Division of Polymer Chemistry (POLY)

Graphical Abstracts

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**Division of Polymer Chemistry (POLY)**

**Table of Contents** [click on a session time (AM/PM/EVE) for link to abstracts]

<table>
<thead>
<tr>
<th>Session</th>
<th>SUN</th>
<th>MON</th>
<th>TUE</th>
<th>WED</th>
<th>THU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellence in Graduate Polymer Research**</td>
<td>AM</td>
<td>PM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials for Energy Harvesting</td>
<td>AM</td>
<td>PM</td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
<tr>
<td>Polymers for Oil and Gas Energy Operations</td>
<td>AM</td>
<td>PM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sustainable Polymers, Processes and Product Applications**</td>
<td>AM</td>
<td>PM</td>
<td>AM</td>
<td>PM</td>
<td></td>
</tr>
<tr>
<td>Undergraduate Research in Polymer Science</td>
<td>AM</td>
<td>PM</td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
<tr>
<td>Frontiers in Polymer Characterization</td>
<td>AM</td>
<td></td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
<tr>
<td>General Topics: New Synthesis and Characterization of Polymers**</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>PM</td>
</tr>
<tr>
<td>Paul J. Flory Polymer Education Award: Symposium in Honor of George Odian</td>
<td>AM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12th International Symposium on Biorelated Polymers</td>
<td>PM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>PM</td>
</tr>
<tr>
<td>ACS Award in Polymer Chemistry: Symposium in Honor of Karen L. Wooley**</td>
<td>PM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Responsive Nanostructures and Nanocomposites</td>
<td>PM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>PM</td>
</tr>
<tr>
<td>Sci-Mix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
<tr>
<td>Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond**</td>
<td>AM</td>
<td>AM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peptide-Based Materials for Nanomedicine**</td>
<td>PM</td>
<td>AM</td>
<td>AM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POLY/PMSE Plenary Lecture and Awards Reception**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
</tbody>
</table>

**Primary organizer of Cosponsored symposium.**

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There is a growing need for environmentally-friendly flame retardants for polymeric materials that are both effective and non-toxic. Traditional organohalogen flame retardants are effective, readily available, and inexpensive. However, they are stable, persist in the environment, and tend to bioaccumulate. Because of this they may pose a risk to human health. Phosphorus compounds are the most likely replacements for these older flame retardants. Since the effectiveness of phosphorus compounds is often enhanced by the presence of nitrogen, it would be desirable to generate materials containing an abundance of both elements. Further, the generation of such materials from a renewable biosource is attractive for several reasons. It would likely degrade in the environment and would not be dependent on a non-renewable petrochemical source. Natural oils are available from several sources and contain unsaturation which may be converted to epoxides. The epoxides may be opened with nitrogen nucleophiles to generate alcohols which can be converted to a variety of phosphorus compounds. This is illustrated below for a commercially-available triepoxide.
2 - Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton

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Thin films of fully renewable and environmentally benign electrolytes, cationic chitosan (CH) and anionic phytic acid (PA), were deposited on cotton fabric via layer-by-layer (LbL) assembly in an effort to reduce flammability. Altering the pH of aqueous deposition solutions modifies both thickness and composition of the final nanocoating. In a vertical flame test, fabrics coated with high PA content multilayers completely extinguished the flame, while uncoated cotton was completely consumed. Microcombustion calorimetry confirmed that all coated fabric reduces peak heat release rate (pkHRR) by at least 50% relative to the uncoated control. This superior performance is believed to be due to high phosphorus content that enhances the intumescent behavior of these nanocoatings. These results demonstrate the first completely renewable intumescent LbL assembly, which conformally coats every fiber in cotton fabric and provides an effective alternative to current flame retardant treatments.
3 - Synthetic design of block copolymer amphiphiles for nanomaterial dispersion

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Amphiphilic block copolymers were prepared with a variety of controlled radical polymerization techniques, including RAFT and ATRP. Length of the hydrophobic and hydrophilic block were adjusted to determine optimum dispersion of various hydrophobic nanomaterials. The prepared water-borne dispersions were subsequently utilized for a wide variety of applications.
Solid-state polymer electrolytes offer a promising alternative to liquid electrolyte supports in lithium ion batteries. Herein, we investigate a diblock system which may offer a nanostructured approach to membrane electrolytes. We have synthesized dicarboximide-functionalized oxanorbornyl diblock copolymers with varying ratios of ethylene oxide (EO)$_2$ and phenyl side groups. Polymerization was conducted under living conditions using a Grubbs third generation catalyst through a ring opening metathesis mechanism. The diblocks were characterized using NMR, GPC, and DSC which shows two glass transition temperatures that correlate with those observed in the phenyl and ethylene oxide (EO)$_2$ homopolymers. Small angle x-ray scattering and AFM of spun cast films will be used to characterize microphase-separated nanostructures, which may be useful in lithium ion conduction.
Microporous polymer scaffolds decorated with nanoparticles could provide functional membranes that are needed in solar-to-fuel technologies. Therefore, efficient production processes are needed for high surface area, porous membranes with distinct catalytic nanoparticles on opposite sides of a support that resists oxidation and separates the products, e.g., hydrogen and oxygen. Breath figure (BF) patterning is an established method to create microstructured honeycomb-patterned porous polymer films. This research shows that surface-active nanoparticles can self-assemble onto the interfaces between the templating BF water droplets and the polymer solution to control micrometer and nanometerscale hierarchical structure. Here, amphiphilic “Janus” nanoparticles serve as both solid surfactants and Pickering emulsion stabilizing agents, thus able to optimize ordering degree of the honeycomb structures and nanoparticle enrichment in the pore walls. Janus nanoparticles were synthesized using literature methods (with improvements that will be presented): functionalizing only the exposed surface of particles embedded on the surface of wax microspheres (colloidosomes) renders half of the particle hydrophobic. They were then employed in the BFs templating method for the first time, resulting in regular, porous films with uniform, high nanoparticle density. Humble materials (silica and polystyrene) demonstrate the method, and can now be replaced by catalyst nanoparticles (e.g., nickel, molybdenum sulfide, or cobalt-based) embedded in a semiconducting polymer to create membranes for photocatalytic water splitting.
The microelectronics industry relies on the ability to continually pattern smaller and smaller features. However, traditional patterning methods are quickly approaching physical limits and economic feasibility, which provides impetus for alternative patterning technologies. Block copolymers (BCPs) can self-assemble into periodic domains of various morphologies (cylinders and lamellae) on the sub-10 nm scale, which surpasses current patterning capability (ca. 20 nm). In order for the self-assembled BCP patterns to be useful, the BCP domains must adopt a perpendicular orientation of domains relative to the substrate. Unfortunately, nearly all BCPs orient their domains parallel to the substrate due to strong preferential interactions between the lower surface energy block and air interface. Non-preferential (“neutral”) interfaces are required to prevent a parallel orientation of the domains. Polarity-switching top coats were designed to replace the air interface with a neutral surface. The top coats promote a perpendicular orientation of BCP domains and were used to control the orientation of a lamellar-forming BCP. Rapid thermal annealing was used to achieve perpendicular domains on the order of ca. 10 nm.
The adhesive capabilities of intertidal marine species, such as mussels, have recently provided a wealth of inspiration toward the design and development of new materials. Mussels show a unique ability to affix themselves to wet, heterogeneous surfaces such as rocks, and maintain adhesion under the high-energy, turbulent environment of the intertidal zones. While the natural adhesives employed by these organisms are a complex mixture of proteins, 3,4-dihydroxyphenylalanine (DOPA) has been identified as a common constituent that plays a central role in the curing and interfacial interactions of the adhesive plaques. DOPA is thought to play two primary roles in such bioadhesives: first, to facilitate cross-linking via the formation of di-DOPA linkages leading to solidification of precursor proteins, where cross-linking may occur via oxidative, enzymatic, or redox induced radical chemistry and, second, to facilitate adhesion to heterogeneous substrates via DOPA’s ability to undergo hydrogen bonding, n−n aromatic interactions, and metal–ligand complexation with a variety of surface functionalities. Inspired by the salient features of natural bioadhesives, interest in designing synthetic polymeric systems that incorporate DOPA and analogous catecholic moieties as active adhesive constituents has proliferated in recent years. In this presentation, we report the synthesis of a dihydroxy eugenol derivative, 4-prop-2-enylbenzene-1,2-diol (EugOH), and its subsequent incorporation into a thiol-ene network based on pentaerythritol triallyl ether (APE) and pentaerythritol tetra(3-mercaptopropionate) (PETMP). The catechol monomer shows improved miscibility with multifunctional thiols and enes commonly used in thiol-ene polymerizations enabling solvent-free resin systems. Comparing to the naturally occurring eugenol and its methylated analogue, methyl eugenol, the effect of the pendant catechol moiety, in the nonoxidized form, on photopolymerization kinetics, thermal, thermomechanical, and adhesive properties has been evaluated.
Synthesis of guanidinium-modified antimicrobial peptide mimics prepared via aqueous RAFT polymerization

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Naturally occurring antimicrobial peptides (AMPs) are amphipathic molecules that selectively eliminate a wide range of bacteria. The hydrophilic regions of AMPs possess an abundance of lysine and arginine amino acid residues, which are protonated and positively charged under physiological conditions. The positively charged AMPs electrostatically bind with the negatively charged bacterial cell membrane and promote cell death. However, literature on AMP mimics has shown a variation in the mechanism of cell death (e.g. membrane disrupting and cell penetrating), depending on the presence of lysine and arginine, respectively. The goal of this research is to determine the predominant mode of antimicrobial activity for statistical copolymer AMP mimics prepared via aqueous RAFT polymerization. The synthesized statistical copolymers are comprised of varying ratios of aminopropyl methacrylamide (APMA), a lysine mimic, and guanadinopropyl methacrylamide (GPMA), an arginine mimic. The prevailing mechanism of cell death was characterized by dye leakage studies with large unilamellar vesicles (LUVs), containing the fluorescent dye calcein, and then directly correlated to the compositional differences of the copolymers. The statistical copolymer AMP mimics utilized have demonstrated well-defined molar ratios of APMA and GPMA, antimicrobial activity, and biocompatibility. Developing a greater understanding of the structure-activity relationship of synthetic AMPs will aid in the future design of systems tailored to target specific bacterial species.
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry was employed to prepare an inimer compound to integrate DA linkages at branching points within a branched polymer backbone. Upon the application of a thermal stimulus, the retro-DA was induced and subsequent branch points were reduced to transform a highly branch architecture into a linear topology.
10 - Design of green materials by building-in a controlled behavior

**Ann-Christine Albertsson**, aila@polymer.kth.se, Fibre and Polymer Technology, Royal Institute of Technology (KTH), Stockholm, Sweden

The need for more sustainable materials and building blocks, as well as green chemistry tools to produce, modify and process them, are raising considerable efforts world-wide. Many attempts are made to replace, or at least increase, the amount of renewable raw materials in a given product on the expense of petroleum derived polymers, thereby hoping to gain competitiveness with products with a better carbon dioxide footprint.

My research focuses on the design of green materials by building-in a controlled behavior into materials aimed at tissue engineering or sustainable commodity applications. A range of pathways have been used to synthesize polymers with various architectures. Strategies for the design of materials with controllable degradability and inherent material properties will be described.
Catalysis is a foundational pillar for sustainable chemical processes; the discovery of highly active, environmentally benign catalytic processes is a central goal of Green Chemistry. Polymers derived from renewable resources provide an attractive alternative to many petrochemical thermoplastics. The challenges in generating new families of biomass polymers that match the performance of petroleum-based plastics are formidable. We have developed new catalytic methods for transforming biomass feedstocks into new monomers and chemical intermediates. With Jim Hedrick of IBM, we have developed a new family of organic catalysts for the synthesis of plastics derived from renewable resources. Mechanistic and theoretical investigations generated new scientific insights on the diversity of mechanistic pathways for organocatalytic polymerization reactions and the opportunities that these new insights have created for the synthesis of renewable polymers.
Our research team developed a mild and efficient biotechnological route for \(\omega\)-hydroxylation of fatty acids. Since this finding, our research group and collaborators have been evaluating how this new platform of biobased building blocks can be of value in the development of unique biobased materials. This paper overviews our research findings which includes published and unpublished work using \(\omega\)-hydroxytetradecanoic acid (\(\omega\)-HOC14) as a model system. \(\omega\)-HOC14 was converted by a condensation polymerization catalyzed by titanium tetraisopropoxide (Ti\([\text{OiPr}]_4\)) to a polymer P(\(\omega\)-HOC14) with \(M_w\) up to 140K. Tensile tests of P(\(\omega\)-HOC14) with \(M_w\) above 78K showed strain-hardening phenomena and tough properties with elongation at break about 700% and true tensile strength about 500 MPa. Furthermore, DSC analysis revealed P(\(\omega\)-HOC14) has a peak melting temperature at about 94 °C and is highly crystalline. Films of P(\(\omega\)-HOC14) were evaluated for compostability by ISO14855 and were found to be readily compostable (unpublished work). Motivated by the biodegradable and useful properties of P(BT-co-BA), a series of aliphatic–aromatic copolyesters from 1,4-butanediol, dimethyl terephthalate and \(\omega\)-HOC14 were prepared by condensation polymerization. NMR analysis showed the polycondensation reactions result in random copolymers. The copolyesters are semicrystalline materials, characterized by the presence of a single crystalline phase (P(\(\omega\)-HOC14) or PBT crystals), according to the composition. The copolymer with 60 mol% \(\omega\)-HOC14 units has similar tensile properties as the commercial product Ecoflex. Finally, Studies were conducted to optimize parameters for reactive extrusion blending of PLA/P(\(\omega\)-HOC14). The objective was that by incorporating relatively rubbery P(\(\omega\)-HOC14) domains within the PLA matrix, PLA can be transformed from being brittle to ductile without significant loss in material strength. By performing reactive extrusion of PLA/P(\(\omega\)-HOC14) 90:10 at 200 °C, screw speed 150 RPM, residence time 15 min and using Ti(\text{OBu})_4 (200 ppm) as the transesterification catalyst, the elongation at break is about 150% relative to 3% for neat PLA. Furthermore, without the transesterification catalyst, PLA/P(\(\omega\)-HOC14) 90:10 was brittle and showed poor adhesion between phases based on cryo-fractured SEM images. The preparation of polyurethanes from polyols built from \(\omega\)-HOC14 units will be briefly introduced and further elaborated in a separate paper given at this meeting.
13 - Syntheses and characterizations of novel, quercetin-based thermoset polymers with natural cross-linkers

Samantha L Kristufek\textsuperscript{1}, samantha.kristufek@chem.tamu.edu, Guozhen Yang\textsuperscript{2}, Jeffery E Raymond\textsuperscript{1}, Megan L Robertson\textsuperscript{2}, Karen L Wooley\textsuperscript{1}. (1) Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States, (2) Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77004, United States

An increased need for lower levels of reliance on petrochemical-derived materials, due in part to the environmental impact of oil-based chemical feedstocks, compels our keen interest in the design and application of engineering polymers derived from renewable biofeedstocks. Quercetin and many of its natural derivatives have been well studied, displaying interesting bioactivities and possessing potentially beneficial properties, though virtually no investigations of its properties as a polymer backbone substituent have been made. Herein, we present a series of novel epoxy thermoset polymers developed from quercetin derivatives cross-linked with various natural materials, such as spermine, spermidine and other naturally derived compounds. Our strategy provides the benefit of possessing both monomers and cross-linkers which are renewable, unlike non-natural analogues synthesized from the diglycidyl ether of bisphenol A (DGEBA) and many traditional cross-linkers. Thorough assessment of the thermal and mechanical properties of these networks will be presented in contrast to those of non-renewable engineering polymers used as protective coatings, adhesives, automotive materials and structural materials in wind-turbine blades. In order to tune the mechanical and thermal response of these systems, cure temperatures and durations will be shown to provide a direct route to control the cross-link density. In total, these epoxy resins represent a new class of environmentally-friendly networks with a potential for the replacement of petroleum-based polymeric systems.
The ability to control the assembly and morphology of nanoscale materials in response to specific biomolecular stimuli is expected to have a significant impact in targeted drug delivery and advanced sensor design. A set of strategies are being developed in our laboratories at UC San Diego to incorporate enzymes, proteins, peptides and nucleic acids into novel polymeric synthetic materials with the aim of programming morphology and function. Together, these efforts involve a concerted effort to develop bioresponsive, and bioactive chemical systems through innovations in synthesis and characterization of dynamic systems at multiple length and time scales.
The development of green plastic materials from sustainable biorenewable sources is important for the advancement of sustainable manufacturing technologies. These materials could be prepared by means of a low energy process of photocuring for making parts in composites, coatings, 3D printing and stereolithography. Our research program is specifically aimed at advancing our ability to tailor the photocationic polymerization and physical properties of sustainable epoxy materials derived from crosslinked epoxidized vegetable oils and terpenes using onium salt photoinitiators. We developed solventless, photopolymerizable epoxy monomer and oligomer systems derived from sustainable biorenewable sources as alternatives to existing highly polluting and energy-intensive thermal curing of epoxy resin chemistry. Two sustainable materials systems will be presented: (1) epoxidized vegetable oils that offer various degrees of crosslinking densities and (2) blends of epoxidized vegetable oils with epoxidized terpenes to tailor their photocuring and mechanical properties for the potential usage in “green” coating, adhesive, 3D printing, and composite applications.
16 - Tailored supramolecular structures for the controlled release of therapeutics

James L. Hedrick¹, hedrick@us.ibm.com, Yi-Yan Yang². (1) IBM Research, San Jose, CA 95120, United States, (2) Institute of Bioengineering and Nanotechnology, Singapore, Singapore

The field of nanomedicine offers significant promise for improving human health by applying the tools of nanotechnology to create and control materials with molecular-level medical effects. The targeting and controlled release of therapeutic agents to specific organs and specific cells in the body is one of the major challenges in developing more effective therapies. We have developed modular self-assembly strategies to investigate the use of non-covalent interactions to assemble multifunctional assemblies that can encapsulate small molecules, probes and exhibit responsive behavior to external stimuli. The foundation for this platform is based on our organocatalytic approach to biocompatible/degradable macromolecules with precisely defined molecular weights, end-group fidelity and backbone functionality. These backbones include polylactide, polycarbonate and related degradable polymers with a wide range of backbone functionalities that mimic the rich and diverse functionality of polypeptides. The use of these synthetic methods to generate well-defined macromolecules and their evaluation to test the functional competence of these constructs as drug/gene delivery vehicle as well as macromolecular antimicrobials will be discussed.

Sunday, March 16, 2014 11:25 AM
Sustainable Polymers, Processes and Product Applications (08:30 AM - 12:05 PM)
Location: Hyatt Regency Dallas
Room: Bryan-Beeman B
17 - Synthesis and characterization of biobased and biodegradable hyperbranched poly(ester)s with different endgroups

Tracy Zhang$^{1,2}$, zhang@mmi.org, Bob A Howell$^2$, Patrick B Smith$^1$. (1) Michigan Molecular Institute, Midland, MI 48640, United States, (2) Science of Advanced Materials, Science of Advanced Materials Program, Mt. Pleasant, MI 48859, United States

Hyperbranched poly(ester)s offer attractive features for applications in a number of areas, particularly as platforms for the support of controlled release actives in the agricultural and biomedical fields. Hyperbranched polymers are well-suited for controlled delivery because of high branching density and high end group content. This permits incorporation of an active agent either through physical entrapment or covalent bonding to end groups. Various endgroup functionalities can be obtained by appropriate choice of monomer stoichiometry, providing opportunities for different chemistry to attach beneficial substances. A series of hyperbranched poly(ester)s based on tri-functional alcohols (trimethylolpropane, glycerol) and diacids (adipic and succinic acid) with –OH and –COOH endgroups have been synthesized using nonlinear polymerization methodology. The resulting polymers were characterized using chromatographic, spectroscopic and thermal methods.

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Sunday, March 16, 2014 11:45 AM
Sustainable Polymers, Processes and Product Applications (08:30 AM - 12:05 PM)
Location: Hyatt Regency Dallas
Room: Bryan-Beeman B
Hydraulic fracturing in the shale oil and gas play is leading the US towards energy independence. A number of technological advancements have also made the upstream, midstream, and downstream operation very efficient. An important direction is the use of new polymers and chemicals for enabling operations in complex well operations and extreme environments. Important classes of polymers, surfactants, and nanomaterials have a role in a number of applications including proppants, viscosity modifiers, polymer cement, anti-scaling, and anti-corrosion applications. This talk will give an overview of the different architectures, stimuli-responsive properties, self-healing, and curing chemistry that can enhance performance in the future. Cost-effectiveness and high performance are important issues in the industry.
19 - Challenges for surfactant enhanced oil recovery

Kishore K. Mohanty, kishore.mohanty@engr.utexas.edu, Petroleum & Geosystems Engineering, University of Texas, Austin, Austin, TX, United States

Surfactants reduce interfacial tension between oil and water and can change the wettability of sandstone and carbonate rocks. Reduction in interfacial tension can increase capillary number and help mobilize oil in porous media. Wettability affects residual oil saturation, relative permeability, and capillary pressure. Wettability can be affected by the ionic composition of the brine as well as the presence of surfactants. Polymers are needed to increase the viscosity of water which displaces surfactant solutions and oil in a stable manner. The challenges in this field are reservoirs with high salinity, high temperature, viscous oils, and reservoir heterogeneity. Recent advances and challenges will be discussed.
20 - Role of polymers in fluid loss control of oilwell cement slurry

Ashok Santra, ashok.santra@weatherford.com, Roderick Pernites. Weatherford, Houston, TX 77086, United States

For successful well-bore cementing, fluid loss control is extremely important in order to prevent rapid dehydration of cement slurry leading to premature gelation, lack of pumpability and incomplete cement hydration. Polymers are excellent candidates for fluid loss control due to its higher molecular weight, water retention capacity, compatibility, and availability. An overview of the different cement fluid loss control polymers and their current developments will be highlighted in this talk. Furthermore, we will also present our new findings about the synergistic effect on the fluid loss control performance of a biopolymer with different friction reducers (or dispersants) commonly used in the oil field cementing. Combination of rheology and high temperature/high pressure (HP/HT) fluid loss analyses were performed to carefully investigate the practical application of the biopolymer as an outstanding cement fluid loss control additive.

Sunday, March 16, 2014 10:10 AM
Polymers for Oil and Gas Energy Operations (08:30 AM - 11:55 AM)
Location: Hyatt Regency Dallas
Room: Moreno B
21 - Shale gas fracturing fluids containing additives of low environmental impact

Anand Viswanath, anand.vithu@gmail.com, Brian C Benicewicz. Department of Chemistry and Biochemistry, University of South Carolina, columbia, South Carolina 29208, United States

The drilling and hydraulic fracturing of typical gas wells in the Marcellus Shale formation underlying most of western, central and northern Pennsylvania requires nearly 4 million gallons of fracturing fluid per well. Several chemical additives are typically added to the fracturing fluid to aid oil recovery, including additives to reduce friction as the fluid is passed through. The friction reducers allow fracturing fluids and proppant (sand) to be pumped to the target zone at higher rates and reduced pressures than if they were not used. Fluid friction reduction is critical to the effective fracturing process. Generally the friction reducer in common use is polyacrylamide. This water-soluble polymer does not easily degrade in the environment and is considered a toxic contaminant when found in ground water. Outlined herein is a facile method for developing fracturing fluids with additives that are environmentally safe. The key to this technology involves the covalent grafting of additives, including polymers such as polyacrylamide, polyethylene glycol, polyacrylic acid to a nano/micro particulate material. The retention efficiency (amount of polymer grafted material that was retained through a filter simulating shale) ranged from 85-98%, suggesting that the addition of such material prevents its leakage to the water table. Given the need for reduced environmental impact for fracturing fluids, this technology directly alleviates this problem and has massive implications for 'green' fracking.

Sunday, March 16, 2014 10:40 AM
Polymers for Oil and Gas Energy Operations (08:30 AM - 11:55 AM)
Location: Hyatt Regency Dallas
Room: Moreno B
22 - Delaying polymer dissolution with degradable crosslinking

S. Sherry Zhu, S.Zhu5@slb.com, Han Li. One Hampshire Street,, Schlumberger-Doll Research, Cambridge,, MA 02139, United States

Water-soluble polymers are of great interest to the oil and gas industry. Water-soluble polymers have been used to modify fluid rheology, to disperse inorganic particles in fluids, and to function as temporary barriers or plugs. The solubility of these polymers mostly depends on temperature and the dissolution usually starts when the polymer is in contact with water above a certain temperature. Rarely, a water-soluble polymer only starts to dissolve after a defined time in water at a certain temperature, i.e. having a delayed onset of dissolution. Such behavior can be quite beneficial for certain applications. Here we report the crosslinking of a water-soluble polymer with hydrolytically degradable crosslinkers. The dissolution of the polymer only starts after the crosslinkers are hydrolyzed in water. The time-to-dissolution at a given temperature can be controlled by changing the crosslinking density. We will present the chemistry used to crosslink the polymer and the characterization of the crosslinking. The time-to-dissolution of the polymer before and after crosslinking also indicates the formation of degradable crosslinking.
23 - Tough polyacrylamide-polyvinylpyrrolidone hydrogels formed by thermal and/or pH triggered gelation

Jazmin Godoy-Vargas, JGodoy-vargas@slb.com, Phil Sullivan, Lijun Lin, Julia F del Valle, Mathilde Lecompte, Jian He.
Schlumberger Pressure Pump & Chemistry (PPC), Sugar Land, TX 77478, United States

Upstream oil and gas operations utilize settable polymeric gels for a variety of applications including sealing of downhole fissures, and blocking of water production zones. Most of these gels consist of polyacrylamide co-polymers crosslinked with either organic or metallic crosslinkers.

In this work we present the synthesis and characterization of tough, elastic, and highly adhesive hydrogels obtained from mixtures of partially-hydrolized polyacrylamide (PHPA) and polyvinylpyrrolidone (PVP). Gelation can be induced by increasing either the pH or the temperature of the polymer mixture. The influence of the pH and temperature on the rheological properties of the gel is discussed. Comparative experiments suggest that a transamidation process between ring-opened PVP and the amide groups in PHPA contributes to the gel formation.
Using polymer-tethered fullerenes in bulk heterojunctions

Joshua A Moore, jamoore1@uair.edu, Brian C Berry. Department of Chemistry, University of Arkansas at Little Rock, Little Rock, AR 72204, United States

The domain size of [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) within the bulk heterojunction of organic photovoltaics (OPVs) is of great importance to the performance and lifetime of the device. This study focuses on the use of polymer-tethered fullerenes (PTFs) as an additive to reduce the initial domain size of PCBM as well as to mitigate the growth of these domains over time that typically results in decreased device efficiency. Films were prepared from a 1:1 mixture of PCBM:P3HT on silicon wafers to approximate a bulk heterojunction system. PTFs were added in concentrations ranging from 0 to 20 percent. The samples were then annealed at 150°C for varying times ranging from 5 to 60 mins and examined by SEM to determine the average PCBM domain sizes for each sample. As expected, the control sample containing no additive showed significant growth in the PCBM domains as the sample was annealed with a final average domain size of 290 μm$^2$. However, addition of as little as 5% PTFs produced average PCBM domain sizes after 60 minutes of annealing of 28 μm$^2$. Addition of 20% PTF resulted in an average PCBM domain size of 2 μm$^2$. Based on these encouraging results, devices containing these architectures were prepared yielding an increase in the lifetime, and in some cases, the efficiency of the device.
25 - WITHDRAWN
26 - Microphase segregation of functionalized block copolymers

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Introducing heterogeneous functionality with precision in polymeric materials provides unprecedented control and means to evaluate various materials properties for technological advancements. While many efforts have focused on top-down lithographic processes and rigid rod–coil block copolymers to make nanostructured heterojunctions, there is a lack of systematic studies on the use of small molecule mesogens in copolymers to study electron transfer in thin-films and bulk. We study the self-assembly of semiconducting block copolymer liquid crystals to obtain highly ordered nanostructured semiconductors. Intrachain electron transfer is studied by photophysical measurement. The latest results will be discussed in the presentation.

Sunday, March 16, 2014 09:45 AM
Materials for Energy Harvesting (09:00 AM - 12:00 PM)
Location: Hyatt Regency Dallas
Room: Cumberland A
27 - Controlling molecular weight of a high efficiency donor-acceptor conjugated polymer and understanding its significant impact on photovoltaic properties

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PBnDT-FTAZ, a high efficiency donor-acceptor polymer, can generate over 7% power conversion efficiency with a noticeably high fill factor over 70% in its bulk heterojunction cells with a relatively thick film (200 – 300 nm). As part of the ongoing study to further understand this peculiar material, we precisely controlled the molecular weight (MW) of PBnDT-FTAZ by adjusting stoichiometric ratio of two monomers, following Carothers equation. A careful study of a library of PBnDT-FTAZ with different MW through various X-ray techniques reveals that the MW significantly influences the morphology and structural order of PBnDT-FTAZ in its bulk heterojunction solar cells, with highest efficiency (over 7%) appearing at a MW of 40 kDa.
We report the synthesis and characterization of a polythiophene diblock copolymer selectively functionalized with 1-N-hexyl isoorotic acid moieties (P4) and a 2,6-diaminopyridine tethered fullerene derivative (PCBP). Self-assembly between P4 and PCBP through “three-point” complementary hydrogen bonding interactions is studied both in solution and in solid state by 1H NMR and UV-Vis spectroscopies as well as optical and atomic force microscopies (AFM). Solar cells employing P4 blended with different weight ratios of PCBP and phenyl-C61-butyric acid methyl ester (PCBM) were fabricated and tested. The best power conversion efficiencies (PCEs) were observed in devices made from P4/PCBP blends (10/8 by wt.) and ternary blends of P4/PCBP/PCBM (10/4/4 by wt.) as active layers. Thermal stabilities of these solar cells were studied in detail by aging tests and corresponding morphological changes were closely monitored by absorption spectroscopy, optical microscopy and AFM. The “three-point” complementary hydrogen bonding interactions between P4 and PCBP, in cooperation with block polymer self-assembly, were found to not only improve the thermal stability of solar cells significantly but also lead to tunable active layer morphologies.
29 - Switching conjugated polymer/fullerene morphologies with solvent annealing in selective solvents

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While low bandgap (LBG) conjugated polymers offer promise as electron donors in bulk heterojunction organic photovoltaic active layers, thermal annealing the as-cast sample often results in a decrease in performance limiting the ability to tune the morphology of the active layer. Therefore, there is an urgent need to develop alternative annealing processes that can be used to tune the morphology of the LBG:fullerene system. We report in this talk our recent work that monitors the structural evolution of LBG polymer:PCBM mixtures during solvent annealing (SA), focusing on the effect of solvent quality on structural evolution and device performance. This result shows that solvent choice can dramatically impact the morphology of the LBG:fullerene mixture, switching from a sample with polymer aggregation to one where the fullerene precipitates in the thin film.

More precisely, solvent annealing (SA) in a solvent vapor which is selective for the LBG polymer results in polymer aggregation, but poor polymer ordering, which limits device performance. SA in a solvent that has similar polymer and fullerene solubility results in a higher degree of polymer ordering and fullerene phase separation, which facilitates charge transport and increases power conversion efficiency (PCE) by 30%. SA in a solvent that is selective for PCBM results in the highest degree of polymer ordering along with fullerene phase separation, which increases PCE by 75%. These results indicate both sufficient polymer ordering and formation of a PCBM pure phase are crucial in the optimization of the morphology of the active layer. More importantly, solvent annealing provides a unique method to precisely tune and optimize the morphology of the LBG conjugated polymer/fullerene mixture, and will be broadly applicable to an extensive range of promising LBG polymer/fullerene mixtures.
Control morphology of low band gap polymer: Bis-fullerene mixed heterojunctions in organic photovoltaics with solvent annealing

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Polymer based bulk-heterojunction (BHJ) photovoltaic cells, based on blends of conjugated polymers and fullerenes, are one potential economically viable option for low cost renewable power generation. The most promising new conjugated polymer:fullerene active layers in organic photovoltaics now utilize low band-gap (LBG) donor-acceptor copolymers. Unfortunately, for most of those LBG devices, there is no further treatment available after film deposition to optimize the morphology. Moreover, replacing PCBM with bis-adduct fullerenes (i.e. ICBA) has been reported to significantly improve device performance in P3HT device. However, in LBG polymers system, replacing PCBM with ICBA results in very poor device performance. So we have completed small angle neutron scattering and neutron reflectometry experiments to study the impact of solvent annealing (SA) and solvent quality on the morphology the LBG/bis-fullerene (i.e. PCPDTBT/ICBA) BHJ photovoltaics. The results show that SA in a solvent which is selective for the LBG polymer results in a decrease in polymer ordering, which limits device performance. SA in a solvent vapor which has similar solubility for polymer and fullerene, results in a higher degree of polymer ordering and fullerene phase separation, which facilitates charge transport and increases power conversion efficiency (PCE) by 100%. The highest degree of polymer ordering along with large amount of fullerene phase separation is obtained by SA in a solvent vapor which is selective for the fullerene. The resultant morphology increases PCE by 190%. These results indicate that solvent annealing and solvent choice provides a unique tool to tune the morphology of LBG/ICBA BHJ system, providing both sufficient polymer ordering and formation of a ICBA pure phase to optimize the morphology of the active layer.
31 - New polymers for energy harvesting

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Conjugated polymers have been investigated for a variety of future electronic and optoelectronic device applications such as sensors, field effect transistors, solar cells, light emitting diodes, etc. Other than the ease of processing and cost efficiency, polymeric materials possess additional desirable properties such as flexibility, property tenability, chemical modification, and conductive properties comparable to metal and inorganic semiconductor materials. Engineering of the HOMO and LUMO molecular orbitals through chemical structural modification has become an effective method to fine tuning opto-electronic properties in conjugated polymers. This research focuses on the frontier orbital engineering through copolymerization of donor and acceptor type monomers. The relationship between structural features, frontier orbitals, and optoelectronic properties will be presented.
32 - Shape amphiphiles based on POSS-polymer conjugates: Systematic molecular design, sequential “click” synthesis, and diverse self-assembly behaviors

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The ordered structures generated by self-assembly of various nano-materials have attracted great amount of interests due to their potentials in advanced material design via the “bottom-up” approach. Shape amphiphiles, constructed by the chemical integration of molecular building blocks with distinct shapes and competing interactions, emerge as a novel class of nano-materials. In this presentation, the molecular design and synthesis of a library of shape amphiphiles with precisely defined structures based on conjugates of functionalized polyhedral oligomeric silsesquioxanes (POSS) and polystyrene (PS) are reported. The development of a “sequential click” approach and the utilization of a series of “click adaptor” molecules facilitate the modular and efficient precision synthesis and the feasible structural diversification of molecular architectures for a systematic investigation. It was subsequently revealed that in the bulk state, driven by the nano-phase separation between the POSS cages and the polymer chains, POSS-based shape amphiphiles can self-assemble into various kinds of ordered phases with sub-10 nm feature sizes, depending on the relative volume fraction of the two components. Moreover, by tuning the molecular architectures of POSS-based shape amphiphiles, some rare phases can be observed, such as a highly asymmetric lamellar phase and an unusual A15 cubic phase. Therefore, POSS-based shape amphiphiles provide a versatile platform for engineering structures with sub-10 nm feature sizes.
Clickable nucleic acids: From click chemistry to sequence controlled polymers

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Abstract: Biopolymers in nature such as peptides and nucleotides have precisely controlled sequences that store their secondary and tertiary structural information. All of these include multiple monomers and variable sequences in their structures. However, traditionally, synthetic polymers are homopolymers or copolymers, which consist of one or two monomers, and the polymer synthesis depends completely on the efficiency of the chemistry used. Among these efficient chemistries, “click” chemistry has unique advantages such as high yields, mild conditions, and rapid kinetics that make it perfect for applications in sequence controlled polymer synthesis. Here, we employed thiol-ene click chemistry to synthesize sequence controlled polymers. We successfully synthesized DNA homologs (Clickable nucleic acids, CNA) whose backbone is a thio-ether formed from the thiol-ene “click” reaction. Additionally, these homologs exhibit binding activity towards complementary DNA strands and our CNA/DNA hybrids have higher melting temperatures as compared to natural DNA double strands. Moreover, the hybridization between our CNA and DNA has been used in surface modification, bio-detection, nanoparticle modification, and hydrogel formation.
34 - Maleic anhydride and ester functionalization of polypropylene with suppressed molecular weight reduction via solid-state shear pulverization

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Synthesis of functionalized polyolefins with limited molecular weight (MW) reduction and functional groups incorporated along the polyolefin backbone is a major challenge for synthetic polymer chemists today. The conventional method of functionalizing polypropylene (PP) is by melt processing, which results in drastic MW reduction of PP and functional groups located at chain ends. This MW reduction occurs as a result of β-scission, a free-radical chemistry that is highly dependent on temperature. By exploiting unique chemistries associated with solid-state shear pulverization (SSSP), we achieve maleic anhydride (MA) and ester functionalization of PP while avoiding the dramatic MW reduction of PP that accompanies functionalization during conventional melt-state processing. Additionally, functionalization via SSSP results in functional groups grafted along the PP backbone and not just at chain ends. For PP-g-MA with \textasciitilde0.5 wt% grafted MA, the frequency of chain scission events per repeat unit is reduced by >90 % when synthesis is done by SSSP as opposed to reactive extrusion. Relative to the parent neat PP, this PP-g-MA synthesized via SSSP exhibits only 8 and 25-32 \% reductions in number-average MW ($M_n$) and weight-average MW ($M_w$), respectively. We also establish, for the first time, synthesis of ester functionalized PP (PP-g-ES) with limited MW reduction via SSSP using a symmetric organic peroxide, benzoyl peroxide, alone. For PP-g-ES with \textasciitilde0.5 wt% graft level, we observe 17 and 36 \% reductions in $M_n$ and $M_w$ respectively.
While amphiphilic block copolymers have demonstrated their utility for a range of practical applications, the behavior of cyclic block copolymers remains largely unexplored due to limited synthetic access. In order to investigate their unique behavior, cyclic copolymers based on biocompatible polyethylene glycol PEG and biodegradable polycaprolactone (PCL), were synthesized by a combination of ring opening polymerization and azide-alkyne click chemistry. In addition, exactly analogous linear block copolymers have been prepared as control samples to elucidate the role of polymer architecture in their self-assembly and acid-catalyzed degradation. The self-assembly of cyclic and linear PEG-PCL block copolymers show that both linear and cyclic PEG-PCL can form micelles in aqueous solution, though the cyclic micelles are notably smaller. Meanwhile cyclic PEG-PCL shows a longer degradation time than linear analogs due to unique properties of the cyclic topology.

The combination of reduced size and unique degradation behavior suggests that they may be useful stimuli-responsive materials in the field of drug delivery carriers and these will be explored in future studies.
Layer-by-layer approach for individual encapsulation of cells based on hydrogen-bonded, complimentary electrostatic and hydrophobic interactions

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Formation of biomimetic coatings capable of protecting cells, retaining their survivability and function, providing attachment with selective transport of molecules is a primary objective for many biotechnology applications. The layer-by-layer (LbL) approach is an attractive method for engineering cell surfaces of individual cells that grants control over many of the issues mentioned above. We have explored the formation of soft hydrogel network shells on the basis of hydrogen-bonded interactions between natural polyphenols and neutral polymers, as well as lightly crosslinked pH-sensitive hydrogel network based on amine-bearing poly(methacrylic acid). Increased viability (85-95%) of yeast cells without loss of cell function makes these polymer-based shells attractive candidates for many cell-based applications. All-natural, biocompatible, highly stable conformal shells based on unmodified silk fibroin protein as well as silk fibroin functionalized with polyamino acids provided additional advantages for sustained long-term performance of cell-based sensors. We explored the formation of silk-based shells with different chemistries of interactions, such as electrostatic factors between ionomer silk derivatives, and intramolecular hydrogen bonding between β-sheets of pure silk protein induced by the treatment with mild concentrations of buffer. Viability and cell function greatly affected by the cell type and the chemistry of interactions used for encapsulation.
37 - Cationic cobaltocenium-containing polymers: From synthesis to advanced applications

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In past decades, metallocene-containing materials have been utilized for applications such as magnetic materials, catalysts and biomaterials. Metallocene-containing polymers with inorganic metal centers and organic framework present unique properties in many aspects. For example, metallocene-containing block copolymers can self-assemble into different nanostructures, which can be utilized as precursors for advanced inorganic nanoparticles. Recently, cobaltocenium-containing polymers have attracted much attention. Compared with widely studied ferrocene-containing polymers, cobaltocenium-containing polymers are a kind of polyelectrolytes that show higher stability, counter-ion dependent solubility and reversible redox chemistry. Cobaltocenium-containing polymers have already been utilized in electrochemistry, biosensing and magnetic materials. We utilized reversible addition-fragmentation chain transfer polymerization (RAFT) to prepare cobaltocenium-containing homopolymers, block copolymers and cylindrical polymer brushes. Besides, with a facile phase transfer counterion exchange method, these cobalt-containing homopolymers, block copolymers and polymer brushes were used as universal precursors to prepare versatile inorganic cobalt-based materials, including cobalt metal, cobalt phosphide, cobalt monoxide, cobalt-iron alloy and cobalt ferrite. Based on self-assembly of block copolymers and the unique architecture of polymer brushes, cobalt-based nanoparticles and nanowires were conveniently obtained from these nanoscale precursors.

References:


Perfluorinated moieties are regularly incorporated into films, coatings, and surface modifications for increased hydrophobicity, antifouling, and degradation resistance for various applications. The inherent nature of perfluorinated species can cause instability in mixing and phase separation in the final product. UV curing provides a means to rapidly introduce perfluorinated moieties into networks leading to properties which are otherwise unattainable. This work looks at the utility of perfluorinated moieties in the development of highly permeable, high free volume UV-cured systems. The first system utilizes a two-step thiol-ene click protocol to develop perfluorinated networks with covalently tethered fluorinated moieties bound within the network. Monomers are modified then combined to form a homogeneous mixture and subsequently UV-cured, locking the incompatible fluorinated moieties into the network. The incompatible fluorine becomes thermodynamically “frustrated” but kinetically bound leading to stretching of the network backbone and ultimately causing high transport of light gases and large hole free volume. The second system studied is a side chain perfluorinated acrylate homopolymer capable of organizing in a well-defined liquid crystalline (LC) lamellar morphology. Disruption of the side chain order, across the thermotropic transition, causes a “switching” behavior in light gas permeability from low permeability to high permeability. Free volume, light gas transport, and morphology were studied with promising results suggesting unique diffusion mechanisms with utility across various applications.
39 - Modular polyelectrolytes based on cyclopropenium cations

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We have synthesized a new class of materials, poly(cyclopropenium) (PCP) cation polymers through both modification of halogen functionalized polymers and RAFT polymerization of easily synthesized CP containing monomers. This PCP cation family, through the aromaticity of the three-member ring and the electron donation of three amino groups, is unique in its larger size relative to other cations and relative stability under various conditions. The materials' design renders them modular to various degrees of functionalization. The side chains can readily be modified to tune the physical properties and a number of functional units can be introduced to explore various polymerization strategies. The monomers can be easily synthesized in gram quantities from readily available starting materials. This paper discusses the use of RAFT polymerization to synthesize polystyrene-based block copolymers, ethylene glycol, and alkyl methacrylate. These materials have potential for many applications and we are testing membranes of these polymers for use in fuel cells.

Sunday, March 16, 2014 01:30 PM
Undergraduate Research in Polymer Science (01:30 PM - 04:45 PM)
Location: Hyatt Regency Dallas
Room: Moreno A
40 - Design and synthesis of pH-responsive block copolymers for use in cancer diagnostics

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Over the past few decades, medical imaging technologies have experienced dramatic growth and currently play a critical role in clinical oncology. With the advent of new and improved imaging techniques, clinicians will not only be able to see where a tumor is located in the body but also envisage biological processes and the expression and activity of specific molecules that influence the response to therapy and behavior of various tumors. One such area is the measurement of the extracellular pH (pHe) in solid tumors. For many years researchers have known the importance of the pHe in relation to cancer morbidity and mortality. As such, the ability to measure the pHe of solid tumors using non-invasive and accurate techniques has become increasingly important and is of great interest to clinicians. Critical to the development of diagnostic techniques for the in vivo measurement of pHe is the development of contrast agents that demonstrate changes in their imaging properties in response to changes in the environmental pH. We have prepared a series of biocompatible pH-responsive block copolymers that demonstrate phase transitions at biologically relevant pH's. These block copolymers have been prepared using reversible addition-fragmentation chain transfer (RAFT) polymerization, which provides polymers with defined structure, molecular weight, and end groups. By systematically varying the structure and molecular weight of our pH-responsive block copolymers, we have been able to produce optimized block copolymers that can be used in the development of new 'smart' contrast agents for magnetic resonance imaging that can be used for the in vivo measurement of pHe in solid tumors.

Sunday, March 16, 2014 01:45 PM
Undergraduate Research in Polymer Science (01:30 PM - 04:45 PM)
Location: Hyatt Regency Dallas
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Alzheimer's disease (AD) is one of the most expensive and prevalent cognitive disorders to plague the elderly population. Despite the prevalence of AD, the mechanism that causes the disease, namely the aggregation of Aβ42, is not fully understood. It is the endeavor of this project to synthesize synthetic mimics of polysaccharides found in GM1 gangliosides, specifically those containing glucose and galactose, for evaluation of their effect on Aβ42 aggregation. GM1 ganglioside is being studied because it can act as a seeding agent for the aggregation of Aβ42. Monomers, 2-(β-D-glucosyloxy)ethyl acrylamide (GlcEAm) and 2-(β-D-galactosyloxy)ethyl acrylamide (GalEAm), and homopolymers, poly(2-(β-D-glucosyloxy)ethyl acrylamide) (polyGlcEAm) and poly(2-(β-D-galactosyloxy)ethyl acrylamide) (polyGalEAm) were synthesized using reversible addition-fragmentation chain-transfer polymerization (RAFT polymerization). The monomers were characterized by 1H and 13C NMR, IR spectroscopy and ESI, and the homopolymers were characterized by 1H NMR or GPC.
42 - Incorporation of cysteine functional groups for novel polymer coupling based upon thiazolidine chemistry

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The development of simple and efficient crosslinking techniques is sought after for a variety of applications including bioconjugation, material synthesis and design, and surface functionalization. This work focuses upon the decoration of latent cysteine functional groups at the terminus and along the backbone that undergo thiazolidine coupling upon the introduction of aldehyde. A protected cysteine residue was prepared and utilized and incorporated via chain end modification and as an initiating site for atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer (RAFT) polymerization techniques.
The synthesis of self-assembling ABC amphiphilic tri-block copolymers as potential vehicles to be utilized in drug delivery systems is described. The A and C end blocks were permanently hydrophilic and hydrophobic, composed of amine and azide functionalized polyethylene oxide and polypropylene oxide, respectively. The synthesis of end group-modified polymers was confirmed by NMR. The center B block consisted of a pH-responsive peptide (i.e. lysine or glutamate) synthesized using ring opening NCA polymerization initiated from the amine functionalized A block. The degree of polymerization was determined by NMR and GPC. Poly(lysine) and poly(glutamate) act as either hydrophobic or hydrophilic blocks depending on side chain ionization. The pH responsive nature of the center block provides a means by which a sudden change in hydrophilic fraction can be triggered using a pH stimulus. Various molecular weights of A and B blocks were synthesized in order to target a change in hydrophilic weight fraction, which would occur upon pH stimulus, resulting in the micelle to vesicle self-assembled morphology transition. These structures were analyzed using light scattering and TEM.
Ice-phobic coatings are extremely promising materials for applications in cold environments, such as aircraft wings, power lines, and radar towers. However, no such surface in nature shows perfect ice-phobicity. By reducing ice adhesion to these surfaces, ice can easily be removed by natural forces before it causes structural damage. Polydimethylsiloxane (PDMS) is a commonly used polymer with low surface energy and extremely low glass transition temperature, which makes it an ideal matrix to fabricate ice-phobic coatings. In this work, ice-phobic coatings were fabricated by PDMS based thiol-ene resins containing SiO₂ nanoparticles via spray deposition method and sequential photopolymerization. Scanning electron microscopy images show the multiscale topography of the surface. Ice adhesion force was measured by normal stress and critical shear stress between ice and the solid surface.
Traditionally, organohalogen compounds, particularly brominated aromatics, have been utilized as flame retardants for polymeric materials. Flame retardancy is a requirement for most polymeric applications. Organohalogen compounds work well for this purpose but are stable, persist in the environment, tend to bioaccumulate, and may pose human health risks. As a consequence, the use of these compounds is coming under intense scrutiny and regulatory pressure around the world. There is an increasing need for suitable replacements. Ideally, replacements should be effective, available at moderate cost, nontoxic and biodegradable. If possible, they should be derived from renewable biosources. Appropriately functionalized tartaric acid esters meet all these criteria. Tartaric acid is an edible by-product of wine making. It is tetrafunctional – two hydroxyls and two carboxyl groups. The hydroxyl groups may be functionalized with a variety of reagents (either phosphorous or bromine) to generate monomers which may be converted to oligomers which display flame retarding properties.
A growing interest in sustainable polymer composites as potential alternatives to petroleum-based products has created a demand for new metrology capable of assessing composite performance non-destructively. This requires development of measurement tools that are able to quantify fundamental structure-property relationships (e.g., characteristic of components at the interface) at multiple length-scales. The National Institute of Standards and Technology (NIST) recently developed a new fluorescence imaging method to reveal the interface in polymer nanocomposites. This was done by employing Förster resonance energy transfer (FRET) through confocal microscopy to probe nanoscale-interactions at the interface of a coumarin (donor dye) dispersed polymer and 5-(4,6-dichlorotriazinyl)-aminofluorescein (DTAF, acceptor dye) labeled nanofibrillated cellulose (NFC) composite. However, coumarin was not covalently attached to the matrix, and this hindered the extension of this model system to other polymers, due to free dye diffusion. Switching donor-acceptor dye pair to DTAF/rhodamine enables DTAF, attached to the NFC, to be used as the donor. We have investigated the differences between these two FRET pairs. In this work, a primary amine containing rhodamine spirolactam (RS), acting as the acceptor to enable FRET measurements of a NFC-epoxy composite, was synthesized for covalent attachment to an epoxy matrix. Introduction of a photoactivatable fluorescent dye in the epoxy matrix reduces dimerization and self-quenching, which can cause low FRET efficiency. FRET measurements were accomplished using both fluorescence lifetime imaging (FLIM) and conventional intensity based measurements.
Pressure sensitive adhesives (PSAs) are widely used in pressure sensitive labels, tapes, stamps, Post-it notes and many other products. At present, PSAs are mainly derived from petrochemicals that are not renewable and not sustainable. In this presentation, we will disclose our new discovery that polyesters from polymerization of epoxidized oleic acid, a bifunctional AB monomer containing a carboxylic acid group (A) and an epoxy group (B), can have superior PSA properties. Oleic acid is a fatty acid that is abundant, renewable, and readily available. A method for preparation of epoxidized oleic acid with high purity has been successfully developed. Effects of various catalysts, the purity of epoxidized oleic acid, and polymerization conditions on the properties of the resulting PSAs have been extensively studied. The resulting PSAs have been characterized for their molecular structures, thermal stabilities, and viscoelastic properties. The peel strength, shear strength, tack, and aging stability of the resulting PSAs have also been evaluated and will be discussed in detail in this presentation.
48 - Polyesters from biomethanol

Ersen Göktürk, Alexander G Pemba, Stephen A Miller, miller@chem.ufl.edu. Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

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 obtained from trees. This presentation describes the synthesis and characterization of a new class of biorenewable polyester thermoplastic that resembles the aliphatic polyester polyglycolic acid (PGA). However, our preparation is much less expensive since it circumvents the multistep production of glycolic acid glycolide currently necessary for PGA synthesis and it avoids fermentation technology upon which polylactic acid (PLA) production depends. Instead, wood or agricultural wastes (non-food resources) can be sustainably converted to the simple C1 feedstocks necessary for production, which are formaldehyde and carbon monoxide—both readily obtained from methanol (bio-methanol, wood alcohol).
49 - Improved method for lignin reactivity quantification for lignin substitution of phenol in preparation of phenol-formaldehyde polymer

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Driven by lignin renewability and high phenol price, application of lignin to replace phenol in preparation of phenol-formaldehyde polymer for applications as resin and adhesive has been one of the attractive research topics in material chemistry and technology field. However, the major difficulty encountered is the lower lignin reactivity than the phenol. Thus it is a key issue to determine and improve the lignin reactivity. Nitrogen content quantification after Mannich reaction of lignin sample has been reported as a determination method for the lignin reactivity, since both the Mannich reaction and the lignin-formaldehyde reaction take place at identical lignin reactive sites and share similar reaction mechanism. However, it can be anticipated that the method is not reliable if the reaction conditions is not properly controlled because the extent of nitrogenation is strongly dependent on the reaction conditions. For example, the Mannich reaction performed at a high pH (above pH 9) will favor the polymerization side reaction between lignin and formaldehyde giving lower nitrogen content. In this study, therefore, model lignin experiment has been performed to establish the optimized relationship between the nitrogen content and the reaction pH of the Mannich reaction for improved reliability. Further on, the improved method will be used to examine the reactivity of various industrial softwood LignoBoost lignins and evaluate their performance in replacing phenol for preparation of lignin-phenol-formaldehyde polymer. The improved method and the results of the lignin application in preparation of lignin-phenol-formaldehyde polymer will be reported in the meeting.
Most of current lubricants originate from petroleum stock, which may be difficult to dispose of and environmentally unfriendly. Triglyceride oils are good platforms for new products that can substitute for conventional mineral oil-based lubricating oils and synthetic esters. As part of our research efforts in sustainability, we have explored the application of pericyclic reactions to produce modified oils. The process required no solvent or catalyst and entailed only the mixing of two appropriate ingredients. Through the use of NMR, the reactions were monitored and the major reaction pathways identified. The product mixture exhibited a self-curing behavior as a function of time, suggesting its possible use as additive in lubricants, caulking, cement and thickener applications. As an example, our recent work involving the reaction between triglyceride and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) will be described.

![Viscosity and fatty acid composition of the reaction products of soybean oil and PTAD with different stoichiometry after 24-hour reaction at 60°C.](image.jpg)
51 - Synthesis and curing of phenol- 5-(hydroxymethyl)furfural (PHMF) novolac resin and its formaldehyde-free curing with organosolv/Kraft lignin (OL/KL)

Yongsheng Zhang, yzhan936@uwo.ca, Zhongshun Yuan, Chunbao (Charles) Xu. Institute for Chemicals and Fuels from Alternative Resources (ICFAR), Western University, London, Ontario N6A 5B9, Canada

The use of formaldehyde to prepare phenol-formaldehyde (PF) resins is one of the primary challenges for the world-wide PF industry with respect to both sustainability and human being health. Lignocellulosic biomass has tremendous potential as a feedstock to make renewable polymers. This study reports the synthesis of novel glucose-based PHMF resin and its curing reaction with OL/KL to produce formaldehyde-free phenolic resins. The use of HMF which was converted from glucose allows an economical and green route to synthesize phenolic resin without formaldehyde consumed or released and enhances its reactivity towards phenol.

The chemical structure of PHMF was characterized by Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance (1H NMR). Polymer molecular weight was determined by Gel permeation chromatography (GPC). OL/KL, which are rich in woody biomass, were proven to be environmentally benign curing agents for PHMF. The curing mechanism was studied by carbon NMR (13C NMR), which demonstrated the occurrence of alkylation reaction between lignin's hydroxymethylene group and PHMF's para- carbon of phenolic hydroxyl group. Further studies regarding curing kinetics were conducted by using dynamic differential scanning calorimetry (DSC) to find out kinetic parameters. For the purpose of its application as replacement of PF resin, performances of OL/KL cured PHMF were tested in terms of thermal stability, and mechanical properties.

This research project realized curing of phenolic resin with OL/KL for the first time among open publications. The results obtained presented OL/KL to be promising curing agents for PHMF and recent results presented here will help make eco-friendly phenolic resins a practical reality.
52 - Sustainable polyacetals and polyspiroacetals derived from lignin

Mayra Rostagno, m.rostagno@ufl.edu, Alexander G. Pemba, Tanner A. Lee, Stephen A. Miller. Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

Current research is strongly focused on the synthesis of polymers that are sustainable and degradable, with the objective of replacing fossil fuel based commodity plastics. In this line of thinking, polyacetals represent an attractive alternative since they are inspired by nature, as cellulose and other natural macromolecules possess this kind of functional group. By including polyacetals in polymer backbones, they can be potentially water degradable.

Dialdehyde monomers were constructed by linking two molecules of an aromatic hydroxyaldehyde derived from lignin with two methylene spacers, having an ether linkage between the two aromatic groups. The dialdehydes were then polymerized with suitable tetraols in solution.

The polymers have a high level of rigidity in the backbones given by the presence of the aromatic rings, added to the new rings that the acetal formation generates (figure 1). By testing different combinations of the monomers, a range of thermal properties was obtained making these polymers comparable to the current commercially available plastics such as poly(methyl methacrylate) and polycarbonate.
Over five million metric tons of bisphenol A (BPA) are produced annually for the synthesis of plastics, such as epoxy resins, vinyl ester resins, and polycarbonates. BPA can mimic estrogen in vivo and can interfere with early reproductive development and cause irreversible physical changes. Therefore, designing sustainably sourced, less toxic BPA alternatives is desirable. We synthesized bisguaiacol F (BGF) as a potential BPA alternative from two lignin model compounds, vanillyl alcohol and guaiacol. Lignin is a promising feedstock for aromatic monomers as the paper and pulping industry produces 70 million tons a year as a waste product and can be depolymerized into useful aromatic compounds. Similar to the industrial synthesis of BPA, the condensation reaction between vanillyl alcohol and guaiacol produce two regioisomers. Selectivity between regioisomers and other byproducts can be tuned by changing reaction conditions such as water content, acidic ion exchange resin proton exchange capacity, and reaction time. DSC was used to determine the effect of regioisomer content on the thermal behavior of BGF. Polyesters containing BGA and BGF were compared using thermomechanical analyses (TGA, and DSC).
Thermoplastic polyurethanes (TPU) are a broad class of macromolecules composed of chemically dissimilar units commonly denoted as hard and soft segments. In a recent report by our laboratory and collaborators, a biotechnological route to biobased ω-hydroxytetradecanoic acid (ω-HOC14) was disclosed. In this work, one family of thermoplastic polyurethanes were prepared using 30 wt% MDI and butane diol as the hard segment and 70 wt-% of soft segments consisting of butanediol capped ω-HOC14 and P(THF) diol (both with $M_n$ about 2000) in varying proportions. By increasing the proportion of ω-HOC14 soft segments from 10 to 30 wt-%, the Youngs Modulus increased from 10 to 80 MPa. The %-elongation at break varied from a maximum of about 1300% at 10 wt% ω-HOC14 soft segments to a minimum of about 600% at 30 wt% ω-HOC14 soft segments. In another study, a second family of polyurethanes were prepared using 40 wt-% MDI and butanediol as hard segments and 60 wt-% soft segments consisting of polyols with varying proportions of ω-HOC14, butanediol and adipic acid units. By increasing the proportion of ω-HOC14 units in polyols from 0 to 75 wt-% the Youngs Modulus increased regularly from 30 to 470 MPa while the %-elongation decreased from 900 to 300%. Thus, the mechanical behavior shifted from elastomeric to semi-crystalline. In conclusion, these two series of polyurethanes showed that by judiciously increasing the content of ω-HOC14 units, important enhancements in elastomer tensile strength and stress at break can be achieved. Furthermore, by replacing short chain diacid and diol building block with ω-HOC14, significant improvements in resistance to hydrolytic and microbial mediated degradation events can be achieved.
Membrane separation is an energy-efficient, small-footprint, cost-effective approach to removal of CO₂ from commercial gas emissions typically consisting of a mixture of this greenhouse gas with other light gases such as N₂, O₂, H₂, and CH₄. Polymeric membrane gas separation is a large and rapidly growing industry. While the gas combinations involved in separations are quite varied, CO₂ is a key component in numerous technological processes. Poly(ethyleneglycol) (PEG) is known for its high CO₂ solubility selectivity. Recently, PEG has been researched as a selectivity-providing component in polymer membranes designed to increase the permeability over pure semi-crystalline PEG. New PEG containing photocurable thiol-ene based membranes were designed and successfully fabricated. A crosslink reduction strategy was employed to simultaneously increase free volume and PEG content. Modulus decreased and elongation increased with increasing dithiol content leading to an increase of molecular weight between crosslinks, $M_c$. Materials with the highest concentrations of dithiol were highly elastomeric with largely improved elongation at break. New membranes exhibited excellent CO₂/N₂, O₂, H₂, CH₄ permeability-selectivity performance [figure 1]. Only a certain minimum PEG content required for “high selectivity”. Free volume based model relating gas diffusion coefficient to crosslink density was developed and successfully applied to experimental diffusion data.
Hydrogen separation via polymer membranes is hindered by low selectivity and weak mechanical strength. In this study, the authors present an ionic cross-linked polymer film, formed using layer-by-layer assembly of a branched polyethylenimine and poly(acrylic acid), capable of combining exceptionally high hydrogen selectivity with remarkable mechanical properties at gas permeabilities in excess of the traditional “upper bound” associated with homogeneous polymeric membranes. The excellent performance of hydrogen selectivity and mechanical strength represents a significant breakthrough in the realization of low-cost, highly manufacturable polymer membranes for hydrogen purification.
Energy-efficient solutions for the separation of oil-water mixtures are desired. Not only does the production and transport of petroleum products engender environmental risk to sensitive ecosystems, but many military applications could benefit from the efficient separation of water from hydrocarbons (oils and fuels). This need also applies to the separation of surfactant-stabilized oil-water mixtures, where additional technical difficulties exist. Traditional membrane-based technologies for oil-water separation are energy-intensive and further limited by membrane fouling or the inability of a single membrane to separate all types of oil-water mixtures. The ideal membrane, which would effectively separate all types of oil-water mixtures, is expected to be both hydrophilic (i.e., water contact angles < 90°) and oleophobic (i.e., oil contact angles > 90°). Such membranes would allow the higher density liquid (water) to flow through the membrane, while preventing the flow of the lower density liquid (oil or fuel). However, as water possesses a significantly higher surface tension value than various oils, most membranes that prevent the permeation of oils also prevent the permeation of water. An update will be provided on the first-ever reconfigurable membranes that, counter-intuitively, are both superhydrophilic (i.e., water contact angles = 0°) and superoleophobic (i.e., oil contact angles > 150°). These membranes were produced through the systematic design of membrane porosity and membrane-water interfacial tension. These fouling-resistant membranes are, for the first time, able to separate all types of oil-water mixtures with greater than 99.9% efficiency. Further, we have produced the first-ever, gravity-assisted apparatus for the continuous separation of free oil-water mixtures and surfactant-stabilized oil-water emulsions.
58 - Magnetic shell crosslinked knedel-like (MSCK) nanoparticles for the environmental remediation of crude oil: A small solution for a big problem

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Well-defined, magnetic shell crosslinked knedel-like nanoparticles (MSCKs) with hydrodynamic diameters ca. 70 nm were constructed through the co-assembly of amphiphilic block copolymers of PAA₂₀₋b-PS₂₈₀ and oleic acid-stabilized magnetic iron oxide nanoparticles using tetrahydrofuran, N,N-dimethylformamide and water, ultimately transitioning to a fully aqueous system. These hybrid nanomaterials were designed for application as sequestering agents for hydrocarbons present in crude oil. Their combination of amphiphilic organic domains, for aqueous solution dispersibility and capture of hydrophobic guest molecules, with inorganic core particles for magnetic responsivity, make these nanomaterials uniquely qualified for oil spill remediation. The employment of these MSCKs in a contaminated aqueous environment resulted in the successful removal of the hydrophobic pollutants at a ratio of 10 mg of oil per 1 mg of MSCK. Once loaded, the crude oil-sorbed nanoparticles were easily isolated via the introduction of an external magnetic field. The recovery and recyclability of these MSCKs was also investigated through the "rinsing" of the loaded MSCK in a sonicating ethanol bath and subsequent drying. These results suggest that deployment of hybrid nanoconstructs, such as these, could aid in environmental remediation efforts, including groundwater clean-up, and at oil spill sites, in particular, following the bulk recovery phase. Furthermore, these studies have led to the design and development of novel MSCK systems for enhanced environmental applications.
To achieve a high efficient of petroleum recovery, the fabrication of high-performance profile control agents has attracted extensive attention because of their scientific significance and urgent requirement in industrial application. The copolymer consisting of Acrylamide (AM) and 2-Ethylhexyl acrylate is thought to be one kind of ideal profile control agent, which has the advantages of high efficiency and low cost. Although AM/2-EHA copolymer profile control agent has made some progress, monomer reactivity ratios for AM and 2-EHA has not been well understood, which seriously inhibit the industrial applications of AM/2-EHA copolymer. Herein, we studied the monomer reactivity ratios of AM/2-EHA by FT-IR by carrying out a serial of controllable experiments. The free radical copolymerization of acrylamide (AM) and 2-Ethylhexyl acrylate (2-EHA) is stimulated by an initiator of benzoyl peroxide (BPO) in a solvent of mixed alcohol and cyclohexane in a molar ratio of 1:1. The FT-IR absorption peaks of C-N and C-O-C were set as the characteristic peaks of AM and 2-EHA, respectively. The relation curve between peak area ratio of both characteristic peaks and the molar ratio of two monomers was obtained on the basis of standard samples. The molar ratio of two monomers in the copolymer was obtained according to the relation curve and the peak area ratio in the copolymer. The monomer reactivity ratios of AM and 2-EHA were calculated by using Fineman-Ross and Kelen-Tudos graphical methods and Yezrielev-Brokhina-Roskin calculative method. The monomer reactivity ratios of AM and 2-EHA were calculated at different temperatures. Based on the results, the mechanism of temperature on the monomer reactivity ratios was proposed.
Although mainly developed and used for polymers, the Hansen solubility parameter concept has proven to be a highly useful tool for developing thermodynamic models that enable improved understanding and optimization of processes involving many types of organic and organometallic compounds. To date, however, there have been relatively few examples of the determination of Hansen solubility parameters for many compounds that are important for fuel treatment operations, such as organic dyes and organosulfur compounds. These small molecules often are not well-suited to traditional methods of Hansen solubility parameter determination, which were developed with polymers in mind. We present both newly modified methods for Hansen solubility parameter determination as well as preliminary results for these compounds, and show how the results can be used in the development of new polymers and processes for fuel treatment.
61 - Pyrolysis products of powdered and powder-free laboratory examination waste gloves

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Finding an appropriate methodology to clean-up the environmental pollution from waste plastic materials by recycling them is one of the objectives of this research. Here, we are reporting the thermal cracking of laboratory safety gloves (LSG), without catalyst, into useful chemicals. Prior to the investigation, the thermal stability of the LSG by thermogravimetric analysis (TGA) was studied. Based on these results, the appropriate setup for the decomposition of the LSG was designed. The thermal stability of both powdered and powder-free LSG, as expected, was very similar since the thermal stability depends on the nature of constituent polymers. The highest decomposition rates were observed at temperatures around 410°C. The leftover ashes of the powder-free LSG were 15% of total mass of LSG at 500°C; whereas the leftover ashes of powered LSG was 30% of its total mass at 500°C. Similarly, the 18% leftover ashes of powdered LSG were higher than 7% ashes of powdered free at 800°C. The GC-MS chromatogram of pyrolysis liquids indicated over 350 chemicals. The most abundant compound, as expected from the chemical constituents of chlorinated plastics, was found to be HCl, followed by eight member carbon isomers, and dimers of butadiene. Also, a variety of highly concentrated phthalic acid derivatives were recognized in all the samples. The liquids obtained from pyrolysis of LSGs were a complex mixture of hydrocarbons and cyclic compounds. Also, it was saturated with inorganic and organic acids, esters, and anhydrides. Therefore, refinement of the liquids resulting from pyrolysis was found to be necessary in order to obtain a quality fuel.
62 - Oligomeric narrow band-gap chromophores: A new class of electron-donating material towards high performance organic solar cells

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Narrow band-gap conjugated polymers and small molecules have both been drawing significant contribution in organic solar cells. Intrinsic advantages and disadvantages relevant to solution processable photovoltaics are often contrary between these two classes of materials. In particular, small molecules possess monodispersity in chemical structures and higher crystallinity, while on the other hand, poorer film formation properties and lower thermal stabilities, as compared with their polymeric counterparts. More importantly, solar cell devices based on small molecular materials are extremely sensitive towards chemical impurities, of which polymers are relatively more tolerant.

Considering the fact that polymers and small molecules provide complementary material properties, we have designed molecular frameworks with successive extension of donor-acceptor characteristics. Materials synthesized following these frameworks are able to adopt some of the most important merits from both polymers (e.g., film quality and thermal robustness) and small molecules (e.g., structural monodispersity and crystallinity). Fabrication of solar cell devices with these materials does not require delicate control over solvent additives or post-deposition treatment, yet reaching power conversion efficiencies close to the highest reported value obtained for discrete molecules to date (6-7%). When integrated in field effect transistors, the most extended molecular system shows device thermal stability beyond 200 °C.
Light upconverting materials are capable of emitting blue-shifted light with respect to the wavelength of incident light. Such materials are useful for many applications such as solar harvesting, drug delivery, optical data storage and bioimaging. Low-power density (0.1 W.cm\(^{-2}\)) continuous-wave upconversion (UC) can be achieved by triplet-triplet annihilation (TTA). These systems usually consist of two dyes: a triplet sensitizer and a triplet annihilator (emitter). As two emitter molecules are involved in the TTA step, it can be expected that the connectivity of the emitter species influences the upconversion process. Thus, 9,10-diphenylanthracene (DPA) emitter molecules were covalently linked with spacers of different length and flexibility to form dimers. These dimers were combined with a palladium octaethylporphyrin (PdOEP) sensitizer and the upconversion of these systems was measured and compared to reference systems based on monomeric DPA. Measurements were carried out in solution as well as in polymer matrices with different glass transition temperatures (\(T_g\)). A systematic study indeed revealed improved upconversion efficiency for some of the dimeric emitters when embedded in polymer matrices.
Conjugated polymers are well-known for their use in organic solar-cells. However, another energy harvesting approach is to use them as photocatalyst for water splitting; producing green hydrogen from only water and sunlight. Some conjugated polymers have been reported to catalyze the proton reduction half-reaction, some the water oxidation half-reaction, and some of them both half-reactions, but not concurrently.

Experimentally it is not easy to elucidate the relationship between polymer structure/composition and its ability to act as a photocatalyst. In part, as it is difficult to measure the position of the ground and excited state energy levels i.e. the HOMO and LUMO. We thus use theory to predict such energy levels (and the theoretical absorption and fluorescence spectra) with calculations on hydrogen-terminated cluster models of the polymers. More specifically, we use a combination of Density Functional Theory (DFT) and Time Dependent-DFT to predict the position of the ground and excited state energy levels relative to the proton reduction and water oxidation potentials.

Here we will discuss our results obtained for polymers reported in the literature as photocatalysts for the water splitting reaction, such as polyazomethine and polyimides networks. We will show how the experimental ability to catalyze both water splitting half-reactions can be understood on the basis of the calculated positions of the polymers energy levels.
65 - Polymer composites for high temperature piezoelectric energy harvesting applications

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We describe a piezoelectric polymer composite with thermal stability up to 152 °C, remnant polarization of 3.71 µC/cm\(^2\) and maximum polarization to 4.50 µC/cm\(^2\). A limiting factor of current piezoelectric polymers such as poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) is high temperature stability, with current materials not able to function above about 100 °C. Conventional P(VDF-TrFE) has 38% lower remnant polarization and 26% lower maximum polarization than our composites, which are also lead free, non-toxic and solution processable—limits of leading ceramic piezoelectric materials. To achieve these metrics, Buckminsterfullerene (C\(_{60}\)) nanoparticles were functionalized with diamine (N-R-N) crosslinking chains and compositied into a (P(VDF-TrFE)) polymer matrix. The composite was spin-coated into films and thermally cured to covalently attach the amine functionalized C\(_{60}\) onto polymer backbones to form crosslinking “bridges”. Differential scanning calorimetry measurement showed the disappearance of the ferroelectric-paraelectric (F-P) transition peak at 106 °C, indicating retention of the ferroelectric phase until the material melt at 152 °C. The loss of this transition in the composite was confirmed through polarization-electric field hysteresis testing at 115 °C, where the pure polymer (dashed) clearly shows a paraelectric response while the composite (solid) retains its ferroelectric state.

These results show promise toward the design of sensors for extreme environments such as structural and pressure sensors in automobiles, and for vibration sensors for machinery supporting oil, gas, mining and manufacturing operations.
Ordered microporous polymer structures have potential application in catalysis, surface engineering and optoelectronics. The Breath Figure Technique (BFT) is a simple method of producing such ordered microporous structures. In this study BFT was applied to a series of commercial conjugated polymer polythiophene derivatives with varying side chain length (n=6,8,10,12). An in-depth study of processing parameters has been carried with the aim of controlling the morphology of the honeycomb film over large, PV relevant areas. Structural and spectroscopic characterization of honeycomb films were performed using Scanning Electron Microscopy (SEM), X-ray scattering, Fluorescence Lifetime Imaging (FLIM) and Spectroscopy [1]. Blends of these polymers with a fullerene derivative, PCBM, were also subjected to BFT and characterized with similar methods to assess their potential use as active layers in solar cells.

Reference:

67 - Rational design of polymers for high energy density capacitors

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Polymers as future materials for high energy density capacitors need to fit many criteria, namely relatively high band gap, high dielectric constant, and low dissipation factor over a broad temperature range, as well as high demands in processability. In the area of high temperature materials, we have systematically explored a new class of polyimides, as well as a class of organometallic polymers, having high thermal stabilities, as well as exhibiting dielectric constants in excess of 7, with loss under 1% over a broad frequency up to temperatures of 100 degrees C. The organometallic class of polymer is especially interesting since different complex formation and hence crystals result in the films wherein crystal preference is brought about by casting solvent. The experimental data is compared to DFT data for the x-ray diffraction and infrared spectroscopy.

Figure 1: Dielectric constant for several different polymer imides as a function of frequency at room temperature. The highest k achieved is approximately 8, based upon a polymer using Jeffamine HK511 and Benzophenone-3,3':4,4'-tetracarboxylic dianhydride (BTDA)

Sunday, March 16, 2014 03:30 PM
Materials for Energy Harvesting (01:30 PM - 04:15 PM)
Location: Hyatt Regency Dallas
Room: Cumberland A
68 - Effects of conjugation in low bandgap donor-acceptor semiconducting polymers for organic photovoltaics

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Charge recombination in organic photovoltaics (OPVs) is a significant factor that limits device performance. In most OPVs, bimolecular recombination, that can be described by the Langevin recombination model, dominates the recombination behavior. In Langevin-type recombination, the recombination rate is limited by the diffusion of charges, and competition between charge extraction and charge recombination can result in short charge carrier drift lengths. Consequently, Langevin systems suffer from fill factors that decrease rapidly as the device thickness is increased, leading to low power conversion efficiencies (PCEs). Some unique systems, however, demonstrate recombination that is significantly reduced compared to diffusion-controlled recombination. These non-Langevin polymers demonstrate high PCEs even for relatively thick active layers (>150 nm). Of the few reported examples of non-Langevin systems, KP115:PC60BM, reported by Peet and coworkers in 2011, is one of the most promising. This polymer demonstrates non-Langevin recombination behavior with no clear correlation between the observed morphology and recombination kinetics. Herein, we report the synthesis, characterization, and electrochemical and photophysical properties of KP115, as well as the fabrication and study of photovoltaic devices made from KP115:PCBM blends. Additionally, it was proposed that the non-Langevin recombination behavior of KP115:PC60BM blends may be attributed to the presence of discrete donor and acceptor units in the polymer backbone. As a result, we also report the synthesis and characterization of KP115 derivatives utilizing conjugation-interrupting linkages to enhance the inherent break in conjugation.
Materials that inherently exhibit both shape memory and self healing properties have been synthesized. These materials are semicrystalline, covalently crosslinked network polymers containing disulfide bonds. The combination of crystallinity and covalent crosslinks gives the material a means to hold a temporary shape and recover to a remembered shape, allowing it to display shape memory properties. The disulfide bonds in the network can be exchanged when exposed to UV light or heat. By activating this disulfide exchange, the network can be allowed to flow and heal small defects and change its shape. Additionally, the disulfide exchange can be used to alter the recoverable shape of the material for shape memory. Shape memory experiments showed high degrees of both fixing and recovery (>95%) and healing experiments showed that the film was able to recover from a scratch whose depth is approximately half the thickness of the film. Finally, large scratches in the material could also be healed using thermal shape-memory to decrease the width of the scratch and then subsequent photohealing to remove the scratch.
The emerging field of depolymerizable polymers offers a unique opportunity to develop materials that provide an amplified response to a specific stimulus. This presentation will focus on polymers that depolymerize from head-to-tail once an end-cap is cleaved from the terminus of the polymer in response to a specific signal. This depolymerization reaction of a polymer chain with $n$ repeating units provides an amplified response either by altering the properties of a material, and/or by providing $n$ monomers with distinct spectroscopic signatures compared to the polymer. This presentation will focus specifically on depolymerizable poly(phthalaldehydes) (PPHA), including their preparation as well as their use for amplification in solution (for analyte detection) and the solid state (to make responsive materials such as microcapsules).
Photodirected confinement of wrinkles on a thiol-ene elastomer

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Wrinkles on polymers are a cost-efficient method to produce surface topography, and have a wide range of applications including antifouling coatings, adhesives, and microarray lenses with tunable focal lengths. However, the precise control over wrinkle confinement and orientation necessary to engineer textured surfaces remains a challenge.

Photopolymerizable thiol-ene chemistry is an attractive technique to spatiotemporally direct wrinkle formation. The base elastomer, embedded with photoinitiator and photoabsorber, is formed using off-stoichiometric amounts of thiols and enes through Michael type addition (see Figure). The strained elastomer is then irradiated with UV light to induce a second stage polymerization of the excess functional groups. While the photoinitiator initiates the second polymerization, the photoabsorber confines the UV light to a thin skin layer, creating the necessary conditions for the wrinkle formation upon release of the strain. Through photomasked UV light, these wrinkles can be selectively confined and oriented, facilitating the formation of complex patterns with multiple distinct wavelengths as well as the formation of gradients containing a continuum of wrinkle wavelengths. Finally, these wrinkles can be “locked in” using a photoorthogonal photoinitiator through additional bulk radical polymerization. With the wide selection of commercially available and synthesizable thiol and ene monomers, photoinitiators, photomasks and stoichiometric control, we present an alternative system to wrinkle formation that is highly versatile, further enabling the a priori design and engineering of textured surfaces.

References:


Sunday, March 16, 2014 02:10 PM
Excellence in Graduate Polymer Research (01:00 PM - 05:45 PM)
Location: Hyatt Regency Dallas
Room: Reverchon A/B
The presentation will introduce surface patterning applications of a visible light-mediated controlled radical polymerization and atom transfer radical addition (ATRA) reaction. The temporal and spatial control enabled by light as an external stimulus for polymerizations and addition reactions is ideal for surface patterning applications. Surfaces with spatially defined regions containing polymer brushes or small molecules can be formed from a uniform initiating layer using a simple photomask. The living nature of the photocontrolled polymerization allows for precise control over chain end functionality and the fabrication of block copolymer architectures. Furthermore, chemical gradients and complex three-dimensional structures can be obtained by modulating light intensity with a grayscale photomask. Together, light-mediated polymerizations and addition reactions offer many advantages over existing techniques for patterning surfaces and generating gradient structures. The unique capabilities of these processes offer significant promise for applications ranging from photolithography to one-step, high throughput patterned substrates.
Engineering network associations for control of responsive reinforcement in nanostructured physical hydrogels

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Shear-thinning hydrogels are particularly promising for use in the minimally-invasive implantation of biofunctional materials for a variety of biomedical applications, including as reinforcing tissue fillers or delivery vehicles for encapsulated cells or drugs. The formation of a robust, injectable implant that can withstand typical stresses in the physiological environment over desired timescales is an ongoing challenge. To address this need while meeting demands for clinically-relevant storage and processing conditions, one strategy has been to engineer thermoresponsive hydrogels that can be injected at low temperatures, but will responsively self-assemble to a reinforced state at high temperatures. Hybrid triblock copolymers made from artificially-engineered associative protein midblocks with poly(N-isopropylacrylamide) (PNIPAM) endblocks form nanostructured associative polymer gels at elevated temperatures, exhibiting large increases in stiffness and toughness, with significant decreases in creep and erosion. Alternative synthetic routes to either all-protein-based elastin-like polypeptide (ELP) triblock fusions or PNIPAM triblocks with dimethylacrylamide-co-N-acryloyl-dopamine midblocks led to responsive hydrogels with altered thermodynamic and mechanical behavior. These designs provide new mechanisms for control over macromolecular structure and association nature. Monodisperse ELP fusions undergo spherical-to-cylindrical transitions at lower concentrations than the hybrid PNIPAM triblocks, while iron-coordinating dopamine-functionalized triblocks exhibit unique pH, temperature, and metal ion-dependent reversible and irreversible behavior. The multiple embodiments of nanostructured associative polymer gels investigated in this study explore new routes to achieving complex morphologies for tuning the reinforcement and toughness of shear-thinning hydrogels for biomedical applications.
A primary aim of covalent mechanochemistry is to develop polymer bound mechanophores that undergo constructive transformations in response to otherwise destructive forces. In our group, we have extensively explored the mechanochemical electrocyclic ring opening of dihalocyclopropanes to 2,3-dihaloalkenes in polybutadiene and polynorbornene based polymers. This transformation occurs readily in solution, via pulsed ultrasound, and in the bulk. Recently, we have leveraged this transformation to demonstrate in situ stress-induced network formation, whereby new bonds are formed in response to otherwise destructive flow forces. Additionally, we have developed a class of non-scissile mechanophores based on a fused bicyclic (bicyclo[3.2.0]heptane and bicyclo[4.2.0]octane) framework, in which the cyclobutane subunit mechanochemically dissociates into tethered alkenes. This versatile platform has enabled us to develop multi-stimuli responsive polymers, expand the toolkit of mechanochemically generated reactive groups, examine stereochemical effects on mechanochemical reactivity, and probe the mechanism of ring opening. Here we will detail our progress to date developing stress-responsive polymers through mechanochemistry.
The field of polymer mechanochemistry, wherein exogenous forces are harnessed to drive chemical transformations in polymeric architectures, is increasingly attracting the attention of the scientific community. Indeed, polymer mechanochemistry has been shown to afford selective access to chemical processes that are otherwise kinetically prohibitive. However, the fundamental role of molecular architecture in such mechanochemical phenomena remains elusive. To elucidate the mechanistic implications of molecular structure in the context of mechanochemistry, we have focused on two model systems that probe regiochemical effects: 1) the formal 1,3-dipolar cycloreversions of 1,2,3-triazoles, and 2) the formal [4+2] cycloreversions of Diels-Alder adducts. We demonstrate that altering the underlying architectures of these mechanically labile scaffolds dramatically modulates any associated mechanical reactivity (i.e., the cycloreversions can be accelerated or suppressed). These reactivity trends can be predicted using simple computational models, which has important implications for the streamlined development of molecular force sensors that have been designed to exhibit tailored responses.
76 - Coupling the Kerr effect and NMR to determine polymer macrostructures

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As protein tertiary and quaternary structures and their resulting functions are determined by their primary sequence of amino acids, so too are the behaviors and properties of synthetic polymers critically dependent on their macrostructures. Relevant structure-property relations developed for polymer materials must also be based on their macrostructures, i.e., the types, quantities, and locations of their constituent microstructures. NMR, usually high field, high resolution $^{13}$C-NMR observed in solution, has repeatedly been demonstrated to be the premier experimental means for elucidating the constituent micro-structural elements present in polymers. Like most spectroscopies, NMR is generally only sensitive to relatively local, short-range microstructures, which do not extend beyond 1 or 2 nm along polymer backbones. To determine polymer macrostructures requires a probe whose consequent observable also depends on the complete macrostructure. We believe that observation of the birefringence produced by application of a strong electric field to dilute solutions of polymers, i.e., their electrical birefringence or Kerr effect, provides a means to characterize the macrostructures of polymers. The contribution made by a polymer solute to the solution Kerr effect depends on and is highly sensitive to both the magnitude and orientation of its overall dipole moment and polarizability tensor. As such, and for the first time, we are able to demonstrate its use to locate along the polymer backbone those short-range microstructural elements that are identifiable by NMR, thus enabling the complete characterization of a polymer chain's macrostructure.

[figure1]
ACOMP has recently become a mature laboratory platform for monitoring multiple characteristics of polymerization reactions as they occur; comonomer conversion, weight average molecular weight and intrinsic viscosity, average composition and drift, and rapid identification of unexpected phenomena such as microgelation, appearance of particulates, premature reaction termination, etc. The approach has been used to monitor a wide variety of reactions, including free radical copolymerization and controlled radical (ATRP, ROMP, NMP, RAFT) homopolymerization and multiblock and gradient copolymerization, heterogeneous phase reactions in emulsions, grafting, postpolymerization modifications, and others. This talk will survey some of the latest results in various applications with a special emphasis on the extension of ACOMP to a ‘second generation’ method capable of monitoring the onset and evolution of polymer stimuli responsive behavior during synthesis. A test case in this is the single-reaction production of a wide variety of copolymer compositions of n-isopropyl acrylamide (NIPAM) and other water soluble comonomers, while monitoring for lower critical solution temperatures with several light scattering cells in series. Progress concerning the ongoing transfer of ACOMP from the R&D lab to the industrial reactor environment will also be reported.
Conjugated polymers evoke the idea of "molecular wires" having strong connection of electrons in one part of a conjugated chain to those in others: electrons, holes and excited states should move freely along the chains. Really good molecular wires might revolutionize solar energy and molecular electronics, but do they exist? Experiments in our laboratory investigate transport of electrons, holes and singlet or triplet excitons along chains to trap groups at the ends. The technique of pulse radiolysis enables rapid injection of charges into the chains with measurements by transient absorption (TA) and complementary measurements by transient microwave conductivity to examine movement of charges. The experiments seek to learn which of two competing pictures is more correct: 1) that conjugated chains are continuous "wires" or 2) that they contain defects that stop transport.

Polymeric "wires" might range from giving fast or slow transport that is continuous along the chains. Alternatively transport might be effective only in segments separated by some kind of defect, or charges or excitons might be trapped by defects. If defects control transport, we will seek to learn what synthetic strategies could reduce or eliminate them. The transient measurements are complimented by DFT calculations that picture (see Figure 1) charges as polarons and provide quantitative descriptions of their properties and measurements that find them to possess infrared band with extinction coefficients to 50,000.
Accelerated in vitro testing, especially high temperature aging, is commonly used to identify degradation mechanisms and predict clinical performance of biostable polymers.

In this analysis, we compare the impact of hydrolytic high temperature aging on the bulk polymer properties of multiphase polyurethane elastomers to their in vivo performance.

Samples of polyurethane (PU) and polydimethylsiloxane-based polyurethane (SPU) were incubated for timed intervals in aqueous buffer (pH 7) at different temperatures (37, 55, 72, 85°C). The time-dependent changes in the specimen's total weight, molecular weight and mechanical properties were examined. Morphology of the polymers were studied with optical (SEM), thermal (DSC) and mechanical (DMA) techniques. Chemistry of the polymers in bulk or surface were studied by FTIR-ATR and GPC. Specimens taken from human explants, through 5 years, were analyzed in the same fashion and compared to those from the accelerated in vitro study.

The in vitro samples water absorption increased significantly with temperature (T), resulting in a non-linear relationship between the logarithm of effective diffusivity and (1/T). For the in vivosamples, high magnification SEM data showed shallow surface cracking of PU and no cracking on SPU samples.

FTIR-ATR analysis revealed weak loss of H-carbonyls responsible for hydrogen bonding between hard segments of PU samples and weak oxidation of the polyether soft segments of both polymers. The molecular weight and tensile property losses in the accelerated testing did not correlate with those from the human implanted samples. The DSC analysis displayed an endothermic transition near 60°C, suggesting morphology changes or phase separation during the aging. Dynamic mechanical thermal analysis presented non-linear relationships of storage versus loss modulus, suggesting molecular rearrangements occurring at high temperatures.

These results suggest that the applicability of time temperature superposition theory in predicting long-term biostability of implanted multiphase polyurethane materials is limited.
Accurate knowledge of polymer brush grafting density will enable direct correlation of tethered chain dynamics and conformational transitions to physicochemical properties and kinetics of polymer thin films. Current methods to estimate grafting density rely on the hypothesis that molecular weight of a planar surface-initiated polymer brush is comparable to molecular weight of a concurrent solution polymerization. Recent Monte Carlo simulations indicate that this assumption may be inaccurate due to differing polymerization rates at the surface and in solution, especially when the density of surface-bound initiator is high.

To address this issue, grafting density was determined by utilizing the stimuli-responsive behavior of dense and highly extended brushes resulting from surface-initiated controlled polymerizations. Brushes swollen with solvents of varying quality change brush height ($h_0$, $h$) and film density; however the distance between tethered chains ($D$) remains constant. In situ x-ray reflectivity measurements were conducted to measure brush swelling upon exposure to solvent vapors and grafting density was determined using modified mean-field theory of one-dimensional swelling. Good solvents demonstrate homogeneous swelling, while heterogeneous density profiles were observed with poor solvents.
Self-healing materials are able to heal mechanical damage caused by any external stress in situ to a degree that the original functionality is – at least partially – restored. As such, these materials hold great promise in prolonging the functional lifetime of devices by repeatedly healing damage inflicted on the materials. However, in order to improve materials’ self-healing capacity in a directed synthetic manner, a detailed understanding of the healing processes in such systems is required.

Figure: Schematic representation of the proposed self-healing mechanism in a terpyridine based metallopolymer. Reversible terpyridine Raman band shifts during heating the metallopolymer indicate partial decomplexation of the metal-ions.

In this contribution we report on our results focussing on developing a molecular understanding of the self-healing processes in polymer coatings bearing metal-terpyridine complexes as reversibly switchable molecular units. The work presented combines (resonance) Raman spectroscopy with QM/MM calculations to unravel different molecular contributions to the self-healing mechanism in a series of polymers constructed from a library of reversibly switchable terpyridine units.

The work presented is supported by the German Research Council in the framework of the Schwerpunktprogramm 1568 Design and Generic Principles of Self-healing Materials.
The molecular motions at the chain end of polystyrene (PS) chemically modified with a nitroxide, cyano group, and deuterium were studied using electron spin resonance (ESR), dielectric spectroscopy (DS), and Fourier transform infrared (FT-IR) spectroscopy, respectively. The segmental mobility at chain end above glass transition temperature ($T_g$) was determined by the ESR and DS techniques. The segmental motional rate at the chain end was approximately double compared to the midchain segments at $T_g + 50$ K. On the other hand, the local $T_g$ around chain ends determined by the ESR and FT-IR was comparable to the bulk $T_g$ of the PS. From these results, it is considered that the chain ends intrinsically have higher segmental mobility compared to the midchain segments; however, the mobilities of chain ends and midchain segments are averaged out in the vicinity of $T_g$ due to the strong cooperativities with neighboring numerous chain segments. Finally, the vibrational frequency of the C-D bond at the chain end was measured by the FT-IR and more rapid vibration of the C-D bond at the chain end compared to that at the midchain of the PS was shown. The difference between the vibrational frequencies of the C-D bond at the chain end and midchain segment almost unchanged even in the toluene solution; therefore, the reduced intramolecular interactions at the chain end were considered as the origin of the rapid vibration.
83 - Probing hierarchical nanomorphologies in high-performance organic solar cells through resonant soft X-ray scattering

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Solar cells based on the polymer:fullerene bulk heterojunction (BHJ) represent one of the most promising technologies for next-generation solar energy conversion due to their low-cost and scalability. In the last fifteen years, research efforts have led to organic photovoltaic (OPV) devices with power conversion efficiencies (PCEs) 12%, but these values are still insufficient for the devices to become widely marketable. To further improve solar cell performance, a thorough understanding of the complex structure-property relationships in OPV devices is required. In this work, by taking advantage of resonant soft x-ray scattering (RSoXS), we have determined that the superior performance of PTB7:fullerene bulk heterojunction (BHJ) solar cells, one of the best-performance OPV systems, is attributed to hierarchical nanomorphologies with optimum crystallinity and nanoscale intermixing of copolymers with fullerenes, which together promote exciton dissociation, and consequently, contribute to photocurrent.

We have also discovered that the formation mechanism of hierarchical nanomorphologies is a competitive yet synergistic mechanism of crystallization and spinodal decomposition phase separation. Fine-tuning morphologies from molecular ordering to nanophases enables us to realize improvement in the performance of PTB7:fullerene BHJ solar cells with PCEs up to 9%. Progress established in the course of these structural and morphological characterizations outline above will serve as the foundation for further improving the efficiency of polymer solar cells to realize their large-scale commercial use.
The calorimetric glass transition (T_g) is measured for single polystyrene ultrathin films using a commercial rapid-scanning chip calorimeter as a function of cooling rate and film thickness. Films have been prepared in two ways: spin-cast films placed on a layer of inert oil or grease and films directly spin-cast on the back of the calorimetric chip. For the films on oil or on grease, the 160 nm thick films show consistent results with bulk sample measured by conventional DSC. On the other hand, the 47 nm thick film on oil and 71 nm thick films both on oil and on grease show a T_g depression which decreases with increasing cooling rate; the magnitude of the T_g depression is similar to results of the most mobile substrate-supported films in the literature. The depression reverts to the bulk values over the course of a day at 160 °C due to films dewetting and thickening to 200 nm. For films directly spin-cast onto the sensor, a T_g depression is not observed for 47 and 71 nm thick films but is observed for a 16 nm thick film. These results are also within the range of the data on supported films in the literature but show a smaller depression than films on oil or grease. The results will be compared to the T_g depression in stacked polystyrene films measured by conventional DSC.
85 - Size exclusion chromatography (SEC) and molecular weight distribution (MWD) analysis of sulfonated polyarylene ether sulfone (SPAES) copolymers in N-methylpyrrolidone (NMP)

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MWD affects both processing and properties of polymers. Engineering polymers incorporate rigid structures which increase T_g and mechanical properties but may also induce limited solubility, making the characterization of the (MWD) more challenging. We have characterized the MWD of random and multiblock SPAES and sulfonated poly(arylene ether ketones) copolymers, using SEC. These materials were soluble in N-Methylpyrrolidone (NMP), but the hydrophilic/hydrophobic nature, rigidity, or aggregation lead to interactions affecting the separations. SEC of SPAES homo and copolymers will be presented comparing the results using light scattering (LS) and universal calibration (UC). Analysis of the MWD of highly sulfonated polymers suggests aggregation and column interaction. Figure 1 shows SEC chromatograms of 15,000 g/mole (NMR M_n) SPAES oligomers. SEC with LS provides weight average molecular weight (M_w) of 22,000 and 28,000 g/mole for 1 and 2 respectively; however, the tailing observed at high elution times indicates column interaction. Asymmetric flow field flow fractionation (AF4) of SPAES copolymers is expected to provide improved results by eliminating column interaction. 100% SPAES are soluble in both aqueous and NMP solvents, partially sulfonated copolymers have limited solubility in aqueous systems so have been analyzed in NMP/0.05M LiBr. Development of AF4 is underway for SPAES with the intention of performing separations in both aqueous and NMP/0.05M LiBr solvents. The limitations of the methods with respect to the level and distribution of the hydrophilic monomers will be reported.

Monday, March 17, 2014 12:05 PM
Frontiers in Polymer Characterization (08:00 AM - 12:45 PM)
Location: Hyatt Regency Dallas
Room: Moreno A
86 - Thermo-mechanical and microscopy of polycarbodiimide optical switching

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Polycarbodiimides are an interesting class of polymers that have a wide range of potential applications. These include optical sensory, data devices, and liquid crystals which are continuing being explored. Great research in the area of synthesis has been of the main focus in polycarbodiimide chemistry. Though the potential for the class of polycarbodiimides has yet been fully realized in materials characterization and application. Of interest has been the polymer poly(N-1-naphthyl-N-octadecylcarbodiime) (PNOC) because of its inherent ability to cause optical switching. The optical switching has been shown in solvent media such as benzene, toluene chloroform and dichloromethane, but has yet been showcased in the bulk polymer without solvent. Bulk PNOC has been evaluated on differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), coupled TGA-FTIR-MS, scanning electron microscopy (SEM), and atomic force microscopy (AFM). It has been discovered via DSC and DMA that this special polycarbodiimide shows a melt at 120 C. While there is a large endotherm at 20 C, it does not correspond to a thermal state change, but is the optical switching of the naphthalene side groups of the imine. This investigation is the opening to further characterization and application of polycarbodiimides.
The addition of a lactide crystallization unit operation at the NatureWorks LLC Blair NE facility has enabled new grades of lactide that are useful in the production of high performance grades of Ingeo™ bioproducts. The new polylactide grades have a lower D-lactic acid content than previous grades. These new grades of resin have a higher melting point, increase of 8 °C to 172 °C; crystallize 3-4x more quickly; and can possess a higher net crystallinity, increase from 45 to 55 J/g. These properties give the resin performance advantages for fiber/non-woven and injection molding applications.
88 - Synthesis of functionalized PLA and PLGA polyesters

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Polyesters of lactic acid (PLA), glycolic acid (PGA) and their copolymers (PLGA) are the most commonly used materials for biomedical, and disposable or non-recoverable polymer goods applications because they degrade under biological and environmental conditions, their degradation products occur naturally in the body and the environment, and their monomers are naturally derived. We recently designed and synthesized acrylate imiders that produced the first truly hyperbranched analogs of linear polyacrylates upon homopolymerization using atom transfer radical polymerization. The key intermediate of this new class of imiders is a 2-halo-3-hydroxypropionic acid (halo = Cl or Br), which we synthesize regioselectively starting from serine, a natural amino acid that can be isolated from soybean protein. Since 2-halo-3-hydroxypropionic acids are halogenated isomers of lactic acid, yet have a primary alcohol group like glycolic acid, we believe they are ideal comonomers to copolymerize with glycolic acid and/or lactic acid to provide PLA and PLGA with sites for attaching biologically active or other functional molecules. We will present the synthesis of halogenated PLGA and PLGA by both acid-catalyzed and enzymatic polymerizations, as well as some functionalization reactions based on the bromine substituent, and the ability of the halogenated PLA to blend with high molecular weight PLA.

Monday, March 17, 2014 09:00 AM
Sustainable Polymers, Processes and Product Applications (08:30 AM - 12:00 PM)
Location: Hyatt Regency Dallas
Room: Bryan-Beeman B
Polylactide (PLA) is a commercially produced bio-based thermoplastic with unique properties such as high strength, biocompatibility and biodegradability. Despite these positive attributes, PLA has a low heat deflection temperature (HDT) such that its mechanical properties fall off at temperatures greater than 55 - 60°C. This paper explores the use of cellulose nanocrystals (CN) as a potential solution to this problem.

Cellulose nanocrystals (CNs) possess many attractive features for use in nano-composites. CNs are derived from cellulose which is highly abundant in nature, non-toxic, biodegradable, and has a low density. A one-step method based on both Fischer esterification and acid hydrolysis was used in this work to obtain functionalized and ready-to-use CNs.

This paper describes an investigation of the reinforcing effect of CNs on PLA-based materials. CNs functionalized with acetate (AA-CN), lactic acid (LA-CN) and unfunctionalized CNs were synthesized and blends of PLA and these CNs were prepared by direct melt blending. The corresponding thermomechanical properties were investigated by DMTA. Blends with LA-CN possessed the highest storage modulus. Based on these results, blends with up to 20% LA-CN were prepared by direct melt blending and an increase of up to 20 °C in the HDT resulted. A decrease in oxygen permeability also resulted from increasing the nano-filler content. This increase in materials properties can potentially expand the applications of PLA based materials.

Sustainable Polymers, Processes and Product Applications (08:30 AM - 12:00 PM)
Location: Hyatt Regency Dallas
Room: Bryan-Beeman B
Various attempts have been made to use renewable polyesters, e.g., polylactic acid (PLA) in different applications such as fibers, injection molded articles, and films. However, a success of biopolymesters in different applications has been limited due to high density that is approximately 30% higher than conventional polyolefins, and certain process and performance deficiencies of typically high stiffness and low ductility polymers. Development of novel biopolyester-polyolefin hybrids can address some of these challenges by reducing material density and enabling hybrid materials with an expanded and novel property profile. Reactive extrusion is used for in-situ hybrid blend compatibilization to develop a biopolyester structure having an extremely uniform dispersion of polyolefin constituents at the nano and micro-meter scale. Interphase modifiers and lubricants (IM) are employed to tune behavior at interfaces and modify matrix polyester mechanical performance. Hybrid blends of PLA and inclusion additives of ethylene vinyl acetate (EVA), polypropylene (PP) and propylene-ethylene copolymer, Vistamax™ (VMX) elastomer were in-situ compatibilized using reactive extrusion with epoxy-functional high molecular weight poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (PEMAGMA) copolymers. Addition of IM did result in a significant improvement in hybrid blend ductility, elongation at break, and toughness. The hybrid PLA-polyolefin blends where successfully processed into fibers, films, and injection molded articles. Electron microscopy imaging, x-ray diffraction, and NMR techniques where used to characterize hybrid blend morphological features and chemical transformations in the blend. An addition of IM modifiers enabled uniform drawing of the hybrid material accompanied by intensive internal cavitation and uniform stress whitening. Solid state orientation resulted in cellular composite structures with up to 60% reduction in density and pore size distribution on a micron and submicron scale. [figure 1] Developed hybrid materials demonstrated novel property profiles characterized by a combination of low density, high impact resistance, ductility and strength.
The use of synthetic polymers from petroleum sources are widespread and can be found in nearly every item we use in our daily lives. There is a growing shift to polymeric materials prepared from renewable sources due to the increased cost of petroleum and sustainability concerns. One of the most widely investigated renewable materials for replacement of polymers derived from petroleum sources is polyactic acid (PLA). Although widely used, PLA is plagued by the brittleness, moisture resistance and deficient thermal performance. To overcome these challenges, we have developed modified lactides which can be co-polymerized to prepare modified PLA.
Nanocomposites based on synthetic polymers grafted from kraft lignin with average particle size of 5 nm were synthesized using atom transfer radical polymerization (ATRP). Lignin macrorinitiators were prepared, and polystyrene and poly(methyl methacrylate) were polymerized with target degree of polymerization of 450. Structural characterization was performed using transmission electron microscopy, and the microstructure was shown to be consistent with well dispersed lignin particles having average diameter of 10 nm in a matrix of the synthetic polymers. Mechanical characterization using tensile testing showed that while the modulus was 10-times lower than that of the corresponding homopolymers, the toughness was more than 20-times greater. These properties are consistent with other single-phase nanocomposite systems and indicate that lignin can be used effectively in preparing advanced materials using renewable resources whose properties are comparable to currently available ones.
93 - Synthesis and characterization of solely biobased polyamides based on furan moieties

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ABSTRACT: Biobased polyamides were successfully synthesized from difuranic diamines and difuranic diacids or diesters solely prepared from furfural moieties. Preliminary studies indicate that there are two synthetic routes enable to produce furan-aromatic polyamide by polycondensation. The structures of these polyamides were confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy ($^1$H-NMR). The properties of biobased polyamide were characterized by thermo gravimetric analysis (TGA), differential scanning calorimeter (DSC), dynamic mechanical analysis (DMA), and tensile tests. The results show that they behave similar as general aromatic polyamides. This study provides sustainable alternatives to fossil-based polyamides since both monomers are derived from biomass.
Recently, Rosin acids and lignin have attracted considerable attention as a renewable source of valuable chemical species. The purpose of this work is to synthetically demonstrate the feasibility of using these natural occurring materials to successfully manufacture environmentally friendly polyester resins. The mono functional rosin acids (1), natural phenols as well as phenolics from lignin based fragments are transformed to organic diols (4) or (5) utilizing a solvent free base catalyzed reaction with bio-based glycerin carbonate (3). The corresponding organic diols, are then polymerization with various diacids, including bio-based succinic acid to afford polyester resins.

These polyester resins are subsequently emulsified to nano-sized particles by various techniques, and coalesced to micron sized composites for use as xerographic marking materials.
95 - Design and synthesis of delivery systems for siRNA therapeutics using RAFT polymerization

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The advent of controlled radical polymerization techniques such as Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization has allowed the design and synthesis of polymeric architectures with quantitative control of block length, microstructure and placement of active and targeting moieties at chain ends or as pendant groups. These structural features are important parameters in advanced delivery systems for protein and gene based therapeutics such as short interfering RNA (siRNA). We have designed and synthesized a range of linear, star and hyperbranched cationic block copolymers based on a combination of N,N-dimethyl aminoethyl methacrylate (DMAEMA), oligoethyleneglycol methacrylate (OEGMA) and butyl methacrylate (BMA) to form cationic, hydrophilic and hydrophobic blocks, respectively. The polymers were characterized by in-vitro test protocols for cell viability, siRNA uptake, serum stability and gene silencing. The presentation will highlight the advantages of RAFT polymerization in the synthesis of polymers with different architectures, and their influence on gene silencing efficiency, and the application of the polymers as siRNA carriers to inhibit the influenza virus replication in-vivo.
Double brush copolymers (DBCs) with each graft site quantitatively carrying two different grafts have been established as a new class of nanostructured Janus copolymers. The earliest examples of DBCs were prepared by tandem living anionic polymerization (LAP) and ring-opening metathesis polymerization (ROMP). However, this synthetic approach is significantly restricted from stringent conditions and narrow monomer scope of LAP. Recently, new synthetic approaches have been developed to afford a broad variety of well-defined DBCs by tandem living radical polymerization (LRP), ring-opening polymerization (ROP), and ROMP. Their Janus morphologies were visualized by TEM imaging, providing direct evidence to verify them as Janus nanomaterials. DBCs with both hydrophilic and hydrophobic grafts can effectively stabilize biphasic systems, and miniemulsions using these JDLCBs as surfactants exhibited remarkably high stability. Moreover, amphiphilic JDLCBs with functional graft ends were utilized as reactive surfactant for the emulsion-based preparation of nanomaterials.

Figure 1. a) Schematic illustration of a DBC macromolecule. b) TEM image of Janus unimolecular morphology of DBC. c) Schematic illustration of emulsion stabilized by amphiphilic DBC. d) Nanoparticles and nanocapsules prepared from emulsion polymerization using amphiphilic DBCs as reactive surfactants.
The oxides of carbon, $\text{C}_2\text{O}_2$ and $\text{CO}_2$, contain double bonds in their structures. The former is very susceptible to polymerization, and the latter is very resistant to reacting with itself. The carbon suboxide monomer readily polymerizes from the vapor or liquid phase into a low molecular weight poly($\alpha$-pyrone) solid without catalysis at room temperature. Carbon dioxide is a much less energetic molecule but can be polymerized under extreme high pressures to an extended solid characterized by an ideal $\text{CO}_2$ Phase V silicon dioxide quartz-like structure. An interesting feature in this transformation is a proposed carbonyl intermediate (trioxane trione) that has been calculated to be of greater stability than the extended $\text{CO}_2$-polymer solid. To be presented are a series of experimental approaches for the preparation and isolation of this intermediate and a measurement of its stability.
98 - Sidearm approach to polymerization catalysts of olefin

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The discovery of new olefin polymerization catalysts is of great fundamental scientific and technological importance. To date, thousands of complexes proved to be active for olefin polymerization but very limited ones are applicable to industry use. Catalyst design for precise-control polymers remain a focus for chemists. Since the performance of the catalyst depends on the electronic properties, the space, and the shape of the polymerization site, we believe that the catalyst design is how to find a simple way to govern these factors. In this presentation, we employ salicylaldeminate as a model and modify a very simple bidentate complex with a “sidearm” into tridentate complexes (we name it as “Sidearm Strategy”). As expected, the coordination pattern of the newly-designed ligands with titanium is different from that of the parental phenoxy-imines due to the interaction of the sidearm with central metal, leading to monoligand ligated complexes instead of bisligand ligated ones. Without alteration of the salicylaldeminate moiety, the installed “sidearm” makes these complexes tunable and excellent copolymerization capability. In addition, they showed also good tolerance to impurity and polar olefins could incorporate into PE backbone efficiently.
In 1984, one year before the passing of Prof. P. Flory, I had the rare opportunity to spend a week with him on the occasion of the 1st International SPSJ Polymer Meeting in Kyoto, Japan. It was at this SPSJ conference, that I presented the first public lecture describing the synthesis and characterization of poly(amidoamine) (PAMAM) dendrimers. During this meeting, there were several historical opportunities to enjoy discussions with Flory concerning his first theoretical concepts for synthesizing highly branched polymers reminiscent of trees. It was in one of those discussions that Flory made a memorable comment concerning his theoretical tree-like polymers. Flory stated--Isn't it strange that we are discussing the synthesis and characterization of symmetrical, ideal tree-branched polymers called dendrimers and yet there are no well characterized examples of my asymmetric, highly branched polymers in the literature? Today dendritic polymers are widely recognized as the 4th major architectural class of macromolecules after: (I) Linear, (II) Cross-linked and (III) Branched polymers (Figure 1). Furthermore, within this dendritic category Flory's theoretical tree-like polymers and dendrimers are actually recognized as subclasses in addition to dendrigraft and dendron macromolecules. It was not until 1988 that the actual synthesis and characterization of Flory's theoretical, highly branched polymers was first reported in a paper by Odian, et al. Although appropriately named and recognized by Webster and Kim in 1988-90, it was unfortunate that the significance of this first report on random hyperbranched polymers was lost in the flurry of attention being given to dendrimers at that time.

References:
We present a new chitosan-based biocompatible self-healing hydrogel system. The hydrogel was generated readily through the formation of Schiff base linkage between the amino groups on chitosan and the aldehyde groups on a telechelic PEG with benzaldehyde chain ends. The Schiff base in the system is in a dynamic equilibrium with the amino and aldehyde groups, which means the crosslink points in the hydrogel keep open and close all the time. Therefore, this hydrogel is self-healable and its gelation state can be altered by many external stimuli, such as temperature, pH, vitamin B6 derivative, some enzymes and amino acids, making it possible for controlled drug delivery applications. We have also found that this hydrogel is biocompatible, suitable for 3D cell culture, tissue engineering and cell free protein expression. Because of its self-healability, the hydrogel containing cells is injectable that could help fix cells at targeted positions for therapeutic and 3D bioprinting applications. In addition, the system can also be further modified with magnetic nanoparticles and electroactive polymers or oligomers to make the gel magnetically and electrically or electrochemically responsive, respectively. Electrical stimulation on electroactive scaffolds was found to affect cell growth and stem cell differentiation.

It is interesting to note that some 30 years ago, my Ph.D. thesis was related to Schiff base polymers under Prof. G. Odian’s direction.

Acknowledgment: This research was supported by the National Natural Science Foundation of China (21104039, 21134004) and the Chinese Ministry of Science and Technology National 973 Project (2011CB935700).
101 - Structure/property relationships of small organic molecules as a prelude to the teaching of polymer science

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The term 'structure-property relationships' and its implications pervade all of polymer science and engineering. For example, subtle changes in the repeating unit of a polyamide can alter its melting point and glass transition temperature, the degree of equilibrium moisture uptake and mechanical properties which can in turn dictate the scope and limitations of a commercial application. While certain properties such as viscoelasticity and the ability to achieve outstanding tensile strengths from molecular orientation are characteristics of only macromolecules, many other properties have dependencies on molecular structure which can parallel those of small organic molecules. Therefore, it can be very useful to introduce students to small-molecule structure-property relationships which can enrich subsequent discussions about polymers.

Simple hydrocarbons such as the C5H12 family will be used to discuss enthalpic and entropic contributions to the melting temperature, and molecular symmetry considerations will be used to identify which isomers may be glass formers upon rapid cooling. These concepts will be extended to structure/property relationships for a wide variety of macromolecules.

Monday, March 17, 2014 11:20 AM
Paul J. Flory Polymer Education Award: Symposium in Honor of George Odian (08:30 AM - 12:10 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm F
Several polymer graduate education efforts were initiated by George Odian beginning in the late 1960’s and developed over the next almost 5 decades:

1) Initiated the Ph.D. program in Polymer Chemistry at The City University of New York (CUNY) in 1972 and led the program for over 25 years. The polymer program has grown from 3 faculty members to 10 faculty at present and has granted over 60 Ph.D. degrees.


3) Taught two courses in the ACS Short Course Program at various sites throughout the United States for 40 years. One course, Polymer Chemistry, was taught jointly with James Mark (Cincinnati). A second course, Polymer Synthesis, was taught by George Odian alone. Between the two courses 1,500-2,000 chemists were educated in the polymer field.

4) Carried out a research program in the areas of radiation graft polymerization and crosslinking, zwitterionic polymerization, and metallocene-initiated polymerization of alkenes. About 20 Ph.D. students were mentored during these efforts, mostly at CUNY but also at Columbia University.

Monday, March 17, 2014 11:45 AM
Paul J. Flory Polymer Education Award: Symposium in Honor of George Odian (08:30 AM - 12:10 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm F
Field-flow fractionation (FFF) is a flow-based one-phase separation methodology. It is capable of separating an enormous assortment of macromolecules and particles with a size range of 1nm to 100µm. FFF is one of the most versatile families of separation technologies known, and applicable within many scientific and technological disciplines that encompass studies of polymers, powders, emulsions, environmental colloids, nanoparticles and biomacromolecules.

This talk will review the principles and theory of field-flow fractionation and introduce the various subtechniques which use flow, sedimentation, thermal and electrical forces to enact separation fields. Then, instrumentations of each subtechnique will be shown, and key applications will be reviewed for macromolecule and colloidal analysis in biological, biomedical, biopharmaceutical, material science and industrial contexts. Detector technology will also be explored including multi-angle light scattering (MALS) and inductively-coupled plasma (ICP) mass spectrometry.

A schematic of the asymmetrical flow FFF experiment:
104 - Detailed polymer characterization is essential to develop high-quality and consistent medical device products

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Naturally occurring and synthetic polymers play an increasingly important role in the medical device and pharmaceutical industries. Polymers are structurally complex, and normally consist of an ensemble of polymeric chains with a distribution of molar masses, chemical compositions, impurities, and architectures. It is critical to completely characterize and understand all polymeric raw materials used in products to ensure processability and batch-to-batch consistency. This characterization is also critical for promoting product quality under the increasingly stringent regulatory requirements that exist for the medical device and pharmaceutical industries. In this study, we characterized several polydimethylsiloxanes (a.k.a. silicones) and hyaluronic acid materials using size exclusion chromatography followed by mass spectrometry, viscometry, refractive index, and multi-angle light scattering techniques. We obtained detailed molecular compositional information such as repeat units, end group chemistry, and identification of impurities of high and low mass ranges. Also, we acquired the structural information of absolute molecular weight averages, molecular weight distribution, radius of gyration, and solution conformation of the polymers. Based on the molecular and structural information acquired by the hyphenated analytical techniques, we established the structure/process/property relationships between the polymeric material and finished products. Figure 1 shows the hyaluronic acid molecule interacts with the contact lens surface. Finally, we will discuss examples of polymer-related challenges and how we overcame the issues.

Hyaluronic acid molecule moisturizes the contact lens surface
105 - Liquid chromatography of multicomponent polymer systems

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Size exclusion chromatography, SEC, cannot discriminate macromolecules of distinct dimensions in solution. Moreover, minor blend constituents cannot be well assessed because of low both sample capacity and detector sensitivity of SEC. Liquid chromatography under limiting conditions of enthalpic interactions, LC LC is a novel approach, which employs the “barrier” effect of appropriate low molecular substances that promote enthalpic interactions of macromolecules within chromatographic column. The pore permeating, slowly eluting barrier is situated in front of sample. It decelerates elution of interacting macromolecules without affecting non-interactive macromolecules. The resulting molar mass independent separation is highly selective. Even minor macromolecular constituents of sample can be identified. The fractions eluted from the LC LC column can be in their entirety forwarded to an online SEC column for assessment of molar masses. Principle and selected applications of LC LC will be presented including one-step discrimination of parent homopolymers from block copolymers. The support of Slovak Grant Agencies VEGA (Project 2/0001/12) and APVV (Project 0109/10) is acknowledged.
106 - Characterization of rubber type, crosslinking, and chain scission in the rubber phase of ABS resins by chromatographic sol fraction analysis

John W Lyons, JWLyon@dow.com, David M Meunier. Core R&D, Dow Chemical, Midland, MI 48667, United States

Described are sample preparation and chromatographic methods of analysis that enable the determination of the weight fraction sol rubber and the molecular weight distribution of the sol fraction rubber. These quantities, when combined with knowledge of the starting molecular weight distribution of the rubber, enable characterization of the extent of crosslinking and the extent of chain scissioning in the rubber domains of acrylonitrile-butadiene-styrene (ABS) copolymers. These structural attributes affect the physical properties of ABS resins.
Two-dimensional (2D) chromatography (gradient polymer elution chromatography x gel permeation chromatography) is playing a growing role in supporting the product developers and process chemists who seek a better understanding of the structure-property relationship and reaction pathways. This is especially important for multistage polymerization reactions because each stage may yield a new population in terms of composition and molecular weight distributions. While bulk acrylonitrile butadiene styrene (BABS) resins have been a commercial success for many decades, the standard analytical methods cannot describe this material in all its complexity. BABS is made by dispersing some butadiene rubber into a mixture of styrene, and acrylonitrile monomers with sometimes the addition of a solvent. In this continuous process, there can be several reactors connected in cascade and styrene acrylonitrile (SAN) copolymer is formed. In general, the process consists of a grafting step and a phase inversion step. The composition and molecular weight distributions of the free and graft SAN copolymers are critical to achieve the desired material structure and targeted properties. Therefore, it is important to determine these distributions and how they relate to each other.

2D chromatography was used to evaluate several BABS resins. The unequivocal relationship between composition and molecular weight was established with IR coupling in the 2D setup for both the free and graft SAN copolymers. The data allowed us to evidence multiple populations in the molecular weight / composition fingerprint that correspond to the stages used during the synthesis.

2D plot of the graft SAN copolymer of a bulk ABS material. The x-axis is the molecular weight axis (GPC). The y axis is a function copolymer composition (GPEC).
108 - Characterization of crosslinked polystyrene nanoparticles by size-exclusion chromatography coupled to differential viscometry

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Conventional size-exclusion chromatography (SEC) and size-exclusion chromatography coupled to differential viscometry (SEC/DV) methodologies have been developed and applied to the dilute solution characterization of crosslinked polystyrene (PS) nanoparticles. A single SEC/DV experiment provides a wealth of information about PS nanoparticle structure including absolute molecular weight distribution, particle size distribution, volumetric swelling factor and solute conformation. Nanoparticle sizes determined by SEC/DV are in excellent agreement with those determined by other techniques such as hydrodynamic chromatography, multi-angle light scattering, dynamic light scattering and transmission electron microscopy. SEC/DV is applicable over a wide range of sizes from a few nanometers to several hundred nanometers. This talk will include discussion of SEC/DV methodology development for nanoparticle PS characterization. The approach for extracting size and volumetric swelling parameters from SEC/DV data will be presented. Solute conformation gleaned from Mark-Houwink plots of PS nanoparticle samples will also be presented. Finally, SEC/DV-based sizes will be compared to those obtained from other techniques.

Figure 1 – Absolute molecular weight distributions and Mark – Houwink plots of large (red traces) and small (blue traces) crosslinked PS nanoparticle examples
109 - Particle characterization by multi-detector HDC

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The “holy grail” of particle sizing can be regarded as the accurate and precise determination of the particle size averages and distribution of a sample that is disperse in size, shape, structure, and chemistry, along with the determination of the averages, distributions, and mutual-interdependences of all these properties. While no single analytical technique will be able to provide all of these for every sample type, multi-detector hydrodynamic chromatography (HDC) has demonstrated the ability to measure a number of these properties for a variety of samples. Advantages of HDC, vis-à-vis size-exclusion chromatography or field-flow fractionation, include its being gentler than the former (thus minimizing the possibility of on-column, flow-induced analyte degradation) and more affordable and easily implementable than the latter.

This talk will focus on the use of packed-column HDC for characterizing particle size, shape, molar mass, and structure, by combining the information obtained from detection methods such as refractometry, viscometry, and light scattering (both dynamic and static).

Figure 1. Mechanism of separation in HDC (from Striegel & Brewer, \textit{Annu. Rev. Anal. Chem.} \textbf{2012}, 5,15).
Probing the TiO₂-polymer composite formation for a new class of latex paint by AFFFF-MALS

Wei Gao¹, weigao@dow.com, James Bohling², Melinda Keefe², Qing Zhang², Michael Leonard², Yogesh Tiwary², Beth Cooper², Stan Brownell². (1) Core R&D, Analytical Sciences, The Dow Chemical Company, Collegeville, PA 19426, United States, (2) Dow Coating Materials, The Dow Chemical Company, Collegeville, PA 19426, United States

Understanding and controlling the interactions of adsorbing latex with inorganic oxides is of great value in waterborne architectural coatings. Unlike the common non-reactive binders, this type of reactive adsorbing latex can be adsorbed onto TiO₂ surface and form TiO₂-Polymer composite. This recently developed TiO₂-polymer composite provides a new approach to enhancing the TiO₂ scattering efficiency in latex paints, resulting in significantly improved wet and dry hiding as well as other paint properties.

Asymmetrical Flow Field-Flow Fraction with on-line Multi-Angle Light Scattering (AFFFF-MALS) was developed to quantitatively characterize the pre-composite latex polymer and the TiO₂-polymer composite. This development enabled us to demonstrate the formation of the TiO₂-polymer composite in the aqueous phase, probe the kinetics of the formation of TiO₂-Polymer composite in different formulations, and predict the reactivity of different grades of TiO₂ with the adsorbing polymer. Using this information, we can make better adsorbing latex polymer by design, and have better understanding and control of the key formulation and process variables affecting the latex-pigment interaction in the paint manufacturing process. Therefore, this analytical technique is essential and has enabled the large scale industrial production of this new adsorbing technology platform.

Figure 1. AFFFF-MALS fractograms of latex, TiO₂ and composite particles.
111 - GPC-IR deformation of complex polymer mixtures with IR spectral database search

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Mid-infrared spectroscopy is a well-established analytical technique to characterize chemical compositions of individual polymers and additives. Coupling an on-line infrared detector with Gel Permeation Chromatography made it possible to take FTIR snapshot spectra of each polymer component and additive in a complex polymer mixture and then identify them one at a time by IR spectral database search. GPC separates the complex polymer mixture into high MW polymer components and low MW additives according to their hydrodynamic sizes. The GPC-IR system removes the solvent and then deposits the chromatographic eluents as a continuous track on an IR-transparent ZnSe disc. The built-in interferometer simultaneously captures a set of time-ordered transmission IR spectra every 0.5 seconds from the solid-phase deposit. The snapshot IR spectra at each elution time can be used for the IR database search to identify the chemical compositions. A case study will be presented to deformulate a complex adhesive sample into 3 polymers and 3 additives by a single GPC-IR run and various IR database search approaches:

(1) Direct IR library matching for the baseline-resolved peaks.

(2) For the partially separated polymer peaks, the snapshot IR spectra at their leading/tailing edges can be used for the component library search. Spectral subtraction and Principle Component Analysis can confirm the results.

(3) In the low-MW region where most additives come out at similar elution times, the snapshot IR spectra in the highly overlapped area can be used for Multiple Component Search to identify each additive component (up to 4 sub-components by BioRad's KnowItAll software).

KnowItAll is a registered trademark of Bio-Rad Laboratories, Inc

GPG-IR chromatogram and identification of peak B
112 - Heparin-mimicking polymer conjugates stabilize basic fibroblast growth factor

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Biomimicry is an important research tool, and since the 1990s, biomimicry has grown to be one of the major innovation tools for drug and therapeutic discoveries. Here, we describe the synthesis and application of a heparin-mimicking polymer, consisting of styrene sulfonate and poly(ethylene glycol) methyl ether methacrylate monomer units. This polymer stabilizes basic fibroblast growth factor (bFGF) upon covalent conjugation. bFGF is a protein that performs crucial roles in diverse cellular functions, such as angiogenesis, tissue and bone regeneration, stem cell self-renewal, and wound healing; however, its therapeutic usefulness is not yet exploited due to issues associated with stability during storage and delivery. The described bFGF-heparin-mimicking polymer conjugate retained bioactivity after synthesis and was stable to a variety of environmentally and therapeutically relevant stressors, such as heat, mild and harsh acidic conditions, prolonged storage and enzymatic degradation. The native bFGF and control conjugate, where the styrene sulfonate monomer units were omitted from the polymer structure, were not stable to the same conditions. Furthermore, a second generation heparin-mimicking polymer has been identified that is capable of replacing heparin in facilitating binding of bFGF to its transmembrane tyrosine kinase receptors, which is the key event leading to cellular responses. These conjugate systems can be beneficial for the clinical use of bFGF and stabilization of heparin-binding growth factors in general. Discovery and synthesis of the polymers, conjugates, biological activity, and medical applications will be discussed.
Recent development of recombinant resilin-like polypeptides (RLPs) has fostered new opportunities for the design of therapeutic biomaterials for mechanically-demanding tissue engineering applications. Here, we describe hybrid hydrogels consisting of an RLP component, synthesized and purified from *E. coli*, which is cross-linked by a synthetic polymer, a multi-arm PEG macromer. We employ two cross-linking strategies: the first is a Michael-type addition reaction between cysteine residues on the RLP and vinyl sulfone groups on the PEG; the second is a photoinitiated thiol-ene cross-linking reaction between norbornene-functionalized RLP and a thiol-containing PEG macromer. Both strategies lead to elastic, resilient hydrogels as confirmed via oscillatory rheometry and tensile testing. Additionally, these hybrid hydrogels demonstrate the ability to viably encapsulate both human aortic adventitial fibroblasts and human mesenchymal stem cells. These RLP-PEG hybrid hydrogels exhibit the utility of a combined approach that harnesses the advantages of synthetic polymers as well as engineered protein polymers.
Towards smart polymeric drug carriers: Self-assembling γ-substituted polycaprolactones with highly tunable thermoresponsive behavior

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In an effort to develop stimuli-responsive polymer-based drug delivery vehicles, functionalized poly(caprolactone)s (PCL) are investigated. This report presents the synthesis of new functionalized ε-caprolactone monomers and diblock copolymers as well as the preparation of thermosensitive micelles for drug delivery applications. A multi-step synthetic procedure yielded two functionalized caprolactone monomers, γ-(2-methoxyethoxy)-ε-caprolactone (MECL) and γ-2-[2-(2-methoxyethoxy)ethoxy]-ε-caprolactone (MEEECL). Diblock copolymers (PMEEECL-b-PMECL) from the two monomers were prepared by ring-opening polymerization (ROP) using stannous 2-ethylhexanoate as catalyst and benzyl alcohol as the initiator. Various MEEECL:MECL monomer ratios were employed to achieve varying block lengths, which were correlated with properties like critical micelle concentration (CMC) and lower critical solution temperature (LCST). The hydrophilic block, PMEEECL, contributes to the thermosensitive nature of the polymer, due to the balance of its hydrophobic caprolactone backbone and hydrophilic MEEE side chain. The block lengths were shown to affect the LCST, which was lowered from 43 °C to 31 °C upon increased incorporation of MECL relative to MEEECL, shown in the figure below. The polymers demonstrated self-assembly into spherical micelles as evidenced by pyrene fluorescence CMC studies, dynamic light scattering, and transmission electron microscopy. Further study of the cytotoxicity and drug loading efficiencies of the polymers will be conducted. This preliminary work suggests the opportunity for polymeric micelles with highly tunable thermoresponsive behavior.
115 - Multivalent 3D display of glycopolymer chains from proteins for enhanced lectin interaction

Ken Lin, ken.zm.lin@gmail.com, Andrea M Kasko. Department of Bioengineering, University of California, Los Angeles, Los Angeles, CA 90024, United States

Synthetic mimetics that resemble natural glycoproteins can have many important tissue engineering and immunotherapy applications. One route towards incorporating saccharide content with proteins is with glycopolymers. Previous examples of protein-glycopolymer conjugates were through the "grafting-to" method. We have synthesized protein-glycopolymers through the "grafting-from" method to directly polymerize glycomonomers from a bovine serum albumin macrorinitiator without any further chromatographic purification. These protein-glycopolymers were shown to interact with recombinant mannose binding lectin. Increasing mannose number (controlled through the polymer chain length) and density (controlled through the comonomer feed ratio of mannose versus galactose) resulted in more interaction with MBL. The 3D presentation of multiple glycopolymer chains around the protein resulted in significantly enhanced interaction with MBL than compared to similarly sized linear glycopolymer chains with no 3D presentation. These enhanced binding results with small quantities of saccharides arranged in a multivalent 3D presentation can have profound impact in how glycopolymer conjugates are constructed, particularly when using compounds available in short supply. The combination of this saccharide presentation method with a protein component could potentially lead to materials with enzymatic activity combined with lectin binding properties.
116 - Pro-adjuvant strategy for delivery of vaccine adjuvants through PRINT nanoparticles

Sarah N Mueller¹, sarah.mueller@unc.edu, Shaomin Tian², Joseph M DeSimone¹,²,³. (1) Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (2) Lineberger Comprehensive Cancer Center, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States, (3) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States

Vaccines consisting of purified soluble antigens rather than killed or attenuated whole pathogens have shown great promise in increasing vaccine safety. However, these subunit vaccines (proteins, DNA, polysaccharides, lipids) are susceptible to degradation and are usually less immunogenic than whole pathogen vaccines. Subunit vaccines have shown increased efficacy when delivered in particulate form compared to soluble form, but there have been few examples of tunable release of active adjuvant from a nanoparticle delivery platform. Herein, we use PRINT® (Particle Replication In Non-wetting Templates) to fabricate polymeric hydrogel nanoparticles for the delivery of novel pro-adjuvants and protein antigens in vitro and in vivo. Resiquimod, a TLR 7/8 agonist, was used to synthesize a polymerizable, acid-labile pro-adjuvant. The pro-adjuvant loaded nanoparticles were capable of steadily releasing the original, active adjuvant when exposed to endosomal pH (pH 5), while protecting the adjuvant from premature release at physiological pH (pH 7.4). This allowed for intracellular delivery of resiquimod and limited systemic side effects.

The model protein antigen, ovalbumin (OVA), was directly conjugated to the surface of nanoparticles through a poly(ethylene glycol) (PEG) linker. Surface presentation of OVA led to antigen processing and presentation by antigen presenting cells and elicited robust immune responses. Therefore, PRINT nanoparticles can be formulated into potent particulate vaccines for controlled and efficiently co-delivery of adjuvants and antigens.

Monday, March 17, 2014 10:25 AM
Excellence in Graduate Polymer Research (08:30 AM - 11:40 AM)
Location: Hyatt Regency Dallas
Room: Reverchon A/B
117 - Structural impact and targeting effect of diblock glycopolymer pDNA delivery system

Yeoying Wu¹, wuxxx729@umn.edu, Miao Wang², Dustin Sprouse¹, Adam E Smith³, Theresa M Reineke¹. (1) Department of Chemistry, University of Minnesota, Twin Cities, Minneapolis, Minnesota 55455, United States, (2) Department of Chemical Engineering and Material Science, University of Minnesota, Twin Cities, Minneapolis, Minnesota 55455, United States, (3) Department of Chemical Engineering, University of Mississippi, University, Mississippi 38677, United States

A series of diblock glycopolycations were created by polymerizing 2-deoxy-2-methacrylamido glucopyranose (MAG) with either a tertiary amine-containing monomer, N-[3-(N, N-dimethylamino) propyl] methacrylamide (DMAPMA), or a primary amine-containing unit, N-(2-aminoethyl) methacrylamide (AEMA). Several structures were synthesized via aqueous reversible addition-fragmentation chain transfer (RAFT) polymerization that varied in the block lengths of MAG, DMAPMA, and AEMA. All of the structures were examined for their ability to complex plasmid DNA into polyplex structures and their ability to prevent colloidal aggregation in physiological salt conditions. Over the experimental time period, the polyplexes formed from these diblock copolymers were all stable from colloidal aggregation, according to dynamic light scattering and cryogenic transmission electron microscopy experiments. In vitro transfection experiments were performed in both HeLa (human cervix adenocarcinoma) cells and HepG2 (human liver hepatocellular carcinoma) cells to examine the role of block length on transfection efficiency and toxicity. The glycopolycation vehicles with shorter DMAPMA blocks exhibit lower cellular toxicity and higher transfection efficiency in both two cell lines than the other analogs. In addition, these analogs revealed higher cellular uptake and transfection efficiency in HepG2 cells than in HeLa cells.
118 - Synthesis of organic nanomaterials for photothermal ablation of cancer cells

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Currently chemotherapy is the most widely used technique to treat cancer. Although this method is effective at treating certain stages and types of cancer, there is a need for a more direct treatment. Recently, one technique that has gained interest due to high selectivity is photothermal therapy (PTT). The PTT approach uses photoabsorptive agents to ablate cancer cells by generating heat from externally applied optical energy via a laser. The vast majority of research focused on PTT is on the inorganic nanomaterials that absorb light in the near-infrared (NIR) region. We are currently developing an organic-based PTT nanomaterial utilizing a hydrophobic photoabsorptive polymer. The monomer 1,4-bis-(3,4-ethylenedioxythien-2-yl)-2,5-dihexyloxybenzene, \([\text{BEB-}(\text{OHex})_2]\) was synthesized and confirmed using NMR spectroscopy. \(\text{BEB-}(\text{OHex})_2\) was polymerized by emulsion polymerization to produce \(\text{PBEB-}(\text{OHex})_2\). After washing and re-suspending in water, the UV-Vis spectrum was acquired; a prominent absorbance was observed in the NIR region ~760nm. Transmission electron spectroscopy (TEM) showed that the morphology of the polymers to be fibril-like and sub 150nm in length. Irradiation of the suspension at 808nm yielded a temperature increase of ~13°C, exceeding the minimum temperature (45°C) necessary for PTT.
119 - Nanocarriers responsive to biological signals

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Over the 40 years of research history for drug delivery, a variety of excellent nanocarriers have been developed. Examples include liposomes, polymeric hollow spheres, polymeric micelles, dendrimers, hyperbranched polymers, and mesoporous silica, which are, in most cases, designed to respond to external stimuli such as pH, light, heat, redox, glucose, and aptamers for releasing drugs. In contrast with such well-explored nanocarriers, we herein report a new type of 1D nanotubular carrier, formed by supramolecular polymerization of a biomolecular machine such as GroEL, a barrel-shaped chaperonin protein. Because of its chemomechanical responsiveness to an endogenous signal ATP, its polymeric form, upon binding with ATP, can break up into short chain oligomers and monomer, thereby releasing guest compounds. The strategy to carry drugs with this machine-based nanocarrier is supported by the fact that the concentrations of intracellular ATP and Inflammatory tissues (cancer tissues) are much higher than those of extracellular matrices. This carrier shows a highly promising biodistribution feature. In addition to the above, we more recently developed a protein-based nanocarrier that selectively responds to other endogenous signals.

References

DNA and poly(N-isopropylacrylamide) are co-assembled onto gold nanoparticles. The DNA sequences can be reversibly exposed or hidden from the polymer surface in response to temperature cues, thereby translating the temperature trigger to the on-off switching of the surface chemistry and function. When exposed (> 33 °C), the DNA rapidly hybridizes to complementary strands, and chain-end biotin groups become readily accessible, while at lower temperatures these activities are largely blocked.
121 - Shape-changing polymer assemblies

Robert Barney Grubbs, robert.grubbs@stonybrook.edu, Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794, United States

A panoply of stimuli-sensitive polymorphic polymer assemblies has been constructed through the intentional synthesis of amphiphilic block copolymers comprising hydrophilic, stimulus-responsive, and hydrophobic blocks. Transformations among canonical micellar forms of polymer assemblies-spherical micelles, wormlike micelles, and vesicles (polymersomes)-have been demonstrated with a number of synthetic systems. This presentation will discuss recent progress in the development and understanding of these systems with a focus on open questions about kinetics of shape change, effects of block copolymer architecture on the rate and nature of the transformation, and potential applications.
122 - Building bone with polymers: An unconventional approach

Matthew L Becker, becker@uakron.edu, Department of Polymer Science, The University of Akron, Akron, OH 44325, United States

The current surgical options to address critical sized orthopaedic defects each have significant limitations. Versatile, resorbable polymeric materials for scaffold construction with sufficient mechanical properties to minimize supplementary external fixation could be used for numerous clinical applications where off the shelf solutions are not viable. The incorporation of the tethered growth factors, such as osteogenic growth peptide, offer a cost-effective solution to the current recombinant bone morphogenic protein-type technologies, which typically costs in excess of $10,000 per treatment. The safety of off label use of freely diffusing growth factors, like BMP, which are used to accelerate healing has been called into question. These concerns highlight the need for new approaches using tethered surface receptor-activated subunits, which remain at the implant site and desired site of action. The proposed osteogenic growth peptide-derivatized scaffolds can provide both mechanical reinforcement and enhance the bioactivity necessary for healing critical sized bone defects in large animal models.
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. 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. New catalysts have been developed that produce highly tactic ROMP polymers with Z double bond geometry.
124 - Polymeric nanocapsules (NCs) by interfacial crosslinking of surfactants in miniemulsion-based systems: Lessons from Wooley’s shell crosslinked knedel-like (SCK) nanoparticles

Chih-Kuang Chen, Yukun Li, Qing Wang, Yun Yu, Jiong Zou, Chong Cheng, ccheng8@buffalo.edu. Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260, United States

This presentation will highlight recent developments toward the preparation and study of polymeric NCs which are prepared by crosslinking surfactants in miniemulsion-based systems. The synthetic design of these materials was inspired by the seminal work in the Wooley lab, demonstrating the synthesis of SCK nanoparticles from block copolymer micelles. A variety of biodegradable polymeric NCs have been obtained by interfacial crosslinking of polymeric surfactants in transparent miniemulsions via UV-induced thiol-ene chemistry. Novel polyelectrolyte NCs have also been prepared by interfacial radical crosslinking of small molecule surfactants using miniemulsion-based templates. With inner cavities and special surface properties, these nanocapsules may have promising potential applications as nanoscopic scaffolds for drug and gene delivery.
125 - Molecular engineering of semiconducting polymers

Lei Fang\textsuperscript{1}, fang@chem.tamu.edu, Zhenan Bao\textsuperscript{2}. (1) Department of Chemistry, Texas A&M University, College Station, TX 77843, United States, (2) Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States

The first part of this presentation involves a polymeric conductive fullerene (C\textsubscript{60}) system. C\textsubscript{60} units were designed to be arranged in one-dimensional close contact by locally organizing them with covalent bonds in a spatially constrained manner. The electron mobility measured for the thin film field-effect transistor devices from the polymers was more than an order of magnitude higher than that from the monomers, as a result of the stronger electronic coupling between the adjacent fullerene units within the long polymer chains. This molecular design strategy represents a general approach to the enhancement of charge transport properties of organic materials via covalent bond-based organization.

The second part of the presentation describes the synthesis of a series of poly(isoindigo-dithiophene) based conjugated polymers with varying amounts of low molecular weight polystyrene (PS) side-chains via random copolymerization. The PS side-chain-decorated copolymers also demonstrated better thin film processability, without affecting the electronic and optical properties when the molar content of the PS-containing repeating units were \leq10\%. Bulk heterojunction solar cell devices fabricated with these PS-containing copolymers demonstrated significantly improved performances [maximum power conversion efficiencies (PCE) \textgreater7\% and open circuit voltages (VOC) \geq0.95 V. The synthesis, processing and device performances of PS-containing copolymers represent a new approach in molecular engineering to achieve a balance between the optical/electronic properties and solubility/processability of reproducible polymeric systems.
This talk will highlight three ongoing research projects in my group that were, in one way or another, inspired by concepts that I was first introduced to while working as an undergraduate researcher in Karen's group. First, our efforts to develop efficient, convergent synthetic routes to polymeric nanostructures with applications in self-assembly, synchronized multi-drug delivery, and multi-modal biological imaging will be described. Second, novel strategies for the synthesis and characterization of responsive polymeric networks will be outlined. Finally, a universal surface modification strategy based on chemically addressable N-heterocyclic carbenes will be discussed.
As a celebration and recognition of the contributions that have been made by my research group and collaborators over many years now, this presentation will highlight a progression of synthetic strategies for the preparation of functional polymer materials, where each strategy and material design is inspired by a targeted application.
128 - Development of sustainable polymers at Bayer MaterialScience

Don S Wardius, don.wardius@bayer.com, Bayer MaterialScience LLC, Pittsburgh, PA 15205, United States

Bayer MaterialScience is a major polymers company operating on a worldwide basis. Sustainability, helping the environment, and conserving resources are important themes at Bayer MaterialScience (BMS). Products and services brought to market by Bayer support the development and growth of renewable energy, energy-efficient buildings, and lightweighting for fuel savings in transportation / mobility sectors for society around the world. Some thermoplastics can be made from biobased chemicals derived from naturally occurring plant material. This talk will discuss part of BMS's recent effort to use more biobased materials, and illustrate the progress being made by discussing a new grade of thermoplastic polyurethane which possesses a higher biobased content and superior performance properties. The talk will also mention a catalysis breakthrough which could be used to incorporate carbon dioxide into the polyether polyols used to make polyurethanes. Typically in industry carbon dioxide is a waste, but in the future it may be recovered from flue gas, purified and employed as a co-reactant. A challenge for humankind is to find ways to move away from one-time uses of our raw materials and more towards a closed loop type of concept. The challenges and rewards of such ideas will be explored in the talk.
This presentation begins with an overview of the space of natural polymers and bio-based polymers and their role in meeting the society’s increasing need of sustainable materials. The concept of sustainability will be discussed based on the three pillars and global drivers of sustainable development, as well as the 2050 sustainability vision.

There are two strategies to utilize renewable feedstocks to produce polymers for sustainable applications. One strategy is using the natural polymers in their native macromolecular forms, the other strategy is to convert biomass into monomers first and then polymerize the monomers into bio-based polymers.

In the first strategy, technologies will be discussed to utilize the widely available natural polymers such as cellulose, starch, proteins, chitosan, algae, etc. for polymer applications. Although these natural polymers inherently have low carbon footprint, however, but due to the performance deficiencies of the natural polymers, various chemical and physical modifications and processes are often required to make natural polymers useful for applications, and these processing steps result in additional carbon emissions. Life cycle assessment (LCA) is needed to determine to true LCA benefits of these materials.

In the second strategy, natural biopolymers were used as starting feedstock to convert into bio-based monomers using biological, chemical, and thermal processes. The resulting monomers are then polymerized into various synthetic bioplastics using well-established polymerization methods. There are several such bio-based polymers on commercial scale including polylactic acid, bio-polyethylene, polyhydroxyalkanoate, partially bio-based polyesters and polyurethanes, etc. 100% bio-based polyethylene terephthalate (PET) is being developed. To make the bio-based polymers useful for commercial applications, further modifications are needed to improve the processing and in-use performance. Developing successful sustainable polymers also need to demonstrate business value in order to justify the cost premium of the bio-based polymers.
Combining renewable polymers, such as alginate, casein, and pectin with inexhaustible natural clays, processed in 100% yield from aqueous suspensions should be as close to a sustainable method of replacing transitional polymer foams as is possible. Both the advantages and the difficulties associated with such an approach will be presenting, including exceptionally low flammabilities, ease of tailoring mechanical properties over several orders of magnitude range, ease of biodegradation within a landfill. The importance of process variables will also be discussed, as will the difficulties of working with freeze drying of large volumes of relatively dilute materials.
**131 - Soybean based amphiphilic copolymer in personal care products**

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Recent 'all natural' and 'green' marketing choices forced industry of personal care products to consider use of bio-based components. Based on soybean oil, (2-vinyl oxyethyl soyate)-co-(penta-ethylene glycol vinyl ether) ((2-VOES)-co-PEGVE) surface-active copolymer was found to be a promising candidate for improving existing commercial shampoo/ body wash formulations. Our studies show that interactions between such copolymer and sodium lauryl sulfate (SLS) are evident in aqueous solutions to improve overall activity of both surfactants, as determined by surface tension, dye solubilization techniques and cosmetic performance tests.

Series of test shampoo formulations were developed, containing either (2-VOES)-co-PEGVE as single active ingredient or in combination with SLS, to further understand feasibility of soybean-based copolymer in personal care market. In a set of experiments, key properties of shampoos were evaluated and compared, such as: i) foam generation and stability; ii) cleaning activity; iii) conditioning action; iv) formulation rheology and shelf-life.

As a result, high potential of (2-VOES)-co-PEGVE as a surface active ingredient in shampoo formulations was observed. While copolymer improves cleaning action of targeted product, it also shows beneficial side-effects – viscosity increase and foam stabilization in the presence of grease. Performance of developed shampoo formulations was contrasted to that of commercial shampoos.

![Figure 1. Scheme of (2-VOES)-co-PEGVE copolymerization.](image)

**Monday, March 17, 2014 02:50 PM**

Sustainable Polymers, Processes and Product Applications (01:30 PM - 05:20 PM)

Location: Hyatt Regency Dallas

Room: Bryan-Beeman B
Sustainable Polymers, Processes and Product Applications (01:30 PM - 05:20 PM)
Location: Hyatt Regency Dallas
Room: Bryan-Beeman B
Cellulose nanocrystals (CNCs) are high-aspect ratio, mechanically stiff fibers which can serve as both a bio-renewable reinforcing agent in nanocomposites, as well as a handle for adding stimuli responsiveness. CNCs can be extracted from a wide range of natural cellulosic materials, with characteristics such as crystal structure, crystallinity and aspect ratio fluctuate widely between sources.

Here, we report lightly phosphorylated CNCs (P-CNCs), prepared using controlled hydrolysis of cotton with phosphoric acid, which are freely dispersable in polar solvents such as dimethyl sulfoxide, water and dimethyl-formamide. Thermal analysis reveals that these P-CNCs exhibit a much higher thermal stability than partially sulfated CNCs (S-CNCs), the current research standard. These CNCs are used to reinforce existing (bio)polymer systems using techniques previously unavailable due to the thermal instability of previous cellulose nanocrystals.

Moreover, we present our research focused on the design and fabrication of reinforced smart bionanocomposite materials created using said CNCs. By being able to tune the filler-filler and filler-polymer interactions, responsive nanocomposites can act as photo-switchable gelators, shape-memory nanocomposites or as a healable materials. Active moieties have been attached to the surface of cellulose nanocrystals and to the polymer matrix, showing we can induce by changing particular interactions.
134 - New innovations in renewable thermoplastic starch based materials

Amy Chen, amy.f.chen@kcc.com, James Wang, Greg Wideman. Corporate Research and Engineering, Kimberly Clark Corporation, Neenah, WI 54956, United States

Starch is a renewable natural biopolymer; it can be converted into thermoplastic starch (TPS). TPS has been investigated in detail in the recent decades for the plastic usage. It is renewable and biodegradable, but pure TPS has limited utility due to poor processability and mechanical properties; Polyethylene (PE) is the most common polymer for manufacturing flexible packaging films today, but it is made from fossil resources and not renewable. Recently, a new type of renewable polyethylene became commercially available; it is made from bio-ethylene from bioethanol through fermentation of sugarcane sucrose from sugarcane. The bio-based PE (Bio-PE) is renewable and has similar properties and processability of petroleum-derived PE.

To enlarge the processing window of TPS, PE and Bio-PE were applied in this study to blend with TPS. The structure-property relationship of different PE/TPS blend systems will be discussed in this presentation. Different film performance was revealed for these two different blend systems-PE/TPS and Bio-PE/TPS.

To improve the dispersion of TPS phase and obtain high performance blend films, TPS was processed into masterbatch (TPSM) first, and then blend with PE or Bio-PE. These new blend systems (PE/TPSM and Bio-PE/TPSM) led to improved mechanical properties of the final films.

Due to the large difference in polarity between TPS and PE, these two biopolymers are not compatible. Without compatibilizer, the film quality of the Bio-PE/TPS films was poor due to severe incompatibility and phase separation. The effect of different compatibilizers on the film quality and mechanical properties were also compared and discussed for PE/TPS and Bio-PE/TPS blend systems.

In summary, multiple blend systems of TPS, TPSM, PE, and Bio-PE with and without compatibilizers were processed into films, their mechanical properties were compared and studied related to phase structure. The morphology of these blend systems was investigated by scanning electron microscopy (SEM).

Monday, March 17, 2014 04:20 PM
Sustainable Polymers, Processes and Product Applications (01:30 PM - 05:20 PM)
Location: Hyatt Regency Dallas
Room: Bryan-Beeman B
The addition of cellulose in micro-nanometer scale increases the mechanical properties of thermoplastic starch also decreases the hygroscopicity of the material. Although, the disadvantage to use cellulose nano-micrometer scale is the process of obtaining the same, requiring different hazardous chemicals and abrasives. Due to this, the use of recycled cellulose from paper mills as reinforcement exhibit the advantage to be a sustainable material.

Different formulations were processed in a prototype extruder brand CINVESTAV, according to an experimental design, varying the type of reinforcement, hydrolyzed maize starch, native maize starch, gelatin and glycerol. Films were analyzed by tensile test, following the norm ASTM D638-00.

The values obtained in the mechanical characteristics of the films reinforced with recycled cellulose were higher than the films reinforced with microcellulose obtained chemically. This implies that use of recycled cellulose as raw material, it is good choice for manufacturing biodegradable packaging, since not only reduces manufacturing costs, but also increases the resistance of the materials.
136 - Environmentally-corrosive, high-performance biopolyamides derived from itaconic acid and their composites with montmorillonite

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Environmentally-corrosive, high-performance biopolyamides with a rigid N-substituted pyrrolidone ring was prepared from the biomonomer itaconic acid (IA), which was mass-produced by the fermentation of Aspergillus terreus. We used salt-type monomers composed of diacidic IA and diamines. These salts thermally converted into polyamides in the presence of sodium dihydrogen phosphate through the aza-Michael addition, followed by intramolecular cyclization to create a pyrrolidone ring in the polymer main-chain.

Figure 1. a) Syntheses of itaconic acid-derived polyamides from its salt with aliphatic diamines, b) Ring-opening conversion of pyrrolidone in polymer backbone.

Polyamides with molecular weights ranging over 28 000 showed Tg values over 87 °C, which were higher than conventional polyamides (around 57 °C). The Young's modulus and mechanical strength of these polyamides also showed high values of 430-2800 MPa and 90-165 MPa, respectively. In addition, the polyamides became soluble in water by ring-opening reaction of the pyrrolidone. Actually the ring-opening reaction was induced by ultra-violet irradiation and landfill in environmental soil as well as alkaline hydrolysis. Especially photo-induced water-solubilization is very important for development of environmentally-corrosive fish line to avoid the damage of creature in the sea. Moreover we will report the composite preparation of biopolyamides with clay such as montmorillonites to improve the mechanical properties.
137 - Adaptive charge transport in reconfigurable materials systems

Brett A. Helms, bahelms@lbl.gov, Changyi Li, Sean E. Doris, Niels L. Meereboer, John P. Lawrence. The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

We will describe our recent efforts in conferring polymer-inorganic nanocomposites with adaptive charge transport capabilities. Our research highlights a critical role played by block copolymers with tailored composition and topology to direct the assembly of inorganic nanocrystals into well-ordered hierarchical materials high interfacial volume, which can be used to direct charge transport. As a result of these characteristics, our polymer-inorganic nanocomposite materials are widely applicable as active layers for energy storage, catalysis, sensors, etc. The key to our success in these endeavors depends on the degree to which we can leverage their prevalence of interfaces, compositional heterogeneity, and structured confinement at the mesoscale to direct charge transport, and to what extent those efforts point towards design rules for achieving molecular level control over transport paths. Systems-level function under non-equilibrium conditions will be discussed, as well as strategies that enable interfacial reconfigurability as necessary to re-wire transduction pathways.

Monday, March 17, 2014 01:35 PM
Responsive Nanostructures and Nanocomposites (01:30 PM - 04:45 PM)
Location: Hyatt Regency Dallas
Room: Moreno A
This talk will describe the layer-by-layer (LbL) self-assembly of wavelength-selective photoresponsive polyelectrolyte multilayers (PEMs) that become soluble upon irradiation with visible or ultraviolet light. Random copolymerization of 2-(dimethylamino)ethyl methacrylate with a nitrobenzyl (NB) or coumarin-containing methacrylate monomer yields photoreactive polycations for layer formation by attractive electrostatic interactions with poly(styrene sulfonate). Irradiation with the appropriate wavelength of light cleaves the photoresponsive group from the polymer backbone resulting in reduced electrostatic attraction between the layers causing their dissolution in aqueous base. This photochemical control of the dissolution of PEMs allows for wavelength-selective patterning of surfaces (as shown in Figure 1) and selective release of guest molecules.
Vertically aligned arrays of multi-walled carbon nanotubes (MWNT forests) possess uncommon responsive properties. Upon infiltration of forests with polymer binder, we obtained highly elastic, electrically conductive composites that provided reproducible changes of resistivity at stretching for strains over 40%. The composites can be used for high deformation strain sensors and skin-like smart materials. When heated with alternating current, nanotube forests generated loud, audible sound typical for thermo-acoustic transducers. The latter can be applied for sound generation, noise cancellation, heat dissipation. If irradiated with low-intensity laser light, forests exhibited bolometric response that became significant with decreasing temperature. A combination of significant bolometric response and nonlinear electrical transport are characteristic features of nanostructured junction array system needed for design of advanced infrared detectors.
140 - Visible light responsive polymeric micelles based on novel organic photoswitches

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Stimuli-responsive micellar systems are an important class of materials with potential applications such as drug delivery and nanoreactors. Polymeric micellar systems are of particular interest because of their response to a wide variety of stimuli including pH, temperature, magnetic fields, and light. Light, of all, is a very attractive tool for altering the micelle formation because it allows spatial and temporal control as well as fine-tuning of parameters. This study introduces amphiphiles comprised of a novel organic photoswitchable molecule conjugated to a linear poly(ethylene oxide) chain end. We demonstrate the self-assembly of these unique amphiphiles into micelles in an aqueous medium and their responsiveness to visible light. Upon exposure, the photoswitchable unit isomerizes from a hydrophobic, extended form to a hydrophilic, compact form triggering micelle disruption and the release of cargo.

The responsiveness of this system to visible light, as opposed to UV light, expands the scope of applications for this technology to personal care, agricultural and home applications. In addition, this system exhibits reverse photochromism thus providing a convenient indicator of photoswitching and the delivery of guest molecules from the interior of the micelles.

Monday, March 17, 2014 02:40 PM
Responsive Nanostructures and Nanocomposites (01:30 PM - 04:45 PM)
Location: Hyatt Regency Dallas
Room: Moreno A
141 - Light and electrical responsive porous materials

Luisa De Cola¹, decola@unistra.fr, Wilfred G. van der Wiel², Henning Luelf¹, Robin N. Mahato². (1) ISIS, University of Strasbourg, Strasbourg, France, (2) MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Mesoporous and microporous materials have recently received a great attention for their potential use in biomedical applications. The use of silica as scaffold is particularly appealing due to the optical transparency and easy preparation and functionalization.

In our laboratories we have devoted a lot of effort to develop strategies to control the functionalization of zeolites and mesoporous nanomaterials. Asymmetric functionalization has been very recently achieved and will be illustrated. Also we have shown that the particles can be decorated with different biocompatible molecules and are able to perform drug and DNA or RNA delivery. The delivery can be probed by a kinetic analyses after the nanoparticles internalization. In particular using confocal fluorescent microscopy it is possible to follow the release of each single component as well as the positioning of the nanocontainers in real time and space.

Finally a new interesting development for the use of the pores as guides to organize in 1D electrically active molecules will be demonstrated. In particular the alignment of electro- or magnetoactive molecules inside the narrow channels of a zeolite L, resulted in the formation of molecular wires. The electrical conductivity measured can be foreseen as possible tool to address the release of the entrapped molecules or as a signaling that can be transferred to the edge of the porous material. Here, we report a very high magnetoresistance at room temperature in molecular wires. The electrical measurements on the 1D molecular wires were performed in a UHV conducting-probe atomic force microscope (CP-AFM). The molecular wire length is tunable between 30 and 100 nm and the resistance scales accordingly. An ultra-high (> 2000%) room-temperature magnetoresistance is observed for only a few mT.

This work has been supported by ERC Advanced Grant no. 247365
The functionality of ionic electroactive polymer (IEAP) actuators is due to the mobility of ions within the ionic membrane and polymer-metal nanostructure (PMNS). The ions are sourced by uptake of electrolyte (aqueous or ionic liquid) into the PMNS, and are mobilized when subjected to an external electrical stimulus. Thus far, the common understanding of the actuation mechanism in IEAP actuators has been that mobility of ions provided by the electrolyte is the primary origin of the mechanical response. Nafion, used as the backbone structure of most IEAP actuators, is an ion permeable polymer with sulfonate end groups and proton counterions. In this work, we have shown that the counterions of Nafion have significant effect on the performance of IEAP actuators and that actuation magnitude, direction and temporal response are closely related to the type of counterions of Nafion. We have studied samples consisting of Nafion in its original (protonated) form and Nafion with 1-ethyl-3-methylimidazolium (EMI) counterions and have shown that the counterions participate in the actuation process and influence the performance of the IEAP actuators. To further scrutinize the relation between polymer counterions and ions sourced by electrolytes, samples with proton (H) or EMI counterions were tested with different electrolytes. It was observed that systems with larger counterions exhibit larger cationic actuation magnitude, suggesting participation of the positively charged counterions in the generation of cationic actuation.
Stimuli-responsive polymers attached on nanoparticles or flat substrates are known to tremendously influence surface properties leading to so-called smart surfaces. Common external trigger can be the change of solvent, light, temperature or ionic strength. Compared to these classical stimuli, the electrical field or using redox reagents as external trigger are less investigated. Especially redox-responsive polymers attracted a lot of attention in the last decade. The most prominent redox couple in such polymers is the ferrocene/ferrocenium moiety which allows a fast and reversible switching. While oxidizing the ferrocene moieties (electro)chemically, the polymer chains undergo a remarkable transition from hydrophobic to hydrophilic accompanied by an induction of charge. The ferrocene oxidation/reduction cycles could be utilized for a responsive release of a dye from patchy nanocapsules, for reversible catalysis modulation, for switching the surface wettability and for ion-selective permselectivity through nano porous channels. The design of ferrocene-containing polymers and amphiphilic block copolymers bearing the lateral redox-active motif is reported. Furthermore, surface immobilization was investigated using surface-initiated atom transfer radical polymerization “grafting from” (ATRP) and “grafting onto” techniques by using end functionalization of ferrocene-containing polymers. These results point towards the importance of redox-active polymers to manipulate fast and reversibly the surface properties for applications in catalysis, membrane gating, sensing and a selective release.

Novel cations for anion exchange membranes remain of great importance. We report novel metal-cations based on supramolecular units capable of stability at 2 M KOH and 80 °C. These novel polymer cations have been fabricated into membranes and characterized. Their conductivity for hydroxide is 29 mS/cm at 30 °C and for bicarbonate is 10 mS/cm.
A new series of synthetic protein transduction domain mimics (PTDMs) was designed to analyze the importance of segregation along the backbone of guanidine and phenyl groups on their membrane interaction and cellular internalization abilities. The structure-activity relationships were evaluated by both a biophysical assay, using dye-loaded vesicles, and by \textit{in vitro} cellular uptake studies of fluorescently labeled chains into Jurkat T cells. The results showed that functional group segregation impacts activity. This study gives new design guidelines for the development of PTDMs.
Photoresponsive and biodegradable biomaterials: A tale of two chromophores

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Photoresponsive materials are advantageous in numerous applications due to the temporal and spatial control they provide. Our lab has developed two classes of photoresponsive polymers. The first of these is a class of photoresponsive polycarbonates incorporating the alkoxyphenacyl chromophore in the polymer backbone. When irradiated at 300 nm, these polymers undergo controlled chain scission (ACS Macro Letters, 2012). The second system is a class of coumarin based polyesters that undergo chain cross-linking at 350 nm and chain scission at 254 nm (Macromolecules 2013). The photoresponsive behaviors of the above polymers enable the fabrication of micropatterned thin films by photolithographic techniques. In addition, these polymers have also been investigated as potential controlled release matrices. In this presentation, we will demonstrate the novelty of these materials, their properties and their potential applications in various areas such as controlled release, fabrication of micropatterned devices, and bone regeneration.
Reperfusion of blood flow to the ischemic tissues results in a large generation of toxic reactive oxygen species (ROS) and exacerbates initial tissue damages. In particular, H$_2$O$_2$ induces release of pro-inflammatory cytokines and triggers apoptosis, leading to the oxidative damage to tissues in ischemia/reperfusion injury. Therefore, H$_2$O$_2$ has great potential as a diagnostic and therapeutic biomarker in I/R injury. We developed novel H$_2$O$_2$-responsive antioxidant nanoparticles formulated from copolyoxalate (PVAX) incorporating bioactive vanillyl alcohol as a novel I/R-targeted nanotherapeutic agent. PVAX was designed to incorporate VA and H$_2$O$_2$-responsive peroxalate ester linkages covalently in its backbone. PVAX nanoparticles therefore degrade and release VA, which is able to reduce the generation of ROS, and exert anti-inflammatory and anti-apoptotic activity.

During hind-limb I/R and liver I/R models in mice, PVAX nanoparticles specifically reacted with overproduced H$_2$O$_2$ and exerted highly potent anti-inflammatory and anti-apoptotic activities that reduced cellular damages.

Therefore, PVAX nanoparticles have tremendous potential as nano therapeutic agents for I/R injury and H$_2$O$_2$-associated diseases.
148 - Targeting cells of the immune system: Glyco-polymers for biomedical applications

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N(2-hydroxypropyl)-methacrylate-based polymers, p(HPMA), are well suited for biomedical applications. They are non toxic and not immunogenic. In addition they reduce toxic side effects and they accumulate in tumor tissue (EPR-effect)\(^1\). Tagged with carbohydrate structures, they have the potential to target specific cells due to interactions with lectins. In this respect mannosylated polymers are of increasing interest in cancer vaccination as they interact with receptors of cells of the immune system, e.g. macrophages. If polymers are tagged with Sialyl-Lewis\(^x\), a known selectin ligand, inflammation can be reduced by inhibition of specific selectins.

Synthesis of HPMA polymers via reactive ester precursor polymers has tremendous advantages for further functionalization. First, well-defined pentafluorophenolester polymers and copolymers can be synthesized by RAFT (reversible addition-fragmentation chain transfer) polymerization. They are easily amenable to GPC and NMR spectroscopy. In a subsequent reaction, the reactive ester copolymers are converted into HPMA-based polymers\(^2\). Simple carbohydrate structures (e.g. mannose), but also complex structures like Sialyl-Lewis\(^x\) can be easily attached during this step to target specific immunological cells. The resulting polymers can also be labeled with different dyes (e.g. NIR dyes) or radioactive tracers and used to track the distribution and specific accumulation in vivo (NIR or PET tomography). Here we describe the synthesis of these polymers and first in-vitro measurements to characterize the binding efficiency of the functionalized polymers.


149 - Organocatalytic methods and postpolymerization modification strategies for functional aliphatic polycarbonate synthesis

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Aliphatic polycarbonates represent a promising class of biodegradable and biocompatible soft materials for various nanomedicine applications. Examples of potential biomedical applications may include drug and gene nanodelivery, imaging, antimicrobial activity, and 'stealth' polymers for evading non-specific protein interactions. Depending on the specific intended application, custom functionality can be rationally incorporated into these polycarbonates at will. Our ability to generate diverse functional polycarbonates depends directly on the synthetic strategies and tools available for the facile and efficient preparation of precursor monomers and polymers. This presentation will focus on our recently reported fluoride-based organocatalytic method for synthesizing functionalized carbonate monomers, as well as the fluoride-promoted postpolymerization modification of a precursor polycarbonate. Additional new strategies for accessing diverse aliphatic polycarbonates via postpolymerization with functional amines will also be discussed.

Monday, March 17, 2014 03:30 PM
12th International Symposium on Biorelated Polymers (01:30 PM - 04:30 PM)
Location: Hyatt Regency Dallas
Room: Reunion Birm C
150 - Semicrystalline polyanhydrides synthesized from thiol-ene polymerization

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Polyanhydrides are traditionally used as drug delivery vehicles due to their surface erosion property, which allows the release rate of the drug to occur at the rate of erosion of the polymer. The most commercially successful polyanhydrides are semicrystalline and are synthesized via melt condensation reactions that require high temperatures and vacuum. Here we present a facile synthesis of semicrystalline polyanhydrides via thiol-ene photopolymerization. These polyanhydrides may be used as pre-polymers that can further undergo chain extension or crosslinking. These polymerizations are very fast (completed within minutes), use commercially available monomers and the polymers have thermal properties that are comparable to the previously developed polyanhydrides.
A new synthetic route for the fabrication of amphiphilic macromolecules containing hydrophilic PEG and lipophilic cholesterol fragments was developed (Fig. 1). The novelty of the synthetic pathway is in combining hydrophilic and lipophilic fragments in a backbone using functional groups of the pyromellitic dianhydride (PMDA). Macromolecules of cholesterol-containing pyromellitates undergo self-assembly and are able to solubilize lipophilic “guest” molecules in aqueous medium. High solubilization capacity and biodegradability, as well as other properties (size distribution, zeta-potential), make the synthesized macromolecules promising candidates for biomedical applications.

Fig. 1. Amphiphilic cholesterol-containing pyromellitates
The treatment of retinal degeneration by cellular replacement therapy is limited to early-stage degeneration due to an overall lack of injected cell support necessary for restoring retinal function. Stem cell scaffolds can offer the needed support, but the material physical properties play a major role in their success. The goal of this project is to provide support to differentiating replacement photoreceptor cells using a stem cell scaffold with controlled nanostructure.

Micro- and nano-porous cell scaffolds were synthesized by direct and lyotropic liquid crystalline (LLC) templating, respectively, of photopolymerizable pre-polymers. Micro-fabrication methods were used to control micron-scaled physical features such as pore size, while surfactant (LLC) chemical structure and concentration were used to control nano-scaled physical features. These physical features were characterized using x-ray scattering and microscopy. The scaffolds were also seeded with differentiating murine induced pluripotent stem (MiPS) cells. Cell growth and differentiation were characterized using microscopy and immunohistochemistry.

Pore size and spacing influenced stem cell growth and differentiation. The presence of nanostructure improved the diffusion properties of the material and thus influenced the growth and differentiation of cells as well. The optimized materials produced were shown to support the differentiation of induced pluripotent stem cells to mature retinal cell types.

An optimized material of this kind could lead to the successful transplantation of replacement cells and ultimately, restoration of retinal function in patients who suffer from retinal degeneration.
An annually produced surplus of elemental sulfur from petroleum feedstocks is only partially used for sulfuric acid production. The development of synthetic polymerization methods to convert elemental sulfur into useful polymeric materials is underexplored. Thermally induced ring-opening polymerization of elemental sulfur yields a chemically unstable polymer with undesirable properties. A facile synthetic copolymerization method, inverse vulcanization, enables direct preparation of chemically stable and processable copolymers with controlled sulfur-sulfur bond content. These novel materials possess properties suitable for infrared optics and high-capacity batteries, offering potential for sustainable energy and optics applications.
A novel π-conjugated donor-acceptor (D-A) poly(benzothiadiazole-sexithiophene-diketopyrrolopyrrole), PBDT6, was synthesized by incorporating a fused electron deficient diketopyrrolopyrrole (DPP) into poly(benzothiadiazole-sexithiophene), PBT6, a promising D-A co-polymeric semiconductor, to enhance the charge carrier transport properties and narrow the bandgap ($E_g$). The incorporation of branched side chains into π-conjugated polymers has been considered as an effective means to enhance polymer processability. However, when the branching position is close to the π-conjugated polymer backbone, steric hindrance inhibits π-π inter-chain stacking. Herein, a branched-linear side chain was synthesized and incorporated into PBDT6, PBDT6-DH, in which the branch session was moved away from the polymer backbone, thus preventing steric hindrance yet maintaining (or even improving) polymer solubility. PBDT6 possessing linear (PBDT6-OD) and branched (PBDT6-DT) side chains were also synthesized to study the impact of side-chain engineering on the macro-scale charge transfer properties. PBDT6 incorporating DPP shows a reduced value of $E_g$ (1.2 eV), compared to PBT6 (1.5 eV). Incorporation of the branched-linear chain increased degree of polymerization: PBDT6-DH attained a much higher MW (50k) compared with PBDT-DT (28k) and PBDT6-OD (14k). Organic field-effect transistor (OFET) devices were fabricated with all three polymer semiconductors via solution-processing. PBDT6-DH allows for a much higher hole mobility (reaching 3 cm$^2$/V$^{-1}$s$^{-1}$) than either PBDT6-DT (0.2-0.77 cm$^2$/V$^{-1}$s$^{-1}$) or PBDT6-OD (0.04-0.42 cm$^2$/V$^{-1}$s$^{-1}$). This side-chain engineering is an effective approach to enhance OFET performance, indicative of the importance of polymer structure-property relationships.
155 - Sorting of semiconducting SWNTs by conjugated polymers and their electronic applications

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Semiconducting single-walled carbon nanotubes (sc-SWNTs), with high charge carrier mobility and solution processibility, hold great promise for high-performance low-cost thin film transistor applications. However, separating the semiconducting (sc) from metallic SWNTs in large quantities still remains a challenge. We reported the sorting of sc-SWNTs with polythiophene derivatives in a simple and high yield method. MD simulation demonstrates that the polymers sides have significant impact on the sorting yield and the selectivity. The increased alkyl side chain lengths can bind the sc-SWNTs better due to the higher surface contact areas while the modeling of the polymer without side chains do not show any selectivity.

Additionally, we used the polymer-sorted sc-SWNTs for fabricating transistors as well as flexible complementary logic circuit. This was achieved by using our molecular n-type dopants to tune the carrier density of polymer-sorted SWNTs films by both vacuum evaporation and solution processing. We can tune the threshold voltage of SWNTs transistors continuously and reliably over a wide range. As a result of tunable doping, we fabricated inverter with unprecedented high noise margin of 28V at $V_{DD} = 80V$ (70% of $1/2V_{DD}$) and a gain of 85 by using inject printed dopants. sc-SWNT CMOS inverters (noise margin at ~72% of $1/2V_{DD}$), NAND and NOR logic gates, with rail-to-rail output voltage swing and sub-nanowatts power consumption, were also fabricated onto a highly flexible substrate for the first time.
Lithium polymer batteries offer a number of advantages to standard lithium ion batteries, including an all-solid state structure, increased safety, and the potential to be combined with lithium metal anodes for increased energy density over lithium intercalation anodes. However, the low-temperature (< 80 °C) ionic conductivity of polymer electrolytes has remained a major limitation over the past 40 years of academic investigation into polymer electrolytes. Progress in understanding strategies for systematic improvement in ionic conductivity has been dominated a single polymer for elucidating structure-property relationships in ionic conducting polymeric solids, i.e., poly(ethylene oxide). By increasing the domain of polymer materials to include a family of structurally related polymers with systematic variation in physical properties, fundamental insight into the relationship between polymer properties and ionic conductivity can be gained. We have synthesized a library of poly(glycidyl ether)s with similar molecular weight and polydispersities. The resultant materials exhibit systematic differences in glass transition temperature (Tg), viscosity, oxygen-content, dielectric constant, and ionic conductivity. No correlation was observed between ionic conductivity and glass transition temperature of the parent polymers or polymer-salt complexes, indicating that ion transport is not rate limited by polymer segmental dynamics in these amorphous electrolytes. Instead, ionic conductivity was observed to increase exponentially as a function of the dielectric constant of the parent polymers, indicating that the concentration of free ions governs the conductivity in these materials. This suggests that efforts should be directed towards increasing the dielectric constant of the parent polymers in electrolytes.
**157 - Improved polymer solar cell performance through new device designs**

**Luyao Lu, luyaolu@uchicago.edu, Luping Yu. University of Chicago, Chicago, Illinois 60637, United States**

In the first part, I will describe a cooperative plasmonic effect on improving the performance of polymer bulk heterojunction (BHJ) solar cells. When mixed Ag and Au nanoparticles are incorporated into the anode buffer layer, dual nanoparticles show superior behavior on enhancing light absorption in comparison with single nanoparticles, which led to the realization of a polymer solar cell with a power conversion efficiency of 8.67%, accounting for a 20% enhancement.

<table>
<thead>
<tr>
<th>NPs</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Best PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>15.0±0.08</td>
<td>0.72±0.01</td>
<td>67.4±0.56</td>
<td>7.2±0.10</td>
<td>7.3</td>
</tr>
<tr>
<td>Au</td>
<td>16.7±0.19</td>
<td>0.71±0.01</td>
<td>68.5±0.39</td>
<td>8.1±0.09</td>
<td>8.2</td>
</tr>
<tr>
<td>Ag</td>
<td>16.4±0.19</td>
<td>0.71±0.01</td>
<td>68.2±0.36</td>
<td>7.9±0.09</td>
<td>8.0</td>
</tr>
<tr>
<td>Dual</td>
<td>17.6±0.18</td>
<td>0.71±0.01</td>
<td>68.7±0.38</td>
<td>8.6±0.15</td>
<td>8.7</td>
</tr>
</tbody>
</table>

The cooperative plasmonic effect aroused from dual resonance enhancement of two different NPs. The idea was further unraveled by comparing Au nanorods with Au nanoparticles for solar cell application. Detailed studies shed light into the influence of plasmonic nanostructures on exciton generation, dissociation and charge recombination and transport inside thin film devices.

In the second part I will show an improved solar cell performance of 8.6% by incorporation of N-doped multi-wall carbon nanotubes (N-MCNTs) into BHJ solar cells composed of PTB7 and PC₇₁BM.

<table>
<thead>
<tr>
<th>N-MCNTs</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Best PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>15.0±0.08</td>
<td>0.72±0.01</td>
<td>67.4±0.56</td>
<td>7.2±0.10</td>
<td>7.3</td>
</tr>
<tr>
<td>1.0%</td>
<td>16.6±0.07</td>
<td>0.70±0.01</td>
<td>68.2±0.57</td>
<td>7.9±0.10</td>
<td>8.0</td>
</tr>
<tr>
<td>1.5%</td>
<td>17.4±0.36</td>
<td>0.70±0.01</td>
<td>68.6±0.45</td>
<td>8.4±0.10</td>
<td>8.6</td>
</tr>
<tr>
<td>3.0%</td>
<td>13.6±0.21</td>
<td>0.70±0.01</td>
<td>67.4±0.49</td>
<td>6.3±0.04</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Incorporation of N-MCNTs leads to not only increased nanocrystallite sizes but also smaller phase separated domain sizes of both PTB7 copolymers and PC₇₁BM from X-ray scattering study. N-MCNTs could also serve as extra exciton dissociation centers and charge transfer bridges. The facilitated charge separation and transport from N-MCNTs is further proved by determining the charge dissociation probabilities and effective charge carrier lifetime in the active layer material.
We report new solution processible n-type polymer semiconductors based on strong electron withdrawing building block naphthalene diimide (NDI) for all polymer solar cells. The new polymers, poly(naphthalene diimide)s (PNDIs), were synthesized by Stille coupling polycondensation reaction between NDI unit and various selenophene derivatives as a co-monomer. PNDIs were achieved with moderate to high molecular weight ($M_w = 12.3 - 177.9$ kg/mol) with a polydispersity of 1.1 – 2.6. By varying the co-monomers, optical properties and HOMO energy levels were varied due to intramolecular charge transfer while LUMO energy levels that governed by NDI unit were remained constant (-4.0 eV). X-ray diffraction analysis revealed highly ordered lamellar crystalline structure of PNDIs with the degree of crystallinity varying with the selenophene co-monomer structure. Charge transport properties were investigated by fabricating organic field-effect transistors, and PNDIs showed ambipolar or unipolar properties with high electron mobility that varied in the range of 0.008 – 0.24 cm$^2$/Vs. PNDIs were evaluated as acceptors in all polymer solar cells with thiazolothiazole based p-type polymer PSEHTT as a donor, and we found that the photovoltaic devices based on NDI-selenophene copolymer acceptor and PSEHTT donor exhibit a record 3.3 % power conversion efficiency with short-circuit current density ($J_{sc}$) of 7.78 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.76 V, and an external quantum efficiency (EQE) of 47 %.

**figure1.** Synthesis of n-type polymer semiconductors (PNDIs).
The discovery that the conductivity of conjugated organic polymers can be controlled through oxidation or reduction led to materials combining the electronic properties of metals with the weight and density of plastics. For this reason, such materials have been studied extensively and their importance recognized with the awarding of the 2000 Nobel Prize in chemistry to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa. The award stemmed from their work on conducting polyacetylene via doping with oxidants which they carried out in the late 1970s. While these studies produced the most dramatic results, investigations of conducting conjugated polymers date back to the early 1960s, particularly with the work of Donald Weiss on polypyrrole and Marcel Jozefowicz on polyaniline. Also commonly overlooked is the work of Berets and Smith who reported conductive polyacetylene doped with gases such as BF$_3$ and BCl$_3$ in 1968. This earlier work will be presented and then compared and contrasted with the later work of Heeger, MacDiarmid, and Shirakawa to try to give a more complete picture of the history of conductive organic polymers.

\[\text{polypyrrole} \quad \text{Weiss and coworkers (1963): } 10^4 - 1 \text{ S cm}^{-1}\]

\[\text{polyaniline} \quad \text{Buvet and Jozefowicz (1966): up to 30 S cm}^{-1}\]

\[\text{polyacetylene} \quad \text{Berets and Smith (1968): } 10^{-4} - 10^{-2} \text{ S cm}^{-1}\]

\[\text{Shirakawa, MacDiarmid, Heeger (1977): up to 560 S cm}^{-1}\]
160 - Traveling the south: The conjugated polymer journey from Texas to Florida to Georgia

John R Reynolds, reynolds@chemistry.gatech.edu, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, United States

Early work in the Reynolds group began at The University of Texas at Arlington synthesizing polyheterocycles, such as the regiosymmetric P(BTP(OR)2) shown below which provided a combination of high electroactivity and structural order. A subsequent program in electrochromic polymers (ECPs) was carried out at the University of Florida directed especially to dioxythiophene and dioxypyrrole type derivatives, such as the multi-color ECP P(BEDOT-Cz) shown below which could switch from a yellow neutral state, to a green intermediate state, and finally to a blue fully oxidized state. Ultimately, completion of the color palette for a full family of cathodically coloring ECPs was accomplished as exemplified by the magenta to highly transmissive switching properties of the PProDOT-(CH2OEtHx)2 shown below. Having these processable polymers on hand now allows a variety of coating and printing methods to be employed at Georgia Tech where we prepare EC films using spray-coating, blade-coating, slot die-coating, and inkjet printing.
Past, present and future of polybenzobisazoles

Malika Jeffries-EL, malikaj@iastate.edu, Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

Polybenzobisazoles were initially synthesized as high performance materials. As a result of their rigid conjugated backbone these materials possess excellent thermal and oxidative stability and can be spun into high tensile strength fibers. At the same time, polybenzobisazoles are also ideally suited for diverse organic semiconducting applications, but have found limited utility due their lack of solubility in organic solvents. Typically, benzobisazoles are synthesized via condensation reactions, in acidic mediums at high temperatures, preventing structural modification. Recently we developed a mild approach for the synthesis of functional benzobisazoles resulting in a new generation of solution processable polybenzobisazoles. The optical electronic and physical properties of these polymers will be presented.
Pi-conjugated polymers have attracted considerable attention over the past decade due to the advantageous combination of their electrical, optical and film-forming properties. A major milestone for this emerging technology consists in achieving functional device fabrication by means of large-area printing. As printing involves liquid solutions of functional substances from a limited variety of solvents, multi-layer devices can, in most cases, only be fabricated by alternating printing and curing steps. The latter can both be achieved by cross-linking or removal of solubilizing groups and can be initiated by chemical, thermal or photochemical stimuli or a mixture thereof.

Our work aims at the immobilization of semiconducting molecules by the external stimulus of heat. Inspiration for our approach is acknowledged to work by Fréchet and Krebs who introduced tertiary esters of poly(thiophen-3-carbocyclic acid-2,5-diyl)s which can be transformed into native polythiophene above 300 °C for use in organic solar cell devices. A major drawback of these materials remains the need for high processing temperatures, which delicately limit their application in functional devices. Thus, we focused on developing new thermally cleavable solubilizing groups that allow immobilization of functional polymers.

We developed a variety of new polymers and intermediates bearing thermocleavable groups employing an easily scalable synthetic route. Our contribution will discuss synthetic aspects of these new materials as well as studies related to their future application in printable organic electronics.
163 - Hyperbranched perfluorinated polymers for proton exchange membranes

Matthew J. Quast, Anja Mueller, muell1a@cmich.edu. Chemistry, Central Michigan University, Mt. Pleasant, MI 48859, United States

A facile, alternative synthesis for hyperbranched perfluorinated polymers with greater molecular weight and lower polydispersity index was developed. The reaction mechanism was explored, the amount of branching was investigated. Cyclization probability was governed by concentration. The reaction conditions also allowed for more controlled and effective substitution with proton transporting groups and crosslinking agents. Initial membrane formation results will be presented as well.

Tuesday, March 18, 2014 10:10 AM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (08:00 AM - 12:00 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blr m C
Materials with high number densities of molecules that exhibit large real third-order optical nonlinearities and that also have low linear and nonlinear loss mechanisms may be of utility for a range of all optical signal processing applications. To date, most molecules and polymers that have large real third-order optical nonlinearities tend to have acceptably large two-photon cross sections. Here, we will report on our studies of cyanine molecules, to better understand both their two-photon cross sections and their third-order susceptibilities. We have found that it is possible to identify systems at particular wavelengths with very small two-photon cross sections but with large third-order susceptibilities. We will discuss recent advances in the design, synthesis, characterization and application of molecules with large real third-order optical nonlinearities, focusing on how variation in chemical structure relates to the observed nonlinearities and how substitution on the molecule (see Figure 1) can help to prevent undesirable aggregation.

Figure 1: Schematic showing some of the structural features of polymethine dyes that can be varied to inhibit aggregation.
We have been studying conjugated polymers, in particular, poly(alkyl thiophene-3-carboxylates) (1) and poly(dialkyl 2,2'-bithiophene-4,4'-dicarboxylates), and examining regiorandom and regioregular backbones looking for intramolecular interactions. Based on spectroscopic data and ab-initio quantum mechanical calculations on bithiophene model compounds it was concluded that there are attractive interactions between the carbonyl oxygen in one ring and the sulfur atom in the adjacent thiophene ring (2). X-ray crystal structures of these model bithiophenes showed conclusively that this was indeed the case. In simple head-to-head methyl esters there was too much steric interaction and so the bithiophene was severely twisted. However, with the carbonyl groups in 5-membered rings, even the head-to-head systems (3) were planar as shown by quantum mechanical calculations and X-ray structure determination. In these systems, when the carbonyl was replaced with a CH₂ group (4) the bithiophenes were calculated to be twisted. Work on additional systems 5 and 6, including syntheses and X-ray structure determination, will be presented. We have looked for a similar electrostatic attraction between the sulfur atom of one thiophene and an electronegative fluorine atom in the benzylic position of the adjacent thiophene. Compounds 7 and 8 were synthesized and studied. Compound 7 was a liquid so 8 was prepared. X-ray structure determination showed that any intramolecular S–F interactions in 8 are very weak at best, however there are significant intermolecular S–F interactions which affect the crystal structure.
Liquid crystalline diblock copolymers containing regioregular poly(3-hexylthiophene) (P3HT) and poly(n-hexyl isocyanate) (PHIC) have been synthesized by the combination of Grignard metathesis polymerization (GRIM) and titanium mediated coordination polymerization methods. The synthesized diblock copolymers displayed solvatochromism in THF/water and THF/methanol mixtures. The field-effect mobilities of the synthesized block copolymers were measured in bottom gate-bottom contact organic field-effect transistors (OFETs). The surface morphology of the polymer thin films were investigated in the channel region of the OFET devices by tapping mode atomic force microscopy (TMAFM). The diblock copolymer displayed nanostructured morphology in thin films and had good mobilities. The X-ray diffraction patterns confirmed the crystallinity the liquid crystalline semiconducting diblock copolymer.
167 - Development of a renewable plasticizer portfolio for vinyl applications

Stephen J Howard, George Poppe, Erik C Hagberg, erik.hagberg@adm.com. Archer Daniels Midland, United States

The development of bio-derived, renewably sourced chemicals presents an opportunity to reduce the environmental footprint of the chemical industry and build new technologies. Applications of bio-derived feedstocks include monomers for a wide variety of polymer systems and additives such as plasticizers and lubricants. In one example, ADM and PolyOne have collaborated to develop and commercialize novel, value added, bio-based plasticizers from corn and oilseeds. Initial work has led to the commercial launch of two materials, reFlex 100™ and reFlex 300™, built upon epoxidized oils technology. Continued efforts have produced a number of unique high value plasticizers such as epoxidized benzyl soyate which bring performance advantages beyond what is possible with conventional plasticizer platforms. The chemistry and properties of these materials will be discussed.

Tuesday, March 18, 2014 08:30 AM
Sustainable Polymers, Processes and Product Applications (08:30 AM - 11:50 AM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm F
A great challenge to overcome is the replacement of traditional petroleum-based polymers with materials derived from sustainable, alternative resources. Of particular interest is the design of nanostructured polymers from sustainable sources with well-defined molecular characteristics and competitive properties to petroleum-derived materials. We have developed sustainable triblock copolymers with hard, glassy outer blocks and a soft, rubbery midblock which can act as thermoplastic elastomers (TPEs). Our previous work has focused on vegetable oils as a renewable source for the TPE components. In this study, we are utilizing rosin-derived polymers to make fully sustainable TPEs. Rosins are obtained from trees such as conifers and offer advantages of cycloaliphatic groups and aromatic structures that are appropriate for the derivation of glassy polymers. In this study, we have synthesized fully renewable TPEs that contain a flexible vegetable oil-derived midblock and rigid rosin-derived end-blocks. We have utilized reversible addition fragmentation chain transfer polymerization for polymerizing methacrylate monomers derived from the renewable resources, for the production of triblock copolymers. The thermal and mechanical properties and thermodynamic self-assembly of the fully sustainable TPEs have been characterized.

**Sustainable Polymers, Processes and Product Applications (08:30 AM - 11:50 AM)**
**Location: Hyatt Regency Dallas**
**Room: Reunion Blrm F**
Cyanate ester monomers and their corresponding cyanurate networks derived from renewable and sustainable resources have exhibited a remarkable range of performance characteristics. These characteristics range from monomers with melting points below room temperature and with low moisture uptake and performance comparable to the best epoxy resins to networks with thermal resistance similar to the best available thermosetting resins of any type. The wide range of performance enables structure-property relationships for thermosetting networks to be utilized to tailor and enhance the properties of these new systems. For instance, oxidation, cyclotrimerization and subsequent functionalization of the renewable essential oil anethole enables the production of trifunctional monomers that, when cured into a macromolecular network, provide superior thermal performance compared to networks generated from bifunctional anethole derived monomers. For improved toughness, interpenetrating and/or graft co-networks can be formed by mixing highly compatible blends of polycarbonate thermoplastics and cyanate ester monomer derived from the same bio-based phenolic precursor, as illustrated with bifunctional eugenol derivatives. These enhancements facilitate the creation of products from renewable and/or sustainable sources that can meet the full range of application requirements typically associated with cyanate ester resins.
170 - Redox-controlled and telechelic polymerization reactions of cyclic esters using iron bis(imino)pyridine catalysts

Jeffery A. Byers, Jeffery.Byers@bc.edu, Ashley Biernesser. Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States

The ring opening polymerization and copolymerization of cyclic esters using iron complexes containing bis(imino)pyridine complexes will be discussed. The ring opening polymerization, which is very sensitive to the electronic nature of the catalyst, can be switched off and on by oxidizing and reducing the metal center, respectively. Additionally, application of the environmentally benign iron catalysts for telechelic polymerization will be disclosed. Application of both redox switching and telechelic polymerization for the synthesis of block copolymers will be discussed.
171 - Processing natural polymer biocomposites under severe shear deformation conditions

Xiaoqing Zhang, Xiaoqing.Zhang@csiro.au, CSIRO Materials Science and Engineering, Melbourne, VIC 3168, Australia

This presentation reports our new success in producing biocomposites from raw wood flour (WF) by equal channel angular pressing (ECAP) method under severe shear deformation conditions. Bulk natural polymer biocomposites were successfully produced from processing cellulose and wood flour powders without additional plasticizers. The processing capability was significantly improved by using wheat gluten (WG) as additives and the processing temperature was decreased to 125°C. Strong intermolecular interactions between the WG segments and the amorphous components of WF were facilitated by such severe shear deformation. The composites displayed high flexural strength/modulus especially when the amount of WG was 20–30 wt%. It provides a promising method to produce bulk biocomposites from cellulose-based raw agriculture waste.
172 - Synthesis of renewable polyester containing oxabicyclic dicarboxylate derived from furfural as inedible biomass

Yuya Tachibana, tachibana@gunma-u.ac.jp, Masayuki Yamahata, Saori Kimura, Ken-ichi Kasuya. Faculty of Science and Technology, Gunma University, Kiryu, Gunma 3768515, Japan

Changing biomass from edible to inedible is essential to solve global food issues. Furan derivatives are ideal chemicals for green chemistry because they are produced from inedible biomass resources. Here, we report the preparation of biomass-based oxabicyclic dicarboxylic anhydride derived from furan derivatives and its polymerization with several diols to polyoxabicyclates. NMR spectra and MALDI-TOF MS measurements verified the chemical structure of the polyoxabicyclates. Polyoxabicyclates prepared using 1,3-propanediol or 1,4-butanediol could be moulded into elastic films by melt pressing. Tensile strength testing of the films indicated that they were highly elastic. Furthermore, the films had good transparency in the visible region.

Figure 1. Stress-strain curves for POBC-c, POBC-a, and polyethylene LDPE.

Figure 2. The POBC-c film (0.10 mm thick) covers the right half of the photograph.
173 - Synthesis and preparation of large iron oxide nanoclusters with various topologies via block molecular bottlebrushes

Alper Nese, nese@mailbox.sc.edu, Jeffery Hayat, Chuanbing Tang. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States

Block molecular bottlebrushes consist of a sustainable/degradable polylactide (PLA) block and an iron oxide precursor polymethacrylate with ferrocene side unit (PFeMA) block were synthesized. A combination of atom transfer radical polymerization, ring opening polymerization, and ring opening metathesis polymerization were used. Once the block molecular bottlebrushes self-assemble into nanoscale morphologies, PLA part was removed and remaining block was converted into iron oxide nanoclusters. By tuning the volume percentage of each block, iron oxide nanoclusters with various sizes and topologies were prepared. Nanoclusters in the level of 100 nm were obtained as a result of the very high molecular weight and extended conformation of the molecular bottlebrushes. Such large size iron oxide nanoclusters formation could not be obtained by using self-assembly of linear diblock copolymers and here emerges as a new application of molecular bottlebrushes. Resulting materials can find wide applications from catalysis to magnetic data storage.
Polyoxalates from biorenewable diols via oxalate metathesis polymerization

John J. Garcia, johngarcia@ufl.edu, Stephen A. Miller. Department of Chemistry, University of Florida, Gainesville, Florida 32608, United States

Oxalate Metathesis Polymerization (OMP) was developed for the synthesis of polyoxalates, which were subjected to molecular weight and thermal property analysis. This methodology employs para-toluene sulfonic acid for the acid-catalyzed ester interchange of dimethyl oxalate and diols. Polyalkylene oxalates were derived from dimethyl oxalate and linear diols HO–(CH₂)ₙ–OH with three to twelve methylene groups (n = 3 – 12). Poly(decylene oxalate), a known polymer based on (potentially biorenewable) decanediol was synthesized in 83% yield with this methodology and exhibited no discernable Tₘ, a Tₘ of 79 °C, and a Mₘₜₜ of 67,600 g/mol. Polyarylene oxalates were derived from dimethyl oxalate and resorcinol bis(hydroxyethyl)ether (RBHE) or hydroquinone bis(hydroxyethyl)ether (HBHE), aromatic diols that can be obtained from biorenewable resources. The poly(resorcinol bis(hydroxyethyl)ether) oxalate (or poly(RBHE) oxalate) was obtained in 56% yield and showed a Tₘ of 34 °C and a Tₘ of 156 °C. The poly(hydroquinone bis(hydroxyethyl)ether) oxalate (or poly(HBHE) oxalate) was obtained in 88% yield and showed a Tₘ of 45 °C and a Tₘ of 190 °C. Aliphatic/aromatic polyoxalate copolymers derived from 1,10-decanediol and RBHE or HBHE in varying compositions were prepared and studied. Incorporation of the aromatic diols into the polymer chain generally afforded increased Tₘ and Tₘ. Solid-state degradation studies indicated facile water-degradation of the polyoxalates as molecular weights decreased 81–92% over the course of 13 months in humid air.
Smart materials have been attracting much attention because of their stimuli responsive nature. We have synthesized biocompatible thermoresponsive crosslinked polyethylene glycol methyl ether methacrylate (PEGMA)-co-vinyl pyrrolidone nanoparticles (PEGMA NPs) using disulfide based crosslinker by surfactant free emulsion polymerization (SFEP) method. Particle characterization studies were carried out by dynamic light scattering (DLS) and scanning electron microscopy (SEM). Polymerization kinetics, effect of crosslinker and initiator concentrations on both average hydrodynamic diameter and polydispersity index were investigated. Hydrodynamic diameters of thermoresponsive PEGMA NPs were decreased from 210 nm to 90 nm upon heating over the lowest critical solution temperature (LCST). Disulfide crosslinked PEGMA NPs were demonstrated as a dual delivery system. Rhodamine B, a model of small sized drug molecule, and PEG-alizarin yellow, a model of large drug molecule, were loaded into PEGMA NPs where the LCST of these NPs was tuned to 37 °C, the body temperature. The rhodamine B was released from PEGMA NPs upon heating to 39 °C. Then, PEG-alizarin content was released by subsequent degradation of nanoparticles using dithiothreitol (DTT) which reduces disulfide bonds to thiols. Furthermore, cytotoxicity studies of PEGMA NPs were carried out in 3T3 cells, which resulted no toxicity effect on the cells.
176 - Rapid degradation mechanisms and novel photocage to allow light-triggered release in vivo

Caroline de Gracia Lux¹,², Jason Olejniczak¹,³, Carl-Johan Carling¹,², Mathieu L. Viger¹,², Arnold Garcia¹,², Adah Almutairi¹,², aalmutairi@ucsd.edu. (1) Center of Excellence in Nanomedicine, UC San Diego, La Jolla, CA 92093-0600, United States, (2) Skaggs School of Pharmacy and Pharmaceutical Sciences, UC San Diego, La Jolla, CA 92093-0600, United States, (3) Department of Chemistry and Biochemistry, UC San Diego, La Jolla, CA 92093-0600, United States

Our long-term goal is to create polymeric materials that allow the activity of any encapsulated molecule to be controlled by light in living organisms. Building on our development of the first polymer to degrade in response to biologically useful powers of near infrared (Fomina et al., Macromol 2011), we have recently turned to polymeric backbones that rapidly translate photo-triggered deprotection into breakdown into small molecules. Inspired by the hydrolysis-independent, spontaneous cyclization of ornithine in peptides, we developed an ornithine-based poly(ester amide) and a poly(ε-caprolactone) bearing ornithine-inspired linkers to triggering groups (de Gracia Lux et al., J Polymer Sci A 2013 and de Gracia Lux and Almutairi, ACS Macro Lett 2013). PEA-Orn degrades 40 times faster than a control lysine-based PEA, and the ornithine-inspired PCL degrades by cyclization alone.

To create a polymer that degrades rapidly upon irradiation and slowly in the absence of light to allow clearance of all nanoparticle material, we are developing a series of polylactide-like polymers that degrade by cyclization. In order to enable near infrared-triggered release from nanocarriers, which is not possible using hydrophobic polymers because bromocoumarins require water for photocleavage, we are incorporating the ornithine structure into a bromocoumarin-bearing hydrogel crosslinker. Finally, since two-photon processes at greater than millimeter depths in tissues require complex beam adjustments, we are developing a polymer that degrades in response to visible light by incorporating a donor-acceptor biphenyl photocage. These advances promise to make light-triggered delivery of a broad range of molecules much more useful in biological research.
177 - Sub-10 nm solid lipid nanoparticles for the topical delivery and thermally activated release of therapeutics

Jason J Benkoski, jason.benkoski@jhuapl.edu, Xiomara Calderón-Colón, Marcia W Patchan, Mellisa L Theodore, Huong T Le, Jennifer L Sample, Julia B Patrone. Research and Exploratory Development Department, The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, United States

Burn injuries, trauma, and surgical procedures result in complex skin wounds that can lead to inflammation, infection, and scarring. Management of complex wounds remains a critical challenge for the medical community due to the lack of localized treatments that provide sustained drug release. Solid lipid nanoparticles (SLNs) are a promising platform for delivering lipophilic compounds topically to skin. Made entirely from ingredients generally regarded as safe (GRAS), the SLNs are biocompatible, stable, accept a wide range of therapeutics, and penetrate the epidermis. In this study, we synthesized sub-10 nm SLNs using the Phase Inversion Temperature (PIT) method. The SLNs are designed to melt at skin temperature (32°C) and thus release their payload in response to skin contact. A systematic Design of Experiments (DOE) approach investigated the role of synthesis parameters on SLN form and function. Particle size and polydispersity were measured as a function of dye solubility, phase inversion temperature, melting point, and latent heat of melting. The particle size distribution was largely invariant to these processing parameters, suggesting that SLNs may serve as a universal carrier for lipophilic therapeutic compounds. Inspection of ex vivo porcine skin samples further demonstrated the penetration of dyes across the entire viable epidermis. Also demonstrated was the delivery of an immunosuppressant drug, rapamycin, through approximately two-thirds of the porcine epidermis. For comparison, the control samples exhibited no penetration due to their sparse solubility in water.

Figure 1. Schematic of solid lipid nanoparticle depicting the outer surfactant layer, inner lipid core, and entrained lipophilic compounds.
We present polycarbonate based hydrogels that contain semibranched polyglycidols entrapped into the polycarbonate-diethylene oxide matrix. The primary OH groups of the polyglycidol can react in a transesterification reaction to form reconfigurable cross-linked materials. Allyl and ethylenoxide functionalized linear polycarbonates react with dithiol oxides derivatives to form cross-linked networks via thiolene click reactions, in the presence or absence of semibranched polyglycidols. Swelling capabilities and degradation in PBS buffer and simulated gastrointestinal fluid are investigated. Paclitaxel is chosen as model drug to study the drug release from a diverse set of carriers. The presence of the polyglycidol as well as the length of the dithiol crosslinker influenced the swelling capabilities and are responsible for a varied drug release behavior. The reconfigurable nature of the transesterification reactions leading to novel materials those are tougher than the comparable hydrogels to carry entrapped semibranched polyglycidols. Furthermore, aminooxy modified polyglycidols are cross-linked to functionalized linear polyesters in buffer without using an external stimulus. The variation in the amount of polyester precursors to polyglycidol and the effect on drug release and swelling are presented. The introduction of a third component in form of 3-D polyester nanosponge materials results in a unique set of modular components that can shape the nature of the prepared hydrogel materials in terms of multicomponent drug delivery systems with tailororable release profiles for the individual drugs of the same or different nature in solubility and molecular weight.
179 - Enzyme-responsive nanoparticles and their utility in tissue targeting

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The goal of targeted therapeutics and molecular diagnostics is to accumulate drugs or probes at the site of disease in higher quantities relative to other locations in the body. To achieve this, there is tremendous interest in the development of nanomaterials capable of acting as carriers or reservoirs of therapeutics and diagnostics in vivo. Generally, nanoscale particles are favored for this task as they can be large enough to function as carriers of multiple copies of a given small molecule, can display multiple targeting functionalities, and can be small enough to be safely injected into the blood stream. The general goal is that particles will either target passively via the enhanced permeability and retention (EPR) effect, actively by incorporation of targeting groups, or by a combination of both. Nanoparticle targeting strategies have largely relied on the use of surface conjugated ligands designed to bind overexpressed cell-membrane receptors associated with a given cell-type. We envisioned a targeting strategy that would lead to an active accumulation of nanoparticles by virtue of a supramolecular assembly event specific to tumor tissue, occurring in response to a specific signal. The most desirable approach to stimuli-induced targeting would be to utilize an endogenous signal, specific to the diseased tissue itself, capable of actively targeting materials introduced via intravenous (IV) injection. We present the development of nanoparticles capable of assembling in vivo in response to selective, endogenous, biomolecular signals. For this purpose, we utilize enzymes as stimuli, rather than other recognition events, because they are uniquely capable of propagating a signal via catalytic amplification.
Responsive soft materials have drawn broad interest in many areas including drug delivery and tissue engineering. Herein, ring opening polymerization (ROP) of racemic allylglycine N-carboxyanhydride (NCA) is utilized to facilely synthesize novel, multi-responsive triblock polypeptide-based hydrogelators. This triblock system, poly(DL-allylglycine)-block-poly(ethylene glycol)-block-poly(DL-allylglycine) (PDLAG-b-PEG-b-PDLAG), is shown to be capable of performing reversible thermo-responsive sol-to-gel transitions within minutes and sonication-responsive gel-to-sol transitions within seconds. An enzyme-responsive gel-to-sol transition is also observed by mass loss measurements as a function of time. Critical gelation temperatures for this system is shown to be tunable with controlled feedstock composition for the PDLAG segments. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), wide-angle X-ray scattering (WAXS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used to study the mechanism of gelation and the results indicate that this hydrogel system is driven by the formation of β-sheet secondary structure between polypeptide segments, with resultant self-assembly into inter-crosslinked fibril networks. In total, these allyl-functionallized smart hydrogelators are suggested to provide a platform to develop multi-responsive hydrogels appropriate for expansion into biomedical applications.
181 - Bioreducible polymeric nanoparticles

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The most common approach to synthesizing responsive materials for drug delivery applications has relied on pH sensitivity because of the known acidity in tumor regions and the acidification known to occur during some modes of endosomal trafficking. Research has shown that the use of bioreducible bonds can be an effective approach to stimuli-responsive activation of molecular metal-based therapeutics, coined “activation by reduction,” which has been observed for Pt, Ru, and Co complexes. Typically, the metal is inert to ligand substitution reactions in its higher oxidation state, but undergoes facile ligand exchange once reduced. This activity capitalizes on intracellular reduction potential (~200 mV), which is 100-1000 fold more reducing than extracellular space. Our work is geared toward expanding this known chemistry to targeted drug delivery where this activity could be used to deliver metal-based therapeutics, or as a stimuli-responsive structural element to trigger particle degradation and release of an additional therapeutic. Application of this strategy using Co and Ru complexes will be discussed.
Delivering and releasing drugs at their target in a controlled fashion remains a key determinant of successful treatment and might contribute to reducing side effects. By using liposomes as basic drug carriers and combining them with hydrophobic superparamagnetic iron oxide nanoparticles (SPIONs), investigations in our lab have led to the development of nanoparticle-liposome hybrids with large nanoparticle clusters directly embedded within the membrane bilayer. SPIONs heat up under the effect of a magnetic field, thus offering a potent release trigger as soon as the target is reached.

Furthermore, these nanoparticles act as contrast agents in magnetic resonance imaging (MRI) and can thus additionally act as a tag for tracking down the present location of the injected medicine. Unlike previous reports, our system enables an incorporation of a far larger quantity of nanoparticles, which in turn improves the resolution and quality of MRI tracking and release efficiency. Finally, we show that the elasticity of liposome membranes is far greater than previously expected and allows the embedding of structures between bilayers far larger than assumed, which consequently opens a large field of biological and medical applications.
Serina Therapeutics, Inc. has developed a patented, proprietary poly(oxazoline) (POZ) platform designed for drug delivery. Drugs are attached to pendant groups along the polymer backbone using "click chemistry". Drug-specific linkers allow one to program the release of drug following subcutaneous, intramuscular or intravenous delivery. Examples of how to employ POZ polymers to address unmet medical needs will be reviewed.

Serina's lead clinical program is SER-214 – a once-per-week subcutaneous injectable designed to deliver continuous dopaminergic tone, a long-sought clinical strategy for treatment of Parkinson's disease. SER-214 is advancing through toxicology and will enter humans in the second half of 2014. Other programs are focused on oncology and include (a) small molecule targeting of POZ-oncolytics using folate to target the high affinity folate receptor alpha (over-expressed in 40 % of solid tumors) and (b) antibody drug conjugates with POZ-loaded toxin designed to be released inside the cell following endocytosis.
Organoplatinum(II) compounds are effective, broad spectrum antitumor drugs. The most prominent of these is cis-dichlorodiammineplatinum(II) [Cisplatin]. Administration of these drugs is accompanied by severe side effects, most prominently extreme nausea and kidney damage. Effective ways to mitigate these side effects would greatly enhance the utility of these compounds. One potentially useful method would be to administer a suitable prodrug that would make the active moiety slowly available as a function of time. Oxidation of platinum(II) compound in ethanol solution generates the corresponding monoethoxo platinum(IV) compound. This confers chemical inertness and, at the same time, introduces ligand, the hydroxyl group, which may be utilized for the generation of a vinyl monomer suitable for copolymerization with biocompatible monomers. The resulting copolymers would contain the organoplatinum unit as pendant groups. The copolymer would represent a platform from which the platinum-containing moiety would be slowly released by hydrolysis. Upon entering the cell, the platinum(IV) species would be reduced to the corresponding active platinum(II) entity.

Equation (copolymer with N-vinylpyrrolidone):

\[
\begin{align*}
\text{O} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H}_2 \text{C} \\
\text{H}_3 \text{N} & \quad \text{P} \quad \text{Cl} \\
\text{H}_3 \text{N} & \quad \text{O} \quad \text{C} \quad \text{H}_2 \text{C} \\
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{C} \quad \text{C} \quad \text{H}_2 \text{C} \\
\text{H}_3 \text{N} & \quad \text{P} \quad \text{Cl} \\
\text{H}_3 \text{N} & \quad \text{O} \quad \text{C} \quad \text{H}_2 \text{C} \\
\end{align*}
\]
Polyphosphoesters (PPEs) have gained increasing interest in polymer science. In poly(phosphonate)s the phosphorus is connected to two oxygen atoms in the main chain and to one carbon atom in the side chain. In contrast to polyphosphates, research interest in polyphosphonates has faded since the 1960s because synthesis is limited to polycondensation methods exclusively.

Although extensive research has been carried out, no single study exists which explores chain growth polymerization techniques to obtain well-defined polyphosphonates. In this study we have overcome this limitation in polymer synthesis and enriched the family of phosphorus based, biocompatible and biodegradable polymers.

We were able to synthesize well-defined water-soluble polyphosphonates over a wide range of molecular weights via anionic ring-opening polymerization (AROP), introducing functional groups by postpolymerization modifications. Furthermore block copolymers were accessible via atom-transfer radical polymerization (ATRP) to alter the properties of an individual block.

 Unsaturated polyphosphoesters were obtained by conducting a ring-opening metathesis polymerization (ROMP), offering another chain-growth technique and emphasizing the versatility of polyphosphoester chemistry.

We have modified the ruthenium catalyzed acyclic diene metathesis (ADMET) polymerization to obtain high molecular weight polyphosphonates. Although the ADMET polycondensation, as a step-growth polymerization, produces a polydispersity index of around 2, it may allow adjusting the mechanical properties and the solubility of the polymer to a specific need. Nanoparticles were prepared from polyphosphonates by the well-established miniemulsion-solvent evaporation strategy. Adhesion to cement mimicking bone tissue was investigated.
186 - Development of degradable diblock copolymer, polyphosphoester-block-poly(L-lactide), and its conversion into well-defined shell crosslinked nanoparticles as delivery carriers for antimicrobial agents

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The combination of state-of-the-art polymerization chemistries, post-polymerization chemical modifications, supramolecular assembly processes and further transformations is allowing for the design of highly well-defined polymer nanoparticles that are demonstrating unique performance toward the effective treatment of infectious diseases. A potentially fully degradable, biocompatible diblock copolymer, polyphosphoester-block-poly(L-lactide) (PPE-b-PLLA), was prepared by one-pot sequential ring-opening polymerizations (ROPs) of two cyclic monomers: alkyne-functionalized phospholane and L-lactide. Photo-induced thiol-ylene "click"-type reactions with small molecule thiols bearing carboxylic acid then afforded amphiphilic diblock copolymers with carboxylate side-chain functionalities along the PPE segment of the diblock copolymer backbone. Subsequently, well-defined (1) spherical micelles with negative surface charges were prepared by direct dissolution of the anionic diblock copolymers (aPPE-b-PLLA) in aqueous solution, and (2) shell crosslinked knedel-like (SCK) nanoparticles were prepared by crosslinking of hydrophilic shell of the micelles, as confirmed by transmission electron microscopy (TEM), dynamic light scattering (DLS) and zeta potential. The Ag-loading capacities of the anionic micelles and SCKs from aPPE-b-PLLA were determined with three different types of Ag-containing molecules, silver acetate (AgOAc) and silver carbene complexes (SCC22 and SCC10). Similarly, Ag-release kinetics of the Ag-loaded nanoparticles, using dialysis cassettes in nanopure water, was studied. We are currently working on the study of (1) degradation capability of micelles and SCKs of PPE-b-PLLA system under hydrolytic or enzymatic degradation, (2) conjugation with target-specific proteins such as FimH to evaluate their ability to perform as target delivery carriers, and (3) determination of their in vitro and in vivo efficacies against bacteria.
187 - Intracellular environment-responsive nanocapsules exhibiting cytosol specific drug release

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The self-assembly of macromolecules is often used as an indispensable molecular tool in functional nanomaterial engineering. The self-assembled polymers with intracellular environment (pH, enzyme and reductive environment) responsive behaviors are of special interest for drug delivery system (DDS) carriers. For DDS, the drug carriers should release entrapped drugs at the target site in response to stimuli in the intracellular environment. We have previously investigated head-tail type polycations composed of a polyamidoamine dendron and poly(L-lysine) (PAMAM dendron-PLL) as a carrier in the DDS field. We recently found that PAMAM dendron-PLL could spontaneously form monodisperse polymer vesicles (self-assembly) through a coil-to-helix transition of PLL tails. In this study, self-assembled polymer vesicles formed from head-tail type polycations were stabilized by the introduction of disulfide bonds through the reaction of Lys residues in PLL tails with 2-iminothiolane. When the cationic dye, rhodamine 6G, was incorporated into the PAMAM dendron-PLL nanocapsules, the dye was not released because of the electrostatic barrier in the cationic cross-linked PLL membrane. However, when the glutathione concentration was increased to a concentration corresponding to that in an intracellular environment the nanocapsules were destabilized through the cleavage of disulfide bonds and the incorporated dyes were immediately released from the nanocapsules. The effective release of a cationic dye that recognizes the intracellular reductive environment was also observed in cultured cells. The obtained results showing intracellular specific release without release in the extracellular environment strongly indicates the applicability of PAMAM dendron-PLL nanocapsules cross-linked by disulfide bonds as a carrier in effective drug delivery.
A series of pseudo-poly(amin acids) (PPAAs) based on dicarboxylic N-substituted amino acids and glycols have been synthesized by esterification process via dicyclohexylcarbodiimide coupling. The use of different N-substituted dicarboxylic amino acids as well as different glycols allows to tailor properties of amphiphilic PPAAs such as hydrophilic-lipophilic balance, micellization energy, solubilization capacity, surface potential, etc. Thus, PPAAs based on N-(fatty acid) substituted amino acids are highly capable of self-assembling in aqueous media and form micelles with the highest solubilization capacity. On the other hand, PPAAs made of temporarily N-protected dicarboxylic amino acids can form micelles with a high positive surface charge in aqueous media. Such amphiphilic PPAAs with protonable amino groups can bind DNA and serve as a non-viral gene delivery vectors. Degradation studies show high hydrolysis rate for amphiphilic PPAAs in aqueous media in physiological conditions. Due to the degradable backbone, high solubilization capacity, tailored micellar surface properties, and functionality, amphiphilic PPAAs can be considered as promising materials for both drug delivery and gene delivery applications.

Figure 1. Scheme of PPAAs structure.
PEGylated poly(amino acid)s: A platform for biomedical copolymers

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Poly(ethylene glycol), PEG, is an established biopolymer that is in clinical use for several decades. It biocompatibilizes substrates by conveying a "stealth character", meaning the PEGylated substrate is not recognizable by the reticuloendothelial system, and therefore longer blood circulation times and diminished biofouling are achieved. However, PEG is chemically inert and therefore cannot be readily attached to a substrate.

By forming a block copolymer with a poly(amino acid), PAA, the PAA block acts as anchoring moiety for PEG. Amino-terminated PEG is used as macroinitiator in the ring-opening polymerization of N-carboxyanhydrides of natural amino acids. The chemical variety of the amino acid building blocks allows for a multitude of applications. If the functional groups of the amino acids are reactive towards a substrate, the copolymer is useful for surface modification, if the PAA-block is hydrophobic or shows a gradual hydrophobicity resulting copolymers will self-assemble into drug or gene delivery vehicles.

**Tuesday, March 18, 2014 11:10 AM**
12th International Symposium on Biorelated Polymers (08:30 AM - 11:40 AM)
Location: Hyatt Regency Dallas
Room: Moreno B
190 - Synthesis and self-assembly of a terpolymer triblock via hydrogen-bonded complexes in organics solvents

Claire Guerlain\textsuperscript{1}, claire.guerlain@uclouvain.be, Sandie Piogé\textsuperscript{2}, Charles-André Fustin\textsuperscript{1}, Jean-François Gohy\textsuperscript{1}. (1) Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium, (2) Institut des Molécules et des Matériaux du Mans (IMMM), Université du Maine, Le Mans, France

For several years, the use of block copolymers in nanotechnology has been widely developed. These polymers can be used to obtain a wide range of nanostructured materials in the solid phase (thin films) or in solution (micelles). Different methods are used to modulate specific dimensions, morphology and properties of these nanostructures. One of them consists in varying the length of each polymer sequence by synthesizing new polymers. Another one is to mix together two block copolymers (AB and CD for example) in which two sequences (B and C) interact thanks to non-covalent specific interactions (electrostatic or H-bond).\textsuperscript{1}

The formation of hydrogen-bonded complexes between polystyrene-\textit{block}-poly(4-vinylpyridine) (PS-\textit{b}-P4VP) and poly(methylmethacrylate)-\textit{block}-poly(methacrylic acid) (PMMA-\textit{b}-PAA) block copolymers has been investigated in organic solvents (THF and DMF) (see Figure 1). Strong hydrogen bond between the P4VP and PMAA blocks induce the formation of complexes which further aggregate into a micellar core surrounded by PS and PMMA chains.

![Figure 1. Micelles formed between PS-\textit{b}-P4VP and PMMA-\textit{b}-PMAA](image)

Moreover, the complexation process of mixtures involving copolymers with the same chemistry as the above AB + CD system, but where the blocks are distributed differently, i.e. mixtures between a ABC triblock copolymer and a homopolymer D or an AD diblock has been studied. A PMMA-\textit{b}-P4VP-\textit{b}-PS triblock copolymer has been synthesized by atom transfer radical polymerization (ATRP), and has mixed with a PAA homopolymer to form hydrogen-bonded complexes in organic solvents (THF and DMF).


**Tuesday, March 18, 2014 08:00 AM**

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)

Location: Hyatt Regency Dallas

Room: Reverchon A/B
A new class of polyisobutylene (PIB)-based thermoplastic elastomers (TPE) has been discovered, using the industrial butyl rubber polymerization system. It has been reported in the literature that living polymerization of isobutylene (IB) initiated by bifunctional or multifunctional initiators and subsequent blocking of a second monomer produces PIB-based TPE materials. However, in general, living IB polymerization systems are expensive, requiring unique, commercially not available initiators and expensive coinitiators. Contrary to this, we found that the polymerization of IB shows living character up to 40 % conversion under the rather inexpensive traditional butyl rubber polymerization conditions (H₂O/AlCl₃ in MeCl at -90 °C to -100 °C), when it is copolymerized with alloocimene, a terpene, by forming a stable emulsion. This is the first example of a two-phase living carbocationic polymerization. The synthesized diblock, triblock and multiblock copolymers exhibit thermoplastic elastomeric properties. This is the first example of a diblock thermoplastic elastomer. The polymerization system solves the problems related to the currently used TiCl₄-based living systems: expensive initiators and coinitiator, high viscosity at low concentration and poor heat transfer.
Injectable and biodegradable supramolecular hydrogels by inclusion complexation between poly(organophosphazenes) and α-cyclodextrin

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Biodegradable poly(organophosphazenes) containing side chains of various oligo(ethylene glycol) methyl ethers (mPEGs) and glycine ethyl ester units were synthesized and characterized. Novel supramolecular-structured hydrogels based on the inclusion complex between the mPEG grafted polyphosphazenes and α-cyclodextrin were prepared in aqueous media.

The gelation time depended on the length of the mPEG, the molar ratio between mPEG repeat units and α-cyclodextrin, and the concentration of the polymeric gel precursors. The hydrogels demonstrated unique structure-related reversible gel-sol transition properties at a certain temperature due to the reversible supramolecular assembly.

<table>
<thead>
<tr>
<th>Gel precursor</th>
<th>Polymer conc.(wt%)</th>
<th>Molar ratio (repeat unit:CD)</th>
<th>Gel name</th>
<th>Gelation time (min)</th>
<th>Gel-sol transition temperature $T_{\text{trans}}$ ($T_{\text{trans}}'$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PmPEG5000</td>
<td>8</td>
<td>4:1</td>
<td>G1</td>
<td>5</td>
<td>60 (42)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4:1</td>
<td>G2</td>
<td>10</td>
<td>58 (40)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>5:1</td>
<td>G3</td>
<td>5</td>
<td>56 (40)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5:1</td>
<td>G4</td>
<td>12</td>
<td>55 (39)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>6:1</td>
<td>G5</td>
<td>6</td>
<td>54 (38)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6:1</td>
<td>G6</td>
<td>20</td>
<td>52 (38)</td>
</tr>
<tr>
<td>PmPEG2000</td>
<td>8</td>
<td>4:1</td>
<td>G7</td>
<td>3</td>
<td>46 (35)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4:1</td>
<td>G8</td>
<td>10</td>
<td>46 (33)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>5:1</td>
<td>G9</td>
<td>5</td>
<td>45 (33)</td>
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<tr>
<td></td>
<td>4</td>
<td>5:1</td>
<td>G10</td>
<td>20</td>
<td>42 (32)</td>
</tr>
<tr>
<td>PmPEG750</td>
<td>8</td>
<td>3:1</td>
<td>G11</td>
<td>6</td>
<td>40 (29)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3:1</td>
<td>G12</td>
<td>15</td>
<td>38 (28)</td>
</tr>
</tbody>
</table>

The rheological measurements of the hydrogels indicated a fast gelation process and flowable character under a large strain. The formation of a channel-type inclusion complex-induced gelation mechanism was studied by DSC, TGA, $^{13}$C CP/MAS NMR and X-ray diffraction techniques. The potential of the new materials for injectable drug delivery application was explored with the use of bovine serum albumin as a model protein for in vitro release studies. All the supramolecular hydrogels studied showed disintegration by dethreading of the α-cyclodextrin. Polymers with longer mPEG side chains had better stability and slower protein release profiles. The molecular weights of the polymers monitored by GPC showed a biodegradability of the new hydrogels.
193 - Photo-controlled polymerization for patterned growth of gel materials

Alexandra M. Cok, acok@mit.edu, Huaxing Zhou, Jeremiah A. Johnson. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Photo-responsive polymerizations offer strategies for controlling the mechanical and chemical composition within polymer gel materials. In-situ polymerizations within polymer networks allow for patterned growth using lithography techniques. This work presents a photo-controlled radical polymerization (PCRP) using trithiocarbonate (TTC) initiators to create end-functionalized polymer chains. We describe the versatility of this PCRP with respect to initiator structure and monomer type, and explore the application of this polymerization to patterning network growth by increasing molecular weight between crosslinks and changing monomer composition. This work presents a new approach to creating stimuli responsive polymer materials.
Polymeric top coat materials containing maleic anhydride have been demonstrated to be spin-coatable on block copolymer thin films in the charged, ring-opened form of maleic anhydride and energetically neutral in the thermally annealed, ring-closed form. The neutrality of the top interface is demonstrated by the rapid perpendicular orientation of the underlying block copolymer thin film in as little as 10 seconds. Block copolymers oriented perpendicularly by this method include high-χ, silicon-containing blocks with potential applications in next-generation nanolithography. Top coats containing maleic anhydride and typically one or more comonomers must be engineered to balance surface energy, solubility, glass transition temperature, and synthetic reproducibility.
195 - Structure and dynamics of block copolymer micelles in the presence of co-solvents

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Amphiphilic block copolymer micelles in aqueous solvents are under broad exploration for drug delivery applications due to their high loading capacity and targeted drug delivery. We aim to understand the kinetic and thermodynamic processes which underlie the self-assembly and exchange dynamics of diblock copolymer micelle systems. The present work focuses on diblock copolymers containing poly(ethylene oxide) (a hydrophilic polymer) and polycaprolactone (a hydrophobic polymer), which spontaneously self-assemble into spherical micelles in water. Addition of a common good solvent (co-solvent) for both of the constituting blocks, such as tetrahydrofuran (THF), reduces the interfacial tension at the core-corona interface. We are currently investigating the effect of this phenomenon on the micelle structural properties and their dynamics, using scattering experiments and pulsed-field-gradient NMR. Structural parameters of interest include hydrodynamic radius, core radius, corona thickness, aggregation number, degree of swelling of the micelle core with the co-solvent, and unimer (free chain) concentration. In addition, dynamic properties of interest are the characteristic time scale of unimer exchange between micelles, micelle diffusion coefficients, and the molecular dynamics of individual (core and corona) blocks. We are examining these structural and dynamic parameters as the interfacial tension at the core-corona interface is varied through changing the co-solvent concentration. Fundamental knowledge from these studies will inform design of drug delivery systems by allowing us to tailor micelle properties for optimal drug loading as well as targeted and timed uptake.

Schematic representation of a time resolved-small angle neutron scattering experiment.

Tuesday, March 18, 2014 09:40 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hyatt Regency Dallas
Room: Reverchon A/B
196 - Synthesis of star architectures from reactive molecular bottlebrushes

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Star-shaped polymers were successfully prepared in high yield under mild reaction conditions based on intermolecular cross-linking of bottlebrush copolymers containing reactive linear end blocks. The utilized brush-linear block copolymers were prepared by grafting-from method to contain poly(methyl methacrylate) (PMMA) brush side chains and poly(glycidyl methacrylate) (PGMA) as the reactive end block. Well-defined poly((glycidyl methacrylate)-b-(2-(bromoisobutyryl)ethyl methacrylate)) diblock copolymer backbones were synthesized using reversible addition-fragmentation chain-transfer polymerization. Subsequent atom transfer radical polymerization of methyl methacrylate from the diblock copolymer backbone as polyinitiator resulted in densely grafted bottlebrush copolymers with narrow molecular weight distributions. Facile ring-opening of the pendant epoxide groups in the block copolymers by ethylenediamine cross-linker in the presence of lithium bromide as a catalyst led to core-cross-linked stars with high yields. Several factors with regards to the star polymer formation, such as the length of PGMA end-chains and PMMA side-chains, reaction temperature and time, and reaction stoichiometry, were assessed for optimization of the reaction conditions. Formation of core-cross-linked molecular star brushes was confirmed by gel permeation chromatography (GPC) and transmission electron microscopy (TEM). Resulting aggregates displayed globular conformation with mostly uniform distributions.
Poly(lactide)-poly(ethylene oxide) (PLA-PEO) block copolymers provide a unique combination of PLA biodegradability and PEO biocompatibility in an amphiphilic molecular structure that can be utilized for drug delivery applications. We report on the synthesis and self-assembly of novel bottlebrush copolymers with PLA and PEO side chains distributed along the backbone in a blocky fashion. Bottlebrush copolymers were synthesized by the grafting-from method combining ATRP, ROP and RAFT polymerization techniques. First, the backbone was synthesized by sequential RAFT copolymerization of solketal methacrylate and 2-(bromoisobutyryl)ethyl methacrylate resulting in a well-defined diblock copolymer backbone with protected hydroxyl and activated bromide initiating sites. PLA side-chains were grafted from the backbone from the liberated hydroxyl functionalities. Subsequently, ATRP of PEO-methacrylate initiated by the pendant bromide functionalities on the backbone produced side chains with PEO-like characteristics. The investigation of the aqueous aggregation of PLA-PEOMA copolymers with varying structural parameters revealed a number of interesting assembly trends and relationships between polymer shape and aggregate morphology. Progressively decreasing side chain asymmetry lead to the formation of micellar aggregates with spherical, cylindrical and bilayer type morphologies, which were characterized by cryogenic transmission electron microscopy.
198 - Synthesis and physicochemical characterization of polymeric micelles based chitosan derivatives by using different preparation methods

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The polymeric micelles were successfully synthesized by introducing hydrophobic and hydrophilic moieties into the chitosan backbone. In this study, the naphthyl group was used as hydrophobic moieties while succinyl group was used as hydrophilic moieties. The N-naphthyl chitosan was synthesized by reacting chitosan with 2-naphthaldehydes under mild acidic condition. The reaction occurred through Schiff base intermediate and then reduced with sodium borohydride. The N-naphthyl-N, O-succinyl chitosan was carried out by succinylation with succinic anhydride. The chemical structure of polymeric micelles was confirmed by ATR-FTIR and $^1$H-NMR spectroscopic technique. The polymeric micelles were prepared by using both dialysis and solvent evaporation methods. It was found that the polymeric micelles prepared by using solvent evaporation method had smaller particle sizes than dialysis method while zeta-potential values of both methods were not different significantly. The critical micelle concentration (CMC) of polymeric micelles was found to be 0.0359 mg/mL and 0.0749 mg/mL for solvent evaporation and dialysis methods, respectively. The morphology of polymeric micelles prepared by both methods was investigated by using Transmission electron microscopy (TEM). It was revealed that the both methods showed spherical shapes, however, the polymeric micelles prepared by using solvent evaporation method can be formed film during production of micelles, leading to small particle sizes. Different preparation methods can be controlled the particle sizes of polymeric micelles that potential applied in drug delivery system.

Figure 1. TEM images of polymeric micelles prepared by dialysis method (A and B) and solvent evaporation method (C and D).
199 - Synthesis and characterisation of gradient polyimide-based porous materials by interfacial polymerisation using emulsion templating

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Naturally porous materials exemplify the benefits of a gradient in pore arrangement. For example, human bone has enhanced strength due to the graduation in its porous microstructure. This was the bioinspiration that motivated us to synthesise gradient porous polymers by layering water-in-oil (w/o) emulsions. We began by curing a surfactant-stabilised w/o emulsion containing polyimides to prepare a highly cross-linked, open-porous layer. This porous polyimide layer was then treated with a dilute amine solution before a second, Pickering stabilised w/o emulsion containing polyimides was cast on top. The amine pre-treatment encouraged interfacial polymerisation, which enhanced the adhesion between the layers. Furthermore, the use of emulsion layers stabilised by surfactants and functionalised nanoparticulates respectively, created unique microstructures [figure 1] with graduation in envelope density or porosity across its thickness and height. The interfacial polymerisation reaction enhanced the properties of these gradient materials. This technique reinvents emulsion templating as a versatile and robust method to produce more complicated gradient structures.

SEM image of emulsion templated layers displaying gradient porosity

Tuesday, March 18, 2014 11:00 AM

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hyatt Regency Dallas
Room: Reverchon A/B
α-substituted styrene such as α-methylstyrene doesn’t undergo homopolymerization under standard radical polymerization condition because the ceiling temperature (Tc) of α-methylstyrene is lower than radical polymerization temperature. According to Ueda et al., α-methyleneindane which is a cyclic analog of α-methylstyrene underwent radical polymerization with AIBN in contrast to α-methylstyrene\(^{(1)}\). They concluded that α-methyleneindane has a lower steric hindrance than α-methylstyrene, therefore the cyclic monomer accelerated the radical polymerization.

We have been studying depolymerizable polymers for a new candidate of extreme ultraviolet (EUV) photoresist component. As a one of model study, we successfully made 1-methyleneisochroman-3-one as a model cyclic monomer and confirmed that this monomer underwent radical polymerization with AIBN. We expect that when this lactone polymer is ring-opened by acid or base then they will depolymerize because of the increasing of steric hindrance. To confirm this hypothesis, we tested base and acid hydrolysis of our product. As a result, this polymer was hydrolyzed by NaOH and generated monomeric 2-(2-acetylphenyl)acetic acid as the product. On the other hand, trifluoroacetic acid didn’t work with this polymer. Although this polymer might not be used for EUV photoresist, this result is very interesting as an aspect of polymer science.

201 - Synthesis and kinetics analysis of imidization of novel poly(benzoxazinone-imide)s

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Polyimides are a class of high performance polymers because of their high-temperature stability, excellent electrical and mechanical properties, and good chemical resistance. The incorporation of heterocyclic moieties, such as benzoxazinone, into a polymer system may improve thermal and mechanical properties of the polymer. T. Takeichi et al. successfully prepared a type of polyimide containing benzoxazinone groups converted from corresponding poly(amic acid) with good thermal and mechanical properties. Imidization reaction is the inevitable stage from poly(amic acid) conversing to polyimide, and imidization kinetics analysis is vital to understand the mechanism and is essential for digital simulation of imidization process. To the best of our knowledge, few papers have been published on imidization kinetics of polyimides with benzoxazinone groups.

In this work, three novel thermoplastic polyimides, poly(benzoxazinone-imide)s (PBEIs)

![Image](image_url)

, were prepared through a two-step method via the corresponding poly(amic acid)s (PAAs) synthesized by the reaction of 4,4’-diamino-6-ethoxycarbonylbenzanilide with 2,3,3’,4’-biphenyltetra-carboxylic dianhydride, 2,3,3’,4’-diphenyl ether tetracarboxylic dianhydride and 3,3’,4,4’-benzophenone-tetracarboxylic dianhydride, respectively. It is indicated that the three thermoplastic polyimides exhibited good thermal stability. The imidization kinetic processes from PAAs to PBEIs were investigated by Differential Scanning Calorimetry (DSC). Two different kinetic models which are Kissinger and Ozawa were used to analyze the date of the imidization reaction and calculate the values of activation energy.

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.
202 - High performance thin-film transistors based on donor-acceptor polymers

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Co-polymers based on the diketopyrrolopyrrole (DPP) acceptor block are very promising for use in field-effect transistor applications. Such polymers have been shown to possess mobilities in the range 2-10 cm²/V-s by a few groups (albeit at high operating voltages and in long channel length devices). In this presentation we will describe results with several new DPP-based polymers and specifically discuss techniques to keep the operating voltage low (< 10 V) in small channel length (< 5 micron) devices. A range of ambipolar and p-channel FET forming materials have been synthesized. We have been able to obtain mobility values of ~4 cm²/V-s with some of the materials in such devices at low operating voltages for channel lengths of 4 microns. These devices possess very high temperature field-induced conductivity of any polymer FET and which exceeds that of most organic single crystal FETs. This research was a result of understanding how to control the deleterious effects of Fröhlich polarons which tend to reduce mobility when high-k dielectrics are used with polymer semiconductors. Employing a thin interfacial low k dielectric, we are able to get record high mobilities. These devices also possess very low off-currents and a high on/off current ratio. A range of ambipolar and p-channel FET forming materials have been synthesized.

Tuesday, March 18, 2014 01:00 PM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (01:00 PM - 05:15 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm C
203 - No need for SAMS in OFETS? Self-layered nanomorphology for enhanced mobility of fluoroalkyl/P3HT block copolymers

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Conjugated block copolymer, P3HT-b-PFMA, undergoes a self-layering effect that provides significant improvement in the electrical charge carrier properties of the semiconductor component without a OTS or other SAM treatment layer. Transmission Electron Microscopy with complementary Energy Dispersive X-ray mapping directly and clearly reveals, the self-organization of the fluorinated block copolymer, with fluorine migrating to the upper surface layer of the block copolymer thin film, driving a P3HT organization at the bare SiO₂ surface. Furthermore, this block copolymer can be used as an minor additive (as little as 2.5%) to P3HT, resulting in a closely packed lamellae configuration which increased the mobility from 0.5 cm² V⁻¹ s⁻¹ for P3HT to 1.7 cm² V⁻¹ s⁻¹. We find that this concept allows the design of a semiconductor material that promotes efficient charge transfer processes, influences the nanoscale architecture of thin film device while simultaneously introducing a self-protective layer; and as such can provide a notable and versatile approach to the design of organic semiconductor systems in optoelectronic devices.

Tuesday, March 18, 2014 01:30 PM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (01:00 PM - 05:15 PM)
Location: Hyatt Regency Dallas
Room: Reunion Birm C
204 - Optimizing conjugated polymers for high efficiency solar cells: A case study of PBnDT-FTAZ

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PBnDT-FTAZ, a “weak donor-strong acceptor” polymer that combines benzodithiophene (BnDT) and fluorinated benzotriazole (FTAZ), has received significant amount of attention because it is a peculiar material with many outstanding features that need to be further explained. For example, with a medium band gap of 2.0 V, PBnDT-FTAZ can still generate over 7% power conversion efficiency with a noticeably high fill factor over 70% in its BHJ cells with a relatively thick film (200 – 300 nm).

In this talk, I will discuss our ongoing efforts to further optimize this interesting polymer. First, we discovered that all these interesting properties shown by PBnDT-FTAZ can only be obtained with polymers of a quite narrow range of molecular weight. Second, molecular engineering of PBnDT-FTAZ by substituting alkylthiol and selenophene in PBnDT-FTAZ give mixed results: both \( V_{OC} \) and \( J_{SC} \) can be varied depending upon the substitutions.
205 - Solar paint: A new paradigm in organic photovoltaics

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Recently, the fabrication of organic solar cells from water-dispersed nanoparticulate materials (solar paint) has attracted increasing interest since it offers the potential of morphological control coupled with device processing in the absence of an organic solvent. This talk will present recent work aimed at developing optimized nanoparticulate organic photovoltaic (NP-OPV) devices from water-based dispersions.

By controlling both nanoparticle morphology [1] and inter-particle interactions, power conversion efficiencies (PCEs) approaching 1% for water-based polyfluorene NP-OPV devices are demonstrated [2,3].

We have shown how NP morphology determines device function in P3HT:PCBM devices with PCEs of 1.3% achieved. Scanning transmission X-ray microscopy (STXM) studies show that annealing leads to gross phase segregation and reduced device performance [4,5]. Finally, the performance P3HT:ICBA NP-OPVs is discussed, which exhibit PCEs of 2.5%. The enhanced miscibility of ICBA in P3HT results in a more efficient intermixed structure [6].

Recently, a variety of polymers that absorb more light by fine-tuning energy levels in the polymer to better match their bandgaps with the solar spectrum have been reported. Many of the systems with high power conversion efficiencies (PCE) utilize derivatives of dialkoxy substituted benzo[1,2-b:4,5-b']dithiophene (BDT) monomers. We have developed dithioalkoxy derivatives of this ring system (S-BDT) that when used either in homopolymers or in low bandgap D-A copolymers, lowers the HOMO level with respect to the LUMO of acceptors such as PCBM and leads to open circuit voltages (Voc) > 1.0V and PCE of ~4% in bulk heterojunction solar cells (BHSC). We will discuss the design and synthesis of these (co)polymers and their performance in BHSCs.
Recent work has demonstrated the potential of all-conjugated block copolymers for solution-processed photovoltaic devices, with power conversion efficiencies near 3%. However, optoelectronic properties and structure-property-processing relationships are poorly understood for this class of materials, and controlled synthetic approaches are lacking. Here, we present a new synthetic approach relying on click chemistry and structure-processing-property analysis of donor-acceptor block copolymers. The implementation of copper-catalyzed azide-alkyne click coupling in the synthesis of all-conjugated block copolymers provides control over the molecular weight of both polymer blocks independently. The morphology of a series of poly(3-hexylthiophene) (P3HT) and poly(3-dodecylthiophene) (P3DDT) all-conjugated block copolymers is analyzed by a combination of grazing-incidence wide- and small-angle X-ray scattering. While co-crystallization is inhibited in P3HT all-conjugated block copolymers, P3DDT block copolymers show significant co-crystallization and a rich processing-dependent morphology. Finally, we present optoelectronic measurements, including photovoltaic device results, of block copolymers incorporating ambipolar poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (PFTBT) polymer block and high-performance p-type PTB7 polymer. OPVs devices based on block copolymers and block copolymer additives are analyzed. These results provide guidelines for optimizing the morphology of all-conjugated block copolymers through materials design and processing.
208 - Material design concepts for printable ink systems for OLED and OPV applications

Elena Sheina, del_72@hotmail.com, Christopher Brown, Christophe Grenier, Chad Landis, Christine McGuiness, Darin Laird, Venkataramanan Seshadri, Neetu Chopra, Sergey Li, Jing Wang, Mathew Mathai. Plextronics, Inc., Pittsburgh, PA 15238, United States

There is a continuous high demand for new organic-based and eco-nomical/-friendly renewable energy and light sources. Plextronics' material developments target several core technologies, printable ink systems that include hole injection/transport layers and photoactive layers for high efficiency OLEDs and organic solar cells. Plexcore inks designed for OPV applications have shown high \( V_{OC} \) (1 V), FF and high efficiency (6.9%, certified). On the hole injection layer side, we have developed unique polythiophene based platform technology both in aqueous and non-aqueous solvent systems, which have been shown to improve the overall performance of OLEDs with state of the art emitter systems. In this talk, various material design considerations for manufacturing friendly HIL and OPV ink systems that enable improved performance will be discussed.
This presentation discusses the synthesis and structure/property relationship of low bandgap polymers containing fused thienobenzothiophene ladder oligomers. Conjugated polymers based on heteroacene 3,7-dialkyl-dithieno[2,3-\(d\):2\(\ell\),3\(\ell\)-\(d\(\ell\))]benzo[1,2-\(b\):4,5-\(b\(\ell\))]dithiophene (DBD) were synthesized. These polymers showed broad UV-Vis absorption with energy bandgaps below 1.7 eV. PTDBD2 showing good miscibility in the polymer/PC\(_{71}\)BM blend film achieved a PCE of 7.6%. The result indicates that copolymers containing DBD are promising candidates for high performance organic solar cells.
210 - Protein amyloid dibrils: From pathological agents, to efficient templates for nanomedicine

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Aggregation of proteins is central to many aspects of daily life, ranging from food technology and pharmaceutical science, to blood coagulation and health disorders. In particular, association of proteins into amyloid fibrils is a highly specific process occurring both in-vivo, such as in the Alzheimer, Parkinson or prion-related neurodegenerative diseases, and in-vitro, as in the case of processed food proteins.

Recently, however, there is a shift of vision on amyloid fibrils, as their occurrence is found in a context much broader than the original neurodegenerative field. In particular, the so-called functional amyloids have been shown to play a vital role in many biological phenomena; furthermore, protein fibrils are emerging as unique building blocks to assist the design of functional materials in a wide range of contexts and applications. The possibility to efficiently mix them with other components, more traditionally used in the design of high-performance materials, enables new opportunities in materials science and nanotechnology. Finally, when protein fibrils occur from non-toxic or food grade proteins, their role in food science and technology is already consolidated. In order to advance our understanding in pathological, functional and artificial amyloid fibrils, it become essential to understand the self-assembly principle from the constitutive peptide to the final collective behavior of the mature fibrils.

In this talk emphasis will be placed on systems made of β-lactoglobulin and hen egg white lysozyme fibrils, since these two proteins are non-toxic (e.g. food-grade) and have both fundamental and practical relevance. By relying on these systems as model functional artificial amyloids, I will discuss our recent contribution to the field and will give three distinct examples to highlight how these protinaceous fibrils can serve in the very broad biological and medical contexts, standing as very efficient delivery vehicles and cellular scaffolds for tissue engineering.

**References**


**Tuesday, March 18, 2014 01:00 PM**
**Peptide-Based Materials for Nanomedicine (01:00 PM - 05:00 PM)**
**Location: Hyatt Regency Dallas**
**Room: Reunion B1rm F**
211 - Peptide functionalized nanofibers for regenerative medicine

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Polymeric nanofibers are attractive for a number of regenerative medicine applications. However, historically nanofibers have been difficult to derivatize with peptides using methods that are translationally relevant. Efficient chemical methods designed to controllably derivatize degradable polymeric nanofibers with peptides and carbohydrates would be widely applicable to the biomaterials community. In our research, we have sucessfully utilized 4-dibenzocyclooctynol (DIBO) and its derivatives to initiate the ring-opening polymerization of a number of different monomers like lactide, e-caprolactone and several copolymer blends. The presence of a DIBO group at the chain end of the polymers enables fast, efficient and metal-free post-electrospinning functionalization with complemetary bioactive species posessing azide groups. We will describe the use of our nanofiber based scaffolds in neural engineering, soft tissue repair and protein stabilization.
A novel biodegradable star-shaped poly-asparamide (SP) was developed for gene delivery. We discovered that the star-shaped polymer showed higher gene transfection efficiency in cell culture than the linear counterparts (LP1 (low MW), LP2 (high MW)). What is more intriguing is that the plasmid DNA nanoparticles formed with the star polymer can specifically deliver the gene to the lung in mice and completely avoid the liver accumulation, where most of the nanoparticle delivery systems end up with. In contrast, the plasmid DNA nanoparticles formed with the linear polymer can only accumulate in the liver and express the gene with much lower efficiency. This novel star polymer is applied in an orthotopic lung cancer model to knockdown oncogenes in order to overcome drug resistance.
Diblock copolymer hydrogels as vehicles for delivery of bioactive hydrophilic and/or hydrophobic molecules into the central nervous system

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Peptides and proteins are present throughout the living world, which can perform tasks as varied as catalyzing complex reactions and serving as the structural framework of living organisms. These unique features make the preparation of synthetic polypeptides an area with the potential for great rewards. Well-defined block copolypeptides, developed in our lab, are novel synthetic biomaterials, whose defined conformations and multitude of block compositions allow for the precise design of materials that can self-assemble into complex associated structures. Amphiphilic diblock copolymer hydrogels (DCH) are synthetic copolypeptides with many features that make them attractive as scaffolds or molecule delivery vehicles for central nervous system (CNS) applications. We are developing DCH as vehicles that can be safely and easily injected into specific sites in CNS tissues to deliver potentially therapeutic molecules. We have previously shown that DCH are biocompatible after injection into brain or spinal cord and self-assemble in vivo into structures with finely tunable properties. Our current work shows that DCH can provide prolonged release of bioactive growth factors that influence local neurons in predictable ways and form gradients that are effective up to 5mm away from the hydrogel depots in mouse CNS. We also demonstrate the facile and predictable tunability of DCH to achieve a wide range of loading capacities and release profiles of hydrophobic molecules while retaining CNS compatible physical properties.
214 - Biodegradable polyesteramide microspheres for controlled drug delivery in ophthalmology

Vanessa Andrés-Guerrero¹, vandres@farm.ucm.es, Blanca Arango-González², Mengmeng Zong³, George Mihov³, Aylvin Dias³, Marius Ueffing², Rocío Herrero-Vanrell¹. (¹) Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, Complutense University of Madrid, Madrid, Spain, (²) Institute for Ophthalmic Research, University of Tuebingen, Tuebingen, Germany, (³) DSM, Geleen, The Netherlands

Amino acid based polyesteramides (PEAs) are a new generation of biodegradable polymeric materials based on α-amino acids, aliphatic dicarboxylic acids and aliphatic α-ω diols. Dexamethasone (DX) is a glucocorticoid widely used in ophthalmology to prevent and/or treat several ocular diseases. The aim of this study was to evaluate the suitability of PEA microspheres (Ms) to be used as carriers of DX for controlled delivery in ophthalmology.

Unloaded and DX-loaded PEA Ms were prepared following an emulsion-solvent evaporation technique. Ms were characterized by particle size, morphology and DX-encapsulation efficiency. In vitro release studies were carried out for 90 days by suspending the Ms in isotonized PBS. PEA Ms were sterilized with ⁶⁰Co radiation source (25 kGy) and then characterized. To determine the toxicity of unloaded PEA Ms, a screening study (0.125-1 mg Ms) was performed in an organotypic culture system of wild type rats’ retinas, by TUNEL assay and conventional histology in short and long term cultures (7 and 20 days in culture, respectively). Toxicity of sterilized DX-loaded PEA Ms was tested in the same system with 0.625 mg of Ms.

The encapsulation efficiency of DX was around 85% (181.57±2.76 μg DX/mg Ms) and the release profile of DX had an initial burst of 17.28±0.44 µg DX/mg Ms in the first 24 h. The cumulative release of DX after 90 days was 98.43±9.65 µg DX/mg Ms (54.10±6.21%). Sterilized DX-loaded PEA Ms did not show any difference with non-sterilized Ms in terms of particle size, morphology, encapsulation efficiency and release profile of DX up to 90 days. Retinas treated with unloaded and DX-loaded PEA Ms did not show signs of toxicity in organotypic retinal cultures up to 0.625 mg.

Biodegradable PEA Ms are potentially useful to develop new controlled drug delivery systems for treating ophthalmic diseases affecting the back of the eye.

Tuesday, March 18, 2014 02:40 PM
Peptide-Based Materials for Nanomedicine (01:00 PM - 05:00 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm F
215 - Well-defined synthetic star-polypeptides as gene delivery vectors

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Recent advances in the ring-opening polymerisation of N-carboxyanhydrides (NCA) allow the synthesis of well-defined synthetic polypeptides with architectural control. Employing a 'grafting from' approach from a range of generations of amino-functional polypropylene imine (PPI) dendrimer initiators, star polypeptides with varying number of arms and molecular weights were obtained.¹ Star shaped poly(lysine)s (PLL) were used to prepare pDNA and siRNA to form "polyplexes" to determine their ability to complex different nucleic acid cargoes.² Significant differences in size and surface charge were seen between star-shaped PLL polyplexes and linear PLL polyplexes for both cargoes. The star-shaped polypeptides were capable of more effective complexation and protection of both nucleic acids at low N/P ratios compared to linear PLL. This was particularly evident in siRNA polyplexes as linear PLL failed to completely complex siRNA into nanocomplexes of appropriate size for cell transfection i.e. <200 nm in size, while star poly(lysine) formed siRNA-polyplexes <100nm at certain N/P ratios. A 300-fold increase in luciferase expression was seen for star-shaped PLL polyplexes with 64 arms compared to linear PLL pGLuc polyplexes in epithelial cells. The results highlight the potential of polypeptide star polymers as gene delivery vectors.

216 - Enzyme responsive 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.
Antibodies, such as IgGs, are widely applied as detection probes, purification ligands and targeting moieties in research and medicine. Protein A from *Staphylococcus aureus* is capable of selectively binding to antibodies. Z$_{33}$, a 33 amino acids peptide sequence derived from Protein A, is a minimized binding domain with comparable interaction potential. This peptide was fused to two different proteins without perturbing the properties of both the protein and the Z$_{33}$-domain. The thermodynamic parameters for the interaction of the fusion proteins with antibodies from various species were determined by isothermal titration calorimetry. This showed that binding was enthalpically driven and entropically unfavorable. A difference in Z$_{33}$ binding affinity of several orders of magnitude was observed between human and bovine antibodies. The selectivity towards human IgGs was employed in a fusion protein of Z$_{33}$ and a stimulus-responsive elastin-like polypeptide for the efficient and selective purification of human IgGs from mixtures containing bovine IgGs and other proteins by affinity precipitation.
218 - PLLA-\textit{b}-peptide-\textit{b}-PLLA nanoparticles in nonaqueous emulsion: Promising platform for bioactive carriers?

\textbf{Robert Dorresteijn,} dorreste@mpip-mainz.mpg.de, \textbf{Nils Billecke, Sapun H Parekh, Klaus Müller, Markus Klapper. Max-Planck Institute for Polymer Research, Mainz, Germany}

The nonaqueous emulsion polymerization method has proven to be a very useful for the generation of bioactive and sensitive systems\textsuperscript{1-5}. Owing to the mild and nonaqueous conditions, this system enabled facile incorporation of a variety of peptides in between two poly(L-lactide) (PLLA) chains in a single step at room temperature by using bifunctional peptides as initiator for the ring-opening polymerization (ROP) of L-lactide\textsuperscript{2}. The resulting nanocarriers consisting of PLLA \textit{block} peptide \textit{block} PLLA copolymers showed high loading capacity of cargo molecules and were dispersed in aqueous medium with retention of the original size of 100 nm, which is ideal for drug delivery systems as it prevents potential recognition and clearance by Kupffer cells and minimizes drainage into blood capillaries, what is associated with potential toxicity\textsuperscript{2,6-7}. Proven peptide tunability makes this method a highly promising platform for the generation of custom designed bioactive systems.

219 - Mechano-responsiveness: Stimulating polymer chemistry

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Materials capable of responding in a useful fashion to given stimuli are particularly attractive both from a fundamental and application-oriented perspective. Here we present specific examples of how architectural control in polymers can be used as a tool to direct function. In particular, we present a class of mechanically responsive materials i.e. both polymers that will react to a mechanical stimulus or materials that will respond mechanically upon application of other types of cues. The practical uses of such materials will also be broached.
220 - Synthesis and properties of novel ionomer nanocomposites without quaternary ammonium salts or surface functionalization

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Nanocomposites of layered silicates have been prepared by a simple process with excellent dispersion and very substantial exfoliation in new, water-self-dispersible ionomers of ethylene/methacrylic acid copolymer. The quaternary ammonium salts that can degrade and discolor during processing are not required for exfoliation. With platelets of a synthetic, 2:1 layered hydrous magnesium lithium silicate (Laponite®, a "synthetic hectorite"), nanocomposite clarity is excellent. Haze and yellowness index are only very slightly affected. Excellent morphology can be obtained at least up to 30 wt % filler. The ionomer's mechanical and thermal properties are substantially improved, especially tensile modulus, storage and loss modulus (DMA), and creep. This approach has been successfully extended to a range of well-known nanofillers, rod-shaped, platy, and spherical.
221 - Thermomechanical behavior of hydrogen-bonded supramolecular polymer nanocomposites containing complimentary hydrogen-bond functionalized silica nanoparticles

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Hydrogen bonded polymers and supramolecular polymers form an important subclass of temperature responsive materials. We have investigated the effect of nanoparticle surface functionality and loading on the thermomechanical behavior of nanocomposites prepared using these temperature responsive hydrogen-bonded polymers with surface functionalized silica nanoparticles. Our prior work (RSC Advances, 3(37), 2012, 16686) showed a complex interplay between nanoparticle surface functionality and thermomechanical response that varies with polymer hydrogen bond content and crystallinity.

In this talk, we expand on our prior work by comparing the thermal and mechanical response of nanocomposites made using nanoparticles functionalized with the self-complementary hydrogen-bonding moiety 2-ureidopyrimidinone (UPy) and nanocomposites made using nanoparticles functionalized with a complementary hydrogen-bonding moiety based on 2,7-diamido-1,8-napthyridine (Napy). Both side-chain hydrogen-bonded polymer matrices and linearly hydrogen-bonded supramolecular polymer matrices will be discussed. Trends in thermomechanical response are explained using a combination of interfacial and dispersion effects.
Layer-by-layer (LbL) assembly is wide-reaching conformal coating "platform" technology capable of imparting a multiplicity of functionalities on nearly any type of surface in a relatively environmentally friendly way. At its core, LbL is a solution deposition technique in which layers of cationic and anionic materials (e.g. colloidal or nano-particles, polymers and even biological molecules) are built up via electrostatic attractions in an alternating fashion, while controlling process variables such as pH, coating time, and concentration. Here we are producing nanocomposite multilayers having 10 – 96 wt% clay that are completely transparent and exhibit oxygen transmission rates below 0.005 cm$^3$/m$^2$•day (at a film thickness below 100 nm). These same 'nanobrick wall' assemblies are very conformal and able to impart flame resistance to highly flammable foam and fabric by uniformly coating the complex three-dimensional geometries. On foam, these coatings can simultaneously cut the heat release rate (HRR) in half, relative to uncoated foam, and eliminate melt dripping without adding halogenated flame retardants. We've also developed intumescent recipes that do not require clay, but rather rely on the foaming action of phosphorus and nitrogen-rich molecules. These 'intumescent' nanocoatings provide an effective, environmentally-benign alternative to the more toxic brominated compounds widely used today. I'll also describe how these films can separate H$_2$ from N$_2$, with selectivity greater than 2000, which exceeds other commonly used gas separation membranes (including zeolites). These films also have exceptional oxygen barrier that makes them interesting for food and flexible electronics packaging. All of the materials described are water-based and processing occurs under ambient conditions in most cases. Our work in these areas has been featured numerous times in C&EN and also highlighted in Nature, ScienceNews, Smithsonian Magazine and various other scientific news outlets.
223 - Structure property relationships in cyclobutanediol based polymers and polymer nanocomposites exhibiting high impact and shape memory

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Over the past decade a great deal of research and commercial activity has occurred on the use of 2,2,4,4 tetramethyl 1,3 cyclobutanediol (CBDO) monomer in polyester polymers. These polyesters exhibit extremely high impact resistance (40% greater than polycarbonate), exceptional ballistics performance, and extraordinary shape memory and self-healing properties. Nanocomposites made with this family of polymers retains these extraordinary characteristics but in addition the composites yield improved modulus and increased elongation at break. The CBDO monomer exist in a trans and cis conformation and in an effort to understand the origin of the unique properties of this family of polymers the the two forms have been purified and utilized to produce polymers with only trans or cis monomer. This paper will report the properties of these two end members and how they correlate with the type of monomer. It is clear from this work that the cis form of the monomer is critical to the observed properties of high impact strength and shape memory.

Tuesday, March 18, 2014 03:20 PM
Responsive Nanostructures and Nanocomposites (01:30 PM - 04:50 PM)
Location: Hyatt Regency Dallas
Room: Moreno A
Stimuli-responsive polymers, which undergo phase transitions in response to an external stimulus (e.g., temperature, pH value) have gained the interest of many researchers in the last decade. Particular attention has been paid to the thermo-sensitive self-organization of amphiphilic block copolymers, especially on the formation of phase separated structures in the bulk, in thin-films or in solution. Block copolymers as building blocks represents a versatile and straightforward methodology for the simple incorporation of different structural or chemical features (e.g., changing the hydrophobic to hydrophilic ratio).

Different block copolymers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) with di(ethylene glycol) methyl ether methacrylate (DEGMA) or styrene (S) were synthesized by controlled radical polymerization techniques. One system, PDMAEMA-b-PDEGMA, showed double lower critical solution temperature (LCST) behavior in water and the respective phase transitions were studied using turbidimetry, dynamic light scattering (DLS), variable temperature proton nuclear magnetic resonance ($^1$H NMR) spectroscopy, zeta potential and cryo transmission electron microscopy (cryo-TEM). Hereby, the formation of multi- and unilamellar vesicles, depending on the solution temperature, could be demonstrated (see Figure1).
Biocompatible albumin NPs are generally nontoxic and easy to prepare. However, the strategies of labeling and tracking albumin NPs using organic fluorescent chromophores are still limited, and most commercial available tags emit in the visible region, in which signals are often obscured by autofluorescence. We report two squaraine (SQ) dyes, N-propanesulfonate-benzothiazolium squaraine (SQ-1) and N-propanesulfonate-benzoindolium squaraine (SQ-2), containing sulfonate groups to increase water solubility. Both dyes are nearly nonfluorescent in aqueous solution with fluorescence quantum yields of 0.03, but exhibited significant fluorescence enhancement after noncovalently binding with bovine serum albumin (BSA). Upon addition of BSA, the fluorescence intensity increased by ca. a factor of 10, along with a 10-fold increase in the fluorescence lifetime. SQ-1 and SQ-2 interacted with BSA efficiently and appeared to show a preference for binding at site II, involving combinational effects of electrostatic and hydrophobic interactions. The fluorogenic squaraine dyes were then used to label BSA, forming BSA-based nanoparticles (NPs) through noncovalent binding. The resulting BSA-SQ NPs exhibited enhanced near-IR fluorescence and reduced aggregation of the squaraine chromophore. The BSA-SQ NPs were used in cell incubation and bioimaging studies.

Uptake of the nanoparticles was conveniently monitored using fluorescence microscopy by determining the red fluorescence emitted from the cells that internalized the BSA-SQ NPs. Consistent with previous reports, both BSA NPs and BSA-coated NPs were uptaken by cells into the endosomes and/or lysosomes. To track the BSA-SQ NPs following their uptake, the lysosomal compartments of HCT 116 cells were stained with LysoSensor Green. The resulting fluorescent images revealed that most of the red-emitting particles overlapped with LysoSensor-stained lysosomes. This strategy overcomes the generally low fluorescence emission of SQ dyes in water and aggregation-reduced fluorescence, providing a versatile strategy for BSA-sensing and BSA-based NP delivery.
FRET efficiency map revealing the interphase in epoxy/NFC composite (left image), and color composite image from donor (blue) and acceptor (green) fluorescence in epoxy/NFC composite (right image).

Composites have percolated into a wide range of material applications, ranging from vehicle light weighting to construction materials. With an increase in demand comes the need for more sustainable sources of components for composites. Understanding the components' interactions at the interphase in composites will help target possible sources for both the reinforcing and matrix portion when designing a composite. Förster Resonance Energy Transfer (FRET) imaging of a composite interphase was pioneered at the National Institute of Standards and Technology previously, through the dispersion of donor dye in a polymer matrix and covalent attachment of the acceptor dye to nanofibrillated cellulose (NFC). In this work, we examine the interphase of an epoxy/NFC composite using FRET. To this end, a donor fluorophore and acceptor fluorophore were covalently attached to the epoxy and NFC, respectively, (see Figure, right image) to prevent dye migration. The chemistry employed optimized spectral overlap, between the donor emission and acceptor absorbance, to maximize energy transfer efficiency at the interphase. Because the dyes are anchored to each phase, an increase in FRET signal is expected where the two phases are more intimately mixed (see Figure, left image). Here we investigated the FRET response to changes at the interphase caused by mechanical and thermal stresses.
227 - Encapsulation of proteins in micro and nano hydrogel carrier systems for controlled drug delivery

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Therapeutic proteins like antibodies or signaling proteins have a high potential for pharmaceutical applications. Drug delivery systems are needed to protect these proteins from in-vivo degradation. Furthermore, the proteins are able to induce unwanted side effects, e.g. an immunogenic response. A local administration close to the diseased area and a slow drug release can minimize these effects. Hydrogels provide a protein friendly environment and can have good biocompatibility. Therefore they are well suited as drug delivery systems. Diffusion and/or degradation are the main release mechanism. To investigate the relation between network structure and release hydroxyethyl starch modified with polyethylene glycolmethacrylate was used to obtain bulk hydrogels or injectable hydrogel microspheres.

The release was investigated and correlated with the mesh size.¹ Green fluorescent protein (GFP) loaded hydrogels have been analyzed by fluorescence methods with two-photon excitation.² Via fluorescence anisotropy the inner rotational motions can be studied. The results suggest an unrestricted GFP rotation within the hydrogel.² Fluorescence recovery after photo-bleaching gives information about the translational diffusion. Here the data indicate that translational mobility of GFP is restricted in the hydrogel.² Furthermore, a nanogel system prepared from chitosan and tripolyphosphate was investigated regarding entrapment efficiency and release of signaling proteins.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is acknowledged.


³ Poth, N. et al. 2013, submitted
228 - Orthogonal and modular approaches for the construction functional biomaterials

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Using hyaluronic acid (HA) as the starting material, we have created various HA-based bulk gels, hydrogel particles (HGPs) and HGP-integrated doubly crosslinked networks (DXNs). Successful installation of orthogonal functional groups to HA has led to the development of various in situ crosslinkable HA bulk gels. The same crosslinking chemistries, when restricted to microscopic compartments, have enabled the production of HA HGPs. Physical entrapment or covalent integration of HA HGPs in a secondary HA network give rise to hybrid networks that are hierarchically structured and mechanically robust, capable of mediating cellular activities through the spatial and temporal presentation of biological cues. Alternatively, self-assembled block copolymer micelles (BCMs) carrying reactive handles on the hydrophilic shell were employed as the microscopic crosslinkers for the construction of mechano-responsive HA hydrogels. Dexamethasone (DEX), loaded into BCMs prior to crosslinking, was released from BCM-crosslinked HA gels in a strain-dependent manner by intermittently-applied external compression. HA-based bulk gels and DXNs are conducive matrices for the engineering of soft connective tissues, as well as the creation of prostate cancer tumor models.

Figure 1: Cryogenic scanning electron micrograph of HA HGPs (left) and HA DXN (right).
229 - Cytocompatible phospholipid polymer hydrogel matrix for higher efficient cell differentiation

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To provide cells as one of the materials for tissue engineering towards regenerative medicine, a large number of uniform cells are imperative. The differentiation of pluripotent stem cells is induced by chemical and physical signals. The differentiation process occurs during the cell turnover, and signal sensitivity is known to be associated with the G1 phase during cell proliferation cycle. We hypothesized that enhancement of differentiation efficiency of cells is achieved using three-dimensional (3D) environments surrounding cells that could control the induction of signaling protein to G1 phase of the cell proliferation cycles. The 3D environment was constructed by the hydrogels composed of poly[MPC-co-n-butyl methacrylate (BMA)-co-p-phenylvinylboronic acid (VPBA)] (PMBV) and poly(vinyl alcohol) (PVA). The proliferation of cells encapsulated in the PMBV/PVA hydrogel was greatly sensitive by its storage modulus of the hydrogels. That is, the modulus of the hydrogels was higher than 1.1 kPa, proliferation of cells in the hydrogel was disturbed. On the other hand, when the modulus became 0.67 kPa, cell proliferation was induced. Using this change in the modulus of hydrogel, we regulated both the proliferation of cells and induction with differentiation signaling protein (BMP-2) to cells. The differentiation efficiency of the cells differentiated in PMBV/PVA hydrogel in this procedure increased by 4.2-fold compared to conventional method on a conventional cell culture plate.

The PMBV/PVA hydrogel would be a promising material to provide cells with high differentiation efficiency.
230 - Synthesis of biomolecule-responsive bioconjugated gel particles for biomedical applications

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Stimuli-responsive gel particles that undergo changes in size in response to environmental stimuli such as pH and temperature have attracted considerable attention as smart biomaterials. We have prepared various biomolecule-responsive hydrogels by using biomolecular complexes as dynamic crosslinks. In this study, we prepared biomolecule-responsive bioconjugated gel particles, which undergo changes in size in response to a target biomolecule such as glucose and antigen, by introducing saccharide-lectin and antigen-antibody complexes as dynamic crosslinks. The glucose-responsive gel particles were prepared as follows: After the synthesis of acryloyl-modified concanavalin A (ConA), the complexes between 2-glucosyloxyethyl methacrylate (GEMA) and acryloyl-modified ConA were formed in a phosphate buffer solution. The GEMA-ConA complexes with acryloyl groups were copolymerized with \textit{N}, \textit{N}-diethylaminoethyl methacrylate (DEAEMA) and poly(ethylene glycol) dimethacrylate (PEGDMA) by surfactant-free emulsion polymerization to obtain the GEMA-ConA gel particles. Similarly, antigen-responsive gel particles were also prepared by the surfactant-free emulsion copolymerization of DEAEMA, PEGDMA, acryloyl-modified antigen and antibody. The resultant GEMA-ConA gel particles were colloidally stable in phosphate buffered saline and had a diameter of approximately 300 nm. The GEMA-ConA gel particles swelled in the presence of glucose. The swelling ratio of the GEMA-ConA gel particles changed in accordance with glucose concentration. Their glucose-responsive swelling was caused by the dissociation of the GEMA-ConA complexes acting as crosslinks. Furthermore, the paper will describe the antigen-responsive behavior of antigen-responsive gel particles having antigen-antibody complexes as dynamic crosslinks.

\begin{figure}
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\includegraphics[width=\textwidth]{glucose-responsive-gel-particles.png}
\caption{Glucose-Responsive Gel Particles}
\end{figure}

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\includegraphics[width=\textwidth]{antigen-responsive-gel-particles.png}
\caption{Antigen-Responsive Gel Particles}
\end{figure}
231 - Quick preparative method and formulation for biodegradable injectable polymers exhibiting temperature-responsive sol-gel transition

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Biodegradable polymers exhibiting temperature-responsive sol-gel transition between room temperature and body temperature are expected to be applied as injectable polymer (IP) systems in biomedical applications. IP solution containing drugs or living cells can be injected by simple syringe injection at the target site in the body to form a hydrogel acting as a sustained drug releasing depot or a scaffold for tissue regeneration. For example, Lee et al. reported ABA-type triblock copolymer of poly(lactide-co-glycolide) and PEG as biodegradable injectable polymer [1]. We also reported several biodegradable IP systems exhibiting relatively high mechanical strength in gel state using block copolymers of polylactide and branched PEG [2]. These copolymers are usually sticky paste in dry state at room temperature, and it takes a long time to be dissolved in aqueous solution. On these issues, Jeong et al. reported solidification of the triblock copolymers containing poly(ε-caprolactone) exhibiting temperature-responsive sol-gel transition [3]. But, the copolymers must be heated above melting temperature upon dissolution. In this study, we developed a very quick preparative method at room temperature for aqueous IP solution. We synthesized triblock copolymers of poly(ε-caprolactone-co-glycolide) and PEG, PCGA-b-PEG-b-PCGA. The obtained copolymers could be freeze-dried to show powder form morphology in dry state at room temperature. We found that some of the best formulations composed of PCGA-b-PEG-b-PCGA and additives could be distributed in PBS to give suspension within 1 min at room temperature. The obtained suspension could be sucked by syringe and exhibited temperature-responsive sol-gel transition between room temperature and body temperature. Therefore, this system should be convenient for instant preparation at clinical scene.


232 - Efficient chemistry for post-electrospinning nanofiber modification

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Polymeric nanofibers are attractive for tissue engineering applications. Nanofibers can be generated easily via electrospinning, and their morphology and dimensions can be tuned easily with solvent, concentration and processing conditions. Apart from the physical characteristics of nanofibers, the biochemical effects that are induced from the bioactive motifs presented on the surface of nanofibers also play an important role in the resulting behavior of cells on the materials. Efficient chemical methods aiming at efficient modification of electrospun fibers are needed to reduce potential biocompatibility concerns. In our research, 4-dibenzocyclooctynol (DIBO) and its derivative were used as initiators for the ring-opening polymerization of a number of different monomers like DIBO-PBLG, DIBO-PCL, DIBO-PLA, DIBO-(P(CL-co-OPD)) and so on. The presence of a DIBO group at the chain end of the polymers enables fast, efficient and metal-free functionalization. For further application of these materials, nanofiber-based scaffolds were generated via electrospinning, the nanofibers generated from these polymers bearing active DIBO groups on the surface of fibers available for post-fabrication functionalization in aqueous solution.

Functionalized nanofiber based scaffolds were used for neuron engineering, soft tissue repair and protein stabilization. Combined with other types of efficient chemical methods, di-functionalized and tri-functionalized nanofibers were also constructed for the study of synergistic effects in tissue engineering.
This paper describes our progress in developing a unique family of functional bioresorbable poly(sophorolipid) biomaterials for use as scaffolds for tissue engineering. Lactonic sophorolipid (LSL\(_{2\text{Ac}}\)) is a natural macrocyclic glycolipid produced in large quantity (>150 g/L) by fermentation of the yeast *Candida bombicola*. Our team used ring-opening metathesis polymerization (ROMP) to convert LSL\(_{2\text{Ac}}\) into P(LSL\(_{2\text{Ac}}\)) (\(M_n>100,000\), \(T_g\) 61°C, \(T_m\) 123°C, semi-crystalline). To extend our understanding of LSL\(_{2\text{Ac}}\) ROMP polymerizations, studies were conducted using Grubbs 2\(^{\text{nd}}\) (G2) and 3\(^{\text{rd}}\) (G3) generation catalysts to determine polymerization kinetics. Polymerizations were shown to be entropically driven toward an equilibrium which consists of about 70% polymer, 10% of oligomer and 20% monomer. The \(k_p\) of G3 catalyzed ROMP continuously decreases as the polymerizations progress. Plots of \(\ln([\text{M}]_0/[\text{M}]_t)\) versus reaction time for G2 are linear, suggesting apparent first-order kinetic behavior. In G2 catalyzed LSL\(_{2\text{Ac}}\) ROMP, a plot of \(M_n\) versus [monomer]/[initiator] ratio resembles the theoretical curve based on living polymerizations. To create a diversified set of macrocyclic glycolipid monomers and polymers, LSL\(_{2\text{Ac}}\) was regioselectively modified at its two primary -OH positions, including deacetylation to prepare P(LSL\(_{\text{OH,Ac}}\)) and esterification with various vinyl esters (e.g. vinyl butyrate to prepare LSL\(_{\text{Bu,Ac}}\)). Clickable groups including methacrylate and azide were also selectively introduced into LSL monomers. There monomers were successfully converted into new SL (co)polymers with tailored properties and potential to conjugate bioactive groups. P(LSL\(_{2\text{Ac}}\)), P(LSL\(_{\text{OH,Ac}}\)), P(LSL\(_{\text{Bu,Ac}}\)) films were selected to test their cytotoxicity and ability to support attachment and proliferation of human mesenchymal stem cells (h-MSC). After a 72 h culture time, h-MSC attachment and proliferation were statistically indistinguishable across the different poly(SL) structural analogs and relative to tissue culture polystyrene controls. In addition, after 72 h, no significant cytotoxic effects for these poly(sophorolipid) film surfaces were detected by lactate dehydrogenase (LDH) relative to tissue culture polystyrene controls.
234 - Fluoralkyl polyhedral oligomeric silsesquioxane (F-POSS) modified structures: Synthesis to applications

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Fluoralkyl Polyhedral Oligomeric SilSesquioxane (F-POSS) has emerged as a promising nanomaterial possessing low surface energy properties for applications in wetting-resistance materials. Recently, a novel synthetic method was developed for the controlled functionalization of F-POSS, enabling these compounds to be further functionalized with a variety organic moieties ranging from long aliphatic chains to various monomers. The chemical structures of these compounds were confirmed using multinuclear NMR spectroscopy, FT-IR and combustion analysis. The crystal structure for an endo,endo disilanol F-POSS compound was determined by single crystal X-ray diffraction. Among these functionalized compounds different macromers using methacrylate, acrylate, styrene, or norbornene functionality were produced. These macromers was used to produce copolymers via free radical polymerization or ring-opening metathesis (ROMP) polymerization. These well-defined copolymers containing a covalently bound F-POSS macromers. These tunable structures provide unprecedented access to fluorinated building blocks for low surface energy materials.

Figure 1. a) General methodology of F-POSS cage functionalization. b) Static contact angle measurement of water droplet on SiO\textsubscript{2} surface coated with methacrylate functionalized F-POSS. c) Water and hexadecane droplets on a cotton fabric coated with poly(methyl methacrylate)-co-poly(methyl methacrylate functionalized F-POSS).
235 - Polymer processing using α -cyclodextrin and its characterization

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ABSTRACT

Host-Guest Inclusion complex (IC) formation is a well known method to reorganize the polymer chains and improve their mechanical and rheological properties. Modifying polymers using cyclodextrins (CDs) is one such way of processing polymers. CDs, cyclic starches containing glucose repeat units, are often able to form non-covalently bonded ICs with guest polymers by threading them through their hydrophobic cavities. Cd-ICs with biopolymers like Poly(ε-caprolactone) ((PCL α-CD-IC ) are bio-absorbable, bio-compatible and bio-Degradable and can be used for biomedical applications. On removal of the host α-CDs, the c-PCL that results is likely transformed into small domains (1/10th the size of the crystalline grains of the IC powder). In each domain the PCL chains are likely partially aligned and have largely un-entangled extended conformations, without, however, directional correlation among the different coalesced domains. In comparison to samples made from randomly-coiled and entangled as-received PCL (ar-PCL), the rheological and mechanical properties of c-PCL are distinct and improved. For example, c-PCL melt exhibits yield stress and shows a zero shear viscosity nearly 3 orders of magnitude below that of an ar-PCL melt, and frequency sweep behavior distinct from that observed in the viscoelastic melt of the ar-PCL. Also c-PCL films and undrawn and drawn fibers were observed to have significantly and greatly higher moduli, respectively, and greatly reduced extensibilities.
Lower back pain is often associated with degeneration and loss of the gel-like nucleus pulposus (NP), a component of the intervertebral discs in the backbone. Therefore, replacement of lost NP with a synthetic gel is under consideration for the treatment of disc degeneration. A biocompatible hydrogel as similar to natural human NP is desired. In present study, we synthesized a novel hydrogel composed of chondroitin sulfate (CS), a major component of NP, and glycidyl methacrylate (GMA) as crosslinker.
237 - Truly monodisperse single-walled carbon nanotube epoxy composites

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Solvent-dispersed single-walled nanotubes (SWNTs) are incorporated into epoxy matrices, followed by evaporation of the solvent before curing. The effect of solvent choice in thermal and mechanical properties of the resulting nanocomposites is evaluated using N-methyl pyrrolidone and dimethyl formamide. In this study, fluorescence is used as the tool to monitor the dispersions of SWNTs in the solvent and epoxy matrix. This study also compares the thermal and mechanical properties of these epoxy nanocomposites with a nanotube loading ranging from 0.001-0.01 wt. %. The presence of residual solvent in the epoxy composites is determined by thermogravimetric (TGA) analysis. Thermo-mechanical properties of the resulting epoxy nanocomposites are determined using dynamic mechanical analysis and differential scanning calorimetry.
Polymer composites attract significant scientific and technological interest due to their major improvements in mechanical properties, gas barrier properties, thermal stability, fire retardancy, and other areas. Polymer network composites are unique, since the reinforcing filler is distributed throughout the matrix of cross-linked polymer chains. C₆₀–polymer composites have potential energy-transfer advantages for light-harvesting and photovoltaic polymer applications. In this work, synthesis of C₆₀–polymer network composites by cross-linking γ-cyclodextrin (γ-CD) molecules together with dodecyl chains will be discussed. The network matrix is covalently bonded and contains essentially equally spaced CD cavities that are dimensionally suited for the intercalation of C₆₀. These C₆₀–CD polymer nanocomposite networks are characterized by guest–host capabilities from the CD nodes, monodisperse filler sizes from C₆₀ and monodisperse 12-carbon tie chain lengths. The network is capable of homogeneously intercalate C₆₀ by apparently via van der Waals guest-host interactions resulting in stable C₆₀ filled networks with improved mechanical properties. The interaction between γ-CD and C₆₀ is enabled by the hydrophobic γ-cyclodextrin cavity and its inner cavity dimension which controls the accessibility of C₆₀. Prepared membranes reveal that the composites maintain a stable C₆₀ concentration, even after multiple extractions with toluene and these membranes are also useful in extracting C₆₀ from C₆₀–solvent mixtures. The synthesis route described in this work is generally applicable for the preparation of reinforced and networked composites involving monodisperse fillers.
239 - Well-ordered nanostructured polyimide films and nitrogen-doped mesoporous carbons by a soft-template approach

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The preparation of a series of mesoporous polymers containing nitrogen-based functional groups and nitrogen-doped mesoporous carbons derived from the same precursor system through soft templating remains challenging, because most nitrogen sources are transformed at an elevated temperature or because the nitrogen-doped carbon matrix decomposes upon calcination. Herein we demonstrate the successful preparation of well-ordered nanostructured polyimides and nitrogen-doped mesoporous carbons with high regularity, tunable morphology, and high surface area, by using highly stable oligoimides and/or polyimides as the nitrogen source. Poly(amic acid)s, the precursors of polyimides, undergo a co-self-assembly process with amphiphilic block copolymer template and transform into polyimides under heating. Upon calcination at 350°C the template is removed without damaging the imide linkage, leading to a highly ordered polymer network with intrinsic imide functionality. Further carbonization at 600 °C allows the formation of nitrogen-doped mesoporous carbon. This newly developed system, which exhibits a high degree of flexibility, allows precise morphological control of 1-dimensional lamellar, 2-dimensional hexagonal and 3-dimensional cubic mesostructures on the basis of adjustments of each component in the system. This homologous series of well-ordered nanostructured polyimides and nitrogen-doped mesoporous carbons have potential applications in the fields of advanced materials.
Segmental dynamics of adsorbed samples of poly(methyl methacrylate) homopolymer and poly(styrene-co-methyl methacrylate) copolymers on silica was studied using deuterium quadrupole-echo NMR. Homopolymer and copolymer samples, with different methyl methacrylate percentages, were synthesized by free radical polymerization and the adsorbed samples were prepared by solution deposition using toluene. Spectra were collected at different temperatures, below and above the glass transition temperature, for the bulk and the adsorbed samples of homo- and copolymers of poly(methyl methacrylate). The effect of the adsorption and the copolymer composition on the segmental dynamics of the above systems was evaluated. An example of the differences in the spectra of the two systems (bulk and adsorbed) is shown in the figure.
241 - Powder coatings as additives for frontal polymerization

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Frontal polymerization is a localized reaction zone that propagates from the coupling thermal diffusion and the Arrhenius dependence of the rate of an exothermic polymerization. Cure-on demand polymerizations with multifunctional acrylates can be created using frontal polymerization for use in rapid repair of wood and floors as well as a cure-on demand sculptural medium.

In order to improve the strength and toughness of the materials, we tested thermoplastic and thermoset powder coatings in frontal polymerization systems. The high temperature of the front (> 200 °C) is sufficient to melt and cure the powders.
The goal of this research is to synthesize and characterize novel polyphosphazenes bearing carboxy terminated amino acid analogues (β-alanine and γ-amino butyric acid) capable of extensive nucleation of hydroxyapatite (HaP) on their surface when exposed to simulated body fluid. Polyphosphazenes are inorganic/organic hybrid polymers with a nitrogen/phosphorus backbone, with each phosphorus atom bearing two additional organic side groups. The amino acid analogues were incorporated onto the phosphazene backbone to coordinate Ca\textsuperscript{2+} and allow for the deposition of HaP on its surface. Previous studies have shown that polymers capable of nucleating HaP, or those containing a HaP filler, increased the ability of osteoblast-like cells to adhere to their surface and proliferate. In order to control the rate of hydrolysis, the amino groups were co-substituted with p-cresol at either 25 or 50% to alter the degree of backbone protection from water. The final polymers containing 50% acidic group showed extensive calcium phosphate deposition as observed by mass gain and SEM/EDS, with one system showing the presence of HaP by XRD.
243 - Investigation of induced crystalline morphology strata in nylon 6,6

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The crystalline morphology of nylon 6,6 is largely responsible for excellent mechanical and chemical properties of this common polymer. Much is known about the formation of nylon 6,6 crystal structure from the unoriented melt. We aim to develop a parallel understanding of the crystalline kinetics through the cross section of an injection molded sample. In this situation, the melt is subject to both thermal and shear gradients, and orientation effects are not negligible. Inducing a desired cross section of crystalline morphology in an injection molded sample is not straightforward and factors such as sample thickness, shear history of the material, orientation of the polymer melt, and rate of heat transfer result in gradient morphologies consisting of both spherulitic and transcristalline structures.

Controlled molding conditions were used to induce both very high and very low shear rates in samples of two different thicknesses. Resulting crystalline gradients were then studied using Fast DSC, FTIR, and polarized light microscopy. An example of the extreme differences between the induced morphology at the outer surface (skin) and the center (core) of the molded samples is observable when comparing the crystalline melting peaks and thermal transitions that are further contrasted with the annealed Fast DSC curve in the following plot.

These crystalline gradients are correlated to mechanical properties via dynamic mechanical analysis. The Brill transition, a triclinic to pseudo-hexagonal crystalline transition which is typically observed over a known temperature range, is also observed at a constant temperature in the dynamic frequency sweep evaluation of the injection molded samples.
244 - Probing the weak interaction of proteins with neutral and zwitterionic antifouling polymers

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Protein-polymer interactions are of great interest in a wide range of scientific and technological applications. Neutral poly(ethylene glycol) (PEG) and zwitterionic poly(sulfobetaine methacrylate)(pSBMA) are two well-known nonfouling materials that exhibit strong surface resistance to proteins. However, it still remains unclear or unexplored how PEG and pSBMA interact with proteins in solution. In this work, we examine the interactions between two model proteins (bovine serum albumin and lysozyme) and two typical antifouling polymers of PEG and pSBMA in the aqueous solution using fluorescence spectroscopy, atomic force microscopy, and NMR. The effect of mass ratios of protein:polymer on the interactions is also examined. Collective data clearly demonstrate the existence of weak hydrophobic interactions between PEG and proteins, while no detectable interactions between pSBMA and proteins. The elimination of protein interaction with pSBMA could be due to an enhanced surface hydration of zwitterionic groups in pSBMA. New evidence is given to demonstrate the interactions between PEG and proteins, which are often neglected in literature because the PEG-protein interactions are weak and reversible, as well as the structural change caused by hydrophobic interaction. This work provides a better fundamental understanding of the intrinsic structure-activity relationship of polymers underlying polymer-protein interactions, which are important for designing new biomaterials for biosensor, medical diagnostics, and drug delivery applications.
Many biopolymers have attained significant attention for biomedical applications due to their biocompatibility. PEGylated poly(amino acids) (PEG-PAA) have been shown to exhibit minimal toxicity and high hydrophilicity, which make them viable for biomedical purposes. Chemical characteristics of specific Poly(ethylene glycol) (PEG) and poly(amino acid) (PAA) copolymers make them suitable for drug delivery applications and gene therapeutics. The key focus of our research was the synthesis of amphiphilic ABC ter-copolymers based on PEG and PAA copolymers through ring-opening polymerization (ROP) of N-carboxyanhydrides. The deprotection of ter-copolymers, utilizing protected polar amino acids (Glutamate and Lysine) in combination with a hydrophobic amino acid (Leucine), was achieved via basic hydrolysis in order to control their amphiphilic character. Self-assembly of these deprotected ABC ter-copolymers in aqueous medium may generate micro and nano scale aggregates for drug delivery. Cationic ABC ter-copolymers may also provide constructs for gene expression through DNA condensation.
246 - Glycosylated bovine serum albumin as model extracellular matrix

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Bovine serum albumin (BSA) is one of the most abundant by-product proteins from the livestock industry, and it has been widely used in biomedical research. In this project, BSA was employed as a model protein to create artificial Model Extracellular Matrix (ECM) for potential tissue engineering applications. For this purpose, reduced BSA was PEGlyated and glycosylated to synthesize a linear glycoprotein as the major component of ECM. A layer-by-layer assembly approach was employed to fabricate an ECM-mimicking scaffold, with EDC (1-ethyl-3-(3-dimethyaminopropyl) carbodiimide) as crosslinking agent. A range of morphologies was created by varying solution concentration and layering technique. Cell adhesion tests are conducted to assess the interaction with cells. Cell vitality tests are performed to evaluate the material’s biocompatibility. It is hypothesized that glycoprotein composition and specific morphology of the assembly will provide favorable circumstances for cell growth. Such ECM could eventually serve as an alternative for the more expensive collagen and elastin based ECM model substances in tissue engineering.
247 - Ink-jet printed arrays of cell-based sensors in silk hydrogel matrices

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Macroscopic arrays of cell-based sensors immobilized on solid and flexible substrates in silk sandwich stacks using ink-jet printing are reported. Engineered bacterial cells (E.coli and B.subtilis) with molecular ribo-switch constructs capable of detecting specific target molecules were encapsulated into the multilayers of ionomer silk derivatives assembled in layer-by-layer (LbL) fashion. Silk fibroin modified with lysine [poly-L-Lys (SF-PL)] and glutamic acid [poly-L-Glu (SF-PG)] was used to assemble LbL structures with concave-shapes that served as pads or cushions for the injected cells. By injecting these silk derivatives on the top of the cells, sandwich structures formed and established stable structures. The formation of biocompatible, thin (~2 μm) hydrogel-like networks of silk multilayered structures, the viability/activity of cells was maintained. After long-term storage of such structures, cellular response was induced to maximum fluorescence intensity within one hour of incubation in media supplemented with the target analyte. This method of forming biocompatible stable platforms for efficient immobilization of cell-based sensors makes ink-jet printing a valuable tool for the rapid fabrication of large-scale multilayer arrays and multiple cell libraries on any substrate with good precision and accuracy.
248 - γ-Substituted ε-caprolactone monomers for the synthesis of diblock copolymers for micellar drug delivery applications

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Polymeric micelles made from functionalized poly (ε-caprolactone) (PCL) diblock copolymers were investigated in an attempt to generate improved drug delivery systems. This report presents the synthesis of γ-substituted ε-caprolactone monomers with varying substituents and polymerization to generate diblock copolymers which can self-assemble into micellar drug delivery vehicles. The functionalized γ-2-[2-(2-methoxyethoxy)ethoxy]ethoxy-ε-caprolactone was synthesized in a multi-step synthesis and used as the hydrophilic block in the diblock copolymers that contain either unsubstituted ε-caprolactone or a cholesterol γ-substituted ε-caprolactone as the hydrophobic block. The polymers were prepared via a ring-opening polymerization (ROP) using tin(II) 2-ethylhexanoate as the catalyst and benzyl alcohol as the initiator. The polymers were synthesized with varying block lengths achieved by using differing ratios of the two monomers to determine the effect of composition on the properties. The composition and the molecular weight of the polymers were determined using size exclusion chromatography (SEC) and $^1$HNMR. The properties of the various diblock copolymer micelles were investigated by the determination of the critical micellar concentration (CMC) using fluorescence measurements with pyrene as a probe as well as the determination of the size of the hydrodynamic diameter by dynamic light scattering (DLS) measurements.
Functional polymer systems play an increasing role for a variety of biomedical applications. Polymer nanoparticles are used to protect therapeutic proteins (like allergens) or drugs from degradation, obtaining higher local concentrations and enabling targeted transport.\cite{1,2} Degradable nanocarriers combine the advantage of providing a physical barrier between the encapsulated cargo and the biological environment as well as responding to certain local stimuli to release their payload. Encapsulation of allergens inside polymeric nanoparticles could aid to avoid severe side effects occurring sometimes during specific immunotherapy (SIT).

We have synthesized a novel type of difunctional, water soluble poly(ethylene glycol) dimethacrylate macromonomer with acetal-sites that degrade at acidic pH, which was analyzed with $^1$H-NMR, GPC and MALDI-ToF. The allergen and the macromonomer were entrapped inside liposomes as templates that were produced by dual asymmetric centrifugation. Radical polymerization of the methacrylate groups inside the liposomes generated PEG-nanocarriers. These nanocarriers were allergen-loaded and approximately 150-200 nm in size. It could be demonstrated in \textit{in-vitro} studies that dendritic cells (DCs) internalize our protein-loaded, non-toxic PEG-nanocarriers. Uptake of nanoparticles into DCs does not lead to cell maturation, but was capable of inducing immune responses necessary for SIT.\cite{3}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Diagram showing the synthesis of PEG-acetal-DMA and the encapsulation process.}
\end{figure}

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\end{thebibliography}
250 - Amphiphilic polycaprolactone block copolymers containing conjugated histone deacetylase inhibitors for delivery of anticancer drugs and HDAC inhibitors

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Aliphatic polyesters such as poly(caprolactones), poly(lactides), and poly(glycolides) are of significant importance in biomedical and pharmaceutical applications due to their biocompatibility and biodegradability. Introduction of functional groups to aliphatic polyesters can be used to conjugate drugs, targeting agents, or stimuli-responsive molecules. Functional poly(lactones) can be synthesized by the polymerization of functional lactones or post-polymerization chemical modification. Monomers can be designed to generate thermoresponsive amphiphilic block copolymers that will self-assemble to form micelles. The micellar cores can be conjugated with functional groups, drug molecules or cross-linked to enhance drug loading capacity, micelle stability, as well as controlled release properties. We report here the synthesis of amphiphilic polycaprolactone block copolymers containing conjugated histone deacetylase inhibitors (HDACi) which are anticancer agents. Valproic acid, phenylbutyric acid, and varinostat moieties, which are known HDAC inhibitors, have been attached to the hydrophobic block through the ester groups which will allow their release upon hydrolysis.
Stereo- and sequence-random nylon-3 copolymers (poly-β-peptides) display exciting biological functions that might be of therapeutic interest, such as antimicrobial activity. The efficient and inexpensive preparation of these polymers and their intrinsic backbone similarity to conventional peptides/proteins makes the nylon-3 class attractive for biomedical applications.

Cationic-lipophilic nylon-3 copolymers are proposed to adopt globally amphiphilic but irregular conformations upon approaching a biomembrane, which causes interactions with the lipid bilayer that degrade its barrier function and ultimately inhibit microbial growth. Our findings suggest that sequence-random nylon-3 copolymers containing both lipophilic and cationic subunits can display prokaryote vs. eukaryote selectivity patterns similar to those of sequence-controlled host defense peptides.
When polycations are used as a non-virus vector, they induce DNA condensation by hydrophobic interaction due to electric charge neutralization and can protect DNA from nuclease and so on. However, it is concerned that the excessive DNA condensation leads to a drop of the gene expression. To improve the stability against serum proteins of a head-tail type polycation (PAMAM dendron-PLL), which is composed of polyamidoamine (PAMAM) dendron head and poly(L-lysine) (PLL) tail, we have designed multi-arm poly (ethylene glycol) (PEG) installed PLL (maPEG-PLL) by PEGlation at the periphery of the PAMAM dendron head. As a result, not only effective stabilization of the PAMAM dendron-PLL polyplexes through PEGlation of the PAMAM dendron block, but also the interesting behavior as the vector was confirmed. In AFM observation, the polyplexes prepared using maPEG-PLL with the largest exclusion volume of maPEG took nanofiber-like morphology with uncondensed state of pDNA. Furthermore, the cell-free gene expression of nanofiber-polyplexes is higher than those of the polyplexes with the other condensed morphologies. It is thought that there is a strong association between morphology of polyplex, that is, DNA condensation state and gene expression from this results. On the other hand, gene expression of nanofiber-polyplexes was remarkably low in cultured cell because of low ability of endosomal escape of nanofiber-polyplexes. In this study, we designed the hybrid vectors composed of nanofiber-polyplexes and lipofectaminewhich had the ability of endosomal escape. When we optimized quantity of lipofectamine and N/P ratio of nanofiber-polyplexes, the hybrid vector was took up by HeLa cell via endocytosis pathway, then carried to nucleus nearby. Furthermore, the hybrid vector showed higher transfection efficiency compared with the lipoplexes using only lipofectamine. Consequently, it is confirmed that creation of the hybrid vector which had both inhibition ability of DNA condensation and ability of endosomal escape.
253 - Bottlebrush polymers: Custom shape, size, and composition of polymer nanoparticles

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Bottlebrush polymers are highly branched macromolecules capable of unprecedented control over biologically relevant factors: shape, size, and chemical functionality. Here, we show that bottlebrush polymer functionality and properties are tuned by varying the composition and molecular weight of the grafted side-chain polymers. We study the shape, solution properties, and biocompatibility of bottlebrush polymers with poly(ethylene glycol)(PEG), poly(lactic acid)(PLA), and fluorescently labeled poly(NIPAAm) side-chains. First we synthesized different side-chain polymers with a norbornene endgroup. The bottlebrush side-chains range in molecular weight from $M_w$ 2000 – 7000 g mol$^{-1}$ while the overall molecular weight is 100 – 11000 kg mol$^{-1}$.

Bottlebrush polymers with amphiphillic PLA-block-PEG copolymer side-chains ($M_w$130 kg mol$^{-1}$) display second order structure in SANS data after dialysis against water. The hydrophobic cores of amphiphillic bottlebrushes can encapsulate drug molecules and the core size is tunable by changing the molecular weight of PLA. The solubility and side-chain extension of mixed bottlebrush polymers, having both PLA and PEG homopolymer side-chains, are compared to copolymer bottlebrushes. Fluorescent bottlebrush polymers were synthesized by random co-polymerization of NIPAAm and fluorescein O-methacrylate (FMA) by RAFT. The resulting bottlebrush material was $M_W$ 420 kg mol$^{-1}$ with side-chain $M_w$4300 g mol$^{-1}$ and is water soluble. Bottlebrush polymers are characterized by H$^1$NMR, GPC, DSC and SANS, and backbone DP is quantified by light scattering.
254 - Responsive disease-inspired hybrid materials: Can polypeptide secondary conformational transitions help understand virus behavior?

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Polypeptide composite particles have become an appealing class of hybrid materials because of their unique properties. 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.

During infection stage viruses need to change their conformation when attaching to living cells. PCPs can serve as platforms to better understand the mechanism behind virus action. Good control over the core and conditions necessary to induce secondary transitions can be easy to achieve. Our system consists of silica beads grafted with poly(\(N^\epsilon\)-carbobenzyloxy-L-lysine), PCBL. This polypeptide undergoes conformational transitions as a function of temperature in m-cresol. We studied the effect of curvature and solvent nature on the transition by using DLS and NMR as the forefront techniques. Upon debenzylation, PCBL-grafted composites yielded pH-responsive hybrid materials.

This work was supported by the Grants DMR-1306262 from the National Science Foundation.
A novel type of pseudo-poly(amino acids) (PPAAs) based on oligomeric glycols and glutamic acid derivatives has been synthesized and characterized. Using of N-Boc-glutamic acid along with hydrophobic N-lauroyl-glutamic acid for the PPAA synthesis results in amphiphilic PPAA oligomers after Boc removal. The polyester type of backbone provides degradability of PPAAs, whereas deprotected protonable amino groups can serve for further DNA complexation. Hydrophilic-lipophilic balance of the synthesized PPAAs can be easily adjusted by N-Boc-glutamic acid to N-lauroyl-glutamic acid ratio and the length of poly(ethylene glycol) or poly(propylene glycol) oligomers. Obtained PPAAs were purified by precipitation, and characterized by NMR, FTIR, GPC, and acid-base titration.

Novel biomacromolecules can be considered as bioresorbable materials suitable for DNA complexation and gene delivery.
256 - Cell surface engineering with silk protein nanoshells

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Natural protein (silk fibroin) nanoshells were assembled on the surface of *Saccharomyces cerevisiae* yeast cells without compromising their viability. The nanoshells facilitated initial protection of the cells and allowed them to function in encapsulated state for some period of time, followed by complete biodegradation and consumption by cells. Gentle ionic treatment stabilized silk fibroin structure in the shell, and preserved the viability of the cells, as indicated by the fast response of the encapsulated cells, with an immediate activation of green fluorescent protein by the inducer molecules. Extremely high viability rates (up to 97%) and preserved activity of encapsulated cells are facilitated by cytocompatibility of the natural proteins and the formation of highly porous shells in contrast to traditional polyelectrolyte-based materials. Moreover, in a high contrast to traditional synthetic shells, the silk proteins are biodegradable and can be consumed by cells at a later stage of growth, thus releasing the cells from their temporary protective capsules.
257 - Surface-modification of P(MAA-co-NVP) microparticles for oral protein delivery

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Hydrogels are three-dimensional hydrophilic structures that imbibe water while maintaining structural integrity. A subset of hydrogels, complexation hydrogels, has found utility as microparticulate carriers for the oral delivery of protein therapeutics. P(MAA-co-NVP), a random copolymer composed of methacrylic acid (MAA) and N-vinyl pyrrolidone (NVP), is a complexation hydrogel that has been successfully used for the transmucosal delivery of proteins such as insulin and growth hormone. While successful oral protein delivery has been shown with unmodified P(MAA-co-NVP) microparticles, a cause for concern is the lack of interaction of the particle with the mucus-lining of the upper small intestine. This interaction leads to increased carrier residence time in the intestine and ensures greater protein delivery across the intestinal wall.

We have developed dextran- or poly(ethylene glycol)- modified P(MAA-co-NVP) microparticles, as both molecules interact readily with mucus. Dextran tethers have been successfully added in a post-synthesis scheme using carbodiimide-linking chemistry that joins primary amine-containing hydrogels to carboxymethylated-dextran. Poly(ethylene glycol) tethers are incorporated during the UV-initiated bulk radical polymerization hydrogel synthesis. The P((MAA-co-NVP)-g-EG) hydrogels have been synthesized with varying crosslinking type (TEG/PEGDMA) and density (0.75-1.25%) to modulate the swelling profile to better protect the protein in the stomach and prompt release in the intestine (see figure). Furthermore, these systems have pore sizes 10x greater than the hydrodynamic radius of the proteins of interest, show no cytotoxicity, and can successfully load and release protein therapeutics.
258 - Synthesis and characterization of thieno[3,4-b]thiophene acceptors with alkyl, aryl, perfluoroalkyl and perfluorophenyl pendants for donor-acceptor low bandgap polymers

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We report the design, synthesis and characterization of a series of thieno[3,4-b]thiophene acceptor blocks with octyl (T8), phenyl (TP), perfluorooctyl (TF8) and perfluorophenyl (TFP) side groups. Their subsequent copolymerization with dithienyl benzodithiophene by direct arylation polymerization afforded novel low bandgap poly(thienothiophene-alt-dithienylbenzodithiophene) (PTB) polymers. The strongly electron withdrawing TF8 and TFP groups were shown to significantly lower both \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) levels, and gave computed copolymer ground-to-excited state dipole changes \( (\Delta \mu_{\text{ge}}) \) that were relatively higher than for the nonfluorinated analogs. These materials show favorably aligned energy levels relative to conventional fullerene type acceptors, which should make them suitable materials for organic photovoltaics (OPVs). Device performances and active layer morphologies will be evaluated and discussed.
259 - Synthesis and characterization of collagen grafted poly hydroxybutyrate valerate (PHBV) scaffold for loading of bovine serum albumin capped silver (Ag/BSA) nanoparticles in the potential use of tissue engineering application

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The objective of this study is to synthesize and characterize collagen grafted poly (3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV film for loading of bovine serum albumin capped silver (Ag/BSA) nanoparticles. Collagen was grafted on poly (hydroxylethylmethacrylate)-grafted-PHBV (PHEMA-g-PHBV) film with carbonyl diimidazole (CDI) as the crosslinking agent, while collagen was grafted on aminated PHBV (NH2-PHBV) with glutaraldehyde (GA) as the crosslinking agent. This was followed by the loading of Ag/BSA nanoparticles on collagen grafted PHBV films. Collagen immobilization on PHBV film was established by the amide peak in the FTIR spectrum, increase in the nitrogen content of the film as noticed in the survey XPS spectra, an increase in the film roughness based on SEM morphological data of the film treatment, and the collagen density of the film as measured by Bradford assay. Using fluorescence techniques, XPS, and AAS, we established the loading of Ag/BSA nanoparticles on collagen immobilized PHBV film. The Ag/BSA nanoparticles loaded matrix could be potentially useful for bone cell growth and inhibition of bacterial cell growth.

Tuesday, March 18, 2014 05:30 PM
Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
The hypervalent bonds I-L in compounds of the type ArIL₂ (Ar = aryl) are easily cleaved homolytically upon heating or irradiation with the generation of the corresponding radicals L·. These can initiate polymerization of variety of monomers or could be reacted with polymeric substrates yielding, in both cases, functional polymeric materials containing one or more L groups. The ligands L can be exchanged with nucleophiles, affording new hypervalent iodine compounds, which serve as precursors of radicals derived from the nucleophile employed. For instance, hyperbranched polymers were prepared by exchange of acetoxy ligands attached to a hypervalent iodine center with polymerizable carboxylates, followed by decomposition. By this strategy, inimers were generated in situ. Likewise, similar exchange reactions with azides and haloacids yielded precursors of azide and halocarboxylate (or the products of their decarboxylation) radicals, which were successfully reacted with several different polymers to yield materials able to participate in click reactions or to serve as ATRP (macro)initiators, respectively. Kinetic studies of the exchange reactions and the generation of radicals, as well as materials synthesis and applications will be described in this presentation.

Acknowledgement. This research was supported by the Petroleum Research Fund of the ACS (PRF# 51030-DNI7).
261 - Synthesis of photo-cross-linkable core-shell bottlebrush copolymers and their transformation into well-defined organic nanotubes

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Bottlebrush copolymers are comb-like macromolecules, which adopt cylindrical shape in solutions due to steric repulsion between densely grafted polymeric side chains. Cylindrical bottlebrushes can be transformed into organic nanotubes via intramolecular cross-linking of the shell layer and degradation of the inner core. Organic nanotubes with controlled nanometer dimensions can be used in many applications, such as ion transport, chemical catalysis, biosensors, selective encapsulation and separation of nanomaterials etc. Herein, we report a new method for the preparation of organic nanotubes with controlled dimensions from photo-cross-linkable core-shell bottlebrush copolymer precursors composed of an inner degradable polylactide block and an outer block containing photoactive coumarin functionalities. Upon UV irradiation at 365 nm, the peripheral coumarin functionalities undergo [2+2] cyclodimerization to form shell-cross-linked bottlebrushes. Subsequent degradation of the polylactide block provides hollow cylindrical nanoparticles held together by dimerized coumarin units in the shell layer. The length and the inner diameter of the nanotubes are determined by the length of the backbone and the polymeric side chains, respectively. Photocleavage of coumarin units upon 254 nm results in disintegration of nanotubes into small fragments. Amphiphilic nanotubes with a positively charged interior could potentially be used for selective encapsulation, separation, and purification of nanomaterials or biomacromolecules.
Charged glycopolymers are natural components of biological tissue, abundant in the mammalian extracellular matrix and provide the mechanical support and biological interaction for cell migration and morphogenetic activities. Chondroitin sulfate (CS) and hyaluronic acid (HA) are the two major anionic glycosaminoglycans (GAG) present in connective tissue which have been used as biocompatible precursors to synthesize 3D matrices for cartilage regeneration purposes. Due to polyelectrolyte nature of these scaffolds, however, retaining the mechanical integrity of GAG based hydrogels has been a challenge. Copolymerization of functionalized GAGs with oligo(ethylene glycol) acrylate was the approach used in this study to improve the moduli of the crosslinked gels. The moduli of copolymers were 2 to 25 times higher than the parent homopolymer (depending on the GAG and comonomer type). Longer oligomers of ethylene glycol (up to 700Da) as well as higher ratios of functionalized groups on the host glycopolymer, and differences in reactivity ratios of the macromer and comonomer effectively increased the moduli and crosslink density of the gels. Improved structures were observed in copolymerization of both CS and HA functionalized GAGs which suggested independence of the reaction mechanism from the host glycopolymer.

Figure 1 – Suggested reaction mechanism for copolymerization of acrylate and methacrylate comonomers with methacrylated GAG. Homogeneity (b) or heterogeneity (c) of the copolymers was attributed to differences or similarities in reactivity ratios of the functional groups. Right picture compares the transparent MCS-acrylate copolymer (b) versus the translucent MCS-methacrylate (c) copolymer.

Tuesday, March 18, 2014 05:30 PM
Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
263 - Thermoresponsive bottlebrush polymers

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Bottlebrush polymers are highly branched macromolecules with polymeric side-chains. The novel structure of bottlebrush polymers may make them particularly useful in specialty applications, and here we explore the surface and solution properties of model thermoresponsive poly(N-isopropylacrilamide) (PNIPAAM) bottlebrush polymers. The resulting PNIPAAM bottlebrush polymers are fully soluble in water only after removal of the terminal chain transfer agent, reflecting a disproportionately strong effect of the side-chain end groups on bottlebrush polymer solubility (Figure 1 (a)). Above the LCST, PNIPAAM bottlebrush polymers aggregate, and PNIPAAM bottlebrush polymers with 9 kg/mol side-chains form a lyotropic liquid crystal phase, evidenced by low-angle scattering peaks and birefringence under polarized optical microscopy at temperatures above the LCST. Small-angle neutron scattering (SANS) measurements of PNIPAAM bottlebrush polymers in D$_2$O demonstrate that the side-chains collapse as the temperature increases towards the lower critical solution temperature (LCST); both the LCST and the collapse of the side-chains is dependent on the side-chain length IFT measurements show that PNIPAAM reduces the interfacial tension to values comparable to linear PNIPAAM homopolymer. Antifouling studies by quartz-crystal microbalance show a reduction in cell attachment onto a gold surface with PNIPAAM coatings. This study demonstrates the potentially useful interfacial and surface properties of bottlebrush polymers.
Fluorescent dyes conjugated to polymers are used in order to visualize these materials in a biological environment. However, when conjugating a dye to a polymer a Poisson distribution of dyes per polymer particle is obtained. A generation 5 poly(amidoamine) (G5 PAMAM) dendrimer has the capability of having the distribution of hydrophobic ligands (rhodamine dyes) separated based on number by using a reverse phase semi-preparative high performance liquid chromatography (rp-HPLC). Materials with either neutral or positive surfaces have been separated providing material with precise numbers of carboxytetramethylrhodamine (TAMRA) dyes and their individual characteristics have been characterized.

The presentation will also include data from biological studies.
265 - Conductive polymer based ultrasensitive potentiometric immunosensors

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Conductive polymers are versatile transducers utilized in diagnostic technologies. The chemical or electrochemical polymerization processes and the bio-conjugation of the synthesized polymers on a surface can be well controlled to endow them with desirable functions. We devised a conductive polymer based quantitative potentiometric biosensor that offers great assay capability. The sensor allows the ultrasensitive and rapid detection of analytes in complex physiological medium with a wide dynamic range. Polyaniline on electrode surface was enzyme labeled with an immuno-complex through thiol or glutaraldehyde based conjugation on the benzoid amine or quinoid imine moieties of its repeating units. The detection is mediated by the direct redox reaction between the polymer and charged product generated through the enzymatic reaction.

The magnitude of the electrical response was found as a function of the polymer layer thickness, dopants and nanostructure. This polymeric bio-sensing approach is proven viable in the traditional open circuit potentiometric system and novel FET-based biochip systems.
Inorganic-organic hydrogel scaffolds for tissue engineering

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Tissue engineering may be useful to repair osteochondral defects – damage extending from cartilage to subchondral bone. Hydrogels could function as 3-D scaffolds to create an environment in which living cells can attach, proliferate, differentiate, and produce new extracellular matrix. In a materials-guided approach, the scaffold's chemical and physical properties alone guide cell behavior. However, the correlation between scaffold properties and cell behavior is not well defined. Also, engineering interfacial tissues is challenged by needing to regenerate a gradual transition between two tissue types. In this work, we utilized a method for altering, and potentially enhancing, organic poly(ethylene glycol) diacrylate (PEG-DA) hydrogel scaffolds via the incorporation of inorganic methacrylated star polydimethylsiloxane (PDMS\(_{\text{star-MA}}\)). We have previously shown that PDMS\(_{\text{star-PEG}}\) hydrogels are both bioactive and osteoinductive. In this work, we produced PDMS\(_{\text{star-PEG}}\) scaffolds having a continuous gradient of PDMS\(_{\text{star-MA}}\) in order to guide the regeneration of a native-like osteochondral interface. Towards this goal, several parameters were tuned to precisely control chemical and physical properties. First, concentration and wt% ratio of the two macromers were systematically varied. Second, both aqueous and organic fabrication solvents were utilized. Further, poration of the scaffold was explored. The impact of composition and fabrication variables on hydration, pore morphology, and modulus was evaluated. Such scaffolds with highly tunable properties, which may be varied within a single scaffold, possess great potential in the application of osteochondral tissue engineering.

**Figure 1.** Chemical structure of PEG-DA (top) and PDMS\(_{\text{star-MA}}\) (bottom).

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**Tuesday, March 18, 2014 05:30 PM**

**Excellence in Graduate Polymer Research (05:30 PM - 07:30 PM)**

**Location:** Dallas Convention Center

**Room:** Hall A
Photochromism is the transformation of a molecule from one structural state to another where at least one of the states must be light-induced. Because of its unique properties, spiropyran is enjoying widespread use in many applications, particularly in light-responsive materials research, namely hybrid materials that utilize spiropyran to induce material changes or provide colorimetric sensing of changes in the microenvironment. In our studies of spiropyran solution kinetics, we have observed deviations in expected behavior, arguing that spiropyran photoisomerization is not a simple first-order process involving two equilibrating structures. These results motivated us to examine details of this interconversion using ion mobility-mass spectrometry (IM-MS) which can separate the spiropyran isomers based on molecular collision cross-sectional area (CCS). Quantum chemical modeling based on Density Functional Theory was used to identify possible theoretical ground-state isomers of merocyanine. CCS calculations from the program MOBCAL were employed to aid conformer assignment to specific isomers. IM-MS experiments reveal the presence of three distinct conformers. CCS values and theoretical structures will be presented. The results indicate that the three conformers are comprised of one single structure and two groups of isomers; the ring-closed isomer, the cis-MC group; CCX, and the trans-MC group; XTX. The designations; cis (C) and trans (T), refer to configuration of the three methylene bonds linking the p-nitrophenolate and indoline moieties of MC. This work represents the first observation of a second isomer group on timescales greater than nanoseconds. A mechanism for the thermal reaction is postulated to occur via the formation of a stable cis intermediate, CCX, which has not been previously identified as a stable isomer in other work.
268 - Mass spectrometry characterization of branched glycopolymers

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Synthetic carbohydrates and carbohydrate-based polymers are increasingly used for the investigation of glycopolymer-protein interactions and tested for pharmaceutical and medical applications. It has been shown that the usefulness of glycopolymers depends on the spatial arrangement of the sugar units in the molecular structure. Creating and identifying specific structures are important in the production of glycopolymers for medical uses. Synthetic glycopolymers with the same compositions can have various architectures, including branched, dendric and comb-shaped. This complexity creates a challenge in deducing their structures. The development of glycostechnology and the potential applications of synthetic glycopolymers have inspired researchers to develop new methods for the characterization of sugar-containing polymers. In this work a new analytical approach for the precise structural characterization of glycopolymers is reported. It starts with matrix-assisted laser desorption ionization (MALDI) mass spectrometry to obtain information about molecular weights and distributions of the glycopolymers. The various possible structures with the same composition are subsequently identified based on collisionally activated dissociation (CAD) tandem mass spectrometry (MS²) studies. The characteristic elimination of bromomethane molecule (shown in Figure) provides convincing evidence of monomer connectivity, which enables the characterization of the branching architectures. The glycopolymer structures deduced this way are corroborated by comparing experimental collision cross-sections from traveling-wave ion-mobility mass spectrometry (TWIM-MS) results with theoretical values obtained from molecular dynamics.
Polycarbodiimides are a relatively novel class of macromolecules with a repeating amidine structure containing two modifiable nitrogens that bear the functionality of the polymer. These polymers adopt a stable, helical structure in both solution and the solid state which can be biased using chiral monomers/initiators to form optically active materials with an excess single-handed screw sense. Specifically attaching bulky aromatic units (i.e., naphthyl, anthryl, pyrenyl, etc.) to the C=N imine nitrogen of the polymer backbone results in an interesting, unique thermo- and solvo-driven chiroptical switching phenomenon where the specific optical rotations (OR) were shown to be modulated reversibly up to 1300°. These chiroptical changes were determined to be caused by the rotation about the N-aryl bond but the specifics of the process are still widely unknown. Poly(N-1-naphthyl-N-octadecylcarbodiimide) displayed the most intense changes in specific OR so this polymer has been the focus of several new studies to determine the specific mechanism of action for this process. The $^{15}$N NMR of the isotopically enriched polymer revealed that the process is consequence of varying populations of two distinct states. Using VCD spectroscopy and DFT calculations, the specific molecular structure of each state was identified and confirmed. In addition to the small molecular alterations, these two states result in an altered supramolecular self-assembly which was studied and identified by several microscopy techniques such as optical polarized microscope, SEM, and AFM.
270 - Understanding the process-structure relationship for building polymer-CNT interphases

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Understanding and controlling the development of interfacial zones in polymer/nano-carbon composites is necessary for achieving efficient interfacial stress transfer. This is crucial for producing nano-composite materials with outstanding mechanical properties. This study demonstrates the use of templated crystallization by carbon nanotubes (CNT) to form specific polymer morphologies. Subsequently, by tailoring polymer crystallization conditions in CNT dispersions, interfacial morphologies which exhibit different chain conformations on CNT can be obtained. These conformational changes arise due to nano-scale assembly that is the result of synergistic effects between CNT templating (i.e., epitaxy) and external parameters used to promote either chain extension or folding. This work demonstrates that extended-chain, folded-chain, and amorphous conformations for both polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) systems can be achieved by utilizing the aforementioned techniques (see figure). Crystallization parameters and shearing mechanisms were further tailored to promote fibrillar crystal growth and increase the thickness of the polymer interphase on the CNT. The influence of temperature and degree of undercooling on the structure and morphology of the polymer interphases were also studied. The results of this work show the ability to control atomic- to nano- to meso-scale registry in polymer nano-composites by fundamentally understanding templated crystallization mechanisms.
271 - Role of polymer stereoregularity on nanocomposites of polystyrene with single-walled carbon nanotubes

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Significant enhancement of the physical and mechanical property of polymeric materials is achieved with the addition of nanofiller content at low loadings. When determining composite formation, the geometry of the nanofiller is usually preferentially considered; whereas the chain orientation of the matrix is commonly neglected. This study uses a combination of theoretical and experimental methods to investigate how nanostructures such as single-walled carbon nanotubes (SWNT), change the dynamics of polystyrene with respect to its stereoregularity. SWNT/polymer complex formation is depicted with matrix type "A". Further addition of nanotube content to the type "A" matrix results in aggregation of the nanotubes referred to as matrix type "B". Matrix type "C" is due to inadequate interaction of the nanostructures with the host material. Differential scanning calorimetry (DSC) shows that isotactic polystyrene is most suitable to solubilize the SWNT in the host polymer in that it has the most favorable interaction with the SWNT nanoparticle or nanofiller when compared to that of its atactic and syndiotactic counterparts. Solution NMR spectroscopy and solid state \(^{13}\)C \(T_{1\rho}\) measurements support the DSC results and suggest that the isotactic polymer is most effective in interacting with the SWNT. The SWNT is well-dispersed in the nanocomposite matrix. Our study demonstrates the feasibility to improve the interaction of the host polymer with the nanofillers by small three-dimensional structural changes.
272 - Remarkably regioselective deacylation of cellulose esters using tetrabutylammonium hydroxide

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Recently our laboratory has discovered an unexpectedly selective, efficient synthesis of highly regioselectively substituted cellulose esters without the need for protection/deprotection steps. With easily synthesized cellulose triesters as the starting materials, reaction with tetrabutylammonium hydroxide (TBAOH) in conventional organic solvents under readily achieved reaction conditions afforded regioselective deacylation of cellulose acetate at the secondary positions and the retention of the ester group at O-6. Evidence from studies of tetrabutylammonium cation size effects supports a chelation mechanism; coordination of the tetaalkylammonium cation by the ester oxygen atoms of the vicinal 2,3-acetate groups could be the source of regioselectivity at the secondary alcohol esters. In order to understand how to carry it out most efficiently, the scope of this regioselective deacylation of cellulose acetates has been investigated. Reaction with TBAOH in pyridine was the most effective process providing the highest regioselectivity. Furthermore, we demonstrate the broad scope of TBAOH-catalyzed deacylation with respect to ester type; similar regioselectivity for deacylation at O-2,3 was observed with cellulose acetate, propionate, butyrate, hexanoate and benzoate triesters. The success of the TBAOH regioselective deacylation opens up new practical possibilities for making these interesting new materials.
273 - Kinetics and thermodynamics of the decarboxylation of glycerol carbonate to produce glycidol: Computational insights

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Carbon dioxide and glycerol are inexpensive, abundant, and renewable carbon feedstocks for chemical manufacture. In principle, they may be combined to give various glycerol carbonates, thereby converting two waste streams into valuable materials.

Glycidol is attractive too. Suitably protected, it participates in the conventional CO$_2$-epoxide copolymerization to give poly(1,2-glycerol carbonate) homo- or copolymers. With the hydroxy groups restored by deprotection, such polymers are more hydrophilic, and they may undergo post-polymerization modifications (below).

1,2-Glycerol carbonate is reportedly decarboxylated to glycidol by acid or base catalysts. Anticipating increasing interest, we studied the pathways for both base- and acid-catalyzed decarboxylation reactions using computational methods (CBS-QB3(+)), and will discuss our findings. Our results will hopefully lead to milder and more energy-efficient decarboxylation processes that we are exploring in the laboratory.

References

Weak acid congeners: Polymer bound 1H-tetrazole vs. carboxylic acid

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Polystyrenic 1H-tetrazole was previously investigated as an anhydrous proton conductor and found to have both promising conductivity and unique physical characteristics for an azole-containing homopolymer. However, 1H-tetrazole retains bound water under operationally anhydrous conditions and exhibits a pK$_a$ similar to its biological congener, carboxylic acid. Polystyrenic hexanoic acid has been synthesized and characterized to compare proton transport in 1H-tetrazole versus carboxylic acid-based ionic conductors. Despite the abundance of biochemical comparisons of the two acids in the literature, physiochemical comparisons between these two moieties are rare, and comparisons as solid electrolytes are non-existant.

Though 1H-tetrazoles and carboxylic acids have similar pK$_a$, the properties of these two polymers are remarkably different. Anhydrous conductivities are four orders of magnitude lower in the carboxylic acid-based polymer than in the 1H-tetrazole functionalized material. When the materials are hydrated, this margin narrows only moderately. Thermal analysis, solid state NMR, and analysis of conductivity, mobility, and charge carrier density come together to show that morphology, side chain and acid dynamics, and the mechanism of conductivity all differ markedly as a function of the tethered acid. The combined amphotericity, propensity for hydrogen bonding, and polarity of 1H-tetrazole likely contribute to its large increase in conductivity compared to carboxylic acid-based proton conductors.
Polythiophenes are among the most widely studied polymeric materials. They are extensively used in organic electronics and in sensory applications. Regioregularity is a key feature that enables a coplanar arrangement of the thiophene rings in the polymer chain, which in turn confers desirable properties such as extended conjugation and high conductivity after doping.

We succeeded in the preparation of a regioregular polythiophene that is functionalized with triorganoborane moieties in its side chains by Stille-type polycondensation. The electron-deficient borane moieties can function as electron acceptors, while the empty p orbital on boron facilitates π-delocalization. Studies on the photophysical properties of the polymer revealed energy transfer from the boron-containing side chains to the conjugated polythiophene backbone. Moreover, fluoride binding to the tricoordinate borane moieties led to a pronounced response in the absorption and emission characteristics.

Amphiphilic thiophene block copolymers that contain boronic acid functionalities were also prepared using GRIM polymerization techniques. Boronic acid-functionalized polymers have drawn much recent attention because of their strong potential for glucose or RNA sensing, and as self-regulated drug-delivery systems. The synthesis, self-assembly properties and sugar binding behavior of these new polymers will be discussed.
Drug and contrast agent delivery into tumor interstitium relies on passive diffusive transport because of poor convection in solid tumors. The size of polymeric nanoparticle therapeutic and diagnostic agents hinders their penetration through tissues and hence can cause inadequate delivery into the interstitium. It is thus vital to characterize the restricted transport of these large particles in order to improve their delivery into tumors. We introduce a simple and reliable method for the measurement of diffusion into tissue-simulating gels utilizing time-resolved MRI. Optimized inversion-recovery and spin-echo imaging sequences validate our methodology and show the consistency between approaches. We measure the diffusion coefficients of different polymer delivery vectors (size range from 10 to 170 nm in diameter) in both agarose and collagen gels with different porosity and internal functionality. Our polymeric nanoparticles include magnetic block polymer particles and clusters that are tailored as drug carriers and sensitive MRI contrast agents, as well as a series of gadolinium-based polymeric theranostic “beacons” that form plasmid-DNA polycplexes for gene delivery and simultaneous \textit{in vivo} MRI tracking of delivery. Diffusion coefficients determined by our method match previous measurements by fluorescence recovery after photobleaching in gels, but allow tracking over macroscopic distances and access to the dynamic time dependence of transport. We will discuss the influence on transport of the size of polymer nanoparticles, the medium tortuosity and porosity, and comparisons with several theoretical models. These results have meaningful implications for designing non-viral polymeric drug and contrast agents for delivery into tumors and tissues, and for enhanced tissue engineering.
277 - Synthesis of tertiary amine-based pH-responsive block copolymers for use as "smart" MRI contrast agents

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Despite recent advances in the understanding of fundamental cancer biology, cancer remains the second most common cause of death in the United States. One of the primary factors indicative of high cancer morbidity and mortality and aggressive cancer phenotypes is tumors with a low extracellular pH (pHe). Thus, the ability to measure tumor pHe \textit{in vivo} using non-invasive and accurate techniques that also provide high spatiotemporal resolution has become increasingly important and is of great interest to researchers and clinicians. Recently, the use of pH-responsive polymer systems in cancer diagnostics and treatment has received considerable attention due to their ability to undergo conformational changes in response to changes in the environmental pH. For example, pH-responsive drug delivery systems have been developed where the drug is encapsulated in a micelle structure when circulating in the blood stream and is selectively released via a hydrophobic to hydrophilic transition once it arrives at the tumor site. We have developed pH-responsive nanoscale multimodal contrast agents for magnetic resonance imaging (MRI) that demonstrate large changes in relaxivity to improve both the selectivity and sensitivity of \textit{in vivo} pHe measurement. A series of pH-responsive biocompatible block polymers with pK\textsubscript{a}'s ranging from 5.0 to 7.5 have been synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. These copolymers have then been used to modify gadolinium nanoparticles to design a smart contrast agent for MRI, which will potentially allow for enhanced diagnostics in the treatment of cancer.
The finite availability and environmental impact of petroleum has increased the intensive interest in developing polymeric materials from sustainable sources. Vegetable oils are an attractive source for polymers, due to their low cost, abundance, annual renewability, and ease of functionalization. Stearyl (SAc) and lauryl acrylate (LAc), derived from vegetable oils such as soybean and palm kernel oil, have been polymerized through reversible addition-fragmentation chain transfer polymerization (RAFT), resulting in poly(styrene-\(b\)-(lauryl acrylate-co-stearyl acrylate)-\(b\)-styrene) (SAS) triblock copolymers. The SAS triblock copolymers exhibit properties appropriate for thermoplastic elastomer (TPE) applications. Small-angle X-ray scattering and transmission electron microscopy experiments have elucidated the microphase separated morphology of the SAS triblock copolymers, consistent with a spherical morphology lacking long-range order. The physical properties of the polymers can be readily tuned by varying the acrylate mid-block composition, including the melting temperature, viscosity, and triblock copolymer tensile properties. Surprisingly, the order-disorder transition temperature of the triblock copolymer is not dependent on the acrylate composition in the mid-block. This indicates that the acrylate composition can be used as a tool to manipulate the physical properties of the triblock copolymers without affecting the order-disorder transition temperature, or processing temperature, of the TPEs.
Infections involving Superbugs (antibiotic resistant bacteria) have become a serious health threat to human population. Unlike conventional antibiotics, cationic amphiphilic synthetic polymers are considered to be agents without bacterial resistance and less demanding to develop in terms of cost and time required. We report our initial promising findings here on two families of cationic amphiphilic polymers which have not been explored before: poly(vinyl ester)s and polyacrylates. We have synthesized a library of amphiphilic polyacrylates and poly(vinyl ester)s via free radical polymerization, and assessed the role of systematic structural variations on their antibacterial and hemolytic activities. Parameters in consideration included molecular weight, structure and composition of hydrophobic alkyl tails, and their position relative to cationic center. Cationic polyacrylate homopolymers displayed >32 times selectivity towards S. aureus over mouse RBCs, and 14 times selectivity towards S. aureus over E. coli. Highly antibacterial but selective (bacteria over RBCs) polyacrylates were synthesized by copolymerizing amphiphilic monomers with two to six carbon spacer arms, at various mole ratios. In Poly(vinyl ester)s, we studied the role of alkyl side chain length, molecular weight, and mol% of hydrophobic comonomers on their biological activities. A random copolymer with 90% cationic mol% was found to be 46 times more selective towards S. aureus over RBCs. For poly(vinyl ester)s, the lowest minimum inhibitory concentrations of 12 µg/mL and 31 µg/mL were obtained towards S. aureus and E. coli, respectively.
Highly porous submicron activated carbon fibers (ACFs) were derived from low sulfonated alkali lignin and fabricated into electric supercapacitors. The ACFs exhibited high surface area, hydrophilicity and electrical conductivities. As a result, they have demonstrated exceptional electrochemical performances. ACFs from KOH activation in particular, have shown a very high specific capacitance of 344 F/g at low electrode mass and scanning rate. A decent specific capacitance of 196 F/g and remarkable areal capacitance of 0.6 F/cm² were obtained at high electrode mass and scanning rate, resulting in high energy density of 8.1 Wh/kg (averaged) at high scanning rate. An outstanding 96% capacitance retention was achieved after 5000 cycles. Such excellent performances that were comparable even superior to graphene and carbon nanotubes based electrodes showed great potentials of converting lignin to functional carbon materials for energy storage.
Block copolymers (BCPs) can self-assemble into periodic domains of various morphologies (e.g. cylinders and lamellae) on length scales that surpass the resolution limits of optical lithography. Orientation control of the domains is critical, and most applications require domains oriented perpendicular relative to the substrate. Unfortunately, the lower surface energy block of most BCPs (and all Si-containing BCPs) preferentially segregates to the air interface during thermal annealing. Polarity switching top coats can be used to eliminate the air interface and generate a non-preferential (neutral) surface. A neutral surface prevents interfacial segregation, which allows for perpendicular domains. Herein, a new top coat design is implemented to control the orientation of a Si-containing BCP, and rapid thermal annealing produces domains on the order of ca. 8 nm.
Polymeric materials are prominent in today's society and largely account for the high standard of living enjoyed by everyone in the developed world. For most applications polymeric materials must be flame retarded. Traditionally, organohalogen compounds particularly brominated arylethers have been used in this application. However, these materials are stable in the environment, tend to bioaccumulate and pose human health risks. For this reason these materials are being removed from the market and suitable replacements must be found. The bis ester prepared from two biomaterials, isosorbide (from glucose, a starch hydrolysis product) and 10-undecenoic acid (from castor oil by pyrolysis) may serve as a useful platform for the preparation of environmentally-friendly flame retardants from polymeric materials. Thiol-ene reaction with 2-ethanethiol converts the diester to a diol from which may be generated a series of phosphorus esters. These materials display good thermal stability. Thermal degradation begins at about 230 °C by elimination of a phosphorus acid. This process may be readily monitored using infrared spectroscopy. These esters have the potential to provide good flame retardancy in a variety of polymers.
Polymeric materials are pervasive in today’s world. The unprecedented standard of living enjoyed by most citizens of the developed world is largely a consequence of the development of polymeric materials which occurred in the latter half of the last century. For most applications, polymeric materials must be flame retarded. Organohalogen compounds, particularly brominated aromatics, have been popular flame retardants. They are effective and readily available at modest cost. However, these compounds are stable, persist in the environment, tend to bioaccumulate, and may present hazards to human health. Because of these limitations, the use of these compounds is increasingly subject to restrictive regulations by governments around the world. Therefore, there is a strong need for the development of replacements that are effective, non-toxic and biodegradable. Condensation of D0P0 [9,10-dihydro-9-oxa-10-phosphaphenonethalen-10-oxide], 4-aminoacetophenone and aniline affords 1,1-di(4-aminophenyl)-1-dopyl[6-oxido-6H-dibenz<1,2>oxaphosphorin-6-yl]ethane. Treatment of this compound with a variety of phosphorous reagents provides phosphoramidates with good potential to function as effective flame retardants for polymeric materials.
Minimizing adhesion of ice has been the subject of extensive studies for applications such as aircraft wings, spacecraft hull and power transmission wires, while a growing interest concerns coatings for wind turbine blades and in refrigeration. Thus far, ice adhesion measurements employed “custom designed” equipment. The absence of a straightforward laboratory-based ice adhesion test using readily available instrumentation has been a stumbling block to fundamental understanding and coatings development. To establish a laboratory method for evaluating ice adhesion with a readily available instrument, a test with a TA Instruments RSA-III has been developed. The method involves removal of an ice cylinder from a polymer coating with a probe and the determination of peak removal force ($P_s$). To validate the test method the strength of ice adhesion has been determined for a prototypical glassy polymer, poly(methyl methacrylate). Surface roughness and probe placement have been identified as critical variables for ice removal. For the first time, removal energy (RE) has been determined.

The new test provides a readily available platform for investigating fundamental surface characteristics affecting ice adhesion.

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Asymmetric flow field-flow fractionation (AsFIFFF) is an elution-based technique for analysis of macromolecules, colloids, and particles. Separation takes place in an open channel, based on differences in the diffusion coefficients of analytes. Because AsFIFFF is a relatively gentle separation technique in comparison with conventional chromatographic techniques, it has found favor in the analysis of water-soluble macromolecules, molecular assemblies, and even entire cells [1]. At the same time, only very few reports can be found describing AsFIFFF work conducted in organic solvents. Here, we present just such application of AsFIFFF, in tetrahydrofuran, for characterization of narrowly distributed polystyrene stars and their linear analogues. A cross-flow gradient was employed to achieve separation of individual polystyrenes in mixtures (Figure 1). Multiple-detection allowed determination of molar mass and size for each separated polystyrene within a single run and without reliance on calibrants or prior knowledge of channel dimensions.

Figure 1. AsFIFFF fractogram and molar mass for mixture of star polystyrenes. Gray dashed line represents cross-flow gradient, red solid line light scattering signal at 90°, black solid line refractive index signal, and red squares molar mass. Nominal molar masses reported by manufacturer (in kg mol$^{-1}$) for polystyrenes are presented in the fractogram ($M_n$ of arm/total $M_w$).

The end groups of linear macromolecules play a critical role in the resulting physical properties of the polymer and can enable the construction of more complex polymer architectures, yet their identity and purity can be difficult to ascertain using traditional analytical technique because any signal that results from the end groups tends to be overwhelmed by the larger signal from the backbone. Recent advances in mass spectrometry techniques have made matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry a rapid and powerful tool for providing detailed information about the identity and purity of homopolymer end groups. In this work, MALDI-TOF mass spectrometry was used to study end groups of linear polyethylene glycols. In particular, amine, hydroxyl and thiol end groups are investigated because these nucleophilic moieties are among the most common within biological and synthetic macromolecules. Through selective reaction with alcohol, amine, and thiol end groups, the presence of these end groups could be confirmed.
287 - Temperature dependent size exclusion chromatography for the investigation of dynamic bonding/debonding reactions

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Dynamic bonding/debonding polymers are in the recent focus for applications in field of smart or responsive materials. Such polymers allow controlled change in their properties and can be used for reversible crosslinking, for instance by thermoreversible Diels-Alder reaction. This makes them interesting for intrinsically self-healing materials or drug-delivery systems.

Assessing the reversible reactions in real time and in a quantitative manner is a special analytical task because it requires methods working under the reaction conditions. Only if the measurement can be performed online reliable data can be obtained. The molecular weight distribution (MWD) of a polymer is a useful characteristic for this scope because it represents the bonding state quantitatively and allows monitoring the extent of bonding/debonding reactions. Setting up a size exclusion chromatography instrument to work in temperature dependent mode gives the opportunity for the online determination of the MWD at different temperatures. Adequate evaluation methods have to be applied for the compensation of temperature effects and for making the results comparable to each other. The method allows monitoring the progress of bonding/debonding reactions and can be used for analyzing not only the extent, but also the kinetics of the reactions, as shown in the figure on the example of a polymer that depolymerizes at 140 °C (chromatograms after various depolymerization times). Verification of the results is achieved by temperature dependent DLS and NMR experiments.
Nowadays, polymeric materials are inescapable in our modern societies and cover a broad range of applications in areas such as automobiles, textiles, packaging, medical and pharmaceutical, to name just a few. This increasing complexity in applications has driven the need to produce new, and often highly complex, polymeric materials. Accurate and detailed sample characterisation is vital to this process.

It is predicted that the 3D structure of a polymer will have functional importance as synthetic polymers become increasingly sophisticated. Traditional techniques used by the polymer industry cannot measure 3D shape, which is greatly influenced by the flexibility of the polymer chain.

Travelling wave ion mobility separations coupled with quadrupole time-of-flight (QTof) mass spectrometry provide unique capabilities for 3D shape characterization.

Different polymers were prepared for analysis; a random and a block co-polymer containing poly ethylene glycol (PEG) and poly propylene glycol (PPG) repeat units and a polylactide. Samples were introduced to the electrospray source of a SYNAPT G2 HDMS instrument via direct infusion. Ion mobility data were processed using MassLynx v4.1 and DriftScope v2.6.

DriftScope can be used to generate mobility plots that display mass to charge ratio on the x-axis, drift time on the y-axis, and ion intensity represented by color. If we observe a roughly straight, diagonal line in the mobility plots this tells us that as the polymer increases in mass there is a predictable relationship with its size. A bend, or a kink, in the ion series indicates that as the polymer increases in mass the 3D arrangement of the polymer chain changes and possibly folds back on itself.

Both co-polymer samples contained PEG and PPG repeat units and had an average molecular weight of approximately 2000 Da. For the block co-polymer, the area with the highest ion intensity runs roughly diagonally across the plot. This is in contrast to the random co-polymer where we see a greater number of bends, or kinks, in the ion series.

This means that we can draw some conclusions about the 3D structure and flexibility of the two polymers. The block co-polymer has the most linear relationship between mass and shape.

Recently, academic research has been carried out on polylactides to determine the degree of polymerization at which the folding occurs, for a given charge state. Calibrating the mobility cell with a known standard allows collision cross section areas to be calculated. This information can then be used to confirm calculated 3D structures for the polymer at various degrees of polymerization and charge state.
Nanoparticles can have a profound effect on a polymer's glass transition temperature ($T_g$). Many layer-by-layer (LbL) assemblies contain nanoparticles for added functionality, but the resulting effect of nanoparticles on an LbL film's properties is not known. Previously, we have shown that a nanoparticle-free LbL film containing strong polyelectrolytes, poly(diallyldimethylammonium chloride)/poly(styrene sulfonate) (PDAC/PSS), exhibited a thermal transition somewhat akin to a glass transition using quartz crystal microbalance with dissipation (QCM-D) and modulated differential scanning calorimetry (MDSC). In the work presented here, layers of negatively charged nanoparticles of either spherical or platelet morphology have been inserted at varying locations throughout PDAC/PSS LbL films assembled.

QCM-D and MDSC were used to determine the effect that these nanoparticles have on the previously measured thermal transitions as a function of placement within the film and particle shape.
290 - Sub-second kinetics studied by fast scanning calorimetry

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In polymers, pharmaceuticals, (amorphous) metal alloys metastability is the rule rather than the exception, and the study of the kinetics of such systems has become an important issue. For a thorough understanding of the kinetics of all kinds of temperature- and time-dependent processes related to metastability there is an urgent need for new techniques. DSC is one of the few techniques that have a large dynamic range in relation to measuring rates varying from (quasi) isothermal measurement to measurements at relatively high rates up to 1 MK/s for thin film chip calorimeters.\(^1\) Fast cooling is gained by decreasign the sample mass and addenda heat capacity of the measuring cell and employing a gas as the cooling medium.\(^2\)

Figure 1: Sample of pure PCL (ca. 20 ng) on the calorimeter chip XI-269 with additional metal particles for temperature calibration on top

Calorimeters with high scanning rates allow creation of far from equilibrium states, e.g. polymers without homogeneously formed nuclei.\(^3\) Different applications of the device are shown like crystallization kinetics of fast crystallizing polymers,\(^2\) melting of proteins without decomposition,\(^4\) evaporation of ionic liquids at elevated temperatures,\(^5\) and some more.

References

This work is focused on developing and applying a systematic methodology for the measurement of kinetics and thermodynamics of the thermal degradation of polymeric materials. This methodology employs a simultaneous thermal analysis instrument capable of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A numerical model is utilized to fit thermogravimetric data to obtain thermal degradation kinetics. This model is subsequently employed to analyze DSC heat flow and extract sensible, melting and decomposition reaction heats. The extracted set of kinetic and thermodynamic parameters is shown to simultaneously reproduce TGA and DSC curves.

This methodology has been applied to 15 polymers that produce with or without a significant amount of carbon rich residue (char) upon thermal decomposition. The following seven non-charring polymers are examined in the study: poly(oxymethylene), poly(methyl methacrylate), high-impact polystyrene, polyamide 6,6, polypropylene, poly(lactic acid), and poly(acrylonitrile butadiene styrene). Eight charring polymeric materials which produce a significant amount of carbon rich residues during their thermal degradation process are also examined: a poly(methyl methacrylate)-poly(vinyl chloride) alloy (Kydex), polymerized diglycidylether of bisphenol A, poly(ethylene terephthalate), poly(paraphenylene terephthalamide) (Kevlar), polymerized bisphenol A cyanate ester, poly(phenylene sulfide), polyetherimide and poly(ether ether ketone).
292 - Challenges in characterization of generic polymer drug substances

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The Drug Price Competition and Patent Term Restoration Act of 1984 (the Hatch-Waxman Amendments) created section 505(j) of the Act (21 U.S.C. 355(j)), which established the current ANDA (Abbreviated New Drug Application) approval process. To obtain approval, an ANDA applicant must demonstrate, among other things, that its drug product contains the same active pharmaceutical ingredient (API), i.e. same drug substance. Characterization of polymer drug substances presents challenges to both the applicants and the Agency in terms of establishing drug substance sameness. A couple of polymer drug substances are presented to illustrate these issues and common approaches in their characterization.

Tuesday, March 18, 2014 05:30 PM
Frontiers in Polymer Characterization (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
We have demonstrated base-catalyzed thiol-isocyanate chemistries as modular post-polymerization modification (PPM) brush platforms for rapid fabrication of highly functional, multicomponent surfaces. Advantageously, these PPM strategies are one-step reactions and require no “activation” of the tethered brush consequently simplifying the PPM process. At constant thickness and grafting density, our results from FTIR and ellipsometry show a definite MW dependence of thiol on conversion of isocyanate groups; however, the distribution of thiourethanes in the z-direction of the brush is unknown. The z-distribution of functional groups, if present in a heterogeneous arrangement, is likely to influence the ultimate properties of the polymer brush. Therefore, the goal of this work is to provide knowledge of structure and distribution of functional groups installed on polymer brush platforms via a thiol-click PPM process. We have studied the influence of thiol molecular weight and brush thickness on the z-distribution of functional groups resulting from the one-step PPM process using neutron reflectivity. This knowledge will not only provide guidelines for the preparation of homogeneous functional polymer brushes, but will also provide avenues to intentionally introduce heterogeneity in the z-direction yielding polymer brushes with structure (i.e. pseudo-block copolymer brushes) and properties unattainable by conventional methods.
294 - Characterization of backbone structure in poly(chlorotrifluoroethylene-vinylidene chloride) copolymer by multidimensional NMR spectroscopy

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Poly(chlorotrifluoroethylene-co-vinylidene chloride), poly(CTFE-co-VDC) is a thermoplastic that has widely applications in industry due to its water repulsion and chemical stability. However, there are a few studies on the characterization of this polymer's monomer sequence. $^1H/$$^{19}F/$$^{13}C$ Triple resonance multidimensional NMR experiments are effective techniques that have been employed in this study to determine the sequence distribution of backbone in poly (PCTFE-co-VDC).

Resonances of low level sequences (3-carbon sequences) have been identified and assigned by two dimensional NMR experiments. The resonance assignments are based on $^{19}F/$$^{13}C$ gradient heteronuclear single quantum coherence (gHSQC), which provides the one and two-bond $^{13}C$-$^{19}F$ correlations. The assignments are further confirmed by 3-5 bonds $^{19}F$-$^{19}F$ correlations obtained by $^{19}F$-$^{19}F$ gradient double quantum correlation spectroscopy (gdqCOSY).

295 - Local Young's modulus of pure and blended polymers using PeakForce™ Quantitative Nanomechanical Mapping

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Recently developed phase-separated polymer blends for gas separation possess a unique droplet-matrix architecture. The extent of the interaction between the polymers at the blend interface may affect a membrane's tensile strength and gas permeability properties. A method was developed to investigate the interaction between phase-separated polymers using the PeakForce™ Quantitative Nanomechanical Mapping (PFQNM, Bruker) mode of atomic force microscopy. In PFQNM, force curves acquired for each pixel are translated into a height image and mechanical property maps (e.g., adhesion, deformation, dissipation, Young's Modulus).

The successful mapping of Young's modulus in polymer membranes was achieved using the Derjaguin-Muller-Toporov model. Analysis of the Young's modulus maps will reveal the degree of interaction between the polymers in the blends. These results will be used to interpret current gas permeation results and to develop future gas separation membranes.

Tuesday, March 18, 2014 05:30 PM
Frontiers in Polymer Characterization (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Conjugated polymers have become the focus of research for sensors, organic field effect transistors, organic solar cells, and many other electronic and optoelectronic devices. Advantages of conjugated polymers for optoelectronic device applications include flexibility and property tenability, and their intrinsic high conductivity. Charge mobility (a critical factor in conductivity) studies have revealed very efficient charge transport in molecular junctions using organized molecular wires and self-assembled monolayers. However, most of the studies involve single molecules or oligomers (<20 repeat units), chemisorbed or physisorbed to a conductive substrate by interactive (docking) functional end groups such as -RSH, -RSiR₃, and –RPO(OH)₂. This work focuses on the synthesis and characterizations of a phosphonic acid end-functionalized PPV self-assembled onto Indium Tin Oxide (ITO) substrates. The materials synthesis, chemical characterizations, and self-assembly studies including UV-Vis and AFM will be presented.
Ultrafast magic angle spinning (UF-MAS, 60 kHz) solid-state $^{19}$F NMR methods at 706 MHz have been used to characterize cross-linking structures in a copolymer of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) and its curing with bisphenol-AF. Assignment of $^{19}$F resonances for the monomer and inverted monomer sequences were identified for various stages of the curing process. Additional CF$_3$ and CF$_2$ resonances after cross-linking corroborate the presence of previously reported cross-linking structures. Measurement of $T_1$ and $T_1\rho$ relaxation times confirmed the formation of fluorine ion in the form of CaF$_2$ during press and post cure. The data suggests rapid cross-linking occurs during the short press cure and continues at a reduced rate over the longer post cure resulting in increased rigidity.
298 - Developments in 2D-chromatography with FTIR detection for the analysis of complex polymers

Derek Lohmann\textsuperscript{2}, dlohmann@pss-polymer.com, Thorsten Hofe\textsuperscript{1}, John McConville\textsuperscript{2}, Peter Kilz\textsuperscript{1}, Peter Montag\textsuperscript{1}. (1) PSS Polymer Standards Service GmbH, Mainz, Germany, (2) PSS USA Inc., Amherst, MA 01002, United States

The task of characterizing polymeric materials has become more challenging as advances in polymer synthesis gave rise to a variety of novel, complex materials with predetermined chemical composition, functionality and architecture. No single analytical technique, alone, provides adequate information regarding the different distributions.

The co-existence of these property distributions require multidimensional (combined) methodologies. 2D-Chromatography combines the separation power of two different chromatographic methods, e.g. HPLC with GPC/SEC. 2D-chromatography results in a significant enhancement of resolution and peak capacity. Addition (hyphenation) of FTIR detection to 2D-chromatography results in a significant increase in information for complex polymeric materials.

The presentation will outline the advantages of the hyphenated approach for determining both molecular weight and chemical composition data.

Details of a fully integrated, software controlled, 2D-FTIR system will be shown.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{homogeneous_product.png}
\caption{Homogeneous product}
\end{figure}
Recent developments in polymerization processes have utilized a wide array of strategies. The development has evolved from simple polymer chains to complex polymers capable of performing multiple functions within a single molecular chains. As these new materials evolve their control and understanding has come under intense scrutiny utilizing a wide range of analytical technology ranging from chromatographic separation to advance mass spectrometry.

Addressing the challenges of material characterization has often been focused on the so called hyphenated techniques such as two dimensional separation followed by multiple dimensional detection. As these analytical schemes become more complex a need for automation and online approaches are required for ease of use as well as quality of data output. One approach, online two dimensional chromatography, has seen significant advances.

Online two dimensional liquid chromatography (LC × LC) offers unique advantages over traditional single dimensional chromatography as it allows for direct investigation of material composition. Polymeric characteristics as well as polymer composition information is obtained allowing for understanding of material composition and distribution.

In this study we demonstrate the ability and flexibility of this two dimensional separation technique to rapidly isolate material based on high speed size separation and ultra performance gradient affinity separation coupled to material specific detection allowing for monitoring material composition for process optimization and control and consistent performance.
300 - Polymer characterization using ambient and high temperature gel permeation chromatography systems with a dual flow differential refractive index detector

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The main utility of single detector ambient and high temperature gel permeation chromatography (GPC) is to extract quantitative information from the elution curves obtained via a concentration sensitive detector with accuracy and precision. Traditionally, molar mass averages and distributions of polymers are determined using peak position calibration involving polystyrene standards of known molar mass and chemistry analyzed by GPC coupled to a differential refractive index detector (RI). The repeatability and reproducibility of the molar mass averages obtained by GPC/RI are directly dependent on the baseline stability of the RI detector. Here, we have studied the repeatability, reproducibility, and baseline stability of a dual flow RI detector coupled to both an ambient and high temperature GPC for the determination of molar mass averages via peak position calibration by GPC compared to that of conventional RI detectors.

The dual flow design is shown to compensate for any changes in the refractive index of the solvent over time by continuously flowing pure solvent through the reference side of the flow cell, thus significantly increasing baseline stability of the RI detector and the repeatability and reproducibility of the molar mass averages.

Monday, March 17, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Dallas Convention Center
Room: Hall F

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Identification, classification, and interpretation of vibrational spectra present ongoing challenges. The objective of coupling vibrational spectroscopy with databases and analysis algorithms is to minimize experimental work, analyze small/intractable samples and maximize the use of data mining tools. The toolboxes currently available include large cheminformatics spectral and property databases and specialized algorithms for queering optimization based on spectra and property. Additionally chemometrics principal component analysis methods, mixture analysis and advanced visualization tools can be incorporated within the toolbox repertoire. In this presentation we will provide examples of solutions to multi-components identification based solely on effective utilization of computational methods. The flowchart shown below provides a logical protocol for efficient utilization of available tools.
The effect of toluene on the molecular mobility of poly(methyl methacrylate) (PMMA) and PMMA adsorbed on the silica surface has been studied. The incorporation of toluene into the bulk polymer and surface-adsorbed polymer was carried out by vapor sorption. The amount of solvent uptake at different times was studied by thermogravimetric analysis (TGA), which was also used to study the diffusion of the toluene into the polymer system. The mobility of the polymer and the surface adsorbed polymer was studied by using differential scanning calorimetry (DSC). A substantial decrease in the glass transition temperature ($T_g$) was observed for the bulk polymer when toluene was absorbed. For surface adsorbed polymers, the effect of toluene was dependent on the amount of polymer adsorbed on surface.
303 - Eliciting tunable mechanical properties in polymers grafted to optically-active metal complexes

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N-isopropylacrilimide (NIPAM) polymers can directly undergo controllable mechanical changes by varying solution pH and temperature. An additional means of controlling this mechanical change can come from grafting complexes containing metal-ligand charge transfer (MLCT) bands, which can change the conformation of the gel upon activation by either an applied voltage or UV light. Thus, a metallopolymer composed from NIPAM and complexes with MLCT bands have high potential for material applications.

Photoactive transition-metal complexes comprised of bipyridyl ligands coordinated to metal centers (Ruthenium and Nickel analogs) were synthesized and characterized in order to pinpoint a reproducible method for synthesizing each metallopolymer sample and to explore the relationship between mechanical properties and synthesis conditions. Polymers were synthesized by combining purified and characterized mixed-ligand metal complex comonomers with organic comonomers in emulsion polymerization. Polymers were tested for size uniformity by dynamic light scattering, while size distribution data was collected using MALDI-MS. Electronic transition data was collected via UV-Vis spectroscopy and spectrofluorometry. Inductively-coupled plasma atomic emission spectroscopy will be used to determine the concentration of successfully bound monomer to the PNIPAM-type polymers in comparison to concentration data taken of polymers synthesized using an alternative method.
304 - Surface immobilization of heparin onto poly(ether ether ketone)

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Photo-grafting of hydrophilic monomer and space arms was used to enhance the hydrophilicity of poly(ether ether ketone)(PEEK) with the aim of extending its application to biological fields. PEEK films were surface modified by UV grafting of acrylic acid(AA) to introduce ―COOH on PEEK surface. Adipic amine was used as a space arm to introduce heparin on PEEK surface based on the condensation reaction between ―NH2 and ―COOH. [figure1] The modified PEEK(PEEK-COOH, PEEK-NH2 and PEEK-Hep) was characterized by energy-disperse spectroscopy (EDS), X-ray photoelectron spectroscopy(XPS) and water contact angle measurements, which show that heparin was grafted on PEEK surface. The contact angles of modified PEEK films were lower than those of original films, demonstrating a significant improvement of surface hydrophilicity.

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Novel pH Responsive Biodegradable Heterograft Copolymers

B. Hazer, Olgu Oruç and Temel Öztürk

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Synthetic biodegradable polyesters are widely used in medicine and bioengineering. Modification reactions on the biodegradable polymers are carried out in order to gain new features. PCL is a hydrophobic polymer and drug delivery systems have a limited field of application. However, hydrophilic groups attached to the polymer chain to give hydrophilic property studies are very common. In this study, a novel RAFT agent, 1,2-propanediol-3-ethyl xanthegonat, was synthesized, in order to use one pot polymerization of ε-caprolactone (ε-CL) and vinyl benzyl chloride (VBC) in one step. In the second step of the work, chloride side groups of PCL-b-PVBC were reacted with potassium salt of ethyl xanthogenate to obtain PCL-b-PVB-Xanthate (PCL-b-PVB-Xa), a new macro RAFT agent. PCL-b-PVB-Xa macro RAFT agent was used to initiate the polymerization of 2-(dimethylaminoethyl) methacrylate (DMAEMA) in order to obtain PCL-b-PVB-g-PDMAEMA comb type graft copolymer. Figure 1 shows the reactions of the heterograft copolymer synthesis. pH-responsive graft copolymer obtained was soluble in water except pH>12. Finally, the polymers obtained in this work were characterized by using spectrometric, optic and physicochemical methods.

Acknowledgment. This work was supported by; both the Bulent Ecevit University Research Fund (#BEU-2012-10-03-13) and TUBITAK (grant # 211T016).

References

306 - Development of dual responsive polymers for bacterial adhesion studies

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Bacterial biofilms can grow in diverse environments: pipelines, ship hulls, heat exchangers and medical devices are commonly affected. Biofilms greatly affect the energy sector by causing biofouling in oil pipelines and offshore engineering equipment and cause billions of dollars of damage. One strategy to inhibit biofilm formation is to design surfaces that resist or prevent adhesion of bacteria. The effect of surface properties, such as wettability and charge, on bacterial adhesion remains poorly understood. In this study, our objective is to design dual responsive copolymer brushes that can serve as model system for understanding the effects of charge and wettability on bacterial adhesion. We synthesized poly(acrylic acid) (PAA), which changes from hydrophobic at low pH to hydrophilic at high pH and poly(N-isopropylacrylamide) (PNIPAM), which is hydrophobic at high temperature and hydrophilic at low temperature. We synthesized PNIPAM and poly(tert-butyl acrylate) (PtBA) in solution using atom transfer radical polymerization (ATRP) and the resulting polymers had low polydispersity indices (PDIs) and well controlled molecular weights. PAA was obtained from PtBA via hydrolysis. Currently, we are optimizing the ATRP procedure for synthesizing copolymers of PAA and PNIPAM. A critical challenge is to identify reaction conditions for which both polymers are soluble in the reaction solvent and have comparable reaction kinetics. We are presently synthesizing copolymer brushes on a silica substrate using surface-initiated ATRP, to be used in bacterial adhesion studies.

Adapted from – Jiang et al., Adv. Mater. 2006, 18, 435
307 - Analysis of spherical polyelectrolyte brushes loaded with $\text{SiO}_2$ nanoparticles and hollow $\text{SiO}_2$ microspheres by SAXS

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Monodispersed silica-coated polystyrene core–shell nanoparticles (CSNs) and hollow silica nanospheres (HSNs) with a well-defined morphology and pH sensitivity were prepared using spherical polyelectrolyte brushes (SPBs) as templates, and systematically characterized by Small angle X-ray scattering (SAXS) in combination with dynamic light scattering (DLS), scanning electron microscope (SEM), transmission electron microscope (TEM), and thermal gravimetric analysis (TGA). The scattering intensity of CSNs and HSNs were higher than that of SPBs, due to the scattering intensity contribution of the silica. Compared to SPBs, the scattering peak positions of CSNs and HSNs moved towards small $q$ zone due to the size growth caused by the load of silica.

The prepared core–shell and hollow silica nanoparticles showed significant pH response and redispersibility as observed by SAXS and DLS, which may be applied as promising carriers in drug delivery, catalysis and functional materials.

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Development of new materials for high energy density capacitor is of great importance to provide high power needed for hybrid electric vehicles, high energy lasers, electromagnetic railguns, etc. Biaxially oriented polypropylene (BOPP) has dominated the market as the primary choice for energy storage capacitors, but it shows a relatively low dielectric constant (~2.2) and reduced breakdown strength above 80°C. Herein, new materials are investigated for replacement of BOPP, but it is challenging to achieve a high dielectric constant as well as low dielectric loss. Polyimides are promising for next generation polymer dielectrics due to their higher polarizability and better thermal stability. Rationally designed polyimide thin films with polyether segments were prepared with high dielectric constants up to 7.8, while maintaining low loss (<1%) at temperatures higher than 100 °C. Our syntheses were guided by high-throughput density functional theory (DFT) calculations and the experimental measurements were found to be in close agreement with the theoretical calculations. Variations on the polyimide structure allowed for a clear demonstration of the relationship between chemical functionalities and dielectric properties in terms of dielectric constant, dielectric loss, band gap, etc. Dielectric properties were found to be greatly dependent on conjugation structures and the length of polyether segment in the polyimide backbone.
In the recent literature, studies on the synthesis and utility of poly(ionic liquids) derived from 1-vinyl- and 4-vinyl imidazolium monomers have been reported. The acidity of the hydrogen atom at the 2 position of these imidazolium polymers can be a limiting factor relative to the utility of these materials in electrochemical devices, particularly lithium-ion batteries. In the present research, vinyl imidazolium monomers with an alkyl substituent at the 2 position are being synthesized and characterized. Specifically, we have focused on the synthesis of 1-butyl-2,3-dimethyl-4-vinyl imidazolium (BuMe-4-VIm+) [1], 3-butyl-2-methyl-1-vinyl imidazolium (3-Bu-2-Me-1-VIm+) [2], and 2-butyl-3-methyl-1-vinyl imidazolium (2-Bu-3-Me-1-VIm+) [3] salts.

[1] was synthesized by alkylation of 2,3-dimethyl-4-vinyl imidazole which was prepared by a procedure analogous reported to that by Schiavone et al [3]. Two pathways for the synthesis of the 1-vinyl imidazolium monomers are being pursued. The first is vinylation of 2-methyl imidazole, followed by alkylation to yield [2]. The second entails the lithiation of 1-vinyl imidazole and subsequent alkylation to yield either [2] or [3].


[2] Thomas W. Smith; Meng Zhao; Fan Yang; Darren Smith; Peggy Cebe; Macromolecules, 2013, 46(3), 1133-1143

310 - Thermal characterization of poly(lauryl methacrylate) adsorbed onto silica

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The effect of the adsorption of poly(lauryl methacrylate) onto silica was investigated. Of particular interest was the melting point and side chain crystallinity of the alkyl side chains. It was found that there is more side chain crystallinity in adsorbed polymers with larger adsorbed amounts. This is likely because in adsorbed samples with larger adsorbed amounts, the polymer chains have more loosely bound sections, allowing them to move into positions that allow greater crystallinity. For smaller adsorbed amounts, the polymer chains may be more tightly bound and as a result, its crystalline domains are disrupted.
We have developed an azide-functional, modified epoxy resin system that cures via copper-catalyzed azide/alkyne cycloaddition (CuAAC). The modified resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A, was synthesized by reaction of commercial diglycidyl ether of bisphenol-A with NaN₃/NH₄Cl at reflux in a reaction medium of H₂O/2-ethoxy ethanol. When this resin is crosslinked with an aliphatic polyalkyne, such as tripropargyl amine, the resulting thermoset has a T_g that is typically ≤ 130°C. To elevate the T_g, a number of tetra-functional aromatic propargyl amines were synthesized by reaction of the corresponding aromatic diamine with propargyl bromide/K₂CO₃ at reflux in 2-ethoxy ethanol. In this paper, we will report the thermal and mechanical properties of the cured thermosets obtained by reaction of the modified resin with the synthesized tetrapropargyl aromatic amines.

![Chemical structure and reaction diagram]

**Tuesday, March 18, 2014 05:30 PM**

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

**Location: Dallas Convention Center**

**Room: Hall A**
The interfacial interaction of Poly(γ-benzyl-L-glutamate)-silica was investigated with an emphasis on its thermal behavior, in particular its heat capacity. PBLG was synthesized by the ring-opening polycondensation method using γ-benzyl-L-glutamate N-carboxyanhydride (NCA) and initialized by triethylamine. The molecular mass by viscosity measurement gave a mass of 190,000 g/mol. FTIR results revealed that the bulk polymer had primarily α-helical structure, but the adsorbed samples had a mixture of conformations. The T_g of the bulk PBLG was found to be 20°C as shown in Figure 1. Heat capacities were measured by quasi-isothermal differential scanning calorimetry in the temperature range of -80 to 200 °C for PBLG and its adsorbed samples. A model is proposed to enable us to compare the heat capacity of adsorbed PBLG to that of the bulk polymer. The specific heat capacity for PBLG adsorbed samples increased with increasing PBLG content. The thermal stability of PBLG and its adsorbed samples were measured via TGA. The decomposition temperature of PBLG increased with the adsorption of silica.
Polycarbonate Scott Iacono, Dylan Boday, Jeffrey Youngblood Tuesday, March 18, 2014

313 - Plasticization effects of various fatty acids on the mechanical properties of styrene ionomers

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The dynamic mechanical properties of sulfonated styrene (PSSA) and styrene-co-methacrylate (PSMA) ionomers containing 30 wt% of fatty acid obtained from soybean oil were investigated. It was observed that when the fatty acid was added to the PSSA ionomer of low ion content, the ionic modulus increased slightly, but the cluster $T_g$ decreased significantly.

On the other hand, for the PSSA ionomer of high ion content, the ionic modulus increased further and the cluster $T_g$ also increased but still much lower than that for the ionomer of low ion content. In the case of PSMA ionomer of low ion content, the addition of fatty acid increased ionic modulus but decreased the cluster $T_g$.

For PSMA ionomer of high ion content, the ionic modulus and well as cluster $T_g$ decreased drastically. The above findings indicated that the plasticization effects depended on the type and amounts of ionic groups.

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
314 - Reversible surface modification of reactive polymer brushes based on dynamic covalent chemistry

Tomoya Sato\textsuperscript{1,2}, t-sato@polymer.titech.ac.jp, Tomoyuki Ohishi\textsuperscript{2}, Atsushi Takahara\textsuperscript{1}, Hideyuki Otsuka\textsuperscript{1,2}. (1) Graduate School of Engineering, Kyushu University, Fukuoka, Japan, (2) Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan

Recently, “Dynamic Covalent Chemistry” attracts attention in the field of polymer science. One can prepare the novel polymeric materials, which could not be created by traditional methods by using dynamic covalent chemistry. We have reported the structural reorganization of polymers via radical crossover reactions of alkoxyamine units. Because of the reactivity of alkoxyamines under heating condition, alkoxyamine-containing polymers can be reorganized after structural determination. In this study, we report the preparation and radical crossover reactions of alkoxyamine-containing polymer brushes on the surface. As shown in Scheme 1, this kind of polymer brushes can undergo reversible grafting of other functionalities in their structures and surface properties could be changed by the composition control.

Polymer brushes containing alkoxyamine units (1) were prepared on the flat substrate and nanoparticles by surface-initiated atom transfer radical polymerization, and characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. To investigate the reactivity of the alkoxyamine-containing copolymer brushes (1), we treated the copolymer brushes (1) with alkoxyamine-terminated linear polymers. For example, when the brush (1) was heated with fluorinated polymer, poly(2,3,4,5,6-pentafluorostyrene) (2), the surface (5) showed more hydrophobicity. On the other hand, when copolymer brush (1) was treated with poly(4-vinylpyridine) (3), the brush surface (6) showed more hydrophilicity after the quaternization. Reversible grafting and de-grafting reactions were also confirmed by XPS and contact angle measurements. The results indicated that the copolymer brushes (1) including alkoxyamine units are useful for reversible surface property control.

Tuesday, March 18, 2014 05:30 PM  
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)  
Location: Dallas Convention Center  
Room: Hall A
On-going demand of passivation materials for the next generation display pursue substitutes with low dielectric constant, high transmittance and thermal stability, low regain, high adhesive property, and patternability that the current silicon nitride and silicon dioxide layer cannot fulfill. In this study, we developed patternable low k systems containing POSS moieties. Negative-tone patterning was utilized. Through optimizing the patterning conditions, such as PAB, PEB, UV exposure dose, crosslinker content, and PAG content, it was possible to achieve successful patterning of the materials. Thermal stability and dielectric property were improved with increasing POSS content. For the system using POSS as a crosslinker, the 5% thermal decomposition temperature and the dielectric constant were 319 °C and 3.20, respectively, while maintaining its transparency higher than 90%.
Various types of dimer acid (DA) esters were prepared as plasticizer for styrene-methacrylate (PSMA) ionomers. It was found that the PSMA ionomers containing 2.3 mol% of ions showed a negligible plasticization effect when DA was added to the ionomer. However, when the DA esters were added, the ionomers exhibited significant plasticization effects. Even, the ionomer containing methyl DA ester showed similar plasticization behavior like DOP-containing ionomer. In the case of 10 mol% ionomers, similar trends in the storage modulus values were observed.

It should be mentioned that the smaller size of alkyl group of the DA ester decreased more significantly, compared to the DA ester with a larger size alkyl group. This suggested that the strength of the interaction between –COO- groups of the DA ester and multiplets of the ionomer played an important role in the ionomer behavior.
317 - Effect of pore size on gas storage in porous polymers

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Porous materials have emerged as promising scaffolds for the storage of energy related gases, including H₂ and CO₂. Porous aromatic frameworks (PAF)s are a subset of porous materials that have been shown to combine high gas storage abilities with high thermal and moisture stability. We have developed an oxidative post-synthetic crosslinking scheme for novel hexobenzocoronene based PAFs. The extent of crosslinking is characterized by change in pore size, and how the pore size affects the enthalpy of H₂ and CO₂ storage in these materials.
Superhydrophobic diatomaceous earth (SHDE) was prepared by treating diatomaceous earth with silane coupling agents. Coatings were prepared using treated diatomaceous earth and different polymers as binders. The contact angle measurement revealed that the hydrophobicity of the treated DE and polymer coatings improved with modification of DE with the silane-coupling agents. The development of hydrophobicity was found to be dependent on the molecular weight of polymer binder and viscosity of the coating mixture. The development of hydrophobicity will be discussed in terms of amounts of treated diatomaceous earth particles in treated diatomaceous and polymer coatings.
319 - Flame retardancy and thermal decomposition mechanism of silicone-based composites

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Silicones have proven to be effective flame retardants in polymers because of their high heat resistance and nontoxicity during combustion. The flame retardant improvements can be elucidated when analyzing the thermal decomposition process of silicone-based composites as characterized by three stages. An early stage is described by the loss of light decomposition compounds, typically reaching stage completion before 20% total mass loss. After the early stage, the activation energies of the flame-retardant polymers rise as thermal decomposition remains constant up to 80% mass loss, indicating that the thermal stabilities of the intermediate products are rather similar. In the final stage, the silicone flame retardant further increases the activation energy of the polymer in thermal decomposition, suggesting that the flame retardant delays the thermal decomposition behavior of the polymer. In comparison to a pure polymer system, the char of silicone-based composites was found to demonstrate more rapid swelling and formed spherical, closed cells that appear to efficiently block escaping gases. It has been revealed that the silicone has the function of both stabilizing the char residue through the formation of crosslinking structures between the polymer substrates and the silicone additives, and improving the flame retardancy of the polymers in the final period of the thermal decomposition process.
The effect on mechanochemically-induced bond scission by changing polymer architecture from a 3-arm star polymer to a linear polymer analog has been explored. Comparing the breakdown rates of linear polymers at different molecular weights to that of a 3-arm star polymer has shown that the traditional relationship between total molecular weight and mechanochemical transduction does not apply to the comparison of these architectures. Our data has indicated that it is the individual arm molecular weight emanating from the center of the star and linear polymers, not the total molecular weight, that determines the rate of mechanochemical bond scission. These findings have revealed that control over mechanochemical transduction in macromolecular systems at a given molecular weight regime may be modulated by changes in the overall macromolecular structure.
321 - Fabrication of low wettable perfluoro-polyisophthaloylester with PET coatings

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A perfluoro polyisophthaloylester (PF-oate-Iso-R) has been synthesized via Scotothen-Baumann reaction of isophthaloyl chloride with different perfluoro alcohols in the presence of a triethylamine in methyl ethyl ketone (MEK). PF-oate-Iso-R was characterized using $^1$H, $^{13}$C NMR, FT-IR, TGA and DSC. In order to fabricate low wettable coatings, PF-oate-Iso-R were blended with PET in different ratios and deposited on Si wafers. The morphology of the coatings was characterized by AFM.

In addition, the wettability of the coatings was determined by contact angle measurements of both water and hexadecane.

It was found that the wettability of coatings reduced with increasing the amount of PF-oate-Iso-R in coatings.
Computed tomography is one of the most widely applied imaging technologies in diagnostic medicine. Contrast agents, which contain atoms with high electron density, are used to enhance the visibility of soft tissue areas; however, the most broadly used contrast agents have several limitations. Current contrast agents are primarily small molecule, aromatic, iodinated liquids that are rapidly excreted, resulting in short imaging times, and display renal toxicity. Nanoparticles have been shown to have longer circulation times as well as controlled biological clearance pathways, typically accumulating in the liver and spleen rather than the kidneys. We have developed a highly iodinated, biodegradable and biocompatible polymer that has high radiopacity and low cytotoxicity. The polymer can be endcapped with a photo-curable methacrylate group, which allows for easy processing. We can formulate monodisperse nanoparticles via a liposomal/nano-precipitation method. These iodinated nanoparticles are unique in that they are much cheaper than currently developed gold or bismuth nanoparticles, and that they are completely nonaromatic. The size of the particles can be tuned within the range of 50-150 nm in order to avoid excretion by the kidney.

In an initial in vivo study, our nanoparticles showed good contrast in comparison to a commercial contrast agent. Further research is being done to improve the biodistribution and characterization of the nanoparticles with the prospect of creating a new contrast agent that can mitigate nephrotoxicity issues and increase circulation times.
323 - Synthesis, characterization, and application of reversible ultrahydrophobic polymer surfaces

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The well-known ultra-hydrophobic properties of a lotus leaf are based on a hierarchal surface structure in the µm to nm range. Polymer science is now able to mimic this naturally occurring phenomenon by combining polymer particles in the µm range with triblock copolymer coatings in the nm range.

By combining different functionalities in one block polymer molecule, multifunctional polymer surfaces can be synthesized, which exhibit ultrahydrophobic and superhydrophilic behavior. This is achieved by the production of core-shell-nanoparticle layers on a variety of substrates (e.g. polymers and metals) which lead to easy-to-clean (anti-soil and anti-staining behavior) or self-cleaning properties.

The synthesized tri-block polymers consist of a block responsible for the anchoring to the substrate, a “hydrophilic” block and a “hydrophobic” block. This offers the possibility to combine the anchoring to a substrate with reversible switching of the wetting behavior in one molecule. The wetting behavior of the prepared tri-block polymer brushes can be switched by external stimuli: temperature, pH-value, solvent atmosphere, salt concentration etc.

Modern LC techniques to determine the molar mass and the composition of the tri-block polymers will be presented, as well as possible applications for the industrial use of these new switchable materials.

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
324 - PU-PDMS fouling release coatings: Effect of surface damage

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Self-stratified polyurethane (PU)-polydimethylsiloxane (PDMS) based coatings are a promising tough fouling-release coating system. To explore the effect of surface damage on the performance of the coatings, coatings were abraded using scotch brite pads with varying roughness, under varying loads. Roughness analysis showed an increase in roughness of the surface for some treatments. Contact angle and surface energy analysis of the abraded coatings showed increase in contact angle, indicating hydrophobicity of the surface. The coatings were tested for algae, diatom settlement and barnacle and mussel adhesion. The results showed unusual fouling-release performance after abrasion, such as reduction in barnacle attachment, depending on the surface structure induced by the abrasion process.
325 - Surface area and porosity of adsorbed polymers on silica

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The specific surface area and porosity of adsorbed poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) PMMA on silica were measured using the Brunauer–Emmett–Teller (BET) model and the Barrett-Joyner-Halenda (BJH) method, respectively. Measured BET surface areas decreased with increasing adsorbed amount of polymers. Specific surface areas increased linearly with increasing the weight fraction of silica. The results also indicated that the adsorption of the polymer changed the pore size distribution compared to the uncoated silica particles. PMMA and PVAc adsorbed on silica showed different behavior in terms of specific surface area. This difference can be attributed to the changes in the tightly-bound amounts of polymers on the surface of silica with the type of polymer.
326 - Self-healing properties of functionalized poly(ether sulfone) thermoplastic elastomers

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There has recently been much interest in developing materials capable of spontaneous self-healing after damage in order to improve a material’s lifetime, safety, and environmental impact. There has been much success in developing soft, low modulus spontaneously healing materials, but tough and stiff self-healing materials have been less readily synthesized. Recently, some microphase-separated systems have been proposed which incorporate more favorable mechanical properties and self-healing capabilities into the same material; a thermoplastic elastomer morphology with rigid glassy domains embedded in a soft matrix endows a material with mechanical stiffness and the ability to heal via hydrogen bonding. Very little is known about the effect that the mechanical properties of the glassy domain have on the mechanical properties of the material as a whole. Here we report the synthesis and self-healing properties of functionalized poly(ether sulfone)s with grafted side chains capable of hydrogen bonding. High Tg poly(ether sulfone)s are functionalized with initiators for ATRP via chloromethylation in preparation for controlled polymerization of the hydrogen bonding monomer 5-acetylaminopentyl acrylate. Synthetic data, mechanical properties, and self-healing data of the resulting materials will be reported. We expect this research to expand the scope of mechanically robust self-healing materials, and to provide valuable structure-property information about self-healing TPE systems.
A set of low polydispersity diblock copolymers HO-PCLₙ-b-PEG₃₂-RX (n= 51, 67, 109, R= -O(CH₂)₃S(CH₂)₂-, X= -CO₂Na, -SO₃Na) were synthesized for comparative studies of micelle formation and relative stability in aqueous solutions from HO-PCLₙ-b-PEG₃₂-CH₂CH=CH₂ by thiol-ene click chemistry. Narrow size distribution micelles with spherical shapes were characterized by dynamic light scattering (DLS) and cryo-transmission electron microscopy (cryo-TEM). Our working hypothesis is that the stability of aqueous dispersions of micelles can be increased by placing ionic end groups on PEG which gives electrically charged micelle corona that both increase interactions of the micelle with the aqueous environment and inhibit aggregation of micelles through electrostatic repulsions. Micelles from [PCLₙ-b-PEG₃₂-RCO₂⁺ Na⁺]⁺ and [PCLₙ-b-PEG-RSO₃⁻ Na⁺] with negatively charged corona showed a significant increase in the stability compared to the parent HO-PCLₙ-b-PEG₃₂-CH₂CH=CH₂ micelles with a neutral corona. Negatively charged corona stabilize relatively large hydrophobic cores for micelles from diblock copolymers with high hydrophobic to hydrophilic ratios which provides a general approach to increase the drug loading capacity for a micelle carriers.
A conjugated boron-dipyrromethene (BODIPY)–platinum polymer possessing low bandgap of 1.7 eV has been synthesized and characterized. This is the first example of conjugated polymer containing both BODIPY chromophores and Pt centers. Bulk heterojunction solar cells employing this polymer have been fabricated and tested. Thermal evaporated MoO$_3$ was found to form Ohmic contact at the anode, which led to high open circuit voltages up to 0.92 V and power conversion efficiencies (PCEs) close to 1%. The still relatively low PCEs are mainly due to the amorphous nature of the polymer and possible energy mis-alignment between polymer triplets states and fullerene LUMO levels.

**Bandgap = 1.7 eV; HOMO = -5.3 eV; $V_{oc} = 0.92$ V**
The synthesis, characterization, and polymerization of bis(4-trifluorovinyl phenyl ether)methylsilane (SiH-TFVE) will be presented. This new TFVE monomer was prepared via nucleophilic substitution of methyldichlorosilane with TFVE Grignard or organolithium reagents, and characterized by $^1$H, $^{19}$F, $^{13}$C, and $^{29}$Si NMR spectroscopy, IR spectroscopy, and elemental analysis. Condensate-free, thermal polymerization of SiH-TFVE was shown to produce optically-transparent, film-forming polymer with full retention of Si-H functionality. Polymer structure was characterized by NMR, FT-IR, and MALDI-TOF mass spectrometry. Bulk thermal properties were determined from thermogravimetric analysis and differential scanning calorimetry. Facile post-polymerization functionalization via hydrosilylation and dehydrogenative coupling will be demonstrated with an emphasis on incorporating crosslinking and/or chromophore moieties for electro-optic applications.
Conjugated polymers attracted great attention over the past two decades owing to their redox properties, flexibilities, adjustable band gaps and low cost. There are many applications of conjugated polymers such as electrochromic devices, smart windows, organic light emitting diodes, organic field effect transistors. Benzoselenadiazole, dihydroquinazoline and thienothiophene are the units preferred in conducting polymers due to their electrochemical properties. There are no reports in the literature on polymers containing both moieties. With this motivation, we designed and decided to synthesize such a monomer. In this study, a novel benzoselenadiazole, dihydroquinazoline and thienothiophene based monomer; 4-(3a,6a-dihydrothieno[3,2-b]thiophen-2-yl)-7-(thieno[3,2-b]thiophen-yl)benzo[c][1,2,5]selenadiazole (M1) and 2,3-bis(3,4-bis(decyloxy)phenyl)-5,8-dibromo-2,3-dihydroquinazoline (M2) synthesized via Stille coupling and characterized in terms of their spectroelectrochemical and electrochemical properties. They can be good candidates for electrochromic devices in terms of their color and absorption. Especially the polymer 1 can be a great postulant for photovoltaic applications on account of its broad absorption.
331 - Electrospun fibers of fluorescent conjugated polymer with 3D backbone as metal cation chemosensor

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Fluorescent conjugated polymers (FCPs) have received significant attention because of their ability to function as chemosensors in the detection of metal cations in environmental and biological systems with both sensitivity and selectivity. Compared to traditional solution based FCPs, a more practical approach to application is to fabricate inexpensive and portable solid state field-based sensing devices. Previous studies in the Jones group have shown that the photophysical properties of the solid state chemosensors are significantly affected by intermolecular interactions among polymer chains. A functionalized fluorescent conjugated polymer, (tmeda-PPpETE) poly[(pentiptycene ethynylene)-alt-(thienylene ethynylene)] with a N,N,N'-trimethylethyleneamino receptor, was designed and synthesized.

The rigid 3-D framework of the polymer backbones can prevent n stacking of polymer chains, and consequently, increase fluorescent quantum yield of the solid state chemosensor. Electrospun fibers of this polymer were fabricated with a poly (methyl methacrylate) (PMMA) and polyethylene oxide (PEO) matrix, which gives more surface/volume ratio in the solid state increasing the probability of contact between metal analyte and receptor. Photophysical characterization including UV-Vis absorption and emission, fluorescent quantum yield and fluorescent quenching with metal cations have been investigated in order to compare results from the solution based FCPs to this newly developed solid state chemosensor.

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
We report the design, synthesis, and characterization of two novel dioxopyrrolopyrrole-difurano-thiophenyl-diethynyl polymers, poly{(2,5-dioctyl-1,4-dioxo[2H,5H]pyrrollo[3,4-c]pyrrole)furan-2,5-diylethyne-1,2-diyl(3-hexylthiophene-2,5-diyl)ethyne-1,2-
diylfuran-2,5-diyl} (DFDOPP-DE3HT) and poly{(2,5-(2-ethylhexyl)-1,4-dioxo[2H,5H]pyrrollo[3,4-c]pyrrole)furan-2,5-diylethyne-
1,2-diyl(3-hexylthiophene-2,5-diyl)ethyne-1,2-diylfuran-2,5-diyl} (DF2EHDPP-DE3HT) for use in organic photovoltaics. An
ethylenylene spacer was incorporated in both polymers to reduce steric hindrance, as well as to create a better interface between
donor and acceptor layers. Alteration between furan and thiophene based monomers has been previously reported to greatly
increase solubility, allowing for shorter alkyl chains to be inserted, thus decreasing steric hindrance. The DFD2EHPP-DE3HT
polymer was shown to be extremely soluble in most organic solvents, while the DFDOPP-DE3HT polymer was moderately soluble
in organic solvents. The length of the polymer chains has been determined via GPC analysis. The photophysical properties of the
polymers is currently under investigation.

![Figure 1](image-url)
Tenets support the construction of large capacitor banks to provide the power needed for modern electrochemical devices currently being constructed, such as rail guns and the electromagnetic aircraft launch system (EMALS). The industrial standard for the dielectric material incorporated into high energy density capacitors is biaxially oriented polypropylene (BOPP), which has an energy density of 5 Jcm⁻³ at a breakdown of 720 Vμm⁻¹, with a dielectric constant of 2.5 and a dielectric loss as low as 0.01%. As a consequence of BOPP’s low dielectric constant, much research has been focused on replacement materials with increased dielectric constant and thermal stability >100°C while maintaining dielectric loss, energy density and breakdown exhibited by BOPP. Herein we present the rational design, synthesis and characterization of an organometallic polymer, poly(dimethyltin glutarate). Density functional theory (DFT) is applied to model the polymer’s theoretical dielectric constant (ε = 6.04), band gap (E_g = 6.14 eV), stable crystal structure and IR spectrum. Comparison of the computed values and spectra to the experimental measurements of poly(dimethyltin glutarate) show a direct correlation. The measured dielectric constant was ε = 7.39 with an E_g = 4.88 eV while the IR and XRD spectra confirm the presence of the four most stable crystal structures in varying proportion dependent upon processing conditions. This work demonstrates the first organometallic polymer as a high dielectric material for energy storage.
To help obviate one of the main logistical barriers for the proliferation of solar cell technologies, a scheme for the storage of massive amounts of energy is required. Polymers with high dielectric constants that are capable of short pulse discharges are necessary for the next echelon of capacitors, which are used in various up-and-coming energy technologies, including hybrid-electric vehicles, grid-level energy storage and electromagnetic weaponry. In this work, polymers are synthesized with the guidance of high-throughput density functional theory, and are characterized in terms of composition and physical properties, as well as dielectric properties. High dielectric constants are shown across polymer classes, including polyureas, polyurethanes, polyimides, and polysulfones, among others. The inclusion of electronegative species into the polymer backbone is demonstrated to increase the dielectric constant enormously. These studies focus on the structure-property relationship between chemical functionalities and dielectric constants.
335 - Synthesis, characterization and thermal studies of a new series of linear saturated polyamides

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A new interesting class of linear saturated polyamide based on acidic amino acid have been synthesized by melt polymerization of Glutamic acid, Isophthalic acid and different diamine such as Oxalic dihydrazide, 2,6-diaminopyridene, Semicarbazide, Thiourea, Ethylenediamine, p-Phenylenediamine, o-Phenylenediamine and Benzidene. The prepared polyamides were characterized by H-NMR, IR spectroscopy and solubility additionally the density were determined, acid value of the final product were determined and used to calculate the mean molar mass and degree of polymerization. Also, the polymer complex of some polyamide with Fe(II), Cd(II), Mg(II) were prepared in different ratios, and the prepared complexes were characterized by different spectroscopic tolls as well as thermogravimetric analysis were determined from TGA and DTA.
336 - Synthesis, electrochemical characterization, and applications of benzooxadiazole bearing low band gap conjugated polymer

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Three scientists Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa were awarded with the Nobel Prize in Chemistry for 2000 for the discovery and development of conductive polymers which are electrically conductive in their oxidized or reduced states. With this discovery, a new research area had been opened. Conjugated polymers have gained attraction due to solution processability, low cost, easy tuning band gap. They are key materials in many applications such as photovoltaics, OLEDs, organic field effect transistors, biosensors and electrochromic devices. Band gap alternation can mostly be achieved by donor-acceptor approach. As an acceptor unit, strong electron-withdrawing units such as benzooxadiazole unit lower the LUMO energy level which in return decreases the band gap. Benzooxadiazole has good electron accepting property and ability to adopt a quinoid structure. Moreover, coplanar structure of this moiety results in air-stable polymers. In this study, 5,6-bis(octyloxy)benzo[c][1,2,5]oxadiazole unit was firstly coupled with electron rich thiophene unit. Then, the polymer which is namely poly[5,6-bis(octyloxy)-4-(5-phenylthiophen-2-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]oxadiazole] was synthesized via Suzuki polycondensation reaction under inert atmosphere. The electrochemical and spectroelectrochemical characterization of the polymer was carried out.

Benzooxadiazole containing polymer has low band gap, fluorescence characteristic and broad absorption therefore it can be good candidate for solar cells, electrochromic devices and biosensor applications.

![Figure 1: The single scan cyclic voltammogram of the polymer](image1)

![Figure 2: The absorption spectra of the polymer](image2)

**Tuesday, March 18, 2014 05:30 PM**
**General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)**
**Location: Dallas Convention Center**
**Room: Hall A**
337 - Redox-active viologen-embedded polymer prepared by atom transfer radical polymerization and its novel fluorescence properties

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Viologen-containing difunctional (2-bromoisobutyrate) atom transfer radical polymerization (ATRP) initiator was synthesized and used in the polymerization of methyl methacrylate and di(ethylene glycol) methyl ether methacrylate. The obtained well-defined polymers with a single viologen group in the middle of the chain were redox-active, as proved by UV-vis spectroscopy, which allowed for monitoring the accumulation of viologen radical cations, formed in the presence of reducing agents. Additionally, the fluorescence properties of the synthesized viologen-containing polymers were studied. It was found that the fluorescence intensity is solvent-dependent, which opens the possibility to use the viologen-containing polymers as fluorescent sensors.

Monday, March 17, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Dallas Convention Center
Room: Hall F

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
n-Conjugated polymers have received much attention because of their semiconducting properties. Synthesis of a variety of n-conjugated polymers were achieved by cross-coupling reactions catalyzed by transition metal complexes. However, the traditional cross-coupling reaction need both organic halides and organometallic compounds, increasing the cost and the waste.

Recently, Fagnou et al. reported indole synthesis from acetanilides and internal alkynes by rhodium catalysts and oxidants. This reaction can construct n-conjugated units without organohalides nor organometallic compounds.

In this work, we applied the oxidative coupling to synthesis of n-conjugated polymers from 1,4-bisacetamidebenzenes and internal alkynes. The properties of these polymers are investigated by UV vis and florescence spectroscopic measurements, CV, and DFT calculations.
339 - One-pot synthesis of poly(N-vinylcaprolactam)-based biocompatible block copolymers using a dual initiator for ROP and RAFT polymerization

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Poly(N-vinylcaprolactam) (PVCL) is a thermosensitive and biocompatible polymer having a lower critical solution temperature (LCST) in water at 32 °C. PVCL-based biocompatible, amphiphilic block polymers have attracted considerable interest because their micelles can be uniquely designed for targeted and controlled drug delivery systems. Thermosensitive, biocompatible poly(ε-caprolactone)-b-PVCL, poly(δ-valerolactone)-b-PVCL, and poly(trimethylene carbonate)-b-PVCL block copolymers were synthesized at 30 °C using a hydroxyl-functionalized xanthate reversible addition-fragmentation chain transfer (RAFT) agent, 2-hydroxyethyl 2-(ethoxycarbonothioylthio)propanoate (HECP), as a dual initiator for ring-opening polymerization (ROP) and RAFT polymerization in a one-pot procedure. This novel one-pot process is convenient and powerful method for the synthesis of the PVCL-based biocompatible block copolymers. The LCST of the PVCL-based biocompatible block copolymer can be readily tuned by controlling the hydrophobicity of the block copolymers. By copolymerizing a hydrophilic N-vinylpyrrolidone moiety to the PVCL blocks by RAFT copolymerization, the LCST of the copolymer was matched with the body temperature for its future biomedical applications.
340 - Efficient synthesis of high purity homo-arm and mikto-arm poly(ethylene glycol) stars using epoxide and azide-alkyne coupling chemistry

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Multi-arm polymers, which consist of multiple linear chains connected to a central core, have a unique set of properties (e.g. crystalline, mechanical, and viscoelastic properties,) when compared with their linear analogs due to their multi-arm structure, globular shape and multiplicity of end groups. However, the synthesis of multi-arms polymer with a tailored number of arms and control over the length of the each arm can be challenging. In this work, high purity homo-arm and mikto-arm poly(ethylene glycol) (PEG) stars were successfully prepared by the combination of epoxide ring openings and azide-alkyne click reactions. First, monohydroxy-PEG was modified via epoxide chemistry to bear one hydroxyl and one azide functionality at the same end. An alkyne functionalized PEG chain was then coupled to the azide. Subsequently, the remaining hydroxyl could be reactivated to an azide again and again to enable stepwise addition of alkyne functionalized polymer arms. The use of efficient reactions for this iterative route provided star polymers with an exact number of arms, and a tailorable degree of polymerization for each arm. Detailed characterization confirmed the high purity of multi-arm poly(ethylene glycol) products
Polymer surfaces possessing polar functional groups such as the hydroxyl, or carboxyl groups are widely utilized for many applications. However, it is difficult to create a polar surface because of overturn or migration of polar groups into bulk phase so that the hydrophobic moieties are reoriented towards the air interface. In this study, we examined a new approach for controlling functionality at polymer surfaces using side-chain liquid crystalline polymers containing hydrophobic group protecting polar functional groups. First the polymer thin film was annealed and hydrophobic groups segregated at the surface. Then, these groups were removed by deprotection reaction resulting in polar functional group polymer surface. We expected that interaction between liquid crystalline molecules keep their alignment at surface. In this presentation, we describe the synthesis and characterization of polymer 1 with 2,2,2-trifluoro ethanol end groups, which forms smectic B phase at room temperature and polymer 2 with pentafluorophenyl end groups, which forms smectic A phase (Fig. 1). Thin films of polymers were annealed and immersed into NaOH aq for 5 min. As a result, water contact angles decreased from 95° to about 50° for polymer 2, although didn’t decrease for polymer 1. This result suggested that carboxyl group appeared at the polymer 2 surface.

Figure 1. Chemical structures of polymer 1 and 2.
Fluorescent conjugated polymers have received a great deal of recent interest due to their ability to act as chemosensors to detect metal cations in environmental and biological systems with both sensitivity and selectivity. Previously, the polymer tmeda-PPETE, N,N,N'-trimethylethylenediamino (tmeda) receptors on a poly[2,5-thiophenediyl-1,2-ethynediyl-1,4-phenylenediyl-1,2-ethynediyl] (PPETE) backbone, showed significant quenching when Cu$^{2+}$ was added. An inorganic/organic hybrid system, tmeda-PPETE polymer preloaded with Cu$^{2+}$, was also created and shown to be a highly selective and sensitive fluorescence “turn-on” chemosensory system for iron cations. In order to further investigate the interaction between the amino receptor and metal cation, a new polymer, tmpda-PPETE, containing N,N,N'-trimethylpropylenediamino (tmpda) receptors, was synthesized. The new receptors have an additional methylene group between the nitrogen atoms compared to the tmeda receptors. The tmeda-PPETE polymer's donor energy as determined by absorbance and emission wavelength maxima were similar to the tmeda-PPETE polymer, with tmpda-PPETE having greater fluorescence quantum yield. The metal cation selectivity for tmpda-PPETE was drastically altered from tmeda-PPETE. When a variety of metal cations were titrated into a solution of tmpda-PPETE in THF, Fe$^{3+}$ showed significant fluorescent quenching. Addition of all other metals resulted in little to no variation in the emission spectra.

Most importantly, the tmpda-PPETE polymer has the ability to distinguish Fe$^{2+}$ from Fe$^{3+}$, both of which play major roles in biological environments.
343 - Switching the adhesive state of catecholic hydrogels using phototitration

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A polyacrylamide hydrogel system that can be liquefied by remote activation using UV irradiation is investigated as a degradable adhesive. The linear polyacrylamide copolymer, formed by conventional free-radical polymerization, contains biomimetic catechol-iron-mediated cross-linkers that are sensitive to pH changes. Hydrogel films and bulk gels are prepared by basic titration of a polymer solution doped with a photoacid generator, diphenyliodonium chloride, generating an ionic cross-linked network via the catechol pendant groups. Irradiation of these hydrogels with UV light affords a viscous liquid solution, demonstrating a gel-sol transition with a subsequent decrease in the adhesive strength of the material. These gels may be prepared in high throughput and require few synthetic steps with commercially available precursors.
A series of sulfone functionalized polyethylenes has been synthesized via Acyclic Diene Metathesis (ADMET) polymerization. Polymers with a sulfone functionality every eight, fourteen, and twenty carbons were produced. Sulfone-containing α,ω-diene monomers were synthesized by alkylation of sodium sulfide with an appropriate alkyl halide, followed by complete oxidation to the sulfone. Grubb’s first generation catalyst was used to promote the metathesis reaction under vacuum at 50 °C in propylene carbonate. The polymers were subsequently hydrogenated using Wilkinson’s catalyst to yield a completely saturated backbone. Monomers and polymers were characterized with $^1$HNMR, $^{13}$CNMR, and FTIR. Future studies will comprise thermal and morphological data collection and interpretation utilizing DSC, TGA, x-ray diffraction.

1 Sauty, N.; Wagener, K. Synthesis and characterization of precision hydrocarbon polymers containing aromatic moieties. Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, 2014
The sulfonimide functional group has been incorporated into a polyethylene-like backbone at varying concentrations utilizing Acyclic Diene Metathesis (ADMET) polymerization. α,ω-diene monomers were synthesized in varying lengths to afford polymers containing a sulfonimide every eighth, fourteenth, and twentieth carbon. Sulfonimide diene monomers were produced by first, alkylating sodium sulfite with a specific alkyl halide, followed by conversion to the sulfonyl chloride. The sulfonyl chloride was converted to the sulfonamide by reaction with ammonia. The sulfonyl chloride and sulfonamide molecules were then coupled to produce the sulfonimide functionalized diene monomer. Grubb’s first generation catalyst was used to induce the ADMET reaction. Hydrogenation using Wilkinson’s catalyst was performed to completely saturate the backbone. Monomers and polymers were characterized with $^1$HNMR, $^{13}$CNMR, and FTIR. We plan to gather thermal and morphological data with DSC, TGA, x-ray diffraction. The sulfonimide polymer will be compared to previously synthesized sulfonic acid-containing polymers made via ADMET.
High periodic mesoporous polyimide films utilizing block copolymers

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Polyimides (PIs) are expected as high performance materials because of their excellent thermal, mechanical and dielectric properties. However, it has not been achieved yet formation of the well-ordered nanostructures and control of morphologies. Because PIs are generally synthesized through polycondensation which can hardly control their primary structures such as molecular weights and polydispersities, which are different from general vinyl polymers synthesized through chain polymerization. This can lead the difficulty to synthesize the corresponding block copolymers. Here, we propose a new approach for formation of nanostructures and control of morphologies of PIs by using soft templates that guide a cooperative self-assembly between PIs and templating block copolymers. We first attempted to prepare PI precursor films by mixing of polyamic acids and a variety of templating block copolymers such as poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) and polystyrene-b-poly(2-vinylpyridine). Then the imidization was carried out by heating at 100 °C for 12 hours. SAXS and TEM characterization confirmed that the resulting PI films form well-ordered microphase-separated nanostructures with cubic and cylinder morphologies. The domain spacings are around 14 nm and matrices are PIs. Subsequent thermal decomposition of the PI films was also performed to prepare high periodic mesoporous PI films.
Uniformed-sized silicon nanocrystals (SiNCs) have attracted much attention because of optical and electronic consequences in quantum confinement of the electrons and holes, including size-dependent molecular-like optical properties, electron/hole overlap for enhanced photoluminescence efficiencies, and discrete single-electron/hole charging. However, it is still difficult to control and tune the accurate sizes of crystals, and the effective method has not been yet established. Here, we propose a new way to prepare uniformed-sized SiNCs by using nanotemplate. Our approach is to carry out the Hessel's SiNCs preparation procedure, which is a calcination of hydrogen silsesquioxane (HSQ) at 1100 - 1400 °C under 90% argon and 10% hydrogen atmosphere, in well-ordered mesoporous carbon molds. We used the mesoporous carbon prepared by soft-template method with Pluronic triblock copolymer and resol resins followed by curing at 100 °C and calcination at 600 °C, which shows a good structural stability in high temperature. After that Fox-16, which is commercially available MIBK solution of HSQ, was incorporated with the mesoporous carbon mold. Finally the sample was calcined at 1100 - 1400 °C under 97% argon and 3% hydrogen atmosphere. We found the formation of SiNCs in this approach. We will show the detail characterization of the resulting SiNCs by using small-angle X-ray scattering (SAXS), X-ray diffraction (XRD) and transmission electron microscopy (TEM) to investigate the effect of mold, especially for the sizes and morphologies.
348 - Synthesis of iminodiacetic acid-glycerol polyesters

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Polyesters that dissolve only in water can be useful in many applications such as the synthesis of temperature and pH-responsive materials, water and soil remediation, and bioerodable hydrogels. Polyesters produced from glycerol and diacids (such as glutaric, adipic, and citric acids) are common synthetic targets. However, such polyesters are very soluble in polar organic solvents but have limited solubility in water. In this study, we describe the synthesis and characterization of linear, branched and cyclic water-soluble polyesters produced from glycerol and iminodiacetic acid. Products were identified by various characterization methods such as MALDI TOF Mass Spectroscopy, NMR, GC and HPLC. Yields and substitution patterns along the glycerol backbone were influenced by a combination of changes to the solvent system, molar ratio or reactants and catalyst type.
349 - WITHDRAWN
A novel cyclic brush-like copolymer, poly(ethylene oxide)-g-poly(3-hexyl thiophene) (PEO-g-P3HT), composed of conjugated polymer P3HT as side chains was prepared by a combination of living anionic ring opening polymerization, quasi-living Grignard metathesis (GRIM) method and click chemistry.

A well-defined linear α, ω-dihydroxyl polymer with protected hydroxyl groups in each repeating unit (linear PEEGE) was synthesized via anionic ring opening polymerization. Subsequent cyclization of linear PEEGE was conducted to yield cyclic polymer. Cyclic PEEGE was hydrolyzed to recover hydroxyl functionalities along the cyclic backbone, which were then converted into azide functionalities. Alkyne functionalized P3HT was synthesized by a quasi-living Grignard metathesis (GRIM) method. Subsequently, it was grafted onto cyclic backbone with azide groups via click chemistry to obtain the final product. The intermediate and final products were systematically characterized and confirmed by GPC, $^1$HNMR, FT-IR and MALDI-TOF. Morphology of cyclic PEO-g-P3HT was also investigated by AFM.
351 - Anthracene–containing acrylics as reversible polymers

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Thermo– and photoreversible polymers containing anthracene groups for subsequent Diels–Alder reaction and photodimerization were investigated as novel high performance reversible networks. Controlled radical polymerization of 9–anthrylmethyl methacrylate (AMMA) was successfully accomplished using RAFT techniques. Well–defined poly(9–anthrylmethyl methacrylate) (PAMMA) having narrow molecular weight distribution (PDI < 1.2) was obtained using 2–cyano–2–propyl benzodithioate (CPBD) and AIBN as a chain transfer agent and an initiator, respectively, in DMF at 80 °C. AMMA and MMA copolymers having different AMMA compositions were also synthesized at the same conditions for homopolymerization of AMMA. It was found that glass transition temperatures of the polymers were in the range of 119–163 °C depending on the AMMA composition as predicted using the Fox equation, and 5 wt% decomposition temperatures were 240–270 °C. Thermo– and photoreversibility studies of PAMMA and polymers from Diels–Alder modification and photodimerization will be also presented.

Tuesday, March 18, 2014 05:30 PM
General Topics: New Synthesis and Characterization of Polymers (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Cyanate ester (CE) resins are thermoset polymers that possess a unique combination of properties such as pre-cure processability, excellent insulation, and low outgassing characteristics which makes them desirable for use in aerospace and microelectronic components. Many of the environmentally demanding operating properties of CE resins are shared with fluorinated polymers including chemical and thermal resistance. By incorporating fluorine into CE monomers, we can further optimize the cyanurate network properties to afford improved polymers for high performance applications. A new semifluorinated aryl dicyanate ester monomer has been prepared containing a perfluorocyclobutane (PFCB) group that when thermally cured, the network (PFCBCy), exhibited excellent thermal stability and exceptionally low dielectric constant and moisture uptake. Work continues to develop other fluorinated dicyanate ester monomers through synthetic design that can potentially exhibit tailororable properties, ultimately achieving low moisture uptake and low dielectric loss.
353 - Synthesis and characterization of precision hydrocarbon polymers containing aromatic moieties

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Precision polymers, class of polymers in which a functionality is placed at perfectly unvarying intervals, emerged from the discovery and development of the ADMET polymerization. The identity and frequency of the functionality, which can be either a pendant group or within the polymer backbone, determine the properties of the polymer. Precision polymers exhibit enhanced properties as compared to their random counterparts. While various types of precision polymers have been extensively scrutinized, limited work have been conducted on precision hydrocarbon polymers containing aromatic moieties. This report describes the synthesis and characterization of poly(p-phenylene alkylene)s and poly(ethylene-co-styrene)s.

All polymers were prepared via ADMET polymerization of symmetrical α,ω-diene monomers with an unprecedented ADMET protocol utilizing organic carbonates as high boiling solvents. This novel methodology afforded polymers having high molecular weights (Mₙ ranging from 70,000 to 100,000), representing a significant improvement of the standard methods. The structure-property relationship of the aforementioned polymers was scrutinized by varying the methylene run length between two consecutive aromatic moieties (up to 40 methylene units). In the case of poly(p-phenylene alkylene)s, a hyperbolic relationship was found between the melting temperature of the polymers and the frequency of the aromatic moiety in the polymer backbone. Also, random polymers were generated by copolymerization with 1,9-decadiene for comparison with their precise counterparts. In a similar fashion, the effect of isomerization was elucidated by copolymerizing two consecutive monomers in different ratios.
The modification of diatomaceous earth (DE) has been carried out using alkyltrimethoxysilanes [methyl (m-TMS), propyl (P-TMS), octyl (O-TMS), dodecyl (DD-TMS), hexadecyl (HD-TMS) and octadecyl (OD-TMS)]. The reactions were carried out at 50°C in toluene for 2 hours with p-toluenesulfonic acid as the catalyst. The samples were prepared to have the same carbon content on the surface. These alkyltrimethoxysilane modified DEs have been used to study the effect of carbon chain length on the surface properties of DE-modified coatings. These materials have been studied using thermogravimetric analysis (TGA), water contact angle and Brunauer–Emmett–Teller (BET) surface area analysis. When measured at similar carbon contents, the water contact angle increased as the carbon chain lengths increased in the coatings as shown in the figure.
355 - Rapid, semi-automated convergent synthesis of low generation triazine dendrimers using microwave assisted reactions

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Microwave assisted synthesis allows for the rapid access of low generation triazine dendrimers in high yields. Products include a macromonomer and alkyne functionalized generation one to three dendrimers. Using a convergent synthetic approach, two nucleophilic aromatic substitution reactions are executed at 60°C on cyanuric chloride for 10 min using primary amines. Substitution of the resulting monochlorotriazine with diamine requires 95°C for 30 min. Purifications are accomplished using an automated chromatography system such that the generation three dendrimer can be prepared from the starting materials in less than one day.
New functional copolymers of styrene and multifunctional trisubstituted ethylenes were prepared as potential building blocks for novel materials. Styrene and oxy ring-substituted methyl 2-cyano-3-phenyl-2-propenoate copolymers 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.
357 - WITHDRAWN
358 - Multigraft copolymer superelastomers: Synthesis and characterizations

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Commercially available polystyrene-b-polysoprene-b-polystyrene (SIS) and polystyrene-b-polybutadiene-b-polystyrene (SBS) are well-known thermoplastic elastomers (TPEs). In general, the sequential anionic copolymerization of styrene and 1,3-dienes has been employed for synthesizing linear ABA triblock copolymers. Since then, the use of branching has been explored to develop the properties of styrene/1,3-diene TPEs. The multigraft copolymers as TPEs can improve the mechanical properties because if the backbone is selected as the soft block with pendent hard block there will be multiple tether points connecting the rubbery backbone to reinforcing rigid domain. In this presentation, the synthesis and characterizations of new poly(butadiene-graft-styrene) copolymers with tetrafunctional branch points will be reported. The main synthetic strategy includes synthesis of macromonomers with double-tailed polystyrene chains and copolymerization with butadiene through high vacuum anionic polymerization techniques: (1) the selective reaction of living polystyrenes with the two chlorines of 4-(dichloromethylsilyl)styrene to prepare double-tailed macromonomers and (2) the copolymerization of the double-tailed macromonomers and butadiene to synthesize the well-defined poly(butadiene-graft-styrene) copolymers with tetrafunctional branch points. Here the developed structures of multigraft copolymers, polystyrene blocks are positioned at both ends of backbone, are in particular synthesized by using living polystyrene as a macroinitiator and introducing styrene monomer prior to termination. Additionally, the effects of the number of branching points on the morphologies and mechanical properties of these materials are investigated by transmission electron microscopy and mechanical testing.
**359 - Controlled solution aggregation of linear and brush conjugated polymer**

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Conjugated polymers, due to its low cost synthesis and unique opto-electronic property, have gained extensive attentions for flexible electronics applications, including organic photovoltaics (OPVs), organic field-effect transistors (OFETs) and organic light-emitting diode (OLEDs). By mixing conjugated polymer with binary good/poor solvents, both intra-molecular chain conformation and inter-molecular assembly are tunable. Such controlled solution aggregation is critical to the improvement of film device performance via solution casting or spin coating. Here, both linear and brush regioregular poly(3-hexylthiophene) (rr-P3HT, one of the mostly-studied, model conjugated polymers) were investigated in a tetrahydrofuran/ water mixed solution. The brush P3HT possesses a poly-(norbornene) backbone and rr-P3HT side chains. At low water content, linear P3HT easily aggregated into micrometer-long nano-fibers due to inter-molecular Pi-Pi stacking, while intra-molecular aggregation drove the brush P3HT assembly into single-molecule particles, which were confirmed by transmission electron microscopy and dynamic light scattering. The corresponding opto-electronic changes due to inter-molecular stacking in linear P3HT or side-chain aggregation in brush P3HT were obtained by optical absorbance and emission measurement and chemometric analysis.

![Diagram](image)

**Figure 1.** (A) Mechanism of aggregate behavior of linear P3HT and brush P3HT in good/poor solvent mixture. Region of aggregate P3HT due to Pi-Pi stacking were highlighted. (B) Fraction of aggregate P3HT component was deconvoluted from optical absorbance spectra of linear P3HT and brush P3HT in THF/water (good/poor solvent) solution by multivariate curve resolution.
360 - Effect of alkyl chain length on the thermal properties of poly(arylene ether)s derived from N-alkyl-N-phenyl-3,5-difluorobenzene sulfonamides

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Meta-activated nucleophilic aromatic substitution leads to poly(arylene ether)s, PAE, in which the activating group resides in a pendant position relative to the polymer backbone. The nitrogen atom in the strongly activating sulfonamide provides a point of chemical diversity that can be exploited to tailor the physical properties of the resulting polymers. Using N-phenyl-3,5-difluorobenzene sulfonamide group as the starting material a series of N-alkyl derivatives, with chain lengths of 3 to 12 carbon atoms, were prepared and characterized followed by conversion to the corresponding PAE. The effect of alkyl chain length on the thermal stability and glass transition temperatures, T_g values was determined.
Dendrimers are well-defined, highly branched, three-dimensional molecules with a large number of reactive end groups. PEGylated dendrimers have received considerable attention as new polymeric materials for applications in areas such as gene therapy, drug delivery, and as MRI contrast agents. In the present work, we have carried out the synthesis of various generations of a novel mPEG-block-poly(aryl-amide-sulfide) dendrimer. The polymer is built from methoxypoly(ethylene glycol)amine (mPEG-NH₂), methyl 3,4,5-trihydroxybenzoate (methyl gallate), allyl bromide, and 2-aminoethanethiol, allowing the alkene functional groups at the periphery of the dendron in half generations to be easily modified for specific applications (generation 3 is shown below). For example, separate reactions of the dendrimer with 2-aminoethanethiol and 3-thiopropionic acid yielded polymers with amino and carboxylic acid groups on the periphery, respectively. Critical micelle concentration studies were carried out by fluorescence spectroscopy, using pyrene as a probe. In addition, the formation of nanoplexes with nucleic acids at various N/P ratios (where N is the number of amino groups present on the dendrimer and P is the number of phosphate groups in nucleic acids) was characterized by gel shift, circular dichroism (CD), and atomic force microscopy (AFM). Synthesis of the above dendrimers, their characterization with techniques such as NMR and MALDI-TOF, and the applications of the dendrimers in gene delivery will be presented and discussed.
362 - Self-initiated photografting of hydrophilic monomer onto poly (aryl ether ketone)

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Super engineering plastic poly (ether ether ketone) (PEEK) has been used in a variety of high-tech fields due to its excellent properties including good mechanical strength, thermal resistance and chemical resistance. In addition, PEEK with a moderate density, being nontoxic and bioinert, is also a promising biomaterial. In this work, photo-grafting of hydrophilic monomer was used to enhance the hydrophilicity of PEEK with the aim of extending its applications to biological fields. PEEK sheets were surface modified by grafting of acrylamide (AAm) with ultraviolet (UV) irradiation in presence or absence of benzophenone (BP). The effects of BP, irradiation time and monomer concentration on the surface wettability of PEEK were investigated. Characterization of modified PEEK using scanning electron microscopy (SEM), energy-disperse spectrometer (EDS) and water contact angle measurements show that AAm was successfully grafted on PEEK surface both in presence and absence of BP [figure1]. With the increase in irradiation time and monomer concentration contact angles decrease to as low as 30°, demonstrating a significant improvement of surface hydrophilicity. In agreement with the decrease in contact angle, under identical conditions, the nitrogen concentration increases, suggesting the increase in grafting degree of the grafting polymerization. This investigation demonstrates a self-initiation of PEEK due to its BP-like structure in the backbone of the polymer. Though the graft polymerization proceeds more readily in the presence of BP, the self-initiated graft polymerization is clearly observed.
Poly(alkyl/arylphosphazenes) are inorganic-organic polymer systems with a phosphorus-nitrogen backbone having two organic groups directly attached by P-C linkages. These polymers are prepared by condensation polymerization of Si-N-P small molecule precursors that contain simple alkyl, aryl, and alkynyl groups already attached to the phosphorus. Once formed, these polymers are readily modified by post-modification reactions. For example, one-step deprotonation-substitution reactions at the methyl group have afforded new materials with silicon, fluorine, carbonyl, and hydroxyl groups, as well as anionically grafted polymer side chains. In this presentation we focus on post-polymerization modification reactions that enable the introduction of multiple azide or alkyl halide groups to the backbone. The products of the former modification were employed in copper-catalyzed azide-alkyne "grafting-to" reactions with alkyne-capped poly(ethylene oxide), while those of the latter were used as macroinitiators for the low-catalyst concentration atom transfer radical polymerization (ATRP) of vinyl monomers, such as di- tri- and oligo(ethylene oxide) methyl ether methacrylate. The synthesis and characterization of the novel graft copolymers with polyphosphazene backbones will be described.
The synthesis of well-defined amphiphilic figure-eight-shaped block copolyether (8-BCP) together with the linear and cyclic counterparts (l-BCP and c-BCP, respectively) was achieved by the t-Bu-P₄-catalyzed block copolymerization of decyl glycidyl ether (DGE) and triethylene glycol glycidyl methyl ether (TEGGE). The synthesis of 8-BCP was carried out through three reaction steps including (i) t-Bu-P₄-catalyzed block copolymerization of DGE and TEGGE using 2,2-bis((6-azidohexyloxy)methy)propane-1,3-diol ((N₃)₂-(OH)₂) as an initiator with the [DGE₀]/[TEGGE₀]/[(N₃)₂-(OH)₂₀] ratio of 50/50/1, (ii) ω-end functionalization using propargyl bromide, and (iii) intramolecular cyclization using click reaction. The product was identified to be targeted 8-BCP by SEC, IR and ¹H NMR measurements. In addition, the number-average molecular weights (M$_{n,NMR}$) of 8-BCP (21800 g·mol⁻¹) was agreed with the calculated values (M$_{n,calc.}$) based on initial monomer-to-initiator ratio (22000 g·mol⁻¹), and the polydispersities (M$_{w}$/M$_{n}$) was narrow (1.06). The hydrodynamic diameters (D$_h$) and aggregate structures of 8-BCP in water was investigated together with l-BCP and c-BCP using dynamic light scattering (DLS). The D$_h$ of the aggregate formed from l-BCP, c-BCP and 8-BCP were calculated to be 44 nm, 30 nm, and 60 nm, respectively. The size of the aggregate formed from 8-BCP was larger than those of l-BCP and c-BCP, indicating that the aggregation behavior was affected by the macromolecular architectures.
We report herein the synthesis of maltose end-functionalized linear polystyrene (Mal-b-PSt) as well as maltose centered two- and three-branched polystyrene (Mal-b-(PSt)_{x}, x = 2 and 3) via combination of “click” chemistry and atom transfer radical polymerization (ATRP). The azide end-functionalized PSt and branched PSt with an azido group at chain center (N_{3}-PSt, N_{3}-(PSt)_{2}, and N_{3}-(PSt)_{3}) were prepared. Based on the results of size exclusion chromatography (SEC), all the obtained PSts showed monodisperse sharp peak with a narrow polydispersity, resulting that precise polymerizations of styrene were achieved without intra or intermolecular coupling. The chemical structures of the obtained PSts were assigned to the expected structures by proton nuclear magnetic resonance (1H NMR), and the characteristic peaks due to the initiating moiety were observed. Afterwards, the click reaction between the azide-functionalized PSts and N-maltosyl-3-acetamido-1-propyne (ethynyl-Mal) was carried out.

As a result, the corresponding maltose end-functionalized linear PSt and maltose centered star-shaped PSt (Mal-b-PSt, Mal-b-(PSt)_{2}, and Mal-b-(PSt)_{3}) were obtained and identified by infrared (IR) and 1H NMR spectrometry.
Block copolymer is one of the powerful tools to control nano structures. This polymer is composed of connection of different polymers have different properties by covalent bond. Therefore, control of polymers block ratio and molecular weight is critical. Poly(ethylene oxide)-b-polyacrylonitrile (PEO-b-PAN) block copolymer can be used as a precursor of mesoporous carbon materials. There have been several attempts to prepare the copolymers using controlled radical polymerization of AN from a PEO macronitiator, but it is not easy to come by if high molecular weight (MW) of PAN block is required. On the other hand, there have been increasing interests of using click chemistry to synthesize well-designed block copolymers. In this study, we used click chemistry to synthesize PEO-b-PAN copolymer. End-functionalized PAN with various MWs were synthesized by RAFT polymerization, and reacted with PEO to undergo click reactions.

End-functionalized PEO + End-functionalized PAN → PEO-b-PAN copolymer
Flexible oxyalkylene ether linkages within the polyimide backbone have been shown to decrease $T_g$ but do not have a deleterious effect on thermal stability. A unique cardo-diamine, 9,9-bis(4-(2-(4-aminophenoxy)ethoxy)phenyl)fluorene was synthesized by the usual reaction of a diol, 9,9-(bis(2-hydroxyethoxy)phenyl)fluorene with p-fluoronitrobenzene followed by chemical reduction. The diamine was converted to a polyimide was using 4,4'-(hexafluoroisopropylidene)-dipthalic anhydride (6FDA) in a one-pot, amic-acid/imidazation procedure in m-cresol. The fully closed imide could be cast into clear, transparent, creasable films and exhibited a 5% weight loss at 407° and appears to exhibit a thermal transitions at 231° by DSC. A corresponding polyimide synthesized using the less constricted diamine, bis(4-(4-aminophenoxy)ethoxy)-phenyl)diphenylmethane will provide a comparison of thermal properties and molecular weights.
Ice accumulation on outdoor surfaces created serious problems for roads, boats, airplanes, and power transmission lines. An ice-phobic coating applied to exposed surfaces appears to be a good solution to prevent ice build-up and avoid the requirement of de-icing which may result in large energy consumption, dangerous operations and expensive equipment investment. In this work, we present a simple approach for the preparation of ice-phobic coatings by thiol-ene photopolymerization of polydimethylsiloxane (PDMS) resin precursors containing silica nanoparticle. The generated porous surface was further modified to produce a liquid infused top layer required to greatly reduce ice adhesion. Three approaches were utilized to evaluate the performance of ice-phobicity. (i) Tensile strength and shear strength between the ice and coatings were tested to measure the ice adhesion of the coatings, (ii) freezing time delay was measured to show the dynamic ice formation, (iii) and the contact angle of super-cooled water was also tested.
Block copolymers (BCPs) can self-assemble into periodic nanoscale structures, which makes them attractive for next-generation lithography applications. The patterns obtained from BCP assembly must be transferred into a functional substrate using the BCP as an etch mask. Key to transferring the pattern is selective removal of one of the BCP domains, which is traditionally accomplished using reactive ion etching. However, significant drawbacks of this approach, such as poor etch contrast between the BCP domains, can significantly impact the quality of transferred pattern. To avoid this problem, a BCP was designed to contain a self-immolating block. Poly(styrene-block-phthalaldehyde) was synthesized and thin films were prepared from a formulation including a photoacid generator. Self-assembly followed by activation of the photoacid generator results in complete depolymerization of the poly(phthalaldehyde) moiety.
370 - Engineering polymer self-assembly via sidechain modification

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Recently, we synthesized a series of high molecular weight poly-chromophore polymers by incorporation flexible chains (alkyl and tetraethylene glycol) with oligomeric bis(2-ethylhexyl)-p-phenylenevinylene (BEH-PPV) chromophores of different conjugation length (trimer, pentamer and septamer). We found that the photophysics and single-polymer chain morphology were considerably influenced by the conjugation length of the constituent oligomers. In this contribution, we have investigated the role of side-chain composition and regioregularity on the order of polymer nanostructures. We detail our synthetic strategies to prepare regioregular (1-3) and regiorandom (2-methoxy-5-(2-ethylhexyl)-1,4-phenylenevinylene) oligomers (MEH-PPV) as well as BEH-PPV oligomers with hydrogen bonding components such as carboxylic acid and urea functionalities (4-6). We also describe our new synthetic strategies to polymerize the hydrogen-bonding oligomers into poly-chromophore structures.
Since the original synthesis of DPPPV, many modifications to the basic structure have been reported. Recently, the synthesis of a unique DPPPV monomer having a pendant benzyloxy substituent was completed. Thus, the alkynes 1-(benzyloxy)-4-(propargyloxy)benzene and 1-(benzyloxy)-4-(5-pentyloxy)benzene were reacted with 2,5-di(carboethoxy)3,4-diphenylcyclopentadienone to yield the corresponding terephthalates. The terephthalates were reduced with lithium aluminum hydride to the corresponding diols which were reacted with thionyl chloride to yield the monomers 5-((4-(benzyloxy)phenoxy)propyl)- and 5-((4-(benzyloxy)phenoxy)methyl)-1,4-di(chloromethyl)-2,3-diphenylbenzene. Polymerization of the dichloro monomers via a Gilch polymerization yielded DPPPVs with pendant benzyloxy substituents. The polymers were partially soluble in chlorinated solvents and fluoresced bluish-green under UV light either in solution or in the solid state.
372 - Is the silanol-isocyanate reaction suitable for forming stable siloxane-polyurethane block copolymers?

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Recent literature has suggested that siloxane-polyurethane segmented copolymers can be synthesized from the reaction of a silanol terminated poly(dimethylsiloxane) (PDMS) with a diisocyanate.

However, literature published in the early 1960s as well as expert opinion in the fields of silicon and isocyanate chemistry has suggested that the silyl carbamate linkage is hydrolytically unstable, and readily decomposes in the presence of water into carbon dioxide, silanol and amine. But, there are no definitive studies in the recent literature. Investigation into this reaction was carried out using silanol-terminated PDMS and aliphatic and aromatic diisocyanates (TDI, H₁₂MDI, MDI, IPDI, and HMDI) as well as monoisocyanates (cyclohexyl isocyanate and phenyl isocyanate). Outgassing of carbon dioxide from the reaction was measured. Once synthesized, analysis of the product using FTIR, ¹H NMR, GPC and MS provide insight into product formation, as well as the hydrolytic stability upon exposure to water.
Cyanoacrylates were homo- and copolymerized with 2-chloroethyl methacrylate in the presence of a disulfide-containing crosslinker, bis(2-methacyryloyloxyethyl) disulfide and an efficient chain transfer agent, carbon tetrabromide, to yield branched polymers with reductively degradable links at the branching points. To prevent anionic polymerization, small amounts of trifluoroacetic acid were added to the reaction mixtures. The polymers contained multiple alkyl bromide peripheral groups, which, along with the alkyl chloride pendant groups originating from 2-chloroethyl methacrylate, were into azide groups. The latter were used to attach various alkyne-functionalized molecules via copper catalyzed click chemistry. The detailed kinetics of the polymerization, reductive degradation in the presence of phosphines, azidation, and click-type functionalization will be presented.
The ready availability of monobenzyl-protected diphenols \( 1 \) has lead to the synthesis of a series of building blocks for use in the preparation of unique monomers. The reaction of benzyloxyphenol, as well as related systems, with \( \alpha,\omega \)-dibromoalkanes followed by deprotection leads to a series of AB monomers exemplified by \( 2 \). Similarly, the reaction of appropriate benzyloxyaryloxyalkyl bromides or tosylates \( 2 \) with 4-fluoro-4'-hydroxybenzophenone leads to a series of unique PEEK related AB monomers illustrated by \( 3 \). Traditional difunctional monomers \( 4 \) can be synthesized by the reaction of bis(bromoethoxy)benzene and related aromatics with 4-fluoro-4'-hydroxybenzophenone. Polymerization of these monomers can be conducted in NMP using \( K_2CO_3 \) as a base and toluene as an azeotroping agent.
This poster will detail the synthesis, characterization and application of donor-acceptor copolymers with 1,2,6,7-tetraaryldicyclopenta[cd,jk]pyrenes as acceptor groups. This acceptor is a unique class of all-carbon based cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) that has low reduction potentials owing to the ability to form cyclopentadienyl anions. We have prepared both small-molecule models, as well as co-polymers, based on thiophene and bithiophene donating monomers. The photophysical and electrochemical properties as well as the field-effect mobilities of these polymers will be described in detail.
Nanographenes have received much attention because of their semiconducting and optical properties. In order to construct the large aromatics, efficient extension of π-conjugation and concentration of aromatic units are important. Recently, rhodium-catalyzed oxidative coupling of arylborons or arylamides with alkynes have been developed. This reaction gave 1,2-arylated and fused arenes.

In this work, we applied transition metal-catalyzed oxidative coupling of arenes with alkynes to synthesis of novel large π-conjugated molecules. Their optical and electronic properties were investigated by UV-vis absorption spectroscopy, cyclic voltammetry and DFT calculations.
377 - Precise synthesis and characterization of novel rod coil diblock copolymers with helical, chiral polycarbodiimides segments

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Polycarbodiimides are a relatively new class of helical, rigid macromolecules that possess a variety of interesting properties such as chiroptical switching and liquid crystallinity. By incorporating specific and modifiable functional groups at the end terminus of the polycarbodiimide chain, an interesting class of block copolymers can be synthesized containing both a chiral, helical block and a random coil block. Herein, we report the precise synthesis of alkyne end functionalized polycarbodiimides using functional Ni(II) initiators. Azide end capped polystyrene and poly(methyl methacrylate) were synthesized using atom transfer radical polymerization (ATRP) followed by post polymerization functionalization of the bromide end group with azidotrimethylsilane. These two specifically functionalized polymers undergo copper mediated alkyne-azide [3+2] cycloaddition (CuAAC) to yield rod-coil diblock copolymers. The thin film morphologies of these polymers are examined with tapping-mode atomic force microscopy (TM-AFM) and powder X-ray diffraction (XRD). Additionally, the chiroptical and thermal characterization of these polymers are reported using electronic circular dichroism (ECD), vibrational circular dichroism (VCD), and differential scanning calorimetry (DSC).
Incorporating silicon into resist materials is a well known method for providing resistance to oxygen reactive ion etching. However, silicon containing materials don't have good resistance to fluorine dry etching. Incorporation of tin into resist imparts resistance to both oxygen and fluorine dry etching. Therefore, we have studied the synthesis of block copolymers in which one block contains tin. Our goal is to facilitate production of imprint templates for manufacturing of hard disk devices with bit patterned media, which requires patterning fused silica (SiO$_2$) imprint templates. The tin materials enable high aspect ratio etching into the fused silica, but they are easily stripped with H$_2$ plasma. Our first approach involved use of trimethylstannylstyrene. We made the homopolymer of the tin compound, and confirmed that it has better resistance to both oxygen and fluorine dry etching than polystyrene and the silicon analog. Next, we made polystyrene-block-polytrimethylstannylstyrne by various polymerization methods including Nitroxide Mediated Polymerization (NMP), Activator Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP), and anionic polymerization. However, none of these controlled polymerization methods worked. We found Reversible Addition Fragmentation chain Transfer (RAFT) worked for this tin monomer and made various Mw tin containing block copolymers were successfully synthesized and characterized.
The synthesis of poly(isobutylene-b-ε-caprolactone) block copolymers containing amorphous rubbery/crystalline block segments was accomplished by the combination of living cationic polymerization of isobutylene (IB) with the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). The synthesis involved the living cationic polymerization of IB using 1,2-propylene oxide/TiCl₄ initiating system and termination with allyltrimethylsilane to yield functionalized allyl-PIB-OH with a $M_n=4,306$ g/mol and $M_w/M_n=1.21$. The structure of hydroxyl end-functional PIB was confirmed by $^1$H NMR and the molecular weight was determined by SEC. The resulting allyl-PIB-OH was successfully used as macroinitiator for the ROP of ε-CL in the presence of Candida Antarctica Lipase B (CALB), giving poly(IB-b-ε-CL) copolymer. The block copolymer exhibited $M_n=7,253$ g/mol and $M_w/M_n=1.26$. Characterization of the block copolymer by SEC, $^1$H and $^{13}$C NMR spectroscopy was performed.
Melt processable carbon fiber precursor of poly acrylonitrile (AN)-co-vinyylimidazole (VIM) was successfully synthesized. This copolymer showed applicability in energy storage devices like super capacitors as well as in nitric oxide (NO) releasing enhanced wound healing suture and bandages. In order to further extend their applications and better performance in already established uses, new terpolymers with isoprene, styrene and vinylcaprolactum were synthesized by free radical polymerization.
Living radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization) was achieved with the use of a methacrylate monomer, DimethylaminoEthylmethacrylate (DMAEMA) acting as the hydrophillic head group. This particular monomer has a lone pair on the nitrogen and gives way to a pH responsive polymer with a polydispersity < 1.4. A dodecylsulfanylthiocarbonyl derivative was used as the chain transfer agent, CTA. A low target degree of polymerization was desired due to the lack of literature on polymers of this size. The polymers were magnetized using an iron counter ion and their critical micelle concentration, CMC was observed.
Isotactic poly(4-methyl-1-pentene), which is sold under the trade name TPX, is a commodity thermoplastic material possessing a high softening point (about 200 °C), low specific gravity and high transparency that has found important commercial use in a variety of applications. The monomer, 4-methyl-1-pentene (4MP), should also enjoy long-term advantage as a polyolefin feedstock as it is produced through highly selective metal-catalyzed dimerization of propene. Accordingly, there is significant interest in applying new polymerization processes with 4MP as a means by which to expand the accessible range of poly(4-methyl-1-pentene) materials that might exhibit additional unique and technologically valuable physical properties. Recently, we have developed several new 'two-state' living coordination polymerizations of \( \alpha \)-olefins that can be used to rapidly generate, in programmed fashion, a broad spectrum of polyolefin microstructures and polymer architectures – and all from a common monomer feedstock using a single metal complex as initiator.\(^1\) This talk will present the results of the successful application of these two-state polymerization processes to 4MP that provide several new unique forms of poly(4-methyl-1-pentene), such as end-group functionalized materials and well-defined block copolymers, and including the stereoengineering\(^2\) of poly(4-methyl-1-pentene) microstructure. Finally, the living coordinative chain transfer polymerization of 4MP has been accomplished which removes the limitation on productivity that is associated with a traditional living polymerization.

(2) Crawford, K. E.; Sita, L. R. *J. Am. Chem. Soc.* 2013, 135, 8778
A polyisobutylene (PIB) telechelic prepolymer with acrylate functionality was synthesized by reacting bromo-terminated PIB with potassium acrylate. The bromo-terminated PIB was prepared by *in situ* end-quenching of living PIB at full isobutylene conversion with 3-phenoxypropyl bromide. Monomethyl ether hydroquinone was used as inhibitor. Use of a phase transfer agent tetrabutylammonium bromide greatly improved the substitution rate. The PIB-acrylate prepolymer was characterized by $^1$H and $^{13}$C NMR, GPC, and MALDI-TOF MS. The end functionality was determined by $^1$H NMR to be 1 and 2 for mono- and di-functional acrylate-terminated PIB, respectively. GPC analysis indicated that targeted molecular weights and relatively narrow polydispersities were achieved and the substitution reaction was free of coupling and degradation. Molecular weight of the summed initiator plus acrylate end group residual determined by MALDI-TOF MS analysis was in close agreement to the theoretical value, supporting the functionality determined by NMR.
In this contribution, we describe the synthesis and characterization of polymers based on cyclopenta-fused rylene frameworks. These polymers offer interesting photophysical and electrochemical properties due to their cyclopenta-fused polycyclic aromatic hydrocarbon (CP-PAH) nature. Using C-H activation chemistry, we prepared functionalized monomers of 1,2-diaryl-acenaphthylene and 1,2-diarylcyclopenta[cd]perylene s. These monomers were polymerized into homopolymer and donor-acceptor type polymer architecture. We will compare the physical properties between these rylene frameworks and will highlight the implications of the cyclopentene rings to their properties.
385 - Effects of polymer brush growth on flexible porous surfaces

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We have grown brushes of PMMA on porous nylon membranes via atom transfer radical polymerization (ATRP). The molecular weight and polydispersity of surface grafted polymer were investigated as a function of brush density by removing polymer from the membrane and compared with that of polymer concurrently grown in solution. Various brush densities were attained by controlling the molar ratio of ATRP initiator (2-bromo-2-methylpropanoyl bromide) to a blocker molecule (2-methylpropanoyl bromide) during the attachment of initiator to the nylon membrane. PMMA growth was observed with attenuated total reflection Fourier transform infrared spectroscopy as well as scanning electron microscopy. The polymerization could be followed visually as membranes expand uniformly and non-reversibly relative to polymer growth. We attempt to shed light on this phenomenon with a combination of rheological measurements and molecular modeling simulation.
Polystyrene-b-poly(isoprene)-g-poly(ethylene oxide) block copolymers having bottle-brush architecture were synthesized using a combination of anionic polymerization techniques and hydroboration chemistry. The behavior of these polymers in was studied by dynamic light scattering in solutions of THF/water. As water content was increased, the polymers were observed to decrease slightly in hydrodynamic radius until a critical concentration at which the solution became turbid and large aggregates were formed. This transition has been referred to as anomalous micellization. As water content was increased further, solutions became clear and more and micelles were formed that appeared stable to further large increases in water content.

The effects of polymer composition, and concentration were observed to affect the sizes of particles formed as well as the solvent composition at which the transition from unimer to aggregate occurred. Anomalous micellization could be reduced or eliminated by fractionating the block copolymers to remove small amounts of homopolymer.
387 - Synthesis and structural studies of the new (R)- and (S)-polycarbodiimides bearing ethynyl groups as potential functional helical polymers

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The synthesis and morphology characterization (SEM, AFM) of a family of new (R)- and (S)-polycarbodiimides of different composition bearing active ethynyl groups was accomplished under the standard carbodiimide polymerization conditions (e.g. using BINOL Ti-catalyst). The alkyne functionalities in repeat units offer an opportunity for further post-modification thru CuAAC “click”-chemistry protocol leading to cross-linked and PEG-polymers suitable for drug delivery applications.
388 - Elucidations of an ethylene polymerization catalyst promoted by bicyclohexyl-bridged Schiff base complexes of zirconium

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In our most recent effort, we have developed new post-metallocene catalysts of some of the early and late transition metal complexes and conducted the synthesis and characterization of the product of polyethylene polymers; In this presentation, we concentrated on some zirconium complexes and the result will be demonstrated. First, we elucidate new three bicyclohexyl-bridged Schiff bases, substituted salicylaldimine derivatives (4, 4’-methylene bis-(2-methylcyclohexylamine), complexes featuring different phenolate constituents (3, 5-di-t-butyl, 3-isoproyl and 5-t-butyl) which were synthesized. These complexes were tested as precatalysts for ethylene polymerizations and compared to their analogs of the titanium and zirconium complexes previously reported. The theoretically calculated structure confirmed the experimentally predicted structure; Moreover, the structure of some of the corresponding polymers is shown.
389 - Post-assembly functionalization of polymeric nanofiber via efficient chemical methods

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Polymeric nanofibers are promising in tissue engineering applications due to its dimensional similarity to natural collagen. While these nanofibers can be generated easily via electrospinning, they lack the bioactive motifs to guide cellular behavior. Efficient method to functionalize these nanofibers after electrospinning is important for improved cellular performance. In this project, 4-dibenzocyclooctynol (DIBO) and its derivatives were used as initiators for ring-opening polymerization to yield different kinds of polymers like DIBO-PBLG, DIBO-PCL, DIBO-PLA, DIBO-(P(CL-co-OPD)) and so on. DIBO group at the chain terminal of polymers enables fast, efficient and catalyst-free functionalization of the polymer. For further applications of these materials, nanofiber based scaffolds were generated via electrospinning. The generated nanofibers bearing active DIBO groups on the surface are capable of post-fabrication functionalization in aqueous solution without catalyst. Within a few minutes of immersion, these fibers were functionalized according to fluorescence staining. The removal of copper catalyst reduces the potential risk due to the toxicity of copper ion. The yielded scaffolds were used for neuron engineering, soft tissue repair and protein stabilization. Moreover, combined with other types of efficient chemical methods, di-functionalized and tri-functionalized nanofibers were constructed for the investigation of synergistic effect in tissue engineering.
In the interest of preparing soluble main-chain alkoxy substituted 2,3-diphenyl-polyphenylenevinylene (DP-PPV) derivatives, a modified Gilch reaction has been utilized to achieve the desired polymers; however, this method has been shown to be difficult to control and produces mostly insoluble material. The soluble product is of interest since it is composed of highly fluorescent oligomers. In an attempt to produce the same polymeric systems under more controlled conditions, the Horner-Emmons variation of the Wittig was investigated as a means to produce a fluorescent model system as well as desired polymeric systems. The resultant polymers from both methods were characterized using DSC, GPC, IR, NMR, TGA, and UV-VIS analyses.
391 - Phase change insulation for energy efficiency based on wax-halloysite composites

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Phase change materials (PCMs) have gained extensive attention in thermal energy storage. Wax can be used as a PCM in solar energy storage but has low thermal conductivity and cannot sustain shape at higher temperature (above 53 °C). Introducing 50 % halloysite into wax yields a stable and homogenous PCM composite (wax/halloysite) with thermal conductivity of 0.36 W/mK and no leaking until 70 °C (preserves layer-shape above the original wax melting point). To increase the base thermal conductivity, graphite and carbon nanotubes were added into the PCM composite. Thermal conductivity of wax/halloysite/graphite (45/45/10 %) composite showed a six-fold conductivity increase to 1.4 W/mK compared to pure wax and had no liquid wax leakage until 81 °C. Wax/halloysite/graphite/carbon nanotubes (45/45/5/10 %) composite showed thermal conductivity of 0.85 W/mK while maintaining the original shape until 91 °C. Vectorial thermal energy transfer for double layers of different composition was demonstrated: heat flux difference in the opposite directions differed on 25 %. This variance in layer conductivity allows for smart building roof insulators with increased absorption during hot weather but limited thermal losses during periods of cooler temperatures. The new composite is a promising heat storage material due to good heat capacity, high thermal conductivity and ability to preserve its shape during wax melting.

Tuesday, March 18, 2014 05:30 PM
Materials for Energy Harvesting (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
The thermoelectric properties of fully organic nanocomposites were investigated, for which meso-tetra(4-carboxyphenyl) porphine (TCPP) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were used as intrinsically conductive and semiconducting stabilizers, respectively. The electrical conductivity ($\sigma$) of these dual-stabilizer organic composites increased to approximately 9500 S m$^{-1}$ as the concentrations of both the multiwalled carbon nanotubes (MWNTs) and PEDOT:PSS were increased. The thermopower (or Seebeck coefficient, $S$) and thermal conductivity, however, remained relatively unaffected by the increase in concentration (40 $\mu$V K$^{-1}$ and 0.12 W m$^{-1}$ K$^{-1}$, respectively). Replacing MWNTs with double-walled carbon nanotubes (DWNTs) increased $\sigma$ and $S$ to approximately 96000 S m$^{-1}$ and 70 $\mu$V K$^{-1}$, respectively, at 40 wt % DWNT. This study suggests that $\sigma$ and $S$ can be simultaneously tailored by using multiple stabilizing agents to affect the transport properties of the junctions between nanotubes. Combining semiconducting and intrinsically conductive molecules as CNT-stabilizers has led to a power factor that is among the best for a completely organic, free-standing film (500 $\mu$W m$^{-1}$ K$^{-2}$). These flexible, segregated-network nanocomposites now exhibit properties that rival the more conventional inorganic semiconductors, particularly when normalized by the mass.
In bulk heterojunction (BHJ) polymer solar cells, benzodithiophene (BDT) based copolymers are among the most frequently used donor materials. There are several reasons for the extensive use and rapid development of BDT based copolymers in BHJ polymer solar cells. First, it is very easy to attach different substituents to the central benzene core by nucleophilic addition thus fine-tuning the solubility and energy levels of the polymers. Second, the BDT core has structural symmetry and rigid fused aromatic system which could enhance the electron delocalization and also the large planar conjugated structure facilitates π-π stacking which is good for improving mobility. Third, for the BDT based polymer, the steric hindrance is small which is good for maintaining the coplanar structure of the polymer. BDT is also a weak donor and it could maintain a low highest occupied molecular orbital (HOMO) energy level of the resulting polymer.

In this work, we designed a thienothiophenyl substituted BDT monomer and synthesized new conjugated polymers by Suzuki polymerization. The molecular weight, thermo-, optical-, electrochemical-properties were studied. Application of the polymer in BHJ solar cells provided 4.3% PCE in the initial test. Further optimization of the device performance is still under way.

394 - Trisubstituted fulvenes: New molecular architectures for donor-n-acceptor dye sensitizers

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Pentafulvenes are currently under investigation as frameworks for donor-n-acceptor molecules with potential application in organic electronics. Our research focuses on using a synthetic method for the selective and stepwise attachment of functional substituents at the 1, 3 and 6 positions of the fulvene core. This provides a versatile entry into dye sensitizers with more than one donor group conjugated to an acceptor arm (cyanoacrylic acid). Other strategies employing Pd catalyzed coupling reactions to further elaborate these molecules into donor-n-acceptor dyes with attached alkyne, aryl, alkyl, thiophenyl and bipyridyl groups have been carried out. Computational studies combined with experimental observations and results will be presented to show the ability of fine tuning the fulvenes with the desired substituents. Synthetic strategies and spectroscopic results, as well as optical, electrochemical, DSSC performance and single crystal X-ray studies of these new molecules will be presented.
The focus of the title work is on the selective and stepwise attachment of functional pyridine and bipyridine (bpy) groups at the 1, 3, and 6 positions of the pentafulvene core. Reaction of 1,3-diphenylcyclopentadiene with 4-alkynylbenzaldehyde (EtOH/pyrrolidine) gave 1,3-diphenyl-6-(p-alkynylphenyl)fulvene \( \text{I} \) as a dark red solid. Sonagashira coupling of \( \text{I} \) with 5-bromo-2,2'-bipyridine gave the monosubstituted bpy-fulvene compound \( \text{II} \). Entry into the synthetic strategy for (bis) bpy fulvenes, in which the bpy is directly attached to the fulvene core, has also been developed using 3-Ph and 3-(p-bromo)Ph 2-cyclopentene-1-ones as starting materials. The reactivity of the lithium reagent as well as the Mg and Ca Grignard reagents of 5-bromo-2,2'-bipyridine with the 3-Ph and 3-(p-bromo)Ph cyclopenteneones will be compared. Reaction of the bpy cyclopentadienes obtained from this strategy with 2,2'-bipyridine-5-carbaldehyde or 2,2'-bipyridine-4-carbaldehyde (EtOH/pyrrolidine) as well as the coordination chemistry and structure property relationships of the resulting new bpy-fulvene compounds will also be presented.
396 - Advantages of poly(3,4-ethylenedioxythiophene) in flexible inorganic/organic hybrid solid state dye-sensitized solar cells

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Poly(3,4-ethylenedioxythiophene) (PEDOT) has been proven to be an excellent electron-conducting polymer, with the potential for use in inorganic/organic hybrid solid state dye sensitized solar cells. PEDOT is an effective replacement for the iodide electrolyte in the transition from liquid to solid state solar cells. PEDOT:PSS has been widely used, but its poly(styrenesulfonate) co-polymer is insulating and reduces PEDOT’s conductivity. The size of the PEDOT:PSS chains inhibits it from penetrating into the porous TiO\textsubscript{2} layer, and as a result it makes poor contact with the dye. Through the method of vapor phase polymerization, PEDOT penetrates into the porous TiO\textsubscript{2} layer creating an inorganic/organic scaffold with good contact between the dye and the PEDOT. Vapor phase monomers enter the TiO\textsubscript{2} layer and utilize oxidants to initiate a carbon-carbon coupling polymerization.

Possible oxidants are Iron(III) p-toluene sulfonic acid and Copper(II) chloride. Solar cells produced using vapor phase polymerized PEDOT show lower resistances than traditional PEDOT:PSS solar cells, resulting in higher conductivities. We present results on solar cell efficiencies obtained using vapor phase polymerized PEDOT as a electron conducting layer.
Despite the importance of mechanical compliance in most applications of semiconducting polymers, the effects of structural parameters on the mechanical properties are typically not emphasized during the design and evaluation of the new materials. This paper examines the effects of the length of the alkyl side-chain—from butyl to dodecyl—on the tensile modulus and the brittleness for a series of regioregular poly(3-alkylthiophenes) (P3ATs: P3BT, P3HT, P3OT, P3DDT) and their blends with a soluble fullerene derivative (PC$_{61}$BM).

The tensile modulus decreases significantly with increasing length of the alkyl side-chain, from 1.87 GPa for butyl side chains to 0.16 GPa for dodecyl chains (Figure 1a). The large effect on the mechanical properties from small structural changes agrees well with the calculations from theory. The results enable the selection of ultra-compliant materials for solar cells that can withstand tensile strains up to 10%, at which the popular P3HT:PC$_{61}$BM cannot (Figure 1b to 1e). Our conclusion suggests a different perspective in optimization of organic semiconductors on the basis of mechanical compliance, as opposed to purely electronic performance, which should be considered for the engineering of flexible and stretchable electronics.
398 - Preparation of hierarchical porous monolith metal-organic-framework (MOF) aerogel

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Metal-organic-frameworks (MOFs) in which the building blocks of metal ions coordinated to rigid ligands are repeated to produce highly porous crystals with high surface area and permanent porosity. These remarkable properties make them become ideal candidates for fuel-gas storage media, high-capacity adsorbents, and excellent catalysts. However, the merit of their properties is closely related to their pore structures and characteristics. Currently the natural micropores in MOFs have been investigated, while the mesopores and macropores are rarely introduced. However, these mesopores and macropores are able to provide MOFs additional advantages such as improved mass transfer, diffusion and adsorption capacity.

The concept of MOF aerogel has been proposed and a series of representative MOF aerogels (e.g., ZIF-7, ZIF-8 aerogel, etc) have been successfully synthesized via an etching-induced method from metal-based alcogel. This method creates pure MOF aerogel with highly inter-connective crystalline MOF particles, which allows the micropores, mesopores, and macropores to exist simultaneously in MOF structures. The Langmuir surface area of new materials is capable to reaches 1.5-3 times of that of common MOFs. This simple and ingenious strategy shows great potential to achieve hierarchical porous MOFs with better properties.

Tuesday, March 18, 2014 05:30 PM
Materials for Energy Harvesting (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
399 - Precise characterization of molecular aggregation state and interfacial structure in ordered heterojunction poly(3-hexylthiophene)-based photovoltaics

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Nano-imprint technique has been investigated as a method for producing optimized morphologies in organic photovoltaics (OPVs) with ordered heterojunction (OHJ). However, the interfacial morphology and the molecular aggregation states of OHJ-OPVs are still unclear. In this study, we evaluated the morphology of OHJ-OPVs by X-ray structure analyses.

A line/space pattern was fabricated on the P3HT thin film surface by nano-imprinting techniques, and then PCBM thin layer was deposited on the surface patterned P3HT thin film. The interfacial morphology and molecular aggregation state of the OHJ-OPVs were evaluated by AFM, SAXS and GIXD. SAXS and GIXD were carried out at BL03XU beam line of SPring-8.

The nanostructure of the P3HT thin film surface could be observed by AFM, while it was 'buried' after the depositing of PCBM thin layer. In contrast, a clear scattering pattern was obtained from the 'buried' structure using SAXS. It was revealed that the interface get parabolic shape, which is represented by Gaussian distribution function, due to the partial phase mixing of P3HT and PCBM. Figure 1 illustrates the molecular aggregation state of OHJ-OPVs estimated by GIXD. The GIXD profiles revealed that the presence of vertically oriented P3HT chains in the nano-imprinted P3HT thin film, and also the face-on chain orientation is not present in prepared thin films. These nano-imprint induced morphologies exactly contribute to the power conversion efficiency improvement of the OHJ-OPVs.
Vapors from a low boiling, non-solvent were employed to manipulate the morphology of polymer crystals and fullerene agglomerates which constitute the active layer of an organic photovoltaic. The effect of choice of solvent for vapor annealing on device characteristics, charge carrier mobility and contact surface potential were studied. It is believed that this process of non-solvent passivation leads to more balanced charge transport in these devices, through reduction of surface traps and induction of favorable surface charge density. Surface potential is considered to be an indicator of surface electronic state, and Kelvin probe microscopy was employed to record contact potential difference caused by changes in electronic states on the surface of these photoactive films. Because of its simplicity, dark injection space-charge-limited current (SCLC) method was used to measure charge carrier mobility in organic solar cells using carrier density- and field- independent transport model. The $J_D^{0.5}$-V characteristics were corrected for the built-in voltage, $V_{bi}$, that arises from the work function difference between the contacts.
401 - Block copolymer templated synthesis of iridium-platinum alloy nanoparticles for catalysis in fuel cells

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Efficiency as well as stability are highly desired properties for fuel cells. Direct formic acid fuel cells (DFAFCs) offer several advantages to polymer electrolyte membrane and direct methanol fuel cells. Platinum is the most commonly used catalyst material in fuel cells. Electrodes composed of pure platinum lack the adequate electrocatalytic activity needed for oxidation reduction reactions in DFAFCs. Furthermore, a pure platinum anode is highly susceptible to CO poisoning rendering the catalyst inactive. Alloy bimetallic platinum-based nanoparticles have been shown to have high electro-oxidation activity, the ability to oxidize surface adsorbed CO species and are more intolerant to CO poisoning. Iridium platinum bimetallic alloy nanoparticles (Ir$_x$Pt$_{100-x}$) have exhibited excellent catalytic activities for anodic and cathodic reactions. Synthetic methodologies that can specify the size, shape, and composition of Ir$_x$Pt$_{100-x}$ nanoparticle alloys are therefore key to advancing DFAFCs.

The synthesis of DFAFCs catalysts from block copolymer templates has not yet been fully explored and offers several methods for tuning the size, shape and composition of bimetallic alloy nanoparticles. In this presentation, polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) diblock copolymers are investigated for the synthesis of Ir$_x$Pt$_{100-x}$ nanoparticles. The nanoparticles were analyzed via scanning force microscopy (SFM) to determine size, morphology, and structure. Elemental composition was determined through x-ray photoelectron spectroscopy (XPS) and laser ablation inductively-coupled plasma-mass spectrometry (LAICP-MS). Electrochemical measurements were examined in a cyclic voltammetry (CV) mode for the formic acid oxidation reaction. The relationship between the diblock copolymer template, the composition and the activity of Ir$_x$Pt$_{100-x}$ electrocatalysts are discussed.

Tuesday, March 18, 2014 05:30 PM
Materials for Energy Harvesting (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Conjugated polymeric bulk heterojunction (BHJ) based photovoltaics represent one of the most promising technologies for energy harvesting due to their low-cost and scalability. Controlling the morphology at the nanoscale to reduce phase separation suggests significant improvements to increase the efficiency of BHJ solar cells. Block copolymers, which naturally self-assemble into periodic ordered nanostructures, are used to precisely control the morphology.

Here, we demonstrate synthesis and characterization of a donor-acceptor block copolymer poly(3-hexylthiophene)-b-poly{[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalene diimide-2,6-diyl]-alt-5,5'(2,2'-bithiophene)} (P3HT-b-PNDI). P3HT is a p-type conjugated polymer. The electron mobility of P3HT is in the order of 0.1 cm² V⁻¹ s⁻¹, and optical absorption at λ_max = 500 nm. PNDI is known by the large electron affinity due to its electron deficient core, therefore a good candidate for n-type block for polymer semiconductors. PNDI has a high electron mobility in the order of 0.85 cm² V⁻¹ s⁻¹, optical absorption at λ_max = 391 and 697 nm, and low-absorption band edge of 1.45 eV.
Fluorinated polymeric matrices are a versatile class of materials because of their applicability for use is vast, to include the use of high performance materials. Specifically, perfluoropolyethers (PFPEs), which are known to undergo accelerated thermal degradation in the presence of native metals. PFPEs have numerous optimal characteristics such as low volatility, minimal shear thinning, and a viscosity that is predominantly independent of temperature. Optimizing systems to harness the energetic behavior resulting from the degradation pathways facilitated by exothermic metal-mediated oxidation has been explored. It will serve as an additive in a number of polymeric matrices such as epoxy resins, poly(urethane)s, and electrospun fibers from Teflon AF. Preparation, properties, and characterization of the various systems will be discussed.
404 - Thermoelectric properties of metal-filled CNT/C composites

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CNTs were prepared by rapid pyrolysis of ferrocene-dissolving cyclohexane at 1000°C and then were heat-treated at 2800°C to remove the iron particles left in the inside of CNTs by thermal decomposition of ferrocene. After the confirmation of no metal in the inside of hollow, the tips of the heat-treated CNTs (GCNT) were removed with mixed acids. Metal-filled CNTs were prepared by heating and stirring the mixture of the open-ended CNT and iron-containing compounds at melting temperature or nickel-containing compounds dissolved in methanol at room temperature. Acetyl ferrocene and nickel acetate tetra hydride were chosen. Existence of those metals in the inside of hollow were determined with both of energy dispersive X-ray spectrometer and transmission electron microscope (TEM). Iron and nickel particles were observed in CNT filaments with Figures 1 (b) and (c), respectively. Metal content in the resulting CNTs was estimated by the weight difference before and after heat-treatment. The content of iron in Fe-filled GCNTs was ca. 14wt% and the case of Ni-filled GCNTs was ca. 6wt%. CNT/C composites were prepared by carbonization of CNT felts impregnated with thermosetting resin. Seebeck coefficient of each composite was preliminary measured by steady-state method. As a result, Seebeck coefficients of Fe-filled GCNT/C and Ni-filled GCNT/C were 30μV/K and 34μV/K, respectively. We will discuss the details of preparation conditions of metal-filled GCNT/C composites and effects of filling metals on thermoelectric properties.

Figure 1 TEM images of GCNT
(a) Opened-GCNT,
(b) Fe-filled GCNT,
(c) Ni-filled GCNT.
Vertically aligned CNT array on Si substrate was prepared by rapid pyrolysis of the mixture of ferrocene and cyclohexane at 1000°C in a flow of N₂. The height of CNT wall was ca. 70 μm as shown in Figure 1(a). The CNT array was detached from the Si substrate by using one side of the polymer film swollen with chloroform. The CNT forest on the polymer film was unidirectionally pushed down by rotational molding to produce a highly-oriented CNT sheet. Figure 1(b) shows that the CNT forest is inclined at 15° degrees. The CNT/polymer composites were prepared by impregnation of chloroform solution of COPNA resin into the above CNT sheet. Figure 1(c) shows that the CNT filaments were rigidly fixed by the impregnated COPNA resin. Seebeck coefficient of such oriented-CNT/COPNA composites were 24.3 μV/K. The CNT felt/COPNA composites were prepared as a comparison sample. In the case of this CNT felt/COPNA composite, Seebeck coefficient was 15.7 μV/K. This difference in the Seebeck coefficient between them would be attributed into the orientation of CNT filaments. We will discuss details of the preparation and thermoelectric properties of the oriented-CNT/polymer composite.

Figure 1. SEM images of the cross sections.
(a) CNT array on Si substrate,
(b) Highly-oriented CNT sheet,
(c) Oriented-CNT/COPNA composite.
Oxidative polymerization of meso-substituted tetraaminophenyl porphyrins creates nano-fibrous films by creating conjugated phenazine linkage between the porphyrin units. Polymer films made by interfacial, chemical, and electrochemical polymerization are characterized by SEM and UV-Vis spectroscopy. Differences between conductivity and morphology of the films as prepared are discussed and compared to polyaniline films synthesized by analogous techniques. Conductivity is proposed to be related to the extent of oxidation of the film, which is analyzed by UV-Vis spectroscopy. The role of protonation in modulating conductivity will also be discussed.
407 - Probing self-assembly of non-fluorescent small molecules inside live mammalian cells

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Self-assembly of biomacromolecules into fibrillar nanostructures is a fundamental process in both prokaryotic and eukaryotic cells. In contrast to the well-defined (dys)functions of endogenous protein filaments, the fate of intracellular assembly of small molecules remains largely unknown. Besides being driven by non-covalent bonds to form ordered filamentous assemblies, the nanofibers of molecular hydrogelators have shown certain unexpected bioactivities, e.g., they promote activation of procaspase-3, disrupt the elongation of microtubules, and serve as a mimic of cytoskeleton in a model protocell. For a better understanding of small molecular self-assembly inside living bio-entities, we have proposed a general imaging method, correlative light and electron microscopy (CLEM), for the investigation of self-assembly of small molecules without fluorescence labeling (native form) inside mammalian cells after a necessary incubation time. The idea is to incorporate dansyl labeled molecules into the nanofibers formed from the native molecules. This method allows us to determine the formation, localization, and progression of molecular assemblies generated from non-fluorescent small molecular hydrogelators by an enzyme-triggered hydrogelation mechanism inside live mammalian cells. We demonstrated that (i) the precursors passively diffuse inside the cells; (ii) molecular assembly occurs on the endoplasmic reticulum (ER); and (iii) CLEM further indicates that the molecular assemblies are localized near or inside the ER and are likely processed via the cellular secretory pathway (e.g., ER-Golgi-lysosomes/secretion) by cells, albeit less efficiently.

This work not only establishes a general strategy to provide the spatiotemporal profile of molecular assemblies inside cells, but indicates that molecular assemblies of small molecules may provide a new model system to mimic and to understand the cellular mechanisms and processes related to endogenous-normal and aberrant-protein nanofibers.
Developing targeted imaging pharmaceuticals that localize via one of cancer’s broad hallmarks rather than a specific biomarker can have a direct impact on decreasing the number of cancer-related deaths. One particularly attractive hallmark is the acidic extracellular microenvironment of tumor tissue (pH 6.6–7.4). Creating a material that is nano-sized in blood, but upon reaching the acidic extracellular tumor environment, transforms into a bulky, more slowly diffusing object could serve as a novel mechanism for achieving high accumulation of imaging/drug delivery agents at a tumor site. Here, we have designed and characterized self-assembling peptide amphiphile (PA) molecules that transform from isolated molecules or nano-spheres into nano-fibers when the pH is slightly reduced from 7.4 to 6.6, in isotonic salt solutions that simulate the acidic extracellular microenvironment of malignant tumor tissue and consequently in blood serum.

. Relaxivity values of water protons in presence of PAs calculated via MRI measurements were found to be higher than a standard control (Magnevist 4.5 mM⁻¹ s⁻¹)
Regenerative medicine and tissue engineering provide promising alternatives to organ transplantation, the most common therapy available to patients with damaged organs. Healthy cells can be encapsulated into a synthetic extracellular matrices (sECM) to grow in vitro and can then be transplanted back into the patient. The Guan laboratory has investigated a hydrogel system, synthesized from a saccharide-peptide (SP) copolymer, as a sECM for tissue engineering. SP hydrogels are attractive candidates for sECM due to their modular design, ease of functionalization and tunability. Recently for the first time, SP hydrogels were successfully applied to encapsulate syngeneic Lewis rat islets. The encapsulated islets maintained function for over four weeks, and were promisingly able to reverse the diabetes in streptozotocin-diabetic rats after transplantation, *(Biomaterials 2013*, 34, 3984–3991). Given the promising success of SP system for islet encapsulation, extending the lifetime of these hydrogels can open exciting avenues for biomedical applications.

As shown in the figure, we hypothesized that limited incorporation of unnatural amino acids/alkylation of the backbone amides can dramatically influence the proteolytic degradation profile of SP hydrogels. Modular design of SP hydrogel allows incorporation of cross-linking sites with D-stereochemistry while N-methylation of backbones can be achieved by post functionalization of polymer backbones. Herein we report the synthesis and characterization of these modified hydrogels and investigate their performances.

Tuesday, March 18, 2014 05:30 PM
**Peptide-Based Materials for Nanomedicine (05:30 PM - 07:30 PM)**
**Location: Dallas Convention Center**
**Room: Hall A**
410 - Influences of size, shape and surface chemistry of gold nanoparticles on dipeptide self-assembly

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Understanding of the interactions between nanoparticles (NPs) and biological molecules offers new possibilities in the application of nanomedicine and nanodiagnostics. Especially, some features of nanoparticles such as size, shape, and surface functionality play a key role in these interactions. In this study, we have investigated the effect of sizes (5–60 nm) and shapes (i.e., spherical, rod, and cage) of gold NPs (AuNPs) on the self-assembly of diphenylalanine (Phe–Phe) dipeptides. In the light of our results, we found that the size of AuNPs smaller than 10 nm did not affect the self-assembly process of Phe-Phe, while bigger AuNPs (>10 nm) caused the formation of starlike peptide morphologies connected to one center. In the case of shape differences, nanorod and nanocage morphologies acted differently than spherical ones and caused the formation of densely packed, networklike dipeptide morphologies. In addition to these experiments, by combining photothermal properties of AuNPs with a Phe–Phe-based organogel having a thermo-responsive property, we also demonstrated that the degelation process of AuNPs embedded organogels may be controlled by laser illumination. Complete degelation was achieved in about 10 min. We believe that our results have a great impact and offers new possibilities for several technological applications including drug delivery, catalysis, tissue engineering, and biosensors.

Tuesday, March 18, 2014 05:30 PM
Peptide-Based Materials for Nanomedicine (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
411 - Synthesis and characterization of non-ionic water-soluble “clickable” polypeptide

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A series of water-soluble non-ionic co-polypeptides consisting of poly(γ-propargyl-L-glutamate) and poly{Nε-2-[2-(2-Methoxyethoxy)ethoxy]acetyl-L-lysine} were synthesized by ring-opening copolymerization (ROP) of the corresponding N-carboxyanhydrides using benzyl amine as initiators. Successful synthesis of the copolymers was confirmed by size-exclusion chromatography (SEC) and 1H NMR spectroscopy. These copolypeptides bearing pendant alkyne groups can be further modified with azide containing agents through copper-catalyzed alkyne-azide cycloaddition chemistry (CuAAC). Cell adhesion pentapeptide GRGDS terminated with azido group was successfully attached to the copolypeptides in varying grafting density (2-9 mol%) in DMF using a copper wire catalyst. Circular dichroism (CD) analysis reveals that both the copolypeptides and the conjugates adopt α-helical conformations in aqueous solution. Increasing GRGDS content appears to promote the α-helical conformations. Cell adhesion assay indicates the conjugates are able to induce integrin-mediated cell adhesion.

Water soluable PEG

Functional alkyne group
412 - Synthesis and characterization of amphiphilic peptide based linear ABC triblock copolymers exhibiting stimuli responsive capabilities

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The self-assembly morphologies and pH stimulated morphological transitions of linear ABC triblock copolymers is being investigated in this research. The ABC triblock copolymer consists of a hydrophilic poly(ethylene oxide) (PEO) A-block and a hydrophobic poly(propylene oxide) (PPO) C-block, which are separated by a pH responsive poly(lysine) (PK) B-block. At pH of 5 and above, the PK block side chains are neutral, and the peptide block adopts an α-helix secondary structure, which contributes to the hydrophobic weight fraction of the copolymer. Reducing the pH to 5 or below, the PK side chains become protonated and positively charged, the neighboring like charges disrupt the α-helix secondary structure, triggering a helix to random coil transition, at which point the PK block contributes the hydrophilic weight fraction of the copolymer. This pH induced change in the hydrophilic weight fraction of the ABC triblock copolymer triggers changes in the self-assembly morphologies adopted by these polymers in aqueous solution. Self-assembly morphology and size as a function of pH was determined using light scattering and TEM; circular dichroism (CD) spectroscopy was used to determine PK block secondary structure as solution pH was varied. A modular synthesis was employed where ring opening polymerization of lysine N-carboxyanhydride (NCA) could be initiated from either the PEO or PPO block, followed by azide-alkyne click coupling of the complimentary block, yielding the final ABC triblock, peptide based pH responsive copolymer.
413 - Influence of secondary structure on polypeptide synthesis and characterization

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The synthesis of well-defined polypeptides based on the ring opening polymerization of \(\alpha\)-amino acid-\(N\)-carboxyanhydrides (NCAs) has attracted synthetic chemists since the early 20\(^{th}\) century. In the last decades various techniques to control the polymerization have emerged focusing on lower dispersities.\(^1\) Polylsine has been applied to a variety of applications like coatings for improved cell attachment or in gene delivery.\(^2\)

In this work, two series of polylysines with Z and TFA protecting groups were synthesized and their behavior in a range of analytical methods was investigated. GPC of the smaller polypeptides reveals a bimodal distribution, which is lost in larger polymers. With the help of GPC, NMR, CD and MALDI-TOF it has been demonstrated, that this bimodal distribution is not due to terminated chains but a change in secondary structure of the growing peptide chain occurring around DP=15.

The two different secondary structures can be separated and analyzed individually. This work shows that secondary structures need to be carefully considered in synthesis and characterization of polypeptides.


414 - Designing synthetic polyesters that mimic the structural features of peptides

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Common biomaterials such as poly(lactic acid) and polycaprolactone are useful because of their mechanical properties and biodegradable properties. Over the past several decades, these materials have been critical in advancing the field of tissue engineering and drug delivery. However, these common biomaterials are incapable of providing any signaling cues that would enable their interaction and eventual integration with the cellular environment. On the other hand, natural materials such as proteins provide both structural and functional roles due to their multivalent and self-organizing nature. In our lab, we attempt to address the drawbacks of current biomaterials, such as a lack of functionality, by synthesizing multivalent biomaterials with functionalized pendant groups. We have recently developed a new class of multivalent 'peptide-like' polyesters whose physical, mechanical and biological properties are modulated by the pendant groups (Biomacromolecules 2013). Due to their multifunctional structure, they have potential applications in numerous areas such as drug and protein delivery, multimodal imaging, antibacterials, wound healing matrices and multivalent inhibitors.
Natural compounds from biological sources may be conveniently used as building blocks to synthesize new functional biomaterials for various biomedical and pharmaceutical applications. Bile acids are natural steroidal compounds that exist in the gastrointestinal tract in most animals and help in the digestion of fat by the formation of micellar aggregates. Their facial amphiphilicity and acid-base properties make them ideal candidates in the preparation of polymeric biomaterials upon chemical modifications. Such polymers are expected to exhibit better biocompatibility and bioacceptance. We have also made degradable polyesters based on bile acids via entropy-driven ring-opening polymerization catalyzed by lipase. The polymers can be made to display tunable mechanical properties and heterogeneous degradation behavior. Shape memory properties have been observed with such materials. The ring opening polymerization of the norbornene derivatives of bile acids provided multi-shape memory materials through broad glass transitions. Glycopolymeric blocks can be incorporated to build amphiphilic polymers that form aggregates in water. Grafting poly(ethylene glycol) and other polyethers via anionic polymerization yielded polymers that can self-assemble into aggregates for use in encapsulation of drugs. Some polymers, after proper functionalization, exhibit interesting thermosensitive properties. Oligomers made of bile acids have shown to behave as invertible molecular pockets for the inclusion of either hydrophilic or hydrophobic compounds based on the polarity of the surrounding media. Such characteristics may be useful to build sensors for the detection of transition metal ions in aqueous systems with sensitivity at a sub-ppm level.
416 - Molecular modeling of supramolecular polymer of drug amphiphiles for drug delivery

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Drug amphiphiles (DAs) are monodisperse and amphiphilic and assemble into discrete, stable supramolecular nanostructures. They have the potential for self-delivery with high and quantitative drug loading. The DA for this study includes the hydrophobic drug camptothecin (CPT), a DNA topoisomerase I inhibitor conjugated to beta-sheet forming sequence derived from Tau protein through the reducible disulfylbutyrate linker. Morphology of the self-assembly depends on the number of drugs tethered, forming either nanofibers or nanotubes with different widths and lengths. We use molecular dynamics simulations to investigate this effect of the number of drugs on the morphology of the assembly at the molecular level. To investigate what triggers the assembly in the initial steps, we start with randomly inserted DAs in implicit and explicit water. This shows clear pi-pi interactions between the planar CPTs from the early stage, forming clusters. Due to the long time scales for the self-assembly to form cylindrical nanostructures, we pre-build the DA assembly in a roughly cylindrical configuration and let it relax in explicit water with physiological ion concentration. The resulting structure is found to be stable for 150ns simulations. The radii of the cylinders are compared with the experimental data. The population of secondary structures of the peptide parts, water and ion penetration to the core of the cylindrical structures, and the decomposition of the interaction energy are discussed. Our finding will be useful for designing new DAs for drug delivery.
Silica nanoparticles (NPs) have been grafted with amphiphilic block copolymers, polycaprolactone-\textit{b}-polyethylene glycol, with varying grafting densities, using both grafting-from and grafting-to processes. It has been shown that brush height scales differently depending on the grafting density. In this reaction, grafting density was controlled by synthesis of a monolayer on the surface of NPs using varied ratios of 3-aminopropyltrimethoxysilane and trimethylethoxysilane. This afforded silica nanoparticle surfaces that ranged from fully saturated with reactive amine groups or very sparsely functionalized. Amphiphilic block copolymers were attached by first using a grafting-from reaction in which the amine-functionalized silica nanoparticles served as the initiating species in a ring opening polymerization ε-caprolactone and catalyst triethyl aluminum to yield polycaprolactone-functionalized silica nanoparticles. The hydroxy-terminated polycaprolactone was then reacted with a carboxylic acid functionalized polyethylene glycol using activated ester coupling in a grafting-to reaction to yield amphiphilic block copolymer functionalized silica nanoparticles. Amphiphilic block copolymer grafted nanoparticles were characterized using dynamic light scattering and transmission electron microscopy. These materials are expected to be excellent candidates for oil remediation.
418 - Synthesis and evaluation of linear and comb-shape polyacrylamide as viscosity improver for oil recovery

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Polyacrylamide (PAM) is a widely used polymer in oil industry since it can act to increase the viscosity of the solution. However, currently most of the PAM used are limited to linear ones. This is because people are still not able to control the structure of the resulting polymer very well.

Here, we use the mechanism of atomic transfer radical polymerization (ATRP) to synthesize comb-shape polyacrylamide, where the acrylamide monomer grafts from macro-initiator which has an alternating bromine group for initiating acrylamide polymerization. In order to get better water solubility before attaching acrylamide, the backbone is co-polymerized with pentafluorophenyl methacrylate. After aminolysis in a post polymerization modification, this part is supposed to provide some hydrophilic function group and make it possible for the following "graft from" reaction.

Then, effect of polymer structure on the viscosity improvement is tested by measuring the viscosity of lab-made linear PAM and comb-shape PAM with similar molecular weight. The branched PAM is believed to get equal or better viscosity improvement compared to its linear analogue. Also, it’s worthwhile to see how the comb-shape PAM performs compared to the commercial viscosity improver. This fundamental research paves the way for the application of different structure PAM in Enhanced Oil Recovery (EOR).

![Synthesis of branched PAM](image-url)
419 - Reversible activity modulation of surface-attached catalysts using redox-responsive polymers

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Immobilized stimuli-responsive polymer layers can tremendously change surface properties leading to so-called smart surfaces for many important applications. Beside more established external triggers like the change of solvent, temperature, ionic strength, light or mechanical stress, the redox-activity of ferrocene-containing polymers can be used. Monodisperse silica nanoparticles and activated silica wafers were functionalized either by using grafting onto protocol of poly(vinylferrocene) featuring a triethoxysilane end group. In a second approach, surface-initiated atom transfer radical polymerization (SI-ATRP) of 2-(methacryloyloxy)ethyl ferrocenecarboxylate (FcMA) was used for immobilizing the redox-active polymers. The swelling behaviour of the surface-attached ferrocene-containing polymer layers upon oxidation was studied for switching the surface wettability and controlling the accessibility of surface-attached Grubb’s catalysts. The ferrocene moieties in such polymers can be reversibly switched between two oxidation levels changing the polarity of the local environment which is accompanied with a swelling of the surface-attached chains. We appreciate the described methodology for activity modulation of surface-attached reactive centres by using redox-responsive polymers can be expanded to various fields in catalysis, sensor applications and drug-delivery.

[Figure 1]


420 - Flame retardant and antimolding coating doped with halloysite clay nanotubes for flake board protection

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Halloysite clay nanotube is a naturally occurring, biocompatible alumina-silica material with a length of 0.5-1μm, with an outer diameter of 50nm and has a lumen size of 15nm. Halloysite can be used as a nanocontainer for drugs, proteins, antifouling and anticorrosion agents. It has been observed that halloysite also improves the mechanical properties of the coating significantly. Halloysite loading efficiency was optimized by treatment of halloysites with sulfuric acid. In this case, halloysite was loaded with an antifouling agent, and used as a dopant in latex paint. Bacterial studies showed that dopant with antifouling agent loaded halloysite inhibited the growth of molds when compared with the control samples. An added application of pristine halloysite clay nanotubes is, when mixed in a proportion of 5wt% in latex paint, it improved flame retardant properties of the coating when compared to the pure paint coating and paint with pure flame retardant.

![Figure 1. Pure latex paint (a), latex paint with 5 wt% halloysite (b) and paint with FR-1 flame retardant loaded halloysite (c) after flame testing](image)

This ability can be further improved by loading halloysite with flame retardant agents. This dual functioning coating will provide cost effective product for household applications.
**421 - Water-tunable photonic colloidal crystals with narrow diffraction bandwidth**

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Novel opal hydrogels with tunable photonic band gap (PBG) were prepared, with sensitive responses to external stimuli in water. These self-assembled colloidal crystals display narrow stop bandwidth, consisting of polystyrene-co-poly(N,N-dimethylacrylamide) (PS-co-PDMAA) microspheres. The polymeric microspheres were engineered in water, exhibiting narrow size distribution; with numerous acrylamide groups on their surface, they are hydrophilic in nature (Figure 1 (a)). Interestingly, each microsphere has two distinguishable compositional regions. The inner and outer regions are rich in PS and PDMAA, respectively; thus, the inner region is hard and hydrophobic, and the outer region is soft and hydrophilic.

Accordingly, the PS-co-PDMAA microspheres are ready to self-assemble, even via centrifugation, producing diffraction with high color purity. Promptly and sensitively, the centrifugation-induced three-dimensional (3D) photonic colloidal crystals (PCCs) responded to the amount of water presented. With an increase of the amount of water, the volume of the opal hydrogels increased, so did their lattice spacing (Figure 1 (b)-top); accordingly, their PBG shifted from the visible to near-infrared region of the electromagnetic spectrum. With narrow full width at half maximum (FWHM) in the range of 20 to 40 nm only, the diffraction could shift its peak position more than 500 nm (Figure 1 (c)). Remarkably, such shift was repeatable via the cycles of centrifugation and water addition. Furthermore, the water-tunable change in color is visible to the naked eye (Figure 1 (b)-bottom).

The aforementioned observations could be reasonably attributed to the structure of the polymeric microspheres, the outer region of which is hydrophilic with a reproducible degree of hydration. Appreciably, the presence of thiocyanate (SCN⁻) ions shapes the hydration, because they break efficiently the hydrogen bonds between the repeat units of DMAA and water molecules. Thus, the diffraction of the opal hydrogels is affected delicately. With far-reaching implications, our PS-co-PDMAA PCCs have the potential in diffraction-based detections.

![Figure 1](image)

**Figure 1.** Schematic drawing of the interaction between water molecules and the repeat units of DMAA that are on the surface of our PS-co-PDMAA microspheres (a). The PBG of the PS-co-PDMAA PCCs is water-tunable, which could be repeatedly controlled by the cycles of centrifugation and water addition, and the resulting change in color of the PCCs is evident to the naked eye (b). The diffraction spectra collected from PS-co-PDMAA PCCs.
422 - Alignment of halloysite nanotubes in composite polymeric films via controlled evaporation

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A procedure for utilizing inkjet printing to deposit films of 50 nm diameter halloysite clay nanotubes (HNTs) with high degree of long-range alignment and controlled orientation is reported. The surface alignment was verified by means of optical and scanning electron microscopy. The "coffee ring" effect is invoked to explain the tube self-assembly in ordered structures. Various parameters to control directional self-assembly were examined including halloysite tube concentration, evaporation rate, the surface charge of the tubes, solvent pH, ionic strength and surface tension. Furthermore, by functionalizing the tubes with polyanions and anionic surfactants allowed for preparation of polymeric composites with drop casting method. These techniques have allowed for the design of new inorganic/organic nanostructures containing oriented nanotubes and the advantages of such a structure.

Tuesday, March 18, 2014 05:30 PM
Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
423 - PH-triggered responses of spherical and cubical multilayer hydrogel capsules

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We report on synthesis and pH-responsive properties of hydrogel capsules of spherical and cubical shapes. Three types of poly(methacrylic acid) (PMAA)-based hydrogel capsules were produced as hollow replicas of inorganic sacrificial templates through chemical cross-linking of hydrogen-bonded layer-by-layer (multilayer) films; one-component PMAA, one-component poly(methacrylic acid-co-(aminopropyl)methacrylamide) [PMAA-co-NH₂], and two-component PMAA-co-NH₂ with poly(vinyl pyrrolidone-co-(aminopropyl)methacrylamide) [PVPON]. We found that while spherical PMAA capsules increased in size due to a shift from pH=3 to pH=8, cubical capsules changed shape and became bulged at the faces. The PMAA-co-NH₂ single component cubical capsules similarly changed shape, while the two-component PMAA/PVPON cubical system maintained cubical geometry while increasing in size upon pH shift. The differing pH-triggered response was hypothesized to be a result of differing hydrogel rigidity, expressed as the ratio of the contour length between cross-links as compared to persistence polymer length. PVPON/PMAA cubical capsules were found to be ten times more rigid than their one component counterparts, that can explain the expansion of two component cubical capsules uniformly in all directions. We believe these results allow for developing new polymeric materials with predictable shape and size transformation useful in drug delivery, cell uptake, and microfluidic sensing applications.

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Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
424 - Highly swellable ultrathin multilayer hydrogels with pH-triggered surface wettability

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We report on synthesis of a new type of highly swellable ultrathin cationic hydrogel with pH-triggered swelling behaviour and surface wettability. The single-component poly(4-vinyl pyridine) (P4VP) hydrogel films are produced by selective cross-linking of P4VP copolymers in layer-by-layer (LbL) films assembled via spin-assisted deposition. These multilayer hydrogels exhibit drastic and reversible 10-fold swelling when the pH is changed from neutral to acidic. The swelling amplitude of the hydrogels is controlled by varying cross-link densities within the films. These densities are varied by the number of cross-linkable amino-containing units in P4VP copolymer chains. We have found surface morphology of the hydrogels to be significantly affected by fabrication conditions. Contact angles vary from 70° to less than 10° for the films prepared from neutral and acidic solutions, respectively.

Our work opens new prospects for developing highly swellable stimuli-responsive nanothin hydrogels for sensing and transport regulation in microfluidic devices.
Aliphatic polycarbonates are an important class of biocompatible and biodegradable materials widely used for drug delivery and tissue engineering applications. The growing need for increasingly versatile biomaterials has spurred the development of functional polycarbonates, to enable facile tuning of their physicochemical and biological properties by installation of sites for covalent conjugation. We report on the synthesis of copolymers of poly(ethylene glycol) (PEG) and a polycarbonate containing pendant boronic acids, to enable dynamic-covalent chemistry at the hydrophobic block. The organocatalytic polymerization of 5-methyl-5-(phenylboronic acid) oxycarbonyl-1,3-trimethylene carbonate, from a PEG macroinitiator, was studied. The functional amphiphilic copolymer that results after deprotection, generates sites for the incorporation of active molecules. We studied the binding affinity between the polymer and the anticancer drug capecitabine, incorporated through the boronic acid pendant group. We studied drug incorporation through Flash Nanoprecipitation, a method based on competitive times of polymer aggregation, drug-polymer conjugation, and drug precipitation. Stimuli-responsive drug release and core-swelling was studied for a range of pH values and in the presence of triggering agents such as hydrogen peroxide. We report differences between particles generated by this method and one where assembly and reaction kinetics do not influence drug loading.
426 - Dual stimuli-responsive, fluorescent probe based on crosslinked poly(N-isopropylacrylamide-co-fluorescein-co-rhodamine) microgel

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Microgels composed of thermosensitive polymers such as poly(N-isopropylacrylamide) (PNIPAM) have widely studied in the application areas of drug delivery, tissue engineering and responsive colloidal arrays. This is due to critical changes in their sizes and physical properties during volume phase transition (VPT). The crosslinked PNIPAM networks are highly swollen below the phase transition temperature, but become shrunk above VPT, according to dissociation of water molecules from the polymer chains occurs.

Fluorescein and rhodamine fluorophores have been used widely to label and track cells, proteins and organelles of human body because of their excellent biocompatibility and high sensitivity under physiological conditions. Under basic or neutral pH conditions, fluorescein gives strong green fluorescence when the cyclolactam ring is opened, but the emission is dramatically reduced at acidic pH, triggered by ring closure. In contrast, rhodamine shows strong red fluorescence at acidic pH because of opening of its cyclolactam ring but becomes non-fluorescent at basic or neutral pH when the ring is closed. Recently, nanoparticle or polymer-based sensors conjugated with pH-sensitive fluorescein and rhodamine dyes were reported for detecting a wide range of pH values.

In this study, we prepared poly(NIPAM-co-fluorescein-co-rhodamine) microgel that has thermo- and pH-responsive properties. Thus, the ratio of the fluorescence intensities can respond to wide range of pH values, which could observe the pH fluctuations in aqueous solution.

Tuesday, March 18, 2014 05:30 PM
Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
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A series of alternating co-polymers were synthesized, composed of tetra-phenylenevinylene derivatives and 2- and 4-carbon tethers. Static absorption and photoluminescence of drop-cast films show that while the monomeric control and the 4-carbon tethered system exhibit a redshift in absorption and quenched fluorescence after thermal annealing, the 2-carbon tethered system shows little change after annealing, favoring a highly fluorescent film. Time-resolved photoluminescence measurements support this trend: the fluorescent decay of the monomeric control and 4-carbon linked system is expedited to favor a faster relaxation pathway (<3 ns) post-annealing, while the 2-carbon linked system adheres to a slower decay (>10 ns) both before and after thermal annealing. TEM images reveal that while the monomer and 4-carbon tethered system form crystalline features during annealing, the morphological characteristics of the 2-carbon tethered system are trapped after film casting; the annealing process produces no alterations to the amorphous pattern afforded in the as-cast film. Geometry optimization calculations of the 2- and 4-carbon systems shed light on experimental data; the 2-carbon tether is too short to allow intramolecular π-stacking between neighboring phenylenevinylene units to occur at a distance typically found in similar oligomers, which may hinder the ability of the polymer to reorganize during annealing. The vast differences imparted by small modifications to the tether length may provide a method of fine-tuning the photophysics and morphological features within the thin films of other polymeric species.
This study involves the divergent and convergent synthesis and characterization of responsive amphiphilic peptide block copolymers which display unique pH-induced morphology transitions. Variations in the molecular architecture lead to diverse morphologies that are conducive for drug delivery, whereby controlling the porosity of the polymeric membrane will directly affect the release rate of loaded cargo. The model systems for this study are star block copolymers which mimic the molecular architecture of phospholipids, in particular the topology of ABC₂. Here the hydrophilic, pH-responsive blocks (A) are composed of poly(lysine) or poly(glutamic) acid. These are attached to a hydrophobic, α-helix forming poly(leucine) (B) spacer. This amphiphilic peptide moiety was then linked via thiol-yne click reaction to various hydrophobic tail blocks (C). Light scattering and TEM were used to determine aggregate size and morphology as a function of pH, and circular dichroism (CD) spectroscopy was used to observe the helix-to-coil transition within the peptide blocks. Drug release profiles were created to show the triggered release of doxorubicin with change in pH. This study demonstrates how controlling the molecular design and pH responsiveness of these systems leads to control on cargo release.
Ionic polymer-metal composite (IPMC) is composed of an ion exchange membrane (IEM) sandwiched between two metal electrodes. When an IPMC is deformed, it produces output voltage between the two electrodes due to the movement of solvent molecules and cations on the compressed side toward the stretched side.

We prepared an IPMC bending sensor employing Aquivion, of which the structure shown below, as the IEM, and compared with the sensor employing Nafion, a more popular IEM. The higher concentration of ionic groups of Aquivion was thought to be advantageous for generating higher sensor signal.

Ion exchange capacity of Aquivion (1.12 meq/g) was significantly higher than that of Nafion (0.89 meq/g). It was clearly ascribed to the increased number of ionic groups in the membrane. Ion conductivity of Aquivion (0.06 S/cm) was slightly higher or similar as compared with that of Nafion (0.05 S/cm). Water uptake was comparable for Aquivion (25 wt%) and Nafion (22 wt%). As expected, signal output of the Aquivion sensor (2.9 mV) was larger than that of Nafion sensor (1.5 mV). The relation between signal and bending displacement was also investigated, and the results will be presented.
430 - WITHDRAWN
431 - Responsive high refractive index thiol-ene/sol-gel hybrid nanocomposite networks

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A considerable amount of work has recently been done in controlling the wettability of solid surfaces. Superhydrophobic and superhydrophilic surfaces display vast potential for use in applications such as self-cleaning materials, microelectronics, and microfluidics. Similarly, combining a responsive hydrophobic/hydrophilic component in a surface material further allows the control and tailorable of wetting properties. Titanium dioxide is a known photocatalyst displaying a reversible, responsive switch from a more hydrophobic state to a hydrophilic state via increased TiO$_2$ hydroxylation upon exposure to UV light. Combined with TiO$_2$’s high refractive index, good thermal and chemical stability, and low toxicity, TiO$_2$ surfaces provide a versatile platform for use in a variety of applications. In this presentation, we report the synthesis of transparent, high refractive index thiol-ene/TiO$_2$ hybrid networks displaying reversible wetting behavior upon exposure to UV light. The combination of thiol-ene and sol-gel chemistry provides increased network flexibility while maintaining the desirable surface effects of TiO$_2$. This presentation will describe our efforts to evaluate the effect of TiO$_2$ content on refractive index, surface roughness, and reversible wettability of the hybrid-organic/inorganic thin films.
432 - Silk-inorganic nanocomposites materials

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Silk-based hybrid nanomaterials are considered as one of most promising materials in the future because of their excellent biocompatibility and biodegradability. Over the decades, researchers have been developing considerable methods to make silk-based nanocomposites including both chemical and engineering methods. However, no one simple and efficient method has been discovered to obtain silk-inorganic nanocomposites. Recently, we develop a novel one-step method that is quick, universal and green to make silk-inorganic nanocomposites with different kinds of inorganic nanomaterials doping. The synthesized hybrid nanomaterials have considerable applications such as bio imaging, cancer therapy and surface-enhanced Raman scattering (SERS) detection.
High-value materials in, for example, the automotive, railroad, and aerospace industries require the multifunctional coatings for improved performance, self-healing, and durability. It is especially urgent to find new routes for the next generation protective coating, especially taking into consideration the banning of carcinogenic Cr(VI) ions. In this respect, the protective coating should provide the specific functionalities in response to the external stimulus. Here, we introduce the polyelectrolytes, branched poly(ethylenimine) (BPEI) and poly(acrylic acid) (PAA), to build the multilayer structures. Polyelectrolyte nanocontainers with controlled release properties can be used to fabricate a new family of active coatings, with quick response to the changes of coating environment or coating integrity. The release of anticorrosion agent, 8-hydroxyquinoline (8-HQ), encapsulated into the polyelectrolyte nanocontainer can be triggered by pH, salt, or surfactant with a narrow window, and thus preventing spontaneous leakage of the agent. The coating can also have several active functionalities when several types of agent or several kinds of nanocontainers are loaded as the sandwich structures in order to achieve staged release with the corresponding active agent incorporated into a coating matrix.
434 - Synthesis and characterization of photo-active amphiphilic porphyrin/poly(ethylene glycol)-b-polycaprolactone copolymer nanoparticles

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Water soluble porphyrin nanoparticles were prepared via self-assembly of Poly (ethylene glycol)-b-polycaprolactone (PEG-b-PCL) conjugated porphyrin copolymer in aqueous solution. The diameters of the nanoparticles were found to be 100 nm as confirmed by Transmission Electron Microscopy (TEM) and Dynamic Laser Scattering (DLS) studies. Furthermore, these nanoparticles showed an increase in fluorescence intensity with increasing PCL molecular weight of the copolymer. These improved photochemical properties could pave the way to enhance porphyrin nanoparticle performance for applications in imaging and photodynamic therapy.
A novel all-carbohydrate-based polymer was synthesized through tetrabutyl ammonium iodide (TBAI)-catalyzed polymerization of di-functional AB monomer, 2,3,4-tri-O-acetyl-alpha-D-glucopyranosyl bromide. The polymerization was highly efficient, giving sugar poly(orthoester) with molecular weights up to 6.9 kDa. Nanoparticles were prepared by an emulsion-evaporation-lyophilization procedure using poly(ethylene glycol, Mn = 10 kDa) as an emulsifier, which gave average SEM sizes of 230 ± 60 nm. These carbohydrate-based polymers, exhibited excellent biocompatibility with minimal non-specific protein adsorption. Furthermore, with acid-labile orthoester linkages in the polymer backbone, the nanoparticles are highly pH-responsive, allowing fast release of Dexamethasone, which was used as a model drug.
436 - Particle size control of porous carbon microspheres with thermosetting resin

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The resin microspheres were made by heating and stirring the mixture of pyrene-based COPNA resin, poly ethylene glycol, and p-toluene sulfonic acid at 130 °C, and then produced carbon microspheres (CMS) through carbonization process at 1000 °C. COPNA resins were prepared by the following polymerization time: 5 min, 6 min, 7 min, 8 min, 9 min and 10 min. Figure 1 show the tendency that the particle size of CMS became larger as polymerization time got longer. Furthermore, the CMS, derived from the resin with different time between 9 min and 10 min as polymerization times, had open pores with ca. 100 nm in diameter. Heat treatment at various temperatures was carried out to investigate the effects on the structures of open pores. As shown in Figure 2, it was confirmed that open pores developed as heat treatment temperature increased. We will report the details of conditions for preparation of the porous CMS.

![SEM images of the CMS which were prepared from resin whose polymerization times were (a) 5min, (b) 6min, (c) 7min, (d) 8min, (e) 9min and (f) 10min.](image1)

![SEM and TEM images of the CMS prepared at various carbonization temperature. (a) 800 °C, (b) 1000 °C,(c) 1500°C and (d) 2500°C.](image2)
Ever since it’s discovery by Geim et al. graphene has evolved as the rising star in the field of material science.\textsuperscript{1} Starting from the low-cost graphite, graphene oxide aqueous solutions are easily achieved and used widely.\textsuperscript{2,3} Apart from the aromatic areas, the graphene oxide surface is covered with epoxy-, hydroxyl- and carboxylic acid groups making the material highly polar and functional. From the experience of CNT and TiO\textsubscript{2}-nanorod functionalization, we are using the various surface chemistry of graphene oxide to attach functional polymers onto the graphene oxide’s surface.\textsuperscript{4,5} For graphene oxide or reduced graphene oxide this provides an increased solubility in unpolar organic solvents. New ways of processing graphene oxide materials are achieved, making them more accessible as a composite material. Considering the anisotropic shape of graphene oxide we obtain liquid crystalline properties of these materials. Bearing further functionality, the polymers can also support interaction with other nanoparticles, such as metal chalcogenide particles. This may e.g. be applied for new electrode materials in Li-Ion batteries.

References:


438 - Thermotropic helicity induction on polyacetylene/chiral amine system having tunable critical one-handed spiralization temperature and perfect solid state storage of the induced helicity

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Polyacetylene prepared by rhodium catalyst, such as [Rh(nbd)Cl]₂, is a typical dynamic helical polymer, and its main-chain conformation can be *cis-transoidal* or *cis-cisoidal* depending on the monomer structure and the environment. In this study, we report that a thermotropic chiral induction system consisting of a chiral amine and a polyacetylene prepared from an achiral phenylacetylene having two hydroxyl groups shows a tunable critical one-handed spiralization temperature (COST) in nonpolar solvents such as toluene, hexane and CCl₄. The conformation of poly(1) in the system of poly(1)/chiral phenylethyl amine/toluene could be induced into one-handed helix along with transformation of main chain conformation from *cis-transoidal* to *cis-cisoidal* by heating the system to a temperature higher than the COST.

![CD and UV spectra of poly1 in the mixture of (R)-phenylethylamine/hexane (amine content =20vol.%).](image1)

Figure 1. CD and UV spectra of poly1 in the mixture of (R)-phenylethylamine/hexane (amine content =20vol.%). at the temperature from 0 °C to 50 °C.

![Curves of intensities of CD and UV absorptions of poly1 in mixture of (R)-phenylethylamine/hexane.](image2)

Figure 2. Curves of intensities of CD and UV absorptions of poly1 in mixture of (R)-phenylethylamine/hexane (amine content (vol.%): a=10; b=20; c=30; d=50; e=70 and f=90) at wavelength of 310 nm versus temperature.

The induced CD absorption of poly(1) was much stronger than the CD absorption of poly(1) prepared by helix-sense-selective polymerization. The COST can be adjusted by changing the chiral amine concentration in the system, and the higher concentration affords the higher COST. This unique thermotropic chiral induction phenomenon may be caused by the difference in strength of H-bonds of -OH/-NH₂ and -OH/-OH at different temperature. In addition, the induced one-handed helical chirality of the polyacetylene can be self-stabilized by intramolecular H-bonds after precipitating the polyacetylene in methanol to remove the chiral amine, i.e. the induced one-handed helical chirality of the polyacetylene can be perfectly saved in solid state.
Novel bioresponsive materials are crucial for the development of controlled drug delivery. For intracellular delivery, three kinds of biological triggers have been extensively used, including the intracellular enzymatic activities, the acidic environment of the endolysosomes and the reductive environment in the cytoplasm. Despite the fact that many enzymatic and acidic triggers have been developed, disulfide remains as the only reduction responsive chemistry used in drug delivery applications. Therefore, there is an urgent need to expand the chemical toolbox for reduction responsive reactions.

We took advantage of the nucleophilicity of glutathione, the chemical responsible for intracellular reducing environment, and introduced thioester as a novel glutathione responsive functionality for drug delivery. Compared with disulfides, thioesters are more convenient to synthesize and have up to an order of magnitude broader tunability in kinetics. Based on the thioester chemistry, we also developed a thioester based traceless PEGylation strategy to modulate the protein activity, which could potentially enhance its in vivo performance. Upon dePEGylation under a reducing environment, the model protein can completely restore its activity. This thioester chemistry can also be used as a controlled release strategy for nanomedicine. We expect thioesters will play an important role in future studies on thiol responsive controlled drug delivery.
440 - Synthesis and self-assembly of amphiphilic diblock copolymers with a crosslinkable segment

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We present the synthesis and characterization of amphiphilic AB diblock copolymers containing a crosslinkable segment. Both sequential anionic, as well as nitroxide mediated polymerization (NMP) techniques were used to obtain well defined block copolymers containing either poly(styrene-co-isoprene) (P(S-co-I)) or poly(furfuryl glycidyl ether) (PFGE)¹ as hydrophobic block. As hydrophilic segments either poly(ethylene oxide) (PEO) or stimuli responsive poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) has been employed (Figure 1). The materials were characterized by size exclusion chromatography and NMR spectroscopy. Crosslinking of the hydrophobic block in different (nanostructured) environments was achieved by UV-induced radical polymerization (P(S-co-I)) or Diels-Alder reactions using a bifunctional maleimide (PFGE). We demonstrate the application of such block copolymers for the formation of nanoporous membranes or the preparation of organic/inorganic hybrid nanoparticles.


Tuesday, March 18, 2014 05:30 PM
Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
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A conjugated polyelectrolyte (figure 1) based on a polythiophene structure was synthesized to disperse and functionalize multi-walled carbon nanotubes (MWCNTs). The polyelectrolyte/MWCNT hybrid was characterized by scanning electron microscopy and transmission electron microscopy. Furthermore, electrostatic and optoelectronic properties of the hybrid were investigated by electrostatic force microscopy (EFM) and photoconductive atomic force microscopy (PCAFM) respectively. EFM detected positive charges on the carbon nanotubes of the hybrid, suggesting that the MWCNTs were effectively wrapped by the polyelectrolyte. The current-voltage curves obtained by PCAFM were analyzed by the Simmons model. The analysis demonstrated that the equilibrium conductance of the hybrid was increased by approximately 100%.
Poly(glycerol sebacate) (PGS) has been proposed to engineering soft tissues due to its elastomeric properties, biocompatibility, linear degradation rate and non-toxic byproducts. However, one of the problems with PGS is low mechanical stiffness, that limits its application to soft tissues engineering. Here we report the synthesis and characterizations of highly elastomeric and mechanically stiff nanocomposites by covalently reinforcing PGS network with synthetic silicate nanoplatelets. Synthetic silicates are plate-like polyions composed of simple or complex salts of silicic acids and are recently shown to induce osteogenic differentiation of stem cells without using any growth factors. When subjected to thermal curing process at 130 °C, the additional hydroxyl groups (-OH) present on PGS prepolymer reacted with (-OH) present on silicate nanoparticles and unreacted sebacic acid to form covalently crosslinked networks (Figure 1a & 1b).

By tailoring the crosslinking density, it is possible to engineer scaffolds with customized mechanical stiffness, hydration properties (contact angle measurements, Figure 2a) and degradation characteristics. The addition of silicate nanoplatelets significantly enhanced the mechanical strength of the polymeric networks (Figure 2b). The compressive strength and the energy absorbed during the compressive cycle (loading and unloading) increased with increasing silicate nanoplatelets (Figure 2c). This was mainly attributed to the covalently crosslinking of silicate nanoplatelets to PGS networks.

The degradation studies showed that the addition of silicates significantly reduced the degradation rate of nanocomposites by more than 50%. The addition of silicate nanoplatelets also enhanced the in vitro bioactivity of polymeric scaffolds. Preliminary in vitro studies showed enhanced cellular adhesion and proliferation of hMSCs on PGS-silicate nanocomposites compared to PGS. Overall, the unique combination of high mechanical stiffness, elastomeric nature and bioactive character of PGS-silicate nanocomposite may be processed to design scaffolds for musculoskeletal tissue engineering.
The first ferrocene-containing epoxide monomer, ferrocenyl glycidyl ether (fcGE), is introduced. The monomer has been copolymerized with ethylene oxide (EO). This leads to electroactive, water-soluble, and thermoresponsive poly(ethylene glycol) (PEG) derived copolyethers. Anionic homo- and copolymerization of fcGE with EO was possible. Molecular weights could be varied from 2000 to 10 000 g mol\(^{-1}\), resulting in polymers with narrow molecular weight distribution (M\(_w\)/M\(_n\) = 1.07–1.20). The ferrocene (fc) content was varied from 3 to 30 mol %, obtaining water-soluble materials up to 10 mol % incorporation of the apolar ferrocenyl comonomer. Despite the steric bulk of fcGE, random copolymers were obtained, as confirmed via detailed \(^{1}H\) NMR kinetic measurements as well as \(^{13}C\) NMR studies of the polymer microstructure, including detailed triad characterization. In addition, the poly(fcGE) homopolymer has been prepared. All water-soluble copolyethers with fc side chains exhibited a lower critical solution temperature (LCST) in the range of 7.2–82.2 °C in aqueous solution, depending on the amount of fcGE incorporated. The LCST is further tunable by oxidation/reduction of ferrocene, as demonstrated by cyclic voltammetry. Investigation of the electrochemical properties by cyclovoltammetry revealed that the iron centers can be oxidized reversibly. Further, to evaluate the potential for biomedical application, cell viability tests of the fc containing PEG copolymers were performed in a human cervical cancer cell line (HeLa). Significant cytotoxic behavior was observed with fcGE content exceeding 5%.
444 - Well ordered polystyrene-silica nanocomposites provided from perhydropolysilazane and partially epoxidized poly(styrene--block--butadiene--block--styrene)

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Perhydropolysilazane (PHPS) composed with Si-H and amino groups is an interesting and useful preceramic material to synthesize organic-silica nanocomposites. The good solubility of PHPS in many organic solvents and high reactivity of Si-H groups result in the combination of PHPS and the organic polymers having functional groups, such as hydroxy group, epoxy group, etc.

In this work, we have successfully synthesized highly transparent and hard polystyrene-silica nanocomposite films with well controlled microphase separation on the PET substrates from the blend solutions of PHPS and partially epoxidized poly(styrene--block--butadiene--block--styrene). The well arranged nanostructures were widely controlled by varying the PHPS content. The selective staining of polybutadiene domains in the TEM specimen indicated that silica domains selectively existed in the polybutadiene domains. The effects of solvent, PHPS content and heating of the coat layer in steam on the properties of the composites were investigated. Very smooth surface was formed from ethyl benzene/dibutyl ether mixtures, while the rough surface was formed from THF/dibutyl ether mixtures. It was due to the precipitation of the block copolymer by the preferential evaporation of THF. The complete conversion of PHPS to silica by heating at 70 °C in water steam was confirmed by FT-IR measurements by ATR method. The transmittance of the composite layer on the PET substrates measured by UV-Vis at 600 nm was higher than 97 %. The surface hardness of the coated film measured by pencil test reached 4H when silica was the matrix in the composites. Glass transition temperature and thermal decomposition behaviors were measured by DSC and TGA.

Tuesday, March 18, 2014 05:30 PM
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Temperature-responsive multilayer hydrogels provide a new platform for designing novel stimuli-sensitive coatings and microcontainers for controlled delivery. We present novel nanothin multilayer hydrogels of poly(N-vinylcaprolactam) (PVCL) with the reversible thermoresponsive behavior. The PVCL hydrogels were produced by selective cross-linking of PVCL in multilayers of PVCL-co-NH₂ copolymers assembled with poly(methacrylic acid) (PMAA) via hydrogen bonding. Non-cross-linked two-component films did not exhibit any temperature responsive shrinkage due to the presence of PMAA. After crosslinking, the nanothin multilayer hydrogels exhibit distinctive and reversible thermoresponsive behavior. We demonstrated that capsules of cubical and spherical shapes with PVCL hydrogel walls could be fabricated as hollow hydrogel replicas of inorganic templates. The temperature-triggered capsule size changes were completely reversible. The cubical capsules retained their cubical shape when temperature was elevated from 25°C to 50°C exhibiting the size decrease. Our work opens new prospects for developing biocompatible and nanothin hydrogel-based coatings and containers for temperate-regulating drug delivery, cellular uptake, sensing, and transport behavior in microfluidic devices.

**Diagram:**

- Glutaraldehyde 5%
- pH 7 – 8
- Heat
- Cool
- PVCL hydrogel

**Presentation Details:**

**Tuesday, March 18, 2014 05:30 PM**

**Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)**

**Location:** Dallas Convention Center

**Room:** Hall A
Saccharomyces cerevisiae yeast cells have been encapsulated in lightly cross-linked pH-responsive layer-by-layer (LbL) hydrogel nanoshells made from amine-functionalyzed polymethacrylic acid. Enhanced cell viability (90%) demonstrated high biocompatibility of such synthetic hydrogels in comparison to electrostatically assembled LbL shells. By keeping encapsulated cells above the isoelectric point, the cell proliferation process was suppressed and delayed in comparison to the cells held at pH below the pKa of methacrylic acid (pKa=5.0). At the same time, expression of green fluorescent protein was not affected by pH variation and showed stable green fluorescence at pH 7. Progressive ionization and charge accumulation within synthetic shells evoked a structural change in the outer shell which affected the membrane transport. We suggest that the variation in surface charges caused by deprotonation/protonation of unbound carboxylic groups in the nanoshells controlled cell growth and cell function, which can be utilized for external chemical control of cell-based biosensors. The ability to manipulate perceptible response from the encapsulated cells by keeping them in "dormant" conditions (constrained replication) for the extended time can be rewarding for biosensing applications when the early onset of cell growth can compromise the long-term performance.
447 - Self-assembly of magneto-plasmonic polymeric/inorganic nanoparticle hybrid vesicles with biomedical applications

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Both organic and inorganic nanoparticles (NPs) have been extensively explored as drug delivery vehicles. Among them, vesicles (i.e., liposomes or polymersomes) are particularly attractive because of their unique ability to encapsulate and deliver hydrophilic and/or hydrophobic compounds simultaneously. Incorporation of inorganic NPs into organic vesicular membranes can endow the system with new advanced functionalities while preserving all the well-established properties of the vesicles.

This paper describes a new strategy for the preparation of magneto-plasmonic polymeric/inorganic nanoparticle hybrid vesicles with both gold NPs (AuNPs) and magnetic NPs loaded in the polymeric vesicular membranes. The distribution of AuNPs and magnetic NPs can be tuned by controlling the lateral phase-separation of the two types of NPs in the membrane. We showed that both segregation and mixing of AuNPs and magnetic NPs within the vesicular membranes can be generated. We are working towards the understanding of the fundamentals behind the phase separation and find out the optimal structures for the multifunctional vesicles.

The magneto-plasmonic vesicles are simultaneously responsive to external magnetic field and light. These vesicles can be manipulated towards specific location with the assistance of magnetic field. Furthermore, the release of payloads from the vesicles can be externally triggered by AC magnetic field or NIR light. We envision that this method would be a general method to generate multifunctional vesicles with well-defined NP domains for various applications.
448 - Responsive properties of luminescent borinic acid polymers

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Preparation of thermally responsive polymers with tunable critical transition temperatures has been a major goal for polymer chemists over the past several decades. Here, a new class of materials is introduced, which takes advantage of the unique properties of borinic acid functional groups.

Well-defined borinic acid homo and block copolymers were synthesized for the first time via reversible addition-fragmentation chain transfer (RAFT) polymerization showing strong luminescence and a tunable upper critical solution temperature (UCST) in DMSO with different amounts of water. With trace amounts of water (from 0 to 2.5 % (v/v)) in DMSO, the UCST of the borinic acid polymer changes gradually from 20 °C (close to the melting point of DMSO) to 100 °C (boiling point of water). Hence the borinic acid polymer solutions in DMSO show potential for trace water detection. Meanwhile, the borinic acid polymers are also responsive to anions and diols, as a result of complexation to the borinic acid functional groups.

Tuesday, March 18, 2014 05:30 PM
Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Erick S. Vasquez, esv13@msstate.edu, Keisha B. Walters, I-wei Chu. (1) Swalm School of Chemical Engineering, Mississippi State University, Starkville, MS 39759, United States, (2) Institute for Imaging and Analytical Technologies, Mississippi State, MS 39762, United States

Nanoparticle based systems with one or more polymer phases attached have potential use in a wide range of applications, from nanometer-scale drug delivery to nanoparticle self-assembly for display and data storage to flow control in microfluidic devices. Here, polymer-metal nanocomposites, with one or two distinct polymer phases, were formed by a sequential synthesis: (1) particle retention on a solid substrate, (2) controlled radical polymerization, (3) particle release, and (4) an optional second back-fill polymerization. Fe$_3$O$_4$ was used as the core with polymer grafted in either a partial or complete shell. For the monophasic assembly, only one hemisphere of the nanoparticle has a grafted polymer. For the biphasic assembly, two chemically dissimilar polymers are grafted on separate hemispheres of the nanoparticle surface. The two polymers examined are responsive to pH (poly (methacrylic acid), PMAA) and temperature changes (poly (N-isopropyl acrylamide), PNIPAM). Thus, evaluation of the mobility and surface charge under different aqueous conditions becomes critical for future applications in in situ applications.

Significant differences were observed due to the macromolecular structure, chemical and physical (a)symmetry, and nano/microstructural conformation. A systematic study is presented to determine the effects of the chemical functionality and macromolecular structure on the isoelectric point, zeta potential, mobility and hydrodynamic diameter of the nanocomposite system. Molecular weight, pH, temperature and ionic strength are the environmental conditions that are compared for these systems.

Tuesday, March 18, 2014 05:30 PM
Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Nano- and microstructured layer-by-layer (LbL) assemblies have attracted considerable interest for various applications. In particular, one-dimensional LbL microtubes have been garnered interest for their ability to shrink or swell in response to changes in pH. Here, it is shown that temperature can also be utilized as a trigger for shape transformations, and the results are markedly different from the case where pH is used. Here, we report on the thermal behavior of LbL microtubes of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). PAH/PAA nanotubes were prepared using the polycarbonate (PC) membranes as porous templates. The thermal behavior of both freely released nanotubes and nanotubes bound to substrates was investigated in aqueous media as a function of temperature and time using confocal laser scanning microscopy and scanning electron microscopy. When free microtube suspensions were incubated at high temperatures, the microtubes became shorter, fatter, and ellipsoid in shape. In contrast, for the template-bound microtubes, periodic voids were formed on the surface following thermal treatment, which was suggestive of Rayleigh instabilities. In both cases, pronounced transformation occurred above the hydrated glass transition temperature of the PAH/PAA multilayer.
451 - WITHDRAWN
452 - Auto-exfoliation/regeneration functionality for CWA threat reduction

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In-the-field protection from of chemical warfare agents (CWAs) such as VX, sarin, or sulfur mustard is a challenging and important goal of the Second Skin concept. Our unique approach is to destroy these extremely toxic agents through the use of reactive catalytic compounds embedded in a reactive thin protective layer. This protective layer mimics living skin in that upon CWA challenge, it actively reacts with the agents, neutralizes the threat and then self-exfoliates, removing the contaminated layer and exposing fresh protective under-layers. We have expertise in network polymer systems (gels, polymer brushes and nanoparticles) that can be triggered to degrade and release upon appropriate chemical signaling events. These network systems can be loaded with appropriate catalytic compounds and the byproduct of the destruction of the CWA will auto-catalyze the degradation of the network. These systems are selective, sensitive and automated, requiring no secondary sensing or external triggering to activate. The chemistries lend themselves to additional function, such as release of secondary compounds that may be used to alert the user of contamination or shutdown and block underlying layers. This talk will disclose the chemical structures and materials that have successfully displayed a triggered response.

Tuesday, March 18, 2014 05:30 PM
Responsive Nanostructures and Nanocomposites (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Unilamellar liposomes of very low polydispersity were synthesized using 1, 2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and cholesterol as main bilayer-forming components. Poly(N-isopropyl-acrylamide) modified with hexylamine and 4-aminodiazobenzene was incorporated into the lipid bilayer. The hydrophobically modified polymer (HMP) showed more stability in comparison to control samples in the temperature range of 35-42°C. The liposomes were then loaded with the dye propidium iodide and were irradiated using a laser or laser diode. The release of the dye from the liposomes was monitored using fluorescence spectroscopy. The increase in fluorescence-intensity of propidium iodide is used to monitor the release of the dye. 4-aminodiazobenzene is known to show cis/trans-isomerization when irradiated, leading to the disruption of the liposomes. The amount of propidium iodide that can be released depends on three factors: 1) chemical composition of HMP, 2) spectral distribution and 3) intensity of the light source.
Carbon nanotubes (CNTs) are known to act as stress sensors, which can be monitored through the peak shifts of the Raman bands ($D$, $G$, and $G'$). Gel spun polyacrylonitrile/few-walled carbon nanotube (PAN/FWNT) composite fibers have been produced, and the stress-induced Raman band shifts in the FWNTs have been monitored to observe the stress transfer during fiber strain. Improvements in FWNT quality, enhanced FWNT dispersion, and post-processing conditions (fiber drawing) are shown to affect the efficiency of stress transfer from the matrix to the FWNT. Through monitoring of the RBM intensity of specific chiralities, the debundling of the FWNTs can be observed from the raw CNT state, to the solution state, and during the fiber processing stages. As-spun and drawn PAN/FWNT fibers containing 1 wt% FWNT show an increase of 12% and 16% in the tensile modulus, respectively. It is determined that when the stress induced Raman band shift reaches a plateau value as the macroscopic fiber is strained, the PAN-FWNT interface has broken down. Correlating this strain with the stress-strain curve of the PAN/FWNT fiber allows for the PAN-FWNT interfacial shear strength to be determined. The as-spun and fully drawn PAN/FWNT (99/1) fibers exhibit interfacial shear strengths of 13 and 40 MPa, respectively, suggesting that the fiber processing increased interfacial interaction. In addition, improvement in the FWNT dispersion led to a further increase in the interfacial shear strength to 60 MPa.
Polymersomes, artificial vesicles made out of amphiphilic block copolymers, have emerged as multifunctional nanostructures in the last decade. The possibility to tailor the chemical design of the membrane allows for a good control over the shape and the stiffness of the vesicle. This has been demonstrated in a number of reports regarding conformational changes of polymeric assemblies. For instance, by applying an osmotic pressure difference over the membrane of polymersomes consisting of poly(ethylene glycol)-block-polystyrene (PEG-b-PS) block copolymers we managed to construct bowl-shaped vesicles containing a mouth, so called stomatocytes. This transformation was proven to be reversible in a controlled way by the introduction of plasticizing agents for the hydrophobic segment of the membrane.

In this presentation we show the latest results of our enduring investigation towards shape transformations of polymeric vesicles. We demonstrate that the addition of an excess of a bicyclo[6.1.0]nonyne (BCN)-crosslinker to a dispersion of polymersomes consisting of poly(ethylene glycol)-b-poly(styrene-co-4-vinylbenzyl azide) (PEG$_{44}$-b---P(S-co-4-VBA) polymers, can cause them to stretch into a tubular morphology. We show that this shape transition strongly depends on the architecture of the block copolymer and the concentration of the crosslinker. Furthermore, we show that the elongation can be reversed by means of a crosslinker with a cleavable disulfide bond.
Preparation and characterization of porous asymmetric polyvinylidene fluoride (PVDF)/multiwall carbon nanotube (MWCNT) mixed matrix membranes

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The important of compatibility of polymers with additives can often play a significant role in the physical modification of the membrane polymer. The role of organic and inorganic additives, such as methyl cellulose, glycerin, poly(vinyl pyrrolidone), poly(ethylene glycol) (PEG), water and zinc chloride (ZnCl₂) in casting solutions has been used as additive that enhances the permeation properties of membrane polymers. Inorganic salt additives in casting solutions are known to change the solvent properties or the interaction between the macromolecular chains. In this study, effect of LiCl addition on pure PVDF and composite membranes were studied. Different PVDF membranes composition were prepared. Different percent of LiCl were added to PVDF membranes to study their effect on membrane performance. Addition of LiCl will enhance mechanical and physical properties of pure and composite the membrane. The hybrid membranes containing the MWCNTs were characterized by higher rejection value than the polymeric membranes. The rejection values are improved up to 95% when using 1% LiCl. Figure 1 present images of different pure PVDF and composite membranes contain different LiCl percentage.
457 - Multilayered composites with high aspect ratio nanoplatelets/low Tg phosphate glass: Controlled interdiffusion and improved barrier properties

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It has been shown that through interdiffusion of polymers in microlayer systems, an increase in the concentration of inorganic particles can be observed in one of the component layers if there is a mismatch in mobilities of the polymers when annealed in the melt. Convective flow or the moving boundary phenomenon of the more slowly diffusing molecules can be observed opposite that of the faster diffusing molecules. The result is shrinkage of the faster diffusing composite layers and the formation of a more tortuous pathway for diffusing penetrants, thus increased barrier properties. This study expands on previous studies with polyolefin systems (LLDPE/LDPE, LLDPE/HDPE) differing in molecular structure/branching while also analyzing this effect in water soluble polyethylene oxides of different molecular weights (POLYOX™ WSR 100,000 and 1,000,000 MW). Nanoplatelet (montmorillonite, synthetic mica, and xGnP® graphene) dispersions were optimized through melt processing and solvent blending at multiple loadings. Low Tg phosphate glass (Pglass: Tg = 75 ± 3°C and 135 ± 3°C) composites were also studied for the creation of high aspect ratio sheets through particle coalescence with interdiffusion and other post processing techniques to drive platelet formation. The microlayer systems were processed through multilayer coextrusion. The morphology changes of the layered systems and their particulates were observed through various stages of interdiffusion and related to gas transport and fire barrier properties.
458 - Dual stimuli - dual response nanoassemblies prepared from a simple homopolymer

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A dual stimuli responsive nanogel-polyelectrolyte complex based on electrostatic coating has been developed. The nanoassembly is designed to elicit two disparate responses (viz. surface property change and guest encapsulation stability) from two different stimuli (viz. pH and redox variations). In this complex, the polyelectrolyte has charge-conversional features - i.e. the charge in the polyelectrolyte will change from negative to positive charge at low pH. The nanogel(NG) is capable of sequestering hydrophobic guest molecules that are released in response to change in the redox environment. The nanogel has a positively charged surface so as to complement the polyelectrolyte during the complex formation. We have shown that a change in the polyelectrolyte charge, in response to lowered pH, compromises this electrostatic complementarity. As shown in Figure 1, the dissociation event causes a change in the surface properties of the nanoassembly.

It has been proved (shown in Figure 2) that electrostatically bound polyelectrolyte enhances the encapsulation stability of the hydrophobic guest molecules inside the nanogel. Dissociating the polyelectrolyte from the nanogel and then subjecting it to a reducing condition causes the guest molecules to be released from the nanogel.
A stimulus responsive or "smart" polymer will respond to stimuli such as solvents, temperature, counter ions, electrical current, pH, or mechanical pressure. One of the most highly studied stimulus responsive polymers is poly(N-isopropylacrylamide) (PNIPAM) due to its potential uses in surface coatings, microfluidics and drug delivery. PNIPAM, a thermoresponsive polymer, exhibits a lower critical solution temperature (LCST) in aqueous solutions. Covalently-bound composite polymer grafts of poly(N-isopropylacrylamide)-c-poly(N-acryloxysuccinimide) (PNIPAM-c-PNASI) and aminated silica nanoparticles were deposited onto a silicon wafer using covalent layer-by-layer assembly. It is known that when grafted to a surface, these polymers’ response to external stimuli causes measureable changes in the surface topography and wettability. In similar polymeric systems, the restructuring of the surface in response to external stimuli is known to affect the Young's elastic modulus. This investigation focuses on altering the elastic modulus of the polymer graft by varying the temperature or by the addition of counter ions to solution. Using colloidal probe microscopy the mechanical properties of the films were investigated. The Hertz contact mechanics model was used to extract the Young's elastic modulus from a series of force distance curves. The elastic modulus was shown to nearly double when the temperature of the polymer composite graft was raised above the LCST in water. The elastic modulus was found to be responsive to variations in exposure for a range of temperatures, counter ions and solvents.
460 - Self-cleaning membrane for increased lifetime of subcutaneous glucose biosensors

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Subcutaneous glucose biosensors suffer from limited lifetimes due to biofouling associated with the host response. Thermoresponsive poly(N-isopropylacrylamide) (PNIPAAm) hydrogels may achieve “self-cleaning” via transdermal thermal cycling above and below the volume phase transition temperature (VPTT) to cause cellular detachment. Conventional, single network (SN) PNIPAAm hydrogels are limited by their poor mechanical properties and thermosensitivity. In contrast, double-network (DN) hydrogels are associated with enhanced mechanical properties as well as a high degree of swelling. In this work, DN PNIPAAm-based hydrogels were modified to achieve these properties. First, nanocomposite membranes were prepared by the incorporation of polysiloxane nanoparticles. Second, an electrostatic comonomer [2-acrylamido-2-methyl-propane-sulfonic acid (AMPS)] introduced at varying levels into the first network. The resulting VPTT, morphology, deswelling/re-swelling behavior, mechanical properties and glucose diffusion was evaluated and compared to SN.
461 - Grafting from macro- and nano-scaled shape memory substrates enabling the fabrication of physically and chemically dynamic surfaces and nanoparticles

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Surfaces and nanoparticles with switchable properties, such as adhesion, wetting, aggregation and optical properties, have generated interest in the field of smart materials for their potential applications in drug delivery, tissue engineering, cell culture, biomimetics, biosensors, coatings, and textiles. Herein, we present a novel technique to achieve switchable surface chemistry that utilizes surface-initiated ARGET ATRP (Activators ReGenerated by Electron Transfer Atom Transfer Radical Polymerization) from shape memory elastomers to physically manipulate the grafting density of polymeric brushes of oligo(ethylene glycol) methacrylates. Using shape memory presents a unique opportunity to fabricate surfaces with switchable properties; a physical shape change can be predetermined and programmed, allowing brushes to be grafted from the surface while the material is in a secondary shape. The primary shape is recovered by the application of an external stimulus, such as heat, triggering a change in the brush density, and thus the surface characteristics of the material. This technique has been demonstrated on the macroscale from flat surfaces, as well as on the nanoscale from particles. Interesting surface wrinkling behavior has been observed on the macroscale surfaces upon a shape memory transition, indicating a transfer of tension between the layers. These surfaces have been characterized with contact angle, XPS, AFM, and SEM. This work has been extrapolated to shape memory nanoparticles, which have been characterized with DLS, NMR, and SEM.
Recenty, there has been interest in preparing micellar drug-delivery vehicles that expel pharmaceuticals in both a spatially and temporally controlled manner upon application of pH, magnetic, or thermal stimuli. In the work described herein, the physical properties, drug loading capacity, and release profiles of thermoresponsive block copolymers bearing a series of novel bio-derived pyrrolidone-based hydrophobic blocks were measured. The results of our investigation show that only minor adjustments to the hydrophobic block are required to tune the properties and performance of these systems that exhibit a cytotoxic effect on breast cancer cells (MCF-7 line) upon application of a thermal stimulus. Indeed, such studies are critical to gaining a comprehensive understanding of the influence that core-structure has on drug loading and thermoresponsive release phenomena, information that is vital for future core-segment design.
Silver cation-exchanged montmorillonite clay is prepared by exchanging cations present in the interlayer spaces of purified montmorillonite (MMT) by Ag(I) ions. Ag⁺ cations present in the ion-exchanged montmorillonite clay are used to oxidatively polymerize anilinium ions to polyaniline (PANI) for the synthesis of the PANI/Ag/MMT composite. PANI nanofibers and silver nanoparticles are intercalated into the interlayer spaces of clay and are bonded to the outer layers as well, in the nanocomposites. The nanocomposites are characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermo-gravimetric analysis (TGA), X-ray fluorescence (XRF) studies, electrochemical methods, DC conductivity measurements, and AC impedance measurements. XRD patterns of composites depict that the intercalation of PANI into the interlayer spaces of MMT by studding the d spaces of (100) plane of MMT at different temperatures and the XRD data also reveal the presence of silver particles as well. Electronic conductivity of PANI has been enhanced by 2 order of magnitude from that of conventional PANI/MMT composite prepared using persulphate as the oxidizing agent. This is due to the deposition of silver nanoparticles in between PANI chains which are supporting the interlayer electronic movement. AC impedance analysis has also proven that the electronic component of conductivity has been increased. Mechanical and thermal stabilities have also been improved from those of neat polymer or neat metal due to their incorporation of within the montmorillonite clay layer spaces. The gas adsorption ability of the clay particles, catalytic properties of noble metals and those of the PANI could also be improved due to the synergistic effects of the two components when they are intercalated within the layer spaces of MMT. As such, although the neat components do not show any oxygen reduction ability the nanocomposites have this remarkable oxygen reduction ability as shown by the cyclic voltammetric studies of the components and the nanocomposite in the N₂-purged, air-purged and O₂-purged solutions. Such cheap and mundane materials as clay would then find as a competitor for very expensive Pt or Pt/Rh catalysts that are used as cathode materials in fuel cells.
Biofouling, the process of microorganisms accumulating on surfaces, causes considerable damage in various settings such as medical clinics, food processing industries and marine environment. In order to reduce biofouling, initial bacterial attachment to surfaces must be inhibited. Smart surfaces, like Poly-(N-isopropylacrylamide) (PNIPAAm) brushes are known to trigger bacterial detachment. PNIPAAm in aqueous environment undergoes a reversible phase transition from hydrophilic to a relatively hydrophobic state when exposed from below to above its lower critical solution temperature (LCST 32°C). We quantitatively studied the effect of applied shear force on bacterial detachment from PNIPAAm brushes above and below its LCST. We also investigated the effect of PNIPAAm brush thickness and nanoscale defects on critical shear force ($\tau_{50}$), 50% bacterial detachment. Nanoscale parallel defects on PNIPAAm brushes were achieved by patterning the ATRP initiator, immobilized on a glass surface, using a laser assisted interferometric lithography followed by ARGET-ATRP reaction. *Cobetia marina*, known to attach to hydrophobic surfaces, was used as a model fouling bacteria for the studies. Controlled shear force was applied using a spinning disk apparatus consisting of a rotating shaft powered by a DC motor and submerged in artificial sea water. Bacterial detachment profiles obtained from spinning disk assays were fitted using a sigmoidal equation to determine the $\tau_{50}$. We observed that (i) $\tau_{50}$ for flat PNIPAAm brushes decreased significantly by about 40 N/m² as the temperature was altered from above to below its LCST, (ii) $\tau_{50}$ values were affected by PNIPAAm brush thickness below the LCST and can be related to its surface wettability and (iii) nanoscale surface defects on PNIPAAm brushes do not alter its bacterial detachment efficiency relative to uniform flat brushes. Our work demonstrates the potential of stimuli responsive polymers, like PNIPAAM, to be used as regenerable fouling-release surfaces.
A large amount of agricultural and industrial water in the U.S. and worldwide is polluted by different types of contaminants that can impact human health. Removing contaminants from waste water by absorbent materials made from abundant, low cost natural polysaccharides is a feasible approach to deal with this severe problem. In this research, a series of bi-polymeric beads from alginate combined with other natural polysaccharides, e.g. cellulose, starch, lignin, were synthesized. Their average diameters and size distributions in both dried and wet conditions were assessed by optical microscopy. Differences in morphology of these beads were observed by SEM.

The swelling ratio for water uptake and their mechanical properties were also investigated in relationship to their composition and their surface characteristics. The beads were evaluated in regard to their entrapment capacity for specific contaminants and the potential regeneration of the sorbent material. Various ways were explored to tailor their surface chemistry for higher efficiency in the entrapment and release process.
466 - Formaldehyde-free phenolic resin

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As the first commercial synthetic resin, phenolic resins have played an indispensable role in the resin industry with wide ranging applications, from commodity construction materials to electronics and aerospace. Un-reacted formaldehyde (a known carcinogen) from these resins, has posed serious challenges in terms of worker safety and human exposure during the product’s life cycle. This is the main motivation for substitution of formaldehyde with non-toxic co-monomers and development of a more sustainable route to the synthesis of phenolic resins with comparable properties. Here we report the synthesis of novel class of formaldehyde-free phenolic resin using naturally occurring aldoses as a replacement for formaldehyde.

Novolacs were synthesized by the reaction of phenol with glucose in the presence of Zinc acetate at 120°C. Preliminary spectroscopic characterization (FTIR) of the resulting viscous resin indicates spectral signatures similar to commercial phenol-formaldehyde novolac resin. These novolacs can further be cross-linked using multifunctional cross-linkers such as hexamethylenetetramine. The thermal analysis of the cured resin indicated satisfactory results. This research has the potential to transform this well-established resin industry by replacing toxic starting materials with safer bio-based alternatives (bio-derived phenols, naturally occurring aldehydes and benign catalysts).

Tuesday, March 18, 2014 05:30 PM
Sustainable Polymers, Processes and Product Applications (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
467 - Preparation of polycarbonate polyols from carbon dioxide and epoxides

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As a cheap, abundant and renewable resource, carbon dioxide is copolymerized with epoxides to produce polycarbonates, and examples have been commercialized in several countries. Recently, the production of low molecular weight polycarbonate diols and polyols has attracted a lot of attention. Such polyols are important building blocks for polyurethanes.

(salen)CoX catalysts are effective for preparing polycarbonates from carbon dioxide and epoxides. Using trifluoroacetate as the X ligand, polycarbonate polyols can be produced by adding water to the reaction mixture (below). Water acts as a chain transfer agent. By varying the amount of water added, the molecular weight of the polycarbonate polyols is controlled.

The effect of amount of water on the molecular weight will be presented. The use of different epoxides to give different polycarbonate polyols will also be explored. These polycarbonate polyols will further be used as initiators for the polymerization of lactide and lactones to give A-B-A type triblock polymers.

References

With increasing concerns about environment and sustainability and depletion of petroleum, more attention has been paid to the uses of renewable feedstock for the production of bio-based materials. Vegetable oil-based epoxy compounds are useful precursors which have a variety of applications in coating, adhesives, polyurethane foams, and composites. Crude glycerol is a low-value byproduct of biodiesel production process—transesterification of vegetable oils or animal fats with alcohols. Compared to pure glycerol, crude glycerol contains various impurities such as methanol, water, fatty acids, fatty acid methyl esters, soap, and glycerides. The present work provides an alternative way for the synthesis of multi-armed epoxy compounds using crude glycerol as a sole feedstock. The produced intermediates and epoxy compounds were characterized by FT-IR, \(^1\)H NMR, GPC, rheometer, and DSC. Crude glycerol derived multi-armed epoxy compounds show comparable properties to vegetable oil-based epoxy compounds and have potential applications in coatings, adhesives, and polyurethane foams.

Scheme 1. Synthesis of crude glycerol derived multi-armed epoxy compound (linoleic acid is used as a representative fatty acid in crude glycerol)
Dimer acid and its ester derivatives were synthesized using waste vegetable oil based by Diels-Alder reaction of fatty acids and esterification to use them as renewable plasticizer for ethyl cellulose. Dynamic mechanical data revealed that these renewable plasticizers presented fairly good incorporation and plasticizing performance. It was observed that dimer acid exhibited enhanced plasticizing behavior, compared with dimer acid esters, probably due to the interaction between ethyl cellulose containing OH group and dimer acid containing carboxylic acid.

It was found that the DA and its esters with short alkyl chain length behaved as effective plasticizer. In the case of esters with relatively longer alkyl chains, their plasticization was less effective, which is due to lower polarity, compared to the ester with shorter chain.
To enhance impact strength of polyketone (PK), two types of rubber were melt-blended; ethylene-octene rubber (EOR) and maleic anhydride-grafted EOR (mEOR). For both of PK/EOR and PK/mEOR blends, impact strength did not increase with increasing rubber content. The FESEM fracture surface morphology (the top two photomicrographs) indicated poor miscibility between the components, showing large rubber particles and clean interface.

We introduced polyamide 6 (PA6) as a polymeric compatibilizer to the blends. Incorporating PA6 to PK/EOR blend was not effectual. Impact strength was just comparable to PK/EOR blends, and morphology also was not improved (bottom left). The incorporation of PA6 to PK/mEOR blend, however, appeared to compatibilize the blend effectively. Impact strength increased with increasing rubber content, and particle size of the rubber was significantly reduced (bottom right). The compatibilizing effect of polyamide on polyketone/rubber blends will be presented.
Epoxidized sucrose soyate is a novel bio-based epoxy resin derived from sucrose and soybean oil fatty acids, and it contains up to 12 epoxy functional groups per molecule. This epoxy resin was crosslinked with cycloaliphatic anhydride, i.e. methyl hexahydrophthalic anhydride, to form polyester thermosets with high crosslink density; this epoxy-anhydride reaction was catalyzed using a zinc-complex catalyst. In this project, we examined the effect of composition variables, i.e. anhydride-to-epoxy molar ratio and catalyst loading, on the chemical, mechanical and thermal properties of the matrix resin. The chemical property was investigated through soxhlet extraction method, which provides us the amount of insoluble materials and the chemistry of the soluble materials. Then, the mechanical properties were studied through tensile test method, which provides us the tensile strength, Young's modulus and elongation at break. Finally, thermal properties were assessed through dynamic mechanical analysis (DMA), which provides us the polymer's glass transition temperature and crosslink density. The experimental results can then be analyzed through a design of experiment (DOE) study to obtain a formulation with the optimum properties. Figure 1 shows the DOE results of the tensile strength measurement.
Polyethersulfone (PESU) is a widely used commercial thermoplastic that is known for its toughness and stability at high temperatures. PESU allows easy manufacturing of membranes with reproducible properties, low protein retention, and durability in extreme environments. Such membranes can be used in applications like hemodialysis, waste water recovery, and gas separation. The current limitations in membrane research are control of surface properties such as pore size, surface roughness, and anti-fouling capabilities. These issues are typically addressed through surface treatments and chemical modifications to the polymer chains. Such treatments can be costly and harmful to the environment surrounding the membrane; therefore, it is the goal of this research to develop a fundamental understanding of the surface behavior of the unmodified PESU systems. Flexible polymer systems have exhibited segmental density distribution near their surfaces due to chain-end localization to the polymer-air interface, however this behavior is not well understood for rigid-rod systems. This research provides a study of the surface and interfacial chain-end behavior in PESU solution cast films. Commercial PESU was fractionated and characterized using static and dynamic light scattering, gel permeation chromatography, and differential scanning calorimetry. Chain-ends were characterized via GATR-FTIR, fluorescence labeling, static and dynamic contact angle, and atomic force microscopy. Experimental results were correlated with molecular dynamics simulations to develop a model of chain-end localization in rigid rod systems.
Many studies have been carried out using phase-selectively soluble polymer-supported catalysts and reagents. Our past work has focused more specifically on alkane-soluble polymeric ligands that facilitate separation of catalysts from polar products that partition into a polar phase most often using polymer bound versions of ligands that strongly coordinate to transition metals. However, while ionic immobilization of catalysts on insoluble polymers using quaternary ammonium catalysts is known, there are few examples where quaternary ammonium salts that form solvent separated ion pairs are used to recycle catalysts using a very nonpolar heptane phase. This paper will describe how vinyl-terminated polyisobutylene (PIB), a commercially available, low cost, and non-toxic polymer, can be used to prepare heptane soluble quaternary ammonium salts that can be used to potentially recycle homogeneous catalysts. Several routes to these ionic ligands will be described along with qualitative and quantitative studies of the phase selective solubility of PIB-bound tetraalkylammonium dye salts and tetraalkylammonium perruthenate salts. Strategies that use these heptane soluble salts in solvent mixtures that involve liquid/liquid separations after either thermomorphic reactions or in latent biphasic chemistry will be described along with studies using polyolefins as solvents for these hydrocarbon species.

Tuesday, March 18, 2014 05:30 PM
Sustainable Polymers, Processes and Product Applications (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
474 - Free radical polymerization of deep-eutectic solvents

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Deep-eutectic solvents (DESs) formed between a variety of acrylates and ammonium salts exhibit certain properties of ionic liquids that make them suitable for free-radical frontal polymerization. The use of DES not only as a monomer but also as the solvent prevents the use of additional solvents and offers a green tool for the synthesis of functional polymers.

We have taken advantage of the customizable composition of polymerizable DESs to incorporate counterparts such as drugs. By the proper combination of these components, a series of drug delivery systems were designed. For instance, by using different acrylates, the polymer swelling can be controlled by temperature, pH, ionic strength, etc., and hence, the release of the drug from the resulting polymer.

On the other hand, the outstanding capability of DESs as solvents allows dispersing carbon nanotubes. Interestingly, the resulting poly(acrylic acid)/carbon nanotubes composites can undergo swelling depending on pH because of the polyelectrolyte character of poly(acrylic acid), but the nanotubes let the formation of a macroporous structure after submission to a freeze-drying process.

Finally, it is possible to control the porosity at different scales by increasing the degree of crosslinking in polymerized DES. Since one of the components acts as precursor (monomer) and becomes part of the network structure while the other one (ammonium salt) acts as guest molecule, the prepolymerization structure of DES can be captured by free radical polymerization.
475 - Impact of reaction conditions on architecture and rheological properties of starch graft polyacrylamide polymers

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We carried out experiments examining the impact that solvent selection and reaction conditions have on the radical initiated graft polymerization reaction of acrylamide onto starch. We have also evaluated the rheological properties of the starch graft polyacrylamide product when a gel is formed in water. It was found that when the reaction was carried out in DMSO, the molecular weight and the number of anhydroglucose units in between grafting sites (AGU/site) decreased. For example, when conducted in water, the number average molecular weight of the polyacrylamide grafts could be as high as 448822 with 6723 AGU/graft, when DMSO was the solvent the molecular weight could be as low as 14013 with 136 AGU/graft. Polyacrylamide content could be measured by %N or by IR (Figure). These differences could be observed in the rheological properties of the resulting gels in water. The linear range rheological property analysis of the two types of gels (water and DMSO) suggested that water-made starch-polyacrylamide graft copolymers should be 'weak' gels at lower concentrations (<7%), but be 'strong' gels at higher concentrations (≥9%); however, the DMSO-made starch-polyacrylamide graft copolymer should be 'weak' gels at all measured concentrations. The ability to control and generate starch graft polymers with dramatically different architecture may allow starch to be tuned to deliver improved properties for current or new applications.
476 - Optimal extraction of chitin from underutilized sources

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Found in everything from fungi walls, insects and crustacean shells, chitin has already seen a significant use in a variety of fields. However, despite the wide variety of sources, most research and commercial applications focus on a small subsection of known source material. We have begun to investigate some underutilized source materials including crawfish, mealworms, and cicadas with the ultimate goal being a test of their commercial viability.

Our research shows that although chitin derived from any source has the same basic properties, including percent deacetylation, the optimal extraction conditions for each can vary wildly. For example, astaxanthin is found in rather large quantities in crawfish giving rise to the red shell. Removing astaxanthin with acetone in crustacean shells is straightforward but completely unnecessary in mealworm and cicada samples. We will show the results of an extensive survey of how these different extraction procedures affect the resulting chitin and the optimal extraction procedures for each species studied.
On-demand dismantlable adhesion system using acrylate block copolymers in response to photoirradiation and postbaking as dual stimuli

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We report the organotellurium-mediated living radical polymerization (TERP) using dialkylditellurides in the presence of a binary azo initiator system with different decomposition rates for the facile synthesis of high-molecular-weight block copolymers containing a polar side group. The block copolymers containing the poly(tert-butyl acrylate) (PtBA) sequence as the reactive segment and the random copolymer sequences of n-butyl acrylate (nBA) or 2-ethylhexyl acrylate (2EHA) with 2-hydroxyethyl acrylate (HEA) as the adhesive segment were synthesized. The produced block copolymers exhibited a high performance for the dismantlable adhesion responding to the dual external stimuli of photoirradiation and postbaking in the presence of a photoacid generator. The change in the peel strength before and after the UV irradiation and postbaking was investigated and the mechanism of the superior adhesion and dismantling properties of the block copolymer adhesives was revealed based on the results of the peel test, DSC and AFM analyses of the adhesives, as well as the model reactions of the cross-linking formation by transesterification. We have demonstrated that the precisely-controlled living radical polymerization technique is important for the fabrication of high-performance adhesive polymer materials with high molecular weights and a controlled molecular weight distribution containing polar repeating units.
478 - Sustainable antimicrobial coatings from resin acids

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Microbial contamination of material surfaces have been problematic in many areas including medical equipment and apparel in hospitals, medical implants, textiles, food packaging and storage, water purification systems and marine equipment. Medical device associated infections significantly contribute to nosocomial infections which have become a devastating and life threatening problem to patients. Bacterial biofilms on medical device surfaces are difficult to eradicate because they exhibit dramatically decreased susceptibility to antimicrobial agents. Despite the presence of efficient surface sterilization techniques there is a great demand for surfaces which can resist bacterial colonization. A major challenge in this field is to develop low-cost antimicrobial materials that kill a broad spectrum of bacteria, but offer significantly low toxicity to human cells. Widely abundant natural resin acids, which are chemically-modified into cationic compounds, efficiently inhibit growth of a wide range of Gram-positive and Gram-negative bacteria, with no or minimal toxicological effects to human cells. We prepared sustainable antimicrobial coatings from resin acids by covalently grafting resin acid derived cationic compounds on to glass surfaces. These contact active coatings exhibited surprising antibacterial properties as well as reduced formation of biofilms. We believe by grafting the surfaces using polymers with pendant cationic moiety will enhance the antimicrobial properties and we can extend the procedure to modify surface of medical devices and implants.

References:


Sustainable Polymers, Processes and Product Applications (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
479 - Use of polypropylene-based oligomers as supports for homogeneous catalysts

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This talk will describe recent efforts toward the development and use of phase-selectively soluble, terminally-functionalized, polypropylene-based supports for greener, recoverable catalysts and reagents.

Tuesday, March 18, 2014 05:30 PM
Sustainable Polymers, Processes and Product Applications (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
480 - Spatial and temporal control of polysaccharide hydrogels through the thiol-norbornene reaction

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The use of hydrogels in biomedical applications provides controlled extracellular matrix mimics to study cell behavior in relation to the cell microenvironment. Moreover, the ability to pattern chemical and mechanical signals in these hydrogels provides complexity akin to that found in biological tissues. Current hydrogels for these studies have a limited range of properties and are crosslinked with chemistry that does not decouple mechanical properties from changes in chemical signals. Here, we present crosslinking of hyaluronic acid and carboxymethyl cellulose (renewably sourced polysaccharides) with thiol-norbornene chemistry that permits orthogonal photopatterning reactions and extensive hydrogel modification. To obtain this control, the polysaccharides were functionalized with pendent norbornene groups that were crosslinked with a di-thiol linker through a UV-light initiated reaction. By limiting the extent of initial norbornene conversion, secondary photopatterned reactions were able to orthogonally and spatially modify mechanical properties and molecule presentation.
Poly(lactic acid) (PLLA) melt-pressed films with low crystallinity were crystallized either by thermally-induced crystallization or by stretching at a constant strain rate. The strain-induced crystallization, thermally induced crystallization and enzymatic degradation of drawn PLLA films in the presence of proteinase-K at 37°C was investigated using weight loss measurements, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy. The results show that drawing has a significant effect on the crystallinity, molecular orientation, and enzymatic degradation whereas thermally induced crystallization effects only crystallinity. The absorbance ratio of the bands at 921 cm\(^{-1}\) and 956 cm\(^{-1}\) (\(A_{921}/A_{956}\)) was chosen to determine the structural changes during strain-induced crystallization and hydrolysis. The DSC crystallinity and \(A_{921}/A_{956}\) showed an increase with the draw ratio. Since we were unable to obtain the transition moment angle for the bands at 921 and 956 cm\(^{-1}\), the dichroic ratios were compared. It was found that the crystalline orientation develops rapidly at lower draw ratios whereas the amorphous orientation develops much more slowly. The enzymatic degradation of annealed PLLA films showed quite different results from the enzymatic degradation of oriented PLLA films. The extent of degradation was lower for the drawn PLLA film than for the undrawn melt-pressed PLLA film. The DSC crystallinity and \(A_{921}/A_{956}\) of drawn PLLA films increased with the degradation time, suggesting an increase in the crystalline phase with degradation. This reveals that degradation occurs in both the free and the restricted amorphous region in the case of drawn PLLA films, whereas it occurs only in the free amorphous phase.

[Figure1]
Recycling of homogeneous catalysts generally and of Ru-catalysts used in metathesis chemistry is an important unsolved problem. This study will discuss how polyolefins and polyethylene (PE olig) in particular can be used as supports and/or solvents to recover Ru-catalysts or separate its residues from products. For example, by using a polyethylene-supported catalyst that is soluble hot and insoluble cold, we have shown that it is possible to affect both ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions with separation of products and catalysts or catalyst residues. In these cases, the quantitative insolubility of these catalysts or its residues and the products' solubility allowed the products to be separated at room temperature as solutions from the insoluble catalysts. These polyethylene-bound second-generation Hoveyda-Grubbs catalysts were formed using N-heterocyclic carbene ligands that contained polyethylene oligomers. Based on other work where polyisobutylene-bound (PIB) species that are phase selectively soluble in heptane have been used for catalyst recovery, other still ongoing work is exploring additional strategies where unfunctionalized polyethylene (Polywax) is used as a solvent in place of heptane to recover either PIB- or PE olig-bound catalysts. Such waxes are low viscosity liquids at ca. 75 °C but separate as solids or gels at room temperature. The results of both of these studies are that products can be prepared with substantially lower Ru contamination. For example, ROMP products have been prepared with 7.48 ppm Ru residues.
483 - Influence of miscanthus variety on the properties of polypropylene-based composites

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The objective of the overall work is to compare the relative and absolute performances of plant-based filled composites coming from several genotypes of miscanthus. For some genotypes, the influence of the stem section and composition (cellulose/lignin content) will also be investigated. Stems have been used as such, without any treatment except drying. In order to perform this comparison, it is an absolute request that any change in the final mechanical performances of composites is due to the filler and not to any other reason. There are many parameters must controlled before being able to make a direct comparison between the different plant samples and be sure that the differences are directly assignable to the reinforcing fibers and not to any other parameter. We defined a clear, traceable and robust 10-step methodology going from the reception of humid miscanthus stems to the mechanical properties of polypropylene-miscanthus composites. The influence of miscanthus variety will be described. Results show a small influence of genotype, as illustrated on Figure 1 (influence of height of the genotype on strength).

[Fig 1]

Tuesday, March 18, 2014 05:30 PM
Sustainable Polymers, Processes and Product Applications (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
The synthesis of functional polymers with well-defined structure, end-group fidelity and physico-chemical properties useful for biomedical applications has proven challenging. Chemo-enzymatic methods are an alternative strategy to increase the diversity of functional groups in polymeric materials. Specifically, enzyme-catalyzed polymer functionalization carried out under solventless conditions is a great advancement in the design of green processes for biomedical applications, where the toxicity of solvents and catalyst residues need to be considered. Enzymes offer several distinct advantages, including high efficiency, catalyst recyclability, and mild reaction conditions.

In our research, we aim to precisely functionalize polymers using two methods: Enzyme-catalyzed functionalization via polymerization and chemo-enzymatic functionalization of polymers for drug delivery. In the first method, well-defined poly(caprolactone)s were generated using alkyne-based initiating systems catalyzed by CALB. Propargyl alcohol and 4-dibenzocyclooctynol (DIBO) were shown to efficiently initiate the ring opening polymerization of ε-caprolactone under metal free conditions and yielded polymers with \( M_n \) 4 to 24 KDa and relatively narrow molecular mass distribution. In the second methodology, we present quantitative enzyme-catalyzed transesterification of vinyl esters and ethyl esters with poly(ethylene glycol)s (PEG)s that will serve as building blocks for dendrimer synthesis. \(^1\)H and \(^{13}\)C NMR spectroscopy, SEC and MALDI-ToF mass spectrometry confirm the structure and purity of the products.
485 - Impact of polyethylene oxide on the assembly of lignin structure in solution

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Carbon fiber produced from lignin has recently become a promising scalable product with potential uses ranging from thermal insulation to reinforcing automobile bodies. The utilization of lignin for carbon fiber production offers a cheap, stable, renewable source, unlike current petroleum based precursors, such as polyacrylonitrile whose cost fluctuates with the petroleum industry. Depending on the source of the lignin, the resultant molecular structure has varying ratios of the monolignols, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The different molecular structures can affect the assembly of the lignin in solution during processing, which will impact the physical properties of the final product. Previously, lignin-based carbon fiber research has shown that mixing 1-2 wt. % polyethylene oxide (PEO) with the lignin before fiber formation can enhance the properties of the final carbon fibers. The purpose of this research is to study the role of the PEO on the assembly of the lignin in solution by monitoring the structure of lignin from different sources in solution with and without PEO. The molecular assembly of lignin in solution was characterized by small angle neutron scattering, where deuteration of the solvent, dimethylsulfoxide, and PEO provides the required contrast. Initial results indicate the addition of PEO increases the aggregation behavior of some lignins, but appears to have the opposite effect on others, by breaking up the aggregates.
486 - WITHDRAWN
Collaboration between Virginia Tech and the University of Texas at Austin has demonstrated that disulfonated poly(arylene ether sulfone) copolymers are attractive candidates for reverse osmosis and several other water purification technologies. These sulfonated copolymers are much more resistant to chlorine derivatives than the state-of-the-art aromatic polyamide thin film composite. Recent fundamental studies of the linear sulfonated copolymers have investigated the tradeoff relationship between salt rejection and water permeability, the effect of free volume on water permeability and the influence of processing history. These materials have demonstrated high water permeability, but salt rejection needs to be further improved for reverse osmosis applications. A systematic series of controlled molecular weight 4,4'-biphenol and bisphenol-A based partially disulfonated polysulfones were synthesized with amine terminated endgroups, which could be further functionalized to afford acrylamide, phenylethynyl phthalimide and maleimide crosslinkable oligomers. Gel fractions up to 99% were achieved, effectively reducing the swelling of the membrane in water and leading to enhanced salt rejection. Several systematic series of crosslinked copolymers with varying degrees of sulfonation were investigated for their transport properties, which varied widely from the linear control series. In particular, the tradeoff relationship between salt rejection and water permeability was very different for the crosslinked networks than the linear copolymers.
Biodegradable polymers have become increasingly important because they can be synthesized biologically and are not petrochemically based. Poly (3-hydroxybutyrate) (PHB), a biopolyester produced by a wide variety of microorganisms as an intracellular carbon and energy storage material, can be differentiated from all other available biodegradable plastics by their water insolubility and resistance to hydrolytic degradation. In general they exhibit good oxygen permeability and are both biocompatible and nontoxic, making them suitable for medical applications such as drug delivery and tissue engineering. Poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHB-HHx) is a new copolymer of PHB that not only possesses all the excellent properties of PHB but also overcomes its stiffness and brittleness caused by the near perfect stereoregularity and high crystallinity. Hence the PHB-HHx copolymers are much more easily processed.

In our present research, we studied the formation of thermally reversible gels from PHB-HHx in various solvent systems and under different thermal conditions. These gels, which are stable at room temperature, were investigated by Ultraviolet-visible (UV-vis), Raman and Fourier Transform Infrared (FTIR) spectroscopy to identify changes in conformational structure due to the gelation process. The resulting spectra indicate the existence of conformational disorder in the gels, although this appeared to be lost gradually upon drying at room temperature. In addition, we found that the freeze-dried gels, which have 3-D interconnected nanofibrous networks with fiber diameters of 40-300 nm and resemble the structure of the natural extracellular matrix, retained some of the conformational disorder that was induced during gelation. We also demonstrated that the HHx content in the copolymers have a large effect on the gel formation and the conformational structure in the gels. This is extremely important because there is an overarching need for non-toxic, biodegradable, synthetic polymers that exhibit thermoreversible gelation and hence can be used as micro-carriers for cells insuring long term survivability and immunoprotection. Although biological polymers have been used extensively in the past, there are associated risks of transmission of bacterial and fungal infections and hence there is a need for synthetic, biodegradable polymers that undergo
We report the catalytic conversion of 5-hydroxymethylfurfural (HMF) to monomers for nylon-6,6 production, which include adipic acid and hexamethylenediamine. It has been shown previously that 1,2,6-hexanetriol can be obtained in high yields from HMF. Selective dehydration of 1,2,6-hexanetriol to produce 1,6-hexanediol was performed over 1wt% Pt supported on various acidic metal oxides (e.g., amorphous silica-alumina, Y-zeolite, H-ZSM5, amorphous niobia). Selective oxidation of 1,6-hexanediol with molecular dioxygen catalyzed by 1wt% Au/C with added base and 3wt% Pt/TiO₂ with added acid have been carried out, resulting in adipic acid yield of 97mol% and 89mol% respectively. Additionally, 1,6-hexanediol can undergo oxidative amination to form adiponitrile in yields greater than 80mol% by a homogeneous iodine-containing organic molecule as oxidant and ammonia as nitrogen source in aqueous media. Subsequently, adiponitrile can be hydrogenated over Raney nickel catalyst to hexamethylenediamine in close to quantitative yields. This integrated reaction pathway of nylon monomers production from renewable biomass-derived platform chemical HMF represents an attractive alternative to their petroleum derived counterparts.
Many current flame retardant (FR) strategies for polymers contain environmentally harmful compounds and/or negatively impact processing and mechanical properties. In an effort to overcome these issues, an effective flame retardant nanocoating comprised of positively charged chitosan (CH) and anionic poly(vinylsulfonic acid sodium salt) (PVS) was deposited onto flexible polyurethane foam using layer-by-layer (LbL) assembly. This coating system completely stops foam melt dripping upon exposure to the direct flame from a butane torch. Furthermore, 10 CH-PVS bilayers (30 nm thick) add only 5.5% to the foam's weight and completely stop flame propagating on the foam due to the fuel dilution effect from nonflammable gases (e.g., water, sulfur oxides, and ammonia) released from the coating during degradation (known as the 'gas blanket' mechanism). Cone calorimetry reveals that this same coated foam has a 52% reduction in peak heat release rate relative to an uncoated control. This water-based, environmentally benign nanocoating provides an effective post-process flame retardant treatment for a variety of complex substrates (foam, fabric, etc.).
491 - Potential of agricultural oil palm mesocarp fiber as filler for biocomposite

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The largest industrial crop in Malaysia is the oil palm which is also the major contributor of agricultural waste. Oil palm mesocarp fiber (OPMF) is the third largest solid waste produced from the oil palm industry, accounted to 11 million ton per year. It is currently used for fuel-burner or as mulch, however is inefficiently utilized. One of the alternative way to manage OPMF is to produce biocomposite by blending with polyolefin such as polypropylene (PP). The drawbacks of using natural fiber in PP-biocomposite production due to poor adhesion and dispersion of the hydrophilic fiber within the hydrophobic PP can be overcome by using compatibilizer. In this study, the compatibility of PP/OPMF biocomposite with and without the use of compatibilizer was compared. Mechanical, morphological and thermal properties of the biocomposites were determined. It was found that the addition of maleic anhydride grafted polypropylene (MAPP) to the PP/OPMF biocomposite at 3 wt.% improved the compatibility of the fiber to the polymer. Tensile strength of PP/OPMF/MAPP biocomposite was improved by 20 - 80 % compared to PP/OPMF biocomposite at 20 - 40 % fiber loading.

. Unexpectedly at 50wt% of fiber loading, the tensile strength of PP/OPMF/MAPP biocomposite is comparable to those having lower fiber loading. This result indicates that OPMF can be used as renewable filler for biocomposite application.

Tuesday, March 18, 2014 05:30 PM
Sustainable Polymers, Processes and Product Applications (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
492 - Synthesis of anionic conjugated polyelectrolytes for biological sensing using intermolecular energy transfer

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Water-soluble conjugated polymers have been attracted a great deal of attention because of their unique optoelectronic properties, which may serve as a basis for a new generation of optoelectronic devices and biochemical detection. Their peculiar properties stem from the combination of optoelectronic properties of conventional conjugated polymers and water solubility induced by ionic nature of polyelectrolytes. Their optoelectronic properties can be easily tuned through the structural alteration of the conjugated structure of the polymer backbones, and the ionic functionality endows them with exceptional features such as electrostatic interaction with oppositely charged species, a high sensitivity toward fluorescence quenchers and fluorescence change with aggregation.

The aggregation-induced blue-to-green solution fluorescence change of 2,1,3-benzothiadiazole (BT) units in polymer backbones was used for sensing of oppositely charged species. In a dilute, well-dissolved ionic conjugated polymer solution, exciton transport can be approximated by a one-dimensional random walk within an isolated polymer chain. However, if the polymers are aggregated within close proximity to each other, interchain exciton migration becomes possible, and a three-dimensional random walk becomes available to the migrating exciton. In this study, we investigate aggregation-enhanced exciton migration in an anionic conjugated polymers containing green- and red-emitting exciton trap sites, respectively. We found that this polymer exhibited a visually noticeable blue-to-green and blue-to-red fluorescence color change upon aggregation with oppositely charged protein.
493 - Synthesis donor-acceptor copolymers containing benzodithiophene with bithienyl substituents for bulk heterojunction solar cells

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Three donor-acceptor copolymers were synthesized by Stille coupling polymerization of benzodithiophene with bithienyl substituents donor and various acceptors. The benzodithiophene donor unit has 6 hexyl chains, which increased the solubility of the polymer and resulted in the synthesis of donor-acceptor polymers with relatively high molecular weights. The HOMO, LUMO and energy gap were calculated from cyclic voltammogram and UV-Vis spectroscopy. These synthesized donor-acceptor polymers are tested in bulk heterojunction solar cells with [6,6]-phenyl-C71 butyric acid methyl ester (PC71BM). The reported polymers had low HOMO levels of -5.6 eV, which resulted in high open-circuit voltages.
Poly(3-hexylthophene)-b-poly((E)-6-(4-((4-methoxyphenyl)diazenyl)phenoxy)hexyl methacrylate) was synthesized by a combination of Grignard metathesis (GRIM) and atom transfer radical polymerization (ATRP) techniques. Allyl-terminated P3HT was synthesized by in situ end capping of nickel terminated P3HT. Hydroboration-oxidation generated the hydroxypropyl-terminated P3HT which was reacted with 2-bromoisobutyryl bromide to generate the P3HT macroinitiator. The composition of synthesized diblock copolymers was estimated by using $^1$HNMR analysis. The P3HT diblock copolymer containing thermotropic liquid crystalline segment is expected to bring unique self-assembly and opto-electronic properties. The field-effect mobility of the diblock copolymer was measured in organic thin film transistors (OTFT). Thermal properties of the diblock copolymers were investigated using differential scanning calorimetry (DSC).
495 - Polyaniline/graphene multilayer films for structural energy and power

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The development of electrode materials that exhibit both exceptional electrochemical and mechanical properties is increasing in importance. Such a material would enable the development of electrodes for energy and power that can dissipate energy, bear a load, or withstand an impact. In this presentation, we report on a composite electrode containing polyaniline, graphene, and Kevlar® fabricated via layer-by-layer assembly for use as a cathode in a non-aqueous battery. Polyaniline, a conjugated polymer, is widely used as a polymer electrode material since it has good electrical conductivity and chemical stability. Graphene has also good electrical properties and mechanical strength due to its unique two-dimensional structure. In addition, Kevlar is of interest for its high mechanical strength. Film growth, structure, and morphology are characterized using scanning electron microscopy, and UV-vis spectroscopy, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy. Electrochemical and mechanical performance are evaluated for the first time.
Nitrogen containing graphene like structures were obtained by the pyrolysis of two pyrimidine polymers at 600 °C. Pyrimidine polymers were prepared by the base catalyzed aldol condensation reactions between 2-decyloxy-4,6-dimethylpyrimidine and two aromatic dialdehydes. Terephthalaldehyde and isophthalaldehyde were employed as the two aromatic dialdehydes to study the effect of the structure of the polymer on pyrolyzed products. The synthesized polymers were characterized by $^1$H-NMR, UV-visible spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and powder X-ray diffraction. Pyrolyzed products were shown to have a graphitic structure as proved by Raman spectroscopy, scanning electron microscopy, and powder X-ray diffraction studies. The presence of nitrogen in the graphitic structures was proved by elemental analysis and energy dispersive X-ray analysis experiments. Fluorescence quenching experiments with poly(3-hexylthiophene) (P3HT) showed that the resultant graphitic materials can act as acceptor materials. Application of these materials in P3HT/graphene hybrid field effect transistors exhibited 10 times higher mobilities and comparable on/off ratios with organic field effect transistors with only P3HT.
Synthesis of block copolymers tends to attract more interest due to the ability of creating new materials with hybrid properties. Poly(3-hexylthiophene) exhibit versatile optoelectronic properties among π-conjugated polymers whereas poly(4-vinylphenol) is a well-known dielectric material. Block copolymers of poly(3-hexylthiophene) and poly(4-vinylphenol) are expected to show hybrid properties with better performance in magnetic field alignment. As controlled polymerizations provide precise control over macromolecular parameters, reversible addition-fragmentation chain transfer (RAFT) and atom-transfer radical polymerization (ATRP) methods have been used to synthesize block copolymers with well-defined molecular weights and compositions. Allyl-terminated poly(3-hexylthiophene) has been used as a precursor for the synthesis of a P3HT macroinitiator for ATRP and a P3HT macro-RAFT agent. Here we report synthesis and characterization of poly(3-hexylthiophene)-block-poly(4-vinylphenol) diblock copolymers and their opto-electronic properties.
498 - Towards the design of new fulvene-derivatized conjugated polymers

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Molecules containing conjugated π-electron building blocks continue as the focus of many investigations in synthesis and structure-property relationships for organic electronics. Compared to these conjugated systems, organic and organometallic materials based upon substituted pentafulvenes have received little research investigation in this area. In the course of our studies on 6-substituted 1,3-diphenylfulvenes, we discovered a synthetic methodology that allows for the selective and stepwise attachment of functional substituents at the 1, 3 and 6 positions of the fulvene nucleus. This substitution pattern provides entry into the versatile design of unique new materials because the 1,3,6-trisubstituted core allows for incorporation of the fulvene skeleton into polymeric or supramolecular networks which have led into investigations of donor-acceptor properties important in electronic materials.
499 - Simple, one–step procedure to make conductive polymers for solid state electrochromic devices

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Electrochromic materials that exhibit the necessary colors for RGB and CMY replication have been sought after by the display industry for the fabrication of lower-power, thinner, and less complex displays. Traditional polymeric electrochromic device fabrication processes involve electrochemical polymerization of monomers from an electrolyte bath, which requires rigorous cleaning of the electrode surface and results in the need for disposal of a large volume of leftover electrolyte solution. Herein, we present a simple, one–step procedure to make solid state polymeric devices, that we call as in situ monomer approach. This technique eliminates the solution step in device preparation, decreases device assembly time, enables open atmosphere fabrication, generates less waste, and is amenable to high volume manufacturing by direct conversion of monomers inside a cross–linked solid polyelectrolyte matrix after device construction. A variety of thiophene–based monomers, such as 3,4–ethylenedioxythiophene, 2,2 disubstituted 3,4–propylenedioxythiophenes, and 1,3 disubstituted 3,4–propylenedioxythiophenes were demonstrated to be viable electroactive species for in situ polymerization, which greatly expands the choice of materials with desired colors for different applications. In addition, complex patterns with high resolution can be easily formed on relatively large area substrates.
Polymeric electrochromic devices (ECDs) have aroused significant interest due to their energy-saving functions and low power consumption in applications such as smart windows and eyewear. With an electrochromic window, the amount of light passing through the device can be limited, hence it can play an important role in reducing energy costs. High contrast smart windows with fast switching speeds and low power consumption have been the main demands in the development of polymeric ECDs. We have optimized a one-step in situ device fabrication to improve performance towards meeting the demands of commercialization.

Compared with conventional device fabrication processes, where polymer films are electrodeposited from solution, the in situ monomer technique realizes open air fabrication, minimizes cost and waste, shortens device construction time, and facilitates large window production. Polymers formed by this approach are highly dependent on the properties of the gel electrolyte. Herein, an extensive study on the components of the gel electrolyte such as salt, solvent, and polymer matrix, was carried out to maximize properties of electrochromic performance. Optimized gel electrolytes yielded devices with photopic contrasts as high as 53% (without background correction) and switching speeds as low as 2 seconds for devices with 19 cm × 9 cm active area. In addition, these devices displayed good optical memory.

![Images of a large area device (active area 19 cm x 9 cm) with 53% Photopic Contrast. Window can be completely colored in 2 seconds and bleached in 6 seconds.](image_url)
501 - High-throughput screening of color for electrochromic polymers

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Diffusion of two monomers and their oxidative copolymerization inside of a solid-state gel electrolyte is utilized as a method to match the monomer feed ratio to a color resulting from a conjugated copolymer having a single absorption in the visible region. Here, we evaluate several different monomers in which the conjugated homopolymers have a single wavelength absorption with a focus on 1,3-di-tert-butyl-3,4-propylenedioxythiophene (ProDOT-tBu2) and 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me2), since their respective homopolymers are at the high and low energy extremes of the visible spectrum. Combining the two monomers generates a solid-state electrochromic device consisting of a gradient of subtractive colors of any single wavelength in the colored state and when the device is switched to the bleached state, this spectrum of colors all transition to transmissive sky blue. This approach is analogous to the paint industry, where two or three dyes can be combined to make any color, various feed ratios of only two or three different monomers in the synthesis of conjugated copolymers (CPs) could yield the same result for electrochromic applications. These findings could have a significant impact on electrochromic applications such as displays, eyewear, windows, and fabric wherein achieving a specific color or color set is critical to its functional use. Further, these colors could be quickly obtained, avoiding tedious tailored synthetic procedures and purification.

Figure 1. (A) and (B) are the high-throughput screening device that shows PProDOT-tBu2, PProDOT-Me2 and the copolymer region in the neutral state, and (B) is the zoomed in picture of the copolymer region. (B) Also illustrates how the feed ratio of ProDOT-tBu2 and ProDOT-Me2 varies. (C) Shows the feed ratios calculated from the diffusion coefficient, and their respective color coordinates. (D) The color spectrum of subtractive color shows the color of the two homopolymers and the copolymers at each point (shown in (B)).

Tuesday, March 18, 2014 05:30 PM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
502 - Importance of stereochemistry of 1,3-substituted poly(3,4-propylenedioxythiophene)s on optoelectronic properties

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Pure cis and trans 1,3-substituted poly(propylenedioxythiophene)s PProDOTs have not been previously reported in the literature. Here, the pure stereoisomers are compared with varying the ratio of the two stereoisomers, systematically, to evaluate structure-property relationships as it pertains to visible absorption, color, and electrochemical redox potentials. A blue shift of approximately 90 nm in the visible lambda max is indicative that the trans 1,3-substituted PProDOT has disruption of conjugation based upon interactions with one of the substituents of the 7-membered ring.

Figure 1. The UV-Vis spectrum of trans 1,3-ProDOT-iP₂, racemic 1,3-ProDOT-iP₂, and cis 1,3-ProDOT-iP₂ that shows a 90 nm shift from cis to trans.

Tuesday, March 18, 2014 05:30 PM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
503 - Synthesis and characterization of VI-TFEMA-DVB anion-exchange membrane for vanadium redox flow battery

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The VI-TFEMA-DVB (VTD) copolymers were synthesised using the vinylimidazole (VI), trifluoroethylmethacrylate (TFEMA) and divinylbenzene (DVB) by solution polymerization. The quaternarized VTD (QVTD) and anion exchange membranes were prepared with bromoethane and casting method, respectively. The membrane's structure and the thermal stability were confirmed by FT-IR, \(^1\)H-NMR spectrometer and TGA, respectively. The basic properties of membrane such as bursting strength, chemical resistance, water content, ion exchange capacity, electrical resistance and ion conductivity were measured. The chemical resistances of membranes were better than that of commercial membrane (AMX). The efficiency of membranes in the redox flow battery were investigated after 150 cycles. The maximum current efficiency, voltage efficiency, energy efficiency and discharge capacity of membranes were 94.6, 79.6, 75.3 and 47.1 %, respectively.

![Synthetic mechanism of quaternarized VTD ion exchanger.](image1)

**Figure 1.** Synthetic mechanism of quaternarized VTD ion exchanger.

**Acknowledgement**

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2. This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government(MSIP)" (2013, Joint Research Corporations Support Program)
Organic conjugated polymers have been shown to have applications in organic photovoltaic devices (OPVs). However, for OPVs to be a viable source of renewable energy it is essential to optimize their ability to convert solar energy into electrical energy. This improvement can come in the form of synthesizing better compounds for the active layer or improving fabrication methodology. In this study we show that simply varying the temperature for the spin-coating of poly(3-hexylthiophene): phenyl-C61-butyric acid methyl ester (P3HT:PCBM) in dichlorobenzene can have as large of an impact on improving power conversion efficiency as thermal annealing. In addition to the temperature study, modified P3HT:PCBM bulk heterojunction device structures containing a thin coat of P3HT or PCBM sprayed on top were characterized and studied. In addition to determined power conversion efficiencies, the charge mobilities of all devices were measured by space charge limited current.
At present, one potential reason why electrochromic polymer devices have not been commercialized could be the limitation of low cost, high volume manufacturability. In situ polymerization of electroactive monomers has simplified the fabrication of polymeric electrochromic devices. With this in situ process, monomers are directly dissolved into a gel polymer electrolyte and sandwiched between two electrodes. With subsequent exposure to UV light, a solid gel electrolyte matrix is formed, where conversion of monomers takes place with the application of appropriate potential. In order to have useful applications, electrochromic devices must have color uniformity, high photopic contrast, fast switching speed and good optical memory. Photopic contrast is an essential property for smart windows and eyewear. It is necessary to study how material and device properties such as monomer loading, diffusion coefficient of monomers, thickness of the gel electrolyte, polymerization time, thickness of the polymer layer, and temperature affect the photopic contrast and switching speed. A relationship between device performance and above-mentioned factors has been established.
Furan as one of the most important heteroaromatic compounds is widely studied in organic chemistry but less developed as a building block in semiconducting polymers. Its unique properties provide many advantages when furan building blocks are introduced in different positions of polymer chains. Compared with the thiophene units in traditional benzo[1,2-b:4,5-b']dithiophene (BDT) polymers, furan segments display weaker steric hindrance to the adjacent units due to the smaller oxygen atom. Consequently, polymers containing benzo[1,2-b:4,5-b']difuran (BDF) are expected to generate more planar polymer backbone which can further increase conjugation length and optimize n-n stacking. The oxygen atom in furan has higher electronegativity than sulfur. Thus, the furan units as conjugated side chains in the BDT/BDF polymers offer an opportunity to tune the HOMO/LUMO level and the band gap. Semiconducting polymers with adjusted band gaps and improved optoelectronic properties could be envisioned by selectively placing the furan building block in different positions of the monomer structures. As many as four variations of the BDT framework can be synthesized by placing the furan units at different positions. Furthermore, it has been shown that the furan moiety could increase the solubility of polymers. The solvent processability of organic semiconducting materials will thus be enhanced by the furan building block as well.

Donor-Acceptor alternative copolymers were synthesized by Stille coupling polymerization of stannylated 4,8-Bis(5-dodecylfuran/thiophene)benzo[1,2-b:4,5-b']difuran/thiophene as electron donors with 1-(4,6-dibromothieno[3,4-b]thiophen-2-yl)octan-1-one as electron acceptor in this work. Perpendicular π-conjugation with furan or thiophene created different electron distributions on the electron donor, leading to a variation in the HOMO/LUMO energy levels of the synthesized polymers. Physical and electrochemical properties of these four semiconducting polymers containing furan building block were investigated. These donor-acceptor polymers were tested in organic thin film transistors and polymer-PCBM bulk heterojunction solar cells.
Grignard metathesis (GRIM) polymerization of 2,5-dibromo-3-hexylthiophene and 2-bromo-5-iodo-3-hexylthiophene monomers was performed using nickel (II) α-diimine catalyst [(ArN=C(H)-C(H)=NAr)NiBr₂, Ar = 2-C₆H₄ (t-butyl)]. The kinetics of the GRIM polymerization of 2-bromo-5-iodo-3-hexylthiophene was investigated and regioregular polymers with 98% head-to-tail couplings and with molecular weights ranging from 3000 to 12000 g mol⁻¹ were synthesized. The nickel α-diimine catalyst was also successfully used for the GRIM polymerization of bulky fused-ring aromatic monomers such as 2,6-dibromo-4,8-bis(4-decylphenylethynyl)benzo[1,2-b:4,5-b′]dithiophene, 2,6-(dibromo)-4,8-bis(5-dodecylthiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene, 2,7-dibromo-9,9-dioctyl-9H-fluorene. Additionally, the nickel α-diimine catalyst was successfully employed for the synthesis of end functionalized polymers and diblock copolymers.
Methylcellulose (MC) is a commercially important cellulose derivative that has been widely used in food, cosmetics, pharmaceuticals and building materials. To date, only a few aqueous solvent systems have been found effective for the dissolution of MC. The goal of this project is to explore the solubility of MC in a variety of ionic liquids (IL). It was found that 1-butyl-3-methylimidazolium chloride (BMIMCl) was able to dissolve MC (Mw = 150,000 g/mol) at concentrations ≤ 1 wt%. Rheological experiments on solutions comprising 1 wt% MC in BMIMCl revealed liquid-like behavior between 20 °C and 100 °C. The absence of a gelation event is drastically different than MC in water, which exhibits gelation at elevated temperatures. MC can now be characterized in solution at temperatures higher than 100 °C.

Tuesday, March 18, 2014 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
We present the synthesis of a poly(lactic acid)-graft-poly(ethylene glycol) copolymer. To obtain a polymer with one poly(ethylene glycol) (PEG) chain per monomer unit, a thiol-functional PEG chain was attached to an alkene lactide monomer through radical thiol-ene chemistry. The resulting lactide derivative was polymerized via ring-opening polymerization using 1,5,7-triazabicyclo[4.4.0]dec-5-ene as organocatalyst. The polymer furthermore contains functional handles on the PEG chain ends to attach biorelevant groups such as peptides or fluorescent dyes through a modular synthesis strategy.
This work focuses on the development of stimuli-responsive surface coatings. By controlling the functionality, the surface energy can be manipulated to be either hydrophilic or hydrophobic, and the resulting change can regulate wet-ability and fluid flow. Here light responsive moieties were tethered to glass surfaces and upon exposure, cleavage was induced to change surface energy and wet-ability.
Thermo-responsive polymeric nanoshell structures have recently been used in literature for localized drug-delivery. Here, one pot synthesis strategies for poly(N-isopropylacrylamide) based nanostructures are reviewed along with the various suspension media used in their applications. These polymer-based hydrogels have also been copolymerized to include more properties such as temperature sensitivity forming interpenetrative polymer networks which in the appropriate conditions can have many relevant biological applications. Other related horizons for poly(N-isopropylacrylamide) research include self-assembled nanospheres and self-propulsive microcrawlers which can have future applications in circulating tumor cell detection more efficient drug-delivery vehicles.
512 - Processing of electrochromic conjugated polymers: Improved film adhesion by surface modification

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With their low operating voltages and useful color changes, electrochromic polymers promise a wide array of energy saving applications, ranging from low energy displays to electrochromic windows for reducing heating/cooling costs. In recent years there have been large steps forward in the synthesis of these materials, significantly expanding the library of solution processable electrochromic polymers. As this catalog of polymers grows, processing devices consistently becomes more difficult as special considerations must be taken for variations between polymers and transparent electrodes. One common problem stemming from these variations is poor film adhesion. Variations in transparent electrode surface energies and wetting of the polymer can lead to decreases in long term film stability and even delamination. We show a simple method of spray coating layers of electrically inactive species that modify the surface energy of the transparent electrode, but don't interfere with the electronic or optical properties of the system. This allows the polymer, which is processed on top of the modifier, to better adhere to the surface while retaining its ability to switch. This work analyzes the relative effectiveness of several different spray processable surface modifiers on a variety of substrates.

![Figure 1 - Electrochemical film stability of an electrochromic polymer on untreated ITO](image1)

![Figure 2 - Electrochemical film stability of an electrochromic polymer on surface modified ITO](image2)

Monday, March 17, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Dallas Convention Center
Room: Hall F

Tuesday, March 18, 2014 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
513 - Synthesis of 2,6-dichloro-2,4,4,6-tetramethyl heptane (DCTMH) and 4-methoxy-2-methyl-1-butene (MMB) for initiation and end-quenching of the cationic polymerization of isobutylene

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4-methoxy-2-methyl-1-butene, synthesized from 3-methyl-3-buten-1-ol, was used to end-quench the polymerization of isobutylene to form exo-olefin terminated polyisobutylene. The polymerization was initiated from 2-chloro-2,4,4-trimethyl pentane, catalyzed by TiCl$_4$ and conducted at -70°C in 40/60 (v/v) hexane/methyl chloride. 4-methoxy-2-methyl-1-butene exhibited limited effectiveness as an end-quencher towards exo-olefin terminated polyisobutylene, demonstrated by only a 10% conversion, and also showed no selectivity towards endo/exofunctionality.

Along with the synthesis of 4-methoxy-2-methyl-1-butene, a proposed synthesis of 2,6-dichloro-2,4,4,6-tetramethyl heptane, an initiator used in the polymerization of isobutylene, was conducted using mesityl oxide in place of 3,3-dimethyl glutaric acid. The main advantage of the proposed synthesis compared to the traditional synthesis is a more cost-effective production of 2,6-dichloro-2,4,4,6-tetramethyl heptane. Thus far, synthesis of 2,6-dichloro-2,4,4,6-tetramethyl heptane via the proposed synthesis has proven to be unsuccessful.
514 - Characterization of the water environments in thermosensitive NiPAAm gels using $^1$H HRMAS NMR

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Thermosensitive gels are polymers that modify their conformation in response to temperature change. Many polymers exhibit this property, including N-isopropylacrylamide (NiPAAm). NiPAAm polymer gels are perhaps the most studied thermosensitive polymer because it has a low critical solution temperature (LCST) at 32 °C, and the transition period from a homogenous mixture to a phase-separated polymer is small, within 1-2°C. The LCST is close to a human's body temperature, making it particularly desirable for drug delivery and tissue engineering. Even with this popularity, the water environments above and below the LCST are not completely understood. In this poster, $^1$H high-resolution magic-angle spinning (HRMAS) nuclear magnetic resonance (NMR) spectroscopy was used to identify and characterize the different water environments present near the LCST. The improved spectral resolution afforded by HRMAS NMR allowed the identification of multiple water environments in these gels, which were observed to depend on the temperature and cross-link ratios. By coupling HRMAS NMR with pulse field gradient (PFG) experiments, it was also possible to measure the self-diffusion rates for these different water environments. Spin-spin relaxation times ($T_2$), and self-diffusion results were obtained as a function of temperature for two different gels preparation protocols. These HRMAS NMR results provide additional insights to develop describe the water environments in thermo-responsive gels such as NiPAAm.

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Tuesday, March 18, 2014 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
515 - Ionic complexation as a method of miscibility enhancement of polystyrene/polypropylene oxide blends

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The blending of different polymers often results in phase separation due to low entropy of mixing and unfavorable enthalpy of mixing. Methods to increase polymer miscibility would allow for mixing of properties of two different materials in one blend. One method of making a miscible polymer blend is by using polymers with complementary functional groups to drive mixing. In this research, sulfonic acid functionalized polystyrene (SPS) and amine-terminated poly(propylene oxide) were used to make such a polymer blend. The percentage of sulfonation and functionality of the PPO were varied and samples were tested for clarity and mechanical properties. Polystyrene sulfonation levels were 2.5, 3.7, and 6.5%. Di-functional, secondary di-functional, and tri-functional Jeffamines were used. Glass transition temperatures were measured by DSC and five of six tested blends showed only one glass transition temperature, suggesting complete miscibility. All samples resulted in optically transparent blends, but displayed variant mechanical properties. Rheology data suggests that the samples behave as viscoelastic liquids at low frequencies, exhibiting properties that are in between the liquid Jeffamine and solid PS. The polymer blends prepared in this research support ionic complexation as a method of miscibility enhancement.
In order to make conductive, biocompatible, and mechanically robust actuators for use in a variety of biomedical applications, we have synthesized new composite materials made from the biopolymer silk fibroin and the conducting polymer poly(pyrrole). Initial proof-of-concept experiments demonstrated that these composites bend under an applied voltage (or current) using a simple bilayer device geometry. Free-end bending actuation and tensile stress testing was conducted in phosphate buffered saline solutions to characterize the material properties in a biologically relevant setting, and identify the actuation mechanism. In addition to material characterization, actuation sequence programming was optimized to explore more efficient modes of actuation. Program sequences can be modified to fit the function of the actuator, allowing for optimized device life spans and strength of actuation. These methods are now being applied towards the construction and characterization of more efficient, complex three dimensional devices.
Tissue engineering may provide a materials-guided approach to repair osteochondral defects (OCDs) - damage extending from cartilage to subchondral bone. Due to the interfacial nature of OCDs, the ideal scaffold must spatially direct tissue regeneration as a gradual transition between the two tissues types. Thus, the scaffold should be comprised of a gradient of physical and chemical properties that can appropriately direct cell behavior. Towards this goal, a library of scaffolds is needed for rapid-screening of cell-material interactions. Conventional poly(ethylene glycol) diacrylate (PEG-DA) hydrogels, prepared from aqueous precursor solutions have been extensively studied for this purpose. However, the ability of PEG-DA hydrogels to regenerate tissues is limited due to a lack of tunable properties as well as bioactivity and osteoinductivity. In this study, we sought to enhance the versatility of PEG-DA hydrogels through the integration of three fabrication parameters. First, methacrylated star polydimethylsiloxane (PDMS_{star-MA}) was incorporated to enhance bioactivity and osteoinductivity. Second, solvent induced phase separation (SIPS) involving an organic fabrication solvent was employed in place of traditional fabrication with an aqueous solvent. Lastly, pore interconnectivity, critical to cell infiltration and neotissue formation, was tailored through salt leaching techniques. Total macromer concentration, weight percent (wt%) ratio of PDMS_{star-MA} to PEG-DA and average salt particle size was studied with regard to their impact on scaffold morphology, hydration, mechanical properties, bioactivity, and degradation.
Using ceric ion initiator in aqueous medium, ethyl acrylate and methacrylic acid were each grafted onto carboxyl methyl-containing holocellulosic materials obtained by treating corn cob-based holocellulosic materials with sodium hydroxide and sodium monochloroacetate. Ethyl acrylate and methacrylic acid were also grafted onto corn cob pulp. The grafted copolymers were characterized using FT-IR. The adsorption of As, Ni, and Mn metal ions were investigated using ICP-AES. The results obtained indicate that the percent ion absorbed per gram of copolymer depended on the polarity of monomer, the polarity of the holocellulose, and the initiator concentration.
519 - Aromatic amino acid-derived stimuli responsive polymer properties

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In this study, aromatic amino acid-derived polymers, such as L-phenylalanine, are radically copolymerized with acrylic acid. These copolymers are analyzed for solubility at varying temperatures and pH values. Stimuli responsive polymers are viable for a vast range of applications from chemical sensors to selective membranes to drug delivery systems. Amino acid-derived polymers have been studied before, but very little work has been done incorporating aromatic amino acids. The goal of this research is to develop an understanding of the effects that aromatic amino acid functional groups on monomer units have on pH- and thermo-sensitive polymers' properties. The polymers were characterized using H¹NMR and IR spectroscopy. Solubility measurements were made using a UV-vis spectrometer with temperature control, with the intent to detect lower critical solution temperatures.
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. For numerous commercial applications of polymers the near-surface properties are critical to performance. Properties such as chemical resistance, wettability, and tribology are determined by the structure within a few nanometers of the polymer-air interface. Despite this, surprisingly little is known about the free surface structure of most polymer systems. The localization of polymer chain-ends to their surface can arise from an entropic penalty or by enthalpic favoritism for chain ends and can dictate several surface properties such as the glass transition temperature ($T_g$), surface energy, and tribology. This has been characterized in several flexible polymer systems, but little work has been done with semi-rigid and rigid rod polymers. It is the purpose of this research to quantify and characterize the localization of hydroxy (-OH) terminated chain-ends to the polymer-air interface of solution cast polyethersulfone(PESU) films and to determine the effect of chain-end localization on the surface properties of PESU films. Commercial PESU was fractionated and characterized using static light scattering. Fractionated films were prepared via solution casting and characterized using GATR-FTIR and dynamic and static contact angle.
Dendrimers offer potential for producing polymers with multifunctional properties synthesized by sequential reactions. Such dendritic polymers are useful as emulsifiers for oil and water. Starting with the divergent synthesis of a PAMAM dendrimer, we use what we learn to synthesize a dendrimer of two different physical properties.

Our project focused first on the divergent synthesis of a PAMAM dendrimer through a two-step process involving exhaustive Michael addition and exhaustive amidation of the resulting ester, the NH groups are regenerated using 1,2-diaminoethane. After carefully analyzing our findings, we move onto adding another functional group onto chain ends.
Polymers may offer a safer alternative to liquid electrolyte supports in lithium ion batteries. We are investigating dicarboximide-functionalized oxanorbornyl homopolymers as potential solid polymer electrolytes. To that end, we have synthesized dicarboximide-functionalized oxanorbornyl polymers with varying ethylene oxide (EO)\textsubscript{n} side chains with 2, 3, and 4 EO units polymers via a ring opening metathesis reaction under living conditions using a Grubbs third generation catalyst. The polymers were characterized with \textsuperscript{1}H and \textsuperscript{13}C NMR as well as GPC. The molecular weights of the polymers are on the order of 36000 g/mol with narrow polydispersities of less than 1.1. Further characterization will include impedance spectroscopy to measure lithium ion mobility, and solid state NMR to measure polymer dynamics.
523 - Synthesis of poly(2-acryl amidoethyl dihydrogen phosphate) as a phospholipid polymer mimic for the study of amyloid-β peptide aggregation

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Alzheimer's disease (AD) is a growing and costly worldwide problem. This research focuses on the specific impact of amyloid-β (Aβ) peptides on AD etiology. In the presence of certain interfaces such as gangliosides and other lipid head groups, Aβ peptides reorganize into individual unstable β-sheets and aggregate to form oligomeric and fibrillogenic species. In this research, a polymeric mimic of phosphatidylserine, an anionic phospholipid, will be synthesized so that evaluation of its impact on Aβ conformational change and aggregation can be done in the future. Specifically, the monomer 2-acryl amidoethyl dihydrogen phosphate (AAEP) was synthesized and then polymerized using aqueous RAFT polymerization. The monomer was characterized using \textsuperscript{1}H NMR to verify the structure, FT-IR to confirm the presence of the phosphate moiety, and ESI to determine the molecular weight. The homopolymer was characterized using \textsuperscript{1}H and \textsuperscript{13}C NMR to determine the chemical structure and ASEC-MALLS to determine the molecular weight.
524 - Synthesis of 1,3-dioxetane by gold-catalyzed cycloaddition of aldehydes in the presence of allenamides

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In an effort to identify novel chemical entities for materials applications, our team is actively engaged in the synthesis of next generation molecular structures that could open the door for the realization of new polymer frameworks. Recently, we discovered that the 1,3-dioxetane moiety could be produced ostensibly from the corresponding aldehyde under gold-catalyzed conditions in the presence of an adjunct allenamide. The success of this approach is highly dependent upon the optimization of various reaction conditions that lead to the 1,3-dioxetane moiety in greatest yield and purity. Efforts to date include varying reaction stoichiometry, type of allenamide utilized, reaction temperature, type of gold catalyst, and the use of aliphatic vs. aromatic aldehydes. Once in hand, the 1,3-dioxetane system may be exploited for the synthesis of novel polymeric frameworks constructed around this unique molecular theme.

\[ \text{Au catalyst, allenamide} \rightarrow \text{R} \quad \text{O} \quad \text{R} \]

Tuesday, March 18, 2014 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
525 - Development of new, polymer-supported catalysts/reagents based on a propylene/hexene copolymer

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Commercially available oligomers of isotactic-poly [propylene-co-hexene] (iPPH) can be used as a synthetic scaffold toward the development of new versatile, polymer supports, which will be described. It was possible to obtain a library of iPPH derivatives that could be isolated as pure solids and in high yields without chromatographic separations. The use of standard organic transformations allows the olefin-terminated oligomers of iPPH to be converted into many derivatives. By using hydroboration/oxidation, additions and substitutions, along with different click strategies, these derivatives of iPPH were formed. To illustrate the usefulness of this material in synthesis and catalysis we have developed an iPPH-supported DMAP derivative and used it as a recoverable catalyst for the Boc-protection of a hindered phenol. Due to this material’s versatility the separation and recovery of this catalyst can be accomplished by using both liquid/solid and liquid/liquid techniques.
526 - Poly(dimethylsiloxane) networks with iron(II) tris(bipyridine) crosslinks

Shannon O Harris, harrisso@appstate.edu, Mallory A Mcvannel, Kristina Vailonis, Meredith Barbee, Miriam L Pippin, Michael S Hambourger, Alexander D Schwab. A. R. Smith Department of Chemistry, Appalachian State University, Boone, NC 28608, United States

Networks of poly(dimethylsiloxane) (PDMS) are created with electrochemically and optically active iron(II) tris(bipyridine) (Fe(bpy)$_3^{2+}$) cross-links which show promise as electrically switchable elastomeric materials or sensors.

First, bipyridine-terminated PDMS (bpyPDMS) is synthesized by attaching 4'-methyl-2,2'-bipyridine-4-carboxylic acid to amine-terminated PDMS using a carbodiimide coupling scheme. BpyPDMS is then blended with FeCl$_2$ in differing proportions and the resulting networks are characterized. UV-vis spectra of network films exhibit a strong absorbance peak at 540 nm indicative of successful Fe(bpy)$_3^{2+}$ cross-link formation though attempts to quantify the absorbance are complicated by film thickness and film uniformity. The network is insoluble in several solvents which readily dissolve PDMS. DSC indicates that crystallization is suppressed by the addition of FeCl$_2$ to bpyPDMS, though the network $T_g$ is not significantly different than the $T_g$ of PDMS or bpyPDMS.

Network films can be placed on electrode surfaces and swollen with solvent in order to perform cyclic voltammetry (CV). CV studies reveal that the Fe(bpy)$_3^{2+}$ cross-links near the electrode are accessible to oxidation, the oxidation is reversible, and the oxidation potential of the cross-links is near that of "free" Fe(bpy)$_3^{2+}$. Spectroelectrochemical measurements indicate that the oxidation of Fe(bpy)$_3^{2+}$ is accompanied by a loss of the absorbance peak at 540 nm, and much of the absorbance can be recovered by reducing Fe(bpy)$_3^{3+}$ back to Fe(bpy)$_3^{2+}$. 

\[
\text{HO-} + \text{H}_2\text{N-}\text{Si-O-Si-}_n\text{NH}_2 \xrightarrow{\text{EDCl}, 0^\circ \text{C}} \text{CH}_2\text{Cl}_2 \\
\begin{array}{c}
\text{Fe}^{2+} \\
\text{FeCl}_2\text{H}_2\text{O} \rightleftharpoons \text{2-butanone} \\
\end{array} \\
\text{NH}_2 \xrightarrow{\text{FE(bpy)$_3^{2+}$}} \text{Si-O-Si}_n \text{NH}_2 \\
\text{2 Cl} \\
\text{Si-O-Si}_n \xrightarrow{\text{Fe(bpy)$_3^{3+}$}} \text{NH}_2 \\
\]
527 - Chain extension in bipyridine-terminated poly(dimethylsiloxane) blended with copper(II) chloride

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When bipyridine-terminated poly(dimethylsiloxane) (bpyPDMS) is blended with CuCl₂, evidence indicates that there is preferential formation of copper(II) bis(bipyridine) (Cu(bpy)₂²⁺) complexes. The formation of these complexes indicates PDMS chain length is effectively extended or PDMS cycles are formed. The electrochemically active Cu(bpy)₂²⁺ linkages can potentially be exploited to create materials with switchable crystallinity or viscosity.

BpyPDMS is synthesized using an EDCI-mediated amide coupling of 4’-methyl-2,2’-bipyridine-4-carboxylic acid to amine-terminated PDMS (2500 g mol⁻¹). Upon blending with CuCl₂, bpyPDMS, initially a waxy solid at room temperature, becomes a pale blue, non-crystalline material capable of fiber drawing. UV-vis spectra exhibit a broad absorbance peak at 740 nm with a broad shoulder at 950 nm consistent with Cu(bpy)₂²⁺ formation rather than Cu(bpy)₃²⁺. The presence of Cu(bpy)₃²⁺ cannot be ruled out entirely because the molar absorptivity of Cu(bpy)₃²⁺ is less than that of Cu(bpy)₂²⁺. DSC studies show that the addition of CuCl₂ effectively suppresses crystallinity in bpyPDMS and has little effect on T_g.

Films of bpyPDMS with CuCl₂ are placed on electrode surfaces allowing Cu(bpy)₂²⁺ and Cu(bpy)₃²⁺ groups near the electrode surface to be studied with cyclic voltammetry (CV). CV is also performed on solutions containing Cu(bpy)₂Cl₂ and Cu(bpy)₃(PF₆)₂ as models for comparison.

Similar studies have been performed on FeCl₂/bpyPDMS blends which will be compared to the CuCl₂/bpyPDMS blends presented here.

Tuesday, March 18, 2014 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
528 - Synthesis and characterization of new acrylonitrile-co-vinylimidazole-co-furfurylmethacrylate terpolymer

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Acrylonitrile/vinylimidazole (AN/VIM) copolymer already has multiple applications in carbon fiber production as a melt processable precursor polymer and in making nitric oxide releasing enhanced wound healing suture and bandages. These polymers were also successfully used in energy storage devices such as supercapacitors. To broaden the applications of AN/VIM copolymer a new terpolymer with furfuryl methacrylate was synthesized by free radical polymerization. Furfuryl methacrylate-containing polymers are used in simple coatings and adhesives while further development of novel co-polymers could be useful for a variety of new applications. The acrylonitrile-co-vinylimidazole-co-furfurylmethacrylate terpolymer was characterized by attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy, ¹H nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC).
Molecular dynamics simulations of the interactions between a series of polythiophenes with single-walled carbon nanotubes

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The interfacial interactions between single-walled carbon nanotubes (SWCNTs) and polythiophene polymer chains were investigated using molecular dynamics (MD) simulations. These simulations produce details about the preferred conformations of the polymers on the SWCNTs as well as the strength of the attractions. The simulations indicate that the polymer alignment relative to the SWCNT axis is significantly dependent on the length of the polymer chain, the chemistry of the polymer, the flexibility of the backbone, and the length of the aliphatic side groups. Radial distribution functions and interaction energy plots are used to characterize these interactions, whereas snapshots from the MD simulations provide a qualitative perspective on the interfacial interactions, as given in Figure 1 for PQT-12. The information from these studies can be used in the engineering of low-cost, high-efficiency polymeric solar cells, as well as in advancing knowledge of the properties of SWCNT polymer nanocomposites.
Polymers have a finite lifetime due to abrasion and strains on the material, and even if there is fracturing in the material and the material mended, the original properties of the polymer would be impossible to recover. Reversible cross-linked polymers contribute the ability to be durable and resilient at operating temperatures while also having the potential for remolding into different geometries at higher temperatures. The use of reversibly cross-linked polymers on prosthesis is a fairly novel idea. The materials usually used to create a prothetic, such as acrylic, epoxy and polyester are all subject to stresses that is unfavorable on the prosthetic and requires the wearer to have a new prosthetic created. Not only are the materials used inadequate, but also atrophying of tissue on the limb coerces the wearer to have new prosthetics constructed. These reasons lead to cost inefficiencies and waste of material. The crosslinking polymer is created using styrene, furfurylmethacrylate (FMA), and benzyl-bis-maleimide utilizing Diels-Alder reactions. The polymer, when subjected to high temperatures, is easily moldable, and remains intact and stable when cooled to room temperature. If the polymer is incorporated properly, it will allow for the remolding of the cup where the body part sits, since atrophy will require for refitting of the prosthetic.
531 - Rigid dithiols: New monomers for thiolene polymers and networks

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Thiol-ene networks are of current interest to the biomedical and flexible electronics communities due to their synthetic accessibility, uniform network formation and excellent adherence to deposited electrodes. Nevertheless, thiol-ene materials often suffer from hydrolytic instability, due to enchained ester functionalities, and low glass transition, due to the flexible nature of the monomers and the small energy barrier of rotation in the thioether bonds. Therefore, the synthesis of rigid, hydrolytically stable thiol-ene monomers is essential to overcoming these shortfalls. Recently we have developed a synthetic methodology for the facile conversion of a commercially available tricyclic diols to dithiols in three steps. Initial studies with commercially available monomers have yielded polymers which are hydrolytically stable (up to 1 week in 1M NaOH at 37 °C without mass loss) and have high glass transition temperatures for thiolene networks (up to 80 °C) while possessing low crosslink density. Herein we report the polymer and network properties of these new dithiol monomers and their potential application to biomedical devices and flexible electronics.

Figure 1. DMA of novel dithiol network (low crosslink density) versus commercially available trithiol network (high crosslink density).

Tuesday, March 18, 2014 05:30 PM
Undergraduate Research in Polymer Science (05:30 PM - 07:30 PM)
Location: Dallas Convention Center
Room: Hall A
Aramid polymers have long been known to possess excellent mechanical properties. Kevlar, possibly the most famous aramid polymer, is often employed in bullet resistant vests and body armor. Aramid polymers derive their strength from their high crystallinity as well as strong inter-chain interactions from hydrogen bonding and pi-pi stacking. High strength and toughness are also important to systems where high cycle life is desired. Flexible electronics often utilizes thiolene materials due to their facile network formation and compatibility with deposited metals; however, thiolene systems often possess poor mechanical properties due to the flexibility of the thiols employed to form the networks. Combining the high mechanical properties of aramid polymers with the versatility of thiolene polymers should yield a unique class of thiolene-aramid polymers which have good physical properties, are compatible with flexible electronics and possess thermal stabilities enabling high temperature processing. Herein we report on the synthesis and properties of a range of thiolene-aramid polymers and their potential application in flexible electronics.

Figure 1. A) Classic aramid hydrogen bonding and stacking. B) Proposed dithiol aramid monomer and hydrogen bonding. C) Proposed dithiol aramid and functionality.
Bottlebrush polymers with poly(lactic acid)(PLA) side-chains have potential applications such as drug delivery vehicles because of their biocompatibility and biodegradability. In our study, we synthesized and investigated thermal properties of PLA bottlebrushes and polymer blends with linear PLA. Ring-opening polymerization was initiated by an alcohol terminated norbornene (Nb) in the presence of D,L-lactide to yield NbPLAm (m = 10 – 104, Mw = 2000 – 10000 g/mol). Ring-opening metathesis polymerization (ROMP) of NbPLAm macromonomers resulted in well-defined bottlebrush polymers with poly(norbornene) backbone and grafted PLA side-chains, PNb(PLAm)X, (X = 25 – 200, overall Mw = 65000 – 970000 g/mol) where X denotes the backbone degree of polymerization (DP). Size exclusion chromatography (SEC) confirmed mass content of bottlebrush polymers after ROMP >95% in all cases. The glass transition temperature, Tg, of NbPLAm and PNb(PLAm)X are determined by DSC. The Tg of NbPLAm ranges from 10 – 46 °C with increasing molecular weight, as predicted by the Fox equation. PNb(PLAm)X bottlebrush polymers have an average Tg = 48.5 ± 2.5 °C which is independent of side-chain and backbone DP. The mixing of bottlebrush polymers with linear chains was investigated by DSC. PNb(PLA58)50 and PNb(PLA57)200 were blended with NbPLA10 and NbPLA58 at various weight percent. PNb(PLA58)50 additives increased the Tg for the shorter NbPLA10 and decreased the Tg for the longer NbPLA58. Tg for NbPLA58 showed a more significant decrease when backbone DP of the bottlebrush polymer additive increased from 50 to 200.
534 - New fluorine-containing polyarylamines for organic electronics

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Superior hole-transporting mobility and excellent photoconductive properties of aryl amine-containing polymers place them among the one of the most studied materials for optoelectronic applications. Solution processability; however, is significant limitation to highly arylated polymers particularly for preparing spin cast coatings for multi-layer organic light emitting devices. Strategies in order to improve solubility include installing long hydrocarbon ethers as side groups or introducing heteroatoms in the main chain to improve flexibility. Notably, the preparation of partially fluorinated arylated a polymer vastly improves solubility, but has also shown to increase thermal and oxidative stability. In this work, octafluorocyclopentene has been used as a coupling agent to prepare a new class of aryl amine-containing monomers ultimately yielding high molecular weight, optically transparent step-growth polymers. A diverse pool of \(N,N'\)-substituted amine monomers terminally substituted with electrophilic perfluorocyclopentene have been prepared. Herein, this work will present strategic routes for monomer/polymer synthesis, characterization, and viability as a new class of processable coatings or bulk components for the broad area of organic electronics applications.
535 - Synthesis and characterization of sulfonyl-containing perfluorocycloalkenyl (PFCA) aryl ether polymers from AB-type monomers

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AB-type monomers derived from commercial bisphenols containing complimentary phenol and perfluorocycloalkenyl (PFCA) functional groups are prepared enabling the synthesis of high molecular weight PFCA aryl ether homo- and co-polymers. This new class of semifluorinated polymer exhibits similar bulk thermal properties as previously established perfluorocyclobutyl (PFCB) aryl ether polymers and fluorinated arylene vinyl ether (FAVE) polymers, but with a more affordable fluoro-olefin starting material and easier monomer preparation. Present research is focused on the synthesis of sulfonyl-containing PFCA aryl ether polymers for use as proton exchange membranes. The AB-type monomer, sulfonyl-bridged biphenyl PFCA-phenol, was prepared from a 3-step process using commercially available bisphenol S and perfluorocyclopentene compounds as key building blocks. Sulfonyl PFCP-phenol monomer was characterized by $^1$H, $^{13}$C, and $^{19}$F NMR spectroscopy, FT-IR spectroscopy, and combustion elemental analysis. The synthesized AB-type monomer was polymerized in the presence of a base to afford sulfonyl-containing PFCP aryl ether polymers (SO$_2$-PFCP). Polymer molecular structure was characterized by Gel permeation chromatography, $^1$H/$^{19}$F NMR and MALDI-TOF mass spectrometry. Bulk physical properties were elucidated by differential scanning calorimetry and thermal gravimetric analysis. The use of this new semi-fluorinated polymer as a proton exchange membranes will be presented and discussed.
536 - Isothermal drug release of doxorubicin from copolymer micelles

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We seek to build a thermally triggered, drug-delivery system for cancer chemotherapy, consisting of polymer micelles made from poly(ethylene glycol-b-caprolactone), a diblock copolymer (PEG-PCL) or poly(ethylene glycol-b-caprolactone-b-lactic acid), a triblock terpolymer (PEG-PCL-PLA), with the cancer therapeutic drug trapped in the hydrophobic core of the micelles. The polycaprolactone in the micelle core is semicrystalline, and it is expected to trap the cancer drug, preventing its release until the core has melted, the basis for thermally triggered release. The loading capacity and isothermal release for dibucaine, a surrogate cancer drug, were determined for seven different polymers. Three of these polymers (MeO-PEG42-PCL19-H, MeO-PEG113-PCL99-H, and MeO-PEG108-PCL50-PLA46-H) were selected for further study using Doxorubicin, a true cancer therapeutic drug. The triblock, MeO-PEG108-PCL50-PLA46-H, had an impressive Doxorubicin loading capacity of 16.5%. Isothermal release curves for Doxorubicin were measured in triplicate at 27°C, 37°C, 47°C, and 57°C.
537 - Completely renewable flame retardant thin films

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In an effort to create an environmentally-friendly flame retardant (FR) system for foam and fabric, layer-by-layer (LbL) thin films were assembled using “green” materials obtained from completely renewable sources. Positively-charged chitosan paired with anionic montmorillonite clay nanoplatelets was deposited on open-celled polyurethane foam. This coating completely stops the melting of flexible polyurethane foam, when exposed to direct flame from a butane torch, with just 10 bilayers (30 nm thick and only 4 wt% addition to the foam). Cone calorimetry confirms that this coated foam exhibited a reduced peak heat release rate, by as much as 52%, relative to the uncoated control. These results demonstrate the first truly “green” LbL flame retardant and set the stage for a new class of FR nanocoatings.
538 - Polymer science curriculum for the 21st century: PUNK

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With the increasing scope of polymer science research, and growing employment in the field, understanding of polymer chemistry
and properties is now an integral need for undergraduate students studying chemistry, chemical engineering and materials
science. There is also a need to engage students in polymer chemistry earlier in their careers, and outreach efforts to high school
classrooms are critical. Faculty members often struggle to find appropriate polymer chemistry instructional items to incorporate in
their courses. Resources for polymer science instruction, particularly for laboratory courses, are outdated and do not adequately
address recent advances in the field. Individual faculty members are developing polymer-based lectures and laboratory
experiments to fill the gaps. To address the growing need for polymer chemistry education, a group of interested faculty members
from institutions across the country have launched the online resource PUNK: The Polymer Undergraduate Network of Knowledge.
We invite you to join the group to help us develop the network, access relevant resources, and create new instructional materials.
539 - Influence of sterics and electronics in metal-mediated cross coupling reactions in confined environments

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Surface-initiated Kumada catalyst-transfer polycondensation (SI-KCTP) is a powerful technique for creating surface-bound conjugated polymer films. The mechanism of polymerization has been under intense investigation because of the promise this technique holds for the development of a diverse array of nanostructured systems in organic electronic devices. SI-KCTP remains rare in the literature due to the difficulty encountered with bulky monomers. In this talk, we will elaborate on recent work in our laboratory that yields further insight into the density and distribution of initiating sites on the surface when deposited using a variety of chemical and electrochemical techniques. Under optimized conditions, thin and uniform films of various poly(thiophenes) and poly(phenylenes) can be produced via SI-KCTP with different transition metal catalysts.
540 - Synthesis of a water-soluble distyrylbenezene derivative

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The objective of this work was the preparation of a water-soluble conjugated material. Accordingly, 2-amino-(1,4-distyrylbenzene) was synthesized from the reduction of 2-nitro-(1,4-distyrylbenzene), which was prepared via the Wittig-Horner reaction. The novel amino-DSB derivative was soluble in various organic solvents like DMSO, THF, methanol, and acetonitrile. More importantly, the amino-DSB derivative was soluble in water upon protonation with trichloroacetic acid and in neutral aqueous solutions containing 20 % acetonitrile. The new material was characterized by FTIR, 1H-NMR, GC-MS, XRD, and by its absorption and emission profiles. The THF solution of the amino-DSB displayed a UV absorption maximum of 330 nm and an emission maximum of 455 nm. To the best of our knowledge, this is the first DSB derivative containing the amino (NH2) group reported in the literature, even though there are several examples of DSBs containing alkyl-amino groups. The synthetic techniques used in the synthesis of the amino-DSB are currently being explored in the synthesis of water-soluble conjugated polymers containing the amino moiety.
Melanins are a class of naturally occurring pigmented macromolecules found in mammals. These compounds have a high degree of conjugation rendering them a powerful radiation absorber with broadband photon absorption spectrum that extends from the ultraviolet into the infrared range. The black-brown variety of melanin is known as eumelanin and is thought to be a heterogeneous network produced by oxidative polymerization of the two monomers, 5,6-dihydroxyindole and 5,6-dihydroxyindole-2-carboxylic acid. Eumelanins are experimentally challenging due to their poor solubility and extreme heterogeneity. Work by McGinness on electrical switching established that eumelanins were organic semiconductors. Current research involving electronic devices based on eumelanin has only employed insoluble eumelanin pellets or electropolymerized films that are thin and brittle and display very poor morphologies. Progress towards the design and synthesis of well-defined, soluble eumelanin-based polymers will be presented.
542 - Synthesis and characterization of novel semiconducting polymers containing pyrimidine

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The aromatic pyrimidine building block has electron withdrawing character, can participate in dipolar interactions and displays pH sensitivity. Moreover, the nitrogen atoms in pyrimidine can participate in hydrogen bonding and also can chelate various metal ions. These desirable properties makes pyrimidine an attractive building block for the synthesis of conjugated polymers for which one can envision the formation of various supramolecular assemblies that can be used in sensing applications. Various cross-coupling reactions with halogenated pyrimidine have been reported. For example, Suzuki, Stille, Negishi, Sonogashira and Kumada cross-coupling reactions have been employed for the synthesis of conjugated systems. The synthesis of various vinyl pyrimidines through aldol reactions of methyl-substituted pyrimidines have also been reported and the compounds have been employed as liquid crystals and non-linear optical materials. We are reporting here the synthesis and characterization of novel pyrimidine conjugated polymers by the aldol condensation reaction of 2-decyloxy-4,6-dimethylpyrimidine and various aromatic dialdehydes. Soluble polymers containing pyrimidine can thus be obtained. The performance of these polymers in various devices will be detailed. In addition, the thermal annealing of suitable pyrimidine polymers will be shown to demonstrate the graphitization of the polymer into layered graphene-like sheets that are nitrogen doped due to the amount of pyrimidine in the preannealed polymer.
Three new donor-acceptor copolymers P1, P2, and P3 were synthesized with benzodithiophene with bithienyl substituents as the donor and 5,6-difluorobenzo[c][1,2,5]thiadiazole, 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole, and 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole as the acceptors, respectively. The synthesized donor-acceptor polymers were tested in bulk heterojunction solar cells with [6,6]-phenyl C71 butyric acid methyl ester (PC71BM) acceptor. The insertion of thiophene spacer between the donor and the acceptor broadened the absorption of the polymers P2 and P3 and resulted in a red shift of 30 nm as compared to that of the polymer P1. However, the inclusion of fluorine atoms on the polymer had detrimental effects on the photovoltaic properties of the polymers. The polymers were tested in Bulk Heterojunction solar cells. Polymer P2 gave a PCE of 3.52% with PC71BM in which the active layer was prepared in chloroform with 3% v/v 1,8-diiodooctane (DIO) additive.
544 - Chain-growth methods for the synthesis of conjugated polymers

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The synthesis of conjugated polymers and aromatic structures has been dominated by transition metal catalyzed cross-coupling reactions and oxidative condensation reactions. New approaches and conditions are needed to create materials with increased structural diversity. This lecture will detail recent ionic chain-growth methods developed in our group for the synthesis of conjugated polymers as well as general end-capping sequences that can be used to make complex block polymers that can be used for the formation of responsive nanoparticles and organized assemblies. New solvent-free methods will also be discussed that produce materials in an economically fashion.

Wednesday, March 19, 2014 10:25 AM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (08:00 AM - 12:05 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm C
Herein, we demonstrated the preparation of 3,4-ethylenedioxythiophene (EDOT) containing polynorbornylene brushes on Au surfaces via surface-initiated ring-opening metathesis polymerization (SI-ROMP). Using solid-state oxidative crosslinking technique, these polymer brushes were electrochemically converted to conjugated polymer networks. Grazing-angle FTIR spectra of polymer brushes clearly showed the characteristic vibrations of EDOT and norbornylene groups. Furthermore, densely covered Au substrates with polynorbornylene brushes were characterized by using scanning electron microscopy and atomic force microscopy.
546 - Synthesis and nanoscale assembly of conjugated bottlebrush copolymers

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While there is a great interest to utilize block copolymer self-assembly strategies for conjugated polymers having poly(3-hexylthiphene) (P3HT) moiety for organic photovoltaics (OPVs), the strong crystallization behavior of P3HT tends to dominate overall microphase separated morphologies. As a result, the majority of linear block copolymers containing P3HT display nanowire-like morphology, where the second block is confined between P3HT fibers. To overcome such a morphological limitation of these copolymers, we have exploited bottlebrush architecture as a handle for accessing various other morphologies for block copolymers containing P3HT. Specifically, we have synthesized a series of well-defined P3HT-poly(lactide) (PLA) bottlebrush block- and random copolymers by grafting through (or macromonomer) approach using ring-opening metathesis polymerization (ROMP). The morphologies were investigated by transmission electron microscopy (TEM) and showed much more diverse morphologies than the usual nanowire-like structures: these morphologies depend on the composition as well as the sequence of macromonomers (Figure 1). Thus, we demonstrate that the use of complex P3HT macromolecular architecture is an interesting way to tailor the nanoscale assembly of block copolymers containing P3HT, and may offer synthetic paths for achieving a useful morphology for OPVs.

Figure 1. Morphologies of P3HT-PLA bottlebrush random and block copolymers under TEM. (a) Random copolymer having P3HT-PLA (44/56 mol%) (b) random copolymer having P3HT-PLA (29/71 mol%), and (c) block copolymer having P3HT-PLA (29/71 mol%).
547 - Fused-Ring ambipolar units and their impact on the donor-acceptor approach to low band gap conjugated polymers

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Significant effort has been applied to production of low band gap conjugated materials, of which the most commonly applied approach is through the utilization of a 'donor-acceptor' (D-A) polymeric framework. This D-A approach to low $E_g$ conjugated materials was first introduced in 1992 by Havinga and coworkers, in which it was proposed that materials with alternating electron-rich (donor) and electron-deficient (acceptor) moieties along the same backbone could result in a hybrid material with HOMO levels characteristic of the donor and LUMO levels characteristic of the acceptor. This approach has since become a critical design factor in the generation of low and reduced band gap materials. Thieno[3,4-b]pyrazines and its analogues are commonly applied as 'acceptors' in D-A frameworks for the successful generation of low $E_g$ materials. However, recent work has revealed that these units are not only strong 'acceptors', but are actually quite strong 'donors' as well, with donor abilities comparable with the electron-rich 3,4-ethylenedioxythiophene. Not only does this ambipolar nature allow the application of new chemistries for the tuning of electronics through simple choice of side chain functionalities, but significantly changes its role and effect in D-A frameworks. The application and effects of this ambipolar nature will be presented.
This presentation will discuss the opportunities provided by modern polymer synthesis and bioconjugation strategies to design novel, bioactive polymer-peptide conjugate nanomedicines. Judiciously combining biologically active peptides or proteins with synthetic polymers provides opportunities to overcome problems related to the limited stability and plasma half life of peptides and proteins, to enhance the efficacy of polymer-drug conjugates and to augment the activity of peptide based therapeutics. This presentation will illustrate this with a number of case studies, which include amongst others (i) polymer-modified HIV fusion inhibitors that show increased stabilities as compared to the unmodified peptides while maintaining activity and (ii) multivalent HIV entry inhibitors based on side-chain peptide – polymer conjugates which allow to augment the activity of the peptide.
Solution assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptidic molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes: intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. These self-assembled materials range from hydrogels for biomaterials to nanostructures with defined morphology and chemistry display for inorganic materials templating. Hydrogels and nanostructure manipulation will be discussed. The local nano- and overall network structure, and resultant viscoelastic properties, of hydrogels that are formed via beta-hairpin self-assembly will be presented. These peptide hydrogels are potentially excellent scaffolds for tissue repair and regeneration due to inherent cytocompatibility, porous morphology, and shear-thinning but instant recovery viscoelastic properties. Slight design variations of the peptide sequence allow for tunability of the self-assembly/hydrogelation kinetics as well as the tunability of the local nanostructure and hierarchical network structure. During assembly and gelation, desired components can be encapsulated within the hydrogel network such as drug compounds and/or living cells. Importantly, once formed into a solid, self-supporting gel the network can be disrupted by the introduction of a shear stress. The system can shear thin but immediately reheal to preshear stiffness on the cessation of the shear stress. Studies revealing an advantageous drug release profile after weeks in vitro will be discussed. Furthermore, new, designed peptides that alter the fibril nanostructure and hydrogel properties will be discussed to show how molecular changes can be manifested in bulk property changes.
Synthetic glycopolymers are promising candidates for biomedical applications and for investigation of carbohydrate-protein interactions [1]. Polypeptide-based glycopolymers are under investigation as structural mimics of natural glycoproteins with their ability to form secondary structures. Especially stimuli-responsive structural switches are very attractive for the design of “smart” polymeric materials. We have combined the versatility and stimuli-responsiveness of a well-known pH-sensitive polypeptide, i.e. poly(α, L-glutamic acid) (PGA), with the biological activity of sugars by direct glycosylation of PGA. For the synthesis we used a facile aqueous amide coupling approach, where the coupling reaction is conducted in water without any buffer or additive except for the coupling agent itself [2]. Thus the sugar density can be adjusted very easily. This coupling strategy has the potential to be applied to already existing polymeric architectures and materials containing PGA.

We studied the secondary structure (e.g. the helix-coil transition), the aggregation behavior and the biological activity of different partially glycosylated PGAs. Circular dichroism (CD) spectroscopy revealed a strong correlation between sugar density and helicity. Preliminary tests for the biological activity demonstrated specific binding of the glycopolypeptides with lectins. Further lectin binding tests were carried out using a quartz crystal microbalance with dissipation monitoring (QCM-D).

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551 - GRGDS-functionalized poly(lactide)-graft-poly(ethylene glycol) copolymers for bone-grafting applications

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Polymer-peptide conjugates can integrate the advantageous properties of both materials, such as bioactive signaling capability, biocompatibility and enhanced stability, into a single entity. Judicious attachment of peptides to synthetic polymers intended for biomedical applications allows for better integration of the resulting material into a living organism. This biomimetic design entails a higher level of the desired interaction between therapeutic and organism, as well as reduced immunogenic reactions, and hence enables fabrication of advanced biomedical materials.

Herein, we present a biodegradable brush copolymer scaffold based on poly(lactide) which is decorated with several copies of a cell-recognition peptide per polymer chain.[1] Pendant poly(ethylene glycol) chains serve to reduce non-specific protein absorption.[2] Certain cell types are thus attracted specifically via integrin receptor binding, while other biomacromolecules such as serum proteins are repelled. Additionally, the fully modular synthesis of the system affords the possibility to tailor the scaffold to specific biomedical applications.

Through introduction of a functional polymerization initiator in addition to the functional lactide derivative, two orthogonal sites can effectively be generated on a polyester backbone. While one site is available for peptide functionalization, the second one can serve as an anchor for immobilization to yield bioactive surface coatings for potential bone-grafting materials.


Wednesday, March 19, 2014 09:50 AM
Peptide-Based Materials for Nanomedicine (08:30 AM - 12:10 PM)
Location: Hyatt Regency Dallas
Room: Reunion Birm F
552 - ELP-based nanoparticles

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Elastin-like polypeptides (ELPs) are based on the structural protein elastin and demonstrate lower critical solution temperature (LCST) behavior, which means that they will aggregate upon raising temperature.¹ This characteristic makes them interesting for usage in “smart” bio-systems, in which an environmental change can lead to the formation or dissociation of assemblies of ELPs. ELPs therefore have the potential to be used in stimulus responsive drug delivery, if the assembly process can be well controlled, leading to particle formation. In order to achieve this goal, different ELP-based block copolymers were developed, of which one of the blocks showed stimulus-responsive behavior. One class of ELPs, prepared by protein engineering, was composed of a fusion of two different ELPs. A second class of block copolymers was obtained by conjugation of a distinct number of poly(ethylene glycol) chains to ELP, creating amphiphilic ELP-polyethylene glycol (PEG) structures. All of these ELP-based block copolymers self-assembled into well-defined nanoparticles, as was confirmed by DLS. Once cross-linked these nanoparticles show great potential to be used in drug delivery.

REFERENCES


ACKNOWLEDGMENTS

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553 - Supramolecular polypeptide-b-peptide amphiphile nanoparticles as a novel allergy vaccine platform

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Peptide and protein-derived materials have come into the spotlight for supramolecular chemists in recent years. Depending on the sequence, peptides can fold into secondary structures such as β-sheets, α-helices or random coils that can further direct the hierarchical self-assembly of these biomacromolecules. Over the last decade, peptide amphiphile self-assembly has been studied extensively. Conjugation of a peptide to a hydrophobic anchor strongly affects the supramolecular assembly and various morphologies have been reported, such as spherical and worm-like micelles, bicelles and vesicles. As a result, applications of peptide amphiphile-based materials are currently being explored. For example in the field of drug delivery, in-vivo imaging, and regenerative medicine.

Only since 2012 these materials have entered the vaccine field where self-assembled peptides enhanced the immune response by acting as an adjuvant. We developed a new class of polypeptide-b-peptide amphiphiles based on a hydrophilic peptide block comprised of a specific amino acid sequence conjugated to a hydrophobic poly-γ-benzyl-L-glutamate (PBLG) block. Selfassembly results in nanoparticles which have been used in vaccine studies.
Supramolecular peptide nanostructures are attractive for targeted systemic therapies given their potential ability to bind specific receptors or tissue matrix components. They are also of interest because they would be fully biodegradable and could easily incorporate therapeutic elements in the peptide sequences that form the drug vehicles themselves. Furthermore, supramolecular design offers the possibility of increasing their half life which could be problematic in the clinical implementation of hundreds of potential peptide drugs. Given all these attributes they could revolutionize disease treatments with greater efficacy and the elimination of serious side effects. This lecture describes the development of novel peptide amphiphile filamentous nanostructures that can be targeted to injured arteries following balloon angioplasty and chemically designed to deliver nitric oxide in order to avoid the clinically important problem of restenosis after stent placement. The lecture will also describe peptide nanostructures that can be targeted to specific receptors expressed in cancer cells while also carrying chemotherapy cargo in their hydrophobic compartments. Ongoing work toward novel systemic strategies to reverse formation of atherosclerotic plaques with multifunctional peptides will be described as well.
Nanomaterials have emerged as very promising tools for the development of antimicrobial agents due to their chemical and physical properties.

Dendrimers are a relatively new class of macromolecules characterized by highly branched architectures, well-defined three-dimensional structures, monodispersity. Thus dendrimers offer unique opportunities in the synthesis of agents with broad-spectrum antiviral activity.

We report here the synthesis and the viral inhibitory activity of a poly(amide)-based dendrimer functionalized with peptides derived from the herpes simplex virus type I (HSV-I) fusion glycoproteins. The conjugate has proven to be biocompatible and shown no toxicity to cells at biologically relevant concentrations.

Using the copper catalyzed 1,3-dipolar alkyne/azide cycloaddition (CuAAC), a high degree of peptide functionalization was obtained. Furthermore the addition of multiple copies of the viral peptide allows the peptidodendrimer conjugate to inhibit both HSV-1 and HSV-2 at a very early stage of the entry process. Herein is presented work on further improving this attractive design to obtain a new class of therapeutics.


556 - Reversibly transforming polymeric nanoparticles into hydrogel materials

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The incorporation of so-called dynamic covalent bonds into polymeric materials has been a topic of much interest in recent years, presenting an approach to prepare responsive and adaptive polymeric materials which also benefit from the chemical robustness of the covalent bond. The further development of these materials will require the combination of different responsive elements, and in this regard, we have been investigating materials which exploit a combination of the thermoresponsive features of poly(oligoethylene glycol)methacrylates with the adaptive features of dynamic covalent bonds. Here we demonstrate that thermoresponsive water-soluble single-chain polymer nanoparticles possessing dynamic covalent cross-links can undergo a remarkable and fully reversible transformation into a macroscopic chemically cross-linked hydrogel network. This transformation involves a synergy of physical and chemical dynamic processes which drive the transition between different polymer architectures.
557 - Invertible nanostructures formed by stimuli-responsive diblock random copolymers

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Synthesis of thermo-responsive block copolymers of random copolymer blocks allows the tuning of the phase transition temperatures of individual blocks and the introduction of multiple cloud points for a single polymer in water. The same technique can be applied for other stimuli. Diblock random copolymers with dual stimuli-responsive blocks have been designed and synthesized via a sequential reversible addition−fragmentation chain transfer (RAFT) polymerization. A well-defined block copolymer in the form of $A_{n}B_{m}-b-A_{p}C_{q}$ was prepared where A, B and C are N-n-propylacrylamide (nPA), 2-(diethylamino)ethyl methacrylate (DEAEMA) and N-ethylacrylamide (EA), respectively. This polymer shows interesting "schizophrenic" behaviors in aqueous solutions.

Both random copolymer blocks are thermo-responsive and one block is also pH-responsive since the tertiary amine group of DEAEMA becomes protonated at a lower pH. The block copolymers can be molecularly dissolved in water at 25 °C (pH 7), self-assembling to form vesicles with poly(nPA$_{0.8}$-co-EA$_{0.2}$) as the hydrophobic membrane inner layer at 37 °C (pH 7), while the inner and outer layers may be switched at 25 °C (pH 10). The random nature of the blocks allows the fine-tuning of their thermo-responsiveness. In addition, the copolymers manifest stepwise responsiveness in both alkaline and neutral media corresponding to the cloud points of the individual blocks. Solution behavior and nanoparticle morphologies have been studied with $^1$H-NMR, DLS, SLS, zeta potential measurements, as well as imaging techniques, including AFM and TEM.
558 - Reversible macromolecular architectures composed of oxime bonds

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The presence of a dynamic bond in a polymeric assembly, by virtue of its reversible nature, enables the system to reconfigure its molecular architecture and provides a mechanism for controlled release of small molecules such as drugs and fragrances. We demonstrate the formation of oxime functional macromolecular architectures that are able to dissociate and reconstruct themselves under external stimuli. The reversible nature of the oxime bond in the presence of additional alkoxyamines enables it to reconfigure via competitive exchange. Conventional radical polymerization was used to prepare keto-functional random copolymers and reversible addition-fragmentation chain transfer (RAFT) polymerization was utilized to prepare well-defined homopolymers and block copolymers possessing keto functionality. The keto groups in the block copolymers were functionalized via highly efficient oxime bond forming reactions with mono- or di-functional alkoxyamines to yield macromolecular stars or gels capable of reversible disassembly.

Figure 1
559 - Responsive nanostructures in solution and at interfaces

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This presentation will describe the preparation of nanoparticle-based structures by solution and interfacial assembly, and the responsiveness of these structures to their environment and conditions (solvent, mechanical, and e-field).
560 - Regulating architecture of nanothin hydrogels: Effect of layering on pH-triggered swelling

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We report on tuning swelling of pH-sensitive poly(methacrylic acid) (PMAA) ultrathin hydrogels by controlling their internal structure. These hydrogels were produced by chemical cross-linking of PMAA layers in hydrogen-bonded layer-by-layer templates. The internal architecture of those hydrogels was strongly correlated with the internal structure of the as-deposited hydrogen-bonded films, which in turn depends on deposition conditions. A high stratification degree with preserved layering was found for hydrogels obtained from spin-assisted templates. In contrast, with conventional dipping, the hydrogels were highly intermixed with a significant decay in layering. The pH-triggered hydrogel swelling was strongly influenced by the network architecture. Highly swollen (up to 18 times the original dry thickness at pH=7.5) hydrogels, are obtained from well-stratified ‘spin-assisted’ templates; while a three-fold lower swelling observed for intermixed ‘dipped’ precursors. In addition, the well-structured hydrogels exhibited a ten-fold increase in thickness when pH was changed from 5 to 7.5 unlike the two-fold swelling observed in less organized hydrogels.

These hydrogels represent a unique example of an ultrathin but highly-swollen film capable of a 94% water uptake at pH=7.5. We believe that regulating swelling behavior of stimuli-responsive hydrogels at the nanoscale is crucial for advanced drug delivery and sensing applications.

Wednesday, March 19, 2014 10:20 AM
Responsive Nanostructures and Nanocomposites (08:30 AM - 11:45 AM)
Location: Hyatt Regency Dallas
Room: Moreno A
561 - Thermally responsive silicone composites

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As high performance computing requires more computing power, device density has significantly increased. Commonly, a single heat sink will connect to numerous devices making workability a challenge. In this study, we have prepared thermally conductive silicone nano-composites which contain reversible Diels-Alder functionalities. The resulting composites are thermally conductive at standard operating temperatures, but allow rework at elevated temperatures, thus reducing the adhesion properties of the silicone nano-composite to allow for rework.

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Chemical structures showing reversible Diels-Alder reactions are shown. The structures indicate how the reversible nature of the composites is achieved.

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Wednesday, March 19, 2014 10:40 AM
Responsive Nanostructures and Nanocomposites (08:30 AM - 11:45 AM)
Location: Hyatt Regency Dallas
Room: Moreno A
New monomers with either spiropyran- or terpyridine functionalities were synthesized and copolymerized to form responsive nanophase-separated amphiphilic polymer composites. The structure and responsive properties of the polymer networks were studied in detail. The incorporation of photochromic spiropyran units in the hydrophilic domains lead to an enormous repeatability of the light-responsiveness while the terpyridine functionalities formed metal-ligand crosslinks in the presence of metal ions like Fe$^{2+}$ or Co$^{2+}$. Moreover the terpyridine-metal complexes provide addressable functionalities being responsive to external stimuli like changes in the oxidation potential.

Due to the low degree of swelling and nanophase-separated co-continuous structure the networks are ideally suited as responsive membranes. These membranes have shown to be easily produced, mechanically stable, adjustable to different basic permeabilities and responsive to light and chemical/redox stimuli making them suitable for controlled release or smart sensing applications.
Fluids with light-tunable rheological properties (i.e., photorheological or PR fluids) have been studied in the recent past by many research groups. One advantage of light over other stimuli lies in its ability to be directed at a precise location from a remote source. A potential application for PR fluids that leverages the spatial selectivity of light is in the area of flow control within fluidic devices, e.g., to stop the flow at a precise location within a network of fluidic channels (valving action). However, despite a wide variety of existing PR fluid formulations, current fluids are not suitable for this application. Here, we report a PR fluid based on the biopolymer, alginate, that could be useful in this context. The fluid is composed entirely of commercially available components: alginate, a photoacid generator (PAG) as a photo-trigger, and a chelated complex of divalent strontium (Sr$^{2+}$) ions (Sr-EGTA). Upon exposure to UV, the PAG dissociates to give H$^+$ ions, which induce the release of free Sr$^{2+}$ ions from the Sr-EGTA. The released Sr$^{2+}$ ions then self-assemble with the alginate chains to give a nanostructured gel with a high gel modulus (~1000 Pa). To test the possibility of fluidic valving, we flow the above fluid through a microchannel and expose a specific point in the channel to UV light. At that point, alginate is converted into a strong gel in a few minutes, and we find that the resulting gel blocks the flow. When the UV light is removed, the gel is gradually diluted by the flow and the channel reopens. We have thus shown a new kind of light-activated fluidic valve; note that the above concept relies entirely on physical (non-covalent) bonds, i.e., on self-assembly, rather than on covalent crosslinking of dissolved monomers or polymers.
Biodegradable and biocompatible polyesters as poly(glycerol adipate) (PGA), poly(sorbitol adipate) (PSA), and poly(glycerol adipate)-graft-poly(ε-caprolactone), bearing OH-groups on their backbones were synthesized by enzymatic polycondensation. They were modified with different fatty acids or converted to macroinitiators for ATRP followed by controlled polymerization of various hydrophilic or hydrophobic monomers. The graft copolymers formed a variety of supramolecular structures in water including micelles, aggregates of micelles, and polymersomes which can be used for the formation of worm-like aggregates. All nanostructures are useful tool for the delivery of drugs or drug-conjugates. This is demonstrated by in vitro and in vivo tests.
565 - Liquid crystal functionalized elastomers, characterization, and biological-material interactions

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Since the beginning of tissue culture in the early 1900’s, researchers have been able to precisely measure cell response within selected environments and leap into the study of stem cells. Research on stem cell research has flourished due to the increasing search for overturning injuries and diseases that affect the population worldwide. Biomaterial scaffolds are promising composite materials for the replacement of diseased or damaged human tissues, as they can be engineered to provide support, adherence and growth of cells under physiological conditions as well as designed for controlled delivery of therapeutic substances. Bioscaffolds are expected to biodegrade after implantation and release of the payload.

The combination of cells with liquid crystalline polymeric scaffolds or LC-bioscaffolds as new composite materials are a promising combination for engineering tissues as they can not only be biocompatible and biodegradable but can also provide support, adherence and growth of cells under physiological conditions.

We have successfully synthesized ε-caprolactone-based elastomers modified with cholesteric-type liquid crystal units that enhance the mechanical properties of the elastomers and promote superior, stimuli-responsive surface properties for cell attachment. Our scaffold materials also offer an increase in cell attachment and viability (i.e. expansion and proliferation) of cells while increasing their biomechanical functionality. We will provide morphological and structural information on the synthesized biopolymeric scaffolds, discuss the macroscopic physical behavior of the elastomers, and focus on interactions between the liquid crystalline SRS with cells depending on applied external stresses/stimuli.
566 - Interaction between spherical polyelectrolyte brushes and proteins

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Interactions between bovine serum albumin (BSA)/β-lactoglobulin (BLG)/Papain and spherical polyelectrolyte brushes (SPBs) were investigated by a combination of turbidimetric titration, dynamic light scattering (DLS), zeta potential measurement, and small angle x-ray scattering (SAXS) which revealed different behaviors, architectures, and phase states of pH dependent protein-SPB interactions. Binding energetics, affinity, and stoichiometry between BSA/BLG and SPBs were determined by isothermal titration calorimetry (ITC). The SPBs consist of narrowly distributed polystyrene core particles (ca. 100 nm in diameter) onto which linear chains of polyelectrolytes are grafted. The polyelectrolyte shell consists of either weak anionic poly(acrylic acid) (PAA) or weak cationic poly(2-aminoethylmethacrylate hydrochloride) (PAEMH). For a particular proteins (BSA and BLG), the binding stoichiometry, affinity, architecture, and phase state between proteins and anionic SPBs were significantly different from those for cationic SPBs. Significantly larger binding affinity and amount were observed for BSA in anionic SPBs versus cationic SPBs, while opposite for BLG, which were explained in terms of the different charge anisotropies of proteins. These findings lay the foundation for SPB applications in the protein purification and selective immobilization of different proteins, enzymes and antibodies.
Aggrecan is a bottlebrush shaped polyelectrolyte that forms supermolecular complexes with linear hyaluronic acid chains. In cartilage aggrecan-hyaluronic acid complexes are interspersed in the collagen matrix and provide the compressive resistance to deswelling under external load. We investigate the self-assembly of aggrecan and its complexation with hyaluronic acid in near physiological salt solutions using an array of complementary experimental techniques (small angle neutron scattering, small angle X-ray scattering, dynamic light scattering, neutron spin-echo and osmotic swelling pressure measurements) to probe the structure and interactions over a wide range of length and time scales. We attempt to bridge the submicroscopic properties of aggrecan-hyaluronic acid complexes probed by scattering techniques to their macroscopic properties. We believe this approach provides insight into the relationship between the structure and function of the main components of cartilage extracellular matrix and may help to tailor the physical characteristics (e.g., osmotic, mechanical and transport properties) of engineered tissue implants to match those of the replaced tissue.

Figure 1. Variation of the osmotic pressure of solutions of aggrecan, hyaluronic acid and aggrecan-hyaluronic acid complexes in 100 mM NaCl. The inset shows the dynamic light scattering correlation functions g(t) of these solutions measured at 90°.
Several lipase enzymes catalyze the degradation of micelles derived from poly (ε-caprolactone) (PCL) block poly (ethylene glycol) (PEG) diblock copolymers (HO-PCL-b-PEG-OMe) through PCL ester hydrolysis. Spherical micelles with charged corona exteriors derived from block copolymers with charged PEG end groups (HO-PCL\_n\_b\_PEG\_32-RX, R=\(-O(CH_2)_3S(CH_2)_2\); X=\(-CO_2^-, -SO_3^-, -NH_3^+\)) were designed and prepared to probe the corona charge effects on enzyme catalysis. The working hypothesis was that when the micelle corona and lipase enzymes have the same charge there will be an increased barrier to reaction which could be used as a design feature to obtain selectivity for therapeutic transport and release. Kinetic studies of \textit{P.cepacia} lipase catalyzed degradation of micelles with charged corona will be described and discussed that illustrate fulfillment of this hypothesis. Two closely related \textit{P.cepacia} lipase isoforms are observed to manifest unprecedented complementary micelle corona charge selective catalysis.
569 - Tracking the transport of intact DNA in gene delivery using FRET labeled beacons

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Our limited understanding of how polymer-DNA complexes, termed polyplexes, are internalized into cells, transported to the cell’s nucleus and then translated into functional proteins hinders the development of new non-viral vectors. It is well known that gene expression is due to a small fraction of the delivered DNA. A major limitation with present imaging techniques is that they cannot distinguish functional intact DNA from degraded DNA. We use a DNA nucleotide labeled with a dye pair that exhibit Forester Resonance Energy Transfer (FRET). As shown in figure 1, this two color DNA construct emits with greater intensity in the red region when intact and emits with greater intensity in the green region when cleaved. Two color molecular beacon oligonucleotides containing are delivered using various polycationic polymers. Flow cytometry and confocal microscopy are used to study the breakdown of the beacon.
The high organization displayed in biological materials can be partly conserved even after significant physico-chemical modifications. Various heat modifications of the polymeric system that constitutes the extracellular matrix can produce materials where complex nanoscale structures are formed while less thermally stable portions leave vacuums. Thus, through specific heat treatments of agricultural byproducts, such as nut shells, we produced highly porous carbonaceous materials (biochars) that could serve as water purifier or filtration system. $^{129}$Xe NMR was found to be a useful technique that is complementary to the conventional porosity measurements such as nitrogen adsorption isotherms. $^{129}$Xe NMR demonstrated the presence of nanoscale porosity that was influenced by the details of the heat treatment and post-treatment processes. In some cases, sustained or more extreme heat treatment caused increase in pore size, probably due to wall collapse. The charring process produced a residue that partially occluded the pores but could be removed by washing with water. These complex processes could be observed with $^{129}$Xe NMR at varying degrees of detail.

Figure 1. Almond shell treated at 800 °C heat to produce biochar. Initial heat treatment (60 minutes) did not produce any measurable porosity (lower left $^{129}$Xe NMR spectrum), but further heat treatment (240 minutes, upper left spectrum) or washing with water (lower right spectrum) made pores appear. The porosity increased when both 240-minute heating and washing were applied (upper right spectrum).
Fullerene (C_{60})-γ-Cyclodextrin (γ-CD) guest-host polymer nanocomposite networks were prepared using inexpensive complexation techniques. The networks were evidenced to have monodisperse filler sizes arising from C_{60} and monodisperse 12-carbon tie chains arising from CD-polymer networks which were prepared separately. Unique membranes having guest-host capabilities emanated by appropriate cavity size of the cyclodextrins were developed. These network membranes have inherent hydrophobicity and could potentially be applied in sequestration and scavenging of small molecular impurities from organic solvents.
Silsesquioxanes (SQs) are being considered for many potential applications from structural materials to electronics, with most focus given to the O$_h$ symmetric cubic cages, [RSiO$_{1.5}$]$_8$. Little time and effort have been devoted to the five-fold (D$_{5h}$) symmetric [RSiO$_{1.5}$]$_{10}$ counterpart, mainly because synthetic paths to these sets of compounds provide low yields at best. We report here the development of efficient routes to [RSiO$_{1.5}$]$_{10}$ where R = Ph and vinyl through fluoride catalyzed rearrangement of their corresponding triethoxysilanes or T-resins, as well as isolation of larger cage SQs. These synthetic procedures allow us to compare their properties (absorption, emission, etc.) with the [RSiO$_{1.5}$]$_8$ and [RSiO$_{1.5}$]$_{12}$ analogs. Isolated yields of [RSiO$_{1.5}$]$_{10}$ are >40%. Oligomeric and polymeric materials can also be made from these structures.
Our group uses acyclic diene metathesis polymerization (ADMET) to synthesize precision polymers, meaning we control the identity and spacing of branches or pendant groups on polyethylene, and in this way can elucidate the effect of specific structural features on polymer morphology, crystallization behavior, and the resulting thermal and mechanical properties. Because of the nature of ADMET and the structure of the monomers, the polymers studied thus far have been atactic. However, a new monomer design has made tactic precision ADMET polymers possible, and the strategy is being used to study, for the first time, the influence of tacticity over varying branch intervals on properties.

This talk will describe the design of C2 symmetric chiral monomers which can be polymerized by ADMET to form tactic precision polymers. In the initial study, a series of syndiotactic poly(ethylene-co-vinyl amine) bearing precisely spaced amino groups with varying frequency was synthesized. These new polymers will be studied by WAXS and SAXS to get an understanding for the crystallization behavioral and morphological effects of such stereocontrol at precise intervals of the amino group. Polymers bearing other functionalities are also being synthesized in our lab, as the amine containing polymers are only the first phase of this fundamental model study.

Figure 1: Our strategy to tactic precision polymers.

References:


In current time, depleting fossil fuel reserves are escalating the exploration of renewable sources of material. Development of new renewable monomer feedstocks for fabrication of next-generation polymeric materials is critical to the future success of the polymer industry. In the present invention we have attempted to address some of these issues by synthesizing an assembly of bisfuran diol (BFD) monomer from commercial furfural over four synthetic steps. The BFD ($C_{13}H_{16}O_4$), crystallized in the monoclinic space group $P2_1/C$ with $a = 11.011(12)$ Å, $b = 10.443(12)$ Å, $c = 11.324(12)$ Å and $R$ value of 0.0358, which will be crucial in understanding the molecular arrangement in space, hydrogen bonding and packing of the molecule. BFD was further reacted with dicarboxylic acid to generate polyester material via classical step-growth polymerization. MALDI characterization of synthesized polyester illustrates low molecular weight ($M_n = 5$ kDa) and DSC experiments reveals amorphous nature of the material.
575 - Stimuli-responsive hydrogels for oral delivery of high isoelectric point-exhibiting therapeutic proteins

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Although protein therapeutics now account for over $100 billion annually in sales, therapy comes with high cost and poor delivery options. The vast majority of protein therapeutics are delivered by injection, an unfavorable method that leads to low patient compliance. The preferred oral route has been unused due to digestive enzymes and harsh conditions in the gastrointestinal tract that prevent proteins from reaching their target site. pH-Responsive delivery vehicles based on poly(methacrylic acid) grafted with poly(ethylene glycol) (P(MAA-g-EG)) or poly(methacrylic acid-co-N-vinylpyrrolidone) (P(MAA-co-NVP)) hydrogels have previously been shown to be capable of protecting proteins through the stomach and releasing proteins in the small intestine for uptake into the bloodstream. We aim to expand on this technology to enable the oral delivery of high isoelectric point-exhibiting proteins such as salmon calcitonin to improve treatment compliance and patient quality of life. We show a 10-fold improvement in time-sensitive pH-responsive swelling resulting from changing the pH-responsive moiety to itaconic acid (IA), as well as sufficient delivery potential from P(IA-co-NVP) microparticles for transition to a standard-sized pill. Additionally, using peptide-crosslinked degradable hydrogels targeted for degradation in the small intestine, we demonstrate nearly complete release of encapsulated salmon calcitonin in simulated intestinal fluid, thus showing two promising vehicle designs for overcoming the limitations imposed by the oral pathway.

Supported by a grant from the National Institutes of Health R01-EB-000246-20.
576 - Synthesis of a family of highly phase selectively soluble poly(4-alkylpolystyrene) supports for palladium-mediated homogeneous catalysis

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Controlled radical polymerization and conventional radical polymerization were used to prepare alkane-soluble poly(4-alkylpolystyrene) polymers and copolymers. Products containing 4-tert-butyl, 4-octadecylstyrene and 4-dodecylstyrene monomers were then used to prepare a dye-labeled homo- and copolymers. When these polymers were prepared with dye labels, they exhibited quantitative phase selective solubility in nonpolar phase in mixtures containing nonpolar solvent and immiscible polar solvent at 25° C making them good polymer candidates for recycling of catalysts as shown in Figure 1.

When these polymers were prepared with 5-10 mol% of 4-chloromethylstyrene to give poly(4-alkylstyrene-co-vinylbenzyl chloride) polymers that can undergo substitution of the benzylic chlorine they afforded useful precursors for catalyst ligands. For example, substitution with dicyclohexylphosphinobiphenyl ligand yields an electron-rich air stable polystyrene-bound phosphine ligand. Palladium complexes of poly(4-alkylstyrene)-bound phosphines were compared to those formed with a polyisobutylene (PIB), whose terminus was also converted into a dicyclohexylphosphinobiphenyl ligand. Both complexes were active and recyclable catalysts in haloarene-amine and haloarene-arylboronic acid couplings. Additionally, a diphenylstyrylphosphine ligand was incorporated onto the poly(4-dodecylstyrene) polymer via RAFT chemistry. The catalytic activity of these polymer-supported phosphine ligands and their recycling will be discussed.
Polycarbodiimides are a young, versatile class of helical, semi-flexible macromolecules with a nitrogen rich backbone and several attractive properties such as liquid crystallinity, chiroptical switching, and chiral sensing. These polymers are synthesized via controlled, “living” transition metal mediated polymerizations with either titanium(IV), copper(I)/(II), or nickel(II) initiators. Herein, we report the synthesis of two functional Ni(II) initiators to specifically end functionalize polycarbodiimides with alkyne and alkene moieties. These end groups were easily observed in the $^1$H NMR spectra of the resulting polymers and further confirmed using MALDI-TOF mass spectrometry. Furthermore, these end capped, helical polycarbodiimides were coupled with conventional random coil polymers through post-polymerization modification of the end groups to form a new class of helical-$b$-random coil and helical-$b$-random coil-$b$-helical di- and tri- block copolymers. Copper-mediated alkyne-azide [3+2] cycloaddition was applied to couple azido and bis(azido) terminated poly(ethylene glycol) (PEG) with alkyne end functionalized polycarbodiimides to form amphiphilic block copolymers. Additionally, the alkene terminated polycarbodiimides were coupled with bis(silane) terminated polydimethylsiloxane (PDMS) via hydrosilation. The nano-phase separation and aggregation behavior of these polymers were studied by tapping-mode atomic force microscopy (TMAFM), polarized optical microscope (POM), and dynamic light scattering (DLS). The thermal and chiroptical properties of these polymers were also studied using differential scanning calorimetry (DSC), polarimetry, and circular dichroism (CD).
578 - WITHDRAWN
579 - Modular surface functionalization of polyisobutylene-based thermoplastic elastomers

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The Puskas group proposed to modify the surface properties of polyisobutylene (PIB)-based thermoplastic elastomers (TPEs) using a modular approach. PIB-based TPEs are emerging biomaterials; the first generation is used as the drug-eluting coating on coronary stents. The surface chemistry of PIB-based TPEs can be modified using this modular approach by “gluing” low molecular weight functionalized PIBs (PIB-X) to the surface of the TPEs. PIB-OH was made by living carbocationic polymerization using propylene oxide as initiator and titanium tetrachloride (TiCl₄) as coinitiator. PIB-PEG was then synthesized from PIB-OH using Candida antartica Lipase B (CALB) as catalyst and spin coated onto the surface of a TPE. Protein adsorption studies using Surface Plasmon Resonance (SPR) demonstrated decreased fibrinogen adsorption to the modified surface. This modular approach is much simpler than attaching functional groups covalently to surfaces, therefore it holds great promise in practical applications.
Isotactic poly(1-butene) is a commodity thermoplastic material that has found important commercial use in a variety of applications. However, complex crystallization kinetics associated with this material can give rise to at least three different crystalline polymorphs upon cooling from the melt, that can further contribute to aging effects through the conversion of one crystalline modification into a more thermodynamically favored one over time. We have previously demonstrated successful stereoengineering of a polyolefin stereochemical microstructure by exerting external control over a two-state living coordination polymerization that involves interconversion between an active configurationally-stable chiral propagating species and a configurationally-unstable dormant state through rapid and reversible methyl group exchange that proceeds at a rate far greater than propagation. By controlling the relative populations of the active and dormant species as a function of time, the frequency of stereoerror incorporation can be established in programmed fashion.\(^1\)\(^-\)\(^3\) In this way, a single catalyst system is capable of providing a broad spectrum of different targeted grades of a polyolefin under nearly identical conditions, including unique stereoblock and stereogradient microstructures. This talk will present the results of a similar investigation of the ability to stereoengineer the physical properties of poly(1-butene) through application of stereomodulated two-state living coordination polymerization of 1-butene.

High-performance functionality along with high physical and chemical stability over time are overarching goals of almost all classes of electronics. Negligible variations in physical and chemical properties of materials over time, ensures continuous and reliable operation of electronics; packaging, circuit design, materials selection and device layout are all configured to accomplish this outcome. However, a new concept would be to design sophisticated electronic devices at the same performance level that are capable of undergoing rapid degradation at prescribed time and controlled rate. The sophisticated electronics used in implantable biomedical devices, military and espionage applications in everything from sensors, radios, data acquisition devices and even phones can now be made at such a low cost that they are pervasive. Many biomedical implantable devices require an extraction surgery once the end of the operation life of the device is reached. In military and intelligence applications, these electronics have become a necessity for operations; but, it is almost impossible to track and recover every device from the operation field. We have developed a novel concept of transient materials in electronic devices with goal of investigating feasibility of transient materials for design and synthesis of substrate and packaging materials for electronic circuits. Transient materials and electronics are capable of dissolving in their surrounding environment with no traceable remains. These devices should maintain full functionality until triggered for degradation. Once triggered to dissolve, the electronics would degrade rapidly at a tunable rate. In this work we have demonstrated precise control over transitory behavior of polymer composites based on biocompatible and biodegradable polymers for potential biomedical applications. We have studied chemical (FTIR) and physical behaviors of these polymer composites and have characterized them for their transiency and mechanical (DMA) properties.
582 - Synthesis and chiral separation of helical poly(phenylacetylene)s having L-amino acid derivatives as side groups

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In recent few decades, enantioseparation and asymmetric synthesis of chiral drugs have attracted considerable attention because of the different pharmacologies of enantiomers. Chiral separation, especially by high-performance liquid chromatography (HPLC), is recognized as a reliable method which can easily provide both enantiomers with a high enantiomeric excess. One key point of this separation technique is to develop effective chiral stationary phases (CSPs) with high chiral recognition abilities, and many polymer CSPs for HPLC have been developed. Moreover, a large number of polysaccharide derivatives have been commercialized as CSPs for HPLC. Among synthetic polymers, helical poly(phenylacetylene)s having chiral substituents have been considered to be attractive and prospective candidates to prepare novel CSPs for HPLC enantioseparation. However, the influence of the chiral side groups and chiral recognition mechanism as CSPs are still not well-known and have been attractive research areas. In this work, helical poly(phenylacetylene)s having L-amino acid derivatives as side groups were synthesized using Rh(nbd)BPh4 as a catalyst to prepare CSPs.

Influences of coating solvents, chiral side groups and eluents on their chiral recognition abilities were investigated by HPLC. The results indicated that some of the poly(phenylacetylene) derivatives showed comparable or higher chiral recognition abilities for some racemates than some commercial CSPs derived from polysaccharide phenylcarbamates.
We will present some of our recent work on the theoretical characterization of the nonlinear optical properties of Π-conjugated materials. In particular, we will focus on the use of cyanine derivatives for all-optical switching (AOS) applications; AOS requires materials with large third-order optical nonlinearities and low nonlinear optical losses [1]. We will first provide a quantum-chemical description of the real and imaginary nonlinear optical properties of relevant polymethine-type molecules [2]. We will then discuss the strategies that need to be followed in order to translate the properties of the isolated molecules into the solid state [3] and describe some recent very promising examples.

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References


584 - Simulating conjugated polymers using density functional theory

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Density functional theory is widely used to model the structure and properties of conjugated polymers. New density functional approximations provide improved accuracy for many properties, while remaining computationally inexpensive enough to model large systems. This talk reviews the development of screened hybrid and "Rung 3.5" density functionals, and our applications to bulk polymer structure, polymer band structures, polythiophene synthesis, and the prediction of new conjugated materials. The figure below, adapted from J. Chem. Phys. 134, 184105 (2011), illustrates these methods' predictions for the band gaps of 11 conjugated polymers.
585 - A walk along the acenes: How properties evolve as conjugation length increases

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Acenes are a unique class of polycyclic aromatic hydrocarbon that delocalize a single Clar aromatic sextet over an ever increasing number of rings. This feature leads to a remarkable evolution of electronic properties, and a rapid decrease in stability, for each linearly-fused ring added to the system.

In this talk, I will present acenes from anthracene to nonacene (and their heteroaromatic counterparts), and describe how changes in acene length influence their optical and electronic properties. Special focus will be given to the functionalization and stabilization of these otherwise reactive materials, and the tuning of substituents to optimize electronic performance in a variety of device applications.

Wednesday, March 19, 2014 02:00 PM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (01:00 PM - 05:15 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm C
586 - Thermotropic, light-emitting, and liquid crystalline properties of novel polypyridinium salts derived from 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrilium)tosylate and 3,3′-dimethylnaphthidine

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Four polypyridinium salts were synthesized from 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrilium) tosylate and 3,3′-dimethylnaphthidine with tosylate, triflimide, 1-naphthalenesulfonate, and 2-naphthalenesulfonate counterions. Their structures and purities were established by FTIR, FTNMR spectroscopies, Gel Permeation Chromatography and Elemental Analyses. Thermo gravimetric and Differential Scanning Calorimetric studies show them having high thermal stabilities. Fluorescence spectroscopy results show that the nature of the counterions influence their thermotropic and light-emitting properties. Polarized light microscopy shows that they all form lyotropic liquid crystals at 24 °C which is not influenced by the counterions.

[figure 1]
587 - Crystallization of conjugated molecules from graphitic surfaces

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Carbon nanomaterials with graphitic surfaces such as carbon nanotubes (CNTs) and graphene can initiate the crystallization of conjugated molecules (CMs) from the surface through the π-π interactions between CMs and graphitic surfaces. The assembly behavior of four thiophene-containing conjugated polymers, regioregular poly(3-hexythiophene) (rr-P3HT), poly(3,3-didodecyquaterthiophene) (PQT-12), poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT-14), and poly(2,5-bis(3-tetradecylthiophen-2-yl)thiophen-2-ylthiazolo[5,4-d]thiazole) (PTzQT-14), on carbon nanotubes was investigated through the microscopic studies of the nanowires formation and theoretical simulation. It is found that crystallization of these molecules on CNTs depends on the molecular structure and CNT size.

Wednesday, March 19, 2014 02:50 PM
Synthesis and Applications of Conjugated Materials: Contributions from Texas and Beyond (01:00 PM - 05:15 PM)
Location: Hyatt Regency Dallas
Room: Reunion Blrm C
588 - Conjugated polymers for ionizing radiation detection

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Conventionally, radioactivity is detected through ionization of gas, typically inert gas, by ionizing radiations emitted from radioactive materials. When exposed to ionizing radiation, naturally insulating gases become locally ionized, meaning that positively charged alpha particles remove electrons from gas atoms; as a result electrically neutral gas atoms become ionized with positive charge. The whole process results in a temporary and incremental increase in conductivity of the gas that can be detected via proper electronic equipment. The drawbacks of the current state-of-the-art ionizing radiation detection systems are: 1) need for high potential deference between electrodes (due to extremely low conductivity of gases); and 2) need for gas tubes (Geiger-Müller tubes) to increase sensitivity, which prevent networking of detectors for real-time monitoring of large areas. In this work, we have investigated the response of doped conjugated polymers as sensors for detection of ionizing radiation. Conjugated polymers have delocalized electrons that can be paired with alpha particles and change electrical properties of the conjugated polymers. This change in electrical properties can be easily detected by ordinary electronic equipment. The main advantages over the current systems are that doped conjugated polymers are conductive; thus, a significantly smaller potential deference between the electrodes will be required for detection. Most importantly, small pieces of doped conjugated polymers can be used to form network of sensors, to construct a large detector to monitor radiations over large areas (nuclear power plants, nuclear submarines, government buildings, military bases, etc.) Conductivity of conjugated polymers can be fine-tuned by level of doping and synthesis methods to control sensitivity of the sensors. Moreover, conjugated polymers can be synthesized to detect beta particles; use of undoped conjugated polymers is more suitable for detection of beta particles.
Our group has developed a series of novel electropolymerizable monomers that utilize specifically designed coordination environments to incorporate well-defined metal complexes directly into conducting polymer backbones. These hybrid materials known as conducting metallopolymers have a variety of applications including light-emitting devices, photovoltaics, catalysis, and molecular storage/delivery. These materials exploit the properties of both the conducting polymers and the metal centers in a cooperative fashion. The synthesis, electrochemistry, and electrodeposition of a collection of these metallopolymers will be presented.
Porosity has a profound impact on performance of conducting polymers. While the electrochemical deposition of conducting polymers may introduce porosity, solution-cast films of conducting polymers typically exhibit low porosity. We have explored hard and soft templating approaches to control porosity in soluble p-doping and n-doping polymers. Methods of templating p-doping and n-doping polymers to control porosity will be discussed along with the impact of polymer porosity on electrochemical properties.
591 - Charge storage in polymer acid-doped polyaniline-based layer-by-layer electrodes

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Polyaniline (PANI) has been of great interest for various applications such as energy storage systems, memory devices, sensors, and fuel cells due to its conductivity, unique doping/dedoping process, and ease of synthesis. Especially, PANI has been extensively studied as an electrode in non-aqueous energy storage systems. However, PANI electrodes demonstrate irreversible charge storage at highly oxidizing potentials > 3.5 V vs. Li/Li⁺, resulting in poor cycle life. Recently, we demonstrated that polymer acid-doped PANI, PANI:poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PANI:PAAMPSA), exhibits reversible charge storage up to 4.5 V, enabling electrodes of high capacity, energy, and power.

Here, we successfully incorporate PANI:PAAMPSA into layer-by-layer (LbL) assemblies. Three different LbL electrodes (PANI/PAAMPSA, PANI/PANI:PAAMPSA, and poly(ethylenimine)/PAAMPSA (LPEI/PANI:PAAMPSA)) were fabricated, and the nature of charge storage in each was assessed in non-aqueous energy storage systems. PANI:PAAMPSA in an LbL film maintains its reversible charge storage at highly oxidizing potentials. These results show that PANI:PAAMPSA is a promising candidate for LbL electrodes, where electrochemical activity and conductivity is required.
Since the early 1990’s there have been gradual and significant strides with improvement of the electrical conductivity of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT-PSS). Here, we report PEDOT-PSS having electrical conductivity in excess of 3,000 S/cm as films on textile, specifically textile made from melt spinning of polyethylene terephthalate or nylon. PEDOT-PSS coated textile is prepared from bulk materials by soaking the textile in aqueous PEDOT-PSS colloidal solution followed by a 60-90 minute heat cure. As a demonstration, we use the PEDOT-PSS textile in a circuit to carry 50 watts either with DC or AC in order to light an incandescent bulb without resistive heating of the PEDOT-PSS textile taking place. We benchmark PEDOT-PSS coated textiles with several metal coated fabrics. Further, comparisons are made with copper wire as it pertains to the current passed per mass and current passed per cross-sectional area of the conductor. The percolation threshold occurs at 0.2 wt% of the PEDOT-PSS and the electrical conductivity of the material is stable at 200°C for 10 minutes without degradation.
593 - Genetically encoded polypeptide nanoparticles for delivery of drugs

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In the first half of my talk, I will discuss the design of drug-loaded nanoparticles of elastin-like polypeptides (ELPs) for systemic delivery of anti-cancer chemotherapeutics. ELPs are a class of artificial polypeptides – also called protein polymers – whose repeat unit is borrowed from a VPGXG motif that recurs in tropoelastin. ELPs undergo a lower critical solution temperature transition, in which ELPs undergo phase separation in response to environmental variables such as an increase in temperature or salt concentration. We have explored the capacity of ELPs to self-assemble into nanostructures in response to a range of stimuli. In one example, we designed a chimeric polypeptide that consists of two segments: (VPGXG)$_n$ repeats followed by a short (GGY)$_n$ segment, and showed that attachment of multiple copies of a hydrophobic molecule at the Y position can impart sufficient amphiphilicity to the polypeptide and thereby drive its self-assembly into near-monodisperse nanoparticles with the attached hydrophobic small molecule embedded in the core of the nanoparticle. This is an interesting finding, because it appears that any molecule with a hydrophobicity that is greater than a threshold value appears to drive attachment-triggered self-assembly of the chimeric polypeptide into a nanoparticle. Because many cancer chemotherapeutics are insoluble hydrophobic small molecules with poor bioavailability, this approach of attachment-triggered encapsulation of small hydrophobic molecules into soluble nanoparticles has great utility to increase the solubility, plasma-half-life and tumor accumulation of cancer chemotherapeutics. I will demonstrate the efficacy of this approach with two cancer drugs, doxorubicin and paclitaxel.

The second half of my talk will summarize two examples of ELPs that can be digitally switched between two states in response to a physiologically relevant trigger. In one example of the utility of ELPs for drug delivery, I will discuss the design of diblock ELPs that self-assemble into monodisperse micelles in response to a thermal trigger, wherein self-assembly in the narrow temperature range between 37 ºC (normal body temperature) and 42 ºC (highest temperature approved for mild clinical hyperthermia) results in the presentation of a functional cell penetrating peptide (CPP) motif. The presentation of a functional CPP only at 42 ºC, but not at 37 ºC opens the way to convert CPPs, which are powerful yet promiscuous agents to promote the uptake of drugs into cells, into an exquisitely targeted system for cancer drug delivery via the application of focused external hyperthermia to solid tumors. In the second example, I will describe the design of the first pH-responsive polypeptide micelle that dissociates in response to the low extracellular pH of solid tumors. This system consists of a histidine-rich diblock ELP that self-assembles at 37 ºC into spherical micelles that are further stabilized by Zn$^{2+}$ and are disrupted as the pH drops from 7.4 to 6.4. These pH-sensitive micelles demonstrate better in vivo penetration and distribution in tumors than a pH-insensitive control and provide a potential solution to the problem of limited tumor penetration of nanoparticle drug delivery vehicles. These examples illustrate the precision with which genetic engineering can be exploited for the design of peptide polymers that digitally switch between an assembled and disassembled state in response to a clinically relevant trigger, with intriguing implications for the in vivo delivery of drugs or imaging agents.
594 - New bioconjugation strategies for the site-selective modification of protein N-termini

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The rapidly growing role of proteins as therapeutic agents and cell-specific targeting groups has created a high demand for new bioconjugation strategies. To be useful, these reactions must be capable of modifying one or a limited number of functional groups on the surface of a complex biomolecule without the use of protecting groups. They must also proceed in aqueous media at mild temperatures and at near-neutral pH. As a result of these requirements, there remain relatively few techniques that can be used for bioconjugate formation. In this presentation, two different chemical strategies will be presented for the single-step modification of the N-terminal positions of proteins and peptides. Both methods are tolerant of free cysteine residues and glycan groups, and thus they can be applied to a very wide substrate scope. As the vast majority of proteins possess free N-termini, these strategies are envisioned to be useful for the preparation of many new types of protein-based materials. The application of these techniques for the efficient preparation of well-defined protein-polymer conjugates will serve as the focus of the presentation.

N-terminus serves as a unique reaction site

Two new reactions feature:
1. Single step N-terminal modification
2. High chemoselectivity
3. High yields on full-sized proteins
4. Mild reaction conditions
5. Facile reagent removal
595 - Peptide-based drug amphiphiles for self-delivering supramolecular nanomedicine

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The creation of vehicles for the effective delivery of hydrophobic anticancer drugs to tumor sites has garnered major attention in cancer chemotherapies for several decades. A successful strategy promises immense benefits to cancer sufferers through both the reduction of side effects and a greater treatment efficacy. Current approaches focus on the use of nanosized carriers, whereby the drug’s pharmacokinetic properties and biodistribution profiles are manipulated by encapsulation within, or by conjugation to the carrier. While these methods can be effective, there are concerns regarding the short-term and long-term toxicities arising from the synthetic nanomaterials other than the drug being delivered. Furthermore, there are inherent difficulties in achieving a quantitative and high drug loading per carrier (typically less than 10%). Our strategy presented here is to devise approaches that enable anticancer drugs to directly assemble into discrete well-defined nanostructures with the potential for self-delivery. In this presentation, I will detail our rational design of monodisperse, amphiphilic anticancer drugs—which we term drug amphiphiles (DAs)—that can spontaneously associate into discrete, stable supramolecular nanostructures with a high and fixed drug loading. Depending on the number and type of the drug in the molecular design and also the chosen peptide sequence, the resulting nanostructures could assume various morphologies, such as nanofibers, nanotubes or toroids. Our results also suggest that formation of nanostructures provides protection for both the drug and the biodegradable linker from the external environment and thus offers a mechanism for controlled release.
596 - Simplifying alternating peptide synthesis by protease-catalyzed dipeptide oligomerization

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Our research group is exploring the use of enzyme-catalyzed peptide synthesis from amino acid ester monomers as a versatile platform to prepare peptide oligomers with useful properties such as self-assembly, antimicrobial activity, metal chelation and more. Relative to alternative methods of peptide synthesis that generally involved tedious protection-deprotection steps, peptide synthesis by protease catalysis can be conducted using amino acid ethyl esters as monomers in aqueous media at nearly ambient temperatures. A strategy is described in this paper by which protease-catalyzed oligopeptides synthesis is used to prepare perfectly alternating oligopeptides sequences. Indeed, alternating oligopeptides motifs prepared by solid-state peptide synthesis have been shown to have a number of attractive physical and biological properties. The first target selected was silk inspired (AG)x sequences. In the first step, we prepared AG-OEt dipeptide 'legos' in nearly quantitative yield. In order to convert these AB dipeptide building blocks to perfectly alternating oligopeptides, initial studies showed the importance of identifying the appropriate reaction conditions so that propagation at the C-terminus of peptide chains dominates other pathways that would tend to randomize oligopeptide sequences. Based on this work, oligomerizations of AG-OEt were conducted using papain as catalyst at pH=8 and 40°C. In 30 seconds (AG)x was prepared in about 80% yield with an average chain length of 9.4 dimeric units. Thus, a simple and scalable route to silk-like β-sheet forming domains was demonstrated. Subsequently, the general utility of preparing dipeptide 'legos' that can be converted to alternating peptides was tested by studying the oligomerization of Lys-Leu ethyl ester (KL-OEt). After exploring a diverse range of protease-catalysts, α-chymotrypsin was found to be most effective for the conversion of KL-OEt to (KL)x oligomers retaining this alternating motif. Indeed, 10 s after addition of α-chymotrypsin to KL-OEt, (KL)x oligomers were formed that resulted in a sol–gel transition. The mixture of (KL)x chain lengths under alkaline conditions self-assembles into β-sheets. Thereafter, intermolecular backbone hydrogen bonding between peptides results in physically entangled nanofibrillar networks. This work is currently being extended to a broad range of interesting alternating peptide sequences.
597 - WITHDRAWN
598 - Biomimetic oligopeptoids: From nanostructured materials to nanomedicines

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Peptoids are peptidomimetic oligomers composed of $N$-substituted glycine units. Solid phase synthesis protocols enable strict control over the sequence of highly diverse side chain groups. Control of the primary sequence permits the design of peptoids as scaffolds for the construction of monodisperse multivalent displays that can precisely position bioactive ligands along the oligomer chain. Control of peptoid oligomer folding through macrocyclization provides stable secondary structures and permits the design of peptoids with amphiphilic features that mimic antimicrobial peptides and that perturb cellular membranes.

We report studies of two families of peptoids indicating these oligomers have promising characteristics for development as "nanomedicines". First, we describe the potent and selective antimicrobial activity of peptoids incorporating both cationic and hydrophobic side chain groups. Enforcing amphiphilic structure through macrocyclization enhances their activity against both gram positive and gram negative bacterial pathogens, including Multidrug Resistant Staphylococcus Aureus (MRSA). Second, we find that multivalent displays of the steroid ethisterone can modulate the activity of the Androgen Receptor (AR, Figure 1). Because AR activity plays a critical role in driving the development and growth of prostate cancer, the discovery of new AR antagonists is a significant goal in cancer pharmacology. Two of the peptoid-ethisterone conjugates exhibit potent anti-proliferative activity in cell culture models of late stage "castration-resistant" prostate cancer, for which new therapeutics are urgently needed. We now report in vivo evaluation of a divalent ethisterone conjugate in mouse xenografts of human prostate cancer tumors.
599 - Peptide-polymer conjugates tools to precisely define interactions in macromolecular systems

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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\(^5\).


Figure. Peptide-polymer conjugates as tools to precisely adjust interaction capabilities with various systems.
600 - Polypeptide-based nanoparticles for ocular drug delivery

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As the world’s population ages, disorders affecting the posterior segment of the eye are occurring at an increasing rate. Treatment of these diseases requires injection of drugs into the eye ball resulting in patient discomfort and secondary complications. A method of sustained drug delivery and release would limit the injections required for treatment and the resultant complications. Polypeptides are ideal materials for ocular drug delivery vehicles due to their biocompatibility and biodegradability. Amphiphilic polypeptides with precise properties can be synthesized from amino acid building blocks using ring opening polymerization (ROP) of N-Carboxyanhydrides (NCAs). Self-assembly of these polymers, yields nanoparticles with potential drug delivery properties. This presentation details the synthesis of a series of peptide-based polymers and their formulation into nanoparticles, both micelles and vesicles. Characterization of the nanoparticles and an investigation into their suitability for drug delivery was carried out and will also be discussed.
601 - Molecular structures of RADA16-I and MAX8 self-assembled β-sheet peptide nanofibers probed by solid state NMR spectroscopy

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The designer peptides RADA16-I and MAX8 self-assemble into nanofiber matrices capable of supporting cell culture and regenerative medicine. The peptides were designed with repetitive amino acid sequences which promote β-strand secondary structure and self-assembly via backbone hydrogen bonding. In the literature, RADA16-I is presumed to form an antiparallel β-sheet structure, minimizing repulsion between like-charged sidechains. MAX8 includes a type II' double proline turn, which is proposed to affect triggered self-assembly via ion-dependent β-hairpin formation. We have tested both structural hypotheses by solid state NMR spectroscopy. NMR data on $^{13}$C chemical shift and $^{13}$C-$^{13}$C dipolar coupling within RADA16-I nanofibers are not consistent with antiparallel β-sheet structure, but support a structure composed of parallel β-strands. Data on $^{13}$C-$^{13}$C dipolar couplings within MAX8 nanofibers are consistent with the proposed β-hairpin conformation. Both peptides have some polymorphic tendency. These results will be discussed in the context of our predictive ability in the design of peptides which self-assemble through β-sheet formation.
Compartmentalization is a key concept in living organisms and provides cells with methods to gain spatiotemporal control over their reaction pathways. In this way, fragile components can be protected against degradation, or incompatible reaction environments can be separated from each other by confining them to different organelles. Mimicking such systems allows for a better understanding of compartmentalization in nature.

The most prominent compartments inside cells are organelles, and to mimic these, we use semi-porous polymeric nanoreactors that can encapsulate enzymes. Their structure allows only for diffusion of small molecules like substrates into the nanoreactor, while larger molecules are excluded. By functionalization of the nanoreactor surface with cell-penetrating peptides, cell uptake is triggered and these nanoreactors can be used as additional functional compartments inside cells, providing them with new functionalities and prolonging activity of entrapped enzymes (A).

Besides application in living cells, organelle mimics can also be used to create artificial cell mimics. For this, the enzyme-filled nanoreactors, together with other enzymes and reaction components, can be loaded into larger, cell-sized, polymer vesicles (B). In these systems we observe that the performed cascade reactions take place exclusively inside the cell mimics and over multiple organelle compartments. Furthermore, compartmentalization of enzymes can also be used to introduce incompatible enzymes into the reaction sequence, while still maintaining activity for a longer period of time compared to when all enzymes are free in solution.
603 - Directed self-assembly of colloids

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The self-assembly of colloidal particles into well-defined 3D structures is of great interest for potential applications in biomaterials, catalyst supports, and photonics. The presentation will introduce a general method to functionalize patchy colloidal particles with well-defined symmetries with either sticky-ended DNA or metal-coordination recognition sites creating colloids with directional interactions; the “valence” is determined by the number of patches. Patch-patch attractions are realized by specific DNA hybridization or by a single metal-coordination step and the binding directionality is predetermined by the patch geometry. This strategy should allow for the possibility of building new low-coordinated open structures, both amorphous and crystalline.
Our research group aims to develop the next generation of supramolecular synthons for the controlled self-assembly in water. Using hydrogen bonding encoded peptides positive contributions are balance out with repulsive forces, which constrains the supramolecular materials in three dimensions. Via a combination of structural features (packing parameter, Fig. 1A)[1] and switchable charged side chains (Fig. 1B),[2] we develop materials that are ordered, well-defined in molecular weight and size, yet molecularly dynamic. This strategy closes an important (size dimension) gap between covalent polymers and self-assembled amphiphiles, whilst taking full advantage of the ability to orientate and position functional groups. These supramolecular polymers will find applications in molecular imaging, dynamic and responsive delivery vehicles and switchable (bio)organic hybrid materials.

We will discuss our recent efforts the synthesis and dipolar assembly of a polymer stabilized Janus nanoparticle composed of a single dipolar cobalt nanoparticle conjugated to a heterostructured semiconductor nanorod. These types of magnetically responsive nanoparticles serve as intriguing nanoscopic monomers to form mesoscopic colloidal polymer like structures. Blending experiments with various types of dipolar nanoparticles and nanorods will be discussed to form “colloidal copolymers” of varying composition and sequence.
This study involves the bottom-up design and tunability of responsive, peptide-based block copolymers. The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic diblock, triblock and star copolymers containing poly(lysine) (PK) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. These materials exhibit hydrodynamic size that is responsive to pH, due in part to the helix-coil transition in the peptide chain, but also due to changes in curvature of the assembly at the interface. This talk will present some recent studies in solution morphology transitions that occur in these materials as a result of the helix-coil transition and associated charge-charge interactions. We exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH due to morphology transitions.
607 - Responsive liquid crystal elastomer for cell sheet growth and alignment

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Clinical trials have shown aligned muscular cell sheets hold promise for the treatment of heart failure via regenerative therapy. Here, we report the development of biocompatible monodomain liquid crystal elastomer composite materials as electrically responsive substrates for cell sheet alignment and growth. Conductive monodomain LCEs are produced using the traditional two-step crosslinking method along with the addition of carbon black particles both before and after crosslinking, resulting in conductive LCEs (resistivity 4-5 Ωm) with as little as 2wt % carbon black nanoparticles. Surface wrinkling with defined wavelength and amplitude is achieved by layering a thin polystyrene film on the LCE top surface [1]. The resulting LCE bilayer composites exhibit rapid (0.1 – 1 Hz) and reversible shape and topography changes in response to modest voltages (10 – 40 V). Electro-mechanical expansion of conductive LCEs was completely reversible with no hysteresis. Neonatal rat ventricular myocytes remain viable on LCE-carbon black bilayer substrates, and aligned myocyte cell sheets were successfully grown on LCE-composite bilayers.

We report a simple one-pot, low temperature polycondensation reaction between paraformaldehyde and either bisanilines or diamines to form a hemiaminal supramolecular network (HSN) that undergoes thermally-induced cyclization at high temperatures to form poly(hexahydrotriazine)s (PHTs). By appropriate selection of monomer and polymerization conditions, either HSNs or PHTs could be preferentially formed, thereby allowing access to the unique and versatile properties of each material. An HSN prepared from low-temperature polymerization of oligomeric poly(ethylene glycol)-based diamines with paraformaldehyde is elastic and entirely reverts back to its starting monomers after immersion in neutral water. HSNs prepared from bisanilines are mechanically strong, and, at elevated temperatures undergo cyclization to form extraordinarily high modulus (14.0 GPa) PHTs. The remarkably different, yet useful, HSN and PHT properties are characterized through a suite of spectroscopic and mechanical techniques. A proposed mechanism for the HSN and PHT forming reactions is presented, and DFT calculations support spectroscopic characterization and model experiments for the formation of HSN as an intermediate to PHT.
Formation of bacterial biofilms is a severe problem for many implants. Such biofilms are difficult to treat by systemic antibiotics and therefore often necessitate a revision surgery. The risk of biofilm formation can be reduced using coatings which minimize microbial colonization, while simultaneously foster a stable tissue adhesion on the implant surface.

Copolymers of vinylpyridine (VP) with vinyl benzylphosphonate (VBP) or dimethyl(2-methacryloyloxy ethyl) phosphonate (DMMEP) in different compositions were synthesized and quarterized with hexyl bromide.

The copolymers were characterized by 1H-NMR- and IR-spectroscopy and coated on titanium disks. After drying of the layers unbound copolymer is washed away by solvent. The phosphonate groups bind the copolymer to the surface. The thickness of the layers is ca. 6-8 nm as evidenced by ellipsometry. Antibacterial activity is assessed by investigation of adherence of S. mutans. Most of the copolymers show a clear reduction in the number of adherent bacteria. Biocompatibility is rated based on human gingival fibroblast adhesion and proliferation as evaluated employing a modified LDH activity assay. Like the antibacterial effect also the biocompatibility strongly depends on the exact composition of the copolymers. There are some compositions which show significant anti-bacterial effect and simultaneously good biocompatibility.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is acknowledged.

610 - Surface morphology of durable, highly effective antimicrobial hybrid coatings

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Infection with pathogenic bacteria is a serious medical complication associated with health care environments. Such contamination ranges from medical devices such as catheters to transmission from frequently touched objects such as doorknobs and computer stations. Antimicrobial coatings that affect contact kill offer promise in helping curb the spread of such infections. However, long-term stability of biocidal coatings is important for antimicrobial effectiveness. In this research, a novel hybrid coating is investigated aimed at improving the stability of antimicrobial effectiveness, mechanical properties and economy. The new hybrid polyurethanes display no-leaching contact kill against several strains of Gram-positive and Gram-negative. Good biocidal effectiveness is retained after storage for at least two months under ambient conditions of temperature and humidity. Surface morphology and topology via TM-AFM imaging of hybrid coatings and zeta potential measurements provide insight into the stability of biocidal effectiveness and polycation concentration at the coating surface.

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Wednesday, March 19, 2014 02:05 PM
12th International Symposium on Biorelated Polymers (01:30 PM - 04:30 PM)
Location: Hyatt Regency Dallas
Room: Moreno B
New antibiotics with novel modes of action are necessary to combat the increasing number of drug-resistant bacteria. In recent years, very few antibiotics have been introduced due to challenges identifying new bacterial targets effective to the current and emerging resistance mechanisms. The long-term goal of this research is to develop new antimicrobial agents based on cationic methacrylate polymers. In this study, we evaluated the activity of these polymers against bacteria and their cytotoxicity to mammalian cells. The minimum inhibitory concentration (MIC) against a panel of Gram-positive and negative bacteria was determined using a standard turbidity-based assay. In general, the polymers were more active against the Gram-positive bacteria as opposed to the Gram-negative bacteria with the exception of \textit{S. enterica}. The cytotoxicity of these polymers to mammalian cells was also evaluated by a cell-viability XTT assay. At high concentrations, polymers significantly reduced the cell viability of HEP-2 (IC\textsubscript{50} = 70 \mu g/mL) and COS-7 cells (IC\textsubscript{50} = 250 \mu g/mL). One polymer was tested against an \textit{S. aureus} nasal colonization in a rat model. This polymer successfully reduced the number of \textit{S. aureus} colonies in the nasal cavity by 99\%, as compared to the antibiotic mupirocin (58\% colony reduction).
The synthesis and characterization of multi-functionalized Fe$_3$O$_4$/SiO$_2$ core-shell magnetic nanoparticles were investigated. The magnetic nanoparticles were prepared by two methods, namely microemulsion and direct-coprecipitation of Fe(III) and Fe(II) salts. Both of the methods generated well-dispersed and mono-distributed magnetic nanoparticles. The direct-coprecipitation of iron salts strategy generated core-shell structure superparamagnetic nanoparticles with a high saturation magnetization of 55.6 emu/g under mild conditions. The surface-initiated reversible addition fragmentation chain transfer (RAFT) polymerization of methylacrylic acid was conducted on CPDB coated magnetic nanoparticles and the resulting nanoparticles are water soluble. TEM images showed that the poly(methacrylic acid) grafted magnetic nanoparticles were well dispersed with diameters of the individual nanoparticles 40 - 50 nm. The grafted PMAA was methylated by trimethylsilyldiazomethane to conduct organic phase GPC characterization. The PMAA grafted Fe$_3$O$_4$/SiO$_2$ magnetic nanoparticles can enhance the bioactivity of Penicillin G over bacteria (both Gram negative and Gram positive) when physically binding with Penicillin G. [figure 1]
613 - WITHDRAWN
614 - RGD peptide-modified dendrimer-entrapped gold nanoparticles enable effective gene delivery to stem cells

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We report the use of RGD peptide-modified dendrimer-entrapped gold nanoparticles (Au DENPs) for enhanced stem cell gene delivery applications. In this study, generation 5 poly(amidoamine) (PAMAM) dendrimers modified with Arg-Gly-Asp (RGD) peptide via a poly(ethylene glycol) (PEG) spacer and monomethyl ether PEG (G5.NH2-(PEG-RGD)10-mPEG10) were used as templates to entrap gold nanoparticles. The formed PEGylated dendrimers and Au DENPs with or without RGD were characterized via different techniques. These dendrimers and Au DENPs were then used as vector to transfect plasmid DNA (pDNA) carrying both luciferase (Luc) reporter gene and enhanced green fluorescent protein (EGFP) gene, and a pDNA reporting human bone morphogenetic protein-2 (hBMP-2) to human mesenchymal stem cells (hMSCs). We show that all vectors are able to transfect both pDNAs to hMSCs. For the former pDNA transfection, this can be demonstrated by quantitative Luc activity assay and qualitative fluorescence microscopy. For the transfection of the latter pDNA, the gene delivery efficiency can be evaluated by the level of osteogenic differentiation of hMSCs via alkaline phosphatase (ALP) activity, osteocalcin secretion, calcium deposition, and von Kossa staining assays. Our results reveal that the stem cell gene delivery efficiency is largely dependent on the composition and the surface functionality of the dendrimer-based vectors and follows the order of K4 > K2 > K3 > K1 > K0 (See and caption). The coexistence of RGD and Au NPs renders the designed vector with specific stem cell binding ability via binding of αvβ3 integrin on the cell surface and improved 3-dimensional shape of dendrimers, which is beneficial for enhanced stem cell gene delivery applications.

Wednesday, March 19, 2014 03:50 PM
12th International Symposium on Bio-related Polymers (01:30 PM - 04:30 PM)
Location: Hyatt Regency Dallas
Room: Moreno B
615 - In vivo delivery of transcription factors with multifunctional oligonucleotides

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Therapeutics based on transcription factors have the potential to revolutionize medicine but have had limited clinical success due to delivery problems. The delivery of transcription factors in vivo is challenging because it requires developing a delivery vehicle that can complex transcription factors, target cells, and stimulate endosomal disruption, with minimal toxicity. In this report we present a multifunctional oligonucleotide that can deliver transcription factors in vivo for the first time, termed DARTs (DNA Assembled Recombinant Transcription factors). DARTs are composed of an oligonucleotide that contains a transcription factor binding sequence and hydrophobic membrane disruptive chains that are "masked" by acid cleavable galactose residues. DARTs have a unique molecular architecture, which allows them to bind transcription factors, trigger endocytosis in hepatocytes, and stimulate endosomal disruption. The DARTs are able to complex transcription factors and target cells due to their oligonucleotide sequence and galactose residues respectively. In addition, the DARTs can disrupt endosomes efficiently with minimal toxicity, because unmasking of their hydrophobic domains only occurs in the acidic environment of the endosome. We show here that DARTs can deliver the transcription factor Nuclear erythroid 2-related factor 2 (Nrf2) to the liver, catalyze the transcription of Nrf2 downstream genes, and rescue mice from acetaminophen induced liver injury.

Wednesday, March 19, 2014 04:10 PM
12th International Symposium on Biorelated Polymers (01:30 PM - 04:30 PM)
Location: Hyatt Regency Dallas
Room: Moreno B
We have designed a new aliphatic polyester that upon formation of a reactive end-group depolymerizes to give carbon dioxide and toluene. The polymer is selectively functionalized with various end-caps allowing for the system to be sensitive to light, acid, base, fluorine, or transition metals. Our research for this new material is focused on its adaptation for EUV resist formulations. As we approach the 10nm half-pitch, the problems with line edge roughness (LER) have become problematic. A main contributor to LER is acid diffusion in chemically amplified resists (CARs), which is exacerbated by the low photon count of EUV light. Improvement requires either a larger photo acid generator (PAG) loading or doses far outside the capabilities of the tools themselves. Our new approach to EUV resists finds amplification through self-immolating polymers. By using a dissolution-inhibiting polymer in Novolac that requires only one non-catalytic photolysis event to undergo a full depolymerization, we aim to achieve high sensitivity, high resolution and decreased LER. The ideal polymer must possess five key properties to be successful: 1) Be miscible with Novolac for our first generation strategy, 2) Contain Lewis acidic sites to block the phenolic groups of the Novolac resin, 3) Depropagate into neutral or Lewis basic monomers to allow dissolution, 4) Have a T<sub>c</sub> above 0º and below 150º for tool and manufacturing compatibility, 5) Be sensitive to EUV exposure via an end-cap or intrinsically via the polymer backbone.
617 - Self-depropagating polyester for extreme ultra violet photoresists

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We have synthesized self-depropagating polyesters with some reactive end-caps as a new candidate for extreme ultra violet (EUV) photoresists. Currently, chemical amplified resist (CAR) system is generally used as photoresists. This system improves the sensitivity by the acid diffusion. But this acid diffusion becomes a problem in EUV lithography. EUV lithography is targeting 10nm half pitch pattern. In this scale patterning, the acid diffusion comes out as pattern blur that is line edge roughness (LER). We are trying to dissolve this issue by the self-depropagating polymers. Those polymers depolymerize by only one trigger reaction and low molecular weight compounds are produced by subsequent self-depolymerization. The depolymerization enhances chemical property's change at exposed area in photolithography. To replace EUV resists from CAR system to self-depropagating system, some properties are needed for the polymers. Those are Inhibition effect for developer, alkali soluble or low b.p. structures after depropagation and depolymerizing below 150 degrees C. By satisfying these requirements, we designed new aliphatic polyesters. We aim to prepare high resolution, small LER and high sensitivity resist materials by the self-depropagating polyesters.
Many organic (opto)electronic devices rely on materials to adopt polyene-like quinoidal structures under operationally-relevant scenarios, a phenomenon that can only be realized by breaking aromaticity. In this context, improving the polyene-character of a material is considered a promising approach to promoting quinoid formation and can be accomplished by introducing non-aromatic \( n \)-conjugated subunits into the system. Unfortunately, the pool of appropriate precursors is severely limited, an issue that must be addressed if materials that exhibit the desirable attributes of a polyene and a polyaromatic are to be prepared. This presentation will describe a convenient and efficient route to cyclopentadiene-containing \( n \)-conjugated (macro)molecules. Highlights include the results of a comparative analysis between the aryl/dienyl hybrids and their aromatic congeners that show a propensity of the diene moiety to reduce the optical band gap of a \( n \)-conjugated system without compromising its planar structural topology.
619 - Toward tough structured thermoset blends for advanced composites

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In pursuit of extending the life cycle of advanced composites, such as those used in wind energy and aerospace applications, the objective of this project is to create structured thermosetting blends, where one component, diglycidyl ether of bisphenol A (DGEBA), contributes a large modulus and tensile strength and the other, polydicyclopentadiene, cured via ring opening metathesis polymerization, contributes high fracture toughness. Differential scanning calorimetry and rheology were used to explore the curing kinetics and gel-times of the individual systems in an effort to match the rate of network formation and thus limiting macroscopic phase separation through kinetically trapping the two networks and creation of interpenetrating polymer networks (IPNs). Given the large difference in curing kinetics, sequential curing of the two polymers was employed as a practical approach but elucidated poor compatibility between the two networks when explored via optical microscopy and glass transition temperature analysis.

The immiscible nature of this system led to the decision to explore *in-situ* compatibilization via special dual-functional molecules that possess reactivity towards Grubbs' catalyst and DGEBA. To supplement the *in-situ* compatibilization efforts, cloud point measurements and small-angle neutron scattering experiments were performed to characterize the Flory-Huggins interaction parameter between the components of this system and identify reaction conditions for the preparation of polymer blends with controlled morphology.

**Wednesday, March 19, 2014 02:00 PM**
*General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:00 PM)*
*Location: Hyatt Regency Dallas*
*Room: Reverchon A/B*
620 - Hydrolytic degradation and thermal properties of epoxy resins derived from soybean oil

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Epoxy resins are a class of polymer that is widely applied in coatings, adhesives, automotive components, wind turbine blades and other applications, due to their superior chemical, electrical and heat resistance, adhesion and mechanical properties. However, most commercial epoxy resins are derived from non-sustainable petroleum, which is a limited resource. For this reason, sustainable biomass derivatives – such as vegetable oils, plant sugars, lignin and cellulose – have attracted much interest to replace traditional epoxy resin components, such as the diglycidyl ether of bisphenol A (DGEBA).

The objective of this work is to develop sustainable and degradable epoxy resins with high mechanical performance and enhanced recyclability. We are utilizing sustainable raw materials derived from biomass to introduce degradable cleavage points throughout the network. Epoxidized soybean oil (ESO), made from high-yield and low-price soybean oil, is an attractive replacement for traditional epoxide-containing molecules to form epoxy resins. The current aim of this research is to add ESO, a flexible molecule that contains ester linkages which are inherently biodegradable, to improve traditional epoxy resins. The thermal properties and degradation behavior of these polymers have been characterized, including thermogravimetric analysis, differential scanning calorimetry, curing kinetics, and hydrolytic degradation in a basic solution.
We have investigated the mechanochemically initiated depolymerization of poly(phthalaldehyde) (PPA), a low ceiling temperature self-immolative polymer. It was found that ultrasound-induced cavitation is capable of causing chain scission in the PPA backbone that ultimately leads to rapid depolymerization of each resulting polymer fragment. An interesting feature of the mechanochemical breakdown is that "half-chain" fragments are not observed, since the depolymerization is rapid following chain scission. These features facilitated the determination of rate constants of activation for multiple molecular weights from a single sample. Finally, an ionic degradation mechanism, which is uncommon in the mechanochemical degradation of polymers, was supported by chain-end trapping experiments.
622 - Novel TMDSC approach to probe the inner structures of hybrid emulsion gel particles

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The inner structures of polystyrene/CTAB/silica and poly(methyl methacrylate)/CTAB/silica hybrid particles were characterized by temperature modulated differential scanning calorimetry (TMDSC). The transitions from the polymers and the surfactants (CTAB) upon heating/cooling were separated using a temperature-modulated mode. The temperatures for the different transitions of CTAB in the thermograms revealed the locations of CTAB inside of the hybrid particles. The enthalpies under each transition were used to estimate the amount of the CTAB at each location. By using a set of normalized thermal transition data as references, the layered inner structures of the hybrid particles were quantitatively analyzed. The new TMDSC method provides not only an objective approach to understand the inner structures of the hybrid particles, but is also a good technique to analyze the surfactants inside of hybrids, which are not obtained by other techniques, such as transmission electron microscopy.
623 - Development of “flex activated” mechanophores: Using bond bending motions to achieve mechanochemical activation

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The ability of macromolecular scaffolds to direct the input of mechanical force to specific reaction sites, i.e. polymer mechanochemistry, has been demonstrated in the past decade to be a versatile strategy for activation of myriad types of reactions. The reaction sites, or mechanophores, are designed such that the desired reaction pathways are consistent with the envisioned effect of mechanical deformation on the moiety. Generally, this strategy results in the incorporation of specific scissile bonds within the polymer backbone, which are elongated to the point of cleavage upon the application of mechanical force. An unexplored aspect of mechanochemical reactivity is the potential for bond scission orthogonal to the polymer main chain, which would enable the release of small molecule side chains while preserving overall macromolecular architecture. We recently demonstrated the first mechanophore capable of this type of “flex activation” in which bond bending motions are harnessed to activate the mechanochemical response. Upon the application of compressive force, the oxanorbornadiene mechanophore undergoes a retro-[4+2] cyclization, resulting in a net strengthening of the polymer backbone with concomitant expulsion of a small organic molecule. The development of the concept of “flex activation” will be discussed, along with experimental and computational investigations into the reactivity of the oxanorbornadiene system and extensions of this concept to other types of polymer matrices and mechanophore structures.
624 - Probing the surface and bulk properties of fluoroPOSS-PDMS amphiphiles

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The synthesis of incompletely-condensed POSS compounds with long-chain fluoroalkyl substituents (fluoroPOSS) has enabled the incorporation of fluoroPOSS moieties into polymers. In the present work fluoroPOSS moieties were grafted to silane-terminated or methylsiloxane-containing polydimethylsiloxane (PDMS) polymers via Pt-catalyzed hydrosilylation with vinylmethyl fluorodecy18T8D1 POSS. The molecular structure of functional fluorodecy1 POSS compounds and PDMS polymers were characterized by ¹H, ¹⁹F, ¹³C, and ²⁹Si NMR spectroscopy, and MALDI-TOF mass spectrometry. Dynamic contact angle analysis using water, hexadecane, and isopropanol was used to elucidate the surface assembly of fluoroPOSS PDMS polymers. Dynamic light scattering and differential scanning calorimetry were used to elucidate bulk assembly. The concentration and macromolecular architecture of synthesized fluoroPOSS-PDMS polymers will be shown to correlate strongly with assembly in both the bulk and on the surface. The potential use of synthesized fluoroPOSS PDMS macromolecules in mechanically robust liquid repellent coatings, and as a well-defined, macro-surfactant with oleophobic-oleophilic interactions will be discussed.
625 - Surface and bulk water in colloidal unimolecular polymer (CUP) systems investigated by spin-lattice ($T_1$) relaxation measurements

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Water-based colloidal unimolecular polymers (CUP) have ultra-high surface area per gram of particles. The surface of these particles should exhibit properties dominated by the surface water. Spin-lattice proton NMR relaxation ($T_1$) experiments were conducted by means of low magnetic field NMR (20 MHz, $^1H$) at 18°C to interrogate the free and surface population of water in the system as a function of concentration and molecular weight, 29kD and 111kD. The inversion recovery data were analyzed by a model equation consisting of the sum of two exponential terms made up of five fit parameters in order to calculate the amount of bound and free water in this system. The spin-lattice relaxation rate $T_1^{-1}$ varies with CUP concentration, the component of the $T_1$ distribution (short $T_1$) that is associated with bound water increases with increasing concentration of CUP. The spin-lattice relaxation time constant of bound water $T_{1b}$ was shorter than the relaxation time of free water $T_{1f}$ by a factor of approximately 50. Two CUP parameters were important in determining the amount of the associated water; size of the particle and the charge density. Smaller particles had more surface area per gram but the larger particles had a higher charge density. As the concentration of CUP was increased the thickness of the bound water layer decreased. This reduction of thickness can be explained on the basis of Manning condensation.
626 - Supramolecular thermoplastic elastomers

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Utilizing fundamental information of well-known thermoplastic elastomers (TPE's) such as Poly(Styrene)-Poly(Butadiene)-Poly(Styrene) (SBS) and thermoplastic polyurethane elastomers (TPU's), the focus of this research has been the synthesis and characterization of a class of novel ABA triblock copolymers and their properties as TPE's.

Thus far, a TPE possessing ABA architecture has been synthesized and characterized. The soft B block is poly(butadiene) and the hard A blocks are made up of oligo(β-alanine) (Nylon 3) units. (See Figure) Nylon 3 is unique to the nylon family because its only observed secondary structure is flat, anti-parallel β-sheets.\(^1\)\(^2\) It is hypothesized that the hard domains formed by this secondary structure will strengthen an elastomer by two mechanisms. First, by physical cross-linking via intermolecular hydrogen bonding and secondly, through a filler effect resulting from the disperse oligo(β-alanine) domains.

DSC confirms two phases are present as a melting point \((T_m)\) can be seen for the hard, crystalline domain and a glass transition temperature \((T_g)\) is observed for the soft, amorphous phase. Oligo(β-alanine) units have been synthesized by solution phase peptide synthesis as well as two different polymerization methods. The differences between these synthetic routes and their effect on TPE properties will be detailed in this research.

References:
627 - Plasticization and melt viscosity reduction of AN/VIM copolymers for filament extrusion

Benjamin L Batchelor¹, ben.batchelor@utdallas.edu, Samsuddin F Mahmood³, Michael W Duff¹, Minhye Jung², HyunKyu Shin², Duck J Yang¹, Dennis W Smith, Jr.¹. (1) Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United States, (2) Korea Institute of Carbon Conversion Technology, JeonJu City, Democratic People’s Republic of Korea

Fibers of Polyacrylonitrile (PAN), or commonly referred to as acrylic fibers, have found to have many uses in the world. Acrylic fibers are used as a textile medium for high quality and high performance yarns and fabrics, and also as the main supply of precursors for carbon fibers. The reasoning for this is because of the high carbon yield of 55% in comparison to other materials which have much lower carbon yield. The current issue with the current acrylic stock is due to its harsh and costly processing conditions. Currently the acrylic fibers are processed by solution spinning in harsh solvents requiring solvent reclamation. We will show to solve this by copolymerizing acrylonitrile with 1-vinylimidazole creating a Tg of 115 °C then can be further plasticized. Melt processing of PAN fibers will be shown by creating and then lowering the processing temperatures to obtain fibers by twin screw extrusion. By incorporation of plasticizers and flow aids, lower operating temperature can be achieved as great as a 25-50 °C reduction.
628 - Synthetic block copolypeptides: A new approach to prevent and treat infections

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Life-threatening infections occur far too frequently when our natural barriers of defense are broken by surgery, trauma, medical instrumentation, or disease. Local wound environments, with dead and damaged tissues (“cracks & crevices”), facilitate microbial growth and invasion. Systemic antibiotics and topical antiseptics are not enough. A-Blocks™ (Amicrobe block copolypeptides) represent a new class of biomaterials designed to fill the treatment “gap”. These long-chain synthetic copolypeptides are composed of one block of cationic amino acids (typically 100 or more) and one block of hydrophobic amino acids (typically 10-60). They self-assemble into microstructures such as fibrils or micelles in aqueous media. A-Blocks are engineered to: (1) kill microbes directly; (2) fill & coat tissue spaces; and (3) be safe for direct application to exposed tissues. They show broad-based antimicrobial activity against Gram-positive bacteria (e.g., *S. aureus*, *S. epidermidis*), Gram-negative bacteria (e.g., *P. aeruginosa*, *E. coli*) and yeast. In animal models, they demonstrate direct antimicrobial activity, as well as antimicrobial barrier function. It is anticipated that A-Block hydrogels and solutions will be applied directly to the exposed tissues of surgery and trauma to help prevent and treat infections.

![Image](https://example.com/image.png)

**Figure 1. Amicrobe's Surgical Hydrogel and Ant-Infective Solution display potent antimicrobial activity in porcine (left) and rodent (right) models. Fluorescently-tagged materials (green) show effective coverage of open wounds.**

**Thursday, March 20, 2014 08:00 AM**

**Peptide-Based Materials for Nanomedicine (08:00 AM - 11:40 AM)**

**Location:** Hyatt Regency Dallas

**Room:** Reunion Blrm C
The self-assembly of globular protein-polymer diblock copolymers into nanostructured phases provides a route for the construction of biofunctional materials with a high density of active protein domains. The thermodynamics of self-assembly in aqueous environments and in solid-state materials shows significant complexity due to the complex shapes and interactions present in folded protein blocks. Herein, we isolate the effect of protein surface interactions on the self-assembly process through comparisons of self-assembly in structurally homologous proteins with significantly different surface potentials. It is demonstrated that under neutral solvent conditions coarse-grained effects dominate the self-assembly process; however, the details of the protein interaction have a larger effect under conditions where the buffer is selective for the protein block. Experiments with varying ionic strength suggest that ionic interactions promote phase separation in the systems studied. Changes in polymer chemistry are also explored as a method to alter protein-polymer interactions, demonstrating a very large impact on self-assembly in concentrated solution, including the observation of new cubic nanodomain structures. Finally, coating materials into thin films enables is shown as a way to produce biocatalytically active materials and coatings.
Peptides that recapitulate the structural and functional properties of proteins serve as models of complex biological systems, as building blocks for synthetic biology, and as a privileged class of nanostructures. However, to mitigate the material properties of these peptides, we conjugate synthetic polymers (i.e., dendrons) to minimalist peptide models of proteins. Understanding how synthetic groups affect the structure of the peptides is desirable for the design of hybrid biomaterials for nanomedicine. Our approach to developing this understanding involves critically testing rules for the de novo design of peptides that mimic protein folding and assembly in the context of dendron-peptide conjugates. The presentation will illustrate spectroscopic and biophysical studies to systematically evaluate how robust are these protein design rules.
Every year in the United States, more than half a million patients undergo surgical operations to remove diseased colorectal tissues, and may require surgical anastomoses of the healthy sections. Standard suturing and stapling techniques rely on piercing healthy tissues and can cause anastomosis leakage leading to life-threatening bacterial infections. In the present study, we demonstrated that plasmonic nanocomposites, generated from cysteine-containing elastin-like polypeptides (CELPs) and gold nanorods (GNRs), facilitated the photothermal welding of ruptured colorectal tissues (ex vivo) to achieve fluid-tight sealing.

GNRs and CELPs were synthesized for fabrication of nanocomposite thin-films. CELPs (2 mg/ml) were self-assembled on GNRs (9.5-190 μg/mL) via gold-thiol bonds at 4°C, a temperature below the transition temperature (Tt) of CELPs, to form nanoassemblies. Heating nanoassemblies above Tt resulted in irreversible phase separation, which leads to the formation of nanocomposites. The photophysical, rheological and biological properties of nanocomposites were evaluated using UV-Vis spectroscopy, rheometer and cell culture, respectively. For laser tissue welding, a titanium sapphire laser pumped by a solid-state laser was employed (800 nm, 20 W/cm², 0.4-2.8 kJ) to re-connect the ruptured porcine intestines in presence of nanocomposites. Post-welding, tissue tensile strength, leakage pressure, bursting pressure and bacteria (E. coli DH5-alfa) leakage were measured.

We have delivered reproducible, stable, light-activable, and biocompatible GNR-CELP nanocomposites. The mechanical property of the nanocomposite can be easily modulated by adjusting the GNR content of the nanocomposites. Biocompatible nanocomposites supported fibroblast cell growth with minimal toxicity up to 72 hours. Heat generated from nanocomposites (monitored via IR camera) enhanced the tensile strength and leaking pressure of ruptured-tissue and created a fluid-tight seal. Welds were examined histologically for thermal injury, nanocomposite-tissue fusion and others. Plasmonic nanocomposites possess enormous translational potential in the repair of colorectal tissues and others. The encapsulation of stem cells and drugs for tissue regeneration/repair will be discussed.
Hydrogels have been found in a variety of biomedical applications ranging from 3-D cell cultures and stem cell differentiation to regenerative medicine, controlled drug delivery and tissue engineering. Polymer gels made of flexible chains have been thoroughly studied to understand the relationship between the physical and functional properties. In contrast, the thermodynamic behavior of supramolecular hydrogels, composed of entangled nanofibers is largely unknown. These systems are formed by self-assembly of small molecules via non-covalent interactions. Enzyme instructed self-assembly allows us to make nanofibers with uniform diameter and infinite length. We investigate the self-assembly of two typical hydrogelators using dynamic light scattering (DLS) and NMR. Measurements have been made on both systems as a function of the concentration and temperature. DLS yields information on the initial stage of fiber formation. Small angle neutron scattering (SANS) is used to determine the structural characteristics (cross-sectional radius of the fibers, average mesh size of the network, etc.) of the nanofibers. We believe a better understanding of the self-assembly process will help us to design supramolecular nanofibers/hydrogels for applications in biology and medicine.
633 - Biomimetic polypeptide-based polymersomes for nanomedicine

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Polymer vesicles (polymersomes) are among the most attractive systems for drug delivery applications. Peptides and polypeptides as building block are of particular interest as they allow both a great control over polymer secondary conformation (driving the self-assembly process) and responsive properties (allowing the formation of smart polymersomes). Furthermore, the use of peptide and saccharide building blocks in the copolymer structure would allow both controlling the self-assembled structure and the resultant biofunctionality. We report recent development 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. Exciting and very promising results about their therapeutic evaluation for tumor targeting and in vivo tumor regression studies will be presented.
Bacterial encapsulins are a class of non-viral protein cages that self-assemble into stable icosahedral structures. Using teal fluorescent proteins (TFP) engineered with a specific oligopeptide, we report the molecular self-sorting and selective packaging of TFP cargo into bacterial encapsulins during *in vivo* assembly. Using native mass spectrometry, we show that loading of TFP cargo occurs with high fidelity and exceptional loading accuracy. Forming highly stable, monodisperse assemblies, bacterial encapsulins are highly promising candidates for future applications in nanotechnology.
635 - Introducing peptomicelles, nanopetogels and peptoplexes: A journey from synthesis of polypeptides to nanoparticles for immunotherapy and diagnostics

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Nanomedicines are expected to have major impact on the development of pharmaceuticals during the 21st century, because they bear the potential to adjust pharmacokinetics of drugs, combine different bioactive agents and deliver them simultaneously.

To design nanoparticles and adjust material properties to the desired application a controlled synthesis of polymers is necessary to ensure polymer functionality and reproducibility. Thus, polymers derived from controlled polymerizations are required to fulfill these needs. In respect to a medical application, polymers need to fulfill further requirements, such as biocompatibility, non-immunogenicity and the ability to be excreted or even better metabolized within the body after performing the desired action.

One remarkable polymeric material fulfilling these needs are polypeptides. One versatile pathway to protein mimics is the polymerization of a-aminoacid-N-carboxyanhydrides. Although this technique cannot provide sequence control it allows to adjust chain length, architecture, functionality and immunogenic properties to a specific need and include functionalities beyond nature’s possibilities.

We have developed various polypeptides based on natural amino acids having molecular weights from 10 – 40 kDa and dispersities around 1.1. While polysarcosine was used a hydrophilic block ensuring stealth-like properties derivatives of lysine, glutamic acid and cysteine carry reactive groups. These groups can be selectively addressed and create amphiphilic block copolypeptides and enable conjugation of bioactive agents or crosslinking of nanoaggregates. By adjusting polymer properties as well as conditions of aggregate formation we were able to synthesize PeptoNanoGels (siRNA and oligoDNA delivery), PeptoPlexes (pDNA delivery) and PeptoMicelles (drug delivery and imaging) in the size range of 40 to 200 nm.

The systems have been applied to cancer immunotherapy, chemotherapy of solid tumors as well as controlled release systems for inhibitors for disease related enzymes.

References
1) M. Barz et al. Polymer Chemistry, 2011, 2, 1900-1918.
In this study, silica nanoparticles, fabricated by the Stöber method, were transformed into multifunctional nanoreactors for use in biosensing applications. Bare silica nanoparticles were modified with 3-aminopropyl trimethoxysilane (APTM) to allow covalent attachment of the luminescent dye, Pd(II) meso-tetra-4-carboxyphenyl porphine (PdP), with EDC and sulfo-NHS. An enzymatically-active region was introduced through layer-by-layer self-assembly (LbL) using poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) to immobilize the enzyme glucose oxidase (GOx) on the particles (Figure 1).

The particles retained activity after being immobilized in a poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogel and tested for optical response to glucose under physiological conditions (Figure 2).

Results demonstrate: 1) silica nanoparticles can be used as templates for immobilizing sensing chemistry to create independently-functioning nanoreactors and 2) these nanoreactors can be incorporated into larger implantable hydrogel structures for in vivo sensing applications.
637 - Synthesis and application of responsive polymeric nanoparticles for gene delivery

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This presentation discussed our recent success on developing a new synthetic strategy to obtain nanostructured responsive polymers and exploring their applications for gene delivery. Functional polymers with uniform size and hierarchical structures, including stars, molecular brushes, hyper-stars, hyperbranched polymers and nanocapsules, can find broad applications in various areas. However, facile syntheses of these materials with precise control on structures and compositions are never easy. We recently applied controlled radical polymerizations in nanometer-sized confine space, such as micelles, and successfully regulated the polymerization behavior of different functional monomers to produce uniform hyperbranched polymers in one pot. The obtained polymers with thousands of preserved initiating sites were used as multifunctional initiators for surface polymerization and produced core-shell structured hyper-stars with functional layers to encapsulate siRNA.
Modern medicine is focusing on the development of new concepts that combine multifunctional compounds with stable carriers or membranes in patient-oriented diagnostics or therapeutic strategies. Suitable amphiphilic block copolymers can self-assemble into supramolecular assemblies, such as compartments with sizes in the nanometer range. The properties of such polymer assemblies can be extensively controlled via chemical composition, molecular weight and the hydrophilic-to-hydrophobic block length ratio of the polymers. Compared to conventional, low molar mass building blocks (e.g. lipids), membranes based on macromolecular self-assembly have advantages of superior stability, robustness, and possibility to tailor their physical, chemical, and biological properties. Other functions, such as catalytic activity can be introduced by combining these polymeric assemblies with suitable biological entities.

Here, we present how polymer compartments that provide distinct spaces for encapsulation/insertion of biomolecules (enzymes, membrane proteins, mimics) in a functional way are designed to serve as artificial organelles inside cells. Channel proteins inserted into the polymer membrane of compartments act as gates for the exchange of substrates and products with the environment, while encapsulated combination of enzymes acting in situ provide the specific functionality (Figure 1). We show that a system based on two enzymes working in tandem in polymer vesicles, with a membrane rendered permeable by inserted channel proteins, mimics peroxisomes, natural organelles involved in regulation of reactive oxygen species. This system was optimized in terms of natural peroxisome properties and function. Uptake, absence of toxicity, and in situ activity in cells exposed to oxidative stress demonstrated that the artificial peroxisomes detoxify superoxide radicals, and H₂O₂ after endosomal escape. Our artificial peroxisome combats oxidative stress in cells, a factor in various pathologies (e.g. arthritis, Parkinson's, cancer, AIDS), and offers a versatile strategy to develop other “cell implants” for cell dysfunction.

Figure 1. Schematic representation of a cell containing both natural and artificial peroxisomes.

References:

639 - Non-toxic coatings with nanoscopically-complex surfaces for anti-biofouling applications

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The need for non-toxic, anti-biofouling surfaces for use in marine environments is increasing due to the number of prohibitions placed on commonly used heavy metal paint formulations. Currently, a number of anti-biofouling coatings have been proposed, with three classes of widely investigated polymers having been shown to inhibit fouling of specific marine organisms; that of fluoropolymers, siloxanes and poly(ethylene glycol) (PEG) based materials. An array of amphiphilic polymeric network generated by the crosslinking of hyperbranched fluoropolymer (HBFP), with varying concentrations of polydimethylsiloxane (PDMS) and PEG, was studied. Crosslinking coincides with and is followed by degrees of thermodynamically-driven phase separation within the bound network and results in a complex surface that displays dynamically-reorganizing heterogeneity in its topography, topology and chemical composition on both the nano- and the micro-scale. Through characterization with atomic force microscopy (AFM), surface force spectroscopy and static water contact angle, the surfaces were observed to display reorganization upon submersion in water. Fouling studies were performed with various marine organisms to test the performance of the systems as anti-biofouling coatings. The findings in this study suggest that the terpolymer system employed has potential to be used as a novel class of anti-biofouling coatings that are non-toxic and offer improved performance due to the heterogeneities generated at the surface from the crosslinking of the three constituents.
Laccases represent a class of enzymes with various industrial and biotechnological applications due to their ability to oxidize lignin compounds and persistent environmental pollutants. As their applications require the ability of the laccase to maintain activity in aggressive environmental conditions (presence of various degrading agents), its protection is mandatory. In order to protect the enzyme, and increase its stability in aggressive environment, we propose a new approach: enzyme encapsulation in polymer vesicles (polymersomes) with oxygen permeable membrane. In situ active laccase (Lac) serves as active component for the design of laccase-based nanoreactors with improved efficiency due to the protective role of polymersomes. Inside polymersomes Lac is simultaneously protected and accessible for its key substrate, oxygen (Figure 1A). Laccase nanoreactors act as a source of reactive oxygen species (ROS) because ROS produced in situ escape the nanoreactor, and react with the corresponding compounds present in the environment of polymersomes. We synthesized poly(N-vinylpyrrolidone)-poly(dimethylsiloxane) (PDMS-PNVP) copolymers for generation of polymersomes due to the high permeability of membrane for oxygen and ROS. Five different PDMS-PNVP polymers were synthesized in order to determine those that are able to self-assemble into polymersomes with the intended permeability and size distribution. The successful Lac encapsulation inside the PDMS-PNVP polymersomes, and its in situ activity were tested by a combination of spectrophotometric methods using ABTS as substrate (Figure 1B).

References:
641 - Binding strength of siRNA/copolymer complexes utilizing aqueous RAFT synthesized hydrophilic-block-cationic copolymers and the effects on gene suppression

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Current research efforts are focused on the development of siRNA carriers that will not only minimize degradation of siRNA during transport but also increase transfection efficiency into cells. Recent advancements in controlled polymerization strategies have allowed for the construction of narrowly dispersed (co)polymers of predetermined molecular weight and architecture. In this research, aqueous RAFT was used to statistically polymerize N-(2-hydroxypropyl)methacrylamide (HPMA) and primary amine containing N-(3-aminopropyl)methacrylamide (APMA), providing biocompatibility and non-immunogenicity from HPMA and a functional handle for post-polymerization conjugation through APMA. This poly(HPMA-stat-APMA) macroCTA was utilized to prepare a series of chain extended copolymers with cationic monomer N,N-(dimethylaminopropyl)methacrylamide (DMAPMA) with varying block lengths. This series of poly[(HPMA-stat-APMA)-block-DMAPMA] copolymers formed narrowly dispersed, neutral complexes with siRNA under physiological conditions allowing for full characterization of binding strength via differential scanning calorimetry and analytical ultracentrifugation. From these analytical methods, increasing binding strength and increased oligonucleotide stability with increasing DMAPMA block length was determined; however, increased intercomplexation bridging was also observed. Use of circular dichroism to probe the changes in oligonucleotide secondary structure found no noticeable alterations upon copolymer complexation, indicating that genetic information remains unaltered during cellular delivery. From these results, we hypothesized that altered binding of these hydrophilic-block-cationic copolymers would greatly affect the gene suppression. No noticeable increases or decreases in gene suppression were observed; however, the kinetics of gene “knockdown” were affected. These findings may allow for fine-tuning for controlled release of siRNA in future applications.
642 - Compartmentlized stimuli-responsive colloidal nanostructure

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Biological systems offer an outstanding ability of multi-compartmentalization that facilitate diversified living functions. Recent advances in the synthesis and assembly of compartmentalized colloidal nanoparticles and nanotubes that exhibit stimuli-responsive behavior have shown that it is possible to produce tunable color and shape responses using simple colloidal synthesis. Ranging from nanoparticles consisting of variable shapes and on-demand color changes to tunable nanowires, nanotubes, and cilia-like morphologies, this presentation will focus on synthetic and physic-chemical aspects of colloidal nano-structures that exhibit stimuli-responsive attributes. Shape-tunable nanotubes as well as Janus nano-particles (JNP) can be synthesized using a simple step-wise emulsion copolymerization resulting in compartmentalized morphologies.
643 - Spiropyran and triazolium functionalized copolymers as stimuli responsive sensing layers for ion selective electrodes

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Thermo- and photo-switchable active layers for ion selective electrodes, ISEs, were developed by covalently attaching spiropyran to the cationic motifs of triazolium-based polymeric ionic liquids, PILs. The reversible light-induced transition from non-polar spiropyrone (SP) to polar mero (MC) produced a drastic change in the polarity of the sensing layer, modulating the ion exchange of the sensor's active layer with its surroundings. This SP to MC transition was used to regenerate the active layer after extended measurement periods and to selectively switch it on and off. Thermally activated control of the sensing layer was achieved via a sol-gel transition of the polymeric ionic liquids blended with triblock copolymer matrices. The sol-gel transition temperature can be controlled by changing the length of the alkyl chain attached to the triazolium groups in the ionic liquid. The selectivity of these ISE membranes is orders of magnitude higher than traditional alkyl ester-plasticized PVC membranes. The stimuli responsive, PIL-containing, sensing layers can be used to produce durable, ion selective, sensors for a wide range of applications such as carbonate levels in seawater and clinical analysis of trace metals in blood serum.
Our research team has been exploring simple and commercially viable techniques for selective transfer of enzyme molecules onto polymer surfaces that catalyze polymer degradation thereby creating lithographically defined patterns in the polymer films. By using thick polymer films (300-500 nm), we studied the ability to retain feature fidelity for holes and channels that penetrate through the film depth.

A Polymer Pen Lithography (PPL) technique was used to deposit an aqueous solution of the lipase *Candida antarctica* Lipase B (CALB) onto a spin-cast PCL film. The PPL printer used in this study employs an array (typically 10 x 10) of polydimethylsiloxane (PDMS) printing tips mounted to a multi-axis robot such that multiple patterns, one from each tip, are created in parallel. By programming the printing sequence, any arbitrary pattern of enzyme ink deposits can be generated, one pattern for each tip in the array. The tips are coated with enzyme before each printing cycle by dipping into an enzyme inkwell. After printing, the film was incubated at 37°C and 87% RH. CALB selectively catalyzes the degradation of the PCL film during incubation, forming etched features through the film thickness with straight sidewalls. Interactions between the enzyme and the PCL film restricts lateral diffusion of the enzyme and improves resolution compared to previous reported methods. The effect of printing parameters and incubation conditions along with the effect of PCL spherulite size on lithographic resolution will be presented.
645 - WITHDRAWN
Proteins as cheap, renewable, degradable and environmentally friendly biopolymers may have potentials to replace oil-based synthetic polymers in different applications. The first necessary step to utilize these polymers is to characterize and control conformational structures of protein chains in denatured status in order to make them industrially processable. Glycinin and β-conglycinin, two major proteins of soybean as two representatives of globular proteins, were chosen in this study. Since proteins are composed of amino acids with different side chain structures and varied polarities, the common practice to dissolve the proteins is to prepare an appropriate solvent system with proper chemical structures interacting with protein molecules. Thus, organic solvent systems with different physiochemical properties were explored in order to find some proper ones for both glycinin and β-conglycinin. As an approach, three dimensional solubility parameters developed by Hansen was employed as a tool in exploration of potential solvent systems for these proteins. Solubility parameters of urea solution that could dissolve the proteins were employed as a reference standard. Different solvent mixtures with varied chemical functional groups were chosen to provide levels of polarity, hydrophobicity and hydrogen bonding in the systems. Circular dichroism, dynamic light scattering, viscosity, turbidity and nano-DSC were utilized to characterize conformational status of the proteins in the solution systems. Results of this study indicate that proteins can be denatured by these organic solvent systems according to the solubility properties of the denaturent agents such as urea alkaline solutions. Alkaline solutions can accelerate the denaturation phenomena due to the effect of increasing electrostatic repulsion between same charges. Shear-thining behavior was detected in reological properties of the soy protein solutions, an indication of conformational structural changes.
Oligonucleotides (ODNs) are easily hydrolyzed in biological fluids, which makes difficult to administrate antisense DNA or CpG motif in the naked state. Polyethylenimine or cationic lipids have been used as a carrier for those oligonucleotides, however, they have drawbacks in cytotoxicity and compaction. Schizophyllan (SPG) is a natural β-(1→3)-D-glucan existing as a triple helix in water and as a single chain in dimethylsulfoxide (DMSO), respectively. When some homo-polynucleotide is added to the SPG/DMSO solution and subsequently DMSO is exchanged for water, the single chain of SPG forms a complex with the polynucleotide. The complex can protect the bound DNA against nuclease-mediated hydrolysis or non-specific binding to serum proteins. We have showed that these characteristics make possible to use native phosphodiester DNAs for antisense therapy. Furthermore, recent immunology revealed that activated antigen presenting cells (APCs) can express a receptor called Dectin-1 on their surface and Dectin-1 recognizes SPG and thus ingested by APCs. This finding suggests that SPG/ODN complex can be specifically ingested by activated APCs and the bond ODN can exert its effect after ingestion. The present talk will show our recent in-vivo and vitro studies to prove this idea and provide a new strategy to specifically transport functional ODNs including antisense-DNA, CpG-DNA, and siRNA to APCs to cure the diseases due to disorientation of immune system.

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Biopolymers such as polynucleic acids and proteins have been widely investigated in order to correlate sequence and structure to function. Polysaccharides (the third class of biopolymers) have historically been recognized as structural materials and as an energy source, and can also play important roles in biological processes such as pathogen recognition, viral entry and immune function, and cell adhesion and signal transduction. However, the lack of tools for the rapid synthesis and characterization of well-defined oligo- and polysaccharides has hampered the investigation of their complex roles in biology, and limited their exploitation for biomedical applications. Synthetic (laboratory) techniques for glycopolymers generally fall into one of two approaches. Well-defined oligo- and polysaccharides can be synthesized via a tedious protection-deprotection sequence, but generally only small amounts of product are obtained. Alternatively, monomers containing a saccharide group are polymerized. Products are high molecular weight, typically linear and only contain one or two residues, and lack specificity in biological interactions beyond the cluster glycoside effect. More efficient synthetic techniques are therefore needed to produce both short and long chain glycomimetics with well-defined biomimetic structures to achieve increased bioactivity. We report a series of glycoacrylates, glycoinitiators and glycoinimers, and optimized their polymerization. We demonstrate that branched polymers incorporating the mannose unit into the branching repeat unit show a higher affinity for mannose binding lectin (MBL) than linear polymers of the same molecular weight. Furthermore, incorporation of the glycoside in the branching repeat unit enhances the polymer's interaction with MBL, and this affinity increases with increasing branching density. In addition to producing linear and branched glycomimetics, we are also polymerizing the glycomonomers and glycoinimers from protein-based initiators to obtain protein-glycomimetic conjugates in which the glycol-component is linear or branched. We have also incorporated glycoacrylate monomers into PEG-based scaffolds and investigate their interaction with cells.
Monomeric sugars, such as glucose, galactose and mannose, are abundant, renewable and inexpensive. They are also biocompatible and therefore are especially useful as starting materials to synthesize polymers for biological and biomedical applications. Numerous efforts have been invested in the syntheses of sugar-containing polymers. Most of these efforts are focused on living radical polymerizations (LRP), wherein the sugar units are chemically attached to vinyl functionalities to form monomers, which are then subjected to radical polymerizations to give glycopolymers that have non-degradable backbones.

For biomedical applications, it is highly desired to synthesize degradable, sugar-containing polymers. However, this practice has proved challenging. Today, most degradable sugar-containing polymers are synthesized by either cationic ring-opening polymerization (ROP) or chemical glycosylation, each of which poses its own set of disadvantages.

Herein, we report two efficient approaches to synthesize polysaccharides using glucose as the starting material. In approach A, 2,3,4-tri-O-acetyl-alpha-D-glucosyl bromide was synthesized as a di-functional AB monomer. The synthesis of the monomer was achieved through a series of chemical manipulations of glucose. The monomer was then subjected to polycondensation using silver carbonate as a promoter. Under microwave irradiation, 1,6-beta-glycosylated polysaccharides were synthesized with molecular weights of 4.1 kDa. In approach B, when tetrabutyl ammonium iodide (TBAI) was used as a promoter, sugar poly(orthoesters) were synthesized with molecular weights up to 6.9 kDa. In this case, all sugar units were connected by orthoester linkages.
Alzheimer’s disease (AD) is a growing problem worldwide, making research on AD pathogenesis a pressing need. Currently, a great deal of research is focused on the specific impact of amyloid β (Aβ) peptides on AD etiology, as these peptides represent a major component of the fibril plaques that are characteristic of AD. Through interaction with various modulators, such as phosphatidylserine and GM1 ganglioside, Aβ peptides have been shown to undergo conformational change and aggregate into toxic species. Until recently, fibrils were thought to be the predominant toxic species; however, current research indicates that oligomers might be the more toxic of the two, as a discrepancy exists between the observed severity of AD and the presence of fibrils. The goal of this research, therefore, is to create synthetic polymer models with substituent groups that mimic the saccharide head group of gangliosides and the anionic phosphate moiety of phosphatidylserine, through the use of RAFT polymerization, in order to investigate the predominance of either oligomers or fibrils in the presence of each modulator. To accomplish this, a series of homopolymers and statistical copolymers, derived from monomers 2-(β-D-glucosyloxy)ethyl acrylamide [GlcEAm], 2-(β-D-galactosyloxy)ethyl acrylamide [GalEAm], and 2-acrylamidoethyl dihydrogen phosphate [AEDP], were synthesized. The polymers were characterized through 1H NMR, and ASEC-MALLS. Conformational changes and aggregation were analyzed through thioflavin (ThT) fluorescence, circular dichroism (CD), polyacrylamide gel electrophoresis (PAGE), and atomic force microscopy (AFM).
651 - Synthesis and application of single-chain polymer nanoparticles from a consecutive ROMP-RCM process

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Linear polymer from ring-opening metathesis polymerization can be facilely functionalized by allyl groups, and intramolecularly crosslinked by ring-closing metathesis to yield single-chain polymer particles controllably with valency control. The particles serve as excellent carriers as functionalities of interest can be loaded in any stage during synthesis, and the particles themselves can be tuned water-soluble through dihydroxylation. Wide application of such particles can be anticipated. For example, the particles showed to be excellent protective carriers for unstable fluorophores such as Fluorescein. Aminated particles showed capability of gene delivery. Dihydroxylated particles can serve as templates for metal nanoparticle formation. We are still actively searching for the capabilities of this material in light harvesting and antimicrobial fields.
Polymer imidazole based ligands are highly useful in coordinating to CdSe nanowires, mainly due to their resistance to degradation and robust attachment. The characterization of attachment is complicated due to the placement of nanowires on flat substrates. Terpolymers were designed to have water soluble groups (PEG), activated esters (NMS) and amine moieties such that dyes can be incorporated. The NMS essentially behaves as an activated ester along the chain and the addition of an amine based imidazole allows for cleavage of the succinimide. As all the three monomers had different and well separated peaks in the NMR, the individual monomer conversions could be determined. By controlling the ratio of monomers, the composition of each monomer in the terpolymer could be exquisitely tuned. This allowed for terpolymers with low polydispersity, high imidazole content and excellent water solubility. The dye functionalized terpolymer was then used to attach to semiconductor nanowires such that the polymer modification could be characterized effectively. Overall, a facile and robust terpolymerization system was designed for the functionalization of semiconductor nanowires with multidentate imidazole moieties is outlined.
653 - 1,1,3,3-Tetramethylguanidine promoted ring-opening polymerization of N-carboxyanhydrides using an alcohol initiator

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N-butyl N-carboxyanhydride (Bu-NCA) was polymerized in THF to produce poly(N-butyl glycine) using benzyl alcohol initiator and 1,1,3,3-tetramethylguanidine (TMG) organocatalyst. Poly(N-butyl glycine) (PNBG) with controlled polymer molecular weight ($M_n=2.9-20.5$ kg/mol) and narrow size distribution (PDI=1.04-1.11) can be obtained by controlling the initial monomer to initiator ratio and conversion. The reaction exhibits characteristics of a living polymerization, as evidenced by the linear increase of $M_n$ with conversion and the successful chain extension experiments. Kinetic studies revealed that the reaction is first-order dependent on the monomer concentration with a slow initiation ($k_i=0.019$ M$^{-1}$s$^{-1}$) relative to the propagation ($k_p = 10^6$ M$^{-1}$s$^{-1}$). MALDI-TOF MS and $^1$H NMR analysis confirmed that the polymer chains were terminated with benzyl alcohol end groups. Polymerization in other solvents such as toluene, DMF and CH$_2$Cl$_2$ or using other alcohol initiators such as EtOH and iPrOH yielded PBNGs whose molecular weights deviated to varying extents from the theoretical values based on single-site initiation. Alcohols with lower pKa appear to initiate the polymerization more efficiently than those with higher pKa, resulting in more controlled $M_n$ in the former than the latter. The polymerization has been successfully extended towards the synthesis of block copolymers based on poly(ethylene glycol) and PNBG by using a PEG-OH initiator and TMG promoter.
Solving modern problems in carbanionic polymerization: Termination and sequence control

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Living anionic polymerization plays an important role in the synthesis of well-defined macromolecules, especially with regard to block copolymers and terminally functionalized polymers. This work describes on the one hand how to adjust the reactivity to guarantee quantitative functionalization of poly(2-vinylpyridine) (P2VP) and poly(ferrocenyldimethylsilane) (PFDMS) with functional epoxide derivatives and on the other hand the monomer sequence distribution monitoring in living carbanionic copolymerization by real-time $^1$H NMR spectroscopy.

Both polymers, P2VP and PFDMS, are stimuli responsive. At a pH value below 4.8 a sufficient number of pyridine rings get protonated to render P2VP water-soluble, whereas PFDMS is redox active and has unique aggregation properties in bulk and solution. However both living polymers cannot be terminated directly with epoxides but by adjusting the reactivity of the propagating specie this throwbacks can be solved.

Direct carbanionic copolymerization represents an almost neglected field in recent decades, although control of the monomer sequence distribution within the resulting polymer chains is of growing interest. In our contribution we focus on in situ monitoring of living carbanionic copolymerizations to study the evolution of the comonomer sequence in great detail to improve the understanding of monomer sequence distribution. Two different comonomer pairs have been investigated, the chemically similarly protected poly$(p$-hydroxystyrene) $(PpHS)$ derivatives, $p$(1-ethoxy ethoxy)styrene $(pEES)$ and 4-tert-butoxystyrene $(tBuOS)$ as well as styrene $(S)$ and $pEES$, which differ in their reactivity.
Our research has focused on the unique properties that can be accessed when functionality is strategically placed in a biomaterial structure. The present research focuses on material properties such as shape memory and x-ray contrast. Since Langer and Lendlein first demonstrated the tremendous potential of SMPs in biomedical applications, there has been a continuing interest in utilizing these materials as intelligent medical devices. Our research focuses on several areas: micro- and nanotopography, reactive functionality and switching stimuli. We have developed thermally responsive micro-patterned poly(ε-caprolactone) (PCL) to examine the interaction of human mesenchymal stem cells (hMSCs) with dynamic surface patterns using PRINT™. We have also begun research on novel polymer structures containing functionality capable of micro- or nanoscopic shape memory and post-functionalization. While this application is accessed by the introduction of functionalization that allows for click chemistry, the second major effort focuses on the incorporation of stable halogens along the polymer backbone for computed tomography contrast agents. Our research efforts towards a processable system based wholly on aliphatic iodinated polyester and the resulting properties will be described.
Extensive research towards development of anti-fouling coatings has been conducted in efforts to replace traditional toxic anti-fouling paints. Amphiphilic polymeric surfaces with complex morphologies and topologies in both the nano- and micro-regimes have demonstrated excellent anti-fouling performance. Additionally, zwitterionic polymeric coatings for anti-fouling applications have been used to generate surfaces that are both energetically and kinetically unfavorable for protein adsorption, due to strong binding of water molecules at the interface. Through a novel synthetic route, a polymeric surface has been designed to combine the properties of both amphiphilic and zwitterionic systems into a single surface. Poly(styrene-co-allyl phospholane), which contains hydrophobic styrene units and reactive phospholane units, is synthesized readily from commercially available polymers. This copolymer is further functionalized via reactive phospholane units which are subsequently modified into zwitterionic phosphorylcholine units through use of a sterically unhindered tertiary amine. The resultant polymeric system was covalently attached onto silanized glass with different crosslinking extents to form amphiphilic, zwitterionic functional crosslinked networks. The polymer surfaces were characterized with atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and static water contact angle. Non-specific protein adsorption studies were performed to test the anti-fouling performance against commercially relevant siloxane standards. The findings in this study show the potential of the amphiphilic, zwitterionic surfaces as a novel class of anti-fouling coatings for future marine applications.
The unique ability of the intertidal marine mussel to adhere to wet, heterogeneous surfaces has recently attracted a tremendous amount of attention. While the natural adhesive employed by this organism is a complex mixture of proteins, the rare amino acid 3,4-dihydroxyphenylalanine (DOPA) has been identified as a common constituent that plays a pivotal role in the interfacial interactions of the adhesive plaques. DOPA's ability to undergo hydrogen bonding, π–π aromatic interactions, and metal–ligand complexation with a variety of surface functionalities facilitates interfacial adhesion. However, under slightly basic conditions DOPA is susceptible to oxidation which diminishes the molecule's adhesive ability and leads to self-polymerization. In this presentation, we report the synthesis of multifunctional halodopamine derivatives showing a decreased oxidation potential and an increased affinity for coordination to a variety of surfaces. The halodopamine monomers show improved miscibility with multifunctional thiols and enes commonly used in thiol–ene polymerizations enabling solvent-free resin systems. This presentation will describe our efforts to evaluate the effect an electron withdrawing substituent in the 2-position of DOPA analogues has on oxidation and coordination behavior, as well as evaluate the effect of the pendant catechol moiety, in the nonoxidized form, on photopolymerization kinetics, thermal, thermomechanical, and adhesive properties of the catechol modified thiol–ene networks.
Hyperbranched polymers are of particular interest for their potential in applications involving drug delivery, imaging, reactive coatings, among others. Several methods are typically employed to prepare such polymers, but one that has attracted recent attention due to its ease of experimental setup is the copolymerization of mono- and multivinyl monomers in the presence of a chain transfer agent, which effectively limits the number of crosslinker units incorporated per growing chain. In this study, CBr₄ was employed as the chain transfer agent. The obtained polymers with multiple alkyl bromide end groups, can be used as macroinitiators for ATRP. Furthermore, the use of monomer with reactive functional groups (glycidyl methacrylate) provides a synthetic route to a universal precursor of a number of functional materials. For instance, the pendant epoxide groups of the resulting polymers were converted to amines or quaternary ammonium compounds, azides, and dihalogenated compounds. Finally, the use of functional crosslinkers allows for the introduction of functional groups at the branching points.
Methyl ester pendant Fluorinated Arylène Vinyle Ether (FAVE) copolymer has been prepared via step-growth polymerization from commercially available starting materials. (Fig 1) Through a series of high conversion post polymerization modifications, the ester functionality of FAVE polymer precursor was transformed into a number of different functionalities including carboxylic acid, N-succinimide activated ester, benzyl alcohol, benzyl bromide, ketene precursor (Meldrum’s acid), azide, alkene, alkyne, and aldehydes. All polymers were confirmed by $^1$H and $^{19}$F nuclear magnetic resonance (NMR) spectroscopy. Bulk polymeric properties were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), and ultraviolet/visible spectroscopy (UV/Vis). In the future, we will investigate to prepare specific functional FAVE polymers by carefully choosing FAVE polymer precursors through different chemical reactions.

Figure 1. Preparation of Methyl ester pendant Fluorinated Arylène Vinyle Ether (FAVE) copolymer
The polymer science community has seen a huge rise in the use of “click” type reactions due to the high efficiency and versatility of these reactions. Thiol-click reactions, being a class of these reactions, offer an attractive approach for polymer modification. Specifically, thiol-isocyanate “click” reactions have been used to synthesize complex polymer architectures, which were otherwise difficult or impossible to achieve, in a facile way. Direct polymerization of isocyanate-functional monomers has been achieved with controlled radical polymerizations (CRP) for precisely engineered modification platforms with highly reactive side chains. However, despite the success of these strategies, the inherent reactivity of isocyanates still leads to adverse side reactions, such as hydrolysis, that are difficult to suppress. Phenol, lactam, and oxime-based blocking agents have been used to limit the reactivity of isocyanates in applications such as multicomponent urethane coating systems. The reactivity of these blocked isocyanates can be restored by thermal deprotection of the blocking agent to achieve the desired reactions. In this work, we synthesize blocked isocyanate-functional monomers for polymerization by CRP in solution and on surfaces. The isocyanate functional group allows facile modification of the side chains by thiol-isocyanate click reactions, while the blocking agent reduces detrimental side reactions like hydrolysis. We investigate thermally labile blocking and report the synthesis and characterization of the blocked isocyanate-functional monomers and polymers, followed by deprotection and modification of the isocyanates by reaction with thiols.
Substantial research is marked in the field of cationic polymers and their derivatives as gene delivery vectors and even resulted in clinical trials. Hydrophobic modifications proved to be a promising approach to improve the efficiency of cationic polymeric gene delivery vectors. A small library of aminoglycoside based polymers were synthesized by taking aminoglycoside as the monomers and the glycerol diglycidyl ether as the linker group. Their transfection profiles were evaluated in different types of cancer cells and proved to be more efficient than the standard poly(ethylene imine). With a view to further enhance the transfection profiles of the lead polymers, lipids of varying chain length were conjugated to the polymers by N-acylation. The conjugates synthesized were well characterized using $^1$H NMR and FTIR spectroscopy. Screening of lipid-conjugated polymers in different cancer cells for evaluation of transfection profiles led to identification of some leads, which showed superior transfection profiles when compared to the parent polymers and poly (ethylene imine). Structure-Activity Investigation revealed that the transfection profiles depends on several factors such as the type of cell line, the kind of polymer, the kind of lipid used for modification, and the degree of conjugation. The influence of the various physicochemical properties including polyplex size, zeta potential, and DNA binding on transgene expression efficacies were also investigated. A characteristic feature of this study is that some of the leads proved to be serum compatible. Taken together, these materials show significant promise in non-viral transgene delivery, and may be attractive for gene therapy applications.
Polymerization reaction with sunlight as energy resource is considered more green and sustainable than that under microwave irradiation and the ring-opening polymerization of ε-caprolactone is selected as the model of sunlight-heated polymerization. Natural sunlight can not be directly used as the energy resource for the polymerization of ε-caprolactone as its power is too weak. Our strategy is to focus natural sunlight by a Fresnel lens that is designed to concentrate the intensity of sunlight by ten thousand times and the solar power increased from below 1 kW/m² to over 500 kW/m² at the focal spot in this way. However, the focused sunlight is not absorbed directly by transparent ε-caprolactone and should be converted to heat that supplies the energy for the polymerization. With ferroferric oxide as the medium of light-heat conversion the temperature of the wall of reaction vessel ranged from 300 to 330°C when the solar power was from 721 to 849 W/m², which is a quite efficient system for the flash-heating polymerization of ε-caprolactone based on our previous work. The ring-opening polymerization of ε-caprolactone proceeded quickly and smoothly with stannous octoate as the catalyst heated by sunlight-absorbed ferroferric oxide. Experimentally, the molar ratio of ε-caprolactone and stannous octoate is 1000 to 1 and the reaction time is twenty minutes. The monomer conversions increased from 78% to 96% with solar power and temperature of ferroferric oxide. The weight-average molar mass ($M_w$) of obtained polycaprolactone ranged from $80.7 \times 10^3$ to $120.3 \times 10^3$ g/mol and the highest one came from the polymerization with solar power at 744 W/m², but with higher solar power $M_w$ decreased (Figure 1). The results indicate that light-heat conversion is a potential approach to utilize sunlight as the energy resource for polymerization reactions and is an energy-saving method for chemical synthesis.

![Figure 1 Results of ring-opening polymerization of ε-caprolactone by sunlight-absorbed ferroferric oxide](image-url)
Collagen, the most abundant protein in mammals, plays a crucial role in tissue development and regeneration, and its structural and metabolic abnormalities are associated with debilitating genetic diseases and numerous pathologic conditions. The ability to target collagens in diseased tissue could lead to new diagnostics and therapeutics, as well as applications in regenerative medicine. In this talk, I will present a new collagen targeting strategy that is based on triple helical hybridization between denatured collagen strands (of diseased tissues) and synthetic collagen mimetic peptide (CMP). This hybridization results in robust collagen specific binding \textit{in vivo} which allows detection of degraded collagens present in normal tissues undergoing fast remodeling (e.g. bones and cartilage) and those in diseased tissues with persistent wound healing activity (e.g. tumor, fibrosis). I will describe various experiments designed to elucidate the mechanism of the hybridization as well as those verifying the CMP’s collagen binding capacity both \textit{in vitro} and \textit{in vivo}. This is an entirely new way to target the microenvironment of malignant tissues and could lead to new opportunity for management of numerous pathologic conditions associated with high collagen degradation and remodeling activity.
664 - Designer synthetic polypeptides for structural hydrogels and responsive nano-delivery

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Synthetic polypeptides provide the basis for new biomacromolecules that can be modified to achieve a broad range of biologically relevant function. We have designed poly(propargyl-L-glutamate) (PPLG) synthetic polypeptides to which different molecules can be "clicked" to achieve dense brush polypeptide backbone structures, helical rod/coil polymers that form the basis of unique hydrogels, and temperature and pH responsive polymers. Crosslinking of dense PEG grafted PPLG molecules with an alpha-helical backbone can lead to gels with more rigid mechanical properties, but with high permeability and water content; whereas, use of coil-like D,L backbones leads to more traditional gel systems. The use of the PPLG backbone can also be used in small quantity within a gel format to present specific peptides for cell adhesion and mobility. By extending the PPLG platform with click chemistry of amino-functional groups, we have developed several new pH responsive molecules. A unique aspect of these new amine-functionalized polypeptides is the ability to buffer, and in some cases, change solubility with degree of ionization, over biologically relevant pHs. These polymers are poly(y-propargyl L-glutamate) (PPLG) homopolymers and poly(ethylene glycol-b-y-propargyl L-glutamate) (PEG-b-PPLG) block copolymers substituted with various amine moieties that range in pKa and hydrophobicity. These systems can be further functionalized to target specific cells, and make unique nanoscale drug carriers for systemic delivery in applications such as targeted cancer chemotherapy.
A series of functional polypeptide-based degradable polymeric nanomaterials (including organogels, hydrogels and nanoparticles) have been developed by using N-carboxyanhydride ring opening polymerizations (NCA-ROP) from both natural and synthetic amino acids. In order to prepare well-defined block copolypeptides on a large scale, the N$_2$ flow accelerated NCA ROP via normal amine mechanism has been explored in detail. The easy operational N$_2$ flow method eliminates the need to use a glove box, and offers a new approach for the synthesis of varieties of block copolypeptides with controllable polymerization rates, predictable molecular weights, and narrow molecular weight distributions. By using different functionalized NCA monomers, polypeptides with tunable pendant side chains could be obtained. The supramolecular interactions between certain polypeptide segments formed secondary structures, such as alpha helices and beta sheets, which could further self-assemble into well-defined fibrous structures and undergo gelation in both organic solvents and aqueous solutions. The functional polypeptide-based hydrogels with tunable mechanical properties can have potential use as wound healing materials and localized drug delivery matrices. Furthermore, several amphiphilic functional diblock copolypeptides with pendant alkyne groups could be synthesized and modified with therapeutic agents, and utilized as a potent platform for delivery of anticancer drugs.
666 - Synthesis, characterization, and lectin binding studies on a series of synthetic glycopolypeptides with varying chain lengths, backbone architecture and epitope densities

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A series of helical and non-helical polypeptides, poly(g-propargyl-L-glutamate (PPLG) and poly(g-propargyl-rac-glutamate (PP-rac-G) respectively, have been synthesized through the ring-opening polymerization of their respective N-carboxyanhydride monomers. Monosaccharides such as mannose and galactose substituents were added to the side chains through copper alkyne/azide cycloaddition reactions. The resulting glycopolypeptides were subjected to turbidity and quantitative precipitation assays to determine both their binding kinetics and binding efficiency to Concanavalin A, a mannose specific lectin. Physical characteristics of the glycopolypeptides such as chain length, backbone conformation and mannose density were systematically varied to enable an assessment of their effects on lectin binding.
667 - Biodegradable nanoparticles of amphiphilic triblock copolymers based on polyoxazoline as a drug carrier

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INTRODUCTION

Dexamethasone is a poorly soluble and crystalline corticoid that is often used for the treatment of diabetic macular edema administered as an implant (Posurdex, Oculex Pharmaceuticals). Micellar systems are known to solubilise poorly soluble hydrophobic drugs in an aqueous solution, thus increasing their bioavailability in the body. The goal of this work is to demonstrate the encapsulation of dexamethasone from biodegradable polymer micelles, composed of a triblock copolymer of poly(L/D-lactide)-b-poly(2-ethyl-2-oxazoline)-b-polymer(L/D-lactide) (PLA-PEtOz-PLA) for intravitreal injection. The potential of PLA-PEtOz-PLA micelles as carriers for dexamethasone was evaluated by estimating the loading efficiency.

EXPERIMENTAL METHODS

The triblock copolymers were synthesized in a three step reaction process. Firstly, PEtOz with di-acrylate end groups was prepared by cationic ring opening polymerization; acrylate end group was introduced by end capping after polymerization. Secondly, monothionic acid PLA block were synthesized by ring opening polymerization and termination with glutaric thioanhydride. The triblock copolymers were then prepared by thioic-ene addition reaction at RT. This block copolymer was self-assembled into micelles in an aqueous phase using nano-precipitation method. The block copolymer were characterized by 1H NMR spectra and GPC. The loading efficiency and content of dexamethasone for micelles was determined by HPLC.

RESULTS AND DISCUSSION

Table 1 show the characteristics of the PLA-PEtOz-PLA triblock copolymer studied.

<table>
<thead>
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<th>MW (NMR)</th>
<th>MW(GPC)</th>
<th>PDI</th>
<th>particle size (DLS)</th>
<th>PDI (DLS)</th>
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<td>1.3</td>
<td>99.26 nm</td>
<td>0.13</td>
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Dexamethasone loading into PLA-PEtOz-PLA micelles occurred simultaneously with self-assembly of block copolymers into micelles. Polymer micelles of PLA-PEtOz-PLA block copolymer exhibited a remarkable capability for carrying dexamethasone. The loading efficiency reached 73 and up to 14 wt% of drug was successfully loaded into particles. No precipitated drug crystals were observed and a clear aqueous solution was obtained, and the particle sizes were in a range of 110 – 140 nm.

CONCLUSION

Dexamethasone was successfully loaded into PLA-PEtOz-PLA micelles using nano precipitation technique. The loading of dexamethasone in micelles was in the range of 7 - 14 % depending on the feed weight ratio of drug to block copolymer. The particle sizes of dexamethasone loaded micelles were in a range of 110 – 140 nm with narrow size distribution. These results suggest that PLA-PEtOz-PLA micelles can be regarded as promising carriers for dexamethasone.

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668 - Injectable materials for co-delivery of stem cells and nanoparticles

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Stem cell transplantation is a promising therapy for a myriad of debilitating diseases and injuries; however, current delivery protocols are inadequate. Transplantation by direct injection, which is clinically preferred for its minimal invasiveness, commonly results in less than 5% cell viability. As a strategy to protect cells, we have designed a reproducible, bio-resorbable, customizable hydrogel using protein-engineering technology. In our Mixing-Induced Two-Component Hydrogel (MITCH), network assembly is driven by specific and stoichiometric peptide-peptide binding interactions. By integrating protein science methodologies with simple polymer physics models, we manipulate the polypeptide chain interactions and demonstrate the direct ability to tune the network crosslinking density, sol-gel phase behavior, and gel mechanics. This is in contrast to many other physical hydrogels, where predictable tuning of bulk mechanics from the molecular level remains elusive due to the reliance on non-specific and non-stoichiometric chain interactions for network formation. Furthermore, the hydrogel network can be easily modified to deliver a variety of other bioactive payloads such as growth factors, peptide drugs, and hydroxyapatite nanoparticles. We present the use of these materials for the co-delivery of adipose-derived stem cells with hydroxyapatite nanoparticles to promote bone tissue regeneration.
Ligand-targeted nanoparticles are emerging drug delivery vehicles for cancer therapy. Here, we demonstrate that the cellular uptake of peptide-targeted liposomes and micelles can be significantly enhanced by increasing the hydrophilicity of the targeting peptide sequence while simultaneously optimizing the EG peptide-linker length. Two distinct disease models were analyzed, as the nanoparticles were functionalized with either VLA-4 or HER2 antagonistic peptides to target multiple myeloma or breast cancer cells, respectively. Our results demonstrated that including a short oligolysine chain adjacent to the targeting peptide sequence effectively increased cellular uptake of targeted nanoparticles up to 100-fold using an EG6 peptide-linker in liposomes and 27-fold using an EG18 peptide-linker in micelles for the VLA-4/multiple myeloma system. Similar trends were also observed in the HER2/breast cancer system with the EG18 peptide-linker resulting in optimal uptake for both types of nanoparticles. Cellular uptake efficiency of these formulations was also confirmed under fluidic conditions mimicking physiological systems. Taken together, these results demonstrated the significance of using the right design elements to improve the cellular uptake of nanoparticles.
INTRODUCTION

The development of polyesteramides (PEAs) bearing amino-acids was accompanied with a successful combination of favorable properties and biocompatibility[1]. Using lysine as a diamine in polymer chain brings additional level of control on polymer properties[2]. These polymers degrade enzymatically via surface erosion mechanism[3]. This study focuses on the exploitation of PEA structural features for biodegradation control and demonstrates that pendant carboxylic groups (Fig. 1) could be the key towards hydrolytic degradation without compromising the polymer performance and biocompatibility.

METHODS

Polymer degradation was studied in presence and absence of α-chymotrypsin. Samples were incubated in buffered medium at 37C and refreshed every 48 hours.

RESULTS AND DISCUSSION

Polymer 1 degrades in presence of α-chymotrypsin via surface erosion as evident on Fig. 1

In contrast, polymers 2 to 4 lose weight in presence of enzyme however Mn of these polymers decreases over time indicating chain scission and bulk erosion. The polymer degradation comprises two independent components (surface and bulk erosion) which synergize at later stage to contribute to the complete degradation of the specimens. These polymers do show bulk erosion patterns of the same rate in absence of enzymes as well.

CONCLUSIONS:

Controlled modification on the pending functionalities of PEAs results in control on polymer degradation mechanism and introduces new hydrolytic degradation properties.

671 - Polyaniline nanofiber formation by interfacial polymerization and its application in resistance welding

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Conducting polymers are attractive as they possess electronic, magnetic, and optical properties similar to metals while retaining the flexibility and processibility of conventional polymers. Compared with other conducting polymers, polyaniline (PANI) is unique due to its relative environmental stability and interesting redox properties. So far, polyaniline (PANI) nanostructures (nanofibers, nanosheets and nanoparticles) have been synthesized by different strategies for various applications. The classical chemical synthesis of polyaniline uses aniline, an oxidant and a strong mineral acid dopant. In the past years, a variety of chemical methods were reported, such as hard or soft template synthesis, nanofiber seeding and electrochemical polymerization. In order to restrain the agglomeration phenomenon interfacial polymerization is employed to synthesize polyaniline nanofibers because it is not dependent on any template or emulsifier.

In this work, by interfacial polymerization we have successfully synthesized polyaniline nanofibers with diameters under 100 nm, which are among the smallest reported for polyaniline nanofibers without using a template. The effect of synthesis conditions such as [An], [APS], solvent, temperature and reaction time on the morphologies of polyaniline nanofibers was investigated, and the mechanism controlling the growth of polyaniline nanofibers was discussed. Conductive polymer matrix composites were prepared by using polyaniline nanofibers as conductive components. The resistance welding of polycarbonate (PC) was investigated using the conductive polymer matrix composites as a heating resistor.

SEM images of polyaniline prepared by interfacial polymerization under 0.1M aniline concentration

Thursday, March 20, 2014 01:35 PM
Responsive Nanostructures and Nanocomposites (01:30 PM - 04:45 PM)
Location: Hyatt Regency Dallas
Room: Reverchon A
Nanocomposites utilizing cellulose nanocrystals (CNCs) are a burgeoning area of research. CNCs are attractive as reinforcing fillers on account of their high tensile stiffness (up to ca. 140 GPa) and relative abundance in nature. They can be obtained from a range of biosources (e.g. plants such as cotton, wood, wheat straw or sea creatures known as tunicates) and can vary in aspect ratio (ca. 10 to 100) depending on the biosource. We have recently reported the ability of these nanocomposites to change their mechanical properties upon application of a stimulus. By controlling the surface chemistry of the CNC we can control not only the stimulus required to illicit the response but also the nature of the response itself. Thus we have been able to access materials (1) that can either transition from stiff to soft or soft to stiff upon exposure to heat/water, (2) that are pH responsive, (3) with tailorable mechanical properties in both the stiff and soft states and (4) water-enhanced mechanical gradient materials. This talk will focus on our latest results on this class on responsive nanocomposites.
673 - Graphene-based polymer nanocomposites as strain sensors

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Graphene is currently inspiring a whole range of research activities in a number scientific areas because of its interesting and unusual electronic and mechanical properties. Excitement was generated originally because monolayer graphene was the world's first 2D atomic crystal and the thinnest material ever produced. It was found to be extremely electrically conductive and to have unprecedented levels of stiffness and strength, consistent with theoretical predictions. Graphene has been shown to give high levels of reinforcement in polymer-based nanocomposites and such materials have been proposed as novel strain sensors.

It is well established that Raman spectroscopy is one of the best methods of both characterizing graphene and following its deformation in nanocomposites. Strong, well-defined resonance Raman spectra are obtained even from single atomic graphene layers and the technique can be used relatively easily to differentiate between monolayer, bilayer, trilayer and few-layer material. In this present study we have followed the effect of deformation upon the 2D band in the Raman spectra of a number of model nanocomposites consisting of exfoliated monolayer, bilayer, trilayer and few-layer graphene flakes embedded in a polymer matrix on a poly(methyl methacrylate) (PMMA) beam. We have monitored the changes with strain in position and FWHM (full width at half maximum height) of the Raman bands. In monolayer graphene the band shifts to lower wavenumber and broadens as the tensile strain in increased as shown in the Figure below.

![2D Raman Band](image)

Examples of the use of graphene-based nanocomposites as strain sensors will be given using both exfoliated and CVD monolayer materials. In contrast to the monolayer materials the stress-induced band shift behavior of the trilayer graphene in the nanocomposite is quite different. The band shifts to lower wavenumber with tensile strain and narrows indicating a loss of Bernal stacking in the trilayer material. Moreover when the stress is removed the Raman band shifts back to lower wavenumber and the shape and width of the band reverts to that of the trilayer before deformation. The mechanisms whereby this takes place will be described and the implications for the use of few-layer graphene in strain sensors discussed.
674 - Nanostructured responsive enzymogel particles for bioconversion

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Responsive enzymogels are a novel type of phase-boundary biocatalysts, i.e. they allow remotely directed performance on insoluble substrates (e.g. cellulosic biomass). Responsive biocatalytic enzymogels are designed as core-shell nanoparticles having superparamagnetic core surrounded by grafted responsive polymer brush scaffold (Fig. 1.). The magnetic core can be used for the recovery of enzymogels from the reaction mixture as well as for their translocations to specified locations of the biocatalytic reaction. Responsive polymeric brushes can be loaded with enzymes at pH 4.0 and can release enzymes when the pH is increased to 7. The structure of enzymogels helps to preserve biocatalytic activity of the loaded enzymes. The responsive brush-like architecture of polymeric scaffold allows for the mobility of loaded enzymes and also favors the efficient interfacial interaction with solid substrate. Application of responsive enzymogels can lead to new approaches in remotely controlled biocatalytic reactions in production of biofuels, drug delivery, recyclable biocatalysts, etc.

Fig. 1. Responsive enzymogel particle
Assembly of small molecules in a controlled manner is useful in the formation of structures with nanoscale dimensions, and moreover defines structure-property relationships. Synthetic chemistry provides a tool to dictate the shape and size of a molecule which impact intermolecular interactions and the ability to assemble molecules in a controlled manner. We will report on the synthesis of functionalized small molecules containing the same core, but differing in substituents, and thus in shape and size. The controlled assembly of these small molecules into well-defined nanostructures with defined functional surfaces will also be reported.
There is an unmet clinical need for designing medical adhesives that provide facile, non-destructive removal from the skin interface. Typical medical adhesives are composed of pressure sensitive polymers that bind to skin with light pressure but removal can cause pain, skin tears, and can further disrupt compromised skin. To address this issue, we have developed a thermally triggered adhesive nanoparticle synthesized through an emulsion polymerization process. Each step in the polymerization adds a specific feature to these viscoelastic nanomaterials. This polymer consists of modified clay encased in thermally responsive poly-N-isopropyl acrylamide (pNIPAM), to create the thermal trigger that controls the nanoparticle's adhesive properties, which is surrounded by a random co-polymer of NIPAM and 2-ethylhexyl acrylate (EHA) shell. Altering the composition of various layers of the nanoparticle affect the chemical and adhesive properties.
677 - WITHDRAWN
High-performance, multi-functional nanocomposites can be created by incorporating carbon nanostructures into polymers. The mechanical, thermal and electrical properties of the composite are dramatically influenced by the detailed arrangement – dispersion, clustering, networking, etc. – of the CNTs within the material. Using energy-filtered transmission electron microscope (EFTEM) tomography we are able to create precise, nanoscale three-dimensional maps of the distribution of CNTs within a composite matrix. Such structural data is necessary for understanding composite behavior, but is time-consuming to obtain. However, a small number of such measurements can be used as the foundation for high-throughput measurements that can be used in a production environment for quality control and assurance. EFTEM data is combined with sophisticated modeling to predict material properties, particularly the electromagnetic response. Once this is known, microwave measurements of bulk composite materials can be used to provide information on the state of dispersion of the nanoscale reinforcement that can be made at high speed. Microwave measurements can be made in both resonant cavity and free-space geometries, with application to fiber and ply characterization respectively.

Figure 1. Tomographic transmission electron microscopy (TEM) reconstruction of complex carbon nanotube structure grown from the surface of a carbon fiber. The nanotubes adjacent to the surface are marked in orange. The image volume is 500 nm x 500 nm x 200 nm.
679 - Extremely robust silk ionomer/graphene oxide microcapsules with tunable permeability

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We have successfully fabricated robust LbL shell microcapsules based on silk fibroin ionomers modified with poly-L-lysine and graphene oxide sheets, which are composed with biocompatible materials in contrast to the usually exploited synthetic polyelectrolytes. The porous shell structures were controlled with varying the number of bilayers, deposition conditions and external pH. Correspondingly, the cut-off molecular weight for the permeation of dextran macromolecules could be tuned. The crosslinked microcapsules are extremely stable in the unusually wide pH range from 1.5 to 12.0 without noticeable disintegration. In contrast to conventional silk microcapsules, the silk ionomer/graphene oxide microcapsules indicated remarkably robust mechanical properties at high osmotic pressure, which enables potential applications in drug delivery and biosensing.
680 - Shells from ionomer silk derivatives and microbial cell responses

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Formation of biomimetic coatings capable of retaining high cell survivability and selective permeability to analytes is a primary objective for cell-based sensor applications. We explored the formation of nanoshells on individual cells based on silk derivative polyelectrolytes: silk fibroin (SF) modified with poly-L-lysine (SF-PL), silk fibroin modified with poly-L-glutamic acid (SF-PG), and grafted to SF-PL polyethylene glycol (SF-PL-g-PEG) with different degrees of grafting (g). Variables included the molecular weight of the poly-amino acids (length of side chains), degree of PEG grafting (g) in order to assess the effect of polycations, even in the form of small side chains attached to large protein macromolecule on properties of microbial cells. We showed that survivability/activity of cells which was initially defined by the type of microbial cells (yeast vs bacterial), also depended on the chemical intermolecular interactions involved in constructing the silk shells. Polyelectrolyte shells had the lowest survivability rates, coatings assembled electrostatically with a low grafting ratio of SF-PL-g-PEG improved cell survivability, and coatings assembled based on hydrogen-bond interactions with high grafting ratios of SF-PL-g-PEG had the highest cell viability.
The fabrication method of a bone scaffold can have substantial impact on mechanical properties and bio-functionality by altering pore size, volume, and interconnectivity. The porosity of thermoset polymers due to their cross-linking densities and viscoelastic properties can be achieved by gas foaming. Gas porogens and foaming apparatuses have the potential to be readily adapted to filling conformal defects in a clinical environment. In order to foam thermoset polymers, the gel time must be tuned to achieve high viscosity to prevent the gas porogen from diffusing out. Gel times are affected by the monomers and initiators used, therefore amines involving triethylamine, glutamine, and water were studied further. The effect of acrylate monomers including polyethylene diacrylate, trimethylolpropane ethoxylated triacrylate, pentaerythritol triacrylate were also analyzed along with a hybrid polymers of these monomers to arrive at the best formulation. Alamar Blue® metabolic assay was performed to measure cell viability.
Poly(butylene adipate-co-terephthalate) (PBAT and Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)) are biopolymers that have the potential to be used in applications of bone healing. In this study, it is hypothesized that the polymer blend has the combined strength and osteoconductivity to support osteoblast collagen formation. PBAT (PBAT 100) and a blend with 20% PHBV (PBAT 80) were extruded in the form of fibers and then knitted in the form of mesh. They were tested in warp as well as in weft direction for the tensile strength; these showed that the weft direction had higher performance than the warp. The individual fibers were kept in phosphate buffered saline (PBS) to record the weight loss over the period of 8 weeks and were tested for the storage and loss modulus using dynamic mechanical analyser (DMA). The results indicated that weight loss over the 8 week period was negligible but mechanical relaxation strength showed a decrease and then an increase. In vitro osteoconductivity studies were done by using differentiating osteoblasts (MC3T3-E1 subclone 4 cells). X-ray diffraction (XRD) was used to determine the change in structure of polymers due to two weeks in vitro degradation. Raman spectroscopy showed that all scaffolds supported the formation of a collagenous network over the scaffold surfaces. For a combination of knittable manufacturing, mechanical performance and osteoconductivity blends offer the best route.
Chitosan has gained much attention as a biomedical product due to its excellent biocompatibility, non-toxicity and biodegradability. One feature detracting from the more widespread in vivo use of chitosan has been its poor solubility particularly at non-acidic pH values [1]. One approach to facilitate solubilization has been to chemically modify the amino functional group, thus yielding a stereoelectronically heterogeneous distribution of chitosan derivatives displaying limited intermolecular H-bonding.

Herein, chemical derivatives of chitosan were yielded under freeze-concentration conditions. The results were notable in the sense that freeze-concentrated reactions yielded chitosan derivatives with enhanced chemical, mechanical and surface properties. For instance, N-alkyl derivatives of chitosan were obtained following Micheal addition of aqueous chitosan solutions frozen in the presence of acrylic, maleic, itaconic and citraconic acid. The bimolecular reactions, which actually proceeded in highly-concentrated unfrozen regions within the ice crystals, were compared against the standard Micheal reaction of chitosan in hot aqueous acrylic acid [2]. Suitable candidates were evaluated as potential biomaterials in several applications.

In addition to enhanced water solubility, the ability to fine-tune the freeze-concentration method, thus yielding a pleurtha of physical and morphological variations, will enable researchers to design biomaterials bearing targeted traits. Continued development of the freeze-concentration method will potentially seed research towards the fabrication of novel biomaterials.

References:

684 - Controlled and versatile synthesis of anion exchange membranes for fuel cell applications

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Fuel cells are attractive alternative energy resources that have the potential to reduce greenhouse gas emissions and dependence on fossil fuels. Anion exchange membrane fuel cells have distinct advantages relative to proton exchange membrane fuel cells, such as fast cathode reaction kinetics and ability to use low-cost, non-noble metal catalysts. In anion exchange membrane fuel cells, cations (typically quaternary ammonium species, \(-\text{NR}_3^+\)) are attached to polymer chains and hydroxide anions (\(\cdot\text{OH}\)) serve as charge carriers. By utilizing our group’s recent polymer functionalization chemistry based on C-H borylation, we have successfully incorporated a variety of stable ammonium-cationic species into aromatic polymers. We will present controlled synthesis and characterization of these anion exchange membranes and their fuel cell membrane properties.

Thursday, March 20, 2014 01:00 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 04:20 PM)
Location: Hyatt Regency Dallas
Room: Moreno B
685 - Polyelectrolytes with tunable charge based on polydehydroalanine: Synthesis and solution properties

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We present the synthesis of poly(tert-butoxycarbonylaminoethylacrylate) (PtBAMA), a derivative of polydehydroalanine (PDha), starting from 2-tert-butoxycarbonylaminoethylacrylate (tBAMA) using free radical polymerization (FRP) and nitroxide mediated polymerization (NMP). Due to the presence of orthogonal protective groups the resulting polymers can be selectively deprotected to yield either a polyanion (poly(tert-butoxycarbonylaminoacrylic acid), PtBAA) or a polycation (poly(aminomethylacrylate), PAMA) (Figure A). On the other hand, deprotection of both the amino- and the carboxyl-functionality in a sequential manner led to the potential polyzwitterion polydehydroalanine (PDha) (Figure A). We investigated the pH-dependent solution behavior of PtBAA, PAMA, and PDha in aqueous solution by ζ-potential measurements and (in parts) potentiometric and turbidimetric titrations (Figure B). All materials were further analyzed using size exclusion chromatography (SEC) and nuclear magnetic resonance spectroscopy (NMR).
Inspired from nature, polymeric materials that undergo phase transitions in response to external stimuli, such as temperature, ionic strength, and pH, represent an important category of materials synthesized by reversible addition fragmentation transfer (RAFT) polymerization, being widely investigated for drug delivery, separation, and diagnostics applications. Temperature-sensitive polymers display lower critical solution temperature (LCST) behavior in some solvents, which leads to a sudden decrease in solubility with the change in temperature, caused by conformational changes, and subsequent aggregation. Polymer stimuli responsiveness has complex relationships to architecture, copolymer distribution, ‘blockiness’, sequence length, etc. The focus of this study is to investigate the effects of the copolymer composition on LCST during synthesis via RAFT of N-isopropylacrylamide (NIPAM)/4-vinylbenzenesulfonic acid sodium salt (VB) copolymers. Due to the high difference in reactivity ratios, VB is rapidly consumed and leads to a composition drift toward NIPAM rich polymer, allowing, thus, tailoring the LCST behavior based on the specific chemical architecture of the resulting polymer.
687 - Design of superionic polymers: New insights from Walden plot analysis

Yangyang Wang², Fei Fan¹, ffan@utk.edu, Alexander L. Agapov¹, Kunlun Hong³, Tomonori Saito², Jun Yang³, Xiang Yu³, Jimmy Mays², Alexei P. Sokolov¹,². (1) Department of Chemistry, The University of Tennessee-Knoxville, Knoxville, Tennessee 37996, United States, (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States, (3) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Solid polymer electrolytes provide many advantages over the traditional liquid electrolytes for potential applications in energy storage and electrochemical devices. However, none of the current dry polymer electrolytes has sufficiently high ionic conductivity at ambient and low temperatures, due to strongly coupled segmental and ionic dynamics. To improve conductivity, significant efforts have been devoted to suppressing crystallization and lowering the glass transition temperature of polyether-based electrolytes. In contrast with these traditional studies, we explore an alternative approach by decoupling the ionic transport from the polymer segmental relaxation.¹ Our modified Walden plot analysis reveals that the ionic conductivity in relatively rigid polymers can be strongly decoupled from the segmental dynamics. Several novel polymers developed in this study can be classified as superionic conductors.

The observed relationship between ionic conductivity and segmental relaxation provides a new paradigm for design of highly conductive polymer electrolytes.

688 - Exploration of diethynyl-thiophene derived polymers as metal ions chemosensors and wide band gap polymers

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This talk will report the characterization of two novel classes of polymers that share ethynyl bridges with thiophene and other monomers. Chemosensors have been developed utilizing fluorescent conjugated polymers (FCP's) to detect metal cations in biological systems or environmental waste streams with enhanced selectivity and sensitivity. Several chemosensor polymers were synthesized and characterized in a collaborative effort between the Jones and Duffy-Matzner groups using a fluorescent backbone poly[2,5-thiophenediyl-1,2-ethynediyl-1,4-(2,5-didodecylphenylenediyl)-1,2-ethynediyl] (PPETE) and poly[2,5-thiophenediyl-1,2-ethynediyl-1,4-naphthalenediyl-1,2-ethynediyl] (PNETE) backbone. These polymers responded with either a "turn-on" or "turn-off" fluorescence response. The relative energy levels of the polymer backbone and the receptor unit with bound metal cations directly influenced this behavior. This work will also examine the electrochemical potential of monomers and oligomers of TMEDA (tetramethylethylenediamine) and diamino-substituted thiophenes using square wave voltammetry studies along with theoretical calculations utilizing Spartan to explain unique turn off/on behavior observed for metal ions with the FCPs. Secondly we would like to develop broad spectrum cost-effective photovoltaic devices using novel organic polymers to provide wide band gap absorption. In that end we report the design and synthesis of two novel difuranodioxopyrrolopyrrole-diethynylthiophene polymers (DFDPP-DET) as shown in Figure 1. Poly{[(2,5-dioctyl-1,4-dioxo[2H,5H]pyrrollo[3,4-c]pyrrole)furan-2,5-diylethyne-1,2-diyl(3-hexylthiophene-2,5-diyl)ethyne-1,2-diylfuran-2,5-diyl]} (DFODPP-DE3HT) and poly{[(2,5-(2-ethylhexyl)-1,4-dioxo[2H,5H]pyrrollo[3,4-c]pyrrole)furan-2,5-diylethyne-1,2-diyl(3-hexylthiophene-2,5-diyl)ethyne-1,2-diylfuran-2,5-diyl]} (DF2EHDPP-DE3HT) have been made. Their chain lengths have been determined by GPC analysis and photophysical characterizations are ongoing.

\[ \text{R}_1 = \text{2-ethylhexyl} \quad \text{DF2EHDPP-DE3HT} \]

\[ \text{R}_2 = \text{octyl} \quad \text{DFODPP-DE3HT} \]
Development of new hydroxide-conducting anion exchange membranes (AEMs) that are chemically stable in alkaline fuel cells (AFCs) is required in order to achieve long-lasting low-cost solid-state AFCs. In this study, we synthesized and investigated the chemical stability of polymerized ionic liquid (PIL) diblock copolymers consisting of various covalently attached cations: trimethylammonium, butylimidazolium, butylmethylimidazolium. Diblock copolymers consisting of a non-ionic component, methyl methacrylate (MMA), and a functional component, 2-bromoethyl methacrylate (BrMA), were synthesized via RAFT and subsequently quaternized with a functional cation. Analogous PIL homopolymers were also synthesized and investigated along with analogous salts: 1-butyl-3-methylimidazolium chloride, 1-butyl-2,3-dimethylimidazolium chloride, trimethylammonium chloride. The extent of chemical stability and degradation pathways of the block copolymers, homopolymers, and salts were determined using $^1$H NMR spectroscopy after exposure to 20 meq of KOH per cation at 30 °C for 168 h. Significant degradation via nucleophilic substitution was observed for the trimethylammonium cation in the polymers. Limited ring-opening degradation was observed for the butylimidazolium cation in both the salt and polymers. No degradation was observed for the C2-substituted butylmethylimidazolium cation in the salt or polymers.
A polymerized ionic liquid (PIL) diblock copolymer was synthesized, poly(MMA-b-MUBIm-Br), comprising of an IL component (1-[(2-methacryloyloxy)undecyl]-3-butylimidazolium bromide) (MUBIm-Br) and a non-ionic component (MMA). This polymer was synthesized via postquaternization from its precursor PIL diblock copolymer, poly(MMA-b-BrUMA) (BrUMA = 11-bromoundecylmethacrylate), which was synthesized via RAFT at various PIL compositions. Remarkably, a high bromide ion conductivity of 0.65 S cm⁻¹ (at 80 °C, 90% RH) was measured for the PIL block copolymer with 1.4 meq/g. At comparable ion exchange capacities (IECs), this long side-chain PIL block copolymer has ionic conductivities that are an order of magnitude higher (with lower water content) compared to a short side-chain PIL block copolymer with similar chemistry, poly(MMA-b-MEBIm-Br) (MEBIm-Br = 1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium bromide). This suggests that ions self-assemble in different arrangements in long side-chain PIL domains, which results in accelerated ion transport. These results could have an impact on the design of block copolymers as polymer electrolytes in numerous applications, such as gas purification, desalination, fuel cells, and batteries.
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Tetraamine 2,6-bis(3′,4′-diaminophenyl)-4-phenylpyridine (Py-TAB) was found to be an efficient, readily accessible, inexpensive monomer for synthesizing pyridine bridge polybenzimidazoles (Py-PBIs). The Py-TAB monomer replaced the frequently and conventionally used 3,3′,4,4′-tetraaminobiphenyl (TAB) monomer for synthesizing polybenzimidazoles (PBIs) structure. Py-TAB monomer showed wider scope for synthesis of PBIs with various dicarboxylic acids (DCAs). Two series of random copolymers (PBI-co-Py-PBI) were synthesized by polymerizing Py-TAB and TAB with isophthalic acid (IPA), and terephthalic acid (TPA) to produce meta (mPBI-co-mPy-PBI) and para (pPBI-co-pPy-PBI) connected copolymers, respectively. All homo and copolymers of Py-PBIs displayed superior solubility in low boiling solvent and hence eliminated the processability issues of PBIs which often restricted the large scale use. Comparable and in some instances superior thermal, mechanical and oxidative stability of Py-PBIs proved that the Py-TAB is the most attractive alternative tetraamine monomer to TAB for synthesis of PBIs. The proton conductivity of acid doped Py-PBI membranes were higher than the conventional PBI membranes and steadily increased with increasing Py-PBI content in the copolymers owing to the higher acid loading and the complex bulky structure. Therefore, 3-fold objectives, namely, (I) alternative tetraamine monomer, (II) soluble PBI, and (III) higher proton conducting PBI based PEM, were achieved in this study.

The acidic methyl protons in 2-decyloxy-4,6-dimethylpyrimidine can be easily deprotonated using a base, because the resultant carbanion is resonance stabilized. This stable carbanion can be used as a substrate for aldol condensation reactions. A series of novel conjugated polymers were synthesized using aldol condensation reactions between 2-decyloxy-4,6-dimethylpyrimidine and various aromatic dialdehydes. The synthesized polymers were characterized by using $^1$H-NMR, UV-visible spectroscopy. Molecular weights of the polymers were determined by size exclusion chromatography. Cyclic voltammetry was used to determine HOMO, LUMO energy levels and electrochemical band gaps of the resultant polymers.
A pH clock reaction is a reaction that has an abrupt change in pH at some point after the start of the reaction. In this work, we studied the bromate-sulfite-bisulfite pH clock reaction and the delay in clock time as a function of ammonium hydroxide. The bromate-sulfite-bisulfite clock reaction proceeds within minutes unperturbed. We observed an increase in clock time with an increase in ammonium hydroxide concentration. After the ammonium hydroxide has evaporated the clock reaction proceeds normally. We also observed that if the system is closed ammonia cannot evaporate, and the clock reaction will remain dormant until the system is opened and ammonia released. We studied the effect of storage time on clock time for varying concentrations of ammonium hydroxide.

We also studied the possibility of coupling the clock reaction with the crosslinking of a poly(carbodiimide) via malonic and maleic acids, creating a programmable pH clock reaction triggered crosslinked coating.

The waterproof coating can easily be applied in single thin layers or multiple layers to create a thicker coating. When the pH of the clock reaction drops the environment becomes the ideal pH for the crosslinking to occur and in thin layers the ammonia evaporates very quickly, allowing the coating to form quickly. The polymer system also has an extended shelf life in the vial with ammonium hydroxide present to keep the pH high.
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- Omni Hotel, San Diego, California, USA
- Chairs: Scott Iacono, Bruno Ameduri

Silicon Containing Polymers and Composites

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- December 9-13, 2015, Grand Hyatt Kauai Resort and Spa, Kauai, HI
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