viscosity over a wide temperature range following a simple Arrhenius law. They behave just like silica, the archetype strong glass-former. I will present the concept and results of phase diagram and dynamics studies. Besides opening intriguing perspectives in both physics and chemistry, vitrimers should rapidly find applications in automotive, electronics, airplane, and coatings industries.


81 - Reversible magnetic memory switch from liquid-crystalline elastomer nanocomposites

Raffaele Mezzenga, raffaele.mezzenga@agrl.ethz.ch, Department of Health Sciences and Technology, Swiss Federal Institute of Technology Zurich, Zurich, Switzerland

Switchable magnetic information found in some inorganic materials is the fingerprint of countless technological applications, but poor control over processability and magnetic anisotropicity imposes severe restrictions, calling for advanced techniques. In this talk I will present a new class of stimuli-responsive materials, which combines the actuation potential of liquid-crystalline elastomers (LCE) with the anisotropic magnetic properties of ellipsoidal iron-oxide nanoparticles. The resulting hybrid nanocomposites exhibit unique shape-memory features allowing via simple low-stress deformation the reversible storage of magnetic information, which can be erased at low temperature by heating above the LCE smectic-isotropic transition. To illustrate the applicability of this concept, it will be shown how the magnetic information can be read, for example, by magnetic torque measurements. These new nanocomposites offer the unprecedented possibility of manipulating magnetic properties at control parameters, such as deformation, stress and resetting temperatures, typical of soft materials, opening up new scenarios in micro-actuators, magnetic storage devices, sensors or artificial muscles applications.

Some of the unique advantages of the use of electrostatic assembly methods to generate drug release systems include the ability to introduce unusually high loadings of biologic drugs, and the ability to incorporate multiple drugs that can be released with exquisite control to achieve unique co- and sequential release profiles from surfaces. New methods of achieving controlled and highly effective mediation of wound healing will be addressed, including the unique release of siRNA and growth factors into chronic wounds, and the use of these systems for the healing of large bone segmental defects as well as the integration of bone on biomedical implants. Finally, new approaches to the release of DNA, antigen, and adjuvants into the skin dermis layer from the surfaces of microneedles demonstrates that the gradual and controlled release of small amounts of DNA can lead significantly enhanced immune responses for vaccine delivery which can significantly outperform other forms of DNA vaccines such as electroporation and intradermal injection. In these examples, the effect of rate of release and the nature of delivery from these unique platforms will be discussed.
Supramolecular polymer chemistry, the science of polymers that are held together and/or functionalized using noncovalent interactions such as hydrogen bonding and metal coordination, has revolutionized polymer science. The field of supramolecular polymer chemistry can be divided into two main areas: side-chain and main-chain supramolecular polymers. Both, classes of materials require polymerization methods that are highly controlled or living, i.e. allow for easy synthesis of multifunctional side-chain copolymers containing a large number of functional groups along their side-chains as well as allow for the controlled incorporation of functional handles at the chain ends of homo- and copolymers. The presentation will focus on design principles of supramolecular copolymers as well as their use for a variety of applications including colloidal assemblies, surface functionalization strategies, and polymer-based foldamers.
A shortage of available organ donors has created a need for engineered tissues. Through combinations of scaffolds, biochemical factors and cells, engineered constructs resembling natural tissue are created. Polymer-based hydrogels that break down inside the body are often employed as scaffold materials, and many different click chemistries have been utilized for this purpose. In this presentation, gels formed by oxime and hydrazone chemistries will be discussed. Both are highly efficient reactions, and the latter is readily reversible. The reversibility of hydrazone bonds allows the gel to reform when the bonds are cut and then brought together (i.e. to self heal). The synthesis of poly(ethylene glycol) based systems, formation of gels, mechanical properties, and kinetics will be discussed. Incorporation of cell binding factors and enzyme cleavable cross-linkers, and viability of mesenchymal stem cells within the hydrogels will be presented.

Monday, September 9, 2013 04:30 PM
2013 Biomacromolecules/Macromolecules Young Investigator Award (01:30 PM - 05:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
85 - Design of stable, unstable, and reactive biointerfaces: A "multilayered" approach

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We are interested in the design of functional polymers, macromolecular assemblies, and surfaces/interfaces that address problems of biotechnological and biomedical importance. The first part of this presentation will describe work on the design of degradable polymer multilayers as coatings for the surface-mediated delivery of bioactive agents, with a focus on (i) fundamental aspects of design and characterization, and (ii) the design of 'multilayered' coatings that promote local transfer of therapeutic DNA and affect beneficial physiological responses in vivo. These approaches make use of conventional approaches to layer-by-layer assembly that exploit weak interactions between polyelectrolytes. We have also developed methods for the 'reactive' assembly of polymer multilayers that exploit fast reactions between mutually reactive polymers and, thus, lead to surface coatings that are covalently crosslinked. The second part of this presentation will describe the design of azlactone-functionalized multilayers as physically stable but chemically reactive platforms for the fabrication and selective functionalization of biointerfaces for applications in controlled release, the control of cell/substrate interactions, and the design of patterned superhydrophobic surfaces of potential utility in new biotechnological contexts.
Precise sequence control in linear and cyclic copolymers of 2,5-bis(2-thienyl)pyrrole and aniline by DNA-programmed assembly

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Linear and cyclic sequence controlled, DNA-conjoined copolymers of aniline (ANi) and 2,5-bis(2-thienyl)pyrrole (SNS) were synthesized. Linear (SNS)₄(ANi)₆ and (ANi)₂(SNS)₂(ANi)₂(SNS)₂(ANi)₂ were prepared from complementary DNA oligomers containing covalently attached SNS and ANi monomers. Hybridization of the oligomers aligns the monomers in the major groove of the DNA. Treatment of the SNS and ANi-containing duplexes with horseradish peroxidase (HRP) and H₂O₂ causes rapid and efficient polymerization. Linear and cyclic copolymers of ANi and SNS were prepared by a DNA encoded module strategy. In this approach, single stranded DNA oligomers comprised of a central region containing (SNS)₆ or (ANi)₅ covalently attached monomer blocks and flanking 5’- and 3’- single strand DNA recognition sequences were combined in buffer solution. Self-assembly of these oligomers by Watson-Crick base pairing of the recognition sequences creates linear or cyclic arrays of SNS and ANi monomer blocks. Treatment of these arrays with HRP/H₂O₂ causes rapid and efficient polymerization to form copolymers having patterns such as cyclic BBA and linear ABA, where B stands for an (SNS)₆ block and A stands for an (ANi)₅ block.

Illustration of the “encoded module” strategy for DNA-templated alignment of SNS and ANi monomers in cyclic and linear arrays. The single-strand DNA recognition sequences are shown as color-coded wavy lines that indicate their affinity with complementary modules and ability to form duplex segments by Watson/Crick recognition. Red spheres represent SNS and blue spheres represent ANi monomers, respectively. B represents an (SNS)₆ block and A represents an (ANi)₅ block.
Under eons of evolutionary and environmental pressure, biological systems have evolved many strong and lightweight polymeric materials with advanced properties. These materials often outperform their man-made counterparts in terms of multifunctionality/tenability as well as adaptability/stimuli-responsiveness. Modularity is ubiquitous in natural protein-based structural materials. This modularity aids the “controlled complexity” of bottom-up construction and hierarchical self-organization across multiple length-scales, ultimately yielding the required advanced mechanical properties, so-called “collective emergent properties”, which dramatically exceed the summed mechanical properties of their individual constituents. The modular design also provides an elegant strategy to combine sequence specificity and synthetic efficiency: while the modules contain precise structural information and programmed properties, polymerization of the modules quickly generates high polymers in an efficient manner. Inspired by Nature, my laboratory has designed and synthesized a series of man-made modular polymers. In this talk, I will discuss three families of modular polymers developed in our lab that are inspired by muscle protein titin, elastic and silk, respectively. Importantly, those synthetic modular polymers not only closely mimics the modularity of their biological counterparts, but also manifests an exciting combination of mechanical properties, including high strength, toughness, adaptive and dynamic properties such as self-healing and shape-memory properties.
88 - Peptide-polymer conjugates as model systems to explore the functional space of precision polymers

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The challenges to establish synthesis routes toward monomer sequence controlled macromolecules require tremendous efforts, but precision polymers promise high gain for functional polymers. The polymer class of oligopeptides [1] offers an established platform, which can be already exploited to explore the functional space available for monodisperse, sequence-defined macromolecules [2] and thus, demonstrate potentials of fully synthetic precision polymers. Here we summarize the recent advances, realizing sequence specific coatings of inorganic particles,[3] enzyme activatable glues [4] or specific drug solubilizers [5].

89 - Elastin-based amphiphilic copolymers as precision building blocks for controlled self-assembly

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Protein-engineering techniques are powerful alternatives to traditional chemical polymerization methods to synthesize monodisperse polymers, as they offer exquisite control over molecular weight, sequence, architecture and functionality. Due to their intrinsic biocompatibility, these systems are highly attractive alternatives to traditional synthetic polymers for biomedical applications, especially drug-delivery where most recombinant polymers are based on the pentapeptide repeat [-Val-Pro-Gly-Val-Gly-] derived from the elastomeric domain of elastin. An essential property of elastin-based sequences is their temperature-triggered phase transition (LCST or Tt). This behavior has been exploited to create temperature-triggered self-assembly of protein block copolymers. Raising the solution temperature can selectively desolvate one block and drive the self-assembly above a critical micellization temperature (CMT) into micellar structures. Self-assembly can be controlled with hydrophilic-to-hydrophobic block ratio, copolymer MW, and distribution of polar and apolar regions along the polymer chain. We have recently designed a series of recombinant amphiphilic diblock copolymers wherein the hydrophobic block (Tt<45°C) contains multiple repeats of hydrophobic (VPGVG) motifs and the hydrophilic block with a higher transition temperature (Tt>60°C) contains repeats of 30 or 60 (VPGXG) motifs with where X is alanine or glycine at a 1:1 ratio. The hydrophilic mass fraction of the copolymer was tuned from 10 to 60%. Extensive analysis (DLS, SANS, TEM, AFM) of the self-assembly behavior of these diblock peptide polymers were performed and relationships between their chemical composition, sequence, and nanoscale structure will be discussed.
The most common strategy for ordered multistep synthesis is to divide the construction of the desired molecule into a sequence of isolated reaction steps, involving: addition of reagents, purification, isolation of intermediate products and the utilisation of protecting group chemistry. However, in nature similar objectives are achieved in a single solution by exquisitely selective catalysis and by increasing the effective molarity of specific reactants at precise moments during biosynthesis. This approach is not only remarkably elegant and efficient but also sufficiently selective to obviate the need for protecting groups.

It has been shown that DNA adapters linked to reactants can direct small-molecule chemical synthesis. If two reactants are linked to complementary oligonucleotide tags then hybridization of the tags ties them closely together, increasing the effective molarity with the potential to greatly increase the reaction rate. The rate enhancement can be sufficient to ensure that cross-reactions with other molecules present in the same vessel but not connected by DNA tags can be neglected. Sequential multistep syntheses have been controlled by the sequential addition of reagents followed by purification at each step, and by controlling stepwise changes in the secondary structure of the template DNA by progressively increasing the temperature.

We present a strategy for the synthesis of ordered oligomeric materials by means of sequential DNA-templated reactions, without the need for addition of reagents or the purification of intermediates. In principle this mechanism allows the synthesis of product of arbitrary length and also precise sequence.
91 - Interfacing DNA nanostructures with synthetic polymers and dendrimers

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The self-assembly of block copolymers into micellar structures has produced great advances in nanoscience, ranging from nanoelectronics to drug delivery. Structural control of polymer micelle morphology is currently achieved by adjusting the chemistry of the polymer chains in the different blocks, the polymer architecture and external environment, and growth of these self-assembled structures is generally isotropic. On the other hand, sequence controlled polymers such as DNA offer the possibility of total anisotropic spatial control. Strand sequences can be programmed to assemble into well-defined two- and three-dimensional structures of any size and shape.

This talk will focus on our group’s current efforts to position synthetic polymers and dendrimers on DNA cages and nanotubes. Using these hybrid cages, we will describe a new mode of protein-inspired interaction: When hydrophobic polymeric units are organized in a specific orientation on a DNA cube, the chains can engage in an intermolecular “handshake” across two cubes, resulting exclusively in a cube dimer. With a different orientation, these units can engage in a “handshake” inside the cube. This forms a monodisperse micelle within a DNA cage. This structure encapsulates small hydrophobic molecules, and releases them with added DNA strands of specific sequences. Thus, when polymeric chains are anisotropically organized on DNA scaffolds, new cooperative, directed interactions emerge. Applications of our structures as tools for conditional delivery of therapeutics inside cells will be discussed.
Smart” polymers that respond to stimuli in their aqueous environments with a pronounced physical change are of great utility in biotechnology and medicine. Currently, however, only few peptide polymers show this behavior. Here, we uncover the relationship between the syntax of peptide polymers and their lower critical solution temperature (LCST) transition behavior. I will show that this syntax ranges from polymers composed of simple repeats of a few amino acids to those whose syntax resembles the complex non-repetitive syntax of protein domains, and that the concept of syntax can be deployed to re-program bioactive peptides to exhibit dual functions, as seen by their stimulus responsiveness and biological activity. I will also describe a class of peptide polymers that show the reverse behavior as they separate from aqueous solution in response to a decrease –as opposed to an increase– in temperature below an upper critical solution temperature (UCST). The unique linguistic features exhibited by these peptide polymers suggests that peptide polymers can be best described as linear macromolecules that are composed of amino acid “letters” that are organized as “words”, with higher order organization of one or more words that repeat or recur to create a “phrase” (the macromolecule) and postulate that the syntax –word order– of this class of polymers controls their function. Hence, by analogy to syntax in natural language —defined as the arrangement of words in a phrase that controls its meaning, I will introduce new concept –syntactomers– to describe polymers whose properties are controlled by their organization as a collection of letters into words and the higher order organization of words into functional phrases.
93 - Sequence-specific peptides synthesis by an artificial small-molecule machine

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The ribosome is an enormous biological molecular machine that joins together amino acids derived from transfer RNA building blocks in an order determined by a messenger RNA strand, creating protein in a process known as translation. Here we report on the design, synthesis and operation of an artificial small-molecule machine that travels along a molecular strand, picking up amino acids that block its path, to synthesize a peptide in a sequence-specific manner. The chemical structure is based on a rotaxane, a molecular ring threaded onto a molecular axle. The ring carries a thiolate group that iteratively removes proteinogenic amino acids from the strand and transfers them to a peptide elongation site through native chemical ligation. The synthesis is demonstrated using $10^{18}$ molecular machines acting in parallel and generates milligram quantities of a peptide with a single sequence, determined by tandem mass spectrometry, corresponding to the original order of the amino acid building blocks on the strand.

94 - Monodisperse, sequence-defined homo- and heterofunctionalized glycooligomers and their multivalent binding modes

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Earlier we introduced a new approach towards monodisperse, sequence-controlled oligo- and polymers based on solid phase synthesis and the stepwise addition of tailor-made building blocks (SPPoS). Through the choice of building blocks applied in each step, we are able to precisely control the physicochemical properties of the macromolecule and tune from hydrophilic to hydrophobic, flexible to stiff, go from linear to branched chains or introduce chirality at different points in the polymer chain. Recently we expanded this approach towards the solid phase synthesis of multifunctional glycopolymers. Through this combination we are now able to control the number of sugar ligands attached to the polymer scaffold, their position on the scaffold as well as their distancing and to go from homomultivalent to heteromultivalent systems presenting different ligands at different positions.

Figure 1: Thiol-ene coupling of building blocks and oligomer precursors to obtain homo- and heteromultivalent glycopolymers

With this toolbox at hand, we look at the fundamental principles of multivalent binding and systematically evaluate the influence of different scaffold parameters using surface plasmon resonance (SPR), NMR and a novel affinity assay based on soft colloidal probe reflection interference microscopy (SCP RICM). This information is then applied for the design of glycomaterials for biomedical applications such as targeted gene delivery and anti-bacterial coatings.
Molecular conjugates and nanoparticles that target antigen and immunostimulatory adjuvant molecules from peripheral tissues through lymphatics to lymph nodes are of great interest for vaccine delivery. A clinical procedure where efficient lymph node targeting is achieved is sentinel lymph node mapping in cancer patients, where small-molecule dyes are efficiently delivered to lymph nodes by binding to endogenous serum albumin. To mimic this process for vaccine delivery, we synthesized well-defined polymeric amphiphiles with the general structure (lipid)-(polar block)-(cargo), where the lipid block controls interactions with serum proteins and the polar moiety controls self-assembly and solubility properties of the constructs. Mimicking sentinel node mapping dyes, the lipid blocks were designed to non-covalently bind vaccine antigens and adjuvants to endogenous albumin on injection. By varying the composition of the lipophilic tail and polar blocks of these amphiphiles, we defined the structural requirements for optimized lymph node targeting of peptide antigens and oligonucleotide adjuvants. These “albumin-hitchhiking” amphiphiles were efficiently captured in lymph nodes following injection, leading to impressively amplified cellular immune responses and anti-tumor immunity. This approaches provides a simple, generalizable strategy to enhance the delivery of vaccine components and other compounds to lymphoid organs.
96 - Single-step grafting of aminooxy-peptides to hyaluronan: A simple approach to multifunctional therapeutics for experimental autoimmune encephalomyelitis

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The immune response to antigens is directed in part by the presence or absence of 'adjuvant'. New therapeutic tools for directing the immune response should, therefore, have the ability to coincidently deliver both antigen and molecules that inhibit or activate specific immune responses. For example, blocking or activating the costimulatory pathway would be a valuable tool for skewing towards tolerization or immunization, respectively. A simple reaction scheme utilizing oxime chemistry allows peptides synthesized with an aminooxy N-terminus to react directly to hyaluronan under slightly acidic aqueous conditions without the need for a catalyst. The resulting oxime bond was found to rapidly hydrolyze at pH 2 releasing peptide, but was stable at higher pH values (5.5 and 7). Two different peptides, a multiple sclerosis antigen (PLP) and an ICAM-1 ligand (LABL) known to block immune cell stimulation fitted with the aminooxy end group showed similar reactivity to hyaluronan and were conjugated in an equimolar ratio. The resulting hyaluronan with grafted PLP and LABL significantly inhibited disease in mice with experimental autoimmune encephalomyelitis, a model of multiple sclerosis. Aminooxy-peptides facilitate simple synthesis of multifunctional hyaluronan graft polymers, thus enabling novel approaches to antigen-specific immune modulation.

Soluble Antigen Arrays (SAgAs)

Antigen Peptide
(PLP, MOG)

Targeting/Inhibitor Peptide
(ICAM-1, LFA-1)

Hyaluronan (or other)
Bacterial infections are a central cause of mortality in the world and affect all areas of medicine ranging from cardiology to oncology. Bacterial infections remain a major health problem despite the availability of effective antibiotics, because their diagnosis is challenging and because they are frequently treated with ineffective antibiotics, due to the widespread rise of bacterial drug resistance. In this report, we present a new PET contrast agent, composed of F-18 conjugated to maltodextrins (MD\textsuperscript{18}F), which can for the first time image bacteria in vivo with the specificity and sensitivity needed to detect early stage infections and measure drug resistance in vivo. We show here that MD\textsuperscript{18}F can detect as few as $10^5 E.coli$ colony forming units (CFUs) in rats, which is 3-4 orders magnitude higher in sensitivity than FDG, the current clinically used bacterial infection contrast agent. In addition, we demonstrate that MD\textsuperscript{18}F can distinguish bacterial infections from inflammation, giving it the potential to identify infections clinically without a biopsy. Finally, we demonstrate that MD\textsuperscript{18}F can monitor treatment efficacy in vivo and can identify beta lactam resistance in \textit{E.coli} in real time, thus providing physicians with a powerful tool for guiding antibiotic selection. We anticipate numerous clinical applications of MD\textsuperscript{18}F given the widespread use of PET and the pervasiveness of infections in medicine.
Intrinsic issues that are associated with chemotherapy, particularly in cancer treatment, include early disease detection, efficient drug delivery with adequate drug dose to reach tumor region, and monitoring therapeutic responses. These issues have facilitated the integration of imaging and therapeutic functions in a single platform to further optimize the therapeutic outcomes based on the imaging information. Since theragnosis allow in vivo real-time imaging of the diseased site, monitoring the biodistribution of drug and determining the optimal therapeutic efficacy following treatments, they have been considered as alternatives and ideal solutions to achieve maximal therapeutic efficacy with minimal unwanted side effect, which enable to attain personalized medicine.

Recently, nanoparticles have received a great interest an application for diagnosis and therapy. Since nanoparticles possess intrinsic features that are often required for drug delivery system and diagnosis, they have potential as platforms for integrating imaging and therapeutic functions, simultaneously. Especially, molecular imaging with theragnostic nanoparticles makes it possible not only to provide useful information for monitoring drug delivery, drug release, and therapeutic efficacy of drug, but also to determine whether the patients are likely to respond to a therapy. To achieve these goals, a variety of imaging techniques have been used, including near-infrared fluorescent (NIRF) imaging, magnetic resonance imaging (MRI) and nuclear imaging (SPECT and PET).

Imaging and monitoring of nanoparticles after systemically administered in living systems play key roles in the development of theragnostic nanoparticles to optimize their physicochemical properties. It has become clear that imaging drug delivery can assist in analyzing the drug delivery and in predicting the therapeutic efficacy of cancer-targeted nanoparticles. This presentation will highlight our recent advances that have been made in the development of multifunctional nanoparticles and the applications of these nanoparticles into theragnostic nanomedicine.
99 - Designing bio-inorganic nanomaterials for ultrasensitive biosensing

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This talk will provide an overview of our recent developments in the design of nanomaterials for ultrasensitive biosensing. Bio-responsive nanomaterials are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering (1). DNA-, protein- or peptide-functionalised nanoparticle aggregates are particularly useful systems since triggered changes in their aggregation states may be readily monitored. Our recent simple conceptually novel approaches to real-time monitoring of protease, lipase and kinase enzyme action using modular peptide functionalized gold nanoparticles and quantum dots will be presented (2). Furthermore we have recently developed a new approach to ultrasensitive biosensing through plasmonic nanosensors with inverse sensitivity by means of enzyme-guided crystal growth (3) as well as a "Plasmonic ELISA" for the ultrasensitive detection of disease biomarkers with the naked eye (4). We are applying these biosensing approaches both in high throughput drug screening and to diagnose diseases ranging from cancer to global health applications.

Understanding and modulating carriers’ cellular interactions and subsequent entries are pivotal to achieve high delivery and labeling efficiency. Using self-assembly of positively charged, non-aqueous soluble semiconducting conjugated polymers (CPs) in water, we have demonstrated that live cell imaging and small interfering RNA delivery to cells to knockdown a target gene. In this presentation, side chain-dependent cellular entries and cancer cell-specific labeling of conjugated polymer nanoparticles (CPNs) will be discussed. CPNs are emerging biomaterials exhibiting excellent photophysical and tunable biophysical properties for biological and biomedical sensing, labeling, and delivery.
101 - Functionalized magnetic nanoparticles as dual chemotherapeutic delivery and magnetic resonance imaging contrast agent

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The application of superparamagnetic iron oxide nanoparticles (IONPs) in Magnetic Resonance Imaging has generated considerable interest in their use as dual contrast agent and drug delivery vehicles. It is well known that high magnetic susceptibility of IONPs core provides strong enhancement of T2 relaxation in a localized tissue region and the integration of a chemotherapeutic drugs on the surface of IONPs can be achieved by physical interactions and chemical linkage. It is essential that the release of the drug should occur after cell internalization via e.g. pH-responsive cleavable linkage. Functional polymers could be utilized to conjugate chemotherapeutics to IONPs, while at the same time impart higher colloidal stability on IONPs in serum. Main advantages of IONPs as dual chemotherapeutic delivery and MRI contrast agent are that they potentially can be used to track the distribution of the drug *in vivo*.

In this work we have functionalized IONPs with block co-polymers followed by the conjugation of anti-cancer drug doxorubicin. These IONP coatings comprise of an inner layer of aldehyde functionalized polymer and an outer layer of poly(oligo ethylene glycol acrylate). Ultimately doxorubicin was conjugated via a pH-responsive imine bond to these hybrid IONP/polymer nanoparticles. Different assays such as colloidal stability, T2 relaxation, cytotoxicity, cell internalization were performed on these doxorubicin functionalized magnetic nanoparticles. Cancer cell uptake (2D and 3D) and intracellular release of doxorubicin were demonstrated using FLIM and confocal microscopy.
One of the challenges for polymer electrolyte fuel cells (PEFCs) used in electric vehicles is the durability which requires PEFC operated at least for 5000 hours. The Nafion ionomer network degradation and the carbon corrosion are two major causes of PEFC performance degradation. The degradation of Nafion ionomer was studied using high resolution TEM and electrochemical characterization methods to reveal the root cause of the Nafion ionomer and the effect on the durability of PEFC. A systematical approach was taken to improve the carbon corrosion in the membrane electrode assembly, starting from the functionalized carbon blacks, then nano-graphite and eventually, graphene. The catalysts using different carbon support was synthesized, characterized for their catalytic performance and their carbon corrosion resistance in the membrane electrode assembly in PEFC using TEM, cryo-TEM, XPS, small angle X-ray scattering and fuel cell characterization methods. The results show that graphene is the best candidate for enhancing the carbon corrosion resistance in fuel cell.
103 - Toward standardization of a laboratory based test for ice release

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Minimizing adhesion of ice has been studied for mitigating problems associated with operations in cold environments for aircraft, space vehicles, and ships. Effects of ice related damage are well known for power transmission lines and wind turbine blades. Thus far, ice adhesion measurements have been based on “custom designed” equipment. To broaden opportunities for the study of ice adhesion, the goal of this research is to establish a method for evaluating ice release with a commercially available instrument. To this end, a test with a TA Instruments RSA-III has been developed and used to determine the strength of ice release for a commercially available PDMS elastomeric coating. Preliminary results suggest a promising path forward for establishing a standard for ice release measurement. Through this work, thickness has been identified as a key variable. A correlation with theory will be presented, including a relationship between critical ice removal force (and removal energy) and $1/t^{1/2}$ for Sylgard 184, where $t$ is coating thickness (Figure 1).

$^1$ The authors thank the National Science Foundation (grants DMR-0802452 and DMR-1206259) for support of this research.

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**Figure 1**: Linear relationship between critical ice removal force (and removal energy) and $1/t^{1/2}$ for Sylgard 184.
Robust systems for autonomic regeneration present challenging problems that demand new concepts and approaches. Major challenges arise from the interplay of mass transport and forces, both intrinsic (e.g. surface tension) and extrinsic (e.g. gravity), that act upon liquid healing agents as they traverse the zone of regeneration. Herein, we demonstrate a bi-phase chemical resin that undergoes two transformations – an acid-catalyzed gelation and independent polymerization of monomer solvent. The resulting crosslinked polymer gel acts as a scaffolding material which exceeds the restorative ability of liquid healing agents alone. Subsequent polymerization of monomer recovers the mechanical properties of the virgin substrate. Careful timing of these chemical changes make it possible to heal multiple stages of damage such as microcracks and large gaps in the material. The combination of the gel scaffold with monomer polymerization defines a new type of healing chemistry and further expands the healing capability of microvascular composites.
105 - Conjugated polymer and carbon nanocomposites with anticorrosion and superhydrophobic wetting properties

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Corrosion and its prevention is a major effort that consumes a significant percentage of the economy. A number of technologies have been reported based on polymer nanocomposites with good initial mitigation properties but require a significant amount of maintenance.

In this report, we describe the use of graphene-oxide and carbon nanotube conjugated polymer composites with anti-corrosion properties. The polythiophenes and polycarbazoles were prepared as solutions with these filler materials and electropolymerized on steel surfaces to demonstrated superior coating properties and thin film formation. The materials were tested with impedance analysis and standard salt solution experiments. Superhydrophobic wetting properties were observed.
Federal Aviation Administration regulations have required the commercial aircraft industry to utilize flame-resistant materials for interior cabin applications. These materials must meet the OSU heat release requirements with a 2 min integrated heat release and a peak heat release rate of ≤65 kW·min/m² and ≤65 kW/m², respectively. A series of polycarbonate and polycarbonate-co-polyester copolymers containing siloxane moieties have been developed, as shown in Figure 1, and the OSU performance mapped. The synthesis and analysis of OSU performance of these polycarbonates will be discussed.

![Polysiloxane block](image)

Polysiloxane block where E = 4 to 100,

![Polyarylate polycarbonate block](image)

Polyarylate polycarbonate block

**Figure 1.** Representative structural considerations for polycarbonate and polycarbonate-co-polyester copolymers, where R = C1-13 monovalent organic group; R¹ = C6-30 arylene group; R² = divalent C1-30 alkylene or C7-30 arylenalkylate moieties.
Designers of automotive, agricultural and construction vehicles all share a common desire to move towards material with molded in color (MIC). Some of the benefits of MIC resins are: Lower volatile organic compounds (VOCs) from painting or coating, less rejects as compared with the painting/coating of complex parts and lower systems costs. For interior parts or parts with lower exposure to UV light, MIC resins have already displaced many of the painted applications. For exterior applications, materials are needed with an excellent balance of UV stability, processability and mechanical properties over the lifetime of the vehicle. Also to be commercially viable, the resin needs, among other attributes, to be manufacturable and available from low cost raw materials.

Polycarbonate (PC) resins have an excellent balance of processability and mechanical properties. Uncoated PC will not withstand the long term weatherability required for these applications. To overcome these shortcomings of PC, we have sought to copolymerize a latent UV absorber into the polymer backbone. To this end, aromatic polyesters were incorporated into the polymers (Figure 1): these units undergo a photo Fries rearrangement when exposed to UV light (Figure 2). The photo Fries products, o-hydroxybenzophenones, are a known class of UV absorbers. This paper will discuss the selection, synthesis and properties of these resins with latent UV absorbers.
Förster resonance energy transfer (FRET) is the result of energy transfer through dipole-dipole interactions between an excited state donor molecule with an acceptor molecule in the ground or lower excited state in a spherical interaction volume. FRET has been studied extensively in the past due to its reliance on proximity (10 – 30 nm) for the energy transfer with primary application to biological systems for the detection of interplay between biomolecules. Previous research at NIST has applied FRET to measure the component interphase of a composite. However, this system employed donor dye dispersed freely in the matrix. The development of dyes functionalized for covalent incorporation into polymer composites in the matrix or reinforcing component is desirable, for the dyes would no longer be prone to migration during heating processes. In this work, a coumarin derivative was functionalized for covalent incorporation into an epoxy matrix to optimize FRET pairing with fluorescein labeled nanoparticles. The coumarin monomer was shown to have high Stokes shift (70 nm) and an emission peak at (476 nm) that makes this monomer an ideal donor for fluorescein. Development of this system will allow for the study of polymer composites. This can be applied to composites containing fibers with different aspect ratios or surface area to aid in the design and characterization of composite systems.
Cationic polymerization of isobutylene by \( t\)-BuCl/FeCl₃/ether initiating system was studied in hexanes at 0 °C. Using \( t\)-BuCl/FeCl₃/ether initiating system highly reactive polyisobutylene in the molecular weight range of 500-2000 g mol\(^{-1}\) with 60-80 mol % exo-olefin end group and acceptable molecular weight distribution \((M_w/M_n = 1.9-2.3)\) was obtained. The polymerization mechanism includes \( \beta \)-proton elimination from the growing chain ends assisted by the ether followed by chain transfer to the monomer. The rate of polymerization and exo-olefin content depend on the nature of ether used for the complex formation with FeCl₃. We have studied a series of linear and branched ethers. Substitution had a large effect on the polymerization rate and a smaller effect on the exo-olefin content. These can be related to the stability and solubility of the FeCl₃ complex with different ethers, which are attributed to steric and electronic effects.
Natural polymers epitomize structural precision. Through controlled monomer sequence and microstructure, natural polymers adopt complex secondary and tertiary structures. This in turn leads to hierarchical self-assembly at a level that is still beyond our reach synthetically. This talk will present our recent work in the area of single-chain folding. Inspired by Ken Wagener's systematic approach in elucidating the structure-property relationship in ethylene-based copolymers, we are taking a similar systematic approach in studying the folding of single polymer chains. The ultimate target of this work is the creation of well-defined secondary or even tertiary structure in a synthetic polymer.
Precise acid- and ion-containing polymers have been synthesized by Ken Wagener's group using acyclic diene metathesis (ADMET). The precision of these molecules produces hierarchical morphologies with unprecedented long-rang order and remarkable uniformity. This talk will summarize our findings from X-ray scattering and will incorporate findings from a variety of collaborators who have studied these precise copolymers using NMR, course-grain molecular dynamics simulations and atomistic molecular dynamics simulations. Three classes of morphologies have been observed in the polyethylene-based copolymers when the acid or ionic groups aggregate. The most common morphology exhibits one scattering peak associated with the separation between ionic aggregates and, while X-ray scattering cannot distinguish the shape of the ionic aggregates, simulations find that the aggregates vary from isolated spherical aggregates to highly branched, percolated aggregates. When the polyethylene spacers are long enough, polymer crystallization drives the formation of layered ionic aggregates perpendicular to the polymer chains, Figure 1. Finally, we have found a few precise copolymers that exhibit cubic symmetry, an astounding result that reflects the exquisitely precise structures formed by ADMET. In addition to static X-ray scattering, in situ X-ray scattering results are underway to evaluate how these morphologies evolve and align during elongation.

Figure 1. X-ray scattering of semicrystalline, precise copolymers with 15 or 21 carbons between functional groups that exhibit layered aggregates.
112 - Herman F. Mark Polymer Award: History and Recipients

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A brief history of the Herman F. Mark Award will be presented with its relationship to other Polymer Division Awards. A review of prior Mark awardees and some interesting relationships in regard to awardees with each other, as for example our present awardee Ken Wagener and his mentor George Butler, will be discussed.

Tuesday, September 10, 2013 09:25 AM
Herman F. Mark Polymer Chemistry Award: Symposium in Honor of Kenneth Wagener (08:30 AM - 12:15 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
113 - Synthesis of polymers with controlled structures using ROMP initiators

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Ruthenium based olefin metathesis catalysts have provided new routes to olefins that appear in a variety of structures. Their functional group tolerance and ease of use allow their application in the synthesis of multifunctional bioactive molecules that are being explored as pharmaceutical agents. The same systems are also useful for the synthesis of an array of new materials from multifunctional polymers to supramolecular systems. Of particular interest are brush polymer systems that phase separate into ordered structures. The long-range order of these periodic structures is controlled by the selection and ordering of the block components. We are exploring the factors that control the spacing and attempting to develop a detailed picture of the phase separation process. The catalysts can also be used to construct telechelic polymers and in the production of composite materials. Underlying these developments has been the discovery of active catalysts with controlled selectivity through the synthesis of new ligands that control the geometry of the intermediate carbene and metallacycle complexes. A recent finding has been a ligand system that controls the geometry of the double bond that is formed in the metathesis process. A particularly efficient catalyst that will dimerize olefins to the Z geometry in high yields has been developed. These systems also generate a family of high Z polymers with controlled tacticity.
Extension of previously developed self-healing concepts to the repair of damage following blast and impact loadings motivates concepts in synthetic materials regeneration. Synthetic materials regeneration aims to restore lost functionality by autonomic processes that mimic biological growth of tissue and appendages. A robust, autonomic regeneration process must first transfer sufficient healing fluid to span the voids in the damaged zone. Delivery of large quantities of healing fluids is achievable using vascular networks that are integrated into composites. Novel healing agents are needed to deal with repair challenges such as gravity, wind, variable temperature, moisture and oxygen. Characterization data on filling prototypical voids created in vascularized polymeric specimens will be presented, including the scaffold-forming chemistry, its transformation to a structural solid and the evolving mechanical properties.
The present interest in graphene, a naturally occurring two-dimensional polymer, makes clear that there is no organic synthetic method available that would allow accessing a covalently bonded molecular sheet with internal periodicity and a thickness of one monomer unit only.[1] After a brief overview of “organic” and “polymer” approaches performed so far, the concepts will be presented which are presently being pursued in the authors’ laboratory. They rest upon designed monomers, interfacial as well as single crystalline ordering, and both metal-complexation[2] and light-induced solid state polymerizations in the single crystal and at interfaces.[3] The lecture will provide a state-of-the-art picture including the first solution to the problem.[3] This work is considered an expansion of Staudinger’s polymerization concept in which (linear) macromolecules with linear repeat units are generated.[4] We are creating sheet-like macromolecules with topologically planar repeat units.

116 - Step-growth polymerization of fluoro-olefins and tetraynes toward high performance cyclopolymers: A Gator tradition!

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Perfluorocyclobutyl (PFCB) aryl ether polymers¹ have been incorporated into a number of platform technologies including: high performance passive optics, electro-optics, polymer light-emitting diodes (PLEDs), space survivability, and polymeric fuel cell membranes (PEMs), to name a few (Scheme 1).² Polymerized via a step-growth [2+2] thermal dimerization of aryl trifluorovinyl ether (TFVE) monomers, PFCB polymers offer a unique platform as semifluorinated cyclopolymer. More recently we have explored nucleophilic step growth, semifluorinated polymers from TFVE and perfluorocycloalkenyl monomers to form fluorinated arylene vinylene ether (FAVE)³ and perfluorocycloalkenyl aryl ether (PFCA)⁴ polymers (Scheme 1). Concurrently we explored a class of processable pre-carbon materials from bis-o-diynylarene (BODA) monomers which undergo thermal Bergman cyclo-rearrangement and polymerization to form carbon networks in > 80 % yield with applications in electronics, composites, light emitting diodes, sensors, dielectrics and conductors.⁵ Additionally this lecture will overview projects in our laboratory on renewable materials, car tire rubber composites, and direct fluorination.


Tuesday, September 10, 2013 11:25 AM
Herman F. Mark Polymer Chemistry Award: Symposium in Honor of Kenneth Wagener (08:30 AM - 12:15 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
117 - Engineering thermoplastics, reactive tougheners for thermosets, and the development of membranes for water, gases, and fuel cells

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Many aspects of this work have been ongoing at Virginia Tech for nearly four decades. In the early days the focus was largely on the generation of engineering thermoplastics, both amorphous systems and semicrystalline materials, such as the poly(arylene ether ketones). They were differentiated from their analogous blends by the fact that the chemical reactions developed a controlled morphology and chemical resistance, which led to very significant fracture-toughness improvements in crosslinked epoxies, other thermosetting materials and carbon fiber composites. Interactions with industrial organizations led to the commercialization of these materials, which are now present as composite materials in both Airbus and Boeing products. More recently, we have turned our attention to the development of membranes, first for fuels cells, and more recently for water and gas separations. In the first two cases, sulfonated copolymers have been investigated, including linear, random, multiblock, and crosslinked systems, which have been able to achieve excellent chlorinated disinfectant resistant compared to the state of the art polyamide systems. Gas separation membranes are also being investigated, building upon our previous experience in the synthesis of high performance materials such as polyimides, poly(amide imides), polybenzimidazoles and polybenzoxazoles. Illustrations of these and typical properties achieved thus far with the great collaboration with Prof. B.D. Freeman at the University of Texas will be presented.
Protein folding is a dynamic process of molecular self-assembly during which a single stranded polypeptide chain folds to form a well-defined, three-dimensional (3D) tertiary structure that exhibits a function. Inspired by nature's way, several approaches have been explored to prepare synthetic analogues of folded proteins. We have recently developed single-chain folding of synthetic polymers bearing a single self-assembling motif. Either benzene-1,3,5-tricarboxamides (BTAs) or 2-ureido-4[1H]-pyrimidinones (UPys) were applied as the recognition motif to induce single chain folding under selected conditions. We found that a wide variety of polymer backbones allow the folding of single polymer chains into single chain polymeric nanoparticles (SCPNs). However, the interaction between solvent and recognition motif is crucial to suppress interparticle aggregation. The addition of catalytic sites or fluorescent moieties provides the SCPNs with a function. For example, bipyridine-based SCPNs are effective for sensing Cu(II) at low concentrations while embedding a catalytically active site in the interior of the SCPNs afforded efficient catalysis in water. Precise location of self-assembling motifs within the polymer chain and enhanced control over polydispersities are of crucial importance to improve the scope of SCPNs. Recent advances in sequence controlled polymerizations and precision polymerizations will undoubtedly provide novel opportunities to achieve this.
119 - Design of novel sequence-controlled oligomers

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Proteins are based on a limited library of monomers, i.e. twenty amino acids, providing a large variety of materials with well-defined characteristics and properties due to the specific sequencing of the amino acids. However, the control of the primary structure of synthetic polymers accessible from a wide range of monomers is more arduous to attain. Few research groups have developed techniques to approach the degree of sequence control existing in proteins. This presentation will focus on an iterative approach inspired by solid-phase peptide synthesis introducing features precisely localized on the oligomer backbone.
Nucleic acids, macromolecules that serve as the ubiquitous information-bearing species throughout biology, present the most versatile, state of the art class of materials for producing diverse, specific nanostructures to date owing to their information-directed self-assembly. Through careful consideration of their nucleobase sequence, nucleic acids can be designed to predictably self-assemble via the hybridization of complementary strands into arbitrary structures. Unfortunately, the versatility of nucleic acid assemblies is tempered by their fragility and susceptibility to thermal and mechanical degradation, attributable to the weak hydrogen bonds holding the strands together. In contrast, covalent bonds exhibit bond energies over an order of magnitude higher than those for hydrogen bonds, providing a route for the fabrication of far more mechanically robust assemblies. We describe the development of sequence-specific oligomers that employ dynamic covalent interactions to effect hybridization between strands of complementary sequences, mimicking the self-assembly commonly observed in complementary nucleic acid strands.
This lecture will discuss recent advances in the design, synthesis, and functions of smart sequence-controlled polymers via living radical polymerization (LRP), especially focusing on the creation of novel sequence-regulated polymerization systems, single-chain nanospace, and unique functions.

(A) **Functional gradient copolymers** were synthesized in one-pot via concurrent tandem LRP, where in situ transesterification of methacrylates ($R_1$MA) into another ($R_2$MA) took place with metal alkoxides, while the two monomers simultaneously copolymerized. Thanks to high controllability (catalysis) and rich diversity (methacrylates and alcohols), this tandem catalysis enables various gradient functionalization and complex sequence regulation (random gradient, gradient block).


(B) **Polymeric pseudo crown ethers** with large in-chain cavities (up to 30-membered rings) were directly obtained from cation template-assisted cyclopolymerization of poly(ethylene glycol) dimethacrylate (PEGnDMA: $n = 4-8$) via the alternating process of intramolecular cyclization and intermolecular chain propagation, to perform selective, unique cation recognition. The key is to select a size-fit metal cation for PEGnDMA to induce a pseudo-cyclic conformation in the bifunctional monomer, where the two vinyl groups are brought into suitable positions for cyclization.


(C) **Single-chain star polymers** with dynamic or patched hydrophobic compartments formed in water from amphiphilic PEGMA/RMA random copolymers via the self-folding by intramolecular hydrophobic interaction. The key is the precision control of random sequence in the copolymers by ruthenium-catalyzed LRP.
Polymers are materials that are widely used in various industries due to their unique properties. Monomer-level sequence control is one of the ultimate goals in polymer chemistry, and if we ever achieve this, the current boundary between biological macromolecules (e.g., proteins, RNA, and DNA) and synthetic polymers would be obsolete, and we could finally have a re-unified polymer science. Compared with the template approach in the biological world, iterative mono-addition has been the strategy used by chemists to achieve monomer-level sequence control in polypeptide and polyester synthesis, but it had never been done for vinyl copolymers. Here we describe such a strategy based on iterative atom transfer radical addition (ATRA) to synthesize sequence-controlled vinyl copolymers. Recent progress and problems after our first publication (ChemComm 2011, 47, 1455) will be presented.

Tuesday, September 10, 2013 10:15 AM
Sequence-Controlled Polymers (08:10 AM - 12:20 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
123 - Engineering hydrolysis behavior of poly(lactic-co-glycolic acid) through precise control of monomer sequence

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Although we have learned from Nature that engineering molecular properties can be accessed by controlling monomer sequences and tacticity, trends to control properties by synthesis of "precision polymers" have just debuted in recent years. Poly(lactic-co-glycolic acid) (PLGA) copolymers have been widely studied as biodegradable and bioabsorbable polymers in the biomedical area. Controlling monomer sequences of PLGA can tune their properties for specific drug delivery and medical device applications. A group of PLGA copolymers with precise sequence and tacticity control were synthesized by condensation polymerization. The hydrolytic degradation rates, thermal properties and the ability to control the release of encapsulated small molecules of sequenced PLGA were investigated. Results showed that sequenced PLGA have potential as components of drug delivery systems.
Gradient sequence copolymers, which exhibit a gradual change in comonomer composition along the polymer chain, are classically interesting materials with unique properties. This intriguing gradient sequence typically requires synthesis by controlled/“living” polymerization, which has been limited to electrically insulating polymers, because conjugated materials are traditionally made by uncontrolled step-growth processes. With the advent of controlled chain growth polymerization for conjugated polymers such as polythiophene, we have recently expanded the cannon of gradient sequence copolymers to include pi-conjugated examples for the first time. Sequence plays a subtle but crucial role in the thermal, optical and electronic properties of these new materials, as well modulating their thin film morphology. While alternating, random, and block copolymers have been examined previously as active components in bulk heterojunction solar cells, no examples of pi-conjugated gradient copolymers were available until recently. Our group has shown synthesis of gradient copolymers with different backbone and side chain functionalities. Ultimately, the goal of our program is to incorporate donor-acceptor gradient copolymers into the active layer of bulk heterojunction organic solar cells to demonstrate their impact on morphology and device performance.
Graphene attracts tremendous interest as a leading candidate for next generation technologies. However, because of its chemical inertness, the structure and properties cannot be modified in a controlled manner. If one can take advantage of organic chemistry to synthesize such an intriguing 2-D structure by design, it may lead to emergence of a large family of artificial 2-D polymers to meet demands for a broad range of applications. However, how to realize an exclusively lateral, periodic growth of monomers remains a key challenge on the synthesis. In the present study, I applied the following two strategies to tackle this problem. In the first, monomers are preorganized into an ordered array prior to their irreversible covalent fixation (2-D topochemical polymerization). In the second, order is created during bond formation by applying reversible reactions for the growth process (2-D equilibrium polymerization). The contribution will present the latest situation showing some concrete examples.
126 - Ring-opening metathesis polymerization for the synthesis of rigid block copolymers and their self-assembly to photonic crystals

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Highly ordered morphologies accessed through the self-assembly of block copolymers yield versatile hybrid materials with diverse applications. The typically slow and complex self-assembly of block copolymers greatly inhibits their ability to assemble to domain sizes greater than 100 nm. Using ruthenium-mediated ring-opening metathesis polymerization, we have synthesized rigid, molecular brush block copolymers that exhibit reduced chain entanglement, drastically lowering the energetic barriers to reorganization. These polymers rapidly equilibrate to nanostructures with domain sizes exceeding 100 nm, providing a bottom-up route to photonic crystals with application-tailored bandgaps that span the entire visible spectrum through modulation of the polymer molecular weight.

![Figure 1. Ring-opening metathesis polymerization of macromonomers to molecular brush block copolymers and their self-assembly to photonic crystals.](image)

**Figure 1.** Ring-opening metathesis polymerization of macromonomers to molecular brush block copolymers and their self-assembly to photonic crystals.
127 - Glycopolymer delivery vehicles exploit active inter-organelle trafficking mechanisms

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Materials that self-assemble with nucleic acids into nanocomplexes (polyplexes) are widely used in many fundamental biological and biomedical experiments. However, understanding the intracellular transport mechanisms of these vehicles remains a major hurdle in their effective usage. Here in, we will present the synthesis of several glycopolycation models that vary in carbohydrate type and cationic functionality. We show that polymer structure impacted the ability of the vehicle to bind and compact nucleic acids (siRNA and pDNA) into polyplexes. We have performed extensive studies to determine the role of polymeric structure on intracellular trafficking. We show that transgene expression duration and toxicity is highly affected by polymer structure. In addition, polymer structure played a large role in the cellular internalization pathways and intracellular organelle colocalization. For example, PEI appeared to promote release of DNA from acidic organelles more than Glycofect, a carbohydrate based polycation vehicle. Immunofluorescence images indicate that both Glycofect and linear PEI delivery vehicles traffic oligodeoxynucleotides (ODNs) to the Golgi and endoplasmic reticulum (ER), which may be a route taken for nuclear delivery. However, Glycofect polyplexes demonstrated higher colocalization with the ER than PEI polyplexes and colocalization experiments indicated retrograde transport of polyplexes via COP I vesicles from the Golgi to the ER. We conclude that slow release and unique trafficking behaviors of glycopolycation polyplexes may be due to the presence of saccharide units, allowing efficacious and benign delivery.
One of the critical challenges for efficient non-viral gene delivery in vivo is the ability to control the transport properties in biological milieu of DNA-containing nanoparticles. Recently, nanoparticle shape has been identified as an important factor determining these properties. However, until now it has not been possible to control the shape of nanoparticles containing packaged plasmid DNA. Here we show that exquisite shape control can be achieved through complexation of plasmid DNA with polyethylene glycol (PEG)–polycation copolymers. Through variation of polymer structure and solvent polarity, we realized shape tunability from spherical and rod-like to worm-like structures. Via matching molecular dynamics simulations we identified that the shape of these plasmid-containing nanoparticles primarily arises from a competition between DNA–solvent interactions, DNA bending rigidity, and entropy of the PEG blocks. More importantly, here plasmid DNA serves both as an active payload and as a shape template. The resulting nanoparticles have a near-neutral zeta potential and surround the DNA with a protective polymeric corona, and thus exhibit high stability in physiological media. Using a liver-targeted gene delivery model, we confirmed shape-dependent levels of transgene expression in the liver of Wistar rats. These findings open up a new avenue for controlling the shape of DNA-compacting nanoparticles and enhancing gene delivery efficiency. More broadly speaking, these micelles closely mimic the typical shapes (spherical, rod-like, and worm-like morphologies), sizes (20 to 80 nm in diameter, hundreds of nm in length for worm-like micelles), and physical features (flexible worm- and rod-like structures, and hydrated surfaces) of viral particles; therefore may serve as a model system for elucidating the role of shape in determining viral transport properties and bioactivities.
129 - Protein transduction domains mimics enable T-cell delivery

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In the last decade, cell penetrating peptides also known as protein transduction domains are highlighted as promising agents for the intracellular delivery of large, hydrophilic molecules which are unable to pass the plasma membrane by themselves. Among the protein transduction domains, arginine-rich peptides are the most efficient subclass. In the light of this information, we designed and synthesized protein transduction domain mimics which contain guanidinium functionality along the polyoxanorbornene backbone. Structure activity relationship has been studied with designed molecules in order to be able to determine the requirements for efficient cellular internalization, as well as the exceptional activity in delivery of bioactive molecules such as siRNA and proteins has been demonstrated.
130 - Helical poly(arginine) mimics exhibit superior cell-penetrating properties

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Cell-penetrating peptides --(CPPs) typically contain a large number of charged arginine residues and consequently adopt random coil conformation due to electrostatic repulsion of the charged side groups. Here, we report the design of the unprecedented, helical, side-chain charged poly(arginine) mimics that show superior membrane-penetrating capability. By inserting an alkyl spacer between the charged guanidinium group and polypeptide backbone, we were able to achieve poly(arginine) mimics that adopted very stable helical conformation. We demonstrated that by incorporating helicity to a short CPP could enhance cell-penetrating efficiency by 5-10 times. Elongating polypeptide backbone length and side chain hydrophobicity further enhanced the cell-penetrating properties of poly(arginine) mimics, up to 130 times more efficient than HIV-TAT for penetrating mammalian cell membranes.

These helical CPPs penetrated cell membranes mainly through the energy-independent, pore formation mechanism; caveolae-mediated endocytosis partly contributed to their penetration kinetics. These poly(arginine) mimics with distinguished cell-penetrating properties and low cytotoxicities can potentially be excellent cellular transporters for the delivery of small molecules and macromolecules into cells.
Efficient and safe delivery of nucleic acids has been a pivotal, technological bottleneck in basic biomedical research as well as in gene therapy. Shielding viral vectors not only ensures safe administration of immunogenic viral particles but also allows to engineer the physico-chemical properties of viral vectors using synthetic macromolecules. Effects of a genetic modification are often insufficient to achieve biological and therapeutic outcomes (e.g., apoptosis of cancer cells) at a desired level, because of an antagonistic pathway (e.g., overly activated survival signal). In this study, adeno-associated virus (AAV) was shelled with acid-responsive polyketal (PK) polymers (viral/nonviral chimeric nanoparticles; ChNPs) in that the PK shell shields the AAV core from the immune response. In addition, the PK assists the AAV core's facilitated intracellular trafficking. Most importantly, the PK shell encapsulates small interfering RNA (siRNA) to obtain simultaneous dual mode expression and silencing of multiple genes. The resulting ChNPs have demonstrated 1) stimuli-triggered, differential release of AAV and siRNA, 2) enhanced transduction by the AAV core, and 3) simultaneous expression and silencing of multiple target genes in a cell. ChNPs consisting of the Bim-encoding AAV core and Mcl-1 siRNA-encapsulating PK shell (BimAAV/Mcl-1siRNA ChNPs) were synthesized in exploration of treating Bcr-Abl(+) leukemia. Bcr-Abl is a molecular cause of chronic myelogenous leukemia (CML) and subsets of other human leukemia. The BimAAV/Mcl-1siRNA ChNPs efficiently interfered with the proliferation of human leukemia cells in vitro and in vivo.
132 - Helical polypeptides mediated nonviral gene and siRNA delivery

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We designed a class of helical, cationic charged polypeptides via the ring-opening polymerization of vinyl benzyl glutamic acid $\text{N}$-carboxyanhydrides. These materials have unusual helical stability and display excellent cell penetrating property, outperforming TAT peptide. By controlling the chemical, morphological and self-assembly structures of these side chain charged, helical polypeptides, we identified a few materials that showed excellent gene and siRNA delivery efficiency in vitro and in vivo.
This presentation will introduce a novel synthetic gene-carrier, hyperbranched polylysine (HBPL), which is structurally related to dendritic polylysine but possesses a randomly branched structure and is obtained in a one-step reaction from lysine. After outlining the synthesis and structural characterization of these hyperbranched polypeptides, their toxicity, cellular internalization and trafficking as well as gene delivery properties will be discussed and compared with those of linear and dendritic polylysine analogies as well as polyethylenimine (PEI). Transient gene expression experiments with CHO DG44 cells revealed that the hyperbranched analogues were superior as compared to the dendritic and linear polylysines. Altogether, the results of this study indicate that hyperbranched polylysine is an interesting, alternative synthetic gene carrier. These polylysine-based polycations can be produced at low costs and in large quantities, are partially biodegradable, which may help to prevent cumulative cytotoxicity, and possesses transfection properties that can approach those of PEI.
134 - Multifunctional dendronized peptide polymer platform for safe and effective siRNA delivery

Hanxiang Zeng, hannah Little, Timothy Tiambeng, Gregory Williams, Zhibin Guan, zguan@uci.edu. Department of Chemistry, University of California, Irvine, Irvine, CA 92697, United States

In this talk, I will discuss our design and synthesis of a novel biodegradable peptide-based dendronized polymer (denpol) platform for siRNA delivery. The novel denpol architecture combines the multivalency of dendrimers and conformational flexibility of linear polymers for optimal siRNA binding. Onto the dendrons multi-functional amino acids were incorporated to overcome various challenges for successful intracellular delivery. The versatile structure could be both systematically and combinatorially tuned to select optimal vectors.

Through screening a focused library, we have identified several denpols that can effectively deliver siRNA to NIH 3T3 cells in vitro and exhibit minimal toxicity. For comparison, the best performing denpol showed significantly improved transfection efficiency over Lipofectamine in serum-containing media. Fluorescence intracellular trafficking study indicated that the amphiphilicity is important for both cell uptake and endosomal escape, and the buffering capacity of histidine facilitates endosomal membrane rupture and therefore enhances the transfection efficacy. The combination of high delivery efficiency in serum and low cytotoxicity suggests the denpol system as a promising new carrier for siRNA delivery.

Tuesday, September 10, 2013 11:50 AM
Biomacromolecules for Therapeutics and Diagnostics Delivery (08:30 AM - 12:10 PM)
Location: Hyatt Regency Indianapolis
Room: Studio One
135 - Chemical origin of shape-memory effect in CP2 polyimide

Loon-Seng Tan\textsuperscript{1}, loon-tan@us.af.mil, David H Wang\textsuperscript{1,2}, Hilmar Koerner\textsuperscript{1,2}, Richard A Vaia\textsuperscript{1}. (1) Materials & Manufacturing Directorate, US Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433, United States, (2) UES, Inc, Dayton, OH 45432, United States

CP2 is a high-T\textsubscript{g} polyimide that was developed in 1980's from the NASA-Langley Research Center “Colorless Polyimides” R&D program toward space applications, where high optical transparency in 300-600nm region was an important requirement. Recently, we have shown that CP2 is promising as a high-temperature shape memory (SM) polymer, and when incorporated with a tris(azobenzene-amine) crosslinker, a CP2 cantilever, upon exposure to a polarized blue light at room temperature, can be rendered photomechanically active as well. However, it was puzzling that when an “uncrosslinked” CP2 film was immersed in a heat-bath at temperatures above its T\textsubscript{g} (\textdegree{C}), it could be easily stretched, bend or twisted, and the temporary shape could be fixed by cooling under a constant stress. When returned to the heat-bath without being under stress, the CP2 film would fully recover its original shape. This SM effect could be repeated (>10 times) and was observed also in CP2-polymers crosslinked with a tris(phenylamine) compound. Interestingly, such SM effect was not observed in other similarly prepared (without crosslinker added) polyimide films (e.g. CP1 and Ultem). Thus, in this work, we have attempted to delineate the source and mechanism of crosslinking, and correlate the crosslinking chemistry and the SM effect apparently unique to CP2.
136 - Shape memory polymer: Fundamentals and applications

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A traditional SMP can only memorize one temporary shape and would recover to its permanent shape upon exposure to an external stimulus (typically heating). This basic concept has been proven quite useful for highly efficient manufacturing (e.g. shrink labeling in packing industry). In this talk, I will give an overview of my recent work on the SMP subject, with the goal of stimulating new ideas in applying such a technology for transportation industry. Particular emphasis will be placed on how the SMP field has evolved scientifically (e.g. multi-shape memory and temperature memory) and how one can take advantage of the polymer shape memory for practical applications (e.g. bioinspired reversible adhesives, self-healing surfaces, and structural colors).
Several biomaterials undergo autonomous repair by a depolymerization-repolymerization sequence of remodeling when damaged by aging or stress. The integration of this concept into synthetic materials systems can be achieved by using low ceiling temperature polymers. These polymers can depolymerize to their monomer, which in turn can be repolymerized as needed. We hypothesized that mid-chain scission of end-capped poly(o-phthalaldehyde) (PPA) by mechanical force would produce two metastable chains which depolymerize back to o-phthalaldehyde monomer. PPA solutions were subjected to acoustic fields generated by an ultrasound horn and depolymerization to monomer was observed. The obtained monomer was repolymerized by a chemical initiator, effectively completing a depolymerization-repolymerization cycle. Mimicking biomaterials, this model system may lead to smart functional polymers where aging or mechanical damage triggers depolymerization and orthogonal conditions regenerate the polymer when and where necessary.
Aerodynamic decelerators in the form of hard aeroshells have been employed on past missions to land small payloads on Mars, but are limited in diameter by the launch vehicle shroud. Inflatable aerodynamic decelerators can allow larger aeroshell diameters for entry vehicles because they are not constrained by the shroud. The inflatable decelerator employs a flexible thermal protection system (TPS) to survive the heat of reentry. The TPS must also endure rigorous handling, high density packing, deployment, and aerodynamic loads. Composite aerogel blankets developed by Aspen Aerogels are considered the baseline insulation for the TPS. However, the matrix used in these blankets is fragile and tends to shed silica aerogel particles. Polyimide aerogel thin films which were designed as a replacement for the composite blankets do not shed particles, and have thermal conductivity comparable or lower than the blankets. This paper will discuss testing of these materials in high heat flux conditions which simulate conditions during planetary reentry. The figure shows thermocouple measurements from a typical high heat flux test. The polyimide aerogels were included as the bottom two layers in the lay-up replacing two of the blanket layers. During the test, it took about 140 seconds for the TC 6K thermocouple to reach 300 °C which is comparable to composite blanket only runs. However, the polyimide layers experienced much less weight loss during the test than the composite blankets.
139 - Modified thiol-ene networks: Tuning the glass transition temperature and energy damping capabilities of thermoset networks

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Utilizing thiol-ene 'click' reactions, it is possible to produce thermoset networks that are highly homogeneous and thus exhibit enhanced energy damping capabilities. This talk will present some recent results in the characterization and impact testing of modified thiol-ene networks with tunable physical properties. In particular, we synthesize ternary networks containing (1) bulky side-chain substituents, (2) isocyanate functionality, or (3) dual thiol components to improve control over the glass transition temperature and strain at break. In addition, we present results in the high-impact compression testing to demonstrate the energy damping capabilities of these materials.
140 - Synthesis and characterization of a new family of polyamide aerogels by cross-linking amine capped polyamide oligomers

Jarrod C Williams, jarrod.c.williams@nasa.gov, Mary Ann B Meador. NASA Glenn Research Center, Cleveland, Ohio 44135, United States

We report the first synthesis of cross-linked polyamide aerogels through step growth polymerization using a combination of diamines, diacid chloride and triacid chloride. Polyamide oligomers endcapped with amines are prepared as stable solutions in N-methylpyrrolidinone from several different diamine precursors and 1,3-benzenedicarbonyl dichloride. Addition of 1,3,5-benzenetricarbonyl trichloride yields gels which form in under five minutes according to the scheme shown. Solvent exchange of the gels into ethanol, followed by drying using supercritical CO$_2$ extraction gives colorless aerogels with densities around 0.1 to 0.2 g/cm$^3$. Thicker monolithes of the polyamide aerogels are stiff and strong, while thin films of certain formulations are highly flexible, durable, and even translucent. These materials may have use as insulation for deployable space structures, rovers, habitats or extravehicular activity suits as well as in many terrestrial applications. Strucure property relationships of the aerogels, including surface area, mechanical properties, and thermal conductivity will be discussed.
141 - Substituent effects on the properties of donor-acceptor conjugated pi-systems: A "Boone" for structure-property studies

Mark D Watson, mdwatson@uky.edu, Mark J Seger, Daijun Feng, Thilanga Liyanage. Department of Chemistry, University of Kentucky, Lexington, KY 40503, United States

This presentation will outline our recent approaches to regulate the solubility, (opto)electronic properties and self-assembly of polymeric and small-molecule organic electronic materials, with a primary focus on structure-property studies. Approaches include systematic changes in the steric bulk of monomer side chains in the near vicinity of polymer backbones and their positions, incorporation of mildly to strongly electron-withdrawing groups, and stringing together electron-withdrawing groups in series.
142 - Synthesis of precision ROMP polymers

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Mo and W catalysts can be designed for synthesis of ROMP polymers with a single structure. Some recent advances in this area will be presented.

Tuesday, September 10, 2013 02:15 PM
Herman F. Mark Polymer Chemistry Award: Symposium in Honor of Kenneth Wagener (01:45 PM - 05:10 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
Unprecedented advances in controlled radical polymerization (CRP) techniques and facile “click” conjugation chemistry now allow synthetic tailoring of precise, nano-scale architectures appropriate for drug/gene delivery. Reversible addition-fragmentation chain transfer (RAFT) polymerization and its aqueous counterpart (aRAFT) afford quantitative control over key synthetic parameters including block length, microstructure, and placement of structo-pendent and structo-terminal functionality for conjugation of active agents and targeting moieties. Amphiphilic (co)polymers synthesized by RAFT appear to be especially attractive for applications ranging from \textit{in vitro} delivery of therapeutics to environmental remediation. In many cases, polymerization, conjugation, loading (capture) and stimulus-induced release can be accomplished directly in aqueous media. This presentation will focus on synthetic strategies utilizing RAFT and facile side- and end-chain reaction chemistries to afford a) modular delivery architectures to aid in stabilization, trafficking and stimulus-induced release of “packaged” therapeutic small interfering RNA (siRNA) and b) unimeric micelles or “polysoaps” for oil spill remediation.
Control of functional group densities and chain flexibility are important parameters for tailoring the properties of macromolecules. The ease of synthesis of various substituted stilbene and maleimide monomers provides an enormous tool box for varying pendant group functionalities of the strictly alternating copolymers that result from radical initiated copolymerization of these comonomers. We have found, from persistence length measurements, that the steric congestion, resulting from incorporation of the stilbene units, along with the rigid cyclic anhydride or imide units in the backbone increases chain stiffness leading to a new class of semi-rigid macromolecules. Various examples of these alternating copolymers, exhibiting a wide range of properties, will be discussed.
Nanoporous polymers with controlled structure and porosity hold tremendous promise for various advanced technologies that include drug delivery and tissue engineering. Our strategy to prepare nanoporous polylactide, a biocompatible and biodegradable thermoplastic, relies on the self-assembly of polybutadiene-polylactide (PB-PLA) diblock copolymers followed by the selective degradation of polybutadiene using olefin metathesis. PB-PLA was obtained by a combination of anionic polymerization and controlled ring-opening transesterification polymerization. The molar mass of each block was tailored to target materials with either a lamellar or cylindrical microphase separated morphologies. Orientation of these nanoscale domains was induced in both thin films and monolithic samples. Selective degradation of polybutadiene was achieved by immersing the samples in a solution containing a ruthenium metathesis catalyst. Successful elimination of polybutadiene was assessed by size exclusion chromatography and $^1$H nuclear magnetic resonance spectroscopy. Direct imaging of the resulting nanoporous PLA was obtained by scanning electron microscopy.
146 - Electroactive polymers: Contrasting electropolymerization and solution processing for film formation

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Early development of electrochemically switchable and electrochromic polymers tended to use concurrent electropolymerization/deposition methods as the main process for electroactive film formation. While highly effective for probing fundamental properties, and providing conjugated polymers directly in their p-doped and conducting forms, low monomer conversions and film insolubility hampered macromolecular characterization and provide limitations to the method. Motivated by suggestions made by Professor Ken Wagener in the 1990s, we will detail how an electropolymerization-dominant synthesis program evolved into a soluble conjugated polymers effort. We will contrast the methods, bringing out situations in which electropolymerization yields materials with otherwise inaccessible properties (see image a), especially in the area of charge storage and supercapacitors. We will demonstrate how solution processable conjugated polymers (see image b) can have properties specifically optimized for photovoltaic and electrochromic properties.
147 - Using metathesis to control polymer morphology

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Precision polyolefins are made using metathesis polycondensation chemistry to regulate, without equivocation, branch identity and the exact location of the branch along a polyolefin backbone. The changes in morphology for these precision materials are clearly different from that found in conventional random ionomers. For example, a high degree of order in the form of layered lamellae becomes apparent in the carboxylic acid polymers that have been formed.

X-Ray scattering demonstrates a change in morphology, changing from clusters of ionic groups in conventional ionomers to sheets interconnected via precision hydrogen bonding – the polymer chain remains orthorhombic in spite of such a large “defect”. When the degree of ionic character becomes significant, then a reversion to highly ordered, cubic centered clusters becomes evident. Such clusters have never been observed previously and serve as a platform for further examination.

Molecular biomass plays an ever-increasing role in the development of renewable polymers. Most often desirable properties and applications are a combination of functions and macromolecular architectures. Over the last few years we have focused on delivering novel sustainable thermoplastics and biomaterials from renewable natural resources. Particularly, we target on a class of hydrocarbon-rich biomass to transform their hydrophobicity into resultant polymeric materials. This presentation will summarize a few projects related with these approaches and objectives.
149 - Characterization of hyperbranched polyesters using NMR spectroscopy

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The controlled delivery of actives is important in a variety of applications including the administration of pharmaceuticals, pesticides and antimicrobials. Dendrimers and hyperbranched polymers are particularly suited for controlled delivery because they are polymeric materials with molecular architectures providing the highest branching density of any polymeric material as well as the highest end group density. One potential delivery mechanism for biobased hyperbranched polyesters is the release of the active as the polymer biodegrades.

A series of hyperbranched polyesters based on glycerol, adipic and succinic acid were synthesized. The molecular weight of these polyesters was targeted using bimolecular nonlinear polymerization methodology which uses the stoichiometry of reactive functionality to control the molecular weight of the resulting hyperbranched polyester. The polyesterification reaction was characterized using both ¹H and ¹³C NMR spectroscopy. Actives were bound to the hyperbranched polyesters and their time-release characteristics defined.

Tuesday, September 10, 2013 02:05 PM
Monomer and Polymer Mimicry with Renewables (01:30 PM - 05:00 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
Polyurethanes are a versatile class of polymers used in industries ranging from construction to apparel. Most polyurethanes are petroleum-derived, but there is growing interest in substituting biorenewable materials. Significant advances have been made in the incorporation of biobased polyols, but there remains a need for practical biobased polyisocyanates. We designed a new class of diisocyanates from sugar-derived rigid bicyclic diols (e.g., isosorbide) and cyclic anhydrides (e.g., succinic anhydride). These diisocyanates are prepared on multi-gram scales in > 99 % purity through a four-step synthesis featuring esterification and a Curtius rearrangement. If a biobased cyclic anhydride is employed, then all of the carbons in the diisocyanate are plant-derived, and no stoichiometric petroleum-based reagents are consumed in the process. Polymerization of the diisocyanates with isosorbide and related diols yielded thermoplastic polyurethanes with molecular weights of ca. 24,000 and polydispersities of ca. 1.5. Thermal and mechanical characterization of these materials is ongoing.
151 - Polyacetals derived from biorenewable feedstocks as potential replacements for commodity plastics

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Commodity plastics (e.g., polyethylene, polystyrene, and polyethylene terephthalate) have become ubiquitous in the day-to-day lives of virtually everybody. Unfortunately, these plastics, however useful, persist in the environment long after use. These plastics also have the added disadvantage in that they still derive from petroleum and natural gas—both non-renewable resources. We have developed polymers that may pose as solutions to these issues. We depart from the all-carbon backbone motif (found in the majority of commodity plastics) to the inclusion of stimuli-responsive functional groups in our polymers. Of special interest is the acetal functionality. We have had great success utilizing our Acetal Metathesis Polymerization (AMP) technique to produce polyalkylene acetals from linear diols (Figure 1A). Now we attempt to broaden the scope of the reaction to include other functional groups like amides, ureas, and carbonates (Figure 1B). We have also had some success producing polyacetals from lignin-derived hydroxyaldehydes—4-hydroxybenzaldehyde, vanillin, and syringaldehyde. Firstly, these hydroxyaldehydes are linked with an ethylene bridge to yield dialdehydes that can then be reacted with either pentaerythritol or erythritol to yield rigid polyacetal ethers (Figure 1C). The inclusion of bulky aromatic subunits and fused ring systems within the polymer backbones imbues these plastics with noteworthy thermal and physical properties. With tunable physical, thermal, and degradation properties, our polymers should be suitable for a wide range of applications currently dominated by commodity (non-degradable) plastics.
The transformation of biomass, such as plant oils, to bicyclic polyesters will be described. In this regard, soybean oil provided a pathway to 1,4-cyclohexadiene (1,4-CHD). Obtaining 1,4-CHD from soybean oil provides an alternative to the Birch reduction of benzene. Isomerization of 1,4-CHD with continuous flow streamlines the synthesis of monomers for polyesters.
153 - Toward vegetable oil based thermoplastic polyurethanes

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In a context of limited supply of fossil resources, numerous initiatives to substitute fossil resources by renewable ones can be reported to prepare polyurethanes (PU). In this light, vegetable oils present an attractive potential thanks to their annually renewable availability, sustainability and variability thanks to present reactive sites.

In this work, vegetable oil based TPU are presented considering three strategies: (i) the classical isocyanate-alcohol approach, (ii) an isocyanate free carbonate-amine route and (iii) a phosgene free acyl azide or acyl hydrazide-alcohol method.

Following the classical route, new diols containing ester or amide linkages were designed from castor and sunflower oils to prepare TPU with amorphous to semi-crystalline morphology and tuned thermo-mechanical properties. [1,2]

Due to the hazard concerns of isocyanate and phosgene, the development of isocyanate and phosgene free strategies to bio-based PU is requested. Isocyanate free TPU with convenient molar masses were synthesized from diamines and castor oil based bis-cyclic carbonates. Using a different phosgene free method, fatty acid derivatives were successfully transformed into diisocyanate precursors such as diacyl azide or diacyl hydrazide. The obtained masked diisocyanates and diisocyanates respectively were reacted with alcohol moieties to obtain fully or partially bio-based TPU with adjusted properties. [3]


154 - Developing new biobased polymer applications from vegetable oils

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Compared with petrochemical polymers, biobased polymers seriously lack product variety. Only a few biobased polymers are available with sizable scales of commercial production, and the performance provided only matches a very small portion of the broad spectrum of properties of conventional polymers. There is a great need to develop new polymers from renewable feedstocks. In this work, we made a series of attempts to use vegetable oils for synthesizing new polymers and developing new applications. Syntheses of epoxies, curing agents, and block copolymers using vegetable oils were explored and properties and performance of the new polymer materials were studied. By manipulating the design of molecular structures of monomers and polymers, thermoplastic and thermosetting polymers of diverse properties can be prepared using these renewable feedstocks.
155 - Stimuli-responsive pyrrolidone-based polymers from pyroglutamic acid, a bio-derived resource

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A key challenge facing the production of bio-derived polymeric materials is the confining property profiles that arise from limitations in monomer diversity and chemical tunability, issues that must be addressed for current sustainable technologies to progress. Replacing non-renewable reagents with bio-derived alternatives that are readily derivatized has emerged as a promising strategy to address this challenge. This presentation discusses the preparation and potential applications of stimuli-responsive pyrrolidone-based polymers from pyroglutamic acid, a bio-derived resource.

Tuesday, September 10, 2013 04:30 PM
Monomer and Polymer Mimicry with Renewables (01:30 PM - 05:00 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
156 - Supramolecular peptide nanosystems for biomimetic extracellular matrix interactions

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Mimicking structure and function of the biological materials through programmed self-assembly of small molecules is important to study cell and extracellular matrix interactions. The self-assembly mechanism that forms the supramolecular aggregates includes noncovalent interactions such as hydrogen bonds, electrostatic and hydrophobic interactions. Diverse functional groups were incorporated into these nanostructures, for example bioactive peptide sequences, metal chelating groups and several other functional chemical groups. We study design and synthesis of peptide nanofiber scaffolds decorated with biologically important signals. We studied effect of three dimensional nanofibrous system on growth factor binding and its effect on cellular mechanisms for regenerative medicine applications. We design self-assembled supramolecular glyco systems for emulating glycosaminoglycan functions in the extracellular matrix. The high surface area of the nanofibrous system with various chemical groups can be also exploited to emulate enzyme active sites for developing biocatalysts in addition to extracellular matrix structural proteins' properties.
We prepared aliphatic polycarbonates with a simple ether functional group at the side chain by organocatalytic ring-opening polymerization of the corresponding cyclic monomers, yielding narrowly dispersed polymers. The number of platelets adhering on the polymer-coated substrates was almost identical to those on well-known antithrombotic polymers such as poly(2-methoxyethyl acrylate) and poly(2-methacryloyloxyethyl phosphorylcholine-co-n-butyl methacrylate). The hydration characteristics of the polycarbonates were evaluated by contact angle against water and thermal analysis of the hydrated polymers. The polymers were insoluble in water but showed decent hydrophilic surface properties, which may influence the platelet adhesion. The polycarbonates were found to be degraded by fairly slow enzymatic hydrolysis. Adhesion of other cell lines on the polymers was also assayed.
158 - New modulation of amyloid aggregation: First acceleration followed by inhibition

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Modulation of amyloid aggregation provides a promising strategy to combat amyloid-related diseases such as Alzheimer's, Huntington's, and Parkinson's. While most modulators of amyloid aggregation often involve simple inhibition or acceleration, we propose a new modulation pathway in which modulators involve both inhibition and acceleration. To demonstrate this concept, we introduce a new class of multivalent polymer small-molecule conjugates to modulate aggregation of amyloid β (Aβ) peptides associated with Alzheimer's. Our results show that the polymer small-molecule conjugates can first promote Aβ nucleation, and then inhibit further aggregation. We expect that this modulation pathway may shed some light on controlling amyloid aggregation and offer a new tool for therapeutics.
159 - Biodegradable polymer-drug conjugates for sustained delivery of anticancer drugs

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A variety of polylactide-based polymer-drug conjugates were synthesized, characterized, and further studied for drug delivery applications. Acetylene-functionalized polylactides were prepared, and then their reactions with functionalized anticancer drug molecules afforded polylactide-based conjugates with hydrolysable linkages connecting drug moieties. Nanoparticles with high drug loadings can be readily prepared from the conjugates without water-soluble groups by nanoprecipitation. On the other hand, the conjugates with hydrophilic poly(ethylene oxide) grafts can directly serve as water-dispersible drug delivery systems. Sustained release of anticancer drugs was achieved in both cases. Their significant therapeutic effects were verified by biomedical assessment.

Figure 1. Structural designs of biodegradable polymer-drug conjugates
a) without water-soluble side groups, and b) with hydrophilic side chains
160 - Drug-initiated, pH-responsive polycarbonate nanoparticles for controlled drug release

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Polymer drug conjugates have offered a promising solution to cancer treatment. The use of a polymeric carrier for therapeutic moieties has led to improved plasma lifetime, as well as enhanced targeting through the enhanced permeation and retention effect. Since their conception from Ringsdorf in 1975, these delivery vehicles have grown in popularity and have expanded to include many architectures including dendrimers, branched, brush, and block copolymers. Polymers such as poly(lactic acid) have found widespread use in this field due to their favorable biodegradable characteristics and safety profiles. The release of drug from poly(lactic acid) may not be controlled, however, due to the release of drug-oligomer species caused by degradation along the ester backbone in addition to the triggerable drug linker. The use of a more robust, slowly degrading backbone may tune the release such that oligomeric drug species are reduced or eliminated. In this study, we investigate the utility of biodegradable poly(trimethylene carbonate) as a more robust polymer backbone for a polymer-drug conjugate. To ensure a high drug loading, polymerization is initiated with our model drug, camptothecin, to form nanoconjugates. These nanoconjugates are then assembled into nanoparticles and their degradation and release properties are investigated.
Poor permeability of cellular plasma membrane remains a major drawback for non-invasive treatment of solid tumors. Therefore, the design of versatile nanocarriers providing long circulation time and promoting the cellular uptake of a various range of cargoes is of prime importance. Towards this goal, we have developed cell-penetrating nanoparticles from amphiphilic peptide-$b$-polymer molecular chimeras. The Tat$_{47-57}$ sequence (YGRKKRRQRRR) from HIV-1 TAT protein is a hydrophilic peptide presenting tremendous cell penetrating abilities.[1] Poly(trimethylene carbonate) (PTMC) is a biocompatible hydrophobic polymer with compelling self-assembly properties.[2] Amphiphilic Tat-$b$-PTMC chimeras were synthesized with high molecular precision, thoroughly characterized and self-assembled in aqueous buffer into size-tunable, highly monodisperse core-shell nanoparticles, presenting a full Tat corona.[3] Their transduction ability in vitro and interaction mode with phospholipid membranes were studied with a view to correlate their highly controlled chemical and physico-chemical profiles with their biological properties. This interdisciplinary approach shed light on the interactions at play in the cellular uptake process. With the ultimate goal of improving pharmacological characteristics, we have developed an ON/OFF PEGylation strategy to harness the cell penetrating power of those biomacromolecular self-assembled systems, which hence represent promising vectors for drug delivery in tumors.

162 - Polymer-peptide conjugates inhibit amyloid β aggregation

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Amyloid β peptide (Aβ) aggregation is the process of forming insoluble proteinaceous aggregates and associated with Alzheimer’s disease. Although it is not yet clear by which mechanism toxic Aβ oligomers and fibrils form, strategies that intervene with the Aβ aggregation and prevent fibril formation have shown their promises in therapeutics for Alzheimer’s disease. Here, we introduce multivalent polymer-peptide conjugates (mPPCs) to design new inhibitors of Aβ aggregation. We designed and synthesized mPPCs by coupling peptide-based inhibitors to polymer backbones. Our preliminary data show that mPPCs exhibit far more effective inhibition against Aβ aggregation than their monomeric counterparts, and that the inhibitory activity may result from stabilization of Aβ oligomers. It can be anticipated that mPPCs may provide a new avenue to develop diagnostics and therapeutics for Alzheimer’s disease and others.
We report a near infrared light (NIR)-responsive polymeric therapeutic system, which can facilitate instant drug release upon NIR irradiation. The polymer is prepared via condensation polymerization of bis-hydroxyl containing drug molecules and NIR-responsive 2,6-bis(hydroxymethyl)aniline (BHA) derivatives. The resulting poly(carbonate) structure releases the incorporated drugs when the pendent NIR-responsive domain is cleaved that results in unstable 2,6-di-substituted aniline structure subject to drug release via self-eliminating processes. Because NIR light is biocompatible and has excellent tissue-penetrating property, the NIR-responsive polymeric therapeutic we designed can potentially be used for in vivo drug delivery applications.
Hyaluronic acid–conjugated graphene oxide (GO) / photosensitizers (Ce6) nanohybrids were developed for cancer targeting and photoactivity switchable nanoplatforms for photodynamic therapy (PDT). HA-GO conjugates with size below 100 nm were prepared and characterized by 1H-NMR, FTIR, UV, TGA, AFM, DLS and MTT assays for the evaluation of chemical structure, morphology and biocompatibility. The high loading of Ce6 onto HA-GO nanocarriers was found to be mainly due to π-π stacking as well as hydrophobic interactions. Through in vitro cell studies, we demonstrate that the cellular internalization of HA-GO/Ce6 nanohybrids was much more effective when compared with free Ce6. The active targeting of HA-GO/Ce6 nanohybrids to cancer cells that overexpresses HA receptors was also confirmed by comparison with several control groups. The photoactivity of Ce6 adsorbed on HA-GO nanocarriers was mostly quenched in aqueous solution to ensure biocompatibility, but was quickly recovered after the release of Ce6 from HA-GO nanocarriers upon cellular uptake. Consequently, the PDT efficiency of HA-GO/Ce6 nanohybrids was significantly improved 10 times more than that of free Ce6, as well documented by MTT and LIVE/DEAD assays. Our work thus highlights the great promise of HA-GO/Ce6 nanohybrids for cancer-targeted PDT.
165 - Acid-labile functional poly(ethylene oxide)-block-polyphosphoester-graft-paclitaxel conjugates as a pH-sensitive platform for paclitaxel delivery

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There has been increasing interest to develop new types of stimuli-responsive drug delivery vehicles with high drug loading and controlled release properties for chemotherapeutics. An acid-labile polyphosphoester-based degradable, polymeric paclitaxel (PTX) conjugate containing ultra-high levels of PTX loading via pH sensitive β-thiopropionate linkage between PTX and polymer has been generated as a potentially effective anti-cancer agent. Poly(ethylene oxide)-block-polyphosphoester PTX drug conjugate (PEO-b-PPE-g-PTX) was synthesized by organocatalyst-promoted ring-opening polymerization of 2-(allyloxy)-1,3,2-dioxaphospholane 2-oxide (ADP) followed by thermo-promoted thiol-ene click conjugation of a thiol functionalized PTX prodrug to the pendant alkene groups of the polymer. The PEO-b-PPE-g-PTX formed well-defined micelles in aqueous solution, by direct dissolution into water, with the number-average hydrodynamic diameter of $114 \pm 31$ nm. The conjugate had PTX loading capacity as high as 53 wt%, and a maximum PTX concentration of 0.68 mg/mL in water, which is much higher than the aqueous solubility of free PTX. The PEO-b-PPE-g-PTX exhibited accelerated drug release under acidic conditions (50 wt% in 8 d) compared to neutral conditions (20 wt% in 8 d), due to their acid-labile β-thiopropionate linkages between PTX molecules and the polymer backbone. The positive cell-killing activity of PEO-b-PPE-g-PTX against two cancer cell lines was demonstrated, and the presence of pendant reactive functionality provides a powerful platform for future work to involve conjugation of multiple numbers and/or types of targeting ligands, other drugs and imaging agents to achieve chemotherapy and bioimaging.
A series of μ-ABC miktoarm copolymers were synthesized via Tier 1 self-assembly from block copolymer precursors. This method involves the association of two block copolymer precursors bearing short complementary associating blocks that are labeled with corresponding carboxylic acid and amine associating groups, respectively. One of these precursors is a triblock copolymer with a short central associating block, while the other precursor is a diblock copolymer that also bears a short associating block. A coupling agent is then added to stitch the pre-associated chains together permanently, thus yielding the m-ABC miktoarm copolymers. In selective solvents, these μ-ABC miktoarm copolymers underwent Tier 2 self-assembly to form various micellar structures, such as hamburger micelles, three-lobed structures, and vesicles. The vesicles were especially fascinating, as they incorporated uniform nanochannels in their vesicular walls. Fluorescence analysis indicated that the rate of fluoresceine release from these capsules into aqueous solution could be tuned by adjusting the pH. These results demonstrated that the vesicular walls incorporated pH-gated nanochannels. These capsules and their future derivatives might be useful for controlled drug delivery applications.
167 - Versatile constructions of asymmetrically-functionalized polymer nanoparticles for the self-assembly of superstructures

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Inspired by the many selective, hierarchical assembly processes that afford complex materials in Nature, the directional organization of asymmetrically-functionalized nanoparticles into complex structures has attracted much attention. However, the routine ability to build hierarchical superstructures from nanoscale building blocks by controllable inter-nanoparticle association is not yet possible due to the challenge of the construction of asymmetrically-functionalized nanoparticles with efficient control over surface chemistries. In this presentation, two strategies towards the symmetrically-functionalized nanoparticles with anisotropic distributions of chemical functionalities will be discussed. A Janus-faced polymer nanoparticle that presents two orthogonally click-reactive surface chemistries, thiol and azido, has been generated by a recyclable strategy that involves reactive functional group transfer by templating against gold nanoparticle substrates. Another stepwise self-assembly strategy produced nanoparticles with sandwich-like distribution of crown ether functionalities by the supramolecular crown ether ammonium interaction-mediated inter-particle association and the local phase separation of unlike hydrophobic polymers.
168 - Block copolymer thin film orientation

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Block copolymer thin film orientation control remains an important area of research for applications ranging from organooptoelectronics, nanoporous membranes, to advanced lithography. Orientation of etch-resistant silicon-containing block copolymers requires control of the top interface that is enabled herein by polarity switching top coats. A versatile 30 second thermal annealing process that produces defect-free perpendicular features of a silicon-containing block copolymer is described that requires only a spin-coater and hot plate.
The need for small-scale structures with controlled morphology and chemical functionality, surface energy and spatial selection continues to grow in importance. New coatings, microelectronic and biomedical applications, sensors and related technologies all call for such surface control. By using self-organizing materials such as block copolymers and block copolymer brushes it is possible to control both surface chemical composition and to determine spatial arrangement. Patterned surfaces can be formed through careful selection of the component blocks from polymers that either crosslink or cleave under appropriate radiation exposure. In this study, block copolymer thin films were produced by spincoating and then solvent annealed to create long-range order. By incorporating photoactive compounds in the block copolymer, it was possible to subsequently crosslink one of the blocks and then photochemically remove the second block to form well aligned dot or line arrays. Chemically similar diblock brushes were grown using surface initiated ATRP on silicon. We have shown that this strategy enables the formation of sub-surface nanochannels and we believe will enable the formation of nanosheets and membranes with controlled surface functionality.
170 - Dynamic-covalent star nanostructures prepared from functional block copolymers obtained by RAFT polymerization

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Macromolecular star architectures, with several polymer chains connected to a central core, are interesting due to their well-defined and compact structure, a high density of functional groups, and unique properties in solution and in the melt. However, adding a characteristic of dynamics (e.g., the potential for controlled degradability) to star polymers is highly desirable in many applications, including coatings, drug-delivery, and biotherapeutics. Both supramolecular and dynamic-covalent chemistry impart dynamics and reorganizability to the polymeric materials. While retaining the benefits of reversibility, the higher strength of many dynamic-covalent bonds, as compared to supramolecular interactions, leads to increased structural stability. The research to be discussed here demonstrates the "arm-first" route to star polymers by dynamic-covalent crosslinking of well defined functional block copolymers synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. Three different types of dynamic-covalent chemistries, namely boronic ester formation, Diels-Alder cycloaddition, and disulfide chemistry were utilized for synthesis of the core-crosslinked stars. The reversibility of the stars induced by specific stimuli (addition of a competing mono/multifunctional diol in case of the boronic ester linkages, heating/cooling in case of the Diels-Alder linkages, and reduction/oxidation in case of disulfide linkages) was further studied over multiple cycles.
New, ordered, nanophase-separated, imidazolium ionic liquid (IL)-based block copolymers (BCPs) were prepared via the sequential, living ring-opening metathesis polymerization (ROMP) of an IL-based monomer and one or more mutually immiscible comonomers. This novel type of ion-containing BCP system forms various ordered nanostructures in the melt state via primary and secondary structure control. Control of block compositions, control of block and overall polymer lengths, and synthetic monomer design were found to directly affect the ordered polymer assembly. Supported, composite membranes of these new BCPs were fabricated, and the effects of BCP composition and nanostructure on CO$_2$/light gas transport properties were studied, since it is known that materials morphology can influence membrane transport performance. These nanostructured BCPs represent innovative polymer architectures for potential CO$_2$/light gas separation applications, given the high solubility of CO$_2$ in imidazolium IL-based materials.
172 - Shape amphiphiles based on molecular nanoparticles: Precision synthesis, versatile self-assembly, and diverse function

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The assembly of shaped amphiphiles is strongly driven by their interactions and the constraints imposed by the rigid shape of the molecular segments. Our research focuses on the structure-property relationship from design and synthesis of specific shape amphiphiles based on molecular nanoparticles up to the organization of these molecules into large scale structures. The particles of interest are fullerene ($C_{60}$) and polyhedral oligomeric silsesquioxane (POSS). By diverse periphery functionalization, they serve as versatile building blocks for the construction of giant shape amphiphiles with controlled hierarchical structures in multi-dimensions across different length scales. For example, a 1D helical line structure was obtained in a porphyrin-$C_{60}$ dyad with a $129_{44}$ helix, where the $C_{60}$ forms three continuous channels around the column of porphyrin. Owing to symmetry breaking both in geometry and chemistry, a 2D sheet structure was obtained in two distinct types of molecular Janus particles: the POSS-$C_{60}$ dyad and the POSS-POSS dyad. The 3D structure with 6-20 nm feature size was generated by a new class of materials called giant surfactants and lipids. In solution, they self-assemble into spheres, cylinders, and vesicles with highly stretched polymer chains in the assemblies. In the bulk, they exhibit diverse phase structures such as sphere, cylinder, double gyroid, and lamellae. The synthesis of these shape amphiphiles with molecular precision has enabled the tailoring of their self-assembling behavior and structure and the elucidation of the structure-property relationship.

Tuesday, September 10, 2013 04:00 PM
DSM Science and Technology Award (01:30 PM - 04:25 PM)
Location: Hyatt Regency Indianapolis
Room: Discovery A
Nanoscale amphiphilic macromolecules (AMs) comprised of a sugar backbone, branched aliphatic chains, and a hydrophilic poly(ethylene glycol) (PEG) tail have shown promise as bioactive delivery systems. These AMs can self-assemble into thermodynamically stable micelles or can be formulated into kinetically trapped nanoparticles, providing the ability to deliver hydrophobic drugs. Furthermore, such AMs have exhibited inherent bioactivity against atherosclerosis, a leading cause of cardiovascular disease, through interacting with macrophage scavenger receptors. As the hydrophobic portion of AMs enables their association with both hydrophobic drugs and receptor binding pockets, manipulation of the aliphatic chain structure may strengthen AMs' interactions with specific target sites or drug molecules and thus enhance their biomedical potential. To this end, novel AMs were synthesized with heteroatom-containing, end-modified aliphatic chains and their physicochemical and biological properties assessed. Within these studies, dibenzyl L-tartrate hydroxyl groups were acylated with modified aliphatic chains, and the resulting intermediate was deprotected to give a sugar-based hydrophobic segment, which was subsequently PEGylated to yield the final AM. The AM structure was confirmed by nuclear magnetic resonance spectroscopy and gel permeation chromatography. Fluorescence spectroscopy and dynamic light scattering were used to determine AM critical micelle concentrations and hydrodynamic diameters, respectively. Upon complete physicochemical characterization, the novel AMs' bioactivities were assessed to measure their potential as delivery vehicles and their abilities to interact with macrophage scavenger receptors.
We report the design of non-viral gene delivery polypeptide template derived from N-carboxyanhydride polymerization and click chemistry. Poly(propargyloxybenzyl-L-glutamate) was synthesized via ring-opening polymerization of propargyloxybenzyl-L-glutamic acid N-carboxyanhydride. The resulting polypeptide was post-functionalized with various side chains through click chemistry. We investigated the side chain length and the types of amine group in attempts to understand their effects on gene transfection efficiency. Polypeptides bearing guanidine-terminated side chains exhibited much higher transfection efficiency than those with amine terminated side chains. Side chain length did not show dramatic effect on transfection efficiency and polypeptides with very long, hydrophobic side chain displayed increasing toxicity.

Figure 1: A) The synthetic route of Poly(propargyloxybenzyl-L-glutamate) (PPOBLG) and PPOBLG-X. B) Side chains bearing primary amine group with different length. C) Side chains bearing guanidine group with different length. D) Schematic presentation of cationic α-helical polypeptide.
Lactosome is a core-shell type polymeric micelle of ca. 35 nm in diameter, which is consisted from poly(L-lactic acid)-block-poly(sarcosine) (PLLA-block-poly(Sar)) amphiphilic polydepsipeptide. Lactosome shows good blood circulation behavior and accumulates highly at transplanted tumor region by the enhanced permeation and retention (EPR) effect. Therefore, utilization of Lactosome as nano-carrier for drug and/or imaging agent delivery has been expected.

In order to evaluate biodistribution of molecular assemblies, radioisotope (RI) labeling method is often utilized. Core-shell type micelle has potential to encapsulate hydrophobic compound in its hydrophobic core, and therefore RI-labeled micelle was prepared by mixing hydrophobic RI-labeled compound. Biodistribution of Lactosome has been discussed by using ¹²⁵I-labeled Lactosome, which was prepared from the mixture of hydrophobic ¹²⁵I-labeled PLLA and the amphiphile.

However, different from low molecular weight compounds, not only decomposition of the micelle, but also degradation of the amphiphilic polymer are occurred in parallel, which make it difficult to clear in vivo dynamics of Lactosome. Biodistribution of ¹²⁵I is expected to be well-correlated with dynamics of Lactosome when ¹²⁵I-labeled PLLA was stably encapsulated into Lactosome, but is strongly reflected hydrophobic PLLA character after Lactosome decomposition. We newly synthesized ³H-labeled PLLA-block-poly(Sar) as Lactosome constituent. ³H-labeled Lactosome was prepared from the amphiphile, and time courses of ³H biodistribution up to 48 h from the administration were evaluated. In this study, effect of RI modification methods on their biodistribution is discussed.
Hydrogen sulfide (H₂S) is known for its distinct smell and has been shown to play an important role in many different biological functions. Most of the H₂S produced in the body originates from the reaction of cysteine with the enzymes cystathionine beta-synthase and cystathionine gamma-lyase. These enzymes facilitate the production of H₂S in many biological systems including the neuronal, cardiovascular, respiratory, liver, immune, renal, gastrointestinal, reproductive, and endocrine systems. A slow, steady release of nanomolar to micromolar concentrations of H₂S is important for its applications as therapies in biological systems because H₂S is toxic at concentrations of 100 mM. Although small molecules are known to deliver H₂S by hydrolysis in water or by reaction with enzymes, no polymers are known that degrade to release H₂S. We developed the first synthesis of polymers based on poly(lactic acid) that contain functional groups known to release H₂S in cells. These polymers release H₂S over prolonged periods of time and at steady rates. The monomers were synthesized by attaching lactide to H₂S-releasing molecules – allyl sulphide and 4-hydroxybenzothioamide – using a thiol-ene reaction and formation of a disulfide bond. The monomers polymerized under mild condition using DMAP as a catalyst. These polymers were readily fabricated into microparticles which released H₂S.
Naturally occurring antimicrobial peptides (AMPs) are amphipathic molecules that have been shown to eliminate a wide range of bacteria. The hydrophilic regions of AMPs have an abundance of lysine and arginine amino acid residues, which are protonated and positively charged under physiological conditions. Due to electrostatic attraction, the positively charged AMPs bind with the negatively charged bacterial cell membrane and promote cell death. Literature on AMPs mimics has shown, however, that depending upon the prevalence of either lysine or arginine, the mechanism of cell death varies from membrane disrupting to cell penetrating, respectively. The goal of this research, therefore, is to determine the bacterial toxicity and selectivity of AMP mimics that are comprised of varying ratios of aminopropyl methacrylamide (APMA), a lysine mimic, and guanadinopropyl methacrylamide (GPMA), an arginine mimic, and analyze how compositional changes affect the mechanism of cell death in gram-positive (B. subtilis) and gram-negative (E. coli) bacteria. This is accomplished through the synthesis, via RAFT polymerization, of various statistical copolymers that demonstrate well-defined compositional ratios of APMA and GPMA, antimicrobial, biocompatibility and membrane disruption testing.
Due to poor water solubility of hydrophobic anti-cancer drugs and inefficient tumor targeting delivery, the development of safe and efficient drug delivery systems (DDSs) for clinic application is still a challenge. Herein, we have constructed a facile DDS based on biodegradable polymeric micelles which cross-linked by stimuli-cleavable drug dimers. Firstly, a double hydrophilic copolymer containing cyclodextrin pendant groups was synthesized by ring-opening polymerization and click chemistry and a drug dimer was formed by linking two doxorubicins with disulfide bond. Secondly, they co-assembled into micelles in water via host-guest interaction and the average size was around 100 nm. It is fit for passive targeting delivery by EPR effect. Drug dimers were utilized as cross-linkers to stabilize the micelles. Owing to the disulfide bonds of drug dimers, these supramolecular micelles were dissociated by treating with dithiothreitol (DTT). In the meanwhile, the free drugs were recovered and released from cavities of cyclodextrins because of dynamic equilibrium. Therefore, it can be served as a novel and controlled drug delivery system.
179 - Functionalization of pentablock copolymers with pathogen-mimicking sugars by click chemistry for targeted delivery

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Biocompatible polymers with controlled architectures such as pentablock copolymers are strong candidates for subunit vaccine adjuvants as they offer sustained gene and drug co-delivery. Functionalization with pathogen-mimicking sugars such as mannose has been shown to increase uptake by antigen presenting cells. Herein, we report studies toward the functionalization of pentablock co-polymers with an azide end and the synthesis of sugars containing an alkyne moiety. The modification of the polymer with carbohydrates by Huisgen-type cycloaddition and analysis of the attachment by various spectroscopic techniques, including the use of N-15 labels, will be discussed.
180 - Maximizing gene delivery efficiencies of cationic helical polypeptides via optimized combination between membrane penetration and cellular targeting

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In non-viral gene delivery, vectors with high transfection efficiencies often suffer from high toxicities, making it unlikely to improve their efficiencies by increasing the dosage. In this study, we developed a ternary polyplex system which comprised of a membrane-active cationic helical polypeptide (PVBLG-8), a cationic helical polypeptide (PVBLG-7) capable of mannose receptor targeting, and a plasmid DNA (pDNA). The presence of PVBLG-7 moiety notably enhanced the cellular uptake and transfection efficiency of the polyplex in a variety of mannose receptor-expressing cells, such as HeLa, COS-7, and Raw 264.7, and showed limited effect on the membrane permeability of PVBLG-8 or overall cytotoxicity of the polyplex. The self-assembly composition of the ternary polyplex could be readily tuned and the optimal formulations of the ternary complexes with a proper balance of the membrane activity and the targeting capability were easily identified in each specific cell type, which displayed desired cell tolerability and markedly outperformed the PVBLG-8/pDNA binary complexes and the commercial reagent Lipofectamine 2000 in terms of transfection efficiency. This study provides an effective and facile strategy to overcome the efficiency-toxicity inconsistency of non-viral vectors and strengthen their delivery efficiencies, providing insights into the design of effective and safe non-viral gene delivery vectors.

Monday, September 9, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Indiana Convention Center
Room: Halls F&G

Tuesday, September 10, 2013 05:30 PM
Biomacromolecules for Therapeutics and Diagnostics Delivery (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
One of the current motivations to improve drug delivery devices is to increase their circulation time in the bloodstream. These devices are usually eliminated before they achieve a therapeutic effect by either a passive or an active mechanism. The passive mechanism is related to diffusion through pores into tissues or into urine. The active mechanism is related to elimination via opsonization, a process that begins with protein attachment onto the device. To reduce elimination by diffusion through pores, the device should have a molecular weight between 30-50 kDa. It is preferable if it has a 3D extended molecular conformation in water, branched structure, and low flexibility.\(^1\) In order to reduce elimination via opsonization, PEG coatings with linear architectures have been used.\(^2\) This presentation will show three different types of architectures and different number of end groups for self-assembled and unimolecular micelles with PEG coatings. Fluorescence and/or biodistribution studies will be shown.

References


Monday, September 9, 2013 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Indiana Convention Center
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Tuesday, September 10, 2013 05:30 PM
Biomacromolecules for Therapeutics and Diagnostics Delivery (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
Axillary lymph node dissection during breast cancer surgery often leads to secondary lymphedema, causing swelling of the patient’s limb, chronic pain and an overall decreased quality of life. Currently, no cure exists for secondary lymphedema. Current treatments focus on manual drainage of fluid or regeneration of vessels through molecular cues such as vascular endothelial growth factor C (VEGF-C), however this technique has not provided a cure for this condition. Previous results by our lab suggest that interstitial flow is required prior to the formation of competent vessels. Here, we propose a novel method combining nanofiber guidance of cells and a drug releasing polymer to repair the severed lymphatic vessel while promoting interstitial flow. Nitric oxide (NO), a potent vasodilator present throughout the body, having a short half-life, and shown to be present within the lymphatic vasculature, will be incorporated into a novel poly L-lactic acid (PLLA) derived material. In this work, nanofiber guides will take the form of electrospun fibers, having been shown previously to promote lymphatic endothelial cell (LEC) migration. Briefly, the PLLA will be modified with an NO releasing nitrosothiol (S-nitroso-N-acetylpenicillamine), capable of controlled release through photolytic cleavage of a nitroso group tethered to the PLLA backbone (see Figure 1). The NO releasing polymer will be electrospun in a highly aligned manner to ultimately develop a small diameter lymphatic conduit capable of regenerating severed lymphatic vessels.
183 - Controlled nitric oxide releasing dendronized poly(vinyl) chloride for improving biocompatibility of implantable devices

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There is huge potential to improve patient treatment by obtaining physiological measurements of important analytes (i.e., $P_{O_2}$, $P_{CO_2}$, pH, glucose, etc.) in real-time data using implantable sensors. Although miniaturized sensors have existed for several decades, most of this technology never becomes widely used due to unreliable analytical data from implanted sensors caused by the biological response from the body. A possible option to overcome this complication with blood contacting devices is through the utilization of nitric oxide (NO). NO is a free radical gas that is produced in our body that has a variety of important functions. A specific example demonstrating the importance of NO is seen in endothelial cells that line our vasculature where NO is produced continuously at an estimated flux of $1\times 10^{-10}$ mol cm$^{-2}$ min$^{-1}$, which prevents platelets from becoming activated and maintains vascular tone. The objective of this research is to develop a high capacity, controlled NO releasing material by covalently linking hyperbranched polyamidoamine molecules to the backbone of poly (vinyl chloride) (PVC) to create a dendronized polymer with high functionality. The structure is then further modified to release NO through homolytic cleavage using light by covalently linking S-nitroso-N-acetylpenicillamine (SNAP) to the primary amine sites. An example of the final derivatized polymer is shown in figure 1. We present the synthesis, characterization and NO release properties of this modified NO-releasing PVC material.
184 - Multistructural domain peptide vesicle design

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Replicating natural structures is a challenge in peptide and protein design. By targeting vesicle-like materials one can explore applications in new drug carriers, novel transmembrane energy transduction processes, and confined space reactivity. Here we employ a multidomain peptide that focuses entirely on structure guided assembly. The aDIMER-A-b design to be presented employs a structural motif where a coiled-coil water soluble dimer is linked to a b-sheet domain by a series of aliphatic amino acids. The overall design elicits a step-wise self-assembly strategy yielding a tapered dimeric structure that ultimately assembles into a vesicle like structure. The polar head is a dimeric coiled-coil, leucine zipper that is rich in positive lysine residues at the vesicle surface to promote electrostatic repulsion that tapers into a neutral, helical poly-alanine segment to initiate a hydrophobic collapse. The second segment is an unstructured and highly aliphatic aminohexanoic acid segment that further promotes hydrophobic collapse. And the final segment, the interior of the vesicle was designed as a b-sheet forming segment to promote a tight attractive interior that is capped by alternating charged (Glu and Lys) residues to complete the overall bola-amphiphilic structure. We submit that the coiled-coil domain initiates the self-assembly process via dimerization. This is followed by hydrophobic collapse of the water insoluble aminohexanoic acid interior. Here, we will present our results from stained TEM and cryoEM studies in addition to SAXS results that suggest vesicles have been formed. A second peptide with a mis-designed helical segment yields extended fibers that suggests the importance of the helical domain of the design.

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Tuesday, September 10, 2013 05:30 PM
Biomacromolecules for Therapeutics and Diagnostics Delivery (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
185 - Synthesis of chitosan:pectin nanoparticles for improved wound healing

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Chronic wounds are a significant problem: among the roughly 2 million nosocomial infections that occur annually within the US, nearly 125,000 result in lower extremity amputation. Chitosan and pectin, natural polysaccharides that behave as weak polyelectrolytes in solution, can create nanoparticles that may exhibit wound healing properties superior to that of current wound healing technology. Chitosan displays antibacterial properties and pectin helps to prevent persistent acute inflammation. Here, 460 nm to 1.0 μm chitosan:pectin nanoparticles were generated via an ionic suspension. Systematically, the physiochemical properties were investigated as a function of mass ratio, concentration, addition order, and pH. The morphology, size, and zeta potential of the chitosan:pectin particles were characterized using transmission electron microscopy, dynamic light scattering, and electrophoretic light scattering, respectively. Due to the presence of chitosan, the generated particles had a high positive surface charge with a zeta potential ranging from +19 to +47 mV. The size and surface charge of the particles were found to have an inverse correlation to solution pH: both decrease with increasing pH until dissociation at pH 6. Particles at various mass ratios demonstrated decreasing surface charge over the course of two weeks before losing stability. Our results indicate that chitosan:pectin particles could potentially be used for degradable wound dressing applications that would benefit from the intrinsic properties of chitosan and pectin.

Proposed structure of chitosan:pectin nanoparticles generated via water-based ionic gelation method.
Successful delivery of therapeutics requires a stable system with minimal drug leakage when circulating in physiological condition but quick release of drugs in pathological sites. To achieve this goal, a pH responsive polymer-based system was developed. The pH-cleavable amphiphilic macromolecules (AMs) consist of a hydrophilic poly(ethylene glycol) (PEG) chain and a sugar backbone modified with hydrophobic alkyl chains connected by a pH-cleavable hydrazone linkage. These AMs can self-assemble into micelles in aqueous media with a hydrophobic core and a hydrophilic PEG shell and thus have the ability to encapsulate hydrophobic drugs. Furthermore, the PEG chains on the micelle surface can prevent any non-specific protein binding leading to enhanced stability when circulating extracellularly. Vitamin E was encapsulated in the micelles using dialysis method. The vitamin E-loaded micelles maintained their integrities under physiological pH (e.g., pH = 7.4). By using HPLC, vitamin E release from the micelle was monitored at pH = 7.4 and 5, which are physiological and intracellular conditions, respectively. It was demonstrated that Vitamin E release was enhanced at pH = 5 compared to pH = 7.4 due to the hydrolysis of the hydrazone linkage which is proved by $^1$H NMR. These studies showed that pH-cleavable AMs have the potential to be used for systemic drug delivery due to their stability under physiological conditions and increased drug release profile under intracellular conditions.
The development of polypeptide composite particles, PCPs, made of a silica core and a polypeptide shell results in unique properties that cannot be achieved by the core or polymer shell alone. Many polypeptides undergo conformational transitions, and when tethered to a spherical bead the resulting hybrid is similar in overall structure to protein-caged materials like viruses. Good control over the core size coupled with the ability to change the secondary structure by changes in pH, temperature or solvent offers a platform to study virus-like conformational transitions on curved surfaces. These transitions may have materials science applications. The polymerization of PCPs through photo-induced cross-linking of unmodified proteins, PICUP, yields unusual polycollloid morphologies. This work was supported by the Grant DMR-1005707 from the National Science Foundation.
188 - Blend system hydrogels with enhanced mechanical properties for islet cell delivery carrier

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Hydrogels are of great interest as potential biomaterials for sustained delivery of various therapeutic agents such as cells, proteins and drugs. Especially, Pluronic F127 is considered as fascinating materials due to its thermo-sensitive gelation behavior in aqueous solution. However, the Pluronic F127 hydrogel is so soft that it easily disintegrated and dissolved out in physiological condition. To overcome this problem, by thiol-disulfide exchange reaction, more robust hydrogel with novel type of thermo-sensitivity was designed. It was hypothesized that the micelle packing induces gelation and further chemical reaction hinders the breaking of highly packed structure. Firstly, the end group of Pluronic F127 was converted to thiol groups (SH) and ortho-pyridine disulfide groups (OPSS), respectively. Each modified Pluronic F127 was blended and the properties of the hydrogel were examined. By in vitro and in vivo experiments, we confirmed that the resultant hydrogel showed highly increased mechanical properties without any noticeable toxicity compared to the same concentration of unmodified Pluronic F127 hydrogel. With this hydrogel, we decided to use it for islet cell delivery, so the rat islet cells were isolated and mixed with the hydrogel and injected to the mouse with diabetes mellitus. As a result, the blood glucose level of the mouse was controlled for more than 10 days and we expect that this blend system hydrogel can be applied to the cell delivery system.
Cardiovascular diseases, especially those triggered by inflammatory reactions which lead to atherosclerosis, are a major cause of mortality in developed countries. Accumulation of pathogenic oxidized low density lipoproteins (oxLDL) in vascular intima and their subsequent uptake by macrophages initiates secretion of inflammatory mediators. Ultimately burst of macrophages and formation of plaque leads to atherogenesis. An innovative way to mitigate this problem is through inhibition of macrophage scavenger receptors responsible for uptake of oxLDL. Nanoscale amphiphilic macromolecules (AMs) based on sugar backbone, aliphatic chains, and hydrophilic poly(ethyleneglycol) (PEG) have shown promising results as anti-atherogenic agents. AMs competitively inhibit binding of oxLDL to scavenger receptors through electrostatic and hydrophobic interactions. Our studies have shown that seemingly insignificant changes in relative orientation of the aliphatic chains had a detrimental effect on the bioactivity. Therefore the effect of chemical modification of key structural motifs, specifically ester linkages which play a great role in molecular stability and binding affinity, was pursued to investigate their influence on the bioactivity. The hypothesis was that their replacement by ethers, amines or amides could reinforce the binding and improve stability. The design, synthesis, and characterization of these modified AMs will be presented. Additionally, their effect on inhibition of oxLDL uptake and specific binding to scavenger receptors will be discussed. These results provide valuable insights towards elucidation of structure activity relationship which guide the development of more potent AMs.
190 - Magnetic field-reactive macroporous ferrogels

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Hydrogels are expected to be the most excellent scaffolds in the field of biomedical engineering such as protein, nucleotides, and cell delivery system. A hydrophilic environment provided by the hydrogels has an excellent condition for cell viability and proteins without denaturation. Especially, porous hydrogels have been widely used in a large field of medical engineering, such as cell-based therapies or drug delivery systems.

Herein, a porous hydrogel was formed with PVP coated iron oxide nanoparticles and acrylamide and N,N-methylenediacrylamide monomers in ammonium persulfate and N,N,N',N'-tetramethylethylenediamine initiating system. The gelation was achieved by cryogel method under the freezing condition, around -20 °C. In freeze-and-thaw process, the iron oxide nanoparticles were homogenously entrapped in the porous hydrogel matrix known as macroporous ferrogel. By Scanning Electron Microscope

![SEM image of the ferrogel. Pore size: 300 – 400 µm](image)

, the average size of the pore in ferrogel was measured around 200 micrometers, which indicated a macroporous structure. A physical property of the hydrogel altered with an encapsulation of iron oxide nanoparticles and at 4 wt% monomer concentrated solution, the proper gelation was formed. The ferrogel was shrunk and expanded under the magnetic field pulse and the extents of shrinkage and expansion was strongly dependent on the magnetic forces. This porous ferrogel can be a potential candidate for applying to regeneration of stem cell differentiation toward specific cell lines with magnetic stimulations.

Tuesday, September 10, 2013 05:30 PM
Biomacromolecules for Therapeutics and Diagnostics Delivery (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
Amphiphilic poly(vinyl ester) copolymers and homopolymers for antimicrobial applications

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Superbug (bacteria) infections have become a serious challenge to the medical communities. Cationic amphiphilic synthetic polymers act to rupture the cell membrane, hence can be expected to minimize the evolution of bacterial resistance. Although, synthetic amphiphilic polymers have attracted substantial research interest in recent years, there are no reported antibacterial polymers based on amphiphilic poly(vinyl esters) known to us. We have synthesized amphiphilic poly(vinyl ester) homopolymers and random copolymers by free radical polymerization of vinyl chloroacetate and vinyl versatate, followed by quaternization with N,N-dimethylethylamine. Minimum Inhibitory Concentration (MIC) of polymers towards Escherichia coli (ampicillin resistant) and Staphylococcus aureus and toxicity towards mouse RBCs (Hemolytic Concentration, HC50) were assessed. Copolymers with 2.5k g/mol molecular weight displayed higher activity against S. aureus (MIC=12 µg/mL) as compared to 5.5k g/mol (MIC=21 µg/mL), or 11k g/mol (MIC=52 µg/mL) series copolymers. Similar trend was observed in the antibacterial activity towards E. coli. For homopolymers, in contrary, 2.5k g/mol homopolymer manifested lower activity towards S. aureus as compared to higher molecular weight homopolymers. Moreover, homopolymers were found to be non-toxic towards RBCs (HC50>2000 µg/mL) and selectively active against S. aureus. Most of the copolymers demonstrated toxicity towards RBCs, but a 5.5k g/mol series copolymer with 90% cationic mole percentage displayed 46 times more selectivity towards S. aureus over RBCs. Similar selectivity was observed in the case of a 2.5k g/mol series copolymer.

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Biomacromolecules for Therapeutics and Diagnostics Delivery (05:30 PM - 07:30 PM)

Location: Indiana Convention Center
Room: Hall I
A new platform for bioconjugation using functionalized TEMPO-oxidized chitin nanocrystals (TCNs) has been developed. These nanomaterials possess unique properties, such as low density, biodegradability, biocompatibility, and nontoxicity, making them attractive for various applications. The crystals were prepared by selective chitin oxidation using TEMPO/NaBr/NaClO, followed by conjugation with a fluorescent dye and derivatives of α-D-mannopyranose (Man) and β-D-galactopyranose (Gal), resulting in the dually functionalized nanocrystals TCN-dye-Man and TCN-dye-Gal, respectively. The biorecognition properties of the nanocrystals were subsequently probed in interaction studies involving two lectins: Concanavalin A (Con A) and Soybean agglutinin (SBA). Con A thus promoted strong TCN-dye-Man aggregation, whereas the solution with SBA remained homogenous. Similarly, TCN-dye-Gal displayed selective aggregation in the presence of SBA. These interactions were visualized by optical, fluorescence and STEM imaging. Our results show that the chitin platform constitutes a straightforward approach to multiply conjugated nanomaterials for potential applications in vivo.
193 - Computational investigation of G-proteins releasing from G-protein-coupled receptors

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G-protein-coupled receptors (GPCRs) mediate various cellular responses in the human body. More than one third of the clinical drugs target on GPCRs to regulate their activation and coupling to G-proteins. Investigation of signal transmission from GPCRs to the G-proteins is thus of great importance for designing better GPCR modulators. The breakthrough in the crystallography of GPCR-G protein complexes has greatly facilitated our study of GPCRs. However, how G-proteins couple to GPCRs to complete the regulation of the human body is still unclear. Here, we carried out steered molecular dynamics simulations (SMDs) to study the release of a G-protein from a prototype of GPCR, the β2-adrenergic receptor. Umbrella sampling of selected states along the releasing pathway was explored to produce the potential of mean force for the uncoupling of the G-protein from the GPCR and detailed information of the G-protein release is elucidated. Our results can be helpful in understanding the signal transmission from GPCRs to the downstream proteins and may provide us with a new perspective on designing molecules regulating G-protein binding.
194 - pH-dependent conformational dynamics of AcrA: Insights into molecular mechanisms

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The Escherichia coli AcrA–AcrB–TolC efflux pump expels a wide range of chemotherapeutic substrates and has been implicated in the intrinsic drug resistance. AcrA has been experimentally demonstrated to exhibit a reversible pH-dependent conformational change and some residues involved have been specified. However, the molecular mechanisms remain unclear. We have conducted constant pH molecular dynamics simulations of AcrA which allow us to offer explanations at the atomic level for the pH-dependent behavior. Our results indicate that some acidic residues undergo protonation at lower periplasmic pH leading to the disruption of an interaction network and change in flexibility (see

at pH 7.0 and

at pH 4.5). Deciphering the origins of the pH-dependent flexibility of AcrA may aid in the development of therapeutic agents targeting the efflux pump.

Tuesday, September 10, 2013 05:30 PM
Biomacromolecules for Therapeutics and Diagnostics Delivery (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
195 - Enzymatic polyesterification to produce functionalized poly(lactic acid) and poly(n-hydroxyalkanoic acid)s

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Poly(lactic acid) (PLA) is a biopolyester that has been widely employed in biomedical applications. Our research group has prepared halogenated PLA and poly(lactic acid-co-glycolic acid) (PLGA) using traditional acid-catalyzed polyesterification conditions.\textsuperscript{1} Although the chemical synthesis is very efficient, it often leaves chemical residues that have health and safety concerns.\textsuperscript{2}

This research initially focused on the study of enzymatic copolymerization of LA with 2-bromo-3-hydroxypropanoic acid (BrA) using Novozym 435 (immobilized CALB), which is considered an effective lipase catalyst for polyesterifications.\textsuperscript{3} However, the molecular weights of the resulting copolymers are low, which seems to be consistent with other enzymatic polymerizations of short hydroxyalkanoic acids.\textsuperscript{4} We are now investigating the effect of the length of the n-hydroxyalkanoic acids on their ability to enzymatically copolymerize with BrA. The molecular weight of enzymatically produced poly(3-hydroxypropionic acid-co-BrA) is similar to that of poly(LA-co-BrA). However, 6-hydroxyhexanoic acid and 12-hydroxydodecanoic acid produce higher molecular weight copolymers with BrA. \textsuperscript{1}H NMR spectroscopy also indicates that lactones copolymerize with BrA under enzymatic conditions.

References

Polyphosphazenes are a class of hybrid organic-inorganic polymers with two organic side groups linked to the polymer backbone. These side groups ultimately determine the final polymer properties, which allows for their use in a variety of applications. One of the main limitations in polyphosphazene synthesis is achieving full substitution, especially when bulky side groups such as phenoxy and phenyl-phenoxy are used. To overcome this, small nucleophiles, such as ethoxy, could be used to finish the reaction. In doing so the hydrolysis properties are changed and the final application is ultimately affected. Typically, aryloxy substituted polyphosphazenes exhibit hydrolytic stability, but the hydrolysis properties of ethoxy are unknown. Due to its small size, ethoxy may not be able to provide sufficient backbone protection under hydrolysis conditions. The objective of this research is to examine the hydrolytic susceptibility of ethoxy containing polyphosphazenes to determine their potential applications. Polymer synthesis and hydrolysis results will be described.
Biofouling on ship hulls calls for immediate attention economically and environmentally as hull clinging creatures increase both friction and weight of vessels resulting in wasted fuel consumption, travel time, and resources cleaning in the shipping industry. There are many efforts in developing polymeric networks as anti-biofouling coatings to replace traditional toxic antifouling paints. Amphiphilic polymeric surfaces with complex morphologies and topologies in nanometer scales demonstrate excellent antifouling performance against proteins that adhere to either larger hydrophobic or hydrophilic region. Zwitterionic polymers coatings are also great candidates as antifouling materials due to their capability of binding a significant amount of water molecules which repel proteins. In this presentation, an amphiphilic zwitterionic polymeric surface, an advanced concept that combines the merits of amphiphilic polymeric surfaces and zwitterionic polymers coatings, will be discussed, as a design that is expected to provide a better solution to combat biofouling. A novel copolymer containing hydrophobic units and reactive units was synthesized and subsequently modified to produce an amphiphilic, zwitterionic polymer. The amphiphilic zwitterionic polymer was covalently attached onto silanized glass with different crosslinking extents to form amphiphilic crosslinked networks. Protein adsorption studies of bovine serum albumin on these coatings against commercially available silicone standards demonstrated that the zwitterionic amphiphilic polymeric system is a promising anti-biofouling solution. This presentation will discuss the detailed design, synthesis, characterization and applications of this novel amphiphilic zwitterionic polymeric system.
198 - “Universal” approach to N-alkyl urea peptoid synthesis and applications

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N-alkyl urea peptoids are biomimetic oligomers that possess large potential synthetic diversity. However, for many applications, control over the oligomer permutation at a single residue level is unnecessary. Therefore, it would be advantageous to prepare sequences in which each residue (i.e. N-alkyl group) is the same, speeding up the synthesis. Furthermore, if the N-alkyl group is reactive functional group it would lead to the potential synthesis of many oligomers from one universal precursor molecule. Oligomers with methoxymethyl (MOM) group as side chain have been used in this strategy. By achieving the deprotection of MOM with HCl in methanol, oligomers with alcohol functional groups were synthesized. Oligomers containing azide, carboxylic acid or chloride groups can be easily obtained from the afforded alcohol moieties. This approach will accelerate projects involving structure-property relationships and the preparation of novel soft materials. Also, incorporating 2, 7-diamido-1, 8-naphthyridine (Napy) with those oligomers will lead to a new application of N-alkyl urea peptoid in supramolecular polymers, which is a further step towards novel functional materials.
199 - Synthesis of biodegradable hyperbranched polyacrylates

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Synthetic biodegradable hyperbranched polymers with complex architectures are valuable in medicine and industry. We recently established a synthetic route to acrylate inimers that homo-polymerize by atom transfer radical polymerization (ATRP)¹ to produce polymers with an ester group attached to every other carbon along the polymer backbone and with a non-functionalized alkyl ester attached as a free side chain.²,³ These polymers were synthesized under aqueous conditions using different initiation mechanisms, such as reverse ATRP, simultaneous normal and reverse initiation (SNRI), and activator generator electron transfer (AGET) polymerization in emulsion and miniemulsion. The optimization conditions for polymerization using AGET/ATRP enabled the synthesis of hyperbranched homopolymers and copolymers in stable colloidal latexes, with number average molecular weight ($M_n$) in the order of $1 \times 10^5$ g/mol, average particle size of 60 nm, and polydispersity index (PDI) from 2.0 to 3.3.⁴

200 - Solubility parameters of immiscible conducting polymers polypyrrole chloride by inverse gas chromatography

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Although the properties of blends of conducting and other polymers were explored, the morphology and the solubility of polypyrrole using IGC are largely unexplored. In this study, the solubility parameters δ₁ and δ₂ of 25 solvents and conducting polypyrrole chloride, PPyCl, were measured using the IGC method in the temperature range of 80-180 °C.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ₂ PPyCl</td>
<td>13.41</td>
<td>13.48</td>
<td>12.52</td>
<td>12.67</td>
<td>12.80</td>
<td>10.70</td>
<td>12.25</td>
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</table>

shows the PPyCl solubility parameter that revealed its miscibility in polar and non-polar organic solvents including alkanes, acetates, chlorinates, cyclic, and oxy groups. It was calculated from the slope of the straight line when the left hand side of a derived equation was plotted versus δ₁.

Our δ₂ values ranged from 10.70 to 14.07 (KJ/L)⁰.⁵ and were not influenced by the change of temperature, consistent with the insoluble nature of PPyCl in any of these solvents. The values of δ₂ of the insoluble PPyCl were compared with those soluble polymers using seven different polymers at a variety of temperature ranges found in the literature. δ₂ values for PPyCl seem to be much lower than those reported except for PECH, PVA and PMA, an evidence of the non-solubility of PPyCl in any of the twenty two solvents used. IGC methods, once again proved its capability, versatility and accuracy in obtaining physico-chemical properties on complex polymeric systems.
201 - Biodegradable poly(anhydride-esters) comprised exclusively of naturally-occurring antimicrobials and EDTA: Antimicrobial and antioxidant activity

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Microbial contamination of food and personal care products is of serious consumer concern. The use of natural, greener preservatives are safer alternatives to synthetic ones. Furthermore, a compound that releases antimicrobials over time would be beneficial for long-term preservation. Carvacrol, thymol, and eugenol are naturally-occurring compounds known to possess antimicrobial activity against a range of bacteria as well as antioxidant activity. Biodegradable poly(anhydride-esters) containing an antimicrobial (carvacrol, thymol, or eugenol) along with ethylenediaminetetraacetic acid (EDTA) chemically incorporated in the polymer backbone were synthesized. EDTA is widely used as a preservative in the food and personal care industries. These polymers are comprised entirely of FDA-approved bioactive molecules in a highly atom-economic way. Polymers were synthesized using a solution polymerization method, and their molecular weights and thermal properties were determined. Release studies were performed under physiological conditions, resulting in free antimicrobial and EDTA release, as determined by high performance liquid chromatography. Antimicrobial activity of the released media against Gram-positive and Gram-negative bacteria in addition to antioxidant activity was tested and compared to that of free bioactives to ensure that the released species retained their activity. These polymers completely degrade into biologically active components that can potentially promote preservation of consumer products via antimicrobial and antioxidant pathways. Therefore, these polymers have potential to be used in food film-wraps or personal care products for sustained release of antimicrobial and antioxidant compounds.
Poly(lactic acid) (PLA) is a compostable and biodegradable thermoplastic derived from starch and sugar. Its low toxicity, along with its environmentally benign characteristics, has made PLA an ideal material for daily use. PLA is also introduced into medical applications such as tissue engineering scaffolds. The Pugh research group copolymerized glycolic acid (GA) and/or lactic acid (DL-LA) with 2-bromo-3-hydroxypropionic acid (DL-BA) to form PLB and PLGB. These copolymers are functionalized with halogen groups on the main chain to allow molecules of interest to be covalently bonded to the polymer backbone.

The stereopurity of P(L)LA has many profound effects on its structural, thermal, and mechanical properties. The deaminohalogenation reaction used to synthesize DL-BA from serine is both regioselective and stereoselective. This poster therefore presents the synthesis of stereopure copolymers by polymerizing L-LA with L-BA in different molar ratios to obtain P(L)LA-co-(L)B and copolymers of their mixed isomers (Scheme 1). The stereorepurity of the copolymers didn’t affect their polymerizability and the molecular weight of the resulting copolymers. However, the stereopure copolymer and the copolymers with L-LA/DL-BA mixed isomer are crystalline at a critical ratio (≥95 mol% LA) for this random PLB. The stereochemical determination of L-LA and L-BA was also investigated by 1H NMR spectroscopy in the presence of a chiral shift reagent.

![Scheme 1. Structures of P(L)LA-co-(L)B and its mixed isomers.](image-url)
Poly(lactic acid) (PLA) is considered to be one of the most promising biodegradable materials in the family of aliphatic polyesters. PLA and its copolymers, such as poly(lactic acid)-co-(glycolic acid), are widely used as alternatives to petrochemical-based polymers and have been used as biomedical materials. PLA has the advantage that it is produced commercially by an efficient method at relatively low cost. However, there are some disadvantages to PLA. It is brittle and difficult to functionalize. Blending is an extremely promising approach to improve the properties of polymers. It is efficient and easy. Blends may exhibit the physical and chemical properties of both individual polymers. The advantages of the two components of the blend may produce a unique and/or superior material. The miscibility of the two polymers can be evaluated by the Tg method. Different chemical properties, such as optimum hydrophilic/hydrophobic balance and the ability to act as a drug-carrier may be relatively easily achieved by functionalization of our recently synthesized brominated PLA copolymers, simultaneously with producing materials with good mechanical properties, by blending functionalized PLA with high molecular weight commercialized PLA. This study investigates the miscibility of brominated PLA with high molecular weight PLA as the first step. The influence of different blends ratios, molecular weights of PLA and configurations of PLA on the miscibility is studied.
We describe the synthesis of graft copolymers of lactic acid and methyl methacrylate using atom transfer radical polymerization of methyl methacrylate from a poly(lactic acid) (PLA) macroinitiator. The PLA macroinitiator ($M_n = 1.7-2.1 \times 10^4$ g/mol; PDI=1.9-2.6) was prepared through acid-catalyzed copolyesterification of lactic acid and 2-bromo-3-hydroxypropanoic acid with a variety of monomer feed ratios.\textsuperscript{1} We established the graft copolymerization conditions using an initiator that models the brominated repeat unit of the macroinitiator: methyl 2-bromo-3-acetoxypropionate. This polymerization is well controlled using CuCl as the catalyst in toluene at 90 °C, as demonstrated by the linear first order monomer conversion and linear growth in number-average molecular weight plots below, as well as by the narrow polydispersity (PDI<1.20). The number-average degree of polymerization ($DP_n$) and glass transition temperature (Tg) of the corresponding graft copolymer also increase with increasing ratios of the monomer to initiating sites, whereas the polydispersity index decreases relative to the macroinitiator.

References:

205 - Robust and degradable hydrogels from poly(ethylene glycol) and collagen interpenetrating networks

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We present an injectable and degradable PEG/collagen hydrogel system with robust networks for use as elastomeric tissue scaffolds. Poly(ethylene glycol) (PEG) and PEG-co-lactic acid were covalently cross-linked and collagen was physically cross-linked to form a semi-interpenetrating hydrogel network. The mechanical strength of the hydrogels depends predominantly on the PEG concentration but the incorporation of collagen into the PEG network enhances hydrogel viscoelasticity, elongation, and also cell adhesion properties. Experimental data show that this hydrogel system exhibits tunable mechanical properties. The hydrogels allow cell adhesion and proliferation in vitro. The results support the prospect of a robust and semi-interpenetrating biomaterial for elastomeric tissue scaffolds applications.

Figure 1. Representative images of an as-prepared PEG hydrogel (far left) and a PEG/collagen hydrogel (center). A schematic of collagen incorporation is presented (right). The hybrid hydrogel is translucent due to the incorporation of collagen into the PEG network.

Tuesday, September 10, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
Poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and their copolymers (PLGA) are used in a wide variety of applications. Uses include sutures, caskets, drinking cups, bone screws, and drug delivery devices. They are well-studied polymers and offer many advantages, such as being derived from renewable resources, being biodegradable, FDA approved for biomedical applications, and commercially available. The main synthetic drawback is that the only sites for post-polymerization functionalization are at the two end groups. By incorporating 3-hydroxy-2-bromopropionic acid as a comonomer with LA and GA, a site for post-polymerization functionalization can be added. Since the halogen is alpha to a carbonyl, it is activated to both nucleophilic substitution and radical formation. Using these two routes, molecules of interest such as drugs, anti-inflammatory agents, and nucleating agents can be covalently bound to the polymer backbone, which may improve the properties of these polymers and/or expand their role in everyday life. This poster will present the synthesis and functionalization of PLGA-based polyesters.
**207 - Synthesis and characteristics of novel fluorinated polyurethanes**

*Jung-Hwan Lee, buffalo878@posco.com, Jong-sang Kim. Surface Technology Research Group, POSCO Technical Research Laboratories, Gwangyang, Jeonnam, Republic of Korea*

Novel fluorinated polyurethane elastomers were synthesized by two step urethane reaction of the fluorinated polyols based on poly(vinylidenefluoride-co-hexafluoropropylene and diisocyanate such as 4,4’-methylene-bis(phenyl isocyanate)MDI in the presence of a solvent, followed by subsequent chain extension with low molecular weight diol such as 1,4-butanediol. Prior to synthesis of fluorinated polyurethanes, the well-defined α,ω-diiodo-poly(VDF-co-HFP) with narrow unimodal molecular weight distribution was polymerized by Iodine Transfer Polymerization, which are one of the controlled “Pseudo-living” free radical telomerization methods. The structure and functionality of these dihydroxy fluoro polymers were characterized by ¹H-NMR, ¹³C-NMR, ¹⁹F-NMR and end-group titration and showed high conversion. As these fluorinated polyol with the molecular weight below 3,000g/mol were used as telechelic fluorinated prepolymer for the synthesis of fluorinated polyurethane with low surface energy and good hydrophobic surface properties.

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**Tuesday, September 10, 2013 05:30 PM**

*General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)*

*Location: Indiana Convention Center*  
*Room: Hall I*
The interest in charge-containing polymers, commonly referred to as ionenes, has increased significantly over the past decade due to their potential application in areas such as electroactive devices and membrane separation sciences. Here, we report the synthesis and thermal properties (T_g and T_d) of several imidazolium-containing thermoplastic polyurethanes. During the course of this study, three key structural deviations were explored: (1) counteranion selection (size and/or hydrogen bonding capability) (2) NCO:OH ratio (hard segment content) and (3) charge density (mono- vs. bis-substitution). The polyurethanes were prepared by reacting an isocyanate prepolymer (polymeric MDI and poly(propylene glycol) oligomer) with an imidazolium-containing diol chain extender. In general, we observed that counteranion selection had a tremendous effect on thermal properties, with larger anions leading to depressed T_g values while use of anions with weak hydrogen bonding affinity resulted in the highest thermal stability (T_d). Increasing the hard segment (NCO content) generally led to an increase in T_g and T_d values while increasing the number of imidazolium rings from one to two per monomeric unit led to depressed T_g values and little change in thermal stability.
209 - Linear and covalently crosslinked polyesters containing a pendant imidazolium group: Synthesis and thermal properties

Carli P. Whittington, kmiller38@murraystate.edu, Lucas A. Daily, Kevin M. Miller. Department of Chemistry, Murray State University, Murray, KY 42071, United States

The scientific and commercial impact of ionic liquids has evolved from developing potential solvent replacements to functional integration into polymeric materials. The interest in polymerizable ionic liquids, particularly those containing the imidazolium group, has increased significantly over the last decade due to its relative ease of functionalization and potential application in areas such as electronic devices and drug delivery vehicles. In an effort to further explore the area of ionically-charged polymers (ionenes), we wish to report on the synthesis and thermal analysis of a series of polyesters (linear and covalently crosslinked networks) in which a pendant imidazolium group has been anchored into the polymer backbone. As part of this study, we wanted to compare changes in thermal properties such as glass transition temperature ($T_g$) and thermal stability ($T_d$) as a function of polyester structure (linear vs. network) as well as anion selection (basicity and size). Linear polyesters were prepared using standard nucleophilic acyl substitution conditions while the covalently crosslinked networks were prepared using the Michael addition polymerization. In addition to the thermal analysis data, a correlation between the $^1H$ NMR chemical shift values of the imidazolium H$^2$ proton and the hydrogen bonding capability of the anion will be discussed.
A new approach to the development of smart materials is through the use of force-activated units called mechanophores. It is generally accepted that mechanophores placed in the center of polymer chains experience the largest force while mechanophores placed at the end of polymers are not activated even under excessively large forces. However, the relationship between mechanophore placement and activity has yet to be explored. With this question in mind, a series of mechanophore-linked PMMA-b-PS diblock copolymers were synthesized. The mechanophore placement in the polymers was varied by changing the length of each block. In order to control the size of each block a bifunctional initiator with an ATRP initiator at one end and an NMRP initiator at the other end was synthesized. The living radical polymerization of the bifunctional initiator provides control over the degree of polymerization of each block. This project will provide quantitative insight about how force is distributed along a polymer chain subjected to elongational flow.
Natural fibrillar structures like cytoskeletal filaments respond to biological signals and autonomously shuttle and deliver subcellular components. In an effort to obtain dynamic and adaptive synthetic analogs, interfacial chemistry and physics between organogels and payloads (particles, micelles, vesicles) based on supramolecular interactions is being investigated. To probe the fibrillar interface, we are developing particles with covalently attached components of gelators or molecules with similar structures, utilizing the multivalency of gelator-bound-particle to allow particles and fibrils to interact. Currently, from various microscopic visualization methods, we have observed different morphologies of a hybrid system consisting of gel and gelator-bound-particle under different conditions. We envision that development of this work will contribute to designing and synthesizing smart polymeric materials.
212 - Superhydrophobic hydrocarbon electropolymerized surfaces as an alternative to fluorine

Melanie Wolfs, Melanie.WOLFS@unice.fr, Sabri Taleb, Thierry Darmanin, Frederic Guittard. Surfaces & Interfaces Group Research, University of Nice Sophia Antipolis, Nice, France

Superhydrophobicity results from the combination of low surface energy materials with the surface structuration at micro and/or nanometer scale. Such surfaces are interesting because of their expected self-cleaning or anti-contamination property that could be useful in various fields such as in biomedical devices or aeronautics for example.

Amongst all the developed techniques in literature to obtain superhydrophobicity, electropolymerization is a fast (deposition and structuration in one-step) and reproducible method. Moreover, electropolymerization of conducting polymers is a versatile technique. Indeed, not only the monomer chemical structure (polymerizable core, substituent) but also the electrochemical parameters such as doping agent, deposition charge or solvent allow to control the surface growth and their morphology in order to obtain surfaces with various water-repellent properties and even reach superhydrophobic properties.

This poster focuses on the electropolymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives bearing an alkyl chain group in the 2-position and the characterization of the obtained films to reach versatile wetting surfaces. This work contributed to the elaboration of bioinspired surfaces with an ecotoxic-friendly approach.

Figure: SEM images of PEDOT-H12 (x10000).

References


213 - Poly(2-isopropenyl-2-oxazoline)s as kinetic hydrate inhibitors

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Kinetic hydrate inhibitors (KHIs) are additives employed in oilfield production lines to delay the nucleation and potentially the growth of gas hydrate crystals. This delay of nucleation is dependent on the subcooling of the system. Poly(2-oxazoline)s are a known class of KHI but previous studies have tested ring opened oxazolines. This study investigates the KHI performance of Poly(2-isopropenyl-2-oxazoline) (PiPOx), a variety of molecular weight PiPOx homopolymers were synthesised by living anionic polymerisation to preserve the ring structure. Furthermore, RAFT polymerisation was utilized to copolymerise iPOx with MMA or NIPMAM at different compositions to determine if a beneficial effect on the KHI performance can be introduced. PiPOx were shown to be effective KHIs and a member of a rare class of non-amide polymer KHIs.
214 - WITHDRAWN
215 - Novel functional copolymers of styrene and ring−disubstituted methyl cyanopropenoates

Ahlam Shahbain, AHLAM.SHAHBAIN@GMAIL.COM, Sonia E Chavez, Gregory B Kharas. Department of Chemistry, DePaul University, Chicago, IL 60614, United States

New functional copolymers of styrene and trisubstituted ethylenes were prepared as potential building blocks for novel materials. Copolymer of styrene and some ring-disubstituted methyl 2-cyano-3-phenyl-2-propenoates were prepared in solution with radical initiation.

The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, $^1$H and $^{13}$C NMR. The copolymers were characterized by GPC, DSC, and TGA.
We have synthesized a group of functionalized polyethylenes containing precisely placed sulfonic acid moieties. Acyclic Diene Metathesis (ADMET) polymerization was conducted to yield a sulfonic acid functionality on every ninth, fifteenth, and twenty-first carbon of the backbone. Ester protected prepolymers were necessarily synthesized first, followed by a novel deprotection procedure to achieve the desired sulfonic acid functionality without poisoning the catalyst. Protected symmetrical diene monomers were afforded by the alkylation of ethyl methanesulfonate. Weight-average molecular weights up to 40,000 g/mol were achieved. Subsequent hydrogenation of the ester protected prepolymers yielded saturated polyethylene backbones. Complete deprotection of the ester moieties is required to retain the precision, or else a random placement of esters and acids would exist throughout the polymers. We have developed a new methodology for quantitative ester deprotection of polymers by suspending the polymer in nonsolvent and beginning a hydrolysis reaction, for which the product is soluble in the solvent. This deprotection procedure ensures that the polymer is quantitatively deprotected by continuing the reaction in solution. Ester hydrolysis was confirmed by $^1$H NMR and $^{13}$C NMR. Future studies will comprise thermal and morphological data development (e.g., DSC, TGA, x-ray diffraction). These sulfonic acid-containing polymers will add to the library of precise acid-containing polymers our group has already developed, including precision boronic, carboxylic, and phosphonic acids. Sulfonic acids are the most interesting due to their greater acidity ($pK_a < 0$) potentially leading to applications.
**217 - Synthesis of P3HT star polymers with gold nanoparticle core**

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Poly(3-hexylthiophene) (P3HT) star polymer with gold nanoparticle (NP) core was synthesized by coupling reaction of thiol terminated P3HT and gold NP. For this, thiol group terminated P3HT (P3HT-SH) first was synthesized by GRIM followed by modification of the end groups. Obtained well-defined P3HT-SHs with different molecular weights (PDI < 1.3) were then reacted with gold NP (size = 7 nm), where the thiol group of the P3HT exchanged the oleic amine group of the gold NP, to give P3HT star polymer with gold NP core. P3HT-SHs with lower molecular weights gave the star polymers with higher molecular weights (Mw = 10^6). Obtained star polymers with gold NP cores were then characterized by SEC, \(^1\)H NMR, FT-IR, UV-vis, PL, TEM, AFM, and DSC analyses and examined the possibility of OPV and OFET applications.
218 - Superhydrophobic and antibioadhesive surface with nanoscale roughness

Jeanne Tarrade, Elena Celia, Mélanie Wolfs, Melanie.WOLFS@unice.fr, Thierry Darmanin, Sonia Amigoni, Elisabeth Taffin de Givenchy, Frederic Guittard. Surfaces & Interfaces Group Research, University of Nice Sophia Antipolis, Nice, France

The bacterial adhesion and the formation of biofilm are natural and spontaneous processes. This phenomenon happens whatever the nature of bacterium, surrounding fluid and receiving substrate.

Bacterial adhesion depends on physical chemistry interactions between the bacteria and the receiving substrate. Tamada and Ikada showed that the nature of substrate and its characteristics of surface, such as superhydrophobic or superhydrophilic character, can affect the development of a biofilm, in order to obtain “anti-bioadhesive” surfaces.¹ In case of superhydrophobic surfaces, the wetting is reduced which may favor the “sliding” of the aqueous medium on the surface. Hence, its ability to interact with bacteria may also be reduced. This phenomenon is associated with the chemical functionality of the coating and its roughness.

For an anti-bioadhesive application, the control of the roughness is very important. In fact, the presence of asperities larger than bacteria favors their mechanical bonding and thus, the increasing of bacterial adhesion. The size of bacteria being about 1µm, it is necessary to develop superhydrophobic surfaces with nano-scale roughness.

Among the methods allowing to structure and functionalize surfaces in order to make them superhydrophobic, electropolymerization is a simple, inexpensive and perfectly manageable.² Here, we present the work realized in designing surfaces by electrodeposition with a potential anti-bioadhesive application.

![Figure: Superhydrophobic polymer with nano-scale roughness](image)

References

(1) Tamada, Y.; Ikada Y.; Polymer, 1993, 34, 2208-2212.
219 - Single chain polymer nanoparticles using 1-functionalized vinylbenzocyclobutenes

William Storms¹, Ajay R Amrutkar², ara31@zips.uakron.edu, James Baker³, Coleen Pugh⁴. (1) Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, United States, (2) Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, United States, (3) Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, United States, (4) Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, United States

There is great interest in making well-defined polymer nanoparticles in the sub-nanometer size range due to useful applications in a variety of fields. Polymer nanoparticles have traditionally been prepared via methods such as miniemulsion, microemulsion and self-assembly of block copolymers into micelles followed by cross-linking. A relatively new method (Hawker, C. et. al. J. Am. Chem. Soc. 2002, 124, 8653-8660) that involves intramolecular cross-linking and collapse of individual polymer chains into discreet nanoparticles is gaining much attention. Since these nanoparticles are formed from single chain precursors of linear polymers, they are obtained in the range of 5-20 nm, which is otherwise difficult to obtain by other methods. Moreover, this method provides the ability to tune the size of the nanoparticle by changing the molecular weight and mole % of cross-linkable moiety in the linear polymer precursor. A cross-linkable group, benzocyclobutene (BCB), which undergoes thermal ring opening and subsequent cycloaddition reactions to form stable carbon-carbon bonds is very attractive. This poster will report the synthesis of 1-functionalized vinylbenzocyclobutenes and their utilization to make discreet single chain polymer nanoparticles (Scheme 1).
Although there have been remarkable advances in living ionic or radical polymerization techniques for synthesizing block copolymers, the monomer choice is rather limited, typically employing vinyl monomers. In contrast, graft copolymers are relatively easy to prepare and a wide range of potential host polymers are available for making nanoscale copolymer structures beyond the vinyl-based polymers. The microphase separation of graft copolymer systems has been previously investigated using branched mikto-arm block copolymers (BPs) as a model graft copolymers. However, the synthesis of such well-defined mikto-arm graft copolymers is still quite demanding. In addition, these systems have been primarily of fundamental interest to elucidate the effects of chain stretching and crowding at the interfaces of ordered structures of BPs. The study of microphase separation in random graft copolymers, where the graft chain is attached at random points along the “host” polymer backbone, has received much less attention and, to our knowledge, the observation of periodic nanostructures in such systems has not been previously reported. We now report the study of microphase separation in a random graft copolymer system which displays a remarkably high level of local order after homopolymer-removal and fractionation using HPLC. Since our graft copolymer system is made using polydisperse backbone polymer chains (polydispersity index, PDI = 1.59) for the grafting, the observed periodic nanostructures from such polydisperse graft copolymers will broaden the choice of polymer components that can form self-assembled nanostructures.
Synthesis of a fluorescent polymethacrylate-based monomer by reversible addition fragmentation chain transfer polymerization

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A novel monomer was synthesized by reacting 2-hydroxyethyl methacrylate with 1-pyrenyl isocyanate, which was generated in situ by treating 1-amino pyrene with triphosgene. The structure of the monomer was confirmed using nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry. The monomer was polymerized using the RAFT chain transfer agent S-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (DDMAT) in DMF at 85 °C (Figure 1). NMR spectra showed the polymerization proceeded to a 79% conversion after 4 h. The polymer was precipitated from cold ether and the number average molecular weight of the polymer was determined by gel permeation chromatography (GPC) to be $4.3 \times 10^4$ g/mol with a PDI of 1.6. The synthesis of fluorescent gels using this polymer is currently under investigation.
223 - Deoxygenation of aromatic ketones by solid formic acid equivalent with Pd/C

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The reduction of aromatic ketones to their corresponding hydrocarbons is a widely used reaction. To avoid the difficulties associated with the use of conventionally employed reagents such as concentrated HCl, hydrazines and H₂ gas for this transformation, we have developed a polymer based solid formic acid complex which has high formic acid content. The synthetic utility of the formic acid equivalent solid complex has been demonstrated in its application in the Pd catalyzed direct reduction of aromatic ketones to their corresponding hydrocarbons.
Polyethylene glycol (PEG) is widely used in medical and pharmaceutical applications for its biocompatibility, water-solubility, and chemically robust nature. Recently, there has been an increasing interest in functionalized PEG-based polymers and their applications, which are highly dependent on the nature of the functional groups. We report that propargyl substituted epoxides can be polymerized to give alkyne substituted PEGs. These polymers are synthons for post-polymerization modification by Cu-catalyzed, "click" reactions with organic azides. The results of the polymerizations and properties of the "click" modified polymers will be presented.
225 - Synthesis of trefoil knotted poly(e-caprolatone) via Cu(I)-template method and ring-expansion strategy

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Knots have gained great interest from arts, mathematics and biologies. Although chemists have successfully synthesized knots of small molecular weight with different strategies, knots with large molecular weight i.e. knotted polymers have not yet been reasonably accessed. Here, we report a synthetic strategy for trefoil knotted polymer derived from the Cu(I)-templated helical knot precursor and by subsequent ring-expansion approach. The expected properties compared to its linear analogue such as reduced hydrodynamic radii and lower intrinsic viscosity, together with an atomic microscopy (AFM) image of individual polymer molecules, confirmed the formation of trefoil knotted polymer.
A synthesis of a catenane comprised of two different polymer rings is demonstrated. The polymer[2]catenane is prepared through the active metal template approach. In this strategy, the metal plays a dual role during the assembly of the catenated architecture, simultaneously acting as both a template for the assembly of the components and as a catalyst for interlocking the final product by covalent bond formation. A linear polymethylmethacrylate (PMMA) was designed with azide and alkyne terminal groups for the subsequent Copper-Assisted Azide-Alkyne Cycloaddition (CuAAC) ‘click’ reaction. In this study, Cu(I) coordinates with a pyridine-containing macrocyclic polystyrene (PS) and to the azide and alkyne end groups of the linear PMMA which leads to a metal-mediated bond formation through the cavity of the macrocycle to form a catenane. The product was characterized by GPC, AFM, FTIR and NMR.
227 - One-pot synthesis of poly(ε-caprolactone)-b-poly(vinyl alcohol) block copolymers using a dual initiator for RAFT polymerization and ROP

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An efficient one-pot procedure for the synthesis of amphiphilic poly(ε-caprolactone)-b-poly(vinyl alcohol) (PCL-b-PVA) block copolymers using a hydroxyl-functionalized xanthate reversible addition-fragmentation chain transfer (RAFT) agent, 2-hydroxyethyl 2-(ethoxycarbonothioylthio)propanoate (HECP), as a dual initiator for RAFT polymerization and ring-opening polymerization (ROP) was successfully developed. The PCL block was first polymerized by the ROP of ε-caprolactone (CL) using diphenyl phosphate as a catalyst, followed by the RAFT polymerization of vinyl chloroacetate (VClAc) after quenching the ROP of CL with 4-dimethylamino pyridine. The resulting PCL-b-poly(vinyl chloroacetate) block copolymers were directly hydrolyzed with hexylamine to PCL-b-PVA block copolymers in the same pot. To the best of our knowledge, this is the most convenient method for the synthesis of well-defined PCL-b-PVA block copolymers.
228 - Addressing the challenges: Improving polymer characterization by size exclusion chromatography

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The ability to accurately and precisely characterize the molar mass distribution and averages of synthetic and natural polymers is essential as the shape and the breadth of a polymer’s molar mass distribution will dictate the end-use properties of the polymer. One of the most highly used tools for characterizing the molar mass of polymers is size exclusion chromatography (SEC). Here, we will show the multiple utilities of SEC along with the time and resource saving benefits of implementing a chromatography system with low dead volume, a dual-flow refractive index detector and semi-micro columns for fast and accurate characterization of polymers. We will demonstrate how single-detector SEC can be used to monitor the synthesis of PEGylated polymers to determine the oligomeric content, as an approach to failure analysis for synthetic polymers, and for the characterization of commercial rubbers. The molar mass distributions of these synthetic polymers was fully characterized in less than 20 minutes and provided significant pictorial and numerical data for the differentiation between products. Finally, we will show how SEC coupled to a train of detection methods can be used to provide a detail picture of molar mass and polymeric size of natural polymers. Through these multiple applications we will also demonstrate how a low dead volume SEC system equipped with a dual-flow refractive index detector and semi-micro columns will save time and resources when analyzing polymers.
229 - Triconstituent assembly of vanadia sol, phenolic resin, and block copolymers for electrochemically active nanoporous vanadia-carbons

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The fast condensation rate of vanadia sols and rapid crystallization of vanadia at modest temperatures creates a challenge for the synthesis of ordered mesoporous vanadia through cooperative assembly with surfactants or block copolymers. Even when the cooperative assembly is successful, vanadia crystallization through the pores formed by the block copolymer tends to disrupt the ordered structure and significantly decrease the porosity.

In this work, we modify the typical synthesis procedure with the addition of an oligomeric phenolic resin that can also assemble with the block copolymer template. The phenolic resin provides a significant carbon yield that can mitigate the breakthrough crystallization of the vanadia at sufficient loadings. A systematic investigation of the impact of resol content on the ordered structure will be presented for the initial assembly and the carbonized structure. These structures can also be fabricated in thin films with the morphology investigated with AFM and GISAXS. A significant improvement in the ordered structure can be clearly observed when phenolic resin (resol) is added to the sol. Finally, we will present the electrochemical properties of these porous composites with an eye towards supercapacitor applications. Structure-property relationships for these composite materials will be discussed with respect to idealized morphology for supercapacitors with porous vanadia-carbon composite electrodes.
Wrinkled surfaces have garnered much interest over the past decade as they provide a facile route to nanostructured surfaces. The typical route to wrinkles is through mechanical stretching of a rigid thin film attached to an elastomeric substrate, typically PDMS. In this work, we describe a simple route to generating wrinkles in a single step through photoinitiated polymerization of furfuryl alcohol coatings. Use of hydrophobic photoacid generators (PAGs) generates a local enhancement of PAG at the air interface from wetting considerations, which in turn leads to increased polymerization at the surface with UV exposure.

Here we will discuss the role of the coating thickness, humidity and selection of the PAG on the morphological characteristics of the wrinkles. As the coating thickness increases, there is an increase in the amplitude of the wrinkles without any statistical change in the wrinkle wavelength. Conversely, humidity impacts the wrinkle wavelength due to changes in the proton diffusion when water is present in the furfuryl alcohol. For samples using triphenyl sulfonium triflate as the PAG, there is a transition from wrinkling (top) to creasing (bottom) that is observed as the thickness of the coating increases.
231 - Spherulitic growth of poly(vinylidene fluoride) in blends with poly(methacrylate-co-methacrylic acid)

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A series of poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-MAA) random copolymers ranging in MAA content from 0-15 mole% have been synthesized and blended with poly(vinylidene fluoride) (PVDF). Using polarized optical microscopy, the spherulitic growth rate of the PVDF in the blends was determined. The results showed that at low MAA comonomer contents (<5 mole%), a significant decrease in the spherulitic growth rate of the PVDF occurred, while at higher MAA contents, the growth of the PVDF spherulites in the blend approached that of pure, unblended PVDF. These results suggest that while the hydrogen-bonding of the PMMA-co-MAA blend component initially produces a greater intermolecular interaction with PVDF, eventually, the intramolecular interaction of the higher MAA content copolymers causes the PMMA-co-MAA to interact less with the PVDF blend component.

Tuesday, September 10, 2013 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
232 - Effective removal of Cu\textsuperscript{2+} from aqueous solution by sulfonic acid modified hypercrosslinked microporous polymer

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In this paper, a new hypercrosslinked microporous polymer SBE-XDC was prepared by continuing Fried-Crafts alkylation polymerization succedent modification of sulfonic groups. The chemical and pore structure of above polymers were characterized by FT-IR, EA and BET. The results showed that the polymer possess high BET specific surface area (583.05 m\textsuperscript{2}/g) and large pore volumes (1.047cm\textsuperscript{3}/g), the surface modification almost did not destroy the porous structure. Adsorption of Cu\textsuperscript{2+} from aqueous solution onto SBE-XDC resin at 283K, 298K and 313K was studied. The Equilibrium adsorption data was fitted very well with Langmuir model. The free energy changes ΔG for adsorption of Cu\textsuperscript{2+} onto the SBE-XDC in the aqueous solution was evaluated. The negative values of ΔG indicated that the overall adsorption processes were spontaneous and thermodynamically favorable.
233 - Bicyclic polyesters derived from plant oils

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The synthesis of aliphatic bicyclic polyesters derived from soybean oil provides an alternative to petroleum based monomers. The synthesis procedure first involves catalytic transformation of soybean oil to 1,3-cyclohexadiene. The use of a cyclic diene provides aliphatic polyesters.
A novel biobased glycidyl ester epoxy (Cin-epoxy) was synthesized from cinnamic acid. Cinnamic acid was first converted to a dicarboxylic acid by Friedel-Crafts reaction, followed by allylation of the carboxylic groups and subsequent epoxidation of the allyl double bonds. Two acylating agents, succinic and maleic anhydrides, were compared in the Friedel-Crafts reaction. The chemical structures of the epoxy and intermediates were confirmed by $^1$H NMR, FT-IR and ESI-MS. The obtained Cin-epoxy was cured with hexahydrophthalic anhydride, terpinene-maleic anhydride and methylnadic anhydride (MNA) respectively. Non-isothermal curing of the epoxy was studied using differential scanning calorimetry. Results show that the cinnamic acid-derived Cin-epoxy was more reactive than the bisphenol A type epoxy resin. The thermal mechanical properties and thermal stability of the cured epoxy resins were studied using dynamic mechanical analysis and thermogravimetric analysis, respectively. Results showed that this new epoxy displayed good properties. The glass-transition temperature and modulus of MNA cured Cin-epoxy were 116 °C and 2100 MPa. This result indicates the Cin-epoxy has the potential to replace the petroleum-based thermosetting resin.

![Reaction scheme of Cin-epoxy from cinnamic acid](image-url)
Development of environmental-friendly "green" polymers for various commercial applications has gained momentum in recent years. Plant oils are amongst the most sought after starting materials in synthesizing green composites. They are composed of triglycerides of fatty acids as shown in Figure 1, and are being explored by researchers as an alternative to petro-based resins widely used today such as polyesters, vinyl esters, epoxies and urethanes that consist of chemicals with major concerns such as styrene and bisphenol A. There are four reactive positions on triglycerides that can act as starting points for different chemistries: ester groups, unsaturated C=C double bonds, α-positions of ester groups and allylic positions. The purpose of this presentation is to report invention of high-bio content, low toxicity, resins derived from functionalized plant oils as matrix resins for reinforced composites. The syntheses are performed using simple fatty acids as model reactions to understand the more complex system of plant oils. The targeted properties of these green composites are high glass transition temperature of at least 120 °C, Young's modulus greater than 2000 MPa and more than 80% bio-content.
The study of a class of materials almost always begins with the development of an understanding of properties in the bulk state. However, pure bulk phases are idealizations rather than widely encountered realities. It is actually the study of surface critical phenomena that has led to a number of new important insights into polymer behavior. Much of what exists in molecular modeling and experimental literature explains the behavior of flexible or modified chains. There is still a lack of accepted models that adequately explain chain conformation, structural organization, and dynamics of semi-rigid and rigid rod polymers at surfaces and interfaces, which limits their effective use in important applications such as coatings and composites for transportation and aerospace industries. This work presents a fundamental study of the environmental and structural parameters that determine polymer behavior at the polymer-air interface for a series of polyethersulfone (PESU) polymer films cast from solution. Commercial PESU was fractionated into systems of varying molecular weight and narrow molecular weight distributions via fractional precipitation. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to observe the evolution of the surface morphology and surface energies were measured via contact angle. Through combined experimental and simulation analysis of these systems, refined models of PESU (and by extension semi-rigid/rigid rod polymers) behavior at the polymer-air interface will be developed that will enable further advancement of PESU applications.
Carbon nanotubes (CNT), as nano-fillers, have the ability to improve the mechanical and electrical properties of the host matrix. The composite properties depend significantly on the distribution of the CNTs within the polymer matrix, and on the nature of the interface between the polymer and the CNTs. Here we aim to study the relation between the nanoscale morphology, obtained through optical fluorescence microscopy, and macroscale properties. The rationale for applying optical microscopy over electron microscopy is three-fold. First, optical microscopy is non-destructive and can penetrate microns deep into CNT/polymer composites to reveal the three-dimensional structure from the nano- to the micro-scale. Second, labeling the matrix and/or CNTs with fluorescent dyes can make such optical measurements visible to regions of particular interest, such as the interphase. Third, super-resolution imaging techniques, which were originally developed in the field of biology, can be implemented to provide resolution ideally at the 10-20 nm scale. We employ photoactivation localization microscopy (PALM) which precisely locates isolated, activated fluorophores over a series of diffraction-limited images. Combining the locations of the fluorophores generates a final super-resolution image. The PALM method requires photoactivatable dye molecules, which are synthesized by a ring closure reaction in alcoholic solvents. We have developed techniques to incorporate such dyes into CNT/polymer nanocomposites. Combinations of different dyes in the polymer and attached to the CNTs can be used to highlight the interfacial regions in nanocomposites.
238 - Electrochemical supercapacitors based on covalently-grafted polyaniline on graphene oxide sheets

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Conventional energy storage devices, such as batteries, have limitations such as short cycle life and relatively slow charging/discharging currents. Recently, electrochemical supercapacitors have attracted much attention due to their excellent cycling performance and higher power density. Especially, much effort has been dedicated to the construction of supercapacitors using polyaniline (PANI). PANI has been considered as one of the most promising and versatile conducting polymers for supercapacitor application due to its high capacitance, low cost, and easy synthesis. However, PANI suffers from poor cycling stability caused by swelling and shrinking of the polymer backbone during charging/discharging. This drawback greatly limits the potential of PANI as the supercapacitor electrode in practical applications.

In the present study, we utilize a facile route to prepare covalently-grafted PANI /GO nanocomposites by in-situ polymerization of aniline initiated on aniline-functionalized GO sheets. This approach involves first the functionalization of GO with p-phenyldiamine via a diazonium reaction, followed by an in-situ polymerization of aniline in the presence of aniline-functionalized GO, HNO₃, and ammonium persulfate. The as-prepared covalently-bonded PANI/GO composites exhibited a hybrid morphology, which consists of GO of layered structure, PANI thin film on GO, and vertically-grown PANI nanorods on GO. The unique structure of this composite material is expected to maximize the synergistic effect between PANI and GO, leading to a higher capacitance and improved cycling stability as supercapacitor electrodes.
239 - Investigation of Nafion ionomer degradation in catalyst layer

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The membrane electrode assembly (MEA) is the core component of PEFCs. The MEA structure consists of two porous catalyst layers which are consisting of recast Nafion ionomer and the precious Pt metal catalyst nano particle sitting on the surface of carbon black aggregates. The Nafion® ionomer network in catalyst layer functions not only as a binder, but also as the necessary proton transport pathway.

In our work, Nafion ionomer degradation in the catalyst layer has been investigated using a simulated process of a series of catalyst layers with different amounts of Nafion content to eliminate the influence from catalyst particles and membrane degradation. The degradation of the Nafion network in the catalyst layer was assumed to result in a shrunk Nafion network, which was simulated using a catalyst layer with a lower Nafion content. Catalyst layers with different Nafion content (A set of MEAs with different Nafion content from 28% to 12% was made by spray method) were fabricated and characterized for polarization curves and AC impedance for the H⁺conductivity to simulate the degradation of the Nafion ionomer network.

The degradation of Nafion affected on performance and structure of the membrane electrode assembly (MEA). With the decrease of Nafion ionomer in catalyst layer, it was shown to have an effect on performance within the entire range of polarization curves, shown in Fig1.
Commercial and military aircraft are equipped with numerous antennas to transmit and receive at various frequencies, each operating for a specific purpose. Each antenna not only adds to the complexity of the electronics of the aircraft, but can also add a substantial amount of weight. Utilizing a lightweight material with low dielectric properties as the antenna substrate has the potential to significantly increase the overall efficiency of operation of an aircraft by allowing a single antenna to cover a much wider bandwidth of frequencies and also by reducing the total antenna weight. Aerogels are extremely porous, lightweight solid materials that possess many unique properties including low relative dielectric constants and low density. This paper will discuss development and refinement of the synthesis of fluorinated polyimide aerogels. In addition, the effect of structure on various properties of the polyimide aerogels will also be presented. Finally, prototype antennas and antenna arrays using the aerogels as substrates will be demonstrated and compared to current state of practice antenna substrates.
241 - Fouling release properties of natural and non-natural amphiphilic oligopeptide side chains on a PS-b-P(DMS-co-VMS) based diblock copolymer

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Amphiphilic surfaces, having both hydrophobic and hydrophilic properties, have been considered for marine antifouling and fouling release applications, as they may provide an environmentally friendly nonbiocidal alternative for surface coating. In previous studies by our group, hydrophobic- and hydrophilic-based polymers have been modified using either epoxidation and etherification or click reactions to attach different functional groups, including amphiphilic side chains. The side chains predominately used are hydrocarbons, silicone, perfluorinated carbon chains, and PEG. Currently we are proposing a new class of amphiphilic side chain using natural and non-natural oligopeptides. These amino acids have a diverse array of functionalities and polarities that can be arranged in any sequence to optimize antifouling and fouling release behavior. Due to advances in solid state peptide synthesis, these peptides can be synthesized on a multiple gram scale in a short period of time. The first two natural oligopeptides that were used were a V-al4Cys residue and a Ser4Cys residue that were 'clicked onto PS-b-P(DMS-co-VMS) diblock copolymer. The first class of non-natural peptides that will be used incorporates a lysine which will be functionalized with PEG or perfluorinated carbon chains. The functionalized PS-b-P(DMS-co-VMS) diblock copolymer was annealed on to glass sides. The polymer surface has been characterized with bubble contact angle measurements, XPS, NEXAFS, protein absorption, and antifouling ability.
Phosphorescent materials have attracted much attention due to potential applications in solid-state lighting and light emitting diode because they can provide three-fold higher internal quantum efficiency than fluorescent alternatives by harvesting triplet excitons through intersystem crossing. While many organometallic compounds are efficient phosphors due to spin-orbit coupling promoted by metals, they require rare and expensive elements such as platinum and iridium. Developing metal-free phosphorescent materials is promising but challenging because suppressing the vibration of triplets, one of the key processes, is not efficient without heavy metal atoms. While recent studies reveal bright phosphorescence can be realized in purely organic crystalline materials through directed halogen bonding, these organic phosphors still have limitations to practical applications due to the stringent requirement of high quality crystal formation. In this presentation, we will report bright room temperature phosphorescence by embedding a purely organic phosphor into an amorphous glassy polymer matrix. Our study implies that the reduced beta (β)-relaxation of isotactic PMMA most efficiently suppresses the vibrational decay and allows the embedded organic phosphors to achieve a bright 7.5% phosphorescence quantum yield. We will also demonstrate a microfluidic device integrated with a novel temperature sensor based on the organic phosphors in the temperature-sensitive polymer matrix. This unique system has many advantages: (i) simple device structures, (ii) bright phosphorescence emission, (iii) a reversible thermal response, and (iv) tunable temperature sensing ranges by using different polymers.
243 - Design and fabrication of localized resonators for acoustic metamaterial applications

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Acoustic metamaterials exhibit a transmission band gap in the sonic range, due to the existence of both a negative bulk modulus and negative mass density at the material's resonant frequency. By taking advantage of the control offered by microfluidic devices, we can fabricate resonators from monodisperse double emulsions. The double emulsion drops include an inner fluid that is a suspension surrounded by a curable liquid rubber. These drops are collected in solution where the core is consolidated in order to achieve a higher volume fraction and the shell crosslinks, forming the resonator. Resonators can be fabricated with diameters ranging from 100 µm to 5 mm. Dried resonators are embedded in an epoxy matrix to form the acoustic metamaterial. This method of rapid fabrication with precise control over the resonator properties will result in the ability to attenuate specific frequencies. This should then lead to other metamaterial applications currently being investigated such as acoustic waveguiding.
Pairs of bifunctional initiators have been designed that carry complementary hydrogen-bonding sites consisting of alternatingly placed multiple acceptors (A) and donors (D) (e.g., –ADA–) between two initiating halogens for metal-catalyzed living radical polymerization. These initiators give well-defined polymers with an A/D hydrogen-bonding sites at the center of a polymer backbone, to form X-shaped supramolecular self-assemblies. Such positionally induced association is interesting in that it would lead to advanced self-assemblies without changing polymer backbone structures.

Following the lead, this work was directed to introducing the multiple complementary A/D interactive sites in a regular interval along a polymer chain. Radical oligomerization was first initiated with the designed bifunctional initiator (e.g., Cl–DAD–Cl or Cl–DADDAD–Cl) to obtain oligomers of controlled molecular weights. Subsequent chain extension by radical coupling led to the target polymers with regularly positioned multiple recognition sites, –(DAD)n– or –(DADDAD)n–, respectively. Supramolecular self-assemblies are also examined for these self-complimentary polymer pairs, such as –(DAD)n– and –(ADA)m–.
A fluorous functional nanospace was created within the fluorine-condensed microgel-core in a star polymer (F-Star), which induced efficient, selective, and stimuli-responsive molecular recognition (see the attached illustration; Macromolecules 2011, 44, 4574). F-Stars were efficiently synthesized by locally crosslinking macro-initiators (PMMACl; arms) with a bifunctional methacrylate (12FODMA or EGDMA; core-forming linking agent) in the presence of perfluorinated monomers [R_FMA; R_F: C_4F_9 (9F), C_6F_13H (12F), C_6F_13 (13F), C_8F_17 (17F)]. For example, the core-formation with 13FMA led to 13F-Star: M_w = 2.0 x 10^6; 86 PMMA-arms; 14800 fluorine atoms/core. The thermal mobility of the fluorine atoms was much smaller in the 13F-Star core than in MMA/13FOMA random and block copolymers with similar fluorine contents, as confirmed by clearly reduced 19F NMR spin-spin relaxation time (T_2). Independent of the total number of fluorine per polymer, all these F-Stars solubilized perfluorinated guests (PFH, PFO, and PFMCH) in DMF. The solubilization efficiency, or fluorous recognition, apparently depended the number of in-core – CF_3 units, rather than the total number of fluorine atoms (–CF_3 + –C_2F_5 –). F-Stars selectively captured PFO even in the presence of fluorine-containing hydrophobic and hydrophilic compounds (TFMB and TFE, respectively) and also released the guest upon mild heating or addition of excess CHCl_3.
246 - Sequence-controlling radical polymerization with template molecules

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The sequence of monomer units along a polymer chain is the most essential structural factor in biopolymers to express unique functions. We have achieved "repetitive and periodic" sequences (e.g., ABABAB and ABAABA) in vinyl polymers by radical polymerizations with designed "template monomers".1)

This work is to propose a new concept of sequence control: the "bipedal walking template" for discretionary or aperiodic sequences via repetitive "single monomer addition" in radical polymerization. The walking templates were designed to carry a pair of cleavable bonds that meet the following criteria. 1) **orthogonal**: independently cleavable by different stimulus without affecting each other; 2) **cleaving**: quantitatively cleavable by "scissors" molecules via substitution (like S_N2); and 3) **renewing**: reproducing the same cleavable bonds. The combination of N-hydroxysuccinimide ester and pyridyl disulfide met the criteria and were thereby employed to attach a pair of initiator and monomer units onto a template framework to demonstrate the validity of this concept by a repetitive cyclopolymerization, as illustrated in the scheme.


**Tuesday, September 10, 2013 05:30 PM**
**Sequence-Controlled Polymers (05:30 PM - 07:30 PM)**
**Location: Indiana Convention Center**
**Room: Hall I**
247 - Synthesis of precision glycopolymers for bioapplications

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Glycopolymers play crucial roles in biological communication events due to a dramatic effect of the carbohydrate units on the affinity of recognition biomolecules. Additionally, the precise synthesis of macromolecules with controlled chain length, architecture, monomer sequence provides both an effective and selective binding to the lectins. Therefore, new generation is interested in sequence controlled precision glycopolymer and also there are some very recent examples of sequence controlled glycopolymer synthesis procedures. In this study, the first part includes classical well-defined synthetic glycopolymer structure that were synthesized via RAFT polymerization technique using trimethylsilyl propargyl methacrylate (TMSMA) and Glycidyl methacrylate (GMA) monomers. In the second part, copolymerization of styrene with pentafluorostyrene (PFS) and poly(ethylene glycol) methyl ether acrylate (PEGA) was performed by the nitroxide-mediated radical polymerization (NMP). Polymerization kinetic of monomers allowed a sufficient control in chain length, architecture, monomer sequence. These obtained glycopolymers were then subject to their potential for biotechnologies applications owing to their recognition of lectins such as targeted drug delivery systems and biocapture analysis as well as therapeutics.

Schematic illustration of the glycopolymers in various compositions and architectures.
248 - Design of 1D single-chain bioarrays

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In the last decade, the challenges for polymer chemists are to control the co-monomer sequences of synthetic macromolecules and their post-functionalization in order to bring new properties. In the present work, polystyrene chains bearing three different silyl protected acetylenic maleimides have been prepared by nitroxide-mediated polymerization. The incorporation of substituted maleimides, at specific locations of the polystyrene chain, allowed creating functionalizable areas. Triethylsilyl (TES), trimethylsilyl (TMS) and triisopropylsilyl (TIPS) protective groups have been chosen in order to orthogonally deprotect and functionalize the acetylenic moieties using the copper-catalyzed azide-alkyne cycloaddition (CuAAC). This strategy permitted the successive insertion of three different carbohydrates units in order to form 1D single-chain sugar-arrays. Such macromolecular objects are of particular interest in many biological fields such as diagnostics or biocatalysis.
Organic semiconducting materials are of increasing technological significance. Among the most promising applications are thin-film organic photovoltaic devices, which can be fabricated by low-cost, solution processing methods. A large number of different materials have been prepared in an effort to enhance the performance of these devices. The “push-pull” strategy is a widely used approach for optimizing oligomeric and polymeric materials, particularly those with small band gaps. By choosing appropriate electron-rich donor and electron-deficient acceptor monomers, the energy gaps of these polymers can be tuned.

There has been an increased interest in investigating the effects of monomer sequence on macromolecular materials. However, studies of sequence effects—changing the order of donor and acceptor—on fully conjugated oligomers and polymers are rare. Indeed, the vast majority of donor/acceptor copolymers and co-oligomers have a simple alternating or random structure. Recently, however, we reported that HOMO-LUMO gap depended on sequence even for oligomers consisting of electronically similar alkoxy and unsubstituted phenylene-vinylenes. We have now extended these studies to include monomers with greater acceptor characteristics. In the figure below the difference in absorption wavelengths for a series of trimeric oligomers is presented (A = benzothiadiazole; D = 2,5-alkoxy-substituted phenyl units; connection through vinylene linkers). We have also noted sequence-based differences in intermolecular packing, which have profound implications for charge carrier mobility in device applications.
250 - Metal-free living cationic polymerization via reversible addition-fragmentation chain transfer (RAFT) mechanism

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In this paper, we report a new metal-free initiating system for living cationic polymerization that proceeds not via the metal-catalyzed activation but via a reversible activation by a carbocation, in which mainly a covalent C-S bond is activated via reversible addition-fragmentation chain transfer (RAFT) mechanism similar to the well-known RAFT radical polymerization (Scheme 1). The cationic polymerization of isobutyl vinyl ether (IBVE) was carried out in the presence of various thioesters employing a trace amount of trifluoromethanesulfonic acid (TfOH) as the cationogen ([TfOH]₀ = 10 ppm). The \( M_n \) of the obtained polymers increased in direct proportion to the monomer conversion with relatively narrow molecular weight distributions and agreed well with the calculated values assuming that one transfer agent generated one polymer chain. In addition, the obtained living polymers with C-S terminal were accessible to novel sequenced block copolymers consisting of cationically and radically polymerized segments via the transformation from cationic into radical RAFT polymerization.

![Scheme 1. Living Cationic RAFT Polymerization](image-url)
Synthesis of specific sequenced vinyl copolymer via radical alternating copolymerization of maleimide-functionalized sequence-regulated oligomers

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In this paper, we report the synthesis of novel specifically sequence-regulated vinyl copolymers via radical alternating copolymerization of maleimide-functionalized sequence-regulated oligomer with styrene (Figure 1). The maleimide-functionalized oligomers were prepared in good yield by one-by-one sequential Kharasch radical addition of vinyl monomers to halogen compounds, followed by S_N2 reaction with furan-masked maleimide. The copolymerization of the oligomers with styrene was investigated in toluene using AIBN as the initiator. The oligomers and styrene were smoothly consumed nearly at the same rate and gave almost alternating copolymers. Moreover, the effects of the highly regulated sequences were also evaluated on the properties of the obtained copolymers.

Figure 1. Radical Copolymerization of Maleimide-Functionalized Sequence-Regulated Oligomer

Tuesday, September 10, 2013 05:30 PM
Sequence-Controlled Polymers (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
252 - Synthesis of sequence-defined oligomers using well-defined soluble polymer supports: Direct access to precision block copolymers

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In this work, soluble polymer supports were used for preparing block copolymers containing sequence-ordered segments. Well-defined cleavable or non-cleavable polystyrene supports were prepared by atom transfer radical polymerization (ATRP) or activators regenerated by electron transfer (ARGET) ATRP and utilized for the iterative synthesis of hexapeptides and other types of oligomers. The presented strategy is not limited to polystyrene supports but can be extended to a wide variety of biorelevant synthetic segments such as biocompatible or stimuli-responsive polymers.
Crystal growing in gel media has been extensively studied with the purpose of understanding bio-metallic behavior in crystalline structures. It is known that a crystal growth phenomenon in polymeric solutions is directly dependent on the methodology carried out.

Here we are reporting about the feasible synthetic strategy to attain useful biomaterials with general formulae $M-(L)_n$; $(M= \text{Ba, Ca, Mg, Sb, Sn}; L= \text{tartaric acid, NH}_4\text{HPO}_4, \text{poly-ethylene oxide})$ that allow us understand some chemical similarities between metal ions under the presence of biological ligands to form stable materials.

In this research endeavor, $\text{Ba}^{\text{II}}, \text{Ca}^{\text{II}}, \text{Mg}^{\text{II}}, \text{Sn}^{\text{II}}$ and $\text{Sb}^{\text{III}}$ have been choice as metal ions due to their proximity in the periodic table as either group or period members. The gels were polymerized by dropwising a solution of $\text{Na}_2\text{SiO}_3-x\text{H}_2\text{O}$ on $\text{NH}_4\text{HPO}_4$, $L-$ (+) tartaric acid or poly-(ethylene oxide) in ultra-pure water to form a mixture at room temperature.

This polymeric solution was placed into test tubes awaiting two days for the gel formation. A solution from 0.1 to 1.0 M of corresponding metallic saltwas added to grow the desired crystal. All $M-L$ solutions demonstrated "fish fin"- like crystal growth upon the second day of addition. After two weeks at stand, colorless-to-yellowish like crystals were take off from the matrix, washed with cold water and dried on $\text{CaCl}_2$.

Further FT-IR, UV-VIS spectroscopy, TGA, and elemental analysis determination suggest compatibility of structures with those proposed by molecular mechanical modeling.
254 - Comparing the effect of chemically modified rice husk reinforcement on properties of urea formaldehyde composites

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Rice husk (RH) is an abundant and inexpensive agricultural residue in most parts of the world where wood resources are limited. The purpose of this study was to investigate the moisture resistance and mechanical properties of the inexpensive, but brittle, urea-formaldehyde (UF) thermoset resin reinforced with unmodified and chemically modified RH. Chemical modifications were designed to modify the interface properties and to determine how thick an interface is required to modify the interface to enhance moisture resistance and toughness. In order to answer these questions we used a type of “controlled radical polymerization” (Atom transfer radical polymerization, ATRP) that allowed us to test the effect of using a hydrophobic interface for moisture resistance “topped” by a polar monomer to adhere to the UF resin. The RH was modified by polymerizing specific numbers of Methyl Methacrylate monomers (giving PMMA), and Acrylonitrile monomers (giving PAN), for the following grafted RH modifications: RH-g-PMMA (for moisture only) and RH-g-PMMA-g-PAN (for moisture and toughness). The interface modifications were analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray photon spectroscopy (XPS), and Scanning electron microscopy (FE-SEM). UF-grafted RH composites were prepared with (66.6 %) UF and (33.3 %) RH, mechanical and moisture properties were measured.

![Figure 1](image-url) Moisture absorption percentage of UF/RH unmodified and chemically modified composites for 12 hours and the relative thickness of the grafted polymer chains at the RH interface.

Tuesday, September 10, 2013 05:30 PM
Structural Composites and Biomaterials: Modeling and Experiment (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
Nanocomposite hydrogels rely on weak physical bonds (e.g., hydrogen bonding, ionic interactions, etc.) between the polymer network and encapsulated nanoparticles to achieve elevated materials properties and recovery after repeated deformation. Here, derivatives of an adhesive amino acid, DOPA, found in mussel adhesive proteins (e.g., dopamine and nitrodopamine) were incorporated into PEG-based nanocomposite hydrogels to enhance the interfacial binding between PEG and nano-silicate, Laponite. Nitrodopamine-modified PEG (PEG-ND) cured instantly as compared to a cure time of 1 minute for dopamine-modified PEG (PEG-D). Nitrodopamine contains an electron-withdrawing group (e.g., -NO₂), which lowers its pKa for faster oxidative crosslinking. From oscillatory rheometry, values for G' and G" for PEG-ND were an order of magnitude higher than those of PEG-D. Nitro-functionalization likely increased the affinity of nitrodopamine to inorganic surfaces, resulting in enhanced viscous dissipation properties. The combination of elevated elastic and viscous properties make these nanocomposites well suited for repeated load bearing.
Electrostatic interactions between oppositely charged polymers can lead to a variety of complexes with diverse structures and properties. Under defined conditions¹ liquid complexes, referred to as complex coacervates, can be formed. Using polypeptides as a model system we studied complex coacervation and identified a series of parameters (e.g. pH, ionic strength, and stoichiometry) that affect this phenomenon. Polypeptide coacervate properties such as interfacial energy² and viscoelasticity³ as well as the thermodynamics⁴ of the complexation between polypeptides were also examined with respect to changes in external parameters. More complex molecular design can be utilized whereby a polyelectrolyte domain is connected to a neutral polymer block. These neutral domains stabilize microphase separation of the coacervate phase. For example, mixing of a polypeptide copolymer with an oppositely charged polypeptide homopolymer results in the formation of nanometer-sized micelles with a coacervate core. Formation of a hydrogel network with linked coacervate core domains is observed when the concentration of the polymers is increased. A number of experimental techniques including TEM, rheology, and light scattering are used for the characterization of the coacervate assemblies.

257 - Self-assembly and stability of small model systems at various pH conditions

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Understanding the physical, chemical and mechanical properties of biomaterials is important for the rational design of biomedical tools such as imaging and drug delivery agents. Of particular interest is a class of new materials termed peptide amphiphiles, made up of hydrocarbon tails and polypeptide headgroups, which can self-assemble into three-dimensional structures under specific solution conditions. Understanding at a molecular level, the mechanisms by which the peptide amphiphiles interact and self-organize at specific pH conditions is important for designing delivery vehicles for cancer therapy.

Towards this goal we applied constant pH molecular dynamics simulations with the pH replica-exchange sampling protocol to study the stability and conformational dynamics of a small model system, the tetramer of IAAEEEE, at various pH conditions. In our preliminary investigation, we observed that below a transition pH, the tetramer remained stable as β-sheet while above the transition pH the tetramer unfolds to random-coil monomers. The results are in agreement with experimental data. Most importantly, we were able to predict the transition pH and offer atomic details regarding how protonation states of Glu control the self-assembly.

Tuesday, September 10, 2013 05:30 PM
Structural Composites and Biomaterials: Modeling and Experiment (05:30 PM - 07:30 PM)
Location: Indiana Convention Center
Room: Hall I
Knowledge of the self-assembly and phase behavior of pH-sensitive surfactants has implications in many technological applications such as formulation of detergents and development of drug delivery vehicles. The recently developed continuous constant pH molecular dynamics (CpHMD) technique has opened a door to atomic-level understanding of such phenomena. As a proof of principle study, we applied CpHMD to simulate the self-assembly of 12-carbon fatty acids. We observed the formation of a micelle at high pH and a bilayer at low pH, as seen in experiment. Both the micelle-bilayer transition pH as well as the apparent pKₐ values are in quantitative agreement with experiment. Additional data show that aggregates containing more fatty acids have a higher pKₐ, and decreasing the tail length decreases the pKₐ. We have also studied the titration behavior of fatty acids in bilayers of 18-carbon surfactants. These results give novel insights into the interplay between protonation, conformational dynamics and phase transitions.
259 - Titratable water models for all-atom constant pH molecular dynamics

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pH is critical for chemical and biological processes. To simulate pH-dependent processes, the continuous constant pH molecular dynamics (CpHMD) method has been developed. The CpHMD method was initially based on the generalized Born implicit-solvent model, which introduces unphysical artifacts. To avoid the drawback of the implicit-solvent model, the CpHMD method was recently extended to all-atom explicit-solvent simulations. For the all-atom CpHMD, titratable co-ions are used to balance charges of titratable groups varying in simulations. However, varying charges of co-ions such as sodium and chloride are unphysical. To replace the unphysical co-ions, we developed titratable water models, which enable interconversion between water and hydroxide/hydronium (Figure 1A). We tested the titratable water models on titration of three proteins, HP36, BBL, and HEWL. The calculated pKa's are in good agreement with experiment with average unsigned and root-man-square errors less than one pH unit (Figure 1B). In addition, coupling of titratable water to titratable groups of solute mimics proton exchange between solute and solvent, opening up opportunities to study proton transfer involved in many biological systems such as proton channels.
The generation of a patterned surface that can be postpolymerization modified to incorporate fragile macromolecules or delicate biomolecules without the need for special equipment is described. Two monomers that undergo different click reactions, pentafluorophenyl acrylate (PFPA) and 4-(trimethylsilyl) ethynylstyrene (TMSES), were sequentially polymerized from a silicon surface in the presence of a shadowmask with UV light, generating 12.5 and 62 micron pitch patterns. Two different dyes, 1-aminomethylpyrene (AMP) and 5-azidofluorescein (AF), were covalently attached to the polymer brushes through aminolysis and dual desilylation/Copper(I)-catalyzed alkyne/azide cycloaddition (CuAAC) in one pot. Unlike most CuAAC reactions, the terminal alkyne of TMSES was not deprotected prior to functionalization. Although a 2 nm thickness increase was observed for poly(PFPA) brushes after polymerization of TMSES, cross-contamination was not visible through fluorescence microscopy after functionalization.
Research on superhydrophobic surfaces (i.e. surfaces with a water contact angle larger than 150° and low hysteresis and sliding angle) has exponentially-grown for the last decade because of the interest in both scientific and industrial communities. Superhydrophobicity results from the combination of low surface energy materials with an appropriate surface structuration. In nature, many biological materials exhibit water-repellency properties. These surfaces inspired scientists to develop various biomimetic and bioinspired approaches to build materials with superhydrophobic properties.

In literature, the general strategy to make superhydrophobic surfaces is to use highly fluorinated compounds during the process or in a post-treatment step. However, as observed in nature, fluorine is not necessary to obtain high water-repellent surfaces. In addition, long fluorinated chains present consequent impacts on environment because of bioaccumulation of these chains.

Electropolymerization is a fast, reproducible and versatile method to make superhydrophobic surfaces. Morphology and surface growth are governed not only by the monomer chemical structure (polymerizable core, substituent)\(^1\)\(^-\)\(^3\) but also by the electrochemical parameters (deposition charge, solvent, doping agent, electropolymerization technique,...)\(^2\). This work presents some examples of bioinspired superhydrophobic polymer surfaces made by electrochemical polymerization.

This work outlines the characterization of poly(3-hexylthiophene) (P3HT) colloids dispersed in aqueous solutions created using a mini-emulsion technique. A blade coating procedure was used to produce high quality films from these colloidal suspensions, and the crystallinity development of the films coated from these colloids was compared with active layers coated from solutions in organic solvents. We show that both size and crystallinity of these colloids and their films can be tuned by controlling the initial solution concentration, type of solvents and surfactants as well as processing parameters.

The colloidal size was measured by dynamic light scattering (DLS), and the results showed that these colloids were stable against aggregation for several weeks. The presence of surfactant affected the crystal structure of P3HT colloids, which in turn could affect the photoelectric properties of active layers. The morphology of both colloids and active layers were characterized using TEM, SEM and AFM. In addition, the optical and photoelectric properties of active layers blade coated from colloids were investigated and correlated to the specific crystallinity and morphology of the films, and compared with active layers coated from organic solutions.
A facile one-pot strategy to synthesize dye-composited microgels was developed. The rationally selected co-monomers and commercially available dye molecules placed in one pot can be readily fabricated into monodispersed dye-composited microgels via free radical precipitation polymerization in water. With a rational design on functional co-monomers, low cost dye-complexed microgels are capable of continuous glucose detection at near physiological pH via intramolecular B⋯N+ bond formation. The glucose sensitive swelling/shrinking of the microgel could shift the π-π stacking of the dye assemblies on the gel network, and thus convert the glucose concentration changes into optical signal changes.

The dye-composited microgels with optimal content of functional co-monomers demonstrated high glucose sensitivity and signal reproducibility at physiological pH, which provides a promise for continuous glucose detection.
We have developed a highly versatile universal approach to grow polymer brushes from a variety of substrates with high grafting density by using a single-component system. We describe a random copolymer which consists of an inimer, \( p-(2\text{-bromoisobutyloylmethyl})\text{-styrene} \) (BiBMS), copolymerized with glycidyl methacrylate (GMA) synthesized by reversible addition−fragmentation chain-transfer (RAFT) polymerization. Thermal cross-linking created a mat that was stable during long exposure in organic solvent even with sonication or during Soxhlet extraction. The absolute bromine density was determined via X-ray photoelectron spectroscopy (XPS) to be \( 1.86 \pm 0.12 \text{ Br atoms/nm}^3 \). Surface-initiated ATRP (SI-ATRP) was used to grow PMMA brushes on the substrate which were characterized by ellipsometry, XPS, and atomic force microscopy (AFM with a grafting density of \( 0.80 \pm 0.06 \text{ chains/nm}^2 \)).

Through the self-assembly of block copolymer on top of the mat, nanopatterned brushes can be grown after selective removal of one domain from the block copolymer. The inimer containing cross-linkable copolymer can be viewed as a single component ultra-thin polymeric coating which can be applied to a range of substrates to grow high chain density polymer brushes by ATRP. The ease of synthesis, chemical tunability, homogeneity of composition, stability in organic solvents and applicability by simple spin-coating to a wide range of substrates makes this a versatile approach to create functionalized interfaces.
The trans-polypentenamer has unique relevance among the synthetic rubbers since it has similar physical properties to the natural rubber. The polypentenamer additives have propitious effect on the tire properties and have been studied extensively for this application. Polypentenamer synthetic rubber was synthetized by ring-opening metathesis polymerization (ROMP) using ruthenium catalyst systems. It was found that the cyclopentene conversion does not depend on the catalyst activity and catalyst loading. However the applied reaction temperature has a significant impact on the polymerization yield. Equilibrium of growing chain and monomer was observed and the thermodynamic parameters were determined as: \( \Delta H = -5.6 \text{ kcal} \cdot \text{mol}^{-1} \); \( \Delta S = -18.5 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \). The effect of cyclopentene ring substituents on the equilibrium was also investigated by experimental and computational methods. The calculated and experimentally determined activation parameters of the synthetic rubbers made from different substituted cyclopentene derivatives are being determined. This unique feature of the equilibrium polymerization opens a way for the synthesis of durable, environmentally friendly elastomers where tires can be not only synthetized by the transition metal catalyst systems but the used tires can be readily decomposed by the same way and the recovered monomers can be easily recycled.
266 - Phenoxy ortho-substituents effects on olefin polymerization with [OSSO]-type bis(phenoxy) complexes

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[OSSO]-type bis(phenoxy) group metal complexes bearing a trans cyclooctylene ansa group have been known to show high activity in olefin polymerization. For instance, the corresponding Zr catalyst, tBu groups on ortho position, can produce iso-poly(1-hexene) with very high tacticity. The investigation of the ligand structure has been continued and resulted in a vast variety of catalysts development. This presentation will focus on the ortho-substituents effect on activity, tacticity, molecular weight of polymer and chain transfer mechanism and discuss the possibilities of [OSSO]-type catalyst system.
Norbornane based bicyclic polymers have great economic significance because their bulk, bridged cyclic skeleton affords unique properties. Most bicyclic compounds used in the industry are made from hydrogenation or oxidization of Diels-Alder adducts obtained from dicyclopentadiene and other chemicals. To develop the new low-cost functional resins for coating, adhesive or plastics, three new synthetic methods were investigated and the results indicate the bicyclic polymers can be produced by the addition of the corresponding carboxylic acids to norbornenyl ring in the Diels-Alder adduct. These three practical synthetic approaches, characterization and properties of cyclic polymers containing norbornyl ester groups will be presented. The possible industry applications of these synthetic techniques for polyester, polyol, polyesterimide, hydrocarbon resins will be described.
268 - Thiocarbonyl and thioester moieties as thiol protecting groups for controlled radical polymerization

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Controlled radical polymerization (CRP) is a very robust and powerful technique that allows preparing well-defined functional architectures from a wide range of monomers. Among the numerous chemistries employed in macromolecular engineering, thiol chemistry currently stands as one of the most versatile tool for synthesis of functional polymers and materials. However, thiol groups are not compatible with controlled radical polymerization processes since they induce irreversible chain transfer. A simple methodology to prepare well-defined polythiol copolymers by controlled radical polymerization was developed to address this issue.

Use of xanthate, dithiocarbamate and thioacetate moieties as thiol protecting groups was investigated. Model reactions were conducted to study the effect of these protecting groups during controlled radical polymerization of acrylates, methacrylates and styrenics. Deprotection of these moieties by aminolysis was also investigated.

A simple two steps procedure allowed preparing monomers carrying S-alkyl-O-ethyl xanthate moiety as thiol protecting group. Polythiols were obtained by copolymerizing the functional monomers with (meth)acrylates and subsequent aminolysis of the protecting groups. Both atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization were successfully employed to prepare well-defined polythiols. Functionalization of polythiol copolymers was achieved via thiol-ene addition, Michael addition and thiol-disulfide exchange. Thiol deprotection and functionalization were conducted in one-pot for Michael addition and thiol-disulfide exchange. A complete conversion of thiol groups was observed for all three types of reactions, exemplifying the potential of polythiols for the preparation of functional materials.
Silica is widely used as a filler in cross-linked silicones to improve material properties, particularly mechanical strength. This reinforcement effect is generally attributed to the high modulus of silica particles and hydrogen bonding between silica and PDMS chains. We report that Stober silica particles actively participate in the chemical cross-linking of linear PDMS prepared by anionic ring-opening polymerization of octamethylcyclotetrasiloxane (D₄). The silica particles serve as reservoirs for the growing siloxane network and crosslinks are equilibrated into the matrix during polymerization. Scanning electron microscopy and a series of swelling tests demonstrate the erosion of silica particles and the presence of covalent bonds between silica and PDMS. The living (self-healing and chemical stress relaxing) nature of these materials will be reported as well as their use in preparing controlled modulus and gradient modulus materials.

Figure 1. SEM image of a silica particle (initially 10 μm in diameter) after equilibration with a living anionic siloxane network and calcination.

Wednesday, September 11, 2013 11:30 AM
General Topics: New Synthesis and Characterization of Polymers (08:30 AM - 12:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
Amphiphilic double-brush copolymers (DBCs) with each graft site quantitatively carrying both a hydrophilic poly(ethylene oxide) (PEO) graft and a hydrophobic polystyrene (PSt) graft were synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene using a PEO-based norborene-functionalized RAFT agent, followed by ring-opening metathesis polymerization of the resulting diblock macromonomer. These DBCs were utilized as giant surfactants and polyfunctional RAFT agents in miniemulsion polymerization of St. Without using a cross-linker, well-defined polymeric nanolatexes with narrow size distributions were yielded; however, with the presence of divinylbenzene as the cross-linker, vesicular polymeric nanocapsules were obtained as the major product.
Catenanes are topologically interesting molecules composed of two or more mechanically interlocked rings. Over the years, various methods have been reported to synthesize low molecular weight catenanes facilitated by inter- and intramolecular interactions. However, synthesis of comparatively high molecular weight catenanes remains a synthetic challenge. We report the synthesis of catenated poly(caprolactone) via a ring expansion strategy from a supramolecularly templated initiator. This approach allowed a high yielding synthesis and simple isolation method of the target catenated polymer. To obtain the catenated polymer free of Sn, alkene-terminated caprolactone monomers were also copolymerized secondly and intramolecular cross linking will result the stable catenated polymer.
Development of high-performance, recyclable bioplastics is an important task for establishment of low carbon society because of long term carbon-stock in the plastic cycles. Here we synthesized aromatic polyesters, polyamides, and polyimides whose monomers were cinnamic acid derivatives which were available by extraction from plant wastes or by fermentation of microorganism. The aromatic polyesters I prepared at first showed a unique function of photomechanics producing a high power, but its thermoresistance was not high enough to apply as a super-engineering plastics. Then we prepared polyamides and polyimides from the difunctional dimers of cinnamic acid derivatives. They had the 10% weight loss temperature and glass transition temperature higher than 360 °C and 270 °C, respectively. The values were high enough to use as super engineering plastics. In addition, the present aromatic polyamides were very efficiently degraded into monomer by a simple combination of photoreaction and hydrolysis and then the recovered monomers were successfully re-polymerized.
273 - Synthesis and characterization of thermosetting furan-based epoxy materials with improved thermo-mechanical properties

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Renewable alternatives to petroleum–based thermosetting polymers have drawn significant research attention due to their potential economic and ecological impact. For this, they must mimic the rigid, phenylic structure of high performance thermoset monomers. Rigid and naturally plentiful in cellulose and hemicellulose, furan is one promising candidate for such phenyl replacement. However, no direct comparison of furan and phenyl–based epoxy monomers has appeared in literature. In this work, parallel furan– and phenyl–based epoxy monomers were synthesized, blended with DGEBA and amine–based curing agents, cured, and characterized. The resulting furan–based polymers presented improved $T_g$ ($\Delta=8–16^\circ C$) and modulus ($\Delta=0.1–0.6$ GPa) relative to their phenylic analog. Furan has thus been shown to be a potential building block for renewable high–performance epoxies, with potential applications in other thermosetting polymers.
274 - Fatty acids: The perfect renewable feedstock for “green” toughening modifiers of poly(lactic acid)?

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Poly(lactic acid) (PLA) is an aliphatic polyester that fits remarkably well with the high demands for greener materials.¹ However, the brittleness of PLA has prevented it from a wide range of applications. Thus environmental friendly solutions such as copolymerization or blending with soft bio-based polymers are needed.

Nowadays, vegetable oils are gaining widespread interest thanks to their availability, sustainability and biodegradability. Indeed, triglycerides bring different functional groups that can be derivatized to design new promising monomers. All these considerations prompted us to investigate the use of fatty acid-based low Tg polymers as ‘green’ toughening agents for PLA. First, triblock copolymers PLA-b-poly(ricinoleic acid)-b-PLA were synthesized by a sequential self-condensation of ricinoleic acid methyl ester and ring-opening polymerization of L-lactide, thus leading to fully bio-based copolyesters.² These copolymers were used as additives leading to an improvement of PLA flexibility. Second, poly(ester-amide)s (PEAs) were synthesized from novel diols from methyl 10-undecenoate.³ One of these PEAs was melt-blended with PLA yielded toughened PLA.⁴ During this presentation, a critical discussion about the potential of fatty-acid based polymers as toughening agents of PLA will be made.

Worldwide efforts have increased greatly to identify polymeric building blocks that are not derived from fossil fuels and to employ these monomers to create polymers that readily degrade in natural environments. We have developed novel methods for synthesizing linear thermoplastic polymers from a variety of biogenic feedstocks, including sugars, triglycerides, lignin, and C1 feedstocks that can be obtained from trees. This presentation will focus on methodology that directly converts renewable aromatic molecules—such as vanillin and ferulic acid—into polyesters. Facile conversion of vanillin and ferulic acid in polymerizable monomers as well as copolymerization strategies are crucial for tuning the polymeric thermal properties. These novel thermoplastics will be discussed in the context of replacing specific fossil fuel-based plastics.
276 - Synthesis and characterization of a novel, degradable polycarbonate derived from 3,7,4’-tribenzyl quercetin

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We have a keen interest in the design, preparation and investigation of engineering polymers that are derived from renewable biofeedstock resources and produce those same environmentally-benign and bioresorbable natural products upon degradation. Quercetin, and many of its derivatives, are well studied molecules with interesting bioactivities, but until now it has not been incorporated to form the backbone of a polymer. Described here is a novel, polycarbonate, 3,7,4’-tribenzyl quercetin polycarbonate (tBQPC), which is synthesized from 3,7,4’-tribenzyl quercetin. This polymer has been characterized by $^1$H NMR, $^{13}$C NMR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). In addition to the inherent opportunity for replacement of bisphenol A-based polycarbonates and bioapplication benefits of it being potentially biodegradable, this polymer expresses bright broad-band auto-fluorescence. Preliminary investigations of the emission properties suggest monomeric, dimeric and higher order delocalized excited states. In total, the tBQPC system presented here represents a new class of environmentally-friendly, degradable polymers, which have the potential for applications as a homopolymer system, a copolymeric signaling agent or a stand-alone photonic material. Moreover, its development in optically-responsive, mechanically-robust materials for orthopedic, dental and other biomedical applications is underway.
Triglyceride oils are currently popular raw materials used for the preparation of a variety of products. They are relatively cheap, renewable, and environmentally friendly relative to petroleum-based materials. Their methyl esters (e.g., methyl soyate) are also gaining increasing attention as biofuel. We have continued our efforts to obtain new materials based on triglyceride oils and their methyl esters. These include derivatives of triglycerides and polymeric materials produced through either the reactions of nitrogen-containing reactive groups or the polymerization of triglyceride oils. These reactions are tools that permit specific molecular weights to be achieved or specific functional groups to be attached in order to impart improved properties to the triglycerides. With appropriate modifications, it may be possible to produce triglyceride-based materials with potential applications as additives for lubricants, coatings, adhesives, and cement applications.
Plant-based compounds bearing a terminal double bond and hydroxyl and ether groups can be used efficiently as comonomers for the copolymerization with olefins including styrene. These copolymerizations are catalyzed by a palladium arylphosphine sulfonate complex, which is less oxophilic than other single-site catalysts. In particular with eugenol as comonomer, copolymers with very high comonomer contents and even polyeugenol can be obtained. The synthesis, properties and applications of these renewable polymers will be discussed.
Polymeric microscale lasers: Fundamentals and applications

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Polymeric micro-spherical lasers will be presented as sensing elements. The sensing element is essentially a polymeric microsphere with embedded a laser dye. When the micro-particle is illuminated with light (laser light or flash lamp), lasing for the micro-particle is observed through the emission spectrum. The excited optical modes of the micro-particles are commonly referred to as whispering gallery mode (WGM). The WGM phenomenon was first observed by Lord Raleigh inside the dome of the St. Paul Cathedral in London while studying the propagation of sound over a curved gallery surface. In optics, WGMs can arise from total internal reflection of light at the internal surface of a high index of refraction dielectric resonator embedded in a surrounding medium of lower index of refraction. These optical resonances (WGM) are characterized by a high optical quality factor. Any change in the morphology of the particle such as shape, size and index of refraction lead to a shift in the optical resonances. Therefore, any change in the physical condition of the surrounding that induces a change in index of refraction or radius of the microsphere can be sensed by monitoring the change (shift) in the resonance (WGM shifts). These micro-scale laser particles can be also embedded into polymeric matrix and used as a functional and sensing element.
280 - Fluorescent dye-doped polystyrene microspheres for particle image velocimetry

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Particle image velocimetry (PIV) is a valuable technique to characterize surface interaction with fluid flows. Reliable seed materials are requisite to accurately determine flow properties using PIV. In particular, low density will reduce the lag time, the delay of a seed particle reaction to changes in the flow, and a narrow size distribution will reduce the measurement uncertainty. Polystyrene latex microspheres (PSLs) have these properties. We are developing multifunctional PSLs to characterize multiple parameters of fluid flow with a single seed material. PSLs doped with a variety of fluorescent dyes were generated by dispersion polymerization. These seed materials may enable ‘near wall’ measurements unobtainable using state-of-the-art seed materials. The dye-doped particles were spectroscopically characterized both dispersed in solution and in the dry state (conditions used during PIV experiments). PSL size distributions were determined using dynamic light scattering and microscopic techniques. PSLs were doped with several fluorescent dyes with temperature sensitivity and the fluorescent emission temperature dependence was evaluated. PSL glass transition temperature was determined to be 105 °C using differential scanning calorimetry. For dye-doped PSLs evaluated in the dry state, the fluorescent emission spectral shape and intensity changed upon increasing temperature from 30 to 100 °C when excited at 532 nm. Preliminary measurements completed using dye-doped PSLs in air flows of known temperature indicating that the detection emission may be sensitive enough to discern both velocity and temperature.
281 - Mechanochemistry of europium-containing metallosupramolecular materials

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A series of lanthanide-containing polymeric networks based on telechelic poly(ethylene-co-butylene) (PEB) with 2,6-bis-(1′-methylbenzimidazolyl)pyridine chain ends (BKB) were coordinated to europium salts to afford a material (BKB\(\cdot\)\[Eu(ClO_4)\_3\]) with metal-coordinate supramolecular motifs. The europium complexes serve both as "weak" crosslinks and built-in optical sensors where the reversibility of the metal-crosslinks upon exposure to ultrasonication can be measured in situ using luminescence spectroscopy. Polymer films of BKB\(\cdot\)\[Eu(ClO_4)\_3\] were exposed to an Fe\(^{2+}\) solution with for extended periods of time with no appreciable color change. Upon ultrasonication or mechanical force, an irreversible color change characteristic of the formation of BKB∙Fe(ClO_4)_2 was observed indicating that solid-state mechanochemical activation is possible. Additionally, cut films of BKB\(\cdot\)\[Eu(ClO_4)\_3\] were mended together upon exposure to ultrasound and the original mechanical properties were recovered. The autonomous repair of materials by mechanical stimulus is rare. The features and properties of this class of metallosupramolecular materials will be discussed.
The measurement of shear stress developed as a fluid moves around a solid body is difficult to measure. Stresses at the fluid-solid interface are very small and the nature of the fluid flow is easily disturbed by introducing sensor components to the interface. To address these challenges, an array of direct and indirect techniques have been investigated with various advantages and challenges. Hot wire sensors and other indirect sensors all protrude significantly into the fluid flow. Microelectromechanical systems (MEMS) devices, although facilitating very accurate measurements, are not durable, are prone to contamination, and are difficult to implement into existing model geometries. One promising approach is the use of engineered surfaces that interact with fluid flow in a detectable manner. To this end, standard lithographic techniques have been utilized to generate elastomeric micropillar arrays of various lengths and diameters. Micropillars of controlled length and width were generated in polydimethylsiloxane (PDMS) elastomer using a soft-lithography technique. The 3D mold for micropillar replication was fabricated using laser ablation micromachining and contact lithography. Micropillar dimensions and mechanical properties were characterized and compared to shear sensing requirements. The results of this characterization as well as shear stress detection techniques will be discussed.
Liquid crystals (LCs) are anisotropic materials with physical properties that depend sensitively on both global and local molecular alignment. The ability to change LC molecular alignment under an external field will lead to dynamic tuning of the mechanical, optical and electric anisotropies of LCs, thus, providing powerful tools in controlling the propagation of light and the assembly of soft materials. LC anchoring is an essential factor in the switching and actuation behavior of LC materials, and much attention has been devoted to the study of LC anchoring on material surfaces with different chemical and topological properties. Here, we fabricated micropillar arrays from nematic liquid crystal elastomers (NLCEs) with diameter of 1-10 µm and aspect ratio (=height/diameter) up to 5 using soft lithography. The LC molecules were aligned planarly or homeotropically along the pillar wall, controlled by the geometry and surface chemistry of the PDMS mold. Upon heating above the isotropic phase, the homeotropically anchored LCE pillars shrank in height but expanded in diameter due to realignment of the LC molecules within the pillars with a strain of ~20%. This change was completely reversible upon cooling. Numerical simulations showed planarly anchored LCE pillars would give out larger strain at both height and diameter direction of the pillars, which makes them more suitable for practical applications. The actuation of LCE micropillars could be potentially of interest to create sensors and actuators for artificial muscles, heart valves, light switches and displays.
AB diblock and ABC triblock copolymers have been studied thoroughly. ABAC tetrablock copolymers, representing the simplest variation from ABC triblock by breaking the molecular symmetry via inserting some of the A block in between B and C blocks, have been studied systematically in this research. The model system is poly(styrene-b-isoprene-b-styrene-b-ethylene oxide) (SISO) tetrablock terpolymers and the resulting morphologies were characterized by nuclear magnetic resonance, gel permeation chromatography, small-angle X-ray scattering, transmission electron microscopy, differential scanning calorimetry and dynamic mechanical spectroscopy. Three novel phases are first discovered in a single component block copolymer melts: hexagonally ordered spherical phase, dodecagonal quasicrystalline (QC) phase and Pm3n cubic phase. In particular, the discovery of QC phase bridges the world of soft matters to that of metals. These unusual sets of morphologies will be discussed in the context of segregation under the constraints associated with the tetrablock molecular architecture. Theoretical calculations based on the assumption of Gaussian chain statistics provide valuable insights into the molecular configurations associated with these morphologies.
Molecular self-organization is ubiquitous in biology. Our aim is to understand the physical mechanisms governing self-assembly of cartilage biopolymers. In cartilage extracellular matrix the bottlebrush-shaped aggrecan molecules form complexes by binding to hyaluronic acid (HA), creating a secondary bottlebrush architecture. The high swelling pressure of the aggrecan-HA complexes keeps the collagen network inflated, thus resisting deswelling under external (compressive) loads. To gain a consistent picture of structure/function relationships and determine the structure of assemblies we make measurements at different length- and time-scales using an array of complementary experimental techniques, such as osmometry, small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), static and dynamic light scattering, and atomic force microscopy (AFM). The organization of different polymer species is studied by SANS and SAXS. We determine the static and dynamic properties of the main polymeric components and their assemblies, and quantify the thermodynamic interactions between collagen, proteoglycans, water, and ions.

Figure 1. Dynamic light scattering autocorrelation function $g(\tau)$ for solutions of hyaluronic acid ($\times$), aggrecan (+) and aggrecan/hyaluronic acid complex (o).
Colloidal Unimolecular Polymer (CUP) particles were prepared from random copolymer of methyl-methacrylate and 2-acrylamido-2-methylpropane sulfonic acid by the process of water-reduction. Because of their true-nano scale size (diameter 2-9 nm) which can be controlled, easy make-up and absence of any additive such as surfactant or emulsifier; these systems are excellent contenders to study electro-viscous effects, electrokinetic behavior and the effect of surface water on the rheology and surface tension behavior. In a fairly dilute concentration regime (< 10% solids wt./wt.), the primary and tertiary electroviscous effects dominated the rheology behavior of CUPs. The primary electroviscous coefficients were calculated using Ruiz-Reina's model and fitted well as a power function of the volume fraction of the CUP particles. The experimental viscosity data fitted well with the Krieger-Dougherty model. The thickness of the bound water on the surface of CUPs was calculated and was found to increase linearly with the molecular weight of the copolymer or with the increasing size of CUP particles. In the same dilute regime, the surface tension of the CUP suspension decreased linearly with increasing concentration of CUP particles.
Nano-structured amorphous bulk polymer samples were produced by processing them with small molecule hosts. Urea (U) and γ-cyclodextrin (γ-CD) were utilized to form crystalline inclusion compounds (ICs) with low and high molecular weight poly (vinyl acetate) (PVAc), poly (methyl methacrylate) (PMMA), and their blends as included guests. Upon careful removal of the host crystalline U and γ-CD lattices, nano-structured coalesced bulk PVAc, PMMA, and PVAc/PMMA blend samples were obtained, and their glass-transition temperatures, $T_g$s, measured. In addition, non-stoichiometric (n-s)-IC samples of each were formed with γ-CD as the host. The $T_g$s of the un-threaded, un-included portions of their chains were observed as a function of their degree of inclusion. In all cases these nano-structured PVAc and PMMA samples exhibited $T_g$s elevated above those of their as-received and solution-cast samples. Based on their comparison, several conclusions could be reached concerning how their molecular weights, the organization of chains in their coalesced samples, and the degree of constraint experienced by un-included portions of their chains in (n-s)-γ-CD-IC samples with different stoichiometries affect their chain mobilities and resultant $T_g$s.
288 - WITHDRAWN
Several new, covalently crosslinked imidazolium-containing polyester networks were prepared using Michael addition polymerization methods to determine how ionic functionality correlates with thermal properties such as glass transition temperature \(T_g\) and thermal stability \(T_d\). As part of this structure-activity study, the length of the methylene spacer \(n\) and the anion \(X^-\) were varied. Analysis of \(T_g\) by differential scanning calorimetry (DSC) indicated that longer methylene spacers \((n = 6\) versus \(2\)) resulted in depressed \(T_g\) values due to an increase in chain flexibility. Use of larger anions such as bis(trifluoromethylsulfonyl)imide \([\text{NTf}_2^-]\) or trifluoroacetate \([\text{CF}_3\text{CO}_2^-]\) also led to a decrease in \(T_g\). Thermal stability \(T_d\), as measured by thermogravimetric analysis (TGA), was found to be the highest when weakly coordinating anions such as \([\text{NTf}_2^-]\) or tetrafluoroborate \([\text{BF}_4^-]\) were employed. Correlations between anion selection and \(^1\text{H}\) NMR chemical shift values of the acetoacetate precursors will also be discussed.
290 - WITHDRAWN
Conventional polymer electrolyte batteries have higher energy densities and are safer than traditional lead-acid batteries, but still have issues with solvent leaking and low transference numbers due to the mobility of both cations and anions. In single ion conducting polymers, or ionomers, the anion is covalently attached to the polymer backbone, which eliminates any anion motion and provides a cation transference number of unity. The cation is dissolved within the polymer matrix, which eliminates the need for solvent, thus eliminating the issue of solvent leaking. However, one of the main limitations with ionomer systems is their typically low conductivity at room temperature. The motion of the lithium cation through the polymer matrix was studied in a model polymer system with the intent to understand how the cation motion relates to the structure and dynamics of the polymer matrix, ultimately influencing conduction. Lithium cation motion in poly(ethylene oxide)-based sulfonate ionomers was investigated using nuclear magnetic resonance spectroscopy in samples with varying ion content and varying molecular weight of the poly(ethylene oxide) spacer. $^7$Li self-diffusion coefficients were determined using a pulsed-field gradient stimulated-echo pulse sequence and compared to results obtained from dielectric relaxation spectroscopy.

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**Figure 1.** A) Chemical structure of PEO$_x$-polymer ionomers where $x$ is the molecular weight of the PEO segment, $y$ is the fraction of sulfonated epoxide units, and $n$ is the number of PEO repeat units. B) Schematic of the bipolar pulse-field gradient stimulated-echo pulse sequence where $2\pi$ and $\chi$ represent rf pulses, and the gradient pulses are represented by the filled boxes.
A photo-responsive nanogel was synthesized from spiropyran (SP) methacrylate. Spiropyran undergoes a photochromic switching from a neutral to a zwitterionic structure under UV irradiation. Isomerization of the pendant SP functionality within the nanogel leads to a change in hydrophilicity that can induce swelling or deswelling depending on the polarity of the monomer used to disperse and infiltrate the 6 nm nanogel particles. With 0.1 to 2 wt% of the SP-modified nanogel added to triethylene glycol dimethacrylate (TEGDMA), colorless, transparent homogenous mixtures were obtained. Upon UV irradiation in the presence of photoinitiator, formation of the glassy, crosslinked polymer is coupled with the rapid photo-switching in the dispersed nanogel structures with potential significant dimensional change. The practical utility is that this provides a new mechanism to alleviate polymerization-induced stress. The formulation with 1 wt% SP nanogel reduced stress by 50% compared to the TEGDMA control. Although the photochromism process competes for the same photons necessary to initiate polymerization, photopolymerization kinetics were only modestly affected for this range of nanogel-modified systems. Interesting surface morphology differences were noted with a change from a wrinkled pattern to a needle-like pattern as the nanogel content was increased.
293 - Investigating the heteroatom effect in new donor-acceptor polymers based on 2,1,3-benzochalcodiazoles and benzo[1,2-b:4,5-b']difuran for use in organic solar cells

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

Laura C Dodge, laura.c.dodge@gmail.com, Michael A Brook. Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

As part of ongoing research into the various properties of a novel class of compounds that have been termed silicone-boronic acids, it was discovered that it is possible to produce elastomeric materials by non-covalent crosslinking methods. The Lewis acidic nature of boron atoms present in the silicone-boronic acid polymers allows for application of Lewis acid/base crosslinking with commercially available amine-containing silicones.

![Diagram of silicone-boronic acid crosslinking](image)

This type of physical crosslinking has never before been demonstrated for silicone-based materials, and has led to elastomers with tunable transparency, hardness and rheological properties. We have also been able to demonstrate the deconstruction and reconstruction of elastomer networks simply by introduction of volatile Lewis bases such as triethylamine or ethereal solvents. The rheological and physical properties of these new elastomers will be presented, as well as some preliminary data regarding swelling and self-healing capabilities.

Wednesday, September 11, 2013 11:40 AM

New Synthesis and Characterization of Polymers (08:20 AM - 12:20 PM)

Location: Hyatt Regency Indianapolis

Room: Discovery A
The long-range alignment of cylindrical domains in polystyrene-poly(ethylene oxide) (PS-b-PEO) diblock copolymer films induced by directional solvent vapor penetration (SVP) is presented. PS-b-PEO sandwich films were prepared between two glass pieces and treated with solvent vapors of 1,4-dioxane, toluene and benzene. Single molecule tracking was used to probe the microdomain alignment upon SVP by recording the trajectories of individual sulforhodamine B (SRB) dyes that predominantly partition into the cylindrical PEO domains. Upon SVP with 1,4-dioxane, the quantitative assessment of SMT data has revealed a majority of probes (70%) moving in one dimension along the SVP direction with a high degree of order, as reflected by a 2-dimensional order parameter of ca. 0.9. In contrast, films treated with benzene and toluene vapors showed a negligible number of SRB dyes diffusing in one dimension. The PEO domain radius (ca. 11nm) determined from the probe positional error was in good agreement to that (14 ± 2 nm) measured by atomic force microscopy. This result suggests the confinement of SRB probes within the PEO domains. The ability of 1,4-dioxane to induce long-range microdomain alignment by SVP might originate from its higher selective partitioning into PEO.
Yaroslava G Yingling, yara_yingling@ncsu.edu, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, United States

Understanding interactions between biopolymers, polymers and nanoparticles is crucial for the development of novel composite materials with tunable properties. We use molecular simulations to test, explain and predict the design and properties of polymer- and biopolymer-nanoparticle composite materials. In this talk, I will discuss how we can manipulate DNA and di-block copolymers by tuning metal nanoparticle (NP) ligand chemistry and solvent. Specifically, we observed that ligand chemistry, surface charge density and concentration of NP can control the binding modes and structural mechanics of DNA. We also showed how the interactions between NPs with PS and PMMA polymers can be controlled via ligand chemistry and solvent, which produces various morphologies. The results of our studies provide an insight into processing conditions and structural ordering of nanoparticles in polymer nanocomposites.
297 - Antimicrobial properties from graphene and CNT nanocomposites in films and fibers

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A variety of films and non-woven fibers are useful for coatings and filters as the topmost layer in a variety of applications including membranes. We demonstrate the preparation of graphene oxide (GO) platelets and carbon nanotubes (CNT) polymer nanocomposites and their anti-microbial properties. The use of polyvinylcarbazole polymers are used for the preparation of films and fibers of these active C-allotropes and their nanocomposites at various compositions. The preparation involves optimized high loading of the nanofillers enabling a high concentration on the films which can be prepared by casting or subsequently cross-linked by electropolymerization. The anti-microbial properties result from the oxidizing properties of the graphene oxide and the CNT or their high aspect ratio shapes capable of disrupting the cell-membrane of the pathogen.

Wednesday, September 11, 2013 02:05 PM
Structural Composites and Biomaterials: Modeling and Experiment (01:30 PM - 05:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
Nanoscale interfaces of tricalcium silicate and organic dispersants in cement: Agglomeration and initial hydration

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Improvements in the sustainability and durability of building materials depend on understanding interfacial properties of various mineral phases at the nanometer scale. Such understanding is often a challenge for current instrumentation, which is why we introduce a force field for atomistic simulations that provides excellent agreement with available experimental data, including X-ray structures, cleavage energies, elastic moduli, and IR spectra (INTERFACE force field). Using this model and measurements, we analyze nanoscale interfaces of tricalcium silicate (C₃S), the major constituent of cement clinker. An extensive set of possible cleavage planes of the non-hydrated mineral shows cleavage energies in a range of 1300 to 1600 mJ/m² consistent with the observation of faceted crystallites with an aspect ratio near one. Using pure and hydroxylated surface models that represent the first step in the hydration reaction, we examined the adsorption mechanism of several organic amines and alcohols at different temperatures. Strong attraction between -20 and -50 kcal/mol is found as a result of complexation of superficial calcium ions, electrostatic interactions, and hydrogen bonds on the ionic surface. Agglomeration of cleaved C₃S surfaces in the absence of organic molecules was found to recover less than half the original cleavage energy (~450 mJ/m²) associated with reduced Coulomb interactions between reconstructed surfaces. Additional adsorption of organic compounds below monolayer coverage reduced the attraction between even surfaces to less than 5% of the original cleavage energy (~50 mJ/m²) related to their action as spacers between cleaved surfaces and mitigation of local electric fields. Computed agglomeration energies for a series of adsorbed organic compounds correlate with the reduction in surface forces in the form of measured grinding efficiencies.
299 - Measuring transport properties in controlled release coatings

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Controlled release coatings comprised of drug-polymer composites have become integrated with many medical devices, which can significantly improve device functionality and performance. Although the performance of these systems is dictated by drug distribution within the polymer matrix, i.e. microstructure, which develops during manufacturing, the transport properties governing microstructure development are virtually unknown for these materials. Films consisting of tetracycline and poly(styrene)-block-poly(isobutylene)-block-poly(styrene) (SIBS) were solution cast. We have used a step-change vapor sorption method to determine the effective solubilities and diffusion coefficients for tetrahydrofuran (THF), a commonly used process solvent, in drug-polymer composite films with varying composition. Using a modified Maxwell-Garnett equation that links the effective properties of a two phase composite material to the properties of the constituent phases, we have computed the kinetic properties of both SIBS and tetracycline phases based on the vapor sorption observations. We have found that the computed properties of the constituent phases are independent of composite composition and are consistent with molecular dynamic simulations. Our results suggest vapor sorption can be used as a facile method to determine the solvent properties in controlled release systems. These data may help guide process development and tailor drug distributions to optimize performance.
300 - Characterization of structural composites and biomaterials using nanomechanical, nanothermal, and nanoscale infrared spectroscopy and imaging

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The enhanced physical and mechanical properties of polymer nanocomposites are likely intimately related to the individual component chemical interactions. Since these critical interactions occur on small spatial scales, enhanced nanoscale chemical characterization techniques will be needed to help understand them. Nanothermal analysis, nanomechanical spectroscopy combined with Lorentz contact resonance imaging, and infrared (IR) nanospectroscopy and imaging are newly emerging approaches that can provide valuable insights into the nanostructure of composites and biomaterials. Each of these techniques will be described and examples of their application presented. Understanding gained from the use of these new nanoscale characterization tools should help to accelerate the development of polymer nanocomposites with superior properties.
301 - Predictive simulations of amorphous composites: Their ultimate thermo-mechanical properties

**Alejandro Strachan**, strachan@purdue.edu, Chunyu Li, Yae-ji Kim. School of Materials Science and Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47906, United States

Thermosetting polymers are a popular matrix for polymer composites because of their higher stiffness, higher creep resistance and higher thermal resistance over thermoplastic polymers. Despite their technological importance, a fundamental understanding of composition-molecular structure-property relationships is still lacking. Furthermore, an understanding of the matrix-fiber interface structure and its properties is critical to understand the ultimate performance of composites.

In this presentation, we will present our efforts in simulating the curing process and predicting material properties of thermoset polymers by using molecular dynamics (MD). Recently, we developed a procedure to mimic chemical reactions in the curing process of thermosets and used reactive simulations to predict their ultimate response. The results are in good agreement with available experimental data and show that atomistic simulations can capture non-trivial trends in polymer physics including the effect of temperature, thermal history and strain rate in yield and post-yield behavior. In addition, the simulations provide insight and properties that are difficult to obtain experimentally. In particular, we characterize how size affects the response of thin films including their glass transition temperature, stiffness and yield stress and develop an energy based yield criteria applicable for a wide range of loadings including different amounts of deviatoric and volumetric loads.

We also used molecular dynamics simulations to characterize the in-situ curing process of the resin and the thermo-mechanical response of the graphite-reinforced epoxy composites. Both cohesive yield with strain localization and nano-void formation within the bulk polymer and interface debonding between graphite and thermoset were observed, depending on the in-plane orientation of graphite. These two mechanisms lead to different post yield behavior and can provide key insight for the development of predictive models of carbon fiber polymer composites.
302 - Simulation of bond scission and viscoplastic flow in thermoset polymer fracture

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Phenomena which pertain to fracture of thermoset polymers has been simulated at electronic, atomistic, and meso length scales. Intra- and inter-chain chemical interactions at high strain are explored using hybrid atomistic and electronic structure methods to capture reactions at bond scission. Results are compared with measurements from a variety of types of experiments. Material flow ahead of the crack tip is predicted with a Dugdale model adapted to include necking and strain hardening associated with polymer viscoplastic deformation. Material models are derived from atomistic simulations which include bond scission. Predictions of the resulting critical strain energy release rate for several epoxy resins are compared with measurements.

\textbf{ABSTRACT}

1. INTRODUCTION
2. FRACTURE DEFORMATION ZONE MODEL
   a. Sheet Thickness
   b. Neck Development
   c. Neck Propagation
   d. Deformation Zone Model
   e. Results
3. HYBRID MOLECULAR DYNAMICS / QUANTUM MECHANICS MODEL
   a. Method
   b. Results
   c. Discussion
4. CONCLUSIONS
5. REFERENCES

Wednesday, September 11, 2013 04:50 PM
Structural Composites and Biomaterials: Modeling and Experiment (01:30 PM - 05:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency B
303 - Injectable dopamine-modified poly(ethylene glycol) nanocomposite hydrogel with enhanced mechanical and adhesive properties

Yuan Liu, yliu23@mtu.edu, Hao Zhan, Bruce P. Lee. Department of Biomedical Engineering, Michigan Technological University, Houghton, Michigan 49931, United States

4-arm poly(ethylene glycol) end-capped with mimics of adhesive moiety found in mussel adhesive protein, dopamine was combined with a biocompatible nano-silicate, Laponite, in creating a nanocomposite hydrogel with improved mechanical and adhesive properties. Dopamine's ability to form both irreversible covalent (cohesive and interfacial) and reversible physical (with Laponite) crosslinks was exploited in creating an injectable tissue adhesive. Increasing Laponite content reduced gelation time as dopamine-Laponite bond reduced the required number of covalent bonds needed for network formation. Incorporation of Laponite also increased compressive materials properties (e.g., max strength, energy to failure, etc.) of the nanocomposite without compromising its compliance as strain at failure also increased. From lap shear adhesion test using wetted pericardium as the substrate, incorporating Laponite increased work of adhesion by 5 fold over that of control. Strong, physical bonds formed between dopamine and Laponite increased bulk materials properties, which contributed to the enhanced adhesive properties.
Dielectric materials with high electric energy density and low loss are of great importance for a broad range of applications in electronics and electrical power systems such as hybrid electric vehicles (HEV), medical defibrillators, and switched-mode power supplies. This talk presents our recent studies in developing polymer dielectrics to meet these application requirements, especially in reducing the dielectric loss and conduction loss at high electric fields. We demonstrate the promise of aromatic, amorphous, polar polymers containing high dipolar moments with very low defect levels for future dielectric materials with ultrahigh electric-energy density (> 20 J/cm³), low loss at high applied fields, and ultrahigh breakdown strengths (> 1 GV/m).
305 - Multilayer polymer films as high energy density and low loss dielectrics

Lei Zhu, lxz121@case.edu, Matthew Mackey, Joel M. Carr, Zheng Zhou, Jung-Kai Tseng, Donald E. Schuele, Baer Eric, Mason A. Wolak, James S. Shirk. (1) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, United States, (2) U.S. Naval Research Laboratory, Washington, DC 20375, United States

In this work, we utilize multilayer film (MLF) coextrusion technology at Case Western Reserve University to develop dielectrics for next generation capacitors. Dielectric MLFs are based on a high energy density polymer such as poly(vinylidene fluoride) (PVDF) and a high breakdown polymer such as polycarbonate (PC). In these MLFs, electronic and atomic polarizations are ubiquitous and contribute exclusively to the dielectric response. Dipolar orientational polarization in ferroelectric PVDF needs to be prohibited. Impurity ion polarization in PVDF is minimized by decrease PVDF layer thickness. At elevated electric fields, Maxwell-Wagner-Sillars interfacial polarization will be resulted and account for the enhanced breakdown strength and dielectric lifetime. DC conduction can be reduced by the interfacial polarization of electrons/holes and anions/cations. Optimization among high energy density, minimized ionic and DC conduction losses will produce high energy and low loss dielectric films for capacitors.
Current state-of-the-art biaxially oriented polypropylene (BOPP) and polyethylene terephthalate (PET) capacitor films are limited by their low energy density, unsatisfactory high temperature and high voltage performance. BOPP dielectric films have low loss (tan delta ~ 0.0002) and low energy density (4.88 J/cm³ at breakdown of 730 MV/m), while biaxially oriented PET film has a slightly higher energy density (6.0 J/cm³ at breakdown of 600 MV/m) and moderate dielectric loss (tan d ~ 0.003). Both polymers exhibit excellent room temperature performance, however, significant deterioration in properties above 80 °C was observed. Improving the high temperature and high voltage capability of polymer dielectric films can enable compact and more efficient systems. These deficiencies can be addressed through multilayer coextrusion of poly(vinylidene fluoride) (PVDF) with a high breakdown strength linear polymer, such as polycarbonate (PC) or PET.

The development and optimization of advanced capacitor films for higher temperature applications with enhanced energy storage density and low dielectric loss was explored using multilayer coextrusion technology. Coextrusion of a high glass transition temperature copolymer of PC with PVDF homopolymer into multilayered polymer films achieved an energy density of 8 J/cc. The PC/PVDF films exhibited a tan d loss of 0.003 at 1 kHz and bipolar hysteresis losses as low as 7% with up to a 400 kV/mm applied field. Utilization of higher glass transition temperature constituent polymers resulted significant improvement in the layered film performance at an elevated characterization temperature of 120 °C. These results provide a unique opportunity to meet the requirements for a higher energy density and operating temperature capacitors potentially without the requirement of external cooling systems for applications such as hybrid vehicles, DC-link capacitors.
307 - Ferroelectric polymer nanocomposites with high energy density

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Electrical energy storage not only plays an important role in portable electronic devices but also enables future transportation and renewable energy. Among various energy storage technologies, capacitors possess the advantage of high power density due to the fast electrical energy storage and discharge capability. Polymers offer an attractive alternative to traditional ceramics as dielectric materials for capacitors, owing to their great processability, low cost, and light weight. As illustrated in Figure 1, the preparation of organic/inorganic hybrid materials composed of ferroelectric polymers and ceramic nanoparticles has also emerged as a promising route to dielectric thin films. As the electrostatic energy that can be stored in a dielectric material is related to its dielectric constant and the applied electric field, it is envisaged that the integration of complementary elements such as large dielectric permittivity from ceramic dopants and high breakdown strength from polymer matrix in the composites could lead to an enhanced charge storage capacity. Our most recent work on the ferroelectric polymer based dielectric composite for electrical energy storage will be discussed in this presentation.
Among thiophene-based polymeric materials, side-chain oligothiophene-containing polymers have been much less explored. Meanwhile, there are few reports on the potentials of such side-chain π-conjugated oligomer-containing polymers in organic optoelectronic devices and molecular electronics, in particular, their applications in capacitors have not been studied yet. We present our recent discovery of a series of side-chain π-conjugated oligomer-containing polymers as novel high-performance all-organic nanodielectric materials, which contain true nano-dipolar domains resulting in high permittivity and low dielectric loss across a wide range of frequency (100 Hz – 10 MHz). The energy density (1.56 J cc⁻¹) is among the highest in all homopolymers at an electric field of 200 MV m⁻¹. Wide-angle X-ray Diffraction and Differential Scanning Calorimetry studies indicated the formation of crystalline domains of terthiophene side chains dispersed in the polymer backbone matrix. The highly polarizable and fast-responsive nano-dipoles from the nanoscale crystalline domains (only 1-2 nm) are believed to be responsible for the performance. This approach can be generalized to a variety of side-chain π-conjugated oligomer-containing polymers for capacitor applications requiring high energy density and fast pulse power response.
High energy density capacitors are required for several pulsed power and energy storage applications, including food preservation, nuclear test simulations, electric propulsion of ships and hybrid electric vehicles. The maximum electrostatic energy that can be stored in a capacitor dielectric is proportional to its dielectric constant and the square of its breakdown field. The current standard material for capacitive energy storage is polypropylene which has a large breakdown field but low dielectric constant. We are involved in a search for new classes of polymers superior to polypropylene using first principles computations combined with statistical and machine learning methods. Essential to this search are schemes to efficiently compute the dielectric constant of polymers and the intrinsic dielectric breakdown field, as well as methods to determine the stable structures of new classes of polymers and strategies to efficiently navigate through the polymer chemical space offered by the periodic table. These methodologies have been combined with statistical learning paradigms in order to make property predictions rapidly, and promising classes of polymeric systems for energy storage applications have been identified.
The current standards for capacitive energy storage applications are polypropylene (PP) and polyethylene (PE) which have large band gap and high breakdown strength, but a small dielectric constant. The envisaged next generation dielectric should provide high dielectric constant, while still preserving the insulating characteristics of PP and PE. To meet these growing needs, we use high throughput density functional theory (DFT) calculations in combination with machine learning (ML) methods to identify classes of polymers with large dielectric constant and band gap.

In our work, we consider various possible local chemical modifications to polyethylene (PE), which would result in much larger dielectric constant than PE, while still preserving its insulating properties. PE is chemically similar to BOPP but with a much simpler physical structure. To be specific, we allow the -CH2- unit in the PE backbone segment to be replaced by -NH-, -C(=O)-, -C6H4- (benzene), -C4H2S- (thiophene), -C(=S)-, or -O- units in a systematic, progressive, and exhaustive manner. All of these units are commonly seen in polymer backbones. Different combinations of these units will allow us to explore various polymer systems, such as polyesters, polyamides, polyethers, polyureas, etc.

High throughput methods were used first to accurately determine the dielectric constant and band gap of the chemically modified PE chains for a set of limited compositions and configurations. ML methods were then used to predict the properties of systems spanning a much larger part of the configurational and compositional space. Based on this screening strategy, we have identified several polymer sub-classes which offer a better tradeoff between the dielectric constant and the band gap.
311 - Structure and properties of new polymeric dielectrics

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Using all-atom molecular dynamics simulation, we predict the structure of polymers that have been predicted to have high energy density by density functional theory. We employ a general method to discover stable crystalline polymer states to investigate a wide variety of polymers. We report the trends relating the polymer building blocks to the bulk morphology. We also relate the trends in structure to those of the dielectric constant and loss as calculated through the simulations.
312 - Crystal structure predictions for novel polymeric capacitor dielectrics

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In recent years, evolutionary algorithms have met tremendous success in correctly identifying the crystal structures of inorganic systems,¹,² thereby leading to numerous important discoveries. However, extension and application of such methods to organic polymers is complicated and challenging, as one has to look for a possible solution within the constraint of a given polymeric topology. In this work, we used a specifically designed constrained evolutionary algorithm³ consisting of well-defined molecular units or motifs that can successfully predict polymeric crystal structures from first principles quantum mechanical computations. We apply our methodology to predict the crystal structures for a new class of polymeric materials with high dielectric constant and high breakdown strength. Such polymers are particularly suitable for applications in high voltage, high energy density capacitor technologies. The candidate materials for this class are identified from our `high-throughput' first principles computations. We believe that the identified polymers are of sufficient technological importance and our systematic theoretical exploration would serve as a possible motivation for future experimental efforts along this direction.


Wednesday, September 11, 2013 04:35 PM
Polymer Capacitor Dielectrics (01:30 PM - 05:40 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
A constrained bond- and bond-angle molecular dynamics for polymers that takes computational advantage of idealized-backbone geometric relations is described. The method uses dihedral degrees of freedom, united atoms, and simplified charge centers to predict the dielectric response of polymers having “permanent” dipoles. Studies were performed on a model polar polymer (“polar polyethylene”), which retains the molecular structure, dihedral potentials, and non-bonded interactions of polyethylene, except for artificial charges placed on the united atoms. Lamellar crystals of folded chains of polar polyethylene were computationally created, and the polarization responses to electric fields were simulated.

Ferroelectric behavior was observed, in which strong polarization would remain after field removal, along with a significant coercive threshold. Subsequent strong field reversal demonstrated a variety of prompt and delayed responses, including a torsional wave mechanism that allows the dipoles on a given fold to progressively rotate with few T-G transitions. Progress towards PVDF simulations will also be presented. (Supported by the U.S. Office of Naval Research)
314 - Synthesis and dielectric spectroscopy of novel polycarbonates for wound film capacitor energy storage applications

David A. Boyles¹, David.Boyles@sdsmt.edu, John J. Fontanella³, Tsvetanka S. Filipova¹, John T. Bendler², Mary C. Wintersgill³, Charles A. Edmondson³, Mark Westgate³. (1) Department of Chemistry, South Dakota School of Mines and Technology, Rapid City, SD 57701, United States, (2) BSC, Inc., Rapid City, SD 57702, United States, (3) Department of Physics, U.S. Naval Academy, Annapolis, MD 21402, United States

Extensive prior investigations of glassy state dynamics in bisphenol-A polycarbonate (BPA-PC) have confirmed that megahertz molecular motions occur in the solid polymer at room temperature, more than 100 degrees Kelvin below the glass transition. Direct evidence for such motions is seen in the dielectric spectrum [figure 1] which displays dielectric loss in BPA-PC over seventeen frequencies between 10 Hz to 100000 Hz as a function of temperature. The large, broad loss peak centered at about -100 °C has been widely attributed to simultaneous, if not synchronous, motions of the three main-chain molecular elements of the polymer consisting of the isopropylidene unit, the phenylene rings, and the carbonate unit. To enhance the energy storage properties of BPA-PC, particularly for potential wound film capacitor applications, new aryl polycarbonates have been synthesized having highly mobile dipoles in the vicinity of those thought to give rise to the room temperature megahertz molecular motions, with the objective of keeping loss low and the temperature of the motion significantly below the working temperature range of the capacitor. The new polycarbonates formed tough and glassy films and demonstrated high heat resistance. Dielectric spectroscopy was employed to investigate the low temperature relaxation of the new polycarbonates and demonstrated the extent of modulation of the intensity and peak maximum of the process. Computational modeling was employed to analyze constraints on free molecular motion.
Cilia, marvelous cellular nanomachines, are ubiquitous in biology. They allow single cell organisms to swim and, within mammals, generate hydrodynamics in the lung, the brain and fallopian tubes. To understand these flows, we engineered arrays of microscale actuating structures at the scale of biological cilia, and have used them to generate long range flows and dramatically enhanced mixing. In developing a new generation of strong actuators needed to move viscoelastic fluids, we appreciated that the cilia sheets can act as microrheometers. The free motion of the cilia are impeded by the viscoelastic response of the media in which they are immersed. We have applied these new microsensors to measure the mechanical properties of the clot strength of whole blood, where they may play a role as a diagnostic for clot pathologies of patients.
316 - Nanoparticle-ejecting microcapsules

Bruno De Geest, br.degeest@ugent.be, Department of Pharmaceutics, Ghent University, Ghent, Belgium

Systems with dimensions in the micrometer range that could provide pulsatile release of nanoparticles could find application in the biomedical and microfluidics field. Here we report on our work on nanoparticle-ejecting capsules. These consist of a degradable hydrogel bead in which the nanoparticles are embedded and that is surrounded by a semi-permeable membrane, i.e. permeable to water but impermeable to the degradation products of the hydrogel. By consequence, degradation of the hydrogel beads allows the osmotic pressure to build up within the capsules. By controlling the mechanical strength of the capsule membrane either stable pressurized capsules are obtained or when the osmotic pressure exceeds the tensile strength of the membrane the capsules ruptures. The latter case leads to so-called self-exploding capsules and we measured velocities of ejected nanoparticles to be almost 800 times faster compared to Brownian motion. Pressurized capsule could also be used to eject their nanoparticle payload by puncture, either via an AFM tip or via 'laser microsurgery' pointed on clustered gold nanoparticles on the capsule surface, thereby inducing heat and rupture of the capsule membrane.
317 - Coarse-grained Brownian dynamics simulations of protein translocation through nanopores

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A crucial process in biological cells is the translocation of newly synthesized proteins across cell membranes via integral membrane protein pores termed translocons. Recent improved techniques now allow producing artificial membranes with pores of similar dimensions of a few nm as the translocon system. For the translocon system, the protein has to be unfolded, whereas the artificial pores are wide enough so that small proteins can pass through even when folded. To study how proteins permeate through such membrane pores, we used coarse-grained Brownian dynamics simulations where the proteins were modeled as single beads or bead-spring polymers for both folded and unfolded states. The pores were modeled as cylindrical holes through the membrane with various radii and lengths. Diffusion was driven by a concentration gradient created across the porous membrane. Our results for both folded and unfolded configurations show the expected reciprocal relation between the flow rate and the pore length in agreement with an analytical solution derived by Brunn et al. [Q. J. Mech. Appl. Math. 37, 311 (1984)]. Furthermore, we find that the geometric constriction by the narrow pore leads to an accumulation of proteins at the pore entrance, which in turn compensates for the reduced diffusivity of the proteins inside the pore.
318 - WITHDRAWN
319 - Polymer microcapsules that exhibit chemically-activated motion

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This talk will describe a class of soft microscale assemblies that can propel themselves in the presence of a chemical fuel. These assemblies are created in situ within a microfluidic platform using the biopolymer chitosan as precursor. Individual microscale droplets bearing chitosan are converted to dimeric microcapsules by controlled cross-linking and coalescence. The size, shape, and functionality of each individual capsule within the dimer can be precisely controlled. Specifically, dimers are prepared wherein one lobe contains nanoparticles of platinum (Pt). Such dimers undergo self-propelled motion in water upon the introduction of hydrogen peroxide (H2O2) to the solution. In this case, the catalytic reaction of H2O2 with the encapsulated Pt produces oxygen gas, and the expulsion of this gas in the form of bubbles propels the dimer forward in a direction away from the Pt-containing lobe. Similarly, magnetically actuable dimers can also be created by substituting the Pt with paramagnetic Fe3O4 nanoparticles. The latter structures undergo controlled rotation in an external magnetic field, much like a magnetic stir bar. The overall approach described here is simple and versatile and can be easily adapted to produce a variety of soft structures with motile capabilities.
As part of our continuing effort to establish the structure-morphology-property relationship for high Tg azopolymides, a new diamine (azoBPAA) containing two azobenzenes was synthesized via a four-step route. It was polymerized with five commercial dianhydrides: pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), oxy-4,4'-di(phthalic anhydride) (ODPA), and 1,1,1,3,3,3-hexafluoro-2,2-bis(4-phthalic anhydrido)-propane (6FDA) to afford a series of amorphous, heat-resistant (Tg ranging from 276-307 °C) linear homopolyimides containing two azobenzenes/repeat unit. In addition to homopolyimides, four copolyimides were also prepared from 6FDA, azoBPAA and 1,3-bis(3-aminophenoxy)benzene (APB). These polymers displayed high thermo-oxidative and thermal stabilities with 5wt% weight-loss temperatures between 451-498 °C in air and 420-456 °C in nitrogen, respectively. The photo-directed bending of cantilevers composed of these materials was examined upon exposure to linearly polarized 445nm light. The photomechanical response of homopolyimides increased from 13° for azoBPAA-PMDA to 84° for azoBPAA-OPDA in parallel with the increasing flexibility of dianhydrides. As expected, the bending angles increased with the contents of azoBPAA for 6FDA-based copolyimides albeit bidirectional bending was observed below 45mol% of AzoBPAA content, and only unidirectional bending was observed thereafter. WAXD results indicated that all the polyimides were amorphous except PMDA and BPDA-based homopolyimides, which contain various degrees of crystallinity.
321 - Microfluidic fabrication and modification of thiol click polymer fibers

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Thiol click chemistry has emerged as a prominent synthetic chemistry tool in recent years. The value of click chemistry reactions, which occur by the binding of a sulfhydryl group to an alkene or an alkyne and proceed via photoinitiation, is evident by their use in a wide variety of research applications including hydrogel drug delivery, dendrimer synthesis and electroluminescent films. Using microfluidics, we recently demonstrated the ability to fabricate thiol–ene and thiol–yne microfibers from a variety of reagent components.

A microfluidic channel with grooves in the top and bottom provided a mechanism to fabricate fibers with predetermined cross-sectional shapes (e.g. round, ribbon-shaped, double anchor), while also controlling fiber size on the sub-micron level. In addition to the control over fiber shapes and sizes, we have performed surface chemistry on stoichiometrically imbalanced microfibers, attaching a fluorescent probe to the surface of the fibers via a biotin-streptavidin linkage. Recently, we extended this work by successfully incorporating gold and silver nanoparticles into thiol–ene and thiol–yne microfibers, which altered their materials properties. The work presented covers several research areas including polymer chemistry, polymer engineering and surface chemistry. The ability not only to fabricate thiol click microfibers, but also to control their size, shape, internal components and subject them to post-polymerization modifications should lead to new smart materials for filtration, optics, sensing and textile applications.

Wednesday, September 11, 2013 04:00 PM
Sensing and Controlling Motion with Polymeric Materials (01:30 PM - 04:20 PM)
Location: Hyatt Regency Indianapolis
Room: Studio One
322 - Highly stretchable and highly absorbent polymer hydrogels

Renu Sharma, Bani H Cipriano, Stephen Banik, Srinivasa R Raghavan, sraghava@umd.edu. Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20740, United States

Polymer hydrogels have been used extensively as super-absorbent materials. These materials can swell up to many times their own weight in water; swelling ratios > 1000 are not uncommon. However, such super-absorbent hydrogels usually possess low toughness. In this work we report the synthesis and characterization of a different type of polymer hydrogel based on an acrylamide derivative. These gels form even in the absence of multifunctional cross-linkable monomers. This is due to self-crosslinking that occurs when interchain covalent bonds are formed between chemical moieties on the growing polymer chains. Gels are formed when as little as 5 wt% monomer is present and the gels are highly stretchable. Unswollen gels can be stretched up to several times their original size. The increased toughness of these gels compared to conventional hydrogels is attributed to a uniform distribution of cross-links throughout the gel. Even in the swollen state, these gels retain a high level of toughness when compared to conventional cross-linked gels. Details on the synthesis and characterization of these gels will be presented in this talk.
323 - Degradation of CPVC sprinkler piping material by simulated sunlight and UVB light

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Chlorinated polyvinyl chloride (CPVC) is a promising candidate for sprinkler piping systems in seismic areas. In spite of numerous advantages, the use of CPVC sprinkler piping in earthquake zones poses various concerns like chemical incompatibilities, environmental degradation and limited field data. In this study, the effect of simulated sunlight and ultraviolet (UVB) light on the chemical structure and physical properties of CPVC was studied. Exposures were conducted in the QSUN xenon test chamber and QUV accelerated weathering tester. CPVC tensile specimens were exposed for 1, 4, 8 and 12 weeks in both the QSUN and QUV chambers. Exposed CPVC samples were then analyzed by tensile testing apparatus, Fourier Transform – Infrared (FT-IR) spectroscopy and Differential Scanning Calorimetry (DSC). The results indicated early degradation of CPVC when exposed in the QSUN chamber. The tensile testing data showed apparent changes in elongation at break (70.40% reduction) after 8 weeks of exposure in the QSUN chamber (1344 hours of noon summer light). Figure below shows FT-IR spectrum of (a) unexposed control, (b) CPVC sample exposed for 4 weeks and (c) CPVC sample exposed for 8 weeks in the Q-Sun chamber. FT-IR analysis conducted on the surface of the exposed side indicated spectral changes (indicated by the blue arrows) in samples exposed in QSUN chamber as early as one week. For example, absorbance peak at 1718 cm⁻¹ is not present in the unexposed control.
Visible-light photoredox catalysis has gained attention as green chemistry for small molecules organic synthesis and functionalization. But, it can also be advantageous in macromolecular synthesis as initiating species are readily produced under mild conditions with a broad variety of compounds (organometallics, organic pigments, amines, onium salts, silanes, among others). Also, chromophore absorbance is easily tunable to match the light-wavelength. Thus, high quantum-efficiency light-triggered polymerization at room temperature with low intensity visible-light is possible. Nonetheless, detailed understanding of the intertwined system is still limited.

We characterized the photoredox mechanism of robust visible-light-mediated photoredox catalysis formulations and its integration into polymer synthesis. The latter was performed with an in-house developed real-time monitoring system for simultaneous UV-Vis, FT-IR, fluorescence and polymer light-scattering tracking with millisecond time-resolution. As a result, we can monitor fast kinetics and get mechanistic information for the photoredox catalytic initiation and the polymerization process simultaneously.

We found a new advantage of photoredox catalysis, namely free-radical light-triggered polymerization that continues after a light pulse and beyond the spatial reach of irradiation via the redox reaction responsible for catalyst regeneration. This is based on fast photobleaching (650 nm) of chromophores with a reductant to form only closed-shell intermediate that reoxidizes more slowly, allowing for its diffusion beyond the excitation site. This demonstrates time-delayed polymer initiation permits the first on-demand triggered redox polymer initiation, advantageous in dental- and biomaterials, among many other applications.
325 - Isolated polyacetylene in an inclusion complex: Synthesis, methodology, and theory

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The computational analysis of polyacetylene (PA) suggests that as an infinite isolated chain may have unique and interesting properties. This is based on the analysis of the zero point vibrational level along the bond alternation (Peierls) coordinate which shows that the average structure has equal bond lengths and that the vibrational pattern shows that the ground state is non-degenerate. Several experimental approaches have been taken to test this finding. The first method has been to simultaneously grow an inclusion crystal around PA formed by olefin metathesis using Grubbs catalyst to grow the polymer with the host molecule tris(o-phenylenedioxy)cyclotriphosphazene (TPP) to form the inclusion channel. The second was to isolate the monomer 1,4-diiodo-1,3-butadiene(1,4-DIBD) in a urea inclusion crystal (UIC) and irradiate to create the isolated polymer.

The formation of a UIC with 1,4-DIBD has been verified with X-ray crystallography and Raman spectroscopy. The crystallographic data was taken at multiple temperatures. Both techniques were used to ascertain the ratio of urea:1,4-DIBD, the overall structure of the crystal, and if any PA was formed before and after irradiations with a 266 nm UV source. The crystal structure is unusual among UIC structures in that it is both commensurate and lacking of disorder.
326 - Aqueous-phase polyurethane synthesis from activated carbonates under isocyanate- and catalyst-free conditions

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Polyurethanes are used in numerous applications such as elastomers, thermoplastics, textile and surface coatings, adhesives, dispersions and foams. Unfortunately, their synthesis usually involves the use of isocyanates, a catalyst, and organic solvents, all of which tend to be toxic and environmentally unfriendly. It is also challenging to perform the polymerization in aqueous solution due to the lack of compatibility between isocyanates and water. On the other hand, it is common knowledge that activated dicarbonates undergo polycondensation with nucleophilic diamines to give polyurethanes. The viability of this reaction in aqueous media is highly dependent on the nature of the dicarbonate leaving group, which determines its chemoselectivity for diamines versus water. Herein we report an expedient aqueous-phase method of synthesizing polyurethanes from activated carbonate precursors under catalyst- and isocyanate-free conditions.

Scheme 1. Isocyanate- and catalyst-free polyurethane synthesis in aqueous media.
Aliphatic polycarbonates have received considerable attention as biocompatible, degradable materials for therapeutic delivery, polymer-based therapeutics, and tissue engineering. These polymers are typically prepared with precise control through the ring opening polymerization (ROP) of cyclic carbonates. The properties of these polymers can be tailored through the preparation of appropriately functionalized monomers; however, many functional groups need to be protected so they do not interfere with the ROP. An alternative strategy for the formation of functional polycarbonates is through post-polymerization modification of a reactive polycarbonate. With this strategy, a single backbone with a narrow PDI can be synthesized, onto which various groups can be installed, allowing for direct comparison of their resultant properties. This presentation will focus on a versatile platform for the formation of functional polycarbonates by acid-catalyzed ROP of a cyclic monomer with a pendant activated ester (MTC-OC₆F₅), followed by an efficient post-polymerization modification.
Properties of novel blocked, biobased diacids and their use in epoxy-acid thermosets

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Biobased dicarboxylic acid molecules are crystalline solids with high melting points due to their high degree of hydrogen bonding. These interactions can be overcome by reacting the carboxylic acids to remove the acidic protons. One such method to remove hydrogen bonding is to form ionic liquids of the diacids. The ionic liquid diacids have several positive attributes: 1) the production of the ionic liquids require moderate temperatures (< 100 °C) and no solvent, 2) the ionic liquids are soluble in organics, 3) the counter ion of the ionic liquid acts as a catalyst for the crosslinking with the epoxy, and 4) if properly selected, the counter ion is volatile under curing conditions. The counter ion identity and the diacid chain length effect on the ionic liquid properties (melting point, degree of reaction, etc.) and the impact on the performance properties of the resulting epoxy-acid thermosets will be presented.

Comparison of the melting points of diacids and the physical state of their 4-ethylmorpholine salts at room temperature. The region represents salts that are liquid at room temperature, while those in are solid.
Polymers provide an attractive and highly tunable scaffold for supramolecular chemists to incorporate designer ionophores into its structure for various applications, i.e., alkali salt extraction, sensing, and ion-selective membranes. As triazole-based molecules have recently garnered much attention for their anion binding abilities, we aim to explore how two previously reported anion receptors (preorganized pentads and rigid macrocycles) operate within polystyrene copolymers (1:10 receptor:styrene). The synthesis and characterization of the monomers and subsequent copolymers will be presented alongside their response towards chloride in solution and at the aqueous-organic interface.
330 - Synthesis of amine functional colloidal unimolecular polymer (CUP) particles and their use as cross-linker for epoxy coatings

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Random copolymers of acrylic acid and ethyl acrylate monomers with ratio 1:9 were synthesized in THF as solvent, AIBN as initiator and butanethiol as chain transfer agent to produce an acid rich copolymer. Acid functionality was then reacted with 2-methylaziridine to produce amine functionality on polymers. The polymers were isolated, water-reduced slowly using peristaltic pump and solvent stripped using rotovap to produce Colloidal Unimolecular Polymers (CUPs) with amine functionality on the particle surface. These particles are typically 3-9 nanometers in diameter depending upon the molecular weight. They were then utilized as cross linking agent for crosslinking an epoxide resin at different temperatures. The formed coatings were evaluated for its MEK resistance, adhesion, hardness, gloss, flexibility, wet adhesion, abrasion and impact resistance properties and were compared with traditional amine crosslinkers. These new amine functional acrylic CUPs were solvent free (low or no VOC).
Bicyclo[4.2.0]octa-1,3,5-triene, or benzocyclobutene (BCB), has been widely used in polymer science based on the ring-opening ability of its strained cyclobutene ring. Stable at room temperature, BCB undergoes an electrocyclic rearrangement to the highly reactive \( \alpha \)-quinodimethane when heated (>200 °C) and will form irreversible carbon-carbon bonds by dimerizing or oligomerizing. Thermal activation, the lack of condensation products, and irreversible reactivity make BCB chemistry attractive for cross-linking applications; however the high temperatures required to isomerize BCB limits its use. Introducing an electron donating or withdrawing group onto the cyclobutene ring decreases the ring opening isomerization temperature by increasing the ground state energy or lowering the transition state energy respectively. Although vinylbenzocyclobutene (VBCB) has been synthesized by several routes, there are no literature reports of 1-substituted VBCBs which undergo isomerization at low temperature. This presentation will report the synthesis, co/polymerization and thermal properties of several 1-substituted VBCBs exhibiting a range of ring-opening isomerization temperatures and application of those monomers for nanoparticle formation by intramolecular chain collapse.
332 - Polymer based formic acid complexes: Convenient reduction systems

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The solid donor-accepter complex prepared from formic acid and solid amine polymer carries a large amount of formic acid. The free flowing solid makes its practical application more convenient in various reduction processes. The reduction of phenylacetylenes, chalcones, stilbenes, ketones etc. can be efficiently carried out using solid amine based formic complexes with Pd/C. Studies on its reactivity, selectivity and its synthetic utility will be discussed.

Wednesday, September 11, 2013 04:50 PM
New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hyatt Regency Indianapolis
Room: Discovery A
333 - Selective 1-butene production via ethene dimerization as comonomer for polyethylene production – an old technology revisited

Roland Schmidt, SchmidtR@SABIC.com, Mohammed Al-Hazmi, Dev Ranjan Pradhan. Department of Performance Chemicals, SABIC, Riyadh, Saudi Arabia

1-butene is a highly important sought after commodity mainly as a co-monomer for polymer production. Several processes to generate this compound are commercially available. One of them is the selective dimerization of ethene via a Ziegler-Natta type oligomerization catalyst system. The commercial process is around for more than 25 years. The current system generates butenes selectively exceeding 90+% purity of which 1-butene exceeds 98+%. Due to the expected significant market growth, new interest in this system has been rekindled. The presentation shows newest results tackling the problems of the 'old' system and improvements to a new catalyst and process generation.

Wednesday, September 11, 2013 05:10 PM
New Synthesis and Characterization of Polymers (01:30 PM - 05:30 PM)
Location: Hyatt Regency Indianapolis
Room: Discovery A
The historical applications of polymeric materials in aviation and aerospace applications have ranged from tires to lubricants to wiring insulation to canopies to matrix materials for composites. This presentation will provide a brief overview of on-going applications of polymeric materials in aviation and discuss polymer needs and opportunities for potential future applications. A sampling of specific current polymer research projects in the Air Force Research Laboratory will be presented. Finally, the status, particulars, and opportunities presented by the President's Materials Genome Initiative as it relates to polymers for aviation will be discussed.
Fibrinogen is a multiprotein complex which, when activated, aggregates to form fibrin, a net-shaped molecular formation which is fundamental for the coagulation of blood following a wound or when an extraneous body comes into contact with blood (i.e., graft implants). Thus, adsorption of fibrinogen on material surfaces play an important role in viability of those materials for implants. It is known that fibrinogen is very flexible in solution, a fact that made it hard to crystallize. The flexibility of fibrinogen can also be observed in adsorption studies. Here we examine the flexibility of fibrinogen using atomistic molecular dynamics simulations. Simulations of fibrinogen in solution are used as a reference to evaluate the behavior of fibrinogen on material surfaces and study the initial adsorption stages.

This in turn may have implications for medical applications such as material design for implants.
336 - Insights into chromatin architecture by mesoscale modeling of oligonucleosomes

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Understanding chromosome tertiary organization and its role in control of gene expression represents one of the most fundamental open biological challenges. Chromatin structure and gene expression are intimately related because the complex nature and dynamics of protein-bound DNA folding in the living cell regulates gene activity at a large range of spatial and temporal scales. Recent advances in experimental studies have revealed important chromatin characteristics under various internal and external conditions but many puzzles remain, including the existence of 10 versus 30nm fiber forms. We will present recent findings regarding chromatin structure and function using our mesoscopic model of oligonucleosome chains and tailored sampling protocols. The studies reveal geometric/electrostatic mechanisms by which linker histones, histone tails, and divalent ions consort to form heteromorphic chromatin higher-order structure; the manner by which linker histones regulate folding/unfolding of the chromatin fiber; and the stability of interdigitated 10nm chromatin fibers compared to compact 30nm fiber forms, underscoring the polymorphic and dynamic nature of the chromatin fiber.

Thursday, September 12, 2013 09:05 AM
Structural Composites and Biomaterials: Modeling and Experiment (08:30 AM - 12:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency D
Polyelectrolytes, such as Poly(Styrene Sulfonate), Poly(Acrylic Acid), DNA, and a myriad of similar polymeric materials, are commonly used in stimuli-responsive or self-assembling materials due to their strong coupling between chemical functionality (i.e. charged groups) and molecular architecture. Despite the ubiquity of these chemical features, fundamental and conceptual understanding of the physical ramifications of these systems still requires significant further development. We present, in a conceptual fashion, thermodynamic attributes of charged interfaces in polymeric systems. In particular, we consider the effect of charge ordering using a novel combined SCFT-liquid state theory calculation that allows the consideration of strongly coupled (high-valency, low-dielectric) systems, hard-sphere repulsions, and spatially inhomogenous polymers in a rigorous statistical-mechanical fashion. This investigation uses the simplified geometry of a polymer blend interface to elucidate novel effects such as valency-dependent interfacial stiffening, ion excluded-volume pressures due to hard sphere repulsions, and the effects of local structure arising from ion-ion correlations. We provide conceptual arguments to supplement the numerical theory presented in order to develop an intuitive understanding of the ramifications of ion correlations in multiphase systems, which will inform the development of more complicated polyelectrolyte materials.
338 - 3D imaging of nanoparticles at atomic resolution

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Visualizing the arrangement of atoms has played an important role in the evolution of modern science and technology. X-ray crystallography has long been used to reveal globally averaged 3D atomic structures. Scanning probe microscopes can determine surface structures at atomic resolution. Electron microscopes can resolve atoms in 2D projections of 3D crystalline samples. In this talk, I will present a general method for determining 3D local structures at atomic resolution. By combining scanning transmission electron microscopy with a novel tomographic technique known as equally sloped tomography, we have imaged metallic nanoparticles at atomic resolution in three dimensions and revealed new atomic structure information that are hidden in conventional 2D projections. We expect this general 3D atomic-resolution imaging method to find application in chemistry, materials sciences, nanoscience and physics.

Figure 1. Three-dimensional imaging of a gold nanoparticle at atomic scale resolution.


339 - Nanoscale infrared spectroscopy and imaging: Advances in spatial and spectral resolution

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Infrared (IR) spectroscopy is a ubiquitous technique for the chemical evaluation of polymeric materials. Its utility in the characterization of nanocomposites and biomaterials is limited by the measurements micron scale spatial resolution which is due to the diffraction limit of the mid infrared illumination. Techniques have been developed which extend the spatial resolution of infrared spectroscopy to the nanoscale through coupling the technique with Atomic Force Microscopy (AFM). The probe in the AFM is used as a local detector of the infrared absorption.

Recent advances in these techniques allow improved spectral resolution in addition to coverage of a larger range of the mid IR. These changes are due to improved IR sources which are typically tunable sources such as optical parametric oscillators (OPOs) or Quantum Cascade Lasers (QCLs). Both improvements allow better band assignments or analysis of subtle shifts in absorption bands. In addition, optimization of the detection methods of the AFM has improved the ability to sense thin layers of materials. This has extended the thickness resolution down to ~20 nm. These improvements will be described and application examples demonstrating their utility in the areas of nanocomposites and biomaterials will be presented.

Figure 1: AFM image (right) and nanor spectra (left) showing the change in absorption bands across an interface in a polymer blend
De novo designed peptides MAX1 and LNK1 is capable of self-assembly into hydrogel of distinct beta-fibril networks. A detailed molecular picture, as well as corresponding quantitative analysis, is necessary to understand the driving forces for their assembly features. We use molecular dynamics (MD) simulation to obtain the molecular structural and dynamic information. Previous experiments are consistent with branched fibrils of MAX1, as observed by cryogenic transmission electron microscopy and oscillatory rheology measurements. Same characterizations with LNK1 are consistent with rigid rod-like fibrils. Each peptide is a single β-hairpin with the same hydrophobic patterning featuring a hydrophobic face and a hydrophilic face; only the identities of the hydrophobic amino acids differ. Molecular dynamics simulations on model octamers are presented. This work provides the molecular insights on the fibril structures and the fluctuations of these assemblies, which can potentially inform the rational design of new peptide-based self-assembling materials.
341 - WITHDRAWN
Montmorillonite Clay (MTM) combined with a biological polymer xyloglucan (XG) is a novel bio-nanocomposite material developed recently. Based on its bio-degradability, one has anticipated a wide range of applications in the paper making industry, in the environmental remediation area as well as in the biomedical field. In the present work a molecular dynamics (MD) simulation approach is employed to investigate the details of XG adsorption onto an MTM surface at the atomic level. Aiming at the adsorption mechanism and conformational properties of XGs, two polymer fragments characterized as Native XG (GXXLGXXXG) and Modified XG (GXXXGXXXG) interacting with the MTM surface were built up both in an explicit water model and in vacuo. Here G denotes an unsubstituted β-D-Glcp unit, X a α-D-Xylp-(1-6)-β-D-Glcp-(1-4) and L a β-D(1-2)-Galp(1-2)-α-D-Xylp-(1-6)-β-D-Glcp-(1-4) unit. Our work indicates that in either phase the electrostatic interaction plays a central role of the adsorption process. The existence of water mediates the formation of hydrogen bonds between the XGs molecules and the MTM surface. Moreover, it is predicted that both XGs prefer a orientation parallel to [100] to adsorb onto the MTM surface and that the native XG exhibits higher interaction energy and binding affinity than the modified one. The variation of L in the side chain of XGs shows no significant influence in the view of free energy and entropy change, while it gives conformational suggestions which indicate that an extension of the side chain could facilitate the adsorption interaction of XG/MTM both on the backbone and the side chain residues. All in all, atomistic level theoretical studies of XG/MTM of this kind hold the promise for detailed learning of the adsorption mechanisms and aids the organization of lab experiments for further improvement.
In this presentation, I will discuss synthesis of new isotactic PP polymers containing various polar groups (including OH, NH₂, NH₃⁺Cl⁻) and cross-linkers, which provide significant benefits to the electric energy storage applications. The current state-of-the-art BOPP capacitors exhibit many desirable properties (high pulsed, high power density, low dielectric loss, cost effective, and reliability), but only delivering low energy storage density (2 J/cc). The increase of energy density without altering other desirable properties, especially the low dielectric loss property, can significantly expand PP to a wide range of energy storage applications. 

Our synthesis scheme involves a direct metallocene-mediated copolymerization using specific iso-specific catalysts and suitable comonomers. Several functional PP copolymers containing few mol% polar groups show a dielectric constant of above 4 (double of BOPP)—which is independent on a wide range of temperatures (between -20 and 100°C) and frequencies (between 100 and 1M Hz)—and high breakdown strength >600 MV/m. They are potential to deliver an energy density 2-3 times of BOPP after an applied electric field 600 MV/m, without showing significant increase of energy loss.

Computer simulation sheds light on the role played by OH groups and the trapped H₂O molecules. In addition, the cross-linked PP dielectrics show good mechanical strength and thermal stability, exhibit high breakdown strength (>800 MV/m) and narrow breakdown distribution.
344 - Improved polymeric dielectrics using additional polar groups

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We use molecular dynamics and density functional theory to study the addition of a small number of polar groups to an apolar hydrocarbon polymer. Earlier work with hydroxyl groups showed an increase in dielectric constant by a factor of 2, without substantially increasing the dielectric loss. We now expand on this work with a systematic study of a wide range of polar side groups and adsorbed solvents. The results suggest that improved polymeric based dielectric materials can be designed by incorporating polar groups on the chain, but only those whose relaxations can be substantially slowed due to cooperative effects, e.g., through long-lived hydrogen bonds.
345 - Probing the structure-property relationship in hydroxyl-functionalized polypropylenes

**Sahil Gupta**, sg63@zips.uakron.edu, M. Cakmak, R. A. Weiss. Department of Polymer Engineering, The University of Akron, Akron, OH 44325, United States

The present state-of-the-art in high voltage polymeric capacitors is dominated by metallized biaxially oriented polypropylene (BOPP). BOPP, however, has a low dielectric constant (\( \epsilon = 2.2 \)) and provides a low energy density of (3-5) J/cm\(^3\) at breakdown. Yuan et al. (Macrom. (2010), 43:4011-4015) recently reported the synthesis of hydroxyl-functionalized polypropylene (PPOH) that exhibited energy density 2-3 times that of BOPP.

In this study, we investigate the effect of incorporation of OH groups (0-4 mol\%) on the structure and thermal and rheological properties of polypropylene. Presence of H-bonding between the OH groups is confirmed using Fourier transform infrared spectroscopy (FTIR). The H-bonding densify the amorphous domains and increases the glass-transition temperature with an increasing degree of functionalization.

![FTIR Spectra](image)

Differential scanning calorimetry (DSC) analysis shows that the incorporation of comonomer in PP reduces the crystallinity by as much as 15%. It also disrupts the growth behavior of PP crystals resulting in a reduction in the lamellar thickness measured using small angle X-ray scattering (SAXS), and therefore the melting point. However, the α-monoclinic crystal structure of PP remains unaffected. Small-amplitude oscillatory shear (SOAS) measurements from 165-250°C show that the storage (\( G' \)) and loss (\( G'' \)) modulus are higher for PPOH copolymers due to H-bonding. For PPOH containing 3.9 mol\% -OH groups, \( G'>G'' \) over the entire frequency range. It appears that the H-bonding in this polymer is sufficient to provide a weak gel network.
346 - What do polymer chains do during stretching? Real time ultrarapid- polarized FTIR spectroscopy, birefringence coupled with true stress, strain measurements

Ido Offenbach\textsuperscript{1}, io9@zips.uakron.edu, Jolanta E. Marszalek\textsuperscript{1}, Emre Unsal\textsuperscript{1}, T. C. Mike Chung\textsuperscript{2}, Mukerrem Cakmak\textsuperscript{1}. (1) Department of Polymer Engineering, UNIVERSITY OF AKRON, Akron, Ohio 44325, United States, (2) Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

Today's common use of high voltage, high energy density capacitors is dominated by metalized biaxially oriented polypropylene (BOPP).

Our approach is to develop new classes of polymers, functionalized polyolefins, and to find the best condition for processing to achieve improved properties for capacitors. We are using a one-of-a-kind machine that allows collection of real-time data: birefringence, true strain, true stress, and simultaneous tracking of full spectrum parallel and crossed polarized infrared spectroscopy of materials during heating, stretching, holding and cooling stages typically encountered in an industrial process. This machine is capable of acquiring spectra at 300 spectra/second during the uniaxial stretching allowing us to follow rapid structural changes. The real-time dichroic ratio is calculated by polarized infrared light, both parallel and perpendicular to the stretching direction. This is particularly useful in examining semicrystalline polymers, multiphase systems such as copolymers, nanocomposites and their blends during melting, orientation, relaxation and crystallization behaviors.

As an example when highly oriented PP films are heated, orientation function of crystalline domain, fc, increases in temperature range of 130-160°C as shown in Figure 1. This increase of orientation of crystalline domain results from complex processes occurring at higher temperatures. There are melted fraction that can recrystallize on template of stretched crystalline structure pulling through tie molecules other crystalline fibrils into more perfect alignment.

Thursday, September 12, 2013 09:25 AM
Polymer Capacitor Dielectrics (08:30 AM - 12:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
347 - Significantly improving dielectric and energy storage properties of PVDF-based fluoropolymer by crosslinking and stretching

Shaobo Tan, Zhicheng Zhang, zhichengzhang@mail.xjtu.edu.cn. Department of Applied Chemistry, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

PVDF-based ferroelectric relaxors have attracted considerable interests in high pulse capacitors application for their high dielectric constant and high energy density. Stretching crosslinked PVDF-based fluoropolymer films has been shown to be able to significantly improve their breakdown strength and the energy storage capabilities. The recent progress obtained in our group would be presented in this work.
348 - Novel mechanisms for high power density energy storage in capacitor dielectrics

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At present, highly insulating polymers with large breakdown fields, such as polypropylene, are the dielectrics of choice in high-power capacitors. However, their energy densities are quite low because of small dielectric constants. Ferroelectric polymers from the PVDF family have significantly larger dielectric constants, yet their energy densities are still rather low. This can be traced to early saturation of their displacement fields with the applied electric field. However, an admixture of a small amount of another polymer, such as CTFE, results in a dramatic increase in the stored energy. We show that this highly non-linear increase in the energy density is due to the formation of disordered nanodomains with different copolymer concentrations, which undergo first-order non-polar to polar phase transitions with an increase of the applied field. The resulting energy density profile reproduces well the experimental data, while its variation with co-polymer concentration and distribution suggest avenues for additional substantial improvements in the stored energy. Most recently, we have identified a low-activation-energy pathway for these successive phase transformations, which provides further confirmation of the viability of the suggested energy storage mechanism. If time permits, we will also discuss the mechanisms of energy storage and release in novel polyurea-based dielectrics, which too can exhibit exceptionally high power densities.

In collaboration with V. Ranjan, R. Dong, M. Buongiorno Nardelli, and L. Yu.
When biaxially oriented polypropylene film (BOPP) is aged at fields above about 480 MV/m, the film breaks down before the current density comes to steady state, i.e., after voltage application, the current drops for some tens of minutes, after which it starts to increase monotonically to breakdown over some minutes to tens of minutes. However, the average conductivity of BOPP at 480 MV/m is in the range of $10^{-16}$ S/m. This suggests that under these conditions in this relatively thin (10 μm) film, aging, and probably current density, are local phenomena based on the statistics of morphology, impurity content, and “defects” in the film, but aging clearly involves a positive feedback mechanism. If the electrical properties are statistically independent on a scale of $10^{-10}$ m² of surface, a 10 cm² sample has $10^6$ statistically independent paths through the sample, and aging/breakdown are dominated by the worst case path. A great deal more is known about the solid state properties and high field aging of polyethylene than polypropylene, but usually for much thicker samples where statistical variability through the sample will be much less. This presentation will bring together the experimental work in this area in the context of relevant theory in an attempt to discern material properties which are likely to be correlated with improved dielectric properties.
350 - Challenges in high field polymeric insulation for electrical engineering applications

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In spite of 50 years of research and development the gap between intrinsic breakdown of insulating polymeric materials and engineering breakdown is still large. In the early time of development of polymeric insulation, engineering fields were limited by the presence of molecular/atomic impurities and defects in the form of voids and contaminants. The former leads to high losses/conductivity with the inevitable thermal runaway when increasing the electric field. The latter is the origin of internal discharges and local field concentration both giving rise to material degradation under the form of electrical treeing. Progress in purification methods, material processing and engineering concepts allow increasing the engineering field where the electronic component of the current shown up. The electrical engineering community is now facing the challenge of pushing the limit further. This needs a better description and control of the electronic transport which is responsible for ageing (degradation of the material properties with time under stress) and breakdown. To do so, approaches must rely on material sciences with the objective to tailor the electronic properties of the polymer through chemical/physical modification aiming at controlling specific chemical functions and at tuning the microstructure. Computation at the quantum mechanical level is of paramount importance to achieve this goal. This must be coupled to an improved description of the physics of charge transport, energy storage and transfer dynamics which are the essential ingredients involved in material ageing and in breakdown. Modeling transport and ageing should be done based on reasonable physical grounds but giving outputs tractable in more macroscopic models directly comparable with experimental data. Our objective in this conference is to give an overview of what has been realized along this approach on polyethylene-based materials for HVDC applications and to discuss the challenge for implementing a similar scheme for thin-films capacitors.

Thursday, September 12, 2013 11:10 AM
Polymer Capacitor Dielectrics (08:30 AM - 12:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
Understanding the mechanisms of engineering breakdown in dielectrics is a prerequisite for the design of substantially improved materials. Intrinsic breakdown, which provides an upper limit of breakdown strength, is determined solely by the physical properties of the material and temperature. A first principles quantum-mechanical method for estimating intrinsic breakdown field has been implemented based on an average electron model which assumes that the breakdown occurs when the average electron energy gain from the electric field exceeds the average energy loss to phonons. The computational approach is based on density functional perturbation theory (DFPT) and direct integration of electronic scattering probabilities over all possible final states, with no adjustable parameters. The computed intrinsic breakdown field for several prototypical covalently bonded and ionic materials compares favorably with available experimental data. Engineering breakdown in solid dielectrics is much more complex and involves many phenomena and “extrinsic” factors even in the absence of “gross defects”, such as chemical impurities at the atomic level, metal-dielectric interfaces including the effects of atomic impurities as those interfaces, cavities at the microscopic and macroscopic scales), as well as statistical variations in morphology and microstructure. This paper will discuss approaches to estimating engineering breakdown and computations based on a Monte Carlo scheme to examine the effect of cavities on high field aging and breakdown in polyethylene (PE).
One approach to increasing capacitive energy storage is to study dielectrics composed of nanoparticles in a polymer matrix. Recently, several of the authors have presented results for nanodielectrics composed of poly(ether imide) (PEI) and nano-sized BaTiO$_3$. This includes dielectric breakdown and audio frequency relative permittivity and loss studies (carried out from 5.5K to 400K), thermal measurements and electron microscopy (scanning and transmission) for a wide range of nanoparticle concentrations. The room temperature relative permittivity vs. nanoparticle content follows a recently proposed modified Hanai equation. A relaxation in the region of 20K was found and shown to be associated with the BaTiO$_3$ nanoparticles, themselves, and gives insight into a long-standing discussion on bonding in perovskite-type ferroelectrics. In addition, a water-associated relaxation is found in the vicinity of 200K. Finally, the dielectric breakdown strength was found to decrease as the nanoparticle content increases. Microstructure-level simulations showed that matrix field intensification cannot account for all of the variation of breakdown strength with nanoparticle concentration. Detailed studies have also been reported for BaTiO$_3$ nanoparticles in a cavity. In that case, the shape and intensity of the low temperature relaxation exhibited size effects. Results for BaTiO$_3$ nanoparticles in polycarbonate are discussed and compared with those for nanoparticles in PEI.

Reference s:


**Thursday, September 12, 2013 11:50 AM**
Polymer Capacitor Dielectrics (08:30 AM - 12:30 PM)
Location: Hyatt Regency Indianapolis
Room: Regency F
353 - Real-time measurement of birefringence, weight, thickness, and surface temperature during drying of novel materials for capacitors

Jolanta E. Marszalek¹, jolanta@uakron.edu, Ido Offenbach¹, Emre Unsal¹, Aaron Baldwin², Rui Ma², Gregory A. Sotzing², Mukerrem Cakmak¹, Robert Weiss¹. (1) Department of Polymer Engineering, The University of Akron, Akron, Oh 44325, United States, (2) Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States

There is a need for development of novel materials for application in capacitors with larger dielectric constant and higher voltage breakdown characteristics.¹ Here a new set of polyimide materials that have been synthesized are processed via solution casting for film preparation and evaluation of processing conditions. The changes in physical parameters during the drying behavior of solutions are followed by one of the kind instrument build in our group.² This instrument follows in real-time in-plane and out-of-plane birefringence, weight, thickness, and surface temperature during the course of solidification of films through solvent evaporation in a controlled atmosphere. It is specifically designed to simulate behavior of polymer solutions inside an industrial size, continuous roll-to-roll solution casting line and allows for quick parameters evaluation on low amounts of material. Controlled processing parameters include air speed, temperature, initial cast thickness, and solute concentration, while measured parameters are thickness, weight, film temperature, in-plane and out-of-plane birefringence. In this paper, we illustrate the utility of this instrument with solution casting of (pBTDA-HAD) and (pBTDA-DAB) from m-cresol solution. As the temperature of air drying is increased the steady state is reached earlier. Larger initial thickness of the solution delay reaching of the steady state.

References:


Our group has worked on developing photo-crosslinkable copolymers as a flexible platform for the fabrication of actuating micro-scale devices. Specifically, we make use of materials containing pendent benzophenone units, which give rise to efficient crosslinking with UV light for appropriate copolymer chemistries. For thin sheets of stimuli-responsive polymers, this provides a route to reversibly generate patterns of swelling, yielding buckling into three-dimensional shapes of prescribed Gaussian curvature. The approach also allows for patterning of multi-layer devices, which opens additional opportunities in controlling shape, as well as optical properties, of micro-scale polymer objects.
355 - Stimuli-responsive, shape and surface morphing in liquid crystal polymer networks

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Liquid crystal polymer networks are anisotropic materials capable of a wide range of stimuli-responsive behaviors. One of the distinguishing features of LCN materials is the ability to arrest complexly patterned domain and defect structures. Here, we present our recent work examining shape and surface morphing in monolithic, spatially patterned LCN materials triggered by either heat or light. Spatial patterning was enabled by employing photoalignment materials and complex optical patterning methods. The resulting response of the films can generate motion (deflection of a cantilever, spiral coiling) or topographical features. The rich and diverse responses are shown to be heavily dependent on the underlying polymer chemistry - most notably the crosslink density.
Liquid crystal polymer networks exhibit a wide palate of mechanically adaptive responses. Here we report on our recent work examining the thermally-induced shape formation observed in highly crosslinked, glassy liquid crystal polymer networks (LCNs). Specifically, this work focuses on the response of films prepared with twisted nematic (TN) orientation. The presentation will report on the baseline properties of the material as well as discuss the ability to generate a number of complex shapes in samples in which the nematic director on the film surfaces were offset to the principal axes of the sample. Accordingly, the thermally-generated strain generates shear that results in large magnitude out-of-plane deformation (coiling). The shape memory response of the materials was found to be highly dependent on the crosslink density of the LCN. The $T_g$ of the LCN is reduced to 35°C by adding 15 wt% of a monoacrylate LC monomer. The reduction in $T_g$ allows for the spontaneous generation of shapes simply with body temperature.
357 - Actuating polymer sheets that self-fold in response to light

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We describe a simple approach to actuate polymer sheets that uses localized light absorption on a pre-stressed polymer film to induce self-folding. Self-folding is a deterministic assembly process that causes a predefined 2D template to fold into a desired 3D structure with high fidelity. Self-folding takes advantage of the multitude of available 2D patterning techniques (e.g., lithography, inkjet printing, screen printing). Self-folding is attractive as a cost-effective 3D fabrication strategy for applications such as packaging, robotic actuators and sensors, biological devices, solar cells, and reconfigurable devices. Most approaches to self-folding use hinges (i.e., regions of a substrate that fold) that have unique chemical composition from the bulk, which requires complicated photolithography or other multiple fabrication steps.

Our approach to self-folding relies on printing patterns of ink on a pre-strained polymer film. The substrates are commercially available pre-stressed polymer sheets. The hinges (black ink) are patterned using a desktop printer on either side of the optically transparent sheets. Hinges absorb selectively the light to heat the underlying polymer and causes the polymer sheets to fold into complex 3D structures (e.g., cubes, tetrahedrons) within seconds. The approach is appealing because it uses inexpensive materials and simple patterning techniques to form complex structures.
Shape memory polymers (SMPs) are materials that can be deformed from an initial shape to a second programmed shape that is retained until the application of a stimulus returning the material to its initial shape. These materials have a range of potential applications including biomedical implants and sutures, adjustable aerospace components, and self-healing coatings. In this research a shape memory polymer has been prepared by the simple blending of an ABA triblock copolymer thermoplastic elastomer and a microcrystalline wax. The thermoplastic elastomer defines the “permanent” network of the SMP, while the melting/crystallization of the wax is used to drive the shape fixing/recovery events. It will be shown that the broad melting transition of the wax can give rise to interesting shape memory properties including multiple shape recovery events and tunable shape memory triggering temperatures. This is a potentially useful SMP as it combines the ease of blending commercially available materials with advanced shape memory behavior.

Thursday, September 12, 2013 10:20 AM
Sensing and Controlling Motion with Polymeric Materials (08:30 AM - 11:20 AM)
Location: Hyatt Regency Indianapolis
Room: Studio One
359 - Design of a self-powered material with a memory for specific external stimuli

Matthew S Baker, msb316@psu.edu, Vinita Yadav, Ayusman Sen, Scott T Phillips. Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

This presentation describes the design of a smart polymeric material that is capable of responding autonomously to a specific applied stimulus, even after that stimulus has been removed. This material includes a sensing reagent that responds to UV light to produce a transduction reagent (fluoride). The transduction reagent initiates an autoinductive reagent on the polymer, which continues responding even when the material no longer is exposed to UV light. This presentation will focus on the design, synthesis and physical organic study of the self-perpetuating mechanism, as well as applications of this polymeric material in the context of autonomous, self-powered microscale pumps.
360 - Buckling, twisting, and creasing in hydrogel membranes: A new mechanism for reconfigurable soft materials

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Reconfigurable soft materials that can bend, fold, or transform the structural symmetry in response to external stimuli have attracted significant interests in design of actuators, sensors, and smart materials and devices. It also presents scientific and engineering challenges to the designs of soft structures with reversible, fast, and controllable deformation.

Here, we patterned hydrogel membranes with micro-pores (Fig. 1a, 10 µm diameter, 15 µm pitch) by replica molding and UV crosslinking hydrogel monomers (Fig. 1b): poly(2-hydroxy ethyl methacrylate) (PHEMA), pH responsive acrylic acid (AA), and thermal responsive N-isopropylacrylamide (NIPAAm) to study its structural reconfiguration upon swelling. Depending on the pH and temperature, the hydrogel matrix swells or contracts, leading to fast and reversible reconfiguration of the pore size, shape and symmetry. We observed four distinctive surface configurations at different swelling ratios of the hydrogel (Fig. 1c): initial state of circular pore arrays, buckled pore arrays of alternating mutually orthogonal ellipses, twisted pores snap-shut to form “S” shaped slits, and crease formation with locally formed surface folds. The pore deformation process can be qualitatively assessed based on the buckling instability and pattern transformation of elastomeric cellular solids having square arrays of pores (Fig. 1d).

Our hydrogel microstructure has demonstrated fast and well-controlled deformation of micro-pore arrays on the membrane at the cusp of instability through buckling, bending and creasing, which may find applications in micro-actuators, micro-robotics, and microfluidics.

Figure 1. (a) SEM images of hydrogel structure fabricated from replica molding. (b) Schematics of the chemical structures of monomers and crosslinker to generate the responsive hydrogel network. (c) Optical images of four distinctive surface morphologies at different pH 2, pH 4, pH 6, and pH 7 respectively. (d) Illustration of the surface reconfiguration mechanism in the hydrogel membrane.
361 - WITHDRAWN
Phosphonic acid functional polymers are important for applications in medicine, and membrane technologies such as water purification, and fuel cells due to the unique combination of the properties of phosphonic acid functionality including acidity, stability, proton conductivity, and metal binding. Despite these attractive properties and potential uses, there is a current gap on direct pathways to make phosphonated polymers with controlled properties from phosphonated monomers, and fundamental properties of such materials. This is due the unusual polymerization behavior of phosphonated monomers leading to difficulties in synthesis.

We highlight the advantages of ring opening metathesis polymerization over other polymerization techniques for the synthesis of well-defined phosphonated polymer ester form, and report the basic properties of the resulting new materials. Phosphonated polymers with precisely controlled molecular weight, composition, and architecture were synthesized via ring opening metathesis polymerization directly from phosphonated norbornene imides for the first time. Ring opening metathesis polymerization gave a broad range of phosphonated poly(norbornene imide)s with low polydispersity. Complete hydrolysis of phosphonated poly(norbornene imide)s under mild conditions yielded phosphonic acid functional poly(norbornene imide)s. The resulting phosphonated polymers both in ester and acid form have good thermal/thermo-oxidative stability, and film forming properties. Synthesizing phosphonated polymers via ring opening metathesis polymerization provides a promising pathway to access well-defined macromolecular structures, and allow fine-tuning of material properties in a straightforward manner.
363 - Effect of hydrogen bonding on determination of epoxy-amine reaction kinetics via FTIR

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The amine-epoxy reaction is important in understanding the cure chemistry of a wide variety of epoxy based thermoset materials, where the extent of the amine-epoxy reaction is directly related to the evolution of the primary and secondary amine hydrogens and the formation of a hydroxyl group. FTIR spectroscopy can be used to monitor the amine hydrogens and hydroxyl; however, the FTIR spectra is complicated by the formation of hydrogen bonds, where both the amine hydrogens and the hydroxyl group can form various kinds of hydrogen bonds with the H-bond acceptors on both the reactants and the resulting polymer. In order to use FTIR spectra for the quantitative analysis of the amine-epoxy cure reaction, hydrogen bond formations were quantitatively analyzed for simple binary and ternary mixture of model amines (i.e. N-methyl aniline and aniline) with alkyl-alcohols and additional model compounds with H-bond acceptor agents (i.e. epoxide, ether, tertiary amine and phenyl groups which indicate π bond). The extensive FTIR spectra from 3200 cm\(^{-1}\) to 3600 cm\(^{-1}\) was quantitatively deconvoluted and optimized equilibrium constants and extinction coefficients of the hydrogen bonding species was determined. Using this information on FTIR line location/shape and equilibrium constants, the FTIR spectra of the amine-epoxy system during cure was quantitatively analyzed.
Polymer mechanical properties ultimately determine final applications. In order for a polymer to be a viable tissue engineering scaffold material it must have similar mechanical properties to the parent tissue. One unique class of polymers known as polyphosphazenes has been investigated for this purpose. These highly tunable polymers consist of a flexible backbone of alternating nitrogen and phosphorus atoms with two labile chlorine atoms attached to each phosphorus that are able to undergo nucleophilic substitution by various alkoxides and amines. The high degree of synthetic tunability gives rise to many different polymers whose properties are determined by the backbone and the side groups. This has made these polymers useful for tissue engineering applications. Various side groups can be attached to generate anything from soft, elastomeric polymers to hard, tough polymers to increase their potential in tissue engineering. This project has focused on the design and synthesis of elastomeric biodegradable polyphosphazenes for ligament and tendon scaffold applications. Mechanical properties of specific polymers have been determined by atomic force microscopy. This application uses small sample sizes allowing for multiple potential polymers to be studied to determine which polymer would be the best candidate for further investigation in tissue engineering.
365 - Cross-linking chemistry in synthetic polymer mimics of mussel adhesive proteins

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Adhesives have long been sought for applications ranging from industrial to biomedical. As the search for high strength, durable glues continues, inspiration for one such class of materials comes from the seas. At the beach there a variety of animals, including mussels, attaching tightly to rocks. The adhesive of these shellfish contains a unique amino acid, 3,4-dihydroxyphenylalanine (DOPA), bringing about protein cross-linking and curing. As we learn how marine biology makes glues, these insights can be used to design new synthetic materials. To mimic the cross-linking chemistry of DOPA proteins, poly[(3,4-dihydroxystyrene-co-styrene] is synthesized via anionic polymerization. Addition of cross-linkers to these catechol-functionalized polymers are being examined to determine the effects upon bulk adhesive bonding. Additional parameters under investigation include molecular weight, cure time, cure temperature, and the addition of fillers. With these systematic studies we are finding adhesive performance greater than that of commercial cyanoacrylate products (e.g., Krazy Glue). Blends of polymers with multiple molecular weights are being targeted synthetically to mimic the variety of proteins found in mussel adhesive plaques. Interestingly, increases of adhesion strength are being found for these blends when compared to the individual polymers. These studies are showing how biology makes adhesives as well as helping us to design new biomimetic polymers.
This work is the first report to prepare surface active solid nanogels particles which has ability to lower the surface and interfacial tension of aqueous and non-aqueous media. Moreover, this work aims to use nanogels as stabilizer for non-aqueous solvents such as formamide, hexane and toluene. The present work synthesized a series of amphiphilic crosslinked N-isopropylacrylamide (NIPAm) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) copolymer nanogel based on temperature program method using polymerizable surfactants based on nonyl phenol ethoxylates. The morphologies of the prepared nanogels were detected by TEM and SEM technique [figure 1]. The lower critical transition temperatures (LCST) were determined from DSC technique. The NIPAm/AMPS nanogels reduced the surface tension of water to about 30.1 mN/m at 25 °C and a little increase at 40 °C. The relationship between surface activity and nanogels morphologies and mol percentages of NIPAm was discussed. The surface adsorption state and surface adsorbed layer of NIPAm/AMPS dispersions were also discussed.
367 - Enzyme catalyzed polymerization of DNA amphiphiles that self-assemble into star-like micelles

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The synthesis of biologically-inspired macromolecules with well-defined sequence, dispersity and assembly function has large potential for applications ranging from drug delivery vehicles, sensing applications, to scaffolds for tissue regeneration. Here we report the progress of our work in exploiting the ability of a specific DNA polymerase, terminal deoxynucleotidyl transferase (TdT), to polymerize long chains of ssDNA and to incorporate unnatural nucleotides with useful functional groups into the growing polynucleotide chain. Specifically we report on a method that allows the facile synthesis of amphiphilic ssDNA biomacromolecules (0.6 to 2.7 kilobases) via enzymatic polymerization of mononucleotides. The amphiphilicity arises from the synthesis of hydrophilic homopolynucleotides and the modification of hydrophobic, unnatural nucleotides into the extended ssDNA chain. The hydrophobicity, resulting from incorporation of unnatural nucleotides, can be tuned to drive the assembly of these polynucleotides into star-like micelles. We used high resolution AFM and cryo-TEM imaging to directly visualize the star-like micelle morphologies with a condensed core and hairy corona. In addition, we investigated the hydrodynamic radius ($R_h$) of homopolynucleotides and polynucleotides amphiphiles that form micelles by dynamic light scattering. The unmodified homopolynucleotides have an $R_h$ ranging from 11.7±0.4nm to 21.3±0.3nm, which correspond to the samples with MW ranging from 0.6 to 2.7 kilobases. In contrast, the micelles formed by the polynucleotide amphiphile have an $R_h$ value ranging from 32.9±0.8nm to 56.6±0.4nm.
Optically active poly(meth)acrylamides were synthesized by the stereospecific radical polymerization of (meth)acrylamides, such as (S)-N-(2-hydroxy-1-phenylethyl)methacrylamide ((S)-HPEMA), (S)-N-(1-hydroxy-3-phenylpropyl)methacrylamide ((S)-NPMA), (R)-N-(1-phenylethyl) methacrylamide ((R)-PEMA) and (S)-N-(2-hydroxy-1-phenylethyl)acrylamide ((S)-HPEA), in the absence and presence of Lewis acids, namely, rare earth metal trifluoromethanesulfonates. The effect of Lewis acids on the radical polymerization of (meth)acrylamides was investigated. In the presence of a catalytic amount of the Lewis acid, the isotactic specificity of the polymers remarkably increased when the radical polymerization proceeded in methanol and n-butanol. However, the isotactic selectivity disappeared when the radical polymerization proceeded in DMSO. The interaction between the Lewis acid and the monomers was investigated by $^1$H NMR. It was found that the monomers strongly interacted with the Lewis acid in methanol-$d_4$, which included the coordination of the amide group to the rare earth metal ion and the hydrogen bond between the hydroxyl group of the monomers and the trifluoromethanesulfonate ion of the Lewis acid. The plausible mechanism of stereocontrol in the radical polymerization of (meth)acrylamides was analyzed based on the Lewis acid-monomer interaction.
369 - WITHDRAWN
We report a novel modular strategy for the synthesis of block copolymers via the combination of a macromolecular azo coupling reaction and RAFT or ATRP polymerization method. One block, with a terminus suitable for an azo coupling reaction, was obtained by RAFT or ATRP polymerization using a synthesized chain transfer agent or initiator with the designed functional group. The other block, with a diazonium salt terminus, was obtained by the diazotization of aniline functionalized PEG. The macromolecular azo coupling reaction between the above two polymer blocks was carried out in a polar organic solvent such as DMF under extremely mild conditions. Block copolymers with well-defined structures can be efficiently prepared through this approach.
The synthesis of polysaccharides through glycosylation, using OH-bearing glycosyl donors as di-functional AB monomers, has achieved limited success with only small molecular weight oligosaccharides obtained. This is due largely to the low reactivity of the glycosyl donors employed. Unfortunately, the use of a reactive glycosyl donor would result in stability problems. Herein we report the synthesis polysaccharides through an "in situ" activation approach. 2,3,4-tri-O-acetyl-α-D-Glucosyl and galactosyl bromides were synthesized as the latent AB-monomers. Upon in situ activation with potent activators, including tetrabutyl ammonium iodide (TBAI) and 4-dimethylamino pyridine (DMAP), polysaccharides with molecular weights up to 9.1 kDa were obtained with narrow PDI. Additionally, microwave energy was employed to boost the reactivity of the monomers to further increase the molecular weights.
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