Division of Polymer Chemistry (POLY)

Graphical Abstracts

Submitted for the 248th ACS National Meeting & Exposition

August 10-14, 2014 | San Francisco, CA • Chemistry & Global Stewardship
**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>Controlled Radical Polymerization</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</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>AM</td>
</tr>
<tr>
<td>Green Polymer Chemistry: Biobased Materials and Biocatalysis**</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
</tr>
<tr>
<td>Metal-Containing and Metallo-Supramolecular Polymers and Materials**</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
</tr>
<tr>
<td>Poly(2-Oxazoline)s and Polypeptoids**</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
</tr>
<tr>
<td>Polymers for Additive Manufacturing**</td>
<td>AM</td>
<td>AM</td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
<tr>
<td>Industrial Polymer Scientist Award: Symposium in Honor of Robert D. Allen, IBM</td>
<td>AM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014 Biomacromolecules/Macromolecules Young Investigator Award</td>
<td></td>
<td></td>
<td></td>
<td>PM</td>
<td></td>
</tr>
<tr>
<td>Industrial Innovations in Polymer Chemistry</td>
<td></td>
<td></td>
<td></td>
<td>PM</td>
<td></td>
</tr>
<tr>
<td>Sci-Mix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EVE</td>
</tr>
<tr>
<td>Transport in Polymer Membranes**</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
</tr>
<tr>
<td>DSM Science and Technology Award: Innovative Polymer Solutions for Biomedical Applications</td>
<td>PM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer Degradation, Performance and Ultimate Stability</td>
<td>EVE</td>
<td>AM</td>
<td>AM</td>
<td>AM</td>
<td></td>
</tr>
<tr>
<td>POLY/PMSE Plenary Lecture and Awards Reception</td>
<td>EVE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Primary organizer of Cosponsored symposium.**

*Note: ACS does not own copyrights to the individual abstracts. For permission, please contact the author(s) of the abstract.*
Aquazol® (poly(2-ethyloxazoline)) is a high performance, water soluble, thermoplastic polymer, produced solely by Polymer Chemistry Innovations. The nontoxic, thermally stable material is one of the few water-soluble polymers that is extruder compatible. Aquazol can be easily extruded due to its thermal stability and low T_g. However, the polymer is a glass at room temperature therefore pure extruded fibers are unable to be spooled. The addition of plasticizers to the polymer affords a flexible fiber suited for various applications, which may include 3D printing.

Control of the monomers, initiators, and concentration allows the polymer to be prepared as homo or copolymers with precise molecular weights with low polydispersity and controlled end groups. Narrow molecular weight distribution has already been shown to be important for transfection agents made from Aquazol.

Diblocks and random copolymers have been prepared from 2-ethyloxazoline and other oxazolines. Difunctional Aquazol has been prepared for incorporation into triblock and multiblock copolymers to make thermoplastic hydrogels.
Polymerization of 2-oxazolines has history of half a century, the reaction mode of which is known as cationic ring-opening polymerization (CROP: reaction 1). Two decades ago, we found that 2-oxazoline compounds acted as useful monomers in enzymatic polymerizations (EROPA: reaction 2). In this presentation we will mention the developments of these polymerizations, which mainly our group explored for these four decades. These two are quite different in reaction mode to produce a variety of functional polymers having completely different structures; poly(N-acylethlenimine)s via CROP and 2-amino-2-deoxy sugar unit-containing polysaccharides via EROPA, respectively.


Two major polymerization modes of 2-oxazolines

1. Cationic ring-ring opening polymerization (CROP)

2. Enzymatic ring-opening polyaddition (EROPA)
Several hydrophilic, amphiphilic and thermo- and pH responsive polymers have been synthesized in our group based on polyoxazoline chemistry. By copolymerization of polyoxazoline macromonomers as well as macromolecular crosslinkers amphiphilic gels have been prepared effectively. The grafting from approach has been used to realize thermo- as well as pH sensitive gels. E.g. graft copolymers with thermo-sensitive poly(N-isopropylacrylamide) backbone and pH-sensitive hydrophilic poly(2-carboxyethyl-2-oxazoline) graft chains were synthesized by combination of free-radical and cationic polymerization and their amphiphilic behaviour was characterized. Stable micelle-like aggregates were formed by increase of temperature in a specific pH range of 4.5 to 5.5. The micelles have been successfully cross-linked by electron-beam irradiation yielding stable core-shell type nanogels of about 100 nm diameter with reversible thermo- and pH-dependent swelling behaviour addressed independently within the core and shell structure. The reversible bi-sensitivity of core-crosslinked nanogels has been verified by dynamic light scattering and atomic force microscopy measurements and demonstrated the predicted core-shell structures of the aggregates. Similar nanogels are ideal candidates to be used as multi-responsive material in microfluidic channels acting on temperature as well as pH changes by opening or closing a channel, a highly interesting feature in chemical transistors.

Figure 1: Chemical structure and DLS measurements of PNiPAAm-g-p(carboxyethylcarboxyethyl-2-oxazoline) nanogels below and above the phase transition temperature of the core against pH.

4 - LipoPOx: Partnership between polyoxazoline and lipids

Vincent Lapinte, vincent.lapinte@univ-montp2.fr, Mylène Stemmelen, Cléo Giardi, Laetitia Korchia, Jean Jacques Robin. Institut Charles Gerhardt de Montpellier UMR 5253, FRANCE, Montpellier, France

Amphiphilic copolymers have the ability to self-assemble into a wide variety of morphologies in solution or in bulk giving soft materials such as spheres, rods, vesicles, micelles, nanofibers, and nanotubes for numerous applications such as drug delivery systems, nanoreactors and nanotemplates.

To build amphiphilic copolymers, numerous hydrophobic blocks have already been linked to hydrophilic polyoxazoline. An interesting association concerns the lipids and the polyoxazoline named LipoPolyoxazoline (LipoPOx). Different lipidic derivatives (triacylglycerol, glycerol and fatty acid) can be explored.¹ For instance, oxazoline monomers based on fatty acids have already been described and allowed the synthesis of amphiphilic copolymers with hydrophobic polyoxazoline block.² The fatty (or alkyl) chains can also be employed in the synthesis of amphiphilic diblock copolymers using them as initiators or terminating agents. Moreover, the use of derivatives of glycerol (by-product of biodiesel) as initiators was investigated in the functionalization of polyoxazolines.³ Finally, the synthesis and the self-assembly in water of amphiphilic star copolymers were examined using functionalized vegetable oils to polymerize oxazolines.⁴,⁵Some of these synthetic routes would be detail in order to show the fruitful lipidic-POx combination.

In recent years poly(2-alkyl-oxazolines) - regarded to be pseudo-polypeptides - have received considerable attention for, amongst others, biomedical applications. The living cationic ring opening polymerization (CROP) leads to good control over dispersity and end group fidelity while by variation of the monomer structure a broad range of polymer properties is easily accessible.1

Poly(2-propyl-2-oxazoline)s are known to exhibit interesting thermo responsive behavior.2 Therefore the polymerization kinetics of \(n\)-PropOx, \(i\)-PropOx and the missing analogue 2-cyclopropyl-2-oxazoline (c-PropOx) were investigated. The polymerization rate constant (\(k_p\)) was found to decrease in the order \(c\)-PropOx > \(n\)-PropOx > \(i\)-PropOx.3 Theoretical free energy calculations confirmed the trend for \(k_p\). Studies of a set of DFT-based reactivity descriptors, electrostatics and frontier molecular orbitals revealed that the observed reactivity is dictated by electrostatic effects.4 Consequently the copolymerization of c-PropOx and 2-ethyl-2-oxazoline yields gradient copolymers which cloud points can be tuned by variation of the composition.


---

**Sunday, August 10, 2014 10:25 AM**

**Poly(2-Oxazoline)s and Polypeptoids (08:00 AM - 11:55 AM)**

**Location:** Hilton San Francisco Union Square

**Room:** Golden Gate 6
6 - Design of electrophoretic poly(2-oxazoline)s using sulfoneimides as the initiator and hybridization with bioactive glass

Terunari Hayashi, t.hayashi.acs@gmail.com, Akinori Takasu. Department of Frontier Materials, Nagoya Institute of Technology, Gokiso-cho, Nagoya-shi, Aichi 466-8555, Japan

In our laboratory, bis[(nonafluorobutane)sulfonyl]imide (Nf₂NH) was used as a catalyst for the polycondensation, because of its high activity property. Furthermore, we also tried to use it as a new initiator for cationic ring-opening polymerization of 2-oxazolines.

First, we investigated the polymerization activity and the livingness of N-methyl bis[(nonafluorobutane)sulfonyl]imide (Nf₂NMe) which was derived from Nf₂NH, acting as the new initiator for polymerization of 2-oxazolines. Cationic ring-opening polymerization of 2-ethyl-2-oxazoline proceeded in acetonitrile at 60 °C with Nf₂NMe and compared it with methyl triflate (TfOMe) as current initiator.

As the result, Nf₂NMe had the similar polymerization activity to that of TfOMe. In addition, we confirmed the livingness by the two-step polymerization and ¹H NMR spectrum.

It is well-known that, poly(2-oxazoline)s have biocompatibility, so we next designed electrophoretic poly(2-oxazoline) to survey the application to biological materials conjugated with bioactive glass (Bioglass®45S5) which is silicate material found to bind directly to bone by electrophoretic deposition (EPD).

We synthesized poly(2-oxazoline) having pendent sulfone [poly(sulfonyl-oxazoline)] by polymerization of sulfide-containing oxazoline, successive Oxone® oxidation ($M_n=3.0\times10^3$, $M_w/M_n=1.3$) and conjugated bioactive glass by EPD. In consequence, the poly(sulfonyl-oxazoline)/bioactive glass composite could be deposited on a stainless-steel anode by EPD. Furthermore, after two weeks immersion in SBF (Simulated Body Fluid), we confirmed the appearance of hydroxyapatite on the poly(sulfonyl-oxazoline) / bioactive glass composite film.

These fundamental results provide new biological material having biocompatibility and characteristic of bone regeneration using EPD technique.

Figure 1. Cationic ring-opening polymerization of 2-oxazolines with Nf₂NMe as the initiator

R = -CH₂CH₃ (2-ethyl-2-oxazoline)
R = -(CH₂)₄SO₂(CH₂)₃CH₃ (sulfonyl-oxazoline)
Oligomeric 2-oxazolines with a methacrylate end-group are versatile building blocks for the synthesis of comb and graft copolymers using the reversible addition–fragmentation chain transfer (RAFT) technique. Mainly 2-ethyl-2-oxazoline (EtOx) was applied as monomer for the cationic ring-opening polymerization (CROP) towards these macromonomers, but also macromonomers derived from 2-cyclo-propyl-2-oxazoline could be used to obtain comb-shaped poly(2-oxazoline)s (POx). The concept was further exploited by utilization of 2-n-nonyl-2-oxazoline (NonOx). Despite the sterically demanding substituents, the oligoNonOx could be homopolymerized via RAFT polymerization extending the series of comb-shaped POx with a methacrylate backbone towards highly hydrophobic polyNonOx.

The copolymerization of oligoEtOx and oligoNonOx macromonomers offered simple access to a series of heterografted polymers with a polymethacrylate backbone and varying composition of oligomeric 2-oxazoline side chains, which were investigated by means of differential scanning calorimetry, wide-angle X-ray scattering, dynamic light scatter und cryo-transmission electron microscopy.


Aqueous solutions of amphiphilic polymers often undergo a reversible heat-induced phase separation. In the case of aqueous poly(2-isopropyl-2-oxazoline) (PIPOZ) solutions, the phase separation is followed, upon prolonged heat treatment, by an irreversible crystallization of the polymer. Vibrational spectroscopy studies combined with molecular orbital (MO) calculations and spectral measurements with model compounds indicate that PIPOZ chains heated above the phase transition temperature undergo a conformational transition to a more stable conformer. This change, which is irreversible upon cooling the solution below $T_c$, leads to the conformation taken by the polymer in the crystalline phase. Polymer crystallization ensues via a nucleation/growth mechanism.

A corollary of this observation would be that if the PIPOZ chains are “frozen” in cold water in conformations unfavorable to crystallization, the heat-induced phase transition of their solutions should be fully reversible. I will describe various situations where the PIPOZ chain conformation in cold water was engineered in order to foil crystallization.

Schematic representation of the conformational changes of PIPOZ in water as a function of solution temperature

9 - State-of-the-art of controlled radical polymerization (reversible deactivation radical polymerization)

Krzysztof Matyjaszewski, km3b@andrew.cmu.edu, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Current status of controlled/living radical polymerization (IUPAC recommends a term reversible deactivation radical polymerization), including atom transfer radical polymerization, nitroxide mediated polymerization and reversible activation fragmentation chain transfer polymerization as well as various degenerative transfer processes will be discussed. Special emphasis will be on mechanistic understanding of new catalytic/initiating systems. Some potential applications of materials prepared by controlled radical polymerization will be presented.
RAFT Polymerization is now one of the most versatile and most used methods for implementing reversible deactivation radical polymerization otherwise known as controlled or living radical polymerization. This presentation will briefly trace the historical development of RAFT with reference to the kinetics and mechanism of the process. It will also highlight the most recent developments at CSIRO in this context specifically covering such areas as RAFT crosslinking polymerization, monomer sequence control and multi-block copolymer synthesis, high throughput RAFT polymerization and RAFT agent development.
11 - Nitroxide mediated polymerization: From alkoxyamines to advanced polymers

Didier Gigmes, didier.gigmes@univ-amu.fr, Aix-Marseille University, CNRS, Av. Esc. Normandie Niemen, Marseille, France, France

In the past 25 years, Controlled Radical Polymerization (CRP) techniques revolutionized the field of material science. Indeed such techniques provide a convenient way to produce a broad range of polymer architectures and compositions exhibiting unprecedented properties. Among the different techniques currently used in CRP, Nitroxide Mediated Polymerization (NMP) has attracted a renewal of interest because of its simplicity, since in most cases it requires only adding the suitable alkoxyamine to the polymerization system, scheme 1.

![Activation-deactivation equilibrium in Nitroxide Mediated Polymerization](image)

**Figure 1.** Activation-deactivation equilibrium in Nitroxide Mediated Polymerization

In this lecture we will present an overview on the NMP technique. More particularly the kinetic aspects, features and achievements of NMP since its discovery will be discussed. Then, the potential of NMP will be illustrated through the preparation of high performance materials finding applications in the fields of energy, health and transport.

A focus on our latest advances on nitroxide mediated photo-polymerization technique will be also presented.

Lewis acid-mediated radical polymerization utilises Lewis acids to alter the reactivity of polar monomers, facilitating control of various aspects of polymer structure. The most exciting application of these additives is their potential to influence main-chain stereostructure and provide a convenient route to stereoregular polymers. Unfortunately, even with these novel additives the stereocontrol achieved in most systems is modest, especially compared to the high stereoregularity of polymers synthesised via ionic or coordination polymerisation. We have been using a combination of theory and experiment to better understand why existing agents fail to achieve high degrees of isotacticy with common monomers such as methyl methacrylate (MMA), and how this might be addressed through improved reagent design. As a case study, we have examined the impact of lithium bis(trifluoromethane) sulfonamide (LiNTf₂) on MMA polymerization. Our experiments show that it fails to control the stereochemistry of the polymer but does catalyse the propagation step. Theoretical calculations reveal that the Li⁺ binds preferentially to the terminal and penultimate side chains of the propagating radical in a manner consistent with stereocontrol. However, this binding mode over-stabilizes the propagating radical and reduces its propagation rate. The propagation step is instead dominated by a less favoured, non-stereocontrolling binding mode, in which the terminal unit of the radical and monomer are bound simultaneously, which activates the monomer to such an extent that it leads to the experimentally observed propagation catalysis.

Sunday, August 10, 2014 09:35 AM
Controlled Radical Polymerization (08:00 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Continental Ballroom 4
13 - Kinetics of reversible deactivated radical polymerization studied via SP-PLP-EPR experiments

Michael Juergen Buback, mbuback@gwdg.de, Hendrik Kattner, Wibke Meiser, Hendrik Schroeder, Nicolai Soerensen.
Department of Chemistry, Institute for Physical Chemistry, University of Goettingen, Goettingen, Lower Saxony 37077, Germany

Instantaneous initiation of pulsed laser polymerization (PLP) by an intense single pulse (SP) in conjunction with subsequent highly time-resolved EPR detection of radical concentration provides a detailed picture of polymerization kinetics and mechanism. This SP-PLP-EPR technique may also be applied to systems where, e.g., by intramolecular chain transfer, more than one type of radicals is occurring, as with acrylic monomers. Moreover, SP–PLP–EPR investigations into systems containing two types of radicals allow for analysis of reversible-deactivation radical polymerizations, such as RAFT and ATRP, and for elucidation of kinetic and mechanistic aspects of these controlled polymerizations. The potential of the new method will be illustrated by investigations into chain-length-dependent termination (CLDT) for bulk homopolymerizations of styrene, for which an SP–PLP–EPR trace is shown the figure, of vinyl acetate and of other monomers, including investigations into radical polymerization in solution. The SP–PLP–EPR studies demonstrate that CLDT is adequately represented by the composite model which encompasses the power-law exponents $\alpha_s$ and $\alpha_l$ for termination of short-chain and long-chain radicals, respectively, a crossover chain-length, $l_c$, which separates these two regions, and the rate coefficient for termination of two radicals of chain length unity, $k_t^{1,1}$. Moreover, determination of deactivation rate coefficients in ATRP and of addition and fragmentation rate coefficients in RAFT polymerization will be illustrated. The potential of the new technique is far from being fully exploited.
14 - Synthesis and behavior of stimuli-responsive hairy particles

Bin Zhao, zhao@ion.chem.utk.edu, Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States

Hairy particles are composed of a core and a layer of polymer chains that are densely grafted by one end via a covalent bond on the surface of the core (i.e., polymer brushes). These hybrid particles can be designed to respond to environmental changes, exhibiting different structures and properties under different conditions; examples include various stimuli (e.g., temperature, pH, and light)-responsive hairy particles and multicomponent polymer brush-grafted particles. In this presentation, I will first give an introduction to the synthesis, structures, and properties of stimuli-responsive hairy particles using examples from recent literature. After that, I will present our latest results on environmentally responsive hairy particles, in particular, thermosensitive hairy nanoparticles. We have developed a robust method to immobilize initiators onto 20 nm silica nanoparticles and to grow thermosensitive poly(oligo(ethylene glycol) (meth)acrylate) brushes with different architectures such as homopolymers, random copolymers, and block copolymers by surface-initiated “living”/controlled radical polymerization. The hairy nanoparticles and their responsive behavior are characterized by thermogravimetric analysis, NMR spectroscopy, size exclusion chromatography, and dynamic light scattering. The applications of these thermosensitive hairy nanoparticles in the fabrication of hybrid stimuli-responsive polymeric hydrogels will be presented.
Perhaps more than any other field of the last two decades, the advent of controlled radical polymerization (CRP) (i.e., reversible-deactivation radical polymerization) has enabled research focused on the preparation and application of well-defined polymers in the areas of medicine and biology. In addition to facilitating access to polymers with well-defined molecular weights and end group functionalities that are useful for the preparation of, for example, polymeric delivery agents, biomaterials, and polymeric therapeutics, the control over basic macromolecular characteristics (e.g., architecture, comonomer sequence, molar mass distribution) afforded by CRP has provided fundamental insight into the role of these attributes in governing the behavior and fate of polymers meant to be applied in vivo. In addition to describing our recent work in this area, this tutorial presentation will overview recent advances in biology and medicine that have benefitted from the control afforded by CRP.
16 - Facile synthesis of polypeptide through polycondensation of activated urethane derivative of \( \alpha \)-amino acid

Shuhei Yamada, syamada@moleng.fuk.kindai.ac.jp, Takeshi Endo. Molecular Engineering Institute, Kinki University, Iizuka, Fukuoka 820-8555, Japan

Polypeptides have been widely employed to prepare a wide variety of the functional biomaterials for the use of drug delivery system (DDS) and tissue engineering, because of their excellent biocompatibility and biodegradability. One of the most efficient routes is the ring-opening polymerization of \( \alpha \)-amino acid \( N \)-carboxyanhydrides (NCAs) to give polypeptides with well-defined structures involving molecular weights and terminal structures. However, the synthesis of NCAs usually requires highly toxic phosgene and its derivatives. Sensitive nature of NCAs to moisture and heat has also prevented the production and the utilization of NCAs in an industrial scale. We will present a facile and phosgene-free synthesis of polypeptide (alanine, methionine, lysine and tryptophan) by the polycondensation of \( N \)-carbamylated tetrabutylammonium salt with diphenyl carbonate as the alternative of phosgene (Figure 1(a)). Their polycondensation proceeded smoothly at 60 \(^\circ\)C in \( N,N \)-dimethylacetamide (DMAc) in the presence of amines such as \( n \)-butylamine along with the elimination of phenol and \( CO_2 \) (Figure 1(b)). The molecular weight of polypeptide was adjusted by varying feed ratio of urethane derivative and amine. The structural analysis with MALDI-TOF mass spectroscopy showed that \( n \)-butylamine was successfully incorporated into the chain end of the polypeptide. The employment of an amine-terminated poly(ethylene glycol) in place of \( n \)-butylamine permitted the successful synthesis of the corresponding diblock copolymers composed of polyether and polypeptide segments.
Biodegradable synthetic polymers for biomedical applications are mainly limited to polyesters, polypeptides and poly(alkyl cyanoacrylate); three polymer families with important constraints in terms of chemistry. Conversely, controlled/living radical polymerization (CLRP) techniques enable the design of functional polymers and complex macromolecular architectures, but developing a strategy affording the degradability of such materials is still challenging.

Although known for more than thirty years, radical ring-opening polymerization (rROP) has been scarcely studied in combination with CLRP techniques. Copolymerizing traditional vinyl monomers by CLRP with cyclic ketene acetics (CKAs), as a source of biodegradable ester functions that polymerize through radical ring-opening polymerization (rROP), should open new perspectives.

Herein is reported the nitroxide-mediated radical ring opening copolymerization of three different CKAs [2-methylene-1,3-dioxepane (MDO), 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and 2-methylene-4-phenyl-1,3-dioxolane (MPDL)] with methyl methacrylate (MMA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA), at 90°C. The resulting copolymers were qualitatively and quantitatively characterized by 1H and 31P NMR spectroscopy, as well as by size exclusion chromatography. Among the tested CKAs, MPDL was the best candidate as it enabled the synthesis of well-defined architectures with a high degree of livingness and a tunable amount of ester functions in the main chain, leading to complete chemical hydrolysis. The high degree of livingness was illustrated by the synthesis of various diblock copolymers containing a degradable block. Finally, the innocuousness of the obtained copolymers was confirmed on three different cell lines (NIH/3T3, HUVEC and J774 cells) by cell viability assays.
18 - Chain-length-dependent activation and termination in SET LRP/SARA ATRP

Simon Harrisson, polyharrison@gmail.com, Université Paul Sabatier, Toulouse, Haute Garonne 31062, France

Single Electron Transfer Living Radical Polymerization (SET LRP), also known as Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization (SARA ATRP), is a form of controlled radical polymerization which is carried out in the presence of copper metal, a ligand (e.g. Me₆tren), and an activated alkyl halide initiator. A simple kinetic model of the polymerization can be generated by adding the elementary reactions of comproportionation, disproportionation and activation by copper(0) to the standard reactions of ATRP. Observed features such as ½-order dependence on the copper surface area and loss of control in strongly comproportionating solvents arise naturally from this model. An interesting feature of the polymerization is that the copper(I) concentration is low and nearly constant, while the concentration of copper(II) species increases as a function of the number of dead polymer chains. Measurement of the rate of generation of copper(II) thus allows measurement of the rate of termination at any point in the reaction. As the chain length is relatively narrowly distributed, and increases as a function of conversion, this provides a means of probing the chain-length dependence of the rate of bimolecular termination. We show that addition of copper(II) halide, while narrowing the molecular weight distribution, can cause a reduction in chain-end functionality due to faster termination of shorter chains. The rate of activation of dormant polymer chains by copper(0) shows similar chain length dependence.
Monomer and polymer syntheses harnessing sustainable catalysis has become a major workhorse of innovation in polymer chemistry. Iron is the most abundant transition metal in the Earth's crust. Its high availability and low toxicity render it extremely attractive as a target for metal-based catalytic platforms. Moreover, and maintaining the economic and environmental benefit of iron catalysis, well-defined molecular iron catalysts provide the opportunity to also control selectivity. In our project, iron catalysis has proven particularly efficient in providing methods to both synthesize cyclooctadiene-based monomers and polydienes from 1,3-dienes. Redox-active ligands such as iminopyridine- and bisimine-type bidendates confer unique reactivity to the iron centers, affording various oxidation states. By adjusting steric and electronic factors, excellent regioselectivity and stereoselectivity have been achieved in productions of cyclooctadiene-based monomers on the one hand, and of polydienes on the other. This chemistry has been extended to biobased 1,3-dienes. The low cost, low toxicity, low catalyst loading, and high turnover frequency of the catalysts presented could translate, with appropriate development, into industrially relevant processes.
20 - WITHDRAWN
21 - Novel amphiphilic graft copolymers from end-functionalized starches: Synthesis, characterization, and thin film properties

Lisa M. Ryno, Jeffrey O’Brien, Kayleen Fulton, Jason Nettleton, Cassandra Reese, Gabriel Short, Gerardo Sorriano, McKenzie Tolan, Peter M. Iovine, piovine@sandiego.edu. Chemistry and Biochemistry, University of San Diego, San Diego, CA 92110, United States

We describe the use of end-functionalized starches to synthesize amphiphilic hybrid polymers that feature polysaccharide pendant chains. A general synthetic approach will be described that relies on high yielding click chemistry and a modular backbone polymer scaffold. Thin film properties of these polymers and their ability to interact with small molecules will also be described with an eye toward establishing structure property relationships.
22 - Thermoresponsive functionalized polycaprolactones for micellar drug delivery systems

Elizabeth A Rainbolt¹, liz.rainbolt@utdallas.edu, Katherine E Washington¹, Jing Hao², Daniel Siegwart², Michael C Biewer¹, Mihaela C Stefan¹. (1) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States, (2) Department of Biochemistry, Simmons Comprehensive Cancer Center, University of Texas Southwestern Medical Center, Dallas, Texas 75390, United States

Functionalized poly(caprolactone)s (PCL) demonstrating thermoresponsive behavior show promise for use in polymeric drug delivery systems. This report outlines the continuing development of substituted ε-caprolactone monomers, as well as diblock, triblock, and ternary copolymers and their self-assembly into micelles. Two functionalized caprolactone monomers, γ-(2-methoxyethoxy)-ε-caprolactone (MECL) and γ-2-[2-(2-methoxyethoxy)ethoxy]ethoxy-ε-caprolactone (MEEECL) were synthesized and polymerized by ring-opening polymerization (ROP) using stannous 2-ethylhexanoate as catalyst and benzyl alcohol as the initiator. A series of amphiphilic copolymers containing MEEECL, MECL, and ε-caprolactone (CL) were also prepared. These polymers demonstrated thermoresponsive and self-assembling behavior, which were affected by the MEEECL : MECL : CL ratios. Furthermore, the polymer assemblies exhibited no cytotoxic qualities and successfully encapsulated the model hydrophobic molecule, nile red. The use of a small portion of CL in the hydrophobic block contributed to more uniform micelles than those formed from MEEECL and MECL alone, which may prove useful in drug loading scenarios. By varying the relative incorporation of the three monomers, as well as their order of addition, the LCST, micelle size and stability, drug encapsulation, biodegradation rate, and cellular uptake of micelles may be fine-tuned. By combining thermoresponsive behavior and fully biodegradable backbones, these polymers represent a new direction in synthetic polymeric micelles for controlled drug delivery applications.
23 - Tailoring the characteristics of collodion/sulfonated polystyrene membranes to improve the electrokinetic power generation efficiency

Sofie Haldrup, haldrup@eng.au.dk, Jacopo Catalano, Anders Bentien. Department of Engineering, Aarhus University, Aarhus N, Not Applicable 8200, Denmark

The core mechanism of membrane-based electrokinetic power generation is the potential difference created by a pressure gradient, i.e. streaming potential, applied across a membrane separating two compartments with identical salt solutions. The streaming potential is a direct consequence of movement of hydrated ions whenever a pressure difference drives a volume flux across the membrane, hence creating a potential difference.

The efficiency of the electrokinetic process [1] can be related with three transport properties: streaming potential, ion conductivity and hydraulic permeability, all correlated with macroscopic characteristics: average membrane pore size (APS) and ion exchange capacity (IEC). The aim of this study was to synthetize and characterize collodion/sulfonated polystyrene, SPS, membranes having a broad range of APS and IECs.

The membranes, 50-110 µm thick, were casted by dissolving collodion(nitrocellulose) in ethanol/ether and adding SPS (content varying from 0 to 7 g L⁻¹). The IEC ranged between 0 and 0.42 meq g⁻¹ dry polymer⁻¹ and the calculated APS-diameter between approximately 1 to 8 nm. The streaming potential, hydraulic permeability and ion conductivity values covered about 2, 4 and 6 orders of magnitude in 0.03 M LiCl solutions, respectively. Interestingly the electrokinetic efficiency (> 20% for membranes with SPS ≥ 2 g L⁻¹) showed a non-monotonous behavior with SPS content. Surprisingly high efficiency of 50% was found in the membrane having SPS=5 g L⁻¹.


Sunday, August 10, 2014 10:20 AM

General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:20 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
24 - Rare example of grafting of polyesters onto polystyrene in one-step by radical polymerization

Yinfeng Shi, yinfeng.shi@uni-bayreuth.de, Zhicheng Zheng, Seema Agarwal. Department of Macromolecular Chemistry II and Bayreuth Center for Colloids and Interfaces, University Bayreuth, Bayreuth, Bayern 95447, Germany

It is well known that, graft copolymers are an important type of polymer architectures. The conventional methods for the preparation of graft copolymers like "grafting onto", "grafting from" and "grafting through" require a multi-step preparation procedure. Formation of graft copolymers in one-step could be highly advantageous, and we present copolymerization of $\beta$-propiolactone ($\beta$-PL) and styrene (St) as a rare example of formation of graft copolymers in one-step by radical polymerization. $\beta$-PL is an interesting 4 membered cyclic ester capable of undergoing radical ring-opening polymerization forming corresponding aliphatic polyester. In an attempt to utilize free radical copolymerization reactions of $\beta$-PL with styrene for the formation of degradable functional polymers we observed interestingly a rare behavior of formation of special polymer architecture (graft copolymers (PSt-$g$-$\beta$-PL)). The radical ring-opening copolymerization of $\beta$-PL and St at 120°C for all monomer feed ratios led to the grafting of polyesters onto the polystyrene backbone. A significant difference in the reactivity of St and $\beta$-PL and radical chain transfer reactions at the PST backbone followed by combination with the active growing poly($\beta$-PL) chains led to the formation of graft copolymers by grafting onto mechanism.

The details of the formation of graft polymers in one step, a rare phenomenon, by radical polymerization together with mechanism of formation will be highlighted in the talk.

Sunday, August 10, 2014 10:40 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:20 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
25 - Novel surface properties by switchable polymer brushes:
Application as a function of grafting density, molar mass, and composition

Thorsten Hofe², THofe@pss-polymer.com, Anja Rollberg¹, Kirsten Oleschko², Derek Lohmann³, John McConville³, Manfred Stramm¹, Petra Uhlmann¹. (¹) Leibniz Institute of Polymer Research Dresden, Dresden, Germany, (²) PSS Polymer Standards Service GmbH, Mainz, Germany, (³) PSS USA-Inc., Amherst, MA 01002, United States

The ultra-hydrophobic properties of a lotus leaf are based on a hierarchal surface structure. Utilizing polymer science, it is possible to copy and improve this natural phenomenon. The lotus leaf surface can be perfectly modeled by the use of a polymer particle in the µm range and a tri-block polymer coating in the nm range.

Multifunctional polymer surfaces based on this structure exhibit ultra-hydrophobic and super-hydrophilic behavior. To realize multifunctionality it is necessary to combine the different functionalities in one polymer molecule. 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 synthesis of the tri-block copolymers using controlled living polymerization techniques and the preparation of the core-shell-nanoparticles will be presented.

In addition, modern LC techniques to determine the molar mass and the composition of the polymers will be introduced, including the advantages and possibilities of 2 - dimensional separation techniques including FT-IR identification.

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.

Super-hydrophilic and ultra-hydrophobic surface behavior was achieved and will be discussed as a function of grafting density, molar mass and composition.

Applications for the possible industrial use of these new surface properties will be shown.
Mono-substituted epoxides such as propylene oxide can be polymerized by several methods to form polyethers that find use in a variety of applications. Nearly all of these polyethers are atactic, as enantiopure epoxides are expensive and few catalysts exhibit significant stereochemical control. Recently we have reported bimetallic catalysts that kinetically resolve racemic mono-substituted epoxides to form semi-crystalline polyethers and enantiopure epoxides. Through a combination of experimental and computational studies, the mechanism of these catalysts was studied and several key insights were revealed, including the role of the ionic cocatalyst salt in the initiation and propagation steps of the polymerization and the structural elements that affect the regio- and stereoselectivity of the catalysts. Variations to the bimetallic catalysts were examined in an effort to improve the scope and efficiency of the catalyst system. Finally, possible applications of the synthesized semi-crystalline polyethers were explored.
Macromolecules featuring distinct aromatic segments are being investigated for use in organic electronic materials. Acyclic Diene metathesis (ADMET) has been used in a unique way to access segmented conjugated polymers containing electro-optically active aromatic segments. In the past, we reported ADMET as a convenient route to yield various macromolecular architectures containing homologous electro-optically active conjugated aromatic segments on the either side of the heteroatom. We report here the further extension of ADMET strategy to build various conjugated polymers featuring alternating distinct fluorophores. Structure/property relationships are investigated, specifically electronic interactions between the aromatic conjugated segments and their influence on the electro-optical material characteristics. In the first step, divinyl monomers based on thiophene and phenylenes, bearing solubilizing side chains have been synthesized. In the subsequent step, the monomers are efficiently polymerized via Acyclic Diene Metathesis (ADMET) to afford segmented conjugated polymers. We are currently applying the synthetic approach to build donor and acceptor based conjugated polymers which are of special interest as materials for organic photovoltaics. Polymers are exclusively trans-configured at the internal vinylene bonds. The structures were confirmed by $^1$H, $^{13}$C, HSQC and HBMC NMR analysis. The polymers are highly fluorescent with the fluorescence quantum efficiencies in the range of 0.40-0.60 The GPC number average molecular weight of the polymers was found out to be in the range of 3200-5600 g/mol.
Bacterial infections are of increased concern due to development of antibiotic resistant strains. This trend is coupled with decreased introduction of new antibiotics. In favorable cases, polycations are strongly biocidal without buildup of resistance. However, limited progress toward development of polycation therapeutics is understood given (1) wide variability for antimicrobial effectiveness (2) uncertain cytotoxicity and (3) new drug development costs that can exceed $1 billion. Recently, we have reported new C12-m copolyoxetane polycations having PEG-like and quaternary side chains.

Unlike most previously reported polycations, G+/− antimicrobial effectiveness is found over a relatively broad compositional range (m = 40-60). Furthermore, these copolyoxetanes are cytocompatible; for example, less than 10% RBC cell death is observed for C12-50 even at concentrations well above the minimal inhibitory concentration. Given these encouraging results, we have explored feasibility for tethering these brush-like polycations to a polymer surface via newly developed hybrid surface modification. Initial results after modification of a conventional polyurethane suggest < 2 wt% polycation introduces highly effective contact kill against spray challenges of G+/− pathogenic bacteria. Preliminary results suggest good cytocompatibility. This is the first time that solution and surface activity has been demonstrated for the same polycation species. These findings open the door to a range of coatings applications for medical devices.

*The authors are grateful for support from the National Science Foundation, Division of Materials Research, Grants DMR-0802452 and DMR-1206259.
29 - Disruptive potential for 3D printing in advanced manufacturing

Daniel Daly, rca41@case.edu, The Alabama Innovation and Mentoring of Entrepreneur Center, The University of Alabama, Tuscaloosa, Alabama 35487, United States

As the ability to make functional devices continues to develop by 3D printing, so does the disruptive nature of this capability to the manufacturing sector. Recently manufacturing has been dominated by economic forces of low cost land and access to work forces. The US has seen many areas of manufacturing relocate where it can take advantage of these forces. However, as 3D printing begins to be able to manufacture an increasing amount of functional devices at the locations of the printer. These dominating economic forces will shift from 3D printing centers to our offices and homes. The potential of these advances and how they are currently impacting the ability of start-up companies in the entrepreneurial efforts will be the discussed.
30 - Advanced polymers for additive manufacturing

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

Additive manufacturing encompasses different manufacturing methods that result in objects, shapes, or patterns that are conceived from a digital or mathematical model resulting in serially produced shapes or structures. A most common association is with 3D printing. This is an additive process, where successive layers of material are laid down in different shapes or the use of precisely photopolymerized resins to form objects. This is contrast to traditional machining techniques, which rely on subtractive processes, such as cutting or drilling. The use of polymers is extensive both as extruded material, resin, or monomeric in form. Other methods, while not forming objects per se but creates artificial structures, 2-D patterns, or films from programmed methods are considered additive processes. This talk will give an overview of the different polymer systems use in additive manufacturing as extrudable, photocurable, thermoformable, polymers and precursor materials. It also shows the possibility of introducing different chemistries and expanding the manufacturing scope beyond the traditional methods.

Sunday, August 10, 2014 09:30 AM
Polymers for Additive Manufacturing (08:55 AM - 11:45 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 8
31 - 3D printing hierarchical polymeric structures: From ionic liquid to block copolymer objects

Timothy E. Long\textsuperscript{1}, telong@vt.edu, Christopher B. Williams\textsuperscript{2}, Philip M. Lambert\textsuperscript{2}, Alison R. Schultz\textsuperscript{1}, Musan Zhang\textsuperscript{3}, Courtney P. Long\textsuperscript{1}, Niki Camateros-Mann\textsuperscript{1}. (1) Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States, (2) Department of Mechanical Engineering, Virginia Tech, Blacksburg, Virginia 24061, United States, (3) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States

Additive manufacturing offers immense promise at the interface of tailored polymeric materials and rapidly emerging lithographic manufacturing technologies. This lecture will introduce the potential synergy of 3D printing block copolymers wherein additional hierarchical structure within additive manufacturing processes configures structural performance of designed objects. Mask projection micro-stereolithography enabled the design of micron scale objects with nanostructural control due to block copolymer nanoscale morphologies and nanoscale aggregations for ion-containing polymers and polyelectrolytes. Photo-rheology enabled photo-crosslinking of telechelic acrylate terminated polyethers and polyesters to enlighten a fundamental understanding of the rheology-3D printing relationship. Recent discoveries have also revealed the potential of 3D printed ionic liquid networks/gels for enhanced thermal stability, bioactivity, and ion conductivity in structured objects.

Sunday, August 10, 2014 10:00 AM
Polymers for Additive Manufacturing (08:55 AM - 11:45 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 8
Weight, performance and durability are critical drivers for any aerospace system. Reduced vehicle and system weight can enable reduced fuel consumption and emissions (aircraft), reduced launch costs and complexity (spacecraft) and increased payload capacity. Performance improvements can enhance vehicle and mission capability. System and vehicle durability are important since they impact mission safety and effectiveness. Nanotechnology and nanomanufacturing have the potential to help address each of these concerns by enabling such developments as lightweight, multifunctional materials, low power and volume sensors with high selectivity and sensitivity, radiation hard, fault tolerant electronics, and higher output energy generation and storage devices. NASA has developed a 20+ year plan for the development of nanostructured materials and devices and their insertion in NASA missions. NASA is pursuing technology needs identified in this roadmap in partnership with other Federal agencies under the National Nanotechnology Initiative's Signature Initiatives, in particular the NNI Nanomanufacturing Signature Initiative. This presentation will provide a perspective on future needs identified in the roadmap, the relationship between NASA’s nanomanufacturing R&D and the NNI Nanomanufacturing Signature Initiative and a few examples of current research activities focused on meeting those needs.
33 - Polymeric nanosystems by adaptive co-extrusion

Eric Baer, exb6@case.edu, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

A highly adaptive solvent-less co-extrusion methodology will be described from which nanolayered and nanofibrillar polymeric systems are produced. Since conventional coextrusion methods can readily be adapted to this unconventional processing technology, this advance in polymer processing of hierarchical systems is an outstanding example of additive manufacturing.

Three value-added examples will be described which are currently being translated for industrial usage. [i] The development of gradient refractive index optics that resulted in bio-mimicking of the lens of the human eye. [ii] The creation of multilayered film systems for lightweight capacitors. [iii] The discovery of solvent-less nanofiber processing for industrial and biological applications.

Finally, the possibility of translating and scaling-up this type of adaptive manufacturing will be addressed.
Currently a trend is occurring to use more sustainable feedstocks for the manufacturing of commodity and specialty polyesters. This endeavor opens up the use of alternative monomers that can find their use in, for example, clothing or automotive applications. In light of this trend we report here on the use of biobased dimethyl itaconate and 1,3-propanediol monomers, in polyesters with the final application in automotive. The presence and reactivity of the double bond in the itaconate building blocks directed us to the use of low temperature polycondensation technologies such as using enzymes as catalysts. With CAL B as the catalyst we reveal the importance of the enzyme carrier for the kinetics of the reaction as well as the detrimental effect of leached enzyme on the mechanical properties of the final product. Using a covalent immobilization technique to introduce the enzyme on a gelatin-chitosan based carrier proved to circumvent the leaching of the enzyme. This led to a successful scale-up from gram scale to 15kg of material thus demonstrating the scalable and robust nature of the enzymatic polymerization. In a next step 2,5-furandicarboxylic ester and dimethylsuccinate were incorporated in the polymers of DMI and 1,3-propanediol to broaden the scope of the applicable monomers and tenability of the thermal and mechanical properties. This range of polymers allowed structure-property relationships to be determined after crosslinking the itaconate double bonds in the different polymers with styrene using free radical, a procedure similar to the final application of the commercial materials applied in automotive industry. Where the pure itaconate based polymers displayed thermally stable, brittle materials, the introduction of the stiff aromatic furandicarboxylate decreased the heat deflection temperature as well as the glass transition temperature slightly, furthermore it led to less brittle materials as evidenced from the outer-fibre strain and the flexural strength.
Non-natural oligosaccharides can be expected to exhibit new functions and applications in glycoscience such as potential as drug candidates. Enzymatic glycosylation is a useful tool for the preparation of oligosaccharides with well-defined structure. The α-(1→4)-glucan chains can be constructed by phosphorylase-catalyzed successive enzymatic α-glucosylations using α-D-glucose 1-phosphate (Glc-1-P) as a glycosyl donor and maltooligosaccharides as a glycosyl acceptor. Since enzymes often express loose specificity for recognition of substrate structures, extension of the phosphorylase-catalyzed glycosylations using analogue substrates of Glc-1-P are an efficient approach to obtain new non-natural oligosaccharides. On the basis of above viewpoints, this presentation reports the enzymatic synthesis of chitin/chitosan stereoisomers, non-natural saccharides, by thermostable phosphorylase-catalyzed α-glucosaminylations using α-D-glucosamine 1-phosphate (GlcN-1-P) as a glycosyl donor. Consequently, it was found that this enzyme catalyzed successive α-glucosaminylations to give a chain of α-(1→4)-linked N-acetyl-D-glucosamine units. Furthermore, N-acetylation of the product gave α-(1→4)-linked N-acetyl-D-glucosamine chain. The structures of these materials correspond to the chitin/chitosan stereoisomers.
36 - Custom-tailored water-insoluble glucans from sucrose via glucansucrases

Gregory L Cote, greg.cote@ars.usda.gov, Christopher D Skory, Ryan S Cormier. National Center for Agricultural Utilization Research, USDA, Agricultural Research Service, Peoria, IL 61604, United States

Dextrans and related glucans produced from sucrose by lactic acid bacteria have been studied for many years and are used in numerous commercial applications and products. Most of these glucans are water-soluble, except for a few notable exceptions from cariogenic *Streptococcus* spp. and a very small number of *Leuconostoc mesenteroides* strains. The ability to produce water-insoluble glucans in situ may be of value in encapsulation technology and in the production of biocompatible films and fibers. There are several different ways in which these enzymes can be exploited to produce water-insoluble glucans with varying properties.

We determined that modifying a single amino acid from a *L. mesenteroides* glucansucrase significantly altered the proportions of linkage types, with correlating changes in the physical properties of the polysaccharide. We will discuss the physical properties of these novel polymers and their potential applications in agriculture, medicine and the petroleum industry.
37 - Improving intracellular UDP-sugar availability for heparosan biosynthesis in *Escherichia coli*

Brady F Cress¹, cressb@rpi.edu, Mattheos AG Koffas¹,², Robert J Linhardt¹,²,³. (1) Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, United States, (2) Department of Biological Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180, United States, (3) Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180, United States

Heparin, a highly sulfated polysaccharide, is the oldest and most successful carbohydrate pharmaceutical of the 20th century that is still in widespread use today, but increasing costs and concern over quality control of this anticoagulant drug led our group to develop a process for producing commercially relevant quantities of bioengineered heparin starting from *E. coli* derived heparosan (Figure 1). *E. coli* strain Nissle 1917 is an archetypal probiotic agent that naturally produces and secretes heparosan, an unsulfated polysaccharide precursor to the glycosaminoglycan heparin, as the primary component of its cell capsule. Supplementing *E. coli* cultures with the nucleotide activated sugar precursors UDP-\(N\)-acetylglucosamine and UDP-glucuronic acid significantly improved heparosan titers, suggesting that intracellular availabilities of these valuable metabolites are limiting and that targeted gene deletions, downregulations, and overexpressions could improve production levels. To this end, we have recently sequenced the genomes of Nissle 1917 and related strain K5 to gain insight on biosynthetic pathways responsible for diversion of UDP-sugar precursors toward undesired, non-essential bacterial glycans. Furthermore, we have heterologously expressed the heparosan biosynthetic gene cluster in acapsular workhorse strain *E. coli* BL21, successfully transplanting the heparosan capsule as confirmed by LC-MS analysis. We demonstrate that simultaneous downregulation of competing pathways and overexpression of UDP-precursor accumulation pathways is an effective strategy to explore metabolic space for green production of biomedically relevant microbial polysaccharides from simple carbon sources like glucose and glycerol. Engineered strains capable of generating high intracellular concentrations of UDP-activated sugar donors will be critical for *in vivo* glycosylation of natural products and for production of other medically important glycosaminoglycans like chondroitin sulfate, dermatan sulfate, keratan sulfate, and hyaluronan.

Figure 1. Heparosan repeating disaccharide unit
38 - Redox enzymes for medical and cosmetic applications

Artur Cavaco Paulo, artur@deb.uminho.pt, Center of Biological Eng., University of Minho, Braga, Minho 4800, Portugal

Laccases were used for the formation for phenolic polymers to induce antimicrobial properties in urinary catheters.

Schematic representation of alkaline hydrolysis and polymerization reaction during poly(catechin) oxidation and coating of catheters surface for polyurethane catheters

When the enzymatic polymerization takes place in presence of latex and polyurethane catheters, the amount of polyphenols entrapped is enough to induce stayed anti-film formation. Different start-up phenolics and different catheter materials were studied on the leaching and anti-microbial properties of laccase formed polymers. In the second part of this presentation we report also the formation of cross-linked fibrous networks using protein disulfide isomerase to fix cysteine-containing compounds (CCC) in keratin hair fibers for possible cosmetic applications.

Schematic illustration of the PDI-assisted reactions of cysteine-containing compounds (CCC) on hair keratin
Biocatalysts immobilization onto nanomaterials has been implemented into a variety of applications ranging from biosensing to biotransformation, and from decontamination to energy storage. However, retaining enzyme catalytic activity at such nanointerfaces was challenged by either the non-specific attachment of the enzyme resulting in catalytic center deactivation at the nanointerface or increased enzyme-enzyme interactions known to lead to crosslinking and subsequent loss of enzyme activity. The next generation of enzyme-based applications need to account for increased enzyme functionality, high operational and storage stability, efficiency and yield of recovery and conversion at the nanointerface, as well as reduced enzyme inhibition. We proposed that user-tailored control of the enzyme-nanointerface reactions could lead to enhanced enzyme catalytic efficiency. Our systematic study shows that the enzyme and the nanosupport characteristics (e.g., surface chemistry, surface charge, physical volume to surface ratio etc.) work synergistically to determine and control enzyme functionality and catalytic behavior at nanointerfaces. Further, our results show that user-tailoring the enzyme immobilization techniques at nanointerfaces could lead to robust enzyme-based nanointerfaces to be used for a variety of applications from enzyme-based biosensors to enzyme-based decontamination platforms.
Green chemistry, which includes - but is not restricted to - the replacement of environmentally hazardous chemicals with safer materials, product biodegradation, and the use of catalysts and renewable resources looks to improve the safety and efficiency of polymer chemistry. In this work, ibuprofen was coupled to malic acid, a naturally-occurring, renewable acid present in fruits, via its secondary alcohol to afford ibuprofen-malic acid (Ibu-MA). Ibu-MA and a diol (e.g., 1,8-octanediol) were then polymerized via biocatalytic methods using Novozym 435 (lipase B from Candida antarctica immobilized on acrylic resin), an increasingly popular green polyesterification catalyst. This work is the first report of such a malic acid polymer with functional pendant ester groups (e.g., ibuprofen). Previously, our lab demonstrated the synthesis of ibuprofen-tartaric acid polyester, but used a metal catalyst during the polymerization; however, the lipase use allows for a more environmentally friendly methodology. Polymer molecular weight and thermal properties were determined. The polyester biodegradation was also evaluated under physiological conditions; the polymer undergoes hydrolysis to yield malic acid and ibuprofen in a sustained, controlled manner. To confirm the polymer safety, cytotoxicity studies were performed using fibroblast cells. Additionally, to ensure the structure of released ibuprofen was retained, NMR analysis was used. Using principles of green chemistry, our polyester synthetic methodology moves toward a more economical and environmentally friendly future in biomaterials and drug delivery.
A family of biocompatible and biodegradable polyesters, based on renewable resources such as glycerol and a variety of sugar alcohols (D-sorbitol, meso-erythritol and D-xylitol), were enzymatically synthesized by using Candida Antarctica type B (CAL-B) lipase. Although glycerol and other sugar alcohols have multiple hydroxyl groups in their structure but due to the regioslectivity of lipase catalyst, they were used along with divinyladipate to generate linear polyesters with free pendent hydroxyl groups on their backbone.

All synthesized polyester chains were hydrophilic in nature but only poly(sorbitol adipate) and poly(xylitol adipate) were water soluble. Pendent hydroxyl groups in the backbone were further modified by different saturated and unsaturated fatty acids with varying degree of grafting. Nanoparticles of these modified polyesters were made by using interfacial deposition method and characterized using dynamic light scattering. All the synthesized products were characterized by NMR- and IR-spectroscopy, and their thermal behavior was analyzed by DSC.

Furthermore, polyester backbones were successfully modified with α-bromoisobutyryl bromide in order to use them as macroinitiator for atom transfer radical polymerization (ATRP). As an evidence of this concept, glycerol monomethacrylate was polymerized by ATRP from a poly(glycerol adipate) (PGA) backbone yielding the amphiphilic graft copolymer PGA-graft-poly(glycerol monomethacrylate). Its self-assembly in aqueous solution was studied using dynamic light scattering.
Fractal attitudes: From dendritic architecture to metallomacrocycles

George R. Newkome\textsuperscript{1,2}, newkome@uakron.edu, Xiaocun Lu\textsuperscript{1}, Ting-Zheng Xie\textsuperscript{1}, Sheng-Yun Liao\textsuperscript{3}, Xin Liu\textsuperscript{3}, Jing-Yi Li\textsuperscript{1}, James Ludlow\textsuperscript{1}, Rajarshi Sarkar\textsuperscript{2}, Timothy Moneypenny\textsuperscript{2}. (1) Department of Polymer Science, The University of Akron, Akron, OH 44325-4717, United States, (2) Department of Chemistry, The University of Akron, Akron, OH 44325, United States, (3) Department of Chemistry, Nankai University, Tianjin, China

An overall perspective of research in our laboratories based on functionalized nanomolecular rational design and construction that integrates the spatial arts, mathematics, and material science will be presented. Discussion encompasses the supramolecular paradigms of chemically and geometrically complementary building blocks, along with balanced thermodynamic metal-ligand parameters, to generate new materials via a one-step assembly process. Towards these goals, the incorporation and utility of the 2,2′:6′,2″-terpyridine scaffold provide an excellent avenue to complex, preprogrammed, macromolecular architectures. Thus, terpyridine rigidity, metal connectivity, and well-developed substituent chemistry have allowed the construction of materials predicated on similar, as well as dissimilar polytopic ligands. Progress from simple ring structures based on 120°- and 60°-juxtaposed bisteryridines to the logical combinations of multiple, polytopic terpyridine building blocks, exemplified by the nearly quantitative synthesis of spoked-wheel architectures (Figure 1), will also be discussed. The structural implications of reaction concentration on the assembly process will be considered, especially where forming labile coordinative bonds and more thermodynamically favored products are concerned. The construction of novel 3D architectures will be demonstrated.
43 - Ruthenium(II) terpyridyl-fullerene assemblies: Synthesis, electrochemical, and photophysical properties

Andreas Winter\textsuperscript{1,2}, andreas.winter@uni-jena.de, Kevin Barthelmes\textsuperscript{1,2}, Christian Friebe\textsuperscript{1,2}, Joachim Kübel\textsuperscript{2,3,4}, Maria Wächtler\textsuperscript{2,3,4}, Benjamin Dietzek\textsuperscript{2,3,4}, Ulrich S. Schubert\textsuperscript{1,2}. (1) Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena, Germany, (2) Jena Center for Soft Matter, Jena, Germany, (3) Institute of Physical Chemistry, Friedrich-Schiller-University Jena, Jena, Germany, (4) Leibnitz Institute of Photonic Technology, Jena, Germany

Photoinduced electron transfer and/or energy transfer in molecular assemblies combining ruthenium(II) polypyridine complexes, as donor components, and fullerene-type acceptors have been extensively studied, and their electrochemical and photophysical properties are of particular interest.

A series of Ru(II) bisterpyridine C\textsubscript{60} dyads linked via para-phenyleneethynylene units of different lengths have been prepared. The functionalization on the fullerene sphere was accomplished via 1,3 cycloaddition reaction to form pyrrolidine and cyclopropane rings. The photophysical properties have been investigated by steady-state as well as time-resolved spectroscopy. Upon light excitation of the Ru(II) center, the emission was strongly quenched by the fullerene. Transient absorption spectroscopy revealed characteristic absorption changes that have been ascribed to the fast decay of the Ru(II)-based 3MLCT transition and formation of the lowest excited C\textsubscript{60} triplet state. Nanosecond flash photolysis allowed to determine the decay ($\tau_{1/2} = 1\ \mu$s) of the latter one towards the ground state.
44 - Terpyridine metal ligand constructs

Jay S Siegel, dean_spst@tju.edu.cn, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin, China

Terpy based ligands form stable 2:1 ligand-to-metal complexes with transition metals. They can be used for topological synthesis of Borromean link precursors, metal-organic dendrimers and molecular grids. They can also form complexes for the construction of thermodynamically-driven assemblies. Combining tridentate and bidentate structural units into normally uses flexible linkers; however, linear rigid-rod analogs with parallel-aligned coordination vectors for terpy and bipy would be a desirable design alternative. Fusion of a five-membered ring to the six-membered flanking rings of terpy modifies the substitution pattern, specifically addressing the linear bilateral geometry mentioned above. This lecture details the synthesis of such ligands, as topological bipy mimics, and the combination of these components via a convergent modular strategy.

Sunday, August 10, 2014 09:25 AM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (08:30 AM - 11:40 AM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 1/2
Supramolecular polymers are of great interest because the nature of non-covalent interactions holding them together imparts dynamic, reversible and degradable characteristics to these materials. Although the study of supramolecular polymers has made considerable progress, it remains a challenge to realize control over supramolecular polymerization.

In this presentation, I'd like to introduce two strategies to fabricate supramolecular polymers, leading to advancement of controlled supramolecular polymerization. One is conventional method, that is, to design and synthesize bifunctional monomers by covalent synthesis, and then to fabricate supramolecular polymers by non-covalent interactions. In recent years, we have developed a series of cucurbit[8]uril based supramolecular polymers on the basis of host enhanced charge transfer interactions or pi-pi interactions. In order to achieve a high degree of polymerization in dilute aqueous solution, a strategy of designing rigid or bulky monomers was adopted to inhibit dimerization and cyclization during supramolecular polymerization. Another method is to fabricate supramonomers by non-covalent interactions and then to prepare supramolecular polymers by covalent polymerization of the supramonomers. By taking advantage of this strategy, non-covalent polymerization can be transformed into covalent polymerization, which not only enrich the fabrication method of supramolecular polymers, but also facilitate the structure control of supramolecular polymers.
We report the synthesis and characterization of a metallo-supramolecular polymer based on 2,6-bis-(1' methyl benzimidazoyl) pyridine (BIP) ligands tethered to a poly(n-butyl acrylate) polymer backbone. The influence of the metal-ligand bond strength and phase separation on the mechanical properties of the polymer was investigated. Metal-ligand bond strength primarily affected the properties of the polymer at high temperatures and strains. The phase separation of the complexes within the polymer complexes acted as physical crosslinks and caused a 10x increase in the rubbery plateau modulus over what would be expected based on the theory of rubber elasticity. In addition, the effect of incorporating unbound metal-ligand complexes into the polymer was explored. It was found that the bound and unbound complexes phase segregated together forming ordered, cylindrical domains. The storage modulus, compressive storage modulus, high temperature stability, and creep resistance increased with increasing concentration of metal-ligand complex in the polymer.
47 - Smart metallo-supramolecular hydrogels from heterotelechelic associating copolymers

Jean-François Gohy, jean-francois.gohy@uclouvain.be, Charles-André Fustin, Jérémy Brassinne. Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Louvain-la-Neuve, Belgium

Metallo-supramolecular micellar hydrogels exhibiting thermo-mechanical responsiveness have been prepared through the hierarchical assembly of a heterotelechelic associating copolymer. The latter consists in a linear thermo-sensitive water-soluble sequence terminated by a short hydrophobic sticker at one end, the other being functionalized by a chelating ligand. As a first level of assembly, the associating copolymer is dissolved in water to yield micellar nanostructures, bearing ligands at the end of the coronal chains. The second level of assembly is achieved when transition metal ions are added to the micellar solutions, resulting in almost instantaneous gelation. The thermo-mechanical response of those materials is investigated in detail.
48 - Synthesis of twisted dinuclear ruthenium(II) bis(2,2′:6′,2″-terpyridine) complexes

Kung K. Wang, kung.wang@mail.wvu.edu, Bo Wen, Jeffrey L. Petersen. C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045, United States

A 4,5-diarylphenanthrene (Ar = terpyridyl) was prepared via the cascade cyclization reactions of the corresponding benzannulated enyne–allene. The presence of two terpyridyl units allowed it to serve as a ligand for the synthesis of dinuclear Ru(II) bis(terpyridine) complexes possessing severe helical twists.

Sunday, August 10, 2014 11:05 AM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (08:30 AM - 11:40 AM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 1/2
49 - Photo-induced disassociation of Fe(II)-containing metallo-supramolecular polymers

Joy Romulus, joy.romulus@case.edu, Stuart J Rowan. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States

Metallosupramolecular polymeric materials prepared from telechelic poly(ethylene-co-butylene) polymers end-capped with 2,6-bis(1'-methylbenzimidazolyl)pyridine (Mebip) ligands and complexed to Zn(II) or Eu(III) were previously demonstrated to repair damage of the material in response to a photo-thermal stimulus. While these systems efficiently heal they require intense light and high temperatures, which can limit the type of polymer backbone employed. Furthermore, the healing is limited if these materials are used as coatings on thermally conducting substrates (e.g., glass or metal) that act as efficient heat-sinks. Thus in an attempt to extend the utilization of these metal-ligand polymer complexes this study focuses on utilizing Fe(II) as the binding metal since many Fe(II) complexes are known to weaken upon exposure to light. We show both damaged free standing films and coatings on either metal or glass substrates of these Fe(II)-based metallosupramolecular polymers can be easily healed with light. We also demonstrate the ability of these materials to act as photo-triggered adhesives. Furthermore, we show that more polar metallosupramolecular polymers derived from Mebip end-capped poly(tetrahydrofuran) complexed with Fe(II) are also photo-healable and have photo-activated adhesive properties.
Poly-N-substituted glycine peptides (peptoids) are non-natural synthetic polymers that are based on a peptide polyglycine backbone with side chain substitutions on the amide nitrogen rather than the α-carbon, leading to novel physical and chemical properties. In the past we have developed several peptoids designed for grafting onto surfaces where they confer resistance to fouling by proteins, cells and bacteria. In this talk we will describe two peptoid variations inspired by the most effective antifouling molecules in nature: the glycocalyx and zwitterions. The precise sequence specificity afforded by solid phase synthesis allowed us to probe several molecular designs in which the placement of mono- and disaccharides is varied. In the case of zwitterionic peptoids, the effect of charge separation on protein fouling resistance was emphasized. Results of protein and cell fouling studies of these surface grafted peptoid systems were coupled with computational studies using molecular dynamics and molecular theory, providing insight into important molecular features of antifouling peptoids and guiding the design and optimization of these systems for optimal performance.
Polypeptoids, a class of peptidomimetic polymers featuring N-substituted polyglycine backbones, exhibit tunable physiochemical properties (e.g., solubility, crystallinity and conformation) that are strongly dependent on the side chain structures. Amphiphilic AB or ABC block copolypeptoids [i.e., poly(N-decyl glycine)-b-poly(N-methy glycine) (PNDG-PNMG) and poly(N-decyl glycine)-b-poly(N-methy glycine)-b-poly(N-allyl glycine) (PNDG-PNMG-PNAlG)] with controlled composition have been synthesized by organo-mediated ring-opening polymerization of N-substituted N-carboxyanhydride monomers. The PNDG100-PNMG10 polymer was shown to self-assemble into cylindrical micelles in dilute alcohol solution and a fibrillar network at elevated concentration at room temperature. While both the cyclic and linear PNDG100-PNMG10 polypeptoids form thermo-reversible gels, their gelation conditions (i.e., concentration, temperature and gelation time), mechanical properties and hydration environment around the polymers are architecture-dependent. In comparison, the PNDG100-PNMG10-PNAlG10 sample undergoes a sol-to-gel transition with increasing temperature in water. The gelation was reversible and rapid, which was attributed to the LCST induced formation of a micellar network. The polymer gel is injectable and exhibits minimal cytotoxicity towards human-derived adipose stem cells, which makes it potentially useful for tissue engineering application.
Poly(N-substituted glycine)s, also referred to as polypeptoids, are interesting polymers for life science and materials science applications. They are available by controlled ring-opening polymerization of N-substituted glycine N-carboxyanhydrides (NCAs) and their properties, for instance solution properties including thermo-responsivity, can be tailored by the nature of the side chain. Polypeptoids with unsaturated side chains can be further functionalized by click chemistry including thiol-ene/yne photochemistry.

Poly(N-C3 glycine)s (C3 = n-propyl, allyl, and isopropyl) with molecular weights ranging from 1.8-6.6 kDa readily soluble in water (up to 20-40 g/L) and show LCST behavior; the cloud point temperatures vary between 15 and 58 °C depending on C3 and molecular weight. Poly(N-propargyl glycine), on the other hand, does not dissolve in water. Long-term annealing of aqueous solutions of poly(N-(n-propyl) glycine) and poly(N-allyl glycine) above their phase transition temperature results in the formation of crystalline microparticles with rose bud type morphology.

Poly(N-(n-propyl) glycine)-block-poly(N-methyl glycine) form core-shell micelles in water at above the phase transition temperature of the first block, i.e. >30 °C. Crystallization of the poly(N-(n-propyl) glycine) core produces sub-micron particles, which are larger in size and have different morphology than the original micelles. Kinetics/mechanism of the aggregation and crystallization processes are currently being examined.
**53 - Step-growth polymerization using N-alkyl urea peptoid chemistry**

_Neil Ayres, Neil.Ayres@UC.edu, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221, United States_

N-alkyl urea peptoids are oligomeric biomimetic molecules that can be thought of as hybrids between oligoureas, N-acyl glycines (peptoids) and 2-γ peptides. By virtue of their iterative synthesis strategy a wide variety of functional side chains can be incorporated, including sugars, fluorophores and supramolecular elements. This presentation will describe the use of N-alkyl urea peptoid oligomers in the synthesis of polymers using a step-growth polymerization strategy. The afforded macromolecules have been used for applications including blood-contacting biomaterials as heparin mimicking polymers (Figure 1).

By varying the identity of pendant sugar groups on the polymer we are able to study structure property relationships with respect to blood compatibility. The polymers have displayed prolonged aPTT times with respect to controls and are within clinical ranges. Furthermore, spin-cast films of the polymers displayed dramatically reduced adhered platelets compared to controls following incubation with platelet rich plasma.
Folding and assembly of sequence-defined peptoid polymers

Jing Sun, Caroline Proulx, Gloria Olivier, Ranjan Mannige, Tom Haxton, Li Guo, Golan Gertler, Michael Connolly, Joo Myung Jun, Jessica Su, Rita Garcia, Stan Yoo, Steve Whitelam, Ronald Zuckermann, rnzuckermann@lbl.gov. Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

The design and synthesis of protein-mimetic nanostructured materials based on the folding of non-natural polymers into defined architectures is a fundamental challenge in materials science. Two levels of "synthesis" are required: (1) the covalent structure - the conventional multi-step solid-phase organic synthesis of the precise monomer sequence in the chain, and (2) the non-covalent structure - the folding/assembly of the chain into a higher order structure. Both of these synthetic processes have been studied in detail for the production of peptoid nanosheets in high yield. Computational tools are also being developed at the atomistic and coarse-grained levels, which provide new insights into the dynamics of chain folding and assembly. The precision synthetic control over the peptoid structure afforded by the submonomer method enables the rapid prototyping of new polymeric materials, as well as the testing of fundamental principles in polymer science and structural biology.
Peptoids, oligomers of N-substituted glycine, are useful biomimetic polymers. To date, examples of peptoids that mimic protein secondary structural motifs (helices, turns, ribbons) have been reported, but very few peptoids exhibit higher order structures that rival the complexity of biomolecular structure. We have prepared and studied water-soluble peptoids that can self-associate. Peptoids comprise the strongly helix-promoting residue N-S-(1-naphthylethyl)glycine (Ns1npe), which is intrinsically fluorescent. CD spectroscopy, fluorescence spectroscopy, and other techniques have been used to explore the influence of a peptoid’s sequence on its propensity to self-associate in water, and spectral features have been correlated with more robust association. Our data are consistent with a hydrophobically-driven self-associative mechanism. Peptoid length, secondary structure, and amphiphilicity all influence aggregation. These results enhance the existing understanding of peptoid sequence-structure relationships, and such peptoids have potential promising applications as sensors or sequestrants.
Polypeptoids are a very interesting class of polypeptide-mimetics. It was shown that, in contrast to polypeptides, (multi-)block copolymers can be synthesized from solution \(^1\) and, as we present here, from solid support \(^2\). Compared to these polymerizations the well-known step-wise synthesis of peptides and peptoids \(^3\) lead to uniform monomer sequences that can be used for example as targeting sequences for selected receptors of tumor tissues or as structural units to generate three-dimensional constructions. Uniting the two approaches, provide a perfect modular toolkit for synthetic biology.

During this work, we could optimize the reaction parameters of the solid-phase supported polymerization to gain polymers with narrow molecular weight distributions and identify the monomer diffusion as bottle-neck of the synthesis. Kinetic investigations revealed a strictly linear pseudo-first-order kinetics to high monomer conversion and a linear correlation of the apparent polymerization rate with the monomer concentration. Further, the molar mass increases in a linear manner with the monomer conversion to quantitative monomer conversion.

As a final step, the synthesis of a pentablock copolymer compromising Sar-NCA and N-ethylglycine-NCA was performed and proofs the living character of the ring-opening polymerization of NNCAs from solid-support.

Extensive efforts are currently devoted to mimic the structure and functions of peptides and proteins with abiotic oligomers. Peptoids are a promising class of biomimetic oligomers composed of N-substituted glycines with enhanced proteolytic stability and permeability relative to peptides. Further modifications have involved the insertion of an additional methylene or an aryl group in the backbone. We have thus prepared two novel families of peptoids: the α,β-peptoids with alternating α- and β-residues and the arylopeptoids composed of aminomethylbenzoic acid monomers. The first part of the presentation will focus on the synthesis and conformational investigation of these novel families. The second part of the presentation will discuss on how to reduce the inherent flexibility of peptoids. The α,β-peptoids [1] and arylopeptoids[2] have been cyclized which allowed us to obtain several X-ray crystal structures. We have also developed novel peptoid side chains that are capable of inducing only cis peptoid amides.[3] These novel tools have also facilitated the crystallisation of several peptoid structures.


**58 - Metal-catalyzed living radical polymerization: Recent progress**

*Mitsuo Sawamoto, sawamoto@star.polym.kyoto-u.ac.jp, Department of Polymer Chemistry, Kyoto University, Kyoto City, Kyoto 615-8510, Japan*

This lecture will discuss the recent progresses and topics in metal-catalyzed living radical polymerization that we have been developing, focusing catalysts design and precision functional polymers.

(A) Living Radical Polymerization: Design and development of Ru and Fe catalysts, highly active, functionality tolerant, and/or water-soluble for user-friendly and sustainable systems. Ligand design has led to a series of Ru and Fe complex catalysts that enable living radical polymerization of functionalized monomers and in water or alcohol.

(B) Precision Functional Polymers: Precision synthesis of tailor-made functional polymers, particularly core-functionalized microgel star polymers and amphiphilic polymers undergoing single-chain folding to nanospace. These star polymers can include transition metal complexes to give robust and active catalysts.

(C) Sequence Control: Concept and strategies for sequence control in chain-growth polymerization to construct novel carbon-chain polymers with a controlled sequence of functionalities.
Transition metal carbonyls and perfluoro/alkyl halides were evaluated in the initiation and control of vinylidene fluoride (VDF) photopolymerizations and block copolymerizations under visible light. While Cp2Cr2(CO)4, Cp2Fe2(CO)4, Co2(CO)8, Mo(CO)6, Cr(CO)6 and Fe(CO)5, did not afford PVDF, a free radical polymerization was observed for CH3(CH2)5Br, CH3(CH2)5I, CH3I, CCl4, CCl3Br, Br(CF2)6Br, CF3(CF2)3I, I(CF2)6I) mediated VDF-CRP via iodine degenerative transfer (IDT) in the presence of Re2(CO)10, Mn2(CO)10 >> Cp2Mo2(CO)6 >> Cp2W2(CO)6.

Hypervalent iodide carboxylates (CX3COO)2I[III]Ph (X = F, H) and (CH3COO)3I[V](C6H4COO) are introduced as a new class of visible light photoinitiators for VDF polymerizations initiated by CX3, where with I2, a controlled radical, iodine degenerative transfer process is mediated by the in situ generated CF3I.

Finally, Re2(CO)10, Mn2(CO)10, Cp2W2(CO)6, Cp2Mo2(CO)6, and Cp2Fe2(CO)4 provide complete activation of both PVDF-CH2-CF2-I and PVDF-CF2-CH2-I chain ends, and were used in the synthesis of well-defined PVDF block copolymers with vinyl acetate, t-butyl acrylate, methyl methacrylate, isoprene, styrene, acrylonitrile, 2,2,2-trifluoroethyl methacrylate and methyl 2-(trifluoromethyl)acrylate.
We have developed living radical polymerizations using iodine as a capping agent and organic molecules as catalysts. The catalysts include amines and organic salts such as tetrabutylammonium iodide. The polymerizations are amenable to various monomers including styrene, methacrylates, acrylates, acrylonitrile and their functional monomers. The molecular weight can be increased to $10^5$ for methacrylates and $10^4$ for other monomers. Diblock copolymers, triblock copolymers, star polymers, and polymer brushes on solid surfaces are obtainable. The system is also unique in that it can be induced not only by thermal heating but also by photo-irradiation in a wide range of wavelength (350-750 nm) with appropriate choice of catalysts, which may widen the scope of application. The chemistry and polymerization performance will be presented.
61 - Controlled polymerization of ethylene using RAFT based mechanisms

Cédric Dommanget¹, Ian German¹,², Sébastien Norsic¹, Christophe Boisson¹, Vincent Monteil¹, Franck D’Agosto¹, franck.dagosto@univ-lyon1.fr. (1) UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP, Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, Villeurbanne, France, (2) Department of Chemistry, Present address: Center for Education and Research on Macromolecules, Liège, Belgium

The tremendous volume and broad utility of polyolefins are related to the ability to make different kinds of material from a simple set of largely available monomers (e.g. ethylene, propylene). Ethylene, the simplest and the cheapest of the olefins, is an extremely attractive monomer with a feedstock that can be independent from oil production and obtained by bio-resources. Polyethylene is industrially synthesized either by coordination catalyses (Ziegler-Natta or Phillips catalysts) or free radical polymerization.

Controlling the growth of the chains during a polymerization process gives access to the fine tuning of the properties of the final material. In addition, being able to efficiently and selectively introduce reactive groups into a very apolar polyolefin such as the polyethylene may open the way to use these segments as building blocks.

Coordinative chain transfer polymerization (CCTP or Catalyzed Chain Growth (CCG)) is the only industrially relevant system to produce polyolefins in a controlled manner according to a catalytic process. This system is conceptually analogue to the well-known reversible addition-fragmentation chain transfer (RAFT) process in free radical polymerization.

Our team, involved in catalytic olefin polymerization and controlled radical polymerization, is identifying efficient and original ways of designing well-defined and reactive polyethylene chains. This paper will show how CCG and RAFT have been used to design for the first time starting from ethylene telechelic polyethylene and to control the RAFT polymerization of ethylene, respectively.
Thermally degradable polymers are of wide interest in the area of sacrificial materials, lithography, and drug delivery systems. A new series of thermally degradable polyesters with tunable degradation rate have been developed by controlled radical polyadditions of a bis(bromoisobutyrate) type monomer and a bis(styrenic) type monomer. These polymers undergo chain scission through intramolecular cyclization of the γ-haloalkanoate groups in the polymer backbone at elevated temperatures.

Kinetic studies showed that tunable rate of degradation can be achieved by changing the molecular structure of the monomers. The polymers with benzyl groups linked to the labile groups degrade much faster than the other polymers, while the polymers possessing rigid bicyclic isosorbide group shows the slowest rate. The effects of solvent on the degradation behaviors were also investigated and a remarkable acceleration of the lactonization was observed as the polarity of the solvent increased. This work demonstrated a facile access to thermally labile polymers with tunable degradation rate.
We will discuss our recent efforts on the polymerization of elemental sulfur to prepare chemically stable copolymers with a very high content of sulfur (50-90 wt% sulfur). While the thermally initiated ring-opening polymerization (ROP) of elemental sulfur to form polymeric sulfur has long been known, this form of polymeric sulfur depolymerizes. Furthermore, polymeric sulfur formed from this process is an intractable, brittle material. We have recently developed a novel polymerization method, termed, inverse vulcanization, to form chemically stable and processable sulfur copolymers by the free radical copolymerization of elemental sulfur and 1,3-diisopropenylbenzene (DIB). The inverse vulcanization process is essentially a bulk copolymerization of sulfur and DIB that mechanistically is a thermally initiated thiol-ene reaction. We will discuss the mechanistic aspects of this process along with novel thermomechanical and electrochemical properties of these sulfur polymeric materials.
A thermoresponsive ruthenium catalyst containing PEGylated triphenyl phosphine derivatives has been used to conduct transition metal mediated living radical polymerizations (ATRP) in miniemulsion, allowing for easy removal of the metal catalyst post-polymerization. The polymerizations of butyl methacrylate in miniemulsion catalyzed by RuCp*Cl(PPh₃)₂ (non-thermoresponsive) or the RuCp*Cl(PPEG) (thermoresponsive) were compared, with the PEG containing ligand found to be significantly more active than the triphenyl phosphine ligand. The reaction temperature was near the cloud point of the thermoresponsive catalyst allowing it to transfer into the monomer droplets upon heating and mediate the polymerization. The polymerization showed good control with molecular weight distributions increasing shifting to higher molecular weights at increasing conversions and relatively low polydispersities. Following polymerization the reaction mixture was cooled allowing the catalyst to desorb from the particles. The latex was precipitated in methanol, producing a colorless polymer product that contained less than 10 ppm of residual metal as measured by ICP-AES. This approach may facilitate the development of waterborne ATRP processes yielding final latexes that are metal-free and enabling catalyst recycle.
Air or TEMPO-mediated oxidation of magnesiated iodoarenes \( \text{A} \) initiates polymerization of \( \text{A} \) to provide highly regioregular poly(\( m \)-phenylenes) \( \text{B} \) via strictly alternating anionic/radical cross-over chain growth polymerization. Poly(\( m \)-phenylenes) \( \text{B} \) with mean molecular weight of up to 20000 g/mol can be prepared under mild conditions by this method. The approach represents a new concept for polyarene synthesis and transition metals are not necessary to conduct these polymerizations. Moreover, postmodification of polymers prepared by controlled nitrooxide mediated radical polymerization (NMP) via photochemical nitrooxide trapping will be presented.
The initial phase of styrene solution polymerizations was studied in detail for cyanoisopropyl dithiobenzoate (CyP-DB) or phenylethyl dithiobenzoate as RAFT agents. The transformation of the RAFT agent into oligomeric RAFT species and the main equilibrium of the polymerization are characterized by two chain transfer constants. The kinetic analysis is based on the measurements of the RAFT agent concentration and the molecular weight distribution by means of size exclusion chromatography with high molecular weight resolution. As shown in the plot the initialization period is ideal for temperatures ranging from 60 to 110 °C: to each cyanoisopropyl dithiobenzoate molecule one monomer molecule is added.

In the case of cyanoisopropyl dithiobenzoate already after 0.6 % of monomer conversion the initial RAFT agent is consumed completely. Total transformation of phenylethyl dithiobenzoate is achieved at a slightly higher monomer conversion of 1.5 %. Employing Monte Carlo methods the chain length distributions were modeled as a function of monomer conversion to derive the chain transfer constants for the pre- and main equilibria. For example, the chain transfer constant of the main equilibrium is 1330 at 80 °C using cyanoisopropyl dithiobenzoate as RAFT agent.

Sunday, August 10, 2014 04:40 PM
Controlled Radical Polymerization (01:00 PM - 05:30 PM)
Location: Hilton San Francisco Union Square
Room: Continental Ballroom 4
Both structural and kinetic investigations of radicals in polymerizations have been conducted by various ESR technique using ATRP.

Time-resolved electron spin resonance (TR ESR) spectra allowed direct observation of transient radicals (chain initiating radical) obtained by the addition reaction of a diphenylphosphinoyl radical to vinyl monomers. Since TR ESR spectroscopy is based on chemically induced dynamic electron spin polarization (CIDEP) phenomenon, highly polarized radical can be detected as ESR signal and signal intensity is not correlated with the radical concentrations. Even if transient radical concentrations are lower than the lower limit of sensitivity of conventional steady-state ESR, highly polarized radicals can be detected by TR ESR spectroscopy. Figure 1 shows TR ESR spectrum of tert-butyl methacrylate (tBMA) initiated by 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TMDPO).

Mechanism of radical migration during polymerizations of acrylates has been clarified using oligo- and polymeric model radicals generated from precursors prepared by ATRP. There are many factors that affect the rate of the migration. Dependencies on chain lengths, side group structures, monomer unit sequences, and stereo-chemical differences have been examined.
68 - Facile and practical route to a versatile intermediate of substituted cyclic carbonates offering diverse smart biomaterials

Kazuki Fukushima, fukushima@yz.yamagata-u.ac.jp, Kohei Kishi, Shunya Takaoka, Yuto Inoue, Chikako Sato, Masaru Tanaka. (1) Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan, (2) Department of Biochemical Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan

Biodegradable polymers with functionalities are a powerful tool for creating high-valued biomedical devices, especially in so-called nanomedicine, smart biomaterials, and regenerative medicine, for which are required to equip at least biocompatibility as well as biodegradability. Chemically synthesized biodegradable polymers such as aliphatic polyesters, polycarbonates, and poly(amino acid)s are often prepared by ring-opening polymerization of the corresponding cyclic monomers. Therefore, introducing a functional group, if necessary, is performed at the stage of monomer synthesis in most cases.

Six-membered cyclic carbonates have drawn attention as a promising monomer platform for functional biodegradable polymers due to stability in ambient condition and diverse accessibility to the functionalization. In particular, several synthetic routes have been reported regarding the cyclic carbonates conjugating functional substituents with ester and amide linkers. The monomers called MTC-XRs are derived from bis(2,2-methyloyl)propionic acid (bis-MPA) known as an affordable building block of biocompatible dendrimers. The synthetic pathway of MTC-XRs must include two principal reactions that are a coupling of the carboxyl group of bis-MPA to an alcohol or amine and a carbonylative cyclization of the diol.

We recently developed a new alternative pathway of producing MTC-XRs that is straightforward, easily accessible, economically feasible, and somewhat green. Recent progress on application of poly(MTC-XR)s to tissue engineering will also be discussed.
Poly(L-lactic acid) (PLLA) was reported to form complex crystals (ε-crystals) with some solvents such as N,N-dimethylformamide (DMF) by exposing its films to the solvents. PLLA dissolved in these solvents was gelated by cooling the solutions to room temperature. The X-ray diffraction patterns indicate that PLLA formed ε-crystals in DMF gels, but α-crystals, which are major crystals in PLLA films without exposing to solvents, in other solvents such as N,N-dimethylacetamide (DMA).

Scanning electron microscopy was carried out for freeze-dried DMF gel and precipitates from DMA solutions. PLLA in the DMF gel showed a fine network structure, while PLLA in the precipitates from DMA solutions had a wrinkled structure.

The structure of PLLA in the DMF gel was also observed by atomic force micrography and polarizing optical micrography, and the microstructures of PLLA and DMF were investigated by infrared spectroscopy.
Since the dawn of the Industrial revolution, carbon dioxide (CO$_2$) emissions from burning fossil fuels have grown exponentially. Increased atmospheric concentrations of CO$_2$, a heat-trapping gas, continue to push the world into a potentially dangerous territory. The ability to directly capture CO$_2$ from flue gas or air has the potential to create a carbon negative process. Carbon capture and storage (CCS) is a potential strategy to reduce CO$_2$ emissions. There are three major approaches for CCS: post-combustion capture, pre-combustion capture and the oxyfuel process. Post-combustion capture is advantageous because existing combustion technologies can be used without radical process modifications. However, Post-combustion capture (PCC) typically requires a huge parasitic load (20-30%) due to the necessity of thermal and/or vacuum techniques to recover the CO$_2$.

**Therefore, the development of new PCC technologies for more effective CO$_2$ capture-release capabilities is vital.**

In this work, we present a polymer platform for the efficient and selective capture and release of CO$_2$ from flue gas. Preliminary results have shown that poly(2-vinyl-4,4-dimethylazlactone), PVDMA, based polymer films modified with MTHP reversibly capture and release CO$_2$ from flue gas type gas mixtures as shown in Figure 1.

![Figure 1. TGA results for CO$_2$ capture-release studies by PVDMA-MTHP polymer at RT.](image_url)
**71 - Highly efficient all-polymer solar cells enabled by control of polymer blend morphology**

*Taeshik Earmme, earmme@u.washington.edu, Ye-Jin Hwang, Samson A Jenekhe. Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, WA 98195-1750, United States*

Organic photovoltaics (OPVs) based on conjugated polymers are promising for low cost, scalable solar energy conversion. Much progress has been made in the field of bulk heterojunction (BHJ) OPVs with polymer/fullerene derivative systems in the last decade, already reporting power conversion efficiencies (PCEs) approaching 10%. In contrast, the performance of polymer/polymer (all-polymer) solar cells comprised of both donor and acceptor polymers and free of fullerenes, has been reported with very low efficiency. Despite their potential advantages including tunable electronic structure, enhanced absorption coefficients, increased photovoltage, superior thermal/mechanical robustness, and facile control of solution viscosity for industrial coating process, the development of highly efficient all-polymer solar cells still remains challenging.

Here we report the control of blend morphology in all-polymer solar cells by casting solvents in order to form nanophase-separated polymer domains in few tens of nanometers length scale. The morphology of thiazolothiazole donor polymer (PSEHTT) and naphthalene-based acceptor polymer (PNDIS-HD) blend was successfully tuned by co-solvent deposition and confirmed by atomic force microscopy (AFM). We show that the domain sizes of the polymers are significantly reduced through using chlorobenzene (CB):1,2-dichlorobenzene (DCB) mixture that led to more than 20% improved photovoltaic performance. Enhanced charge carrier mobilities of the polymer blend tuned via the blend morphology were also confirmed by space-charge-limited current (SCLC) measurements. The best photovoltaic parameter was observed in polymer/polymer solar cells, even exceeding similarly fabricated polymer/fullerene solar cells. These results suggest that control of polymer blend nanomorphology is a promising strategy to achieve high-performance polymer/polymer BHJ solar cells.
72 - Metal particulate containing conformal coatings for anti-corrosion applications

Jason T Wertz¹, jtwertz@us.ibm.com, Jing Zhang¹, Joseph P Kuczynski², Dylan J Boday³. (1) Materials Engineering, International Business Machines (IBM), Poughkeepsie, NY 12601, United States, (2) Materials Engineering, International Business Machines (IBM), Tampa, FL 33607, United States, (3) Materials Engineering, International Business Machines (IBM), Tucson, AZ 85744, United States

Common protection of electronics, from harsh environmental conditions, is through the use of silicone conformal coatings (CCs). It has been found that silicone CCs act as a "sponge", with high levels of sulfur soluble in the coatings, thus expediting component failures in sulfur rich environments. CCs routinely contain silica for rheology controls and improvement of mechanical properties. However, these fillers do not protect the metal conductors from corrosion. Here, we demonstrate the inclusion of silver and copper particulate into CCs to provide corrosion protection in harsh environments. The metal particulate can serve the same function as the silica fillers and could even replace a small fraction of the silica filler in some CCs formulations. Copper and silver particles were selected due to their affinity to react with sulfur, thus preventing the diffusion of the corrosive agent through the CCs.

Electrical testing was performed by coating resistors with the metal particulate containing silicone and tested within a sulfur-rich environment to determine the effectiveness of the coating. Details relating to the preparation, characterization, and application in preventing corrosion will be discussed.
73 - Identification and classification of malodorants in low VOC architectural coatings

James Bohling, jbohling@dow.com, Paul Doll, Michelle Gallagher, David Frattarelli. The Dow Chemical Company, Collegeville, PA 19446, United States

The amount of Volatile Organic Compounds (VOC) found in architectural paints has been reduced from over 400 g/L to often less than 50 or even 5 g/L as the industry has progressed from the solvent borne paints of the 1940's to the waterborne coatings of today. This progress has reduced the amount of solvents released to the atmosphere by hundreds of millions of pounds each year, but has also raised the expectation that the coatings of today will have very low odor. Consumers may correlate low odor with healthier, greener and cleaner, although this association is not always the case. In today's lower VOC paints, malodorants with a very low odor threshold can have a much larger impact on odor than their relative quantity would predict. A range of raw and formulation materials were evaluated through the use of analytical tools such as GC-Olfactory analysis, as well as human odor panels. A number of the malodorants in the headspace of a typical low VOC latex paint have been identified and categorized by potency, functional group and source. These results, combined with an understanding of the human olfactory system, have led to a better understanding of how to develop low odor coatings. Background and results of this study will be discussed.
Aggrecan is the predominant proteoglycan in cartilage extracellular matrix. This high molecular weight polymer ($1 \times 10^6 < M < 3 \times 10^6$) possesses a bottlebrush structure, consisting of an extended protein core, to which many chondroitin sulfate and keratan sulfate side-chains are attached. Aggrecan-hyaluronic acid assemblies, enmeshed in a collagen matrix, govern the resilience of cartilage and its ability to withstand compressive load. The compressive properties of cartilage depend on the density of the charged functionalities of the rigid side-chains. In normal physiological conditions, sodium counter-ions provide the required electroneutrality. Multivalent ions, however, can modify both the local and the long-range structure of the system, as well as its dynamic response. In linear polyelectrolytes, multivalent counterions gradually reduce the effective repulsive forces and ultimately cause collapse and precipitation. Aggrecan in cartilage is exposed to an environment containing both mono- and divalent cations, since mineralization requires calcium ions. We report an investigation into the effects of calcium ions on the structure and dynamics of aggrecan assemblies in solution, over an extended range of length scales using small angle neutron scattering, static and dynamic light scattering, along with macroscopic measurements of the osmotic pressure and osmotic modulus.
Polymer gradient networks (PGN) play crucial role in the development of functional coatings for various biological applications (e.g., tissue engineering). PGN exhibit position-dependent continuous variation of network modulus on a flat solid support. We have developed a novel strategy to generate surface-attached PGN with tunable stiffness by copolymerizing acrylamides with 5% of methacryloyloxybenzophenone (photo-activable) and styrenesulfonylazide (thermally-activable) crosslinkers. The incorporation of thermal and photo crosslinkers allows for complete control over the crosslink density in an orthogonal fashion (i.e., light vs. heat). The effect of crosslink density on wettability and swelling was studied. The tensile modulus (E) and mesh size of swollen networks were determined using modified Flory-Rhenar model. It was found that increasing the crosslink density resulted in stiffer (i.e. high modulus) materials. The results of swelling, mesh size and modulus of the PGN were correlated with protein adsorption on the PGN substrate.

Figure 1: (A) Photographs of poly(N-isopropylacrylamide) gradient networks. (B) Graph shows the film thickness as a function of photo energy dosage (J/cm²) used for photo crosslinking. The film thickness was found to increase with increasing UV light energy.
For more than two decades a great deal of research effort worldwide has been devoted to the development of light-emitting and transport materials for organic light-emitting diode (OLED) devices. Despite the tremendous progress achieved to date, the preparation of highly efficient and long-lived multilayer solution processed OLED devices still has challenges that need to be overcome. Some of the most important issues encountered in this area are thermal and morphological stability, solubility and film-forming ability of materials employed. We will discuss our recent progress in designing polymeric hole transport materials for the use in solution processed OLED devices that combine the high OLED device performance demonstrated by small-molecules with the solution processing advantages offered by polymers.
Cyclic polymers were embedded in crosslinked polymer networks to enable investigations on the properties of the resulting materials. The zwitterionic ring-opening polymerization of 2-isoproxy-1,3,2-dioxaphospholane 2-oxide (iPP) with N-heterocyclic carbenes afforded cyclic poly(phosphotriesters) c-p(iPP) with molecular weights of $M_n = 144$ kDa. These cyclic polymers were entrapped in a poly(hydroxyethylmethacrylate) p(HEMA) hydrogels by carrying out the free-radical polymerization of HEMA in the presence of a dimethacrylate crosslinker and various amounts of cyclic and linear p(iPP). Spectroscopic (FT-IR) and extraction studies revealed that the cyclic p(iPP)s were entrapped in the crosslinked p(HEMA) networks whereas the majority of the linear p(iPP) was extracted from the gels. The resulting hydrogels could be swelled in water to generate novel double network hydrogels.
78 - Redox responsiveness and electroactivity for preparation of smart micelles

Lidia Glavas, lidija@kth.se, Karin Odelius, Ann-Christine Albertsson. Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Triggered drug release has proved to be an interesting route, where the drug release occurs through a disruption of the lipophilic environment of micelles as a result of external stimuli. However, under certain circumstances it may be difficult to apply any type of stimuli. Therefore, we have developed a micelle system that dissociates with time rather than as a response of an external stimulus.

The electroactive and redox responsive aniline pentamer was introduced into the amphiphilic and biodegradable PEG-PLA oligomers in two different oxidation states. Spectroscopic measurements indicated that the aniline pentamer retained its electroactive and redox-properties after the coupling reaction. These measurements also revealed that the aniline pentamer underwent time-dependent oxidation while in solution. The introduction of the aniline pentamer led to a decrease in the critical micelle concentration (CMC) regardless of oxidation state. However, the decrease was significantly larger for the oxidized form than for the reduced form of the polymers.

These results show that the micelle core will oxidize with time in solution and thereby increase the CMC of the polymer. If the micelle solutions are formulated correctly, this increase will lead to dissociation of the micelles and consequently release of any incorporated drugs. This effect could thereby be used as a potent tool for designing dissociation of micelle systems without the need of an external stimulus.
79 - Preparation and evaluation of well-defined di- and triblock copolymers based on poly(2-(dimethylamino)ethyl methacrylate) and poly(ε-caprolactone)

Carl Bruce¹,², cbruce@kth.se, Simon Utse³,², Irakli Javakhishvili³, Torbjörn Pettersson¹,², Linda Fogelström¹,², Anna Carlmark¹,², Søren Hvilshed³, Lars Wågberg¹,², Eva Malmström¹,². (1) Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, School of Chemical Science and Engineering, Stockholm, Sweden, (2) KTH Royal Institute of Technology, BiMaC Innovation, Stockholm, Sweden, (3) Department of Chemical and Biochemical Engineering, Danish Polymer Centre, Technical University of Denmark, Kgs Lyngby, Denmark

In this work, di- and triblock copolymers based on poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(ε-caprolactone) (PCL) have been prepared. The PDMAEMA length was kept constant for both di- and triblock copolymers, while in the diblock copolymers the PCL length was varied in three different lengths, yielding three separate block copolymers. For the triblock copolymers, on the other hand, also the PCL blocks were of the same length yielding one ABA- and one BAB-type block copolymer. In the next step, the PDMAEMA-part was quaternized to yield polyelectrolytes with either one or two charged block(s). In the final step, difference in adsorption behavior onto a negatively charged cellulose surface and subsequent alteration of surface properties was investigated. Overall, the polymers were evaluated in solid state, in solution, in water dispersion, and on cellulose surfaces with techniques including differential scanning calorimetry, size exclusion chromatography, dynamic light scattering and quartz crystal microbalance.

References

Alginate hydrogels formed by cross-linking of alginate salts with metal cations are versatile biomaterials. We report on controlling the process of iron(III) crosslinked alginate hydrogel formation and dissolution by changing oxidation state of iron cations. Cross-linking of alginate by iron cations strongly depends on their oxidation state. We have demonstrated that oxidation of alginate solutions containing iron(II) cations by air produces homogeneous and transparent iron(III) cross-linked alginate hydrogels. Chemical reduction of iron(III) cations in iron(III) cross-linked alginate beads by ascorbate results in their disintegration and subsequent dissolution. Photochemical reduction of iron(III) cations to iron(II) can be done in the presence of carboxylic acids of which alpha-hydroxy carboxylic acids, such as lactic acid, produce the best result. Exposure of iron(III) cross-linked alginate gel containing small amounts of sodium lactate to visible light results in rapid photodegradation of the gel making it soluble in 0.9% saline.

This process allows easily photochemical patterning of the hydrogel making it a biocompatible photoresist. Depth of photochemical patterning can be adjusted by controlling access of alpha-hydroxy carboxylic acids to the hydrogel. The obtained patterned hydrogel can serve as a template for preparation of other ionically cross-linked hydrogel as cross-linked iron(III) cations can be subsequently exchanged to other metal cations.
81 - Fully degradable poly(carbonate) materials in microstereolithography

Ian A Barker¹, Matthew P Ablett³, Hamish T Gilbert³, Simon J Leigh², James A Covington², Judith A Hoyland³, Stephen M Richardson³, Andrew P Dove¹, a.p.dove@warwick.ac.uk. (1) Department of Chemistry, University of Warwick, Coventry, Warwickshire CV4 7AL, United Kingdom, (2) School of Engineering, University of Warwick, Coventry, Warwickshire CV4 7AL, United Kingdom, (3) Institute of Inflammation and Repair, Faculty of Medical and Human Sciences, The University of Manchester, Manchester, Lancashire M13 9PT, United Kingdom

A major limitation to the success of current approaches for the fabrication of precisely-defined 3D tissue engineering scaffolds is the limited range of materials available for application with many commercially available materials being non-degradable. While some studies have reported developments to incorporate degradable polymers within such materials, they typically lack functional handles for orthogonal fabrication/functionalization and display a limited range of degradability profiles. We report the application of an allyl-functional aliphatic poly(carbonate) as the basis of a new resin for 3D microstereolithography. The application of radical thiol-ene chemistry in the presence of a biologically inert photo-inhibiting dye will be presented to demonstrate a range of versatile degradable and potentially renewable materials. Fabricated constructs and hydrogels from this material demonstrated good biological compatibility with cells and are proposed to provide excellent materials for a range of applications.
82 - Conductance bistability in non-conjugated polymers: Optically erased nonvolatile memristors

Christopher F. Huebner\textsuperscript{1}, Mary K. Burdette\textsuperscript{1}, Jamie A. Shetzline\textsuperscript{2}, Stephen E. Creager\textsuperscript{2}, Charles Tonkin\textsuperscript{3}, Stephen H. Foulger\textsuperscript{1}, foulger@clemson.edu. (1) Department of Materials Science, Clemson University, Clemson, SC 29634, United States, (2) Department of Chemistry, Clemson University, Clemson, SC 29634, United States, (3) Sonoco Institute of Packaging Design and Graphics, Clemson University, Clemson, SC 29634, United States

The long-term goal of this line of research is to develop a disruptive printed memory resistor or “memristor” in the form of multifunctional colloidal particles that can be printed into devices using additive manufacturing tools. The central hypothesis is that sub-100 nm particles can be formed from non-conjugated polymers that exhibit inherent path-dependent conductive (PDC) characteristics and printed into memristors. This new memory alters its conductivity based on its electronic history and instead of encoding “0” and “1” as the amount of charges stored in a traditional silicon-based cell, the low and high conductivity condition is interpreted as the OFF and ON states. One of the very appealing aspects of this device is that both information retention and processing could be combined in a single device. Two specific objectives will be presented: (1) the structure/property relationships that underlie resistive switching in non-conjugated polymers with pendant carbazole and oxadiazole moieties can be determined and (2) printable inks can be formulated from these resistive switching polymers and employed in printing equipment to produce colloidally-derived memristors.
Nanofluids are solvent-free viscous liquids composed of suitably surface functionalized nanoparticles. Some few examples are uncharged, but the majority of examples reported to date may be viewed as supramolecular ionic liquids. Applications in producing new materials include magnetic fluids and novel resins. Such nanofluids may be viewed as 100% concentrated dispersions (all nanoparticles – no solvent). Previously reported nanofluids have been derived by surface modifying core nanoparticles to produce a shell or corona that induces viscous liquid behavior with apparently classical glass transition and melting transitions. These nanofluid nanoparticles may be synthesized as bulk condensation products, and a recent example is illustrated in the graphical abstract. Such dispersions are being applied as carriers for metal catalysts in formulating advanced catalytic monoliths, investigated as gene transfection carriers, and as new classes of ferrofluids, quantum dot carriers, and as supramolecular reaction media. When core-free or core-based nanofluids are also surface functionalized with reactive groups, they represent a new class of supramolecular monomers and reactive inks. Performance features may be designed into the core, and the supramolecular corona serves as binder and provides tethering functionality.
84 - Digital fabrication of an amperometric glucose sensor

Xiaosong Du, Joshua Motley, Gregory S. Herman, greg.herman@oregonstate.edu. School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States

Type 1 diabetes is a pancreatic disease where individuals are not able to produce insulin to control blood glucose levels. A promising approach to control blood sugar for type 1 diabetics is an artificial endocrine pancreas, which continuously reads blood glucose concentrations and automatically controls the insulin/glucagon injections. In this presentation, we will discuss the digital fabrication of a novel flexible amperometric glucose sensor. Additive manufacturing approaches, including electrohydrodynamic (e-jet) printing and electroplating, are being evaluated for rapid optimization of the sensor, improved uniformity, and ultimately reductions in manufacturing costs. The sensor incorporates a plated Ag/AgCl reference electrode and plated platinum indicating electrodes. E-jet printing is used for the deposition and patterning of the glucose oxidase (GOx) enzyme layer and the polymeric permselective membrane, and provides a precise method to control both the thickness and shape of these layers. Details on optimization of the GOx enzyme and polymeric permselective membrane inks and e-jet printed patterns will be discussed, along with electrochemical characterization of the sensors.
High performance thermoplastics are perhaps the most promising candidates for the adoption of engineering resins into high demanding applications. Hence, the fundamental understanding of their structure and its effect on their expected performance in critical environments is crucial for the development of new technologies and complex processing techniques.

This study describes the morphology of poly(etherketoneketone) (PEKK) resins, focusing on their polymorphic behavior under various conditions traditionally observed in Selective Laser Sintering and other additive manufacturing processes. Precise control over these morphological changes is critical for the successful introduction of PEKK and other high-performance engineering resins in applications such as aerospace, medical and oil and gas exploration.
Additive Manufacturing is rapidly changing how we think about constructing useful products. The area of polymer science and materials engineering is ripe with potential for developing new materials that can be printed into a wide array of shapes and sizes, with high precision and functionality. In collaboration with LLNL, the Kansas City Plant is developing materials and techniques to utilize Direct Ink Writing (DIW), a 3D printing process. Of critical importance is matching the flow characteristics of the material with the desired mechanical properties. In order to produce materials with more uniform properties, we have evaluated the differences between volumetric and pressure-driven flow of commercially-available silicone systems. Additionally, we are in the early stages of compounding boron-containing cage compounds called carboranes into silicone-based materials. We have previously shown that carboranes can selectively plasticize one component (polyurethane) while reinforcing another component (polybutadiene) of polybutadiene-polyurethane multiblock copolymers without imparting crystallinity. This seminar will focus on our efforts to develop DIW including progression of our process, materials used and incorporated into printed products, and the (thermo)mechanical properties of the final parts.
Manufacturing in the US is on the rebound. It is now sexy again to be known as a manufacturing community. The Administration is making this a key focus for projects and grants to bolster, enhance and promote America’s Manufacturing base. This does not mean that the flood gates will now swing the other way. Companies in the US have a distinct advantage when it comes to supply chain and logistics for locally produced components desired by OEMs. Higher quality, on time delivery, short lead times, and flexibility are all attributes that manufacturers desire. Manufacturers typically pay higher wages than other companies and the multiplier for manufacturing is typically 3x to 5x of that for other companies. This means that for every job in manufacturing there are 3 to 5 other jobs created. We will discuss issues that are affecting US and in particular CA companies.
Microbial polyhydroxyalkanoates (PHA) have been developed as bioplastics for the past many years. Commercial PHA are normally poly-3-hydroxybutyrate (PHB), copolyesters of 3-hydroxybutyrate and 3-hydroxyhexanoate (PHBHHx), copolyesters of 3-hydroxybutyrate and 4-hydroxybutyrate (P3HB4HB), as well as copolyesters of 3-hydroxybutyrate and 3-hydroxyvalerate (PHBV). Recently, it becomes possible to produce a series of novel PHA including homopolymers, random copolymers and block copolymers. For example, poly-3-hydroxypropionate (P3HP), poly-4-hydroxybutyrate (P4HB), poly-3-hydroxydecanoate (P3HD) and poly-3-hydroxydodecanoate (P3HDD) et al. Random copolymers containing defined monomer compositions can also be microbially produced. More importantly, block copolymerization containing various block such as diblock copolymers of PHB-b-P4HB, PHB-b-PHHx, P3HP-b-P4HB, PHBHHx-b-PHDD et al have been produced. They remarkably increased the diversity of PHA structures and properties. By manipulating the block compositions, the polymer properties can be easily controlled. Now, PHA industry will be entering a functional polymer era, which allows PHA competitiveness not by the low cost but by its functionality. We will soon experience ultra-strong, shape memory, gas selective permeability and other environmentally responsive PHA.
Bacterial polyhydroxyalkanoates (PHAs) are attractive material as a bio-based alternative to petroleum-derived thermoplastics. We developed a microbial factory expressing engineered PHA synthetic enzymes that synthesizes a variety of novel biomaterials with superior properties. The finding of an engineered PHA synthase with lactate (LA)-polymerizing activity (Lactate-Polymerizing Enzyme, LPE) was a major breakthrough to achieve the microbial production of unusual polymers, particularly LA-based polymers [1]. The chemically synthesized LA-based polymers, such as poly(lactic acid) (PLA) are most widespread bio-based polymers because of their superior transparency and processability. Unlike the most of current chemical processes for PLA production including the LA fermentation and chemical polymerization of LA, our microbial processes produce LA-based polymers from renewable resources via one-pot fermentation. In addition, the enzymatic polymer synthesis under mild conditions allowed us to obtain extremely high enantio-pure polymers (nearly 100% ee) [2]. Further interesting feature is that the microbial factory synthesizes copolymers consisting of LA and bacterial PHA constituents, as a typical example, P(LA-co-3-hydroxybutyrate (3HB)). We have also synthesized copolymers containing the other monomers with varied side-chain-lengths of 3-hydroxyalkanoates (3HAs) using an evolved LPE [3]. In this talk, topics for the engineering approaches to synthesize new biopolymers will be introduced [4]. Especially, it should be noted that the unusual substrate specificity of LPE was found to be applicable to the synthesis of even other 2-hydroxyalkanoate (2HA) monomers; glycolate and 2-hydroxybutyrate [5]. This finding further expands the structural diversity in microbial polyesters. Xylose utilization was also an effective for production of LA-bases polymers [6].

Acknowledgement The researches were financially supported by CREST project (5100270) of JST.

References


5) K. Matsumoto et al., Biomacromolecules, 2013, 14(6), 1913-1918.

Biocatalytic oxidation and amination reactions are great tools for the highly selective functionalization of cheap and simple starting materials, such as alkanes.

Recently we developed a technology platform that allows the one-pot synthesis of chemical intermediates, such as alkanols and acids, building blocks for polymers, as well as more complex performance chemicals from alkanes and fatty acids.
91 - Engineering static and dynamic tuning of malonyl-CoA derived metabolite biosynthesis in microorganisms

Mattheos Koffas, mkoffas@gmail.com, Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

Our research goal is to utilize the richness, versatility but also simplicity of microbial organisms in order to make them ideally suited to convert cheap, renewable resources into high-value and commodity chemicals.

For the purpose of reprogramming the cellular network in order to achieve optimal phenotypes supporting high-yield production, we have developed an in silico model of the genome-wide metabolism of Escherichia coli. Through the application of Metabolic Flux Analysis, we can predict genetic modifications such as deletions and gene expression attenuations that lead to dramatic increases in production levels. Such Systems Biology approaches, in combination with traditional genetic engineering have resulted in robust production levels that can result in the commercially viable processes for the synthesis of important molecules, in particular ones that derive from malonyl-CoA. We also report the engineering of both positive and negative feedback controls for dynamic tuning of metabolic flux in E. coli. Specifically, we have identified a dual transcriptional regulator that can act either as an activator or a repressor for two different promoters. The level of activation or repression is dependent on the level of intracellular malonyl-CoA. As a proof of concept, we demonstrated that the expression of two reporter proteins can be exclusively switched between the on and off state. By engineering this synthetic malonyl-CoA controller, we envision that both the malonyl-CoA source pathway and the malonyl-CoA sink pathway can be dynamically modulated so that carbon flux can be efficiently redirected to synthesize our target compounds. Implementation of this dynamic control will maintain the intracellular malonyl-CoA at the optimal level and improve both the productivity and yield of value-added metabolites in E. coli.
Molecular evolutionary engineering is a method used to harness the power of natural selection to evolve proteins or RNA with desirable properties not found in nature. The possibility of evolving a commonly existing biomolecule into a variety of functional biomolecules has now been realized in the form of aptamers through the development of in vitro selection. In addition to their high affinity and high specificity for the desired targets, aptamers are easily synthesized chemically and can be modified for downstream applications.

Although aptamers were originally selected from a library containing only natural components, the past decade has seen a wealth of new aptamers selected from libraries containing unnatural components to provide new aptamer functions artificially. Here I highlight this transition (the shift between selection from natural components and selection from unnatural components) and the applications of the selected aptamers.

The first is development of a peptide that binds and emits fluorescence in response to the conformational change of target protein. The second is preparation of photo-responsive peptide that binds to and is released from target molecule in response to photo-irradiation. The third is the enhancement of inhibitory activity of small molecule against target enzyme by increasing the extent of interaction between the inhibitor and the target by coupling a peptide aptamer to small molecule. For each selection, a fluorescent molecule which is sensitive to environmental conditions, a photo-isomerizable molecule azobenzene, or an inhibitor molecule was attached to tRNA through amino acid and bioorthogonal evolution was performed.
93 - Yellow fluorescent protein senses and reports mechanical damage in fiber-reinforced polymer composites

Nico Bruns¹, nico.bruns@unifr.ch, Samuel Lörcher², Katarzyna Makyla²,³, Christoph Müller², Thomas Winkler², Claudiane Ouellet-Plamondon⁴, Michaela Eder⁵, Ingo Burgert⁴. (1) Adolphe Merkle Institute, University of Fribourg, Marly, Fribourg 1723, Switzerland, (2) Department of Chemistry, University of Basel, Basel, Basel 4056, Switzerland, (3) Department of General Chemistry, Jagiellonian University, Kraków, Poland, (4) Institute for Building Materials, ETH Zürich, Zurich, Zurich 8093, Switzerland, (5) Department of Biomaterials, Max-Planck-Institute of Colloids and Interfaces, Potsdam, Germany

Mechanophores are molecules that change their color or fluorescence in response to mechanical forces. When incorporated in polymeric materials, they become useful probes that enable the detection of micron scale-damage or render stress distributions visual. The fluorescence of fluorescent proteins is linked to their native structure, which can be distorted by mechanical forces. Enhanced yellow fluorescent protein (eYFP) loses its fluorescence when subjected to macroscopic forces. This protein was implemented as a mechanophore in fiber-reinforced composites by using it as a force-responsive layer at the interface between epoxy resin and glass- or carbon-fibers. The biomolecule reports barely visible impact damage, such as the fracture of fibers and the debonding of resin from fibers, by loss of fluorescence. The resulting self-reporting materials could find application as a safety feature in load-bearing components to prevent catastrophic material failure. Moreover, fluorescent proteins could be used as analytical tool to investigate damage propagation in materials under load.
Cyanophycin is a non-ribosomally synthesized polypeptide that is naturally found in cyanobacteria, where it is used as a nitrogen storage protein. While the material has been widely investigated in order to improve its biosynthesis and it is currently attractive for use in nutraceuticals and as a source of polyaspartic acid for surfactants, its materials properties have not been widely explored. Here, we explore two important material properties of cyanophycin. First, we study the solution properties of cyanophycin, identifying an upper critical solution temperature in the material that is a function of amino acid composition, salinity, and pH. We show that this UCST behavior is due to ion pairing effects which are present in similar synthetic zwitterionic polymers and vary depending upon the amino acid composition of the cyanophycin. The presence of UCST behavior significantly limits water uptake by cyanophycin and facilitates its easy isolation from cellular systems. Second, we investigate the structural, thermal, and mechanical properties of cyanophycin. The material is found to be brittle with a modulus of about 1.4 GPa at room temperature, consistent with other unentangled polymer systems. Recombinant cyanophycin has a molar mass range of 15 to 30 kDa by protein gel electrophoresis, with a bimodal distribution consisting of a lysine-rich and an arginine-rich fraction. The mechanical properties are consistent with those typically observed for lower molecular weight polymers. Cyanophycin is thermally stable in air up to 230 °C by TGA, and shows no reversible glass transition or melting transition below this temperature. However, it does show a large, irreversible endothermic peak upon heating, indicative of annealing from a kinetically trapped structure into a more equilibrium structure. X-ray scattering is applied to understand the protein structure. Cyanophycin can also be readily derivitized using a variety of processes such as acylation in order to change its solubility and mechanical properties. Based on these results, we are exploring cyanophycin as a potential rigid block in renewable elastomers.
Current state of the art solid propellant binders are comprised of hydroxyl-terminated polybutadiene (HTPB) that are cross-linked by diisocyanates. However, isocyanates are known to cause respiratory irritation, occupational asthma and some evidence of carcinogenic effects in animals. Furthermore, the decreasing permissible exposure limits currently being considered by OSHA highlight the need for new propellant binder systems in the future that do not rely on isocyanate cure chemistry. Ideally, these new propellant binders will use cross-linking mechanisms already found in nature that are unlikely to introduce new environmental or safety concerns. One such system is nucleobase binding that holds together DNA strands in plant and animal cells. The synthesis and characterization of polybutadiene containing nucleobase pairs capable of cross-linking by complementary base binding will be presented.

![Polymer diagram]
Supramolecular chemistry has evolved into a powerful strategy for the creation of new materials. Metal-ligand bonds exhibit both strong and directional interactions in which the selection of metal ion and ligand can guide the strength of the association. To this end, we have established a program to incorporate metal binding ligands into polymers and copolymers to create new materials with tunable properties. A focus on blocky architectures and networks will be discussed.
Metal-ligand coordination interactions are widely employed for the self-assembly of supramolecular architectures. Depending on the building block(s) and metal ion(s) used, this process is kinetically controlled, leading irreversibly to several strongly bound products; or it proceeds through thermodynamically controlled equilibria favoring a specific, albeit more weakly bound product that may be difficult to purify. In both cases, electrospray ionization mass spectrometry (ESI-MS) offers an effective method for the determination of the compositional heterogeneity and structure(s) of the resulting assemblies. As a soft ionization method, ESI minimizes fragmentation; meanwhile, as a dispersive method, MS permits direct analysis of the stoichiometries of individual product components without prior separation. With complex product mixtures, further resolution is achieved by combining MS with ion mobility (IM) separation of the ions formed by ESI. In the IM dimension, assemblies are dispersed by charge and size/shape, which enables the deconvolution of overlapping charge states and the separation of isomeric complexes with distinct architectures (figure). Additional analytical information can be obtained by interfacing IM-MS with gradient tandem mass spectrometry (gMS²), in which the separated species are energetically excited to dissociate; the energies causing complete fragmentation reflect relative complex stabilities and help to distinguish isomers and to assess the assemblies' applicability as thermal sensors. These analytical capabilities will be demonstrated with applications to a variety of metallo-supramolecular polymers.
Developments of polymers that are capable of spontaneous repairs upon mechanical damage have generated significant scientific challenges and technological interests. If designed properly, self-healing due to reversible reformation of chemical bonds in metal-containing polymers offers significant advantages. These studies focused on the development of UV repairable polyethylenimine-copper sulfate (C₂H₅N-Cu) supramolecular polymer networks that exhibit high efficiency of converting electromagnetic radiation to chemical energy with negligible temperature changes (< 5 °C), thus minimizing network decomposition, yet allowing repetitive damage-repair cycles. Taking this step further, combining polyurethane and polydimethylsiloxane networks with the coordination chemistry by utilizing CuCl₂ and reformation of Si-O covalent bonds have led to self-repairing networks with the ability of forming coordination bonds and covalent Si-O bonds. These studies show that combining reversible covalent bonding and coordination chemistry offer unique self-repairing polymer networks.
99 - Metallosupramolecular polymers based on semisynthetic chlorophyll derivatives

Frank Wuerthner, wuerthner@chemie.uni-wuerzburg.de, Sanchita Sengupta, Charlotte Grzeszkiewicz. Center for Nanosystems Chemistry, University of Wuerzburg, Wuerzburg, Bavaria 97074, Germany

The spatial arrangement of chlorophyll and bacteriochlorophyll dyes enables pivotal functions in the light-harvesting systems of purple and green bacteria which contain a large number of these chromophores organized in cyclic arrays or tubular architectures by non-covalent interactions. During the last years, we have intensively investigated the self-assembly behavior of semisynthetic zinc chlorin dyes into metallosupramolecular polymers which is directed by oxygen-zinc(II) coordination, pi-pi-stacking and in some cases by additional hydrogen-bonding interactions. The focus of this contribution will be devoted on our most recent studies on the self-assembly mechanism and the elucidation of the charge transport properties of self-assembled zinc chlorins.
100 - Stimulus triggered self-assembly in cholesterol-based terpyridyl/bipyridyl platinum complexes

**Tao Yi**, yitao@fudan.edu.cn, Keyin Liu, Yueyuan Mao. Department of Chemistry, Fudan University, Shanghai, China

Organometallic terpyridyl/bipyridyl platinum complexes containing hydrophobic cholesterol, whose self-assemblies can be controlled by sonication and the polarity of solvent are synthesized and characterized. The complex with bulky tert-butyl terpyridyl groups (1a) can form stable gel in several kinds of solvent, such as alcohol, ethyl acetate and toluene with ultrasound irradiation. These sonogels display different color and enhanced photoluminescence comparing with their related solution and precipitate. The morphology as well as the surface wettability of 1a can be also reversibly adjusted by sonication and heating. Mechanism of molecular self-assemble pattern indicates that sonication may change the molecular conformation of 1a and promote the ionic dipolar interaction and hydrophobic interactions for gelation, and thus switch the optical properties of the complex in the aggregation state.

As cholesterol is one of the most effective hydrophobic chiral function groups, three alkynylplatinum(II) bipyridyl complexes in which two cholesterol groups are combined with bipyridyl group via alkyl chains and amide with difference length of ether chains in the para-position of 1-phenylethyne are designed. All the three complexes (2a-2c) can self-assemble to gels in DMSO while the morphology of 2a shows well defined right-hand helical structure. However, 2c forms perfect regular left-hand helical structure in water/ethanol with a proper ratio and reverse the chirality as the ratio of water increases, which indicates that water can act as a trigger to control the self-assembly of the chiral structures.
Combining a self-complementary zwitterion with metal-ligand binding sites (e.g. terpyridines, catechols, bipyridine) self-assembling molecules with two orthogonal interactions are obtained. Depending on the conditions (e.g. pH, presence/absence of metal ions) different types of self-assembled aggregates are formed such as ion-paired dimers, metal-complexes, linear or three-dimensional polymers. Aggregation can also lead to gel formation in polar solvents. The gels respond to different stimuli such as pH, temperature or competing ligands. One such example is shown in the following figure.
102 - Design of self-oscillating polymer gels coupled with supramolecular chemistry

Ryo Yoshida, ryo@cross.t.u-tokyo.ac.jp, Department of Materials Engineering, School of Engineering, The University of Tokyo, Tokyo, Japan

Herein, we summarize recent developments of self-oscillating polymeric materials based on the concepts of supramolecular chemistry, where aggregates of molecular building blocks with non-covalent bonds evolve the temporal or spatiotemporal structure. By utilizing the rhythmic oscillation of the association/dissociation of molecular aggregates coupled with the redox oscillation by the BZ reaction, novel soft materials that express a similar function as those of living matter, e.g., autonomous swelling-deswelling oscillation, viscosity oscillation, periodical high-ordered structure changes will be achieved. Further, from the viewpoint of materials science, our recent approach to prepare self-oscillating materials that operate long-term under mild conditions will be introduced.
103 - Stimuli-responsive metalo-supramolecular polymer films

Masayoshi Higuchi, HIGUCHI.Masayoshi@nims.go.jp, Electronic Functional Materials Group, National Institute for Materials Science, Tsukuba, Japan and CREST, JST, Japan

Metallo-supramolecular polymers, which are synthesized by the 1:1 complexation of metal ions and ditopic ligands, are a new type of polymers and unique electronic and optical properties, which are difficult to be achieved in conventional organic polymers, are expected based on the intramolecular metal-ligand or metal-metal interaction through the polymer chain. In addition, electrochemical redox of metal ions in the metallo-supramolecular polymers is anticipated to bring reversibly electrochemical control of the unique properties. Here described are (1) synthesis of Fe(II)-, Ru(II)-, Cu(II)-, Ni(II)- and Eu(III)-based metallo-supramolecular polymers and Fe/Ru- and Eu/Fe-based heterometallo-supramolecular polymers, (2) their unique properties of electrochromism, multi-colour electrochromism, ionic conductivity, humidity sensing, vapoluminescence and electrochemical emission switching and (3) the solid-state device fabrication.
The binding strength of metal-complexes can be varied very easily by changing the metal-ligand combination. Therefore, metal complexes could be utilized for the design of self-healing polymers. For this purpose, terpyridine moieties were incorporated into the side chain of a linear polymer (i.e. polymetharylates, polybutadienes). The following crosslinking reaction leads to metallopolymer networks which feature self-healing properties. Furthermore, different parameters (e.g., metal ion, crosslinking density, counter ion) were varied in order to understand the basic self-healing mechanism. Thus, we used different cadmium salts for the crosslinking reaction in order to analyze the molecular structure. Furthermore, the polymer backbone was varied from methacrylic polymer to a polybutadiene. The different obtained substructures have a great influence on the self-healing performance of the metallopolymer networks.\(^{[1]}\)

105 - Assembling metal complexes for tuning their photophysical properties

**Luisa De Cola**, decola@unistra.fr, Matteo Mauro, Alessandro Aliprandi, Dedy Septiadi. ISIS, Universite de Strasbourg, Strasbourg, France

Self-assembly of metal complexes leading to soft and crystalline structures able to possess different properties in relation with the packing of their components is an emerging field with great potential for the development of new materials, sensors, biolabels.... The talk will illustrate some of the recent results on soft structures based on metal complexes able to aggregate in fibers, gels and soft mechanochromic materials [1]. The emission of the compounds can be tuned by an appropriate choice of the coordinated ligands as well as of their aggregation in different structures. The formation of soft assemblies allows the tuning of the emission color, by pressure and temperature leading to a new class of materials possessing reversible properties. The versatility of the systems allowed us to have water soluble complexes that can form luminescent assemblies in living cells suggestig a possible use as a new tool for in vitro imaging [2].


106 - Smart poly(2-oxazoline) particles

Christina Diehl, Niels ten Brummelhuis, Christian Secker, Helmut Schlaad, schlaad@mpikg.mpg.de. Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Poly(2-alkyl-2-oxazoline)s can undergo crystallization in phase-separated aqueous solutions to produce hierarchically structured microspheres built of nanofibers or lamellae. Crystallization occurs for polymer-solvent systems showing LCST behavior, e.g. poly(2-isopropyl-2-oxazoline) (PIPOX)/water, or UCST behavior, e.g. poly(2-isobutyl-2-oxazoline) (PIBOX)/ethanol-water 55:45 w/w. Annealing of PIPOX solutions at 60 °C or PIBOX solutions at room temperature for 24+ hours yields crystalline materials with melting points of ~200 °C or 140 °C, respectively. Morphology and size of the particles can be controlled by the annealing temperature and the presence of co-solvent or surfactant. Kinetics/mechanism of the crystallization process in solution and possible applications of the materials will be discussed.

Core-shell micelles of poly(2-(3-butyl)-2-oxazoline)-block-poly(2-ethyl-2-oxazoline) are converted into functional polymer particles (star polymers) by simultaneous modification/crosslinking with thiols in water. Samples with core-confined ionic groups exhibit stimuli-responsive properties and are sensitive to changes in temperature, pH, ionic strength, and type of salt. The salt-induced shifts of the cloud point temperatures are found to correlate with the Hofmeister series.

Monday, August 11, 2014 08:00 AM
Poly(2-Oxazoline)s and Polypeptoids (08:00 AM - 11:50 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
Amphiphilic copolymers based on poly(2-methyl-2-oxazoline) (POXZ) were prepared to give two types of architectures: block copolymers and grafted copolymers (Figure 1). Poly(2-methyl-2-oxazoline) is a hydrophilic and non-ionic polymer showing interesting properties such as biocompatibility and lack of toxicity. The polymer chosen for the hydrophobic block is a biodegradable polyester: poly(D,L-lactide) (PLA). The synthesis of the amphiphilic copolymers was made by combination of cationic ring opening polymerization (CROP) and click chemistry (Huisgen 1,3-dipolar cycloaddition reaction).

A new monomer 2-(5-azidopentyl)-2-oxazoline bearing an azido group was synthesized. The cationic ring-opening copolymerization of this monomer with 2-methyl-2-oxazoline resulted in a well-defined linear polymer backbone with pendant azido groups that could be used for the cycloaddition reaction. Self-association of these amphiphilic copolymers could lead directly to core-shell nanoparticles, made of a hydrophobic core and a hydrophilic POXZ shell. The synthesis of copolymers with different self-association properties was developed by varying the molecular weight of polymer, the length of each block in order to modify the hydrophilic/hydrophobic balance or the graft density.
Amphiphilic block copolymers containing hydrophilic polyoxazoline blocks is very useful for biomedical applications. Macroinitiation is the common method of synthesizing these polymers. However, macroinitiation results in low yields and block lengths are difficult to control. We have recently shown a modular method of synthesizing well defined triblock copolymers consisting of polyoxazoline-polysiloxane-polyoxazoline using copper catalyzed click chemistry. However, the stealth property of these polymers diminishes when synthesized via copper catalyzed click. We have recently investigated copper free methods for synthesizing these polymers and these polymers show that polyoxazoline is a viable alternative to PEG for drug-delivery.
109 - Hydrogen bonded polymeric multilayer films assembled below and above the cloud point temperature

Bruno G. De Geest, br.degeest@ugent.be, Richard Hoogenboom. Ghent University, Ghent, Belgium

Polymeric multilayer thin films, assembled via layer-by-layer (LbL) deposition of interacting species, have since their advent in the early nineties attracted major attention by scientist active in different fields of research. Whereas initially LbL assembly involved the use of oppositely charged polyelectrolytes there is a steady interest in hydrogen-bonded multilayers. Hydrogen bonded multilayer films based on tannic acid (TA), a naturally occurring polyphenol, are stable over a wide pH range (i.e. pH 2-11), while the multitude of phenolic groups on the TA form strong complexes with neutral polymers bearing ether, ester or amide bonds. Poly(2-alkyl-2-oxazolines) are an attractive class of neutral hydrophilic polymers that are highly biocompatible and that can be engineered with tailored temperature-responsive properties by varying the nature of the alkyl side chains. Here we report on multilayer thin film formation based on hydrogen bonding between TA and Poly(n-propyl-2-oxazoline). In particular we demonstrate that both below its TCP of 25 °C, with the polymer chains being in extended state, and above the TCP, with the polymer chains being in collapsed aggregated state, multilayer formation with TA is possible. Such multilayers could find interesting applications for the design of functional coatings.
110 - High molecular weight uniform poly(2-ethyl-2-oxazoline)

Bryn Monnery, bryn.monnery@ugent.be, Richard Hoogenboom. Supramolecular Chemistry Group, Department of Organic Chemistry, Ghent University, Ghent, Belgium

The polymerisation of 2-oxazolines is well established, but it does not usually give narrow unimodal molecular weight distributions, especially not when targeting high molar mass polymers. The distribution is typically trimodal. This is usually attributed to transfer to monomer via β-elimination.\(^1\) Attempts to produce narrow unimodal polymers are invariably limited to polymers with low degree of polymerization (DP).\(^2\)

In this contribution we report our endeavours to improve the control over the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline and how we have been able to synthesise near uniform (\(\bar{D} < 1.10\)) poly(2-ethyl-2-oxazoline) with a degree of polymerization > 500 and a reactive endgroups. The size exclusion chromatogram of such a polymers is shown in the Figure.


Studies of the self-assembly in water of poly(2-isopropyl-2-oxazolines) bearing perfluorodecyl end-groups by light scattering and $^{19}$F, $^1$H, and $^{13}$C NMR spectroscopy

Na Xue, na.xue@umontreal.ca, Xing-Ping Qiu, Francoise Winnik, Julian Zhu. Department of Chemistry, University of Montreal, Montreal, Quebec H3C3J7, Canada

Telechelic perfluorodecyl poly(2-isopropyl-2-oxazolines) (FPIPOZ) self-assemble in cold water in the form of flower micelles ($R_H$ 9.0 nm, $R_g$ 10.0nm) with a perfluorinated core and a PIPOZ corona. Information on the core mobility was obtained by monitoring the $^{19}$F NMR signal intensities, chemical shifts and the $^{19}$F $T_1$ and $T_2$ relaxation times. Their solutions undergo a phase transition when heated above their cloud point temperature. The mobility of the PIPOZ main chain and side groups was investigated by NMR relaxation techniques for $D_2O$ solutions of PIPOZ and FPIPOZ of different concentrations. The $^1$H and $^{13}$C $T_1$ and $T_2$ relaxation times of PIPOZ and FPIPOZ were measured as a function of temperature.

The temperature dependence of $T_1$ values for the main chain methylene protons was completely opposite to that of the side chain methyl protons, which indicates that the side chain methyl groups motion slows down whereas the main chain motion speeds up upon increasing temperature. Larger $^{13}$C $T_2$ values for the main chain carbons and side chain methyl carbons of PIPOZ, compared to FPIPOZ suggest that the motion of the main chain is restricted in the micelles formed by FPIPOZ.
Many of current research strategies in polymer science are inspired by the functioning of living systems in creating innovative technologies for medicine, industry and various other fields. In this view, the potential of poly(2-alkyl-2-oxazoline)s (PAOx) - that can be regarded as pseudo-polypeptides - has been explored in a wide array of applications, ranging from biomedical applications via additives for (paper) coatings to solid poly-electrolytes for Li-ion batteries. However, up to now bulk material applications of PAOx have remained largely unexplored, mainly due to limited synthetic accessibility of high molar mass PAOx, resulting in poor mechanical properties. This research shows that suitable side-chain functionalization leads to PAOx that exhibit interesting properties for use in high performance bulk materials, i.e. high melting temperatures, high thermal stability and solvent resistance.

To this end, a range of poly(2-cycloalkyl-2-oxazoline)s were synthesized and their physico-chemical properties were investigated (Figure 1).

Figure 1. Cationic ring-opening polymerization of poly(2-oxazoline)s (top) and 2-cycloalkyl-2-oxazolines used in this study (bottom).

Firstly, the kinetics of the different homopolymerizations of the 2-cycloalkyl-2-oxazolines shown in Figure 1 was studied, proving that the polymerizations proceed in both a living and controlled manner. Moreover, the kinetics revealed substituent dependence of the polymerization rate constant (k_p), with an unexpectedly high k_p value for 2-cyclopropyl-2-oxazoline ascribed to a higher monomer nucleophilicity by molecular modeling. Poly(2-cyclobutyl-2-oxazoline), poly(2-cyclopentyl-2-oxazoline) and poly(2-cyclohexyl-2-oxazoline) showed thermal stability up to 350 °C and melting temperatures between 250 °C – 330 °C. The melting temperature could be further fine-tuned by copolymerization of 2-cyclopentyl-2-oxazoline with 2-ethyl-2-oxazoline or 2-butyl-2-oxazoline with varying monomer ratios.

References


113 - Poly(2-alkyl-2-oxazoline)s: Bulk crystallization and solution self-assembly

A. Levent Demirel, ldemirel@ku.edu.tr, Chemistry, Koç University, Istanbul, Turkey

The physicochemical properties of poly(2-alkyl-2-oxazoline)s (PAOX) depend on the alkyl side chain length. As the alkyl side chain length decreases, LCST of aqueous solutions increases, glass transition temperature \( T_g \) increases and bulk crystallization is significantly hindered. Among PAOX having shorter side chains, poly(2-ethyl-2-oxazoline) (PEOX) is the only member whose bulk crystallization was previously not reported. We have shown that self-assembled crystalline PEOX fibers form (Fig. 1) when aqueous PEOX solutions are kept above the cloud point temperature \( T_c \) for long times (days to weeks).

In order to understand the role of alkyl side chain length in PAOX crystallization and the factors affecting the formation of crystalline fibers in aqueous solutions, we have investigated PAOX crystallization in bulk and the self-assembly in aqueous solutions as a function of alkyl chain length, temperature, molecular weight and ionic strength. We identified different crystallization behavior depending on the length of the alkyl side chain. The self-assembly into water insoluble fibers above \( T_c \), a slow crystallization process, was enhanced by the addition of various sodium salts. The specific anion effects on \( T_c \) of aqueous PEOX solutions will be presented and the contribution of different mechanisms to phase separation at \( T_c \) and self-assembly will be discussed.

Monday, August 11, 2014 11:20 AM
Poly(2-Oxazoline)s and Polypeptoids (08:00 AM - 11:50 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
A facile approach to unique 3-D, patterned polymer brushes based on visible-light mediated controlled radical polymerization is reported. The temporal and spatial control enabled by light as an external stimulus allows for the patterning of polymer brushes from a uniform initiating layer using a simple photomask. Furthermore, gradient polymer brushes, patterned block copolymers and complex 3-D structures can be obtained by modulating light intensity.
Every chemical reaction occurs only when a molecule is provided the necessary activation energy. When activation energy is provided in the form of light then the reaction is known as photochemical reaction. The spectrum of solar light is mostly spread across the visible and near infrared ranges with a small part in the near ultraviolet. Apart from that, handling visible light compare to UV light is very easy and safe and it can be potentially applied on an industrial scale. The use of light in controlled radical polymerization also brings several distinct advantages, including temporal and spatial control over chain growth, easy preparation of well-defined polymers at room temperature and minimization of possible higher temperature side reactions. Although extensive efforts have been made in this area, it is still crucial to explore an effective light-induced controlled radical polymerization method in synthetic polymer chemistry. The commonly used light-induced CRP methods are adapted from thermal counterparts including iniferter, nitroxide-mediated radical polymerization, atom transfer radical polymerization (ATRP), cobalt-mediated radical polymerization, organotellurium-mediated radical polymerization and reversible addition-fragmentation chain transfer polymerization etc. Among them, light-induced ATRP has been studied extensively because of the broad range of monomers and mild polymerization conditions. The light-induced ATRP is based on photoredox reactions of copper catalysts under various radiation sources with or without various photoinitiators. Many UV and visible light free radical photoinitiators were reported to be powerful promoters for light-induced ATRP. The infinitely available, easily handled and environmentally friendly visible light makes it attractive for polymer chemists to promote it for CRP methods. Recently, visible light-induced ATRP of vinyl monomers using type I and type II photoinitiators in the presence of copper(II) catalyst, iridium based photoredox catalyst, dimanganese decacarbonyl/copper(II) catalyst and mesoporous graphitic carbon nitride/copper(II) catalyst systems have been developed. In this presentation, the synthetic possibilities for visible-light induced ATRPs and their mechanistic insights are discussed.

Figure 1. General mechanism for visible light induced ATRP


(2) Tasdelen, M. A.; Uygun, M.; Yagci, Y. Macromolecular Rapid Communications 2011, 32, 58.


A new alkoxyamine based on a highly thermally stable nitroxide is used for the controlled polymerization of styrene at temperatures up to 200 °C. High monomer conversions are reached in a few minutes with a linear increase in polymer chain-length with conversion, a final polydispersity index (PDI) of ~1.2 (Figure 1), and successful chain-extension of the resulting material. The alkoxyamine concentration was altered to target various chain lengths, with autopolymerization dictating the polymerization rate regardless of alkoxyamine concentration. Controlled polymerization of acrylate and methacrylate monomers under similar reaction conditions was successful, with the addition of 5-10 mol% styrene leading to improved control. The new material opens the possibility to increase the range of specialty products made for applications in coatings, inks, overprint varnishes and adhesives.

Figure 1. Molar mass distributions measured for the alkoxyamine-mediated batch polymerization of bulk styrene at 200 °C; the initial molar ratio of alkoxyamine to styrene is 1:50 (DPn = 50). Reaction time, conversion and polydispersity index (PDI) are presented in the legend.
Over the past two decades, the number of publications on various controlled radical polymerization (CRP) systems, such as NMP, ATRP and RAFT, has dramatically increased, demonstrating their potentials in numerous application areas. However, reviewing these publications revealed that in almost all of the papers the polymerization experiments were stopped at low to medium conversions. Purposely or unintentionally, high conversion data were omitted and little information about high conversion kinetics was provided. Several papers that reported some scattered high conversion data showed severe loss of controllability. It is understandable that claiming of “well control” could immediately become unsupported and be criticized by reviewers in paper submission. Most bulk CRP systems lose control before 80% conversion. It means more than 20% residual monomer. Reclaiming such high level of monomer residues is costly and not feasible in commercial practice. Recently, we launched a research program aimed at developing strategies for achieving high monomer conversions in bulk CRP systems while maintaining good control. Such a development must be based on good understanding of the mechanism and kinetics involved at high conversion polymerization. Our approach employed both modeling and experimentation. We targeted on complete monomer conversion and examined the effect of thermal history on various diffusion-controlled reactions and polymer molecular weight distribution. As shown in the figure, designing temperature profile could improve the controllability of CRP at high conversions.
Atom transfer radical polymerization (ATRP) has been developed rapidly since the first example of ATRP reported by Matyjaszewski’s and Sawamoto's groups, respectively, in 1995. In view of the intrinsic toxicity of the copper compound, iron salts are particularly attractive for using as the ATRP catalyst due to its good biocompatibility and low toxicity. Herein, a series of different iron-mediated ATRP systems including normal ATRP, reverse ATRP, initiators for continuous activator regeneration for ATRP (ICAR ATRP) and activators generated by electron transfer for ATRP (AGET ATRP) were developed by our group, and the polymerization kinetics was studied in detail. In addition, the iron-mediated AGET ATRP was also successfully applied to the surface modification of different substrates such as chitosan, silica and magnetic nanoparticles to obtain functional materials.

(figure1 here)
This lecture will highlight the relevance of radical chemistry for preparing near-monodisperse and monodisperse sequence-controlled copolymers. Firstly, monomer sequence-regulation in controlled radical polymerizations such as atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP) will be discussed. A wide variety of sequence-controlled copolymers were prepared using time-controlled additions of small amounts of highly-reactive N-substituted maleimides comonomers during the ATRP or NMP of styrenics monomers used in large excess. Moreover, ultra-precise sequence-encoding can be attained using successive feeds of donor and acceptor comonomers. Beyond controlled radical polymerization, radical chemistry can also be used to synthesize monodisperse sequence-encoded copolymers. For instance, rapid “spin-trapping” reactions were used to prepare monodisperse oligomers on soluble and solid-supports.
Radical ring-opening polymerization (radical ROP) is a category of polymerization, which has attracted considerable interest from the following viewpoints: 1) Its potential to afford polymers with main chains containing various hetero atoms that are inherited from the corresponding heterocyclic monomers. 2) Its potential applicability to copolymerization with conventional vinyl monomers such as styrenic and acrylic monomers. These polymerizations undergo no shrinkage, because the highly compact structures of monomers are transformed into acyclic structure that occupies much larger space. Therefore, these “volume expandable monomers” can be expected to be used as sealants and adhesives, which are free from formation of voids and cracks caused by the volume shrinkage during the polymerizations of conventional monomers. We will present a synthesis and polymerization of new monomer containing bulky adamantane structure. Their radical ROP showed the volume expansion value of +6.1%. We also present the radical ROP of other monomers such as cyclic vinyl sulfone, approaching to industrial application.
121 - Organometallic-mediated radical polymerization: From head-to-head addition in vinyl acetate homopolymerization towards well-defined ethylene-based copolymers

Antoine Debuigne, adebuigne@ulg.ac.be, Anthony Kermagoret, Christine Jérôme, Christophe Detrembleur. Department of Chemistry, University of Liege, Liege, Belgium

Organometallic-Mediated Radical Polymerization (OMRP) has received renewed interest in recent years since proving its efficiency for polymerization of non conjugated monomers.\(^1\) In particular, Co(acac)\(_2\) has been effective as a control agent for radical polymerization of vinyl acetate (VAc), \(N\)-vinylamides, \(N\)-vinylimidazolium, etc. Despite developments in the understanding of the OMRP mechanism, important questions and challenges remained, some of which are addressed in this communication. Until recently, it was unclear why the control of the VAc polymerization by OMRP is not affected by the formation of a primary radical \(^4\) resulting from head-to-head addition, a drawback of other controlled radical systems. An in-depth NMR study revealed that Co(acac)\(_2\) does not alter the probability of head-to-head enchainment and indicates that dormant chains \(^1\) and \(^3\) reactivate at similar rates (See scheme below).\(^2\) This observation provided a strong incentive to evaluate the copolymerization of VAc with ethylene by OMRP, confident that the dormant species \(^5\), featuring a terminal ethylene-cobalt moiety, would be reactivated. As a result, well-defined statistical and block-like ethylene-based copolymers were prepared.\(^3\)

123 - Development of nonaqueous proton conducting polymers for high efficient PEMFCs

Minghui Chai, chai1m@cmich.edu, Ewa K. Gorski, Daniel R. Holycross. Department of Chemistry, Central Michigan University, Mt. Pleasant, Michigan 48859, United States

The performance of polymer electrolyte membrane fuel cells (PEMFC's) can be dramatically reduced at elevated temperatures due to the humidity loss. It is critical to develop anhydrous conducting membranes that can conduct protons over a non-water phase and have stable performance under hydration or dehydration. In this project, a new type of high temperature anhydrous novel proton conducting membrane is being synthesized as the potential polymer electrolyte membrane (PEM) material for PEMFC's. Membranes made of this novel type of polymers potentially conduct protons under nonaqueous condition and have high thermal stability, strong mechanic strength, as well as optimal operational durability. The novel polymer contains a conjugated backbone containing nitrogen atoms (as potential proton acceptors) with hydrophobic perfluorinated side chains as well as hydrocarbon chains terminated with hydrophilic sulfonic acid group as potential proton donors. Therefore the novel conjugated polymers can self-conduct protons within a single polymer chain, and/or across different polymer chains. Synthesis of this new PEM material consists of three steps; synthesis of two novel monomers followed by linking both of them via click chemistry. Each synthesized product is characterized by NMR, MS, IR and UV-Vis.

![Chemical structure of the novel polymer for PEMFC's](image)

Figure. (a) Chemical structure of the novel polymer for PEMFC's; and (b) the computer optimized structure of four polymer chains each with four repeating units.
Degradation studies on CPVC sprinkler piping material in QSUN xenon arc chamber and QUV weathering chamber

Swathilekha Chivukula, swathilekha.chivukula@fmglobal.com, Paul (Po-Cheng) Su. Engineering and Research, FM Global, Norwood, MA 02062, United States

Chlorinated polyvinyl chloride (CPVC) is a promising material candidate for sprinkler piping systems in seismic areas. CPVC samples were obtained from a pipe supplier and refabricated according to the dimensions in ASTM D638. Exposures were conducted in the Q-SUN xenon arc chamber with a window glass filter and a day light filter and also in QUV accelerated weathering tester. The Figure below is a graph from Q-Lab Products showing irradiance from different exposure methods.

The left top corner in the figure lists the different exposure methods. The curves pertaining to a) Direct Sunlight, Noon Summer, b) Q-SUN Daylight-Q, c) Q-SUN Window-Q and d) QUV with UVB-313 are of interest in this study. Total energy exposed to the CPVC tensile specimens from QUV with UVB-313 lamps, Q-SUN xenon arc lamp used with a daylight filter and window glass filter in comparison with that of ASTM G177 sunlight over a period of 1 week, 4, 8, and 12 weeks was calculated. Energy levels used to expose the samples in the Q-SUN xenon arc chamber were 12 - 13 times greater than those used in the QUV accelerated weathering chamber. Literature shows that the shorter wavelengths in UVB light are more damaging. However, only minor tensile property changes were observed in the samples exposed to UVB light. A 70.4% reduction in the elongation at break was observed after 8 weeks of exposure in the Q-SUN xenon arc chamber with a daylight filter and a 67.7% reduction in the elongation at break was observed after 12 weeks with a window glass filter. Fourier Transform – Infrared Spectroscopy (FT-IR) analysis and preliminary Gel Permeation Chromatography (GPC) analysis revealed considerable changes. Field aged CPVC pipes were also analyzed.
Fluoride ion batteries offer advantages over currently used lithium ion batteries due to fluorine's high electronegativity and potentially high energy density, but a suitable electrolyte must be chosen to serve as a fluoride ion shuttle. Conventional polymer electrolytes have several problems including build-up of counter-ions, solvent leaking, and low transference numbers. As an alternative to conventional polymer electrolytes, a single ion conducting polymer, or ionomer, was designed. The ionomer consists of a polysiloxane backbone with poly(ethylene glycol) and tetrabutyl phosphonium side chains and a freely diffusing bromide or fluoride anion. In this system, the phosphonium cation is covalently bound to the polymer matrix and does not contribute to the conductivity, producing an anion transference number approaching unity. The restriction of cation motion and removal of organic solvent eliminate the complications that arise from the buildup of cations at the electrodes and leaking of the organic solvent. These ionomers have very low glass transition temperatures (between -70 and -80°C, due to the flexible nature of the polysiloxane backbone) that increase weakly with ion content and are independent of anion type. Spin lattice relaxation rates (1/T1) for 19F and 31P nuclei in polysiloxane-based ionomers of varying ion content were investigated using nuclear magnetic resonance spectroscopy. The resulting dynamics, including activation energies for motion, are compared to results from conductivity measurements using dielectric relaxation spectroscopy.
Anion metathesis enabled a systematic study focused on the thermal, viscoelastic, and conductivity properties of a 4P,12 phosphonium ionenes with various counterions. Aqueous size exclusion chromatography confirmed the well-defined synthesis of 4P,12-Br from the step-growth polymerization of 1,4-bis(diphenylphosphino)butane and 1,12-dibromododecane at a 1:1 stoichiometric ratio. Subsequent anion-exchange employing a dialysis method exchanged the Br⁻ counterion to trifluoromethanesulfonate (TfO⁻), bis(trifluoromethane) sulfonimide (Tf₂N⁻), and tetrafluoroborate (BF₄⁻) counterion. Chemical and thermal characterization revealed that anion-metathesis to more bulky and delocalized anions had resulted in profound differences in fundamental polymer properties including the glass transition temperature and thermal stability. Melt rheology was employed for time-temperature superposition analysis and suggested that larger counterions have a plasticizing effect on the viscoelasticity of the 4P,12 ionene. Additionally, ionic conductivity increased with increasing size of the counterion (Br⁻ < BF₄⁻ < TfO⁻ < Tf₂N⁻) and demonstrated the viability of these novel materials as potential anion-exchange ionomeric membranes.
Cyclic polymers, while possessing interesting physical properties, have presented a synthetic challenge for chemists. Zwitterionic ring-opening polymerization (ZROP) is an efficient and reliable method of producing cyclic polymers. The N-heterocyclic carbene (NHC)-mediated ZROP of δ-valerolactone was investigated in the presence of various concentrations of LiCl. It was found that the rate of polymerization depends sensitively on [LiCl], especially at low concentrations. Furthermore, polymer molecular weights were well-controlled with narrow polydispersities (PDI < 1.2) in the presence of LiCl. It is hypothesized that LiCl acts to break up aggregates of the propagating zwitterionic species to speed up polymerization, but forms a highly coordinated and less reactive alkoxide at high concentrations. MALDI-TOF characterization of polymer products after isolation from aqueous methanol workup revealed that a mixture of linear and cyclic polymers is formed at lower concentrations of LiCl, whereas linear polymers are formed at the highest [LiCl], which is likely due to less efficient cyclization in the presence of LiCl.
There exists a widespread interest in solar energy not only as an alternative to fossil fuel, but also to grow a synergistic energy portfolio consisting of the right blend of renewable and non-renewable approaches. Distinct advantages of polymer organic photovoltaic (OPV) cells over silicon-based conventional solar cells include their ease of fabrication, low-weight, flexibility and lower cost, however they are plagued by their low efficiency in converting light to electricity. Among other things, this deficiency stems from the lack of control of the donor polymer self-assembly, nanoscale morphology of the separated phases of donor and acceptor in the OPV, and the exact nature and chemical constitution at interfaces of their complex multi-layered architectures. Here, we describe our pathways toward increasing the efficiency of air-processed OPV cells by controlling the morphology and absorption through incorporation of organic/inorganic hybrid polyhedral oligomeric silsesquioxane (POSS) nanoparticles with tailored processing techniques. We also investigate the evolution of morphology and change in chemical constitution through different stages of these tailored processing techniques. Vapors from different solvents are shown to affect the morphology and distribution of polymers and fullerenes amongst the crystalline and amorphous regions of the bulk hetero junction (BHI). The effect of such changes on charge carrier mobility and contact surface potential were exhibited through various characterization techniques.
129 - Engineering effective fibrocartilage replacement technologies: Replicating the mechanics of complex tissues through spatial control of nanostructure

Jackson T Lewis, jtlewis@rams.colostate.edu, Travis S Bailey. Chemical and Biological Engineering, Colorado State University, Fort Collins, CO 80523, United States

The meniscus, located in the knee, is a crescent shaped fibrocartilaginous tissue that distributes tibiofemoral contact pressure. Damage to the meniscus leads to osteoarthritis. Due to its primarily avascular nature and high water content it is a prime candidate for a hydrogel based soft tissue replacement. The difficulties in recreating the properties of the meniscus in a hydrogel platform lie in the highly anisotropic and mechanically robust nature of the meniscus. However, creating a nanostructure in a hydrogel platform that more closely resembles the meniscus may overcome these difficulties in creating a hydrogel based soft tissue replacement.

Through the spatial control of nanostructure in polystyrene (PS) polyethylene oxide (PEO) block copolymer based hydrogels we are able to develop a mechanically robust gel while maintaining high water content (90% by mass). Tuning these highly controlled nano-scale morphologies into a structure that more closely resembles that of the native soft tissue may produce a material that is able to perform the highly specific function of the meniscus.
We report the synthesis and characterization of highly exfoliated polyolefin block copolymer nanocomposites via Surface-Initiated Ring Opening Metathesis Polymerization (SI-ROMP). ROMP-active hydrophobic montmorillonite (MMT) clay surfaces were prepared through ion exchange with a norbornene-terminated alkyl-ammonium surfactant. We were then able to polymerize block copolymer brushes of (substituted) norbornene (e.g., ethylidene norbornene) and cyclopentene via SI-ROMP using a Grubbs catalyst. Subsequent hydrogenation yielded highly crystalline linear polyethylene block and rubbery saturated polynorbornene block. Nanocomposites were characterized for thermal (TGA, DSC), morphological (XRD, TEM), and mechanical (DMA, Rheology) properties. A fraction of the polymer brushes were removed from their substrate by reverse ion exchange with a salt and then characterized in parallel with their corresponding nanocomposite analogs. In this way we were able to assess the role of the filler particle in the thermal properties, melt rheology, morphology, and tensile properties.
Controlled graft copolymerization on multiwalled carbon nanotubes from binary mixture of monomers

Kailash C Gupta, guptakc03@yahoo.co.in, Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247 667, India

The polymer functionalized multiwalled carbon nanotubes have been prepared by controlled graft copolymerization of N-isopropylacrylamide and acrylic acid monomers from their mixture at fixed and variable feed composition. The presence of acrylic acid has enhanced the activity of N-isopropylacrylamide for graft copolymerization (52%) on multiwalled carbon nanotubes in comparison to graft copolymerization of N-isopropylacrylamide (38%) in absence of acrylic acid. The atom transfer radical graft copolymerization of N-isopropylacrylamide and acrylic acid monomers has produced graft copolymers (Scheme 1) with high molecular weight ($42 \times 10^3$ g mol$^{-1}$) and low molecular weight dispersity (1.13) at fixed feed molarity (0.1M) and composition.

The copolymer grafted multiwalled carbon nanotubes have shown high dispersity in water in comparison to pristine multiwalled carbon nanotubes. The grafted poly(N-isopropylacrylamide-co-acrylic acid) were characterized by FT-IR for structural information (Figure 1) and variation in thermal stability is evaluated by thermogravimetric analysis.

Poly(N-isopropylacrylamide-co-acrylic acid) grafted multiwalled carbon nanotubes were used to control the sensitivity and selectivity of glassy carbon electrode in cyclic voltammetric detection of dopamine in presence and absence of interfering ascorbic acid in phosphate buffer solution. The modified glassy carbon electrode has shown improved sensitivity and working range with a response time of 4 seconds in comparison to unmodified glassy carbon electrode. The presence of acrylic acid on multiwalled carbon nanotubes has improved the selectivity of electrode for dopamine. These studies have clearly indicated that multiwalled carbon nanotubes with controlled molecular weight and structures of poly (N-isopropylacrylamide-co-acrylic acid) could be useful in cyclovoltammetric detection of dopamine in presence of ascorbic ascobic acid at different temperature and pH.
A novel poly(N-substituted p-benzamide)-b-poly(propylene oxide) (PMAB-b-PPO) multiblock copolymer with controlled architecture was synthesized, and the thermal and mechanical properties were investigated. The amide block was prepared by the step-wise condensation reaction using terephthalic acid (TPC) as the core, N-methyl p-laminobenzoic acid (MAB) as the building block, and thionyl chloride as the condensation reagent. The set numbers of MAB monomers were reacted at both ends of TPC, giving the rigid-rod macro-molecule (MABx-TPC-MABx). The corresponding copolymer was successfully prepared by the direct polycondensation of this molecule with PPO having diamine function at both ends. The molecular weights and polydispersity of the copolymers were about 10,000 and 1.5. From differential scanning calorimeter the copolymers MAB5-TPC-MAB5 have two glass transitions at around -50°C and 145°C, corresponding to PPO and PMAB segregated domains, respectively. The copolymer film was prepared by the ordinal solvent-casting method, and the mechanical properties were evaluated by using stress-strain profile, in which the tensile strength and the elongation at break were 3 MPa and over 1,150%, which indicate the possibility of the thermoplastic elastomer.
A cross-coupling reaction between dihaloarylene monomers and unsubstituted arylene monomers in the presence of a palladium catalyst, the so-called palladium-catalyzed direct arylation, has been paid numerous attention for environmentally-friendly, efficient, and low-cost method for the synthesis of conjugated polymers compared to conventional cross-coupling reaction, such as Stille coupling reaction and Suzuki coupling reaction. In recent years, the synthesis of conjugated donor polymers by direct arylation has been reported; in contrast to synthesis of conjugated donor polymers, the direct arylation synthesis of conjugated acceptor polymers is far less developed. Horie et al. reported the synthesis of a naphthalene bisimide (NBI)-based acceptor polymer, a potential acceptor polymer for organic photovoltaics and organic field-effect transistors, by direct arylation; however, the molecular weight of the obtained NBI-based acceptor polymer was extremely low ($M_n \approx 2000$). Such a low molecular weight does not meet the requirements for the device applications, which may cause the low stability and low performance of devices; therefore, the development of conjugated acceptor polymers with high molecular weights by direct arylation remains a big challenge.

In this work, we found that efficient direct arylation methodology for the synthesis of a NBI-based acceptor polymer ($PNBI3T-Dr$) using a newly designed thiophene-extended NBI monomer under the optimal reaction conditions, which yielded a polymer with a high molecular weight ($M_n > 30000$) in a relatively high yield. To the best of our knowledge, our work is the first example for the efficient synthesis of conjugated acceptor polymers by direct arylation. This result revealed that direct arylation could be an alternative synthetic method even for conjugated acceptor polymers.

| Entry | Phosphine ligand | Concentration (wt%) | $M_n^{a,b}$ | $M_w/M_n^{a,b}$ | DP$^c$ | Yield (%)$^b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCy$_3$ · HBF$_4$</td>
<td>20</td>
<td>10000</td>
<td>1.63</td>
<td>7</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>PCy$_3$ · HBF$_4$</td>
<td>6</td>
<td>25000</td>
<td>2.49</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>nBu$_2$Me · HBF$_4$</td>
<td>6</td>
<td>29000</td>
<td>2.04</td>
<td>21</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>nBu$_3$ · HBF$_4$</td>
<td>6</td>
<td>31000</td>
<td>2.86</td>
<td>23</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>P(o-tol)$_3$</td>
<td>6</td>
<td>3000</td>
<td>1.05</td>
<td>2</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>P(o-PhOMe)$_3$</td>
<td>6</td>
<td>14000</td>
<td>1.65</td>
<td>10</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>PPh$_3$</td>
<td>6</td>
<td>10400</td>
<td>1.80</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>None</td>
<td>6</td>
<td>17000</td>
<td>2.67</td>
<td>12</td>
<td>21</td>
</tr>
</tbody>
</table>

$^{a}$Determined by SEC using polystyrene standards in chloroform. $^{b}$Chloroform fractions in Soxhlet extraction. $^{c}$degree of polymerization.
134 - WITHDRAWN
Dynamic covalent linkages are stable bonds formed as a result of an equilibrium established between starting material and product that can be reversed under a specific set of conditions. Hydrazone bonds make up an important class of dynamic covalent linkages useful for applications ranging from self-healable materials to attachment and release of molecules of interest for therapeutics. Installing dynamic covalent linkages on polymers has become a rapidly growing area of research due to its potential impact on a wide range of applications.

Herein, we report the synthesis of monomers for direct and indirect polymerization of hydrazide functional groups by reversible addition-fragmentation chain transfer (RAFT) polymerization in order to synthesize hydrazone functional polymers. A couple of examples of hydrazide functional polymers by post-polymerization modification have been reported, however, direct polymerization of a hydrazide moiety has, until recently, yet to be achieved. We investigated the polymerization of N-methacryloyl hydrazide directly by aqueous RAFT at various pH's and the polymerization of N-methacryloyl carbazate by RAFT in organic media as an indirect route to achieve hydrazide functional polymers. The synthesis of hydrazide polymers by controlled radical polymerization opens the door to new types of dynamic covalent polymer architectures in solution. The dynamic nature of these hydrazone linkages enables the functionalized polymers to shuffle or exchange pendent groups providing a versatile polymer scaffold for development of dynamic combinatorial polymer libraries. Different monomer structures were also designed to determine its influence on hydrazone formation and exchange after polymerization.
136 - Translating basic science into products and the role of diversity in making that happen

Joseph M DeSimone, desimone@unc.edu, Departments of Chemistry and Pharmacology and Department of Chemical and Biomolecular Engineering, University of North Carolina at Chapel Hill and North Carolina State University, Chapel Hill, North Carolina 27599, United States

Those of us who participate in convergence science know how extensive and difficult the challenges are to executing it. Beyond pursuing scientific problems through research, we are faced with questions about advocacy, public policy changes, restructuring funding systems, peer review and tenure issues, and other administrative—and crucially important—questions about the structures in which we operate as academic scientists. These questions are vast and aren’t associated with any discipline in particular, and I believe the approach to addressing them would be best informed by joining a diverse range of perspectives.

As scientists, we may be doing ourselves a disservice by not being more deliberate in drawing others who are not scientists into our conversations about convergence. Indeed, when solving scientific problems, I have found in my career that the best, most innovative solutions arise from diverse teams composed of talented individuals with different backgrounds, experiences, and expertise. In this context, I will share my perspective about how diversity should be considered for our ongoing dialogue about convergence science in the 21st century.

Monday, August 11, 2014 08:30 AM
Industrial Polymer Scientist Award: Symposium in Honor of Robert D. Allen, IBM (08:30 AM - 12:05 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 7/8
137 - Is living anionic polymerization dead or just radically changed?

Timothy E. Long¹, telong@vt.edu, Sean T. Hemp², Alison R. Schultz¹, Chainika Jangu¹, Keren Zhang¹, Michael H. Allen³. (1) Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States, (2) Michelin, Greenville, South Carolina 29602, United States, (3) Adhesives Research, Glen Rock, Pennsylvania 17327, United States

Ionomers and polyelectrolytes represent families of macromolecules that incorporate cationic or anionic sites either pendant or within the polymer main chain. These charged compositions enable tunable physical properties such as ionic conductivity, thermal and chemical stability, water transport, and anion exchange capability. Ion-containing polymers are versatile materials that continuously enable emerging technologies such as water purification, gas separation, gene delivery, biosensors, fuel cells, and electro-mechanical devices. Multiple hydrogen bonding in block copolymers serve as directional analogues to the non-directional electrostatic interactions. Living anionic polymerization with organolithium initiators enables block copolymers containing low Tg 1,4-polyisoprene sequences, and complementary controlled RAFT radical polymerization employs a rich library of synergistic functional monomers including many ionic liquid monomers. Living anionic polymerization has experienced a recent commercial resurgence due to the critical needs for functional polymers in emerging technologies, and controlled radical polymerization continues to provide multifunctional polar polymers with unprecedented performance that are often unattainable using anionic polymerization. Clearly, both anionic and radical polymerizations continue to enable high performance materials that address global grand challenges of our time.
138 - Resurgence of high performance polymers

James L. Hedrick, hedrick@us.ibm.com, Department of Advanced Materials, IBM Research, San Jose, CA 95120, United States

The chemical depolymerization of poly(ethylene) terephthalate (PET), one of the most pervasively used plastics, is being explored as an alternative feedstock of specialty chemicals. The chemical transformation of PET refuse into functional monomers and subsequently into high performance materials employed in engineering applications such as automotive and aerospace structural materials will have significant societal impact. The transesterification or aminolysis reactions used to depolymerize PET employ an organocatalyst with enzyme-like functionality that provides a “green” alternative to traditional organometallic catalysts. This has become increasingly more important as the European Union has banned many of the organometallic promoters used for important commodity polymers. In addition to diols, diamines and amino alcohols, protected carboxylic acid derivatives have been surveyed as possible nucleophiles to organocatalytically depolymerize PET generating a library of monomers.

These new diamines, bisphenols, diols and related monomers have been used to generate value added materials. It is anticipated that the teraphthalamine structural building motif will provide rigidity and cohesive density owing to the hydrogen-bonding donor and acceptor combination of the amide moiety. Moreover, this structural motif is expected to enhance solvent resistance to the subsequent material and enhance ductility without sacrificing modulus and other important properties. A number of possible enchainment strategies are being explored such as thermoplastics for engineering incorporating polyimides, polyamides, poly(aryl ethers) or combinations of each, as well as thermosetting resins. This talk will provide an overview of this work and our direction.
Lithography, the workhorse technology enabling microelectronics manufacture, has reached astonishing success in producing nanoscale features. Despite this, even higher resolution is needed if plans for next generation electronics are to be achieved. This presentation summarizes approaches to the design of photoresists that abandon the traditional polymer based strategy and explore the use of structures with molecular dimensions on the order of 5 nm and less. In this presentation phenolic molecular glass photoresists are first discussed. Built from organic small molecules, these materials have been synthesized with a variety of structures and patterned at high resolution using EUV radiation. Conventional negative tone and positive tone chemically amplified strategies have been explored and are described.

In a recent development, metal oxide nanoparticles based on hafnia or zirconia with ligands of organic acids have been examined. These materials are extremely sensitive to EUV radiation (less than 10 mJ/cm2) and produce high-resolution patterns. These photoresists which incorporate photoactive compounds function via a ligand exchange mechanism that gives the materials their very high sensitivity. The preparation, imaging and properties of these materials will be discussed.

Figure. Metal oxide nanoparticle resist consisting of oxide core, organic ligands and photo active compounds. These nanoparticles are patterned via a completely new, non-chemically amplified ligand exchange mechanism.
Various incredibly clever process tricks based on chemical principles have been devised that extend the resolution limits of photolithography, some of which are already in use in full scale manufacturing. One promising approach is based on the directed self-assembly of block co-polymers. We have tried to design block co-polymers that are optimized for this application and capable of forming structures with minimum dimensions below 100 Å in width. Doing so requires blocks with very high interaction parameters, $X$ and for some applications, incorporation of silicon in one of the blocks. Polymers of this sort form very small structures, but aligning the structures and orienting them in a way that is useful for microelectronics has been a challenge. For example, achieving orientation by a long solvent annealing process is simply not compatible with the serial nature of microelectronics manufacturing as it is currently practiced and the structures once formed must be useful for patterning a variety of materials including insulators, semiconductors and conductors. We have therefore worked to develop new high $X$ block copolymers and processes that enable very fast, thermal annealing and aligning of these materials. A progress report on our design, synthesis and process development efforts will be presented.
141 - Self-aligned customization of block copolymer directed self-assembly for device-relevant patterning

Daniel P. Sanders¹, dsand@us.ibm.com, Joy Y. Cheng¹, Gregory S. Doerk¹, Charles T. Rettner¹, Gurpreet Singh¹, Srinivasan Balakrishnan¹, Noel Arellano¹, Melia Tjo¹, Hoa D. Truong¹, Elizabeth M. Lofano¹, Jed W. Pitera¹, Markus Brink², Hsin-Yu Tsai², Michael A. Guillorn². (1) IBM Research - Almaden, San Jose, CA 95120, United States, (2) IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598, United States

The directed self-assembly (DSA) of block copolymers (BCPs) is a promising resolution enhancement technology to extend lithographic patterning capability. Chemoepitaxy and graphoepitaxy-based DSA approaches have been demonstrated to generate arrays of sub-lithographic features. In recent years, the availability of semiconductor grade DSA materials and fab-compatible processes has caused an explosion of DSA activity in the semiconductor industry. Now, the focus has turned to the issue of how one can use BCP DSA to make suitably complex, device relevant patterns. The sub-lithographic BCP domain sizes which make DSA so attractive in overcoming the resolution limitations of optical lithography tools at the same time require levels of edge placement control in any cut (or customization) step that challenge the capabilities of those same exposure tools.

To address this challenge, we have developed self-aligned customization processes for chemoepitaxy and graphoepitaxy BCP DSA in which select customization information is incorporated into the guiding prepatterns. While examples of both methods will be presented; the focus of the talk will be a self-aligned customization technique for chemoepitaxy, which we have named CHEETAH (CHemoEpitaxial Etch Trim using a self-Aligned Hardmask). Examples of customized DSA-based patterns prepared using CHEETAH for sample device layouts will be shown. In addition, some fundamental studies of this process will be discussed.
142 - Development of ArF photoresists

Mitsunobu Koshiba, Mitsunobu_Koshiba@jsr.co.jp, JSR, Japan

Robert Allen was the lead inventor of US6,165,678 (Dec. 6, 2000) that is the most critical patent for all (meth)acrylate based ArF photoresists, and this patent is honored by all the major photoresist suppliers that support advanced lithography. JSR has been a development partner for IBM Corp. since 2000, and Bob has been one of the key members of our joint development program. This joint development program was one of the most successful joint programs for JSR that yielded successful photoresist formulations which supported the initial stages of ArF lithography. In addition, the top coat (TCX) formulations developed through the collaboration became a de-facto standard of immersion ArF lithography to date. Collaborations with IBM are expected to continue to deliver innovative lithography solutions to bridge the gap between immersion ArF lithography and EUV that include next generation multilayer and DSA (Direct Self-Assembly) solutions.
Materials innovation enables advances in semiconductor technology. Polymer chemistry plays an important role in the semiconductor roadmap. Contributions from our laboratory toward advancing patterning technology through creative chemistry will be reviewed and also a diverse set of applications of polymer chemistry in non-traditional areas of potentially great societal benefit will be discussed.
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. Plastics are ubiquitous and highly useful modern materials, but their widespread utility and indiscriminate disposal has left an adverse and enduring environmental legacy. We have developed a broad class of highly active, environmentally benign organic catalysts for the synthesis of biodegradable and biocompatible plastics. Conventional routes to polyester plastics rely on metal catalysts; this technology describes the application of metal-free organic catalysts for the synthesis and recycling of polyesters. Several new families of organic catalysts have been discovered which rival or exceed metal-based alternatives for polyester synthesis, both in terms of activity and selectivity. These new synthetic strategies provide an environmentally attractive, atom-economical, low energy alternative to traditional metal catalyzed processes. This technology includes organocatalytic approaches to ring-opening, anionic, zwitterionic, group transfer, and condensation polymerization techniques. Fundamental mechanistic and theoretical investigations have provided 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 well-defined macromolecular architectures. The monomer feedstocks have focused on those from renewable resources such as lactides derived from biomass, but also from petrochemical feedstocks. An emphasis will be placed on functional polycarbonates.

This talk will focus on application of organic catalysis towards functional degradable polymers as well as the degradation of plastic refuse to generate high-end materials for antimicrobial applications, as well as alternative strategies to lithography based on probe-base techniques.
145 - Recent advances in the development of benign polymeric materials

Geoffrey W. Coates, gc39@cornell.edu, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, United States

Society depends on polymeric materials now more than at any other time in history. Although synthetic polymers are indispensable in a diverse array of applications, ranging from commodity packaging and structural materials to technologically complex biomedical and electronic devices, their synthesis and post-use fate pose important environmental challenges. The focus of our research is the development of new routes to polymers with reduced environmental impact. In this work, we aim to transition from fossil fuels to renewable resources, and are developing synthetic methods that limit energy and raw-material consumption. In addition, we are designing materials that will eventually degrade into non-toxic materials, and have properties comparable to current commodity plastics. In this lecture, the development of new methods for the synthesis of sustainable polymers will be presented.

Monday, August 11, 2014 08:55 AM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (08:30 AM - 11:30 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
146 - New route to glucose-derived terephthalic acid using zeolite catalysts

Joshua J Pacheco, jpacheco@caltech.edu, Mark E. Davis. Department of Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

A new series of zeolite-catalyzed Diels-Alder cycloaddition and dehydrative aromatization reactions between oxygenated furan dienes and ethylene are reported. It is found that pure Lewis-acid zeolites (Sn-BEA) are catalysts for the conversion of 5-substituted furoic acid derivatives and ethylene to 4-substituted benzoic acid derivatives. For example, the diene, methyl 5-(methoxymethyl)-furan-2-carboxylate, is converted to the dehydrated Diels-Alder product upon reaction with high-pressure (1000 psig) ethylene at 190°C (selectivity can be over 50%). The aromatic product of this reaction, methyl 4-(methoxymethyl)benzoate, can be used to produce terephthalic acid or its diester via oxidation. This new reaction pathway opens a completely new route for the production of terephthalic acid starting from glucose-derived HMF (5-hydroxymethyl-2-furfural) and ethylene, and avoids any costly reduction steps.
A key challenge for polymer science is to control polymer sequence from mixtures of monomers. Sequence controlled multi-block copolymers are of high interest due to their enhanced properties and the potential for designed functionality. Generally, when using mixed monomer feedstocks, the relative reactivities of the monomers, determined from homopolymerization experiments, are used to predict the sequence of the copolymer – i.e. kinetic control.

Here, we present a novel chemoselective control mechanism which is applicable to both the ring-opening polymerization (ROP) of lactones and the ring-opening copolymerization (ROCOP) of epoxides and carbon dioxide.¹

A straightforward strategy to ‘switch’ between ROP and ROCOP will be discussed. The method applies exogenous ‘switch’ reagents to direct the polymerization pathway and enables a single zinc catalyst to be used for both ROP and ROCOP, sequentially and in one pot.

Designed aluminum salen, salan and amine-bis(phenolate) complexes support the living and immortal ring-opening polymerization of rac-lactide. We have expanded the monomer scope of these classic catalysts, allowing the homo- and co-polymerization of propio-lactone derivatives. Herein we report our work on expanding and optimizing these reactions, including three specific targets. First, aliphatic polyester block copolymer synthetic strategies are explored, ranging from gradient copolymerizations to block copolymerizations with phase separated blocks. Second, the development of epoxidation carbonylation methodology for monomer synthesis increases the scope of readily available monomers. Finally, functional polymers and copolymers are prepared through gradient and sequential ring-opening polymerizations. Exploitation of these polymers in pharmaceutical and medical applications is briefly discussed.
149 - Stereoblock polylactide: New, highly active, and iso-selective catalysts based on group 3/lanthanide phosphasalen complexes

Charlotte K Williams¹, c.k.williams@imperial.ac.uk, Clare Bakewell¹, Nicholas Long¹, Audrey Auffrant². (1) Chemistry, Imperial College London, London, United Kingdom, (2) Chemistry, Ecole Polytechnique, Paris, France

Polylactide (PLA) is a leading bio-derived polymer, in this field there is considerable attention and interest in stereoblock PLA due to its improved thermal and mechanical properties. Currently, stereoblock PLA can be prepared from racemic lactide using aluminum salen catalysts, however, these species are slow and require high catalyst loadings. This presentation will introduce a series of new Group 3 and lanthanide catalysts, based on coordination complexes of phosphasalen ligands, as an alternative to aluminum salens.[1] The new catalysts show excellent rates, high degrees of iso-selectivity ($\Pi_i$: 0.85, 298 K) and high degrees of polymerization control. The presentation will focus on our investigations into the factors which influence and control the polymerization kinetics and stereoselectivity. Our hypotheses regarding control will be presented, together with strategies to further improve stereoselectivity. The thermal properties of the stereoblock PLA will also be presented.


Monday, August 11, 2014 10:45 AM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (08:30 AM - 11:30 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
150 - Aliphatic polycarbonate materials: From heavymetal-ion sequestration to self-assembled nanocarriers applications

Laetitia Mespouille, laetitia.mespouille@umons.ac.be, Philippe Dubois. Chemistry, University of Mons, Mons, Belgium

The development of polymeric materials that possess desirable physicochemical properties but also answer to environmental concerns are required to realize a new generation of materials that can be valorized in added-value applications such as micro-electronics, medicine, coatings and adhesives amongst others. Among various polymer families being investigated, aliphatic polycarbonates (APCs) are gaining increasing credibility for biomedical applications owing to their biocompatibility and bioreabsorbability. Moreover, *in vivo* application of APCs is also strongly motivated by the absence of an acidic microenvironment being generated in the surrounding tissue upon degradation, unlike that generated by polyester degradation preventing a local aseptic inflammation response and deactivation/denaturation of sensitive loaded drugs. Their recent commercialization and clinical use justify the need to develop aliphatic polycarbonate materials free of any toxic compounds. This realization has driven scientists to implement macromolecular engineering processes by replacing potentially toxic and carcinogenic metal-based catalysts by safer and greener organic compounds. Among the different synthetic approaches available, the ring-opening polymerization (ROP) of cyclic carbonates is traditionally preferred as it occurs under benign conditions and offers better control over macromolecular parameters. In this context, new generation of metal-free catalysts inspired by nature itself (amidine, guanidine, betaine) has been successfully applied to the ROP of lactones and cyclic carbonates.

Cytotoxicity tests performed on these catalysts and on the resulting unpurified polymers have demonstrated the absence of toxic response of HepaRG and FHs74Int over a broad range of concentration. Such observations allow the direct use of the APCs materials without the need of time-consuming and expensive purification steps involving large amount of organic solvent.

Beyond these greener synthetic consideration, valorization of these materials in environmentally oriented application as support for heavy metal-ion sequestration or in biomedical fields has been promoted.

Monday, August 11, 2014 11:05 AM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (08:30 AM - 11:30 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
Metallosupramolecular polymers (MSPs) offer a range of useful stimuli-responsive properties, if motifs with dynamic binding characteristics are used. We recently demonstrated that damaged MSPs based on a telechelic poly(ethylene-co-butylene) (PEB) with 2,6-bis(1'-methylbenzimidazolyl)pyridine (Bip) ligands at the termini and Zn$^{2+}$ or La$^{3+}$ salts can be healed upon exposure to UV light.

Light-heat conversion causes disengagement of the metal-ligand motifs, which leads to a decrease of the molecular weight and viscosity. This allows defects to be filled with the constituting components, which re-polymerize when the light is switched off. The same MSPs can also be applied as reversible adhesives, which permit bonding and debonding on demand. Lap joints bonded with the MSPs display an appreciable shear strength, but can be rapidly debonded upon exposure to heat or UV light. Reversible and irreversible disassembly is also possible through mechanochemical transduction in MSPs assembled from Bip-PEB-Bip and Eu(ClO$_4$)$_3$. The Bip- Eu$^{3+}$ complexes serve as mechanically responsive motifs and their characteristic fluorescence allows monitoring the extent of (dis)assembly. Dose-dependent, reversible metal-ligand dissociation occurs upon exposure to ultrasound. This effect is also possible in the solid state and permits mending of damaged objects. Mechanochemical transduction also allowed triggering a solid-state metal-exchange reaction: When the MSP was imbibed with a solution of Fe(ClO$_4$)$_2$, no appreciable color change was visible, whereas ultrasonication or compression caused an irreversible color change, as a result of the formation of Fe$^{2+}$ complexes with Bip-PEB-Bip.
Over the past few years, we have developed an "on-surface synthesis" of 1D and 2D covalent nanostructures involving chemical reactions between thermally activated monomer building blocks in the confinement of a metallic substrate. The underlaying metal surface plays at least two important roles since it has to provide sufficient mobility to the activated monomers to achieve polymerization and it has to aid activation through catalysis. The latter leads to metal-bridged intermediates, which either reductively eliminate to covalent organic chains and networks or remain as metallosupramolecular polymers. The stability of the intermediate metallosupramolecular polymers depends strongly on the nature of the metal as well as the reconstruction of its surface.

Here, this specific aspect of our on-surface polymerization will be presented and other related recent developments will be described.
At present, supramolecular transformations are mainly realized as structural alterations, where connectivity patterns and/or spatial arrangements within a single self-assembly are toggled between two states by changing molecular binding properties through either light, chemical or redox input. Only recently, the Stang group and our team have been able to additionally manage compositional changes in supramolecular transformations. In detail, both groups have mimicked an intricate biological process, called gene shuffling, by setting up spontaneous and catalytic supramolecule-to-supramolecule transformations where two distinct self-assemblies fused into a new assembly via shuffling of their components, requiring to fully reorder both compositional and constitutional connectivities. The present paper will report about further fascinating developments in this direction, i.e. multiple cascading supramolecular fusions A → AB → ABC, their thermodynamics and kinetics.

It is argued that the emerging principles from the present studies will become valuable for the design of adaptive materials operating on the principle of supramolecular fusion.

References:
Europium(III) complexes show unique photophysical properties such as narrow emission bands, large Stokes shifts and long luminescence lifetimes and have found application in emissive materials, molecular imaging and sensing.

However, the forbidden nature of the f-f transitions requires so-called sensitizers or “antenna ligands” to make these interesting features more widely accessible via energy transfer. These “antenna ligands” can also be used to connect Eu(III) coordination compounds to a polymer backbone which is illustrated herein by different approaches ranging from copolymerization to post-polymerization functionalization.

The first part of this contribution discusses Europium containing monomers and analogous acrylates with terpyridine, imidazophenanthroline and dipyridyl-1,3,5-triazine ligands carrying norbornoyl side chains and theonyl trifluoracetacetonate (TTA) as coligand. While the former can be copolymerized by ROMP (ring-opening metathesis polymerization), the latter serve as termination reagents. Thereby, precise placement in random copolymers and amphiphilic block copolymers (within or at the end of the respective polymer chain segments) was achieved. The non-radiative deactivation of Eu(III) luminescence by water can be used for trace water vapour detection and depends on the number of free coordination sites which also was demonstrated for the aforementioned copolymers.

Finally, inverse-electron demand Diels Alder (IEDDA) reactions between di(pyridyl)-1,2,4,5-tetrazine and residual double bonds in the polymer backbone to graft di(pyridyl)pyridazines to emulsion-templated poly(dicyclopentadiene) (pDCPD) foams with a high loading (2 mmol/g) and the subsequent preparation of immobilized europium complexes will be presented.
There is great current interest in the synthesis of well-defined and functional polymers using controlled radical polymerization (CRP) techniques. The advances in the development of these techniques has enabled access to a wide range of functional and responsive materials for a diverse range of applications. In the O'Reilly group we use CRP techniques to synthesize functional and responsive amphiphilic diblock copolymers from a range of monomers which have unique properties such as responsive capabilities, catalytic activity or selective recognition. We are interested in the solution self-assembly and the characterization of the resultant aggregates along with their exploration in a range of applications. One interesting example is in the design of catalytically active nanoreactors which can exhibit enhanced rates of catalysis and also excellent recovering and reuse. Furthermore, these nanostructures can be designed to undergo fast and reversible transitions between different morphologies (and hence give rise to a change in physical properties) as a result of an alteration in the packing parameter of the constituent polymers in response to applied external stimuli. We have explored the application of these responsive materials in controlled release and also catalysis applications.
156 - Redox-driven fluorescence and photo-induced electron transfer in organometallic supramolecular dyads and triads with porphyrin, subphthalocyanine, BODIPY, and azaBODIPY chromophores

Victor N. Nemykin, vnemykin@d.umn.edu, Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, United States

A large number of ferrocene-containing aza-BODIPYs, BODIPYs, subphthalocyanines, and porphyrins have been prepared and characterized by UV-Vis-NIR, MCD, NMR, APCI MS/MS, and X-ray crystallography.\(^1\)\(^-\)\(^3\) The redox properties of target compounds were investigated by electrochemical and spectroelectrochemical methods as well as by the chemical oxidation using variety of oxidants. Fluorescence properties and non-radiative decay pathways were investigated by steady-state and time-resolved techniques in the picosecond and femtosecond regimes. Influence of the metallocenyl substituents’ coordination mode (i.e. peripheral vs. axial connectivity; direct vs. trough spacer connectivity) on formation of the redox-induced mixed-valence and photoinduced charge separation states will be discussed. The experimental electronic, spectroscopic, and geometric parameters of neutral, mixed-valence, and charge separated states in the metallocenyl-containing aromatic macrocycles will be correlated with DFT and TDDFT calculations.

References:

Light harvesting polymers featuring non-conjugated polystyrene or n-conjugated polyfluorene backbones functionalized with Ru-polypyridyl metal complex chromophores have been constructed. The metal complex units are attached to the polymer backbone by using an azide-alkyne “click” reaction. The dynamics of energy transfer and charge transfer in these functional polymers have been explored in solution and at TiO2 interfaces by using emission and time-resolved absorption spectroscopy. The results clearly reveal that energy transfer occurs within the polymer assemblies on timescales that depend on the mechanisms. For example, in all of the polymers, energy transfer among the pendant Ru-polypyridyl complexes occurs on the nanosecond timescale via Dexter hopping. By contrast, transfer from the n-conjugated polyfluorene backbone to the pendant Ru chromophores occurs within a few picoseconds via Forster coupling. The light harvesting polymers can be adsorbed onto mesoporous TiO2 and give rise to moderately efficient photocurrent generation. Time resolved spectroscopy reveals clear evidence of the light harvesting effect for the surface adsorbed polymers, with charge injection occurring on timescales ranging from a few picoseconds to 100 nanoseconds.
The tetradeutate complex \([\text{Ru(dpp)(pic)}_2]\text{Cl}_2\) (dpp = 2,9-di(pyrid-2'-yl)-1,10-phenanthroline and pic = 4-picoline) has been shown to be an effective water oxidation catalyst both in Ce(IV) and light-driven processes. Other tetradeutate ligands related to dpp have been incorporated into similar complexes and examined for activity. The synthesis of another tetradeutate ligand, 2-(pyrid-2'-yl)-8-(1''',10'''-phenanthrolin-2'''-yl)-quinoline (ppq), is reported and its use in a Ru(II)-based water oxidation system as well as a Co(II)-based water reduction system is described.
Metal-organic frameworks (MOFs) are coordination network materials that are composed of metal ions and organic molecules. MOFs have exceptionally high specific surface areas and chemically tunable structures. Due to their unique inorganic–organic hybrid nature and porous structures at the nanometer scale, it is expected that MOFs are rich in fundamental properties that promise revolutionary new device concepts. Research in the fields of MOFs is rapidly expanding into broader applications of 1D micro/nanostructures and 2D coatings into MOF-based devices.

Recently, we developed the first example of a novel and unique MOF-based 1D vertical micro/nanopillars on gold surface by using a facile surface-assisted method. One end of each micro/nanopillar is mechanically connected to the surface when the micro/nanopillars are fabricated. The uniqueness and advantage of the micro/nanopillar technique is that the structures are directly connected to the surface by being grown in place. Being porous, the MOF micro/nanopillars may have applications for unique photonics, surface catalysis, surface gas adsorption, purification, sensing devices etc.
Comparing the degradation of poly(2-oxazoline)s and polypeptoids with polyethylene glycol and other biomaterials

Juliane Ulbricht, Moritz Faust, Robert Luxenhofer, robert.luxenhofer@uni-wuerzburg.de. Functional Polymer Materials, Chair of Advanced Materials Synthesis, Department of Chemistry and Pharmacy, University Würzburg, Würzburg, Deutschland 97070, Germany

Poly(2-oxazoline)s and polypeptoids are similar in structure with an tertiary amide in every repeat unit. While the polypeptoids poly(L-proline) is known to be biodegradable, poly(2-oxazoline)s are considered non-degradable. In contrast, polysarcosine is discussed as biodegradable by some authors, but, to the best of our knowledge, no experimental evidence has been provided to support this statement.

The sensitivity of polyethylene glycol (PEG) against oxidative degradation is well known, yet very little information on the decomposition of PEG under biologically relevant oxidative stress can be found in the literature. Here, we present first evidence that PEG, poly(2-oxazoline)s, polypeptoids and other biopolymers are degradable by oxidative degradation under biologically relevant conditions.[1] Incubation with different reactive oxygen species (ROS) leads to a pronounced time and concentration dependent degradation of all polymers investigated. The oxidative degradation may not be relevant in the short-term usage of these polymers but mid- and long-term biodegradability in vivo appears possible.

oxidative degradation by ROS

References

161 - Peptoid-protein hybrids

Paul Levine, Timothy Craven, Kent Kirshenbaum, kent@nyu.edu. Department of Chemistry, New York University, New York, NY 10003, United States

Introduction of abiotic constituents into protein architectures can generate hybrid macromolecules that exhibit novel functions and enhanced pharmacological profiles. Chemical synthesis of such constructs can be achieved using chemoselective ligation protocols. We have elaborated a rapid and site-specific ligation strategy to bioconjugate synthetic oligomers, termed 'peptoids', to N-terminal serine or threonine residues of peptides and proteins, generating native amide linkages at the ligation site. Peptoids are composed of specific sequences of diverse N-substituted glycine monomers and have been shown to populate distinct secondary structures not readily accessible to polypeptides. Modifications of current expressed protein ligation techniques were implemented to generate synthetic variants of a therapeutic polypeptide. The future prospects of peptoid-protein hybrids for materials and biomedical applications will be evaluated.
Despite numerous advances in drug development approaches as well as understanding of biology of cancers, no perfect drug is developed to date. Nonspecific chemotherapies carry side effects and targeted therapies are expensive in addition to failures on larger patient populations. This is mainly because, most of the targets of these conventional drugs are 'protein' biomarkers and their expression levels are highly heterogeneous from patient to patient. This suggests that effective cancer treatments need to be either personalized or target universally expressing biomarkers beyond proteins. In addition, paucity of economical and biologically amenable molecular classes as drugs further worsens the problem. We are exploring peptoids as alternative class of economical and bio-compatible molecules. Peptoids are serum stable, non-immunogenic, cell permeable, easy to synthesize and can be optimized at will, and the cost of peptoid development is significantly lower than for small organic molecules, peptides and antibodies. Our approach is to develop variety of large and complex on-bead polypeptoid combinatorial libraries and screen them to identify potential lead compounds. We developed a unique on-bead two-color (OBTC) cell screen to directly identify most specific compounds targeting biomarkers on cancer cells. OBTC assay was used on two approaches: First we identified peptoids targeting protein biomarkers such as VEGR2, EGFR, Fibln-S broadly found on tumor microenvironment and validated those as antagonists both in vitro and in vivo. As an approach to overcome the protein biomarker heterogeneity, we applied our OBTC assay at an 'unabised' fashion and uniquely identified a lipid- phosphatidylserine (PS) binding peptoid. PS is universally found on the outer layer of tumor endothelium and on many cancer cells as opposed to normal cells. This peptoid also found to be cytotoxic on various tumor types such as lung, breast and prostate and not on normal cells, indicating a wider but tumor specific treatment method.
163 - Revisiting the enzymatic digestion of polypeptoids

Juliane Ulbricht, Juliane.Ulbricht@uni-wuerzburg.de, Fabian Wieghardt, Robert Luxenhofer. Department of Chemistry, Chair for Chemical Technology of Materials Synthesis, Functional Polymer Materials, University Würzburg, Wuerzburg, Bavaria 97070, Germany

Recently, polypeptoids as well as polyethylene glycol and poly(2-oxazoline)s have been shown to be susceptible to oxidative degradation by a system comprising hydrogen peroxide as well as cupric ions.\textsuperscript{[1]} By this means, highly reactive hydroxyl radicals are formed through Fenton-like reaction, inducing decomposition of the investigated polymers.

\textit{In vivo}, increased levels of oxidative species are referred to as oxidative stress and associated with various diseases,\textsuperscript{[2]} however, they are also connected with physiological processes like respiration and host defense. Although these findings are not considered to be of relevance for short-term usage of polypeptoids \textit{in vivo}, long-term stability may be affected by oxidative degradation. Furthermore, the possibility of enzymatic digestion of pseudo-polypeptides has to be taken into account. As reported by Sarid et al., proline iminopeptidase acts as an exopeptidase cleaving N-terminal proline from polyproline as well as other substrates.\textsuperscript{[3]} Thus, proline iminopeptidase may also be able to digest other N-substituted polypeptides like polysarcosine, which was investigated in the presented study.

This work was supported by the Fonds der Chemischen Industrie and the State of Bavaria.

1 Ulbricht J., Jordan R., Luxenhofer R. (2014), Biomaterials, accepted.
164 - Smart polymeric sensors based on poly(2-oxazolines)

Victor R. De la Rosa, Richard Hoogenboom, richard.hoogenboom@ugent.be. Supramolecular Chemistry Group, Department of Organic Chemistry, Ghent University, Ghent, Belgium

In this work, we will demonstrate the utilization of thermoresponsive poly(2-oxazoline)s as basis for smart polymeric sensors. This first part will deal with thermoresponsive copolymers based on 2-ethyl-2-oxazoline and 2-nonyl-2-oxazoline (see Figure). By shielding the hydrophobic nonyl side chains with supramolecular host-guest complexation with cyclodextrins, not only the phase transition temperature can be tuned but also large hysteresis (up to 40K) is observed. This hysteresis results from the formation of a meta-stable soluble state based on cyclodextrin host-guest complexation. When heating this solution above its phase transition temperature at 50 °C, the hydrophobic association of the free nonyl side chains prevents redissolution until the solution is cooled down to the original phase transition of the polymer without cyclodextrin, which is around 10 °C. Importantly, this large hysteresis window could be exploited as memory function for the thermal history of the solution.

In this second part of this contribution we will discuss the preparation of poly(2-oxazoline) decorated gold nanoparticles and their temperature and salt induced association behavior. This agglomeration of the nanoparticles is associated with a change in surface plasmon resonance and results in a color change from red to purple. Finally, this system will be demonstrated to function as AND logic gate with both temperature and salt concentration as input parameters.
During the past few years, in polymer science, great efforts have been made on a new generation of functional polymeric materials by design at the molecular level. Polypeptoids that combine the advantages of sequence-specific proteins and traditional synthetic polymers, perhaps provide the most convenient platform for achievement of precise architectures. We studied a series of chemically-defined diblock copolypeptoids containing a poly-\(N\)-2-(2-(2-methoxyethoxy)ethoxy)ethylglycine (pNte) block in combination with both a crystalline poly-\(N\)-decylglycine block (pNdc), and an amorphous poly-\(N\)-2-ethylhexylglycine block (pNeh)(Figure 1). A fixed length composition scan was performed for each diblock, where the main chain polymer length was fixed at 36 monomers, and the volume fraction of each block was systematically varied. Both block copolymers formed lamellar structures over an unexpectedly wide range of compositions. In the case of the pNdc-containing diblocks, the lamellar structure is driven by the crystallization of the pNdc block. Interestingly, the crystalline pNte-\(b\)-pNdc diblock copolymer consists of two crystalline lamellar phases, even though the pNte homopolymer is amorphous. In contrast, the same pNte block is amorphous in the pNte-\(b\)-pNeh diblock copolymer. We believe that in the crystalline diblock copolymer, the preorganization of the pNdc chains induces crystallization of pNte chains due to the nearly identical molecular volumes of the side chains. This study enhances our understanding of block copolymer phase behavior and crystallization, and demonstrates that sequence-specific polypeptoid materials are excellent candidates for studies on the effect of composition and sequence design on physical properties and self-assembly of block copolymers.
166 - Bioswitchable antimicrobial poly(2-methyloxazoline)s

Christian Krumm, christian.krumm@udo.edu, Joerg Christian Tiller. Department of Biochemical- and Chemical Engineering, TU Dortmund, Dortmund, Nordrhein-Westfalen 44227, Germany

Alternatives to commonly used biocides, which cause unpredictable long-term environmental problems, are required. A biocide which can be deactivated after its application would be a tremendous progress to reduce the spread of microbial resistances.

Here, biocidal Poly(2-methyloxazoline)s were prepared by introducing a biocidal and an antimicrobial inactive satellite group (SG). The SG was chemically modified and this revealed a loss in antimicrobial activity. This hydrolysis was proven by $^1$H-NMR-spectroscopy and ESI-MS and the reduction of activity was followed by determining the minimal inhibitory concentration of the polymer. The hydrolysis of the satellite group and though the reduction of antimicrobial activity, was also performed under physiological conditions by enzymatic catalysis.
167 - Straightforward post modification of poly(2-ethyl-2-oxazoline) by transamidation of side chain methyl ester groups

Maarten A Mees, maarten.mees@ugent.be, Richard Hoogenboom. Department of Organic chemistry supramolecular chemistry, Ugent, Ghent, Oost-Vlaanderen 9000, Belgium

Poly(2-alkyl-2-oxazoline)s (PAOx) are biocompatible pseudo-polypeptides that received significant interest for biomedical applications in recent years. This popularity of PAOx is also driven by the fact that its chemical reactivity and versatility is much higher compared to the gold standard in this field, poly(ethylene glycol) (PEG), while the biocompatibility and the stealth behaviour of PAOx and PEG are similar. The introduction of functionalities is crucial for further applications in a biomedical context. Here, we report a synthetic methodology to further expand the chemical versatility of PAOx based on a straightforward post-polymerization modification platform. At first, controlled partial hydrolysis of poly(2-ethyl-2-oxazoline) (PEtOx) is performed resulting in a copolymer of PEtOx and poly(ethylene imine) (PEI). Subsequently, side-chain methyl ester groups are introduced, via addition of various methyl ester containing electrophiles, including bromo acetate, methyl-chlorosuccinate and methoxycarbonyl ethyliso(thio)cyanate to the secondary amine groups of PEtOx-PEI. Alternatively, copolymerization of 2-methoxycarbonylethyl-2-oxazoline with PEtOx also led to similar copolymers with methyl ester groups in the side chains. The incorporated methyl ester groups are demonstrated to be versatile for further modification by direct transamidation with a wide variety of different amines as is demonstrated by introducing a range of side-chain functionalities including acid, amine, alcohol, hydrazide and propargyl groups.
168 - Commercialization of atom transfer radical polymerization (ATRP): Telechelic polyacrylate

Yoshiki Nakagawa, yoshiki_nakagawa@kn.keneka.co.jp, KANEKA CORPORATION, Japan

We commercialized Atom Transfer Radical Polymerization (ATRP) first in the world on a metric ton scale for development of telechelic polyacrylate. The telechelic polyacrylate has well-designed and well-controlled structure, which has crosslinkable end-functional group at both ends.
169 - Synthesis and characterization of controlled polymer architectures for reduced biofouling and enhanced biocompatibility of medical devices

Charles W Scales, cscales@its.jnj.com, Brent M Healy, Shivkumar Mahadevan, Zohra Fadli. Research and Development, Johnson & Johnson Vision Care, Inc., Jacksonville, FL 32256, United States

The development of materials which exhibit low bio-fouling (e.g. reduced uptake of certain lipids and proteins) is essential to enhance biocompatibility and in vivo performance of biomedical devices. In hydrogel-based medical devices, e.g. silicone hydrogel contact lenses, enhanced in vivo biocompatibility can be achieved by imbibing a polymeric wetting agent into the lens to reduce the uptake of certain lipids and proteins. Herein, we report the use of controlled radical polymerization (CRP), namely, reversible-addition fragmentation chain transfer (RAFT) polymerization, to synthesize novel classes of amphiphilic block copolymers and block copolymer nanogels comprising blocks of poly(dimethylsiloxane) (PDMS) and poly(N,N-dimethylacrylamide) (PDMA) or PDMS and poly(vinyl pyrrolidone) (PVP) for use as wetting agents with a well-known and marketed silicone-hydrogel contact lens material, senofilcon A. Copolymers were characterized via \(^1\)H NMR and size exclusion chromatography with multi-angle light scattering (SEC-MALS) and the performance of each copolymer composition was assessed via in vitro lipid and protein uptake assays of copolymer-treated lenses, demonstrating that both the copolymer molecular weight and architecture have a significant impact on in vitro protein and lipid uptake of senofilcon A.
Advanced microlithography photoresist technology and decreasing imaging wavelengths have enabled the semiconductor industry to fulfill the prediction by Intel's Gordon Moore ("Moore's Law") that chip circuit density will double approximately every 18 months. Critical feature sizes under 100 nm (650 C-C bond lengths) are being sought with the current generation of Deep Ultraviolet (DUV) photoresists imaged at 248 nm. In 2004, 90 nm circuit features were first commercialized with 193 nm (ArF) photoresists using methacrylate polymer systems. Recent advances in 193 nm photoresists including immersion lithography and double patterning enable resolution at or below 32 nm. Extreme Ultraviolet (EUV), E-Beam direct write and Directed Self Assembly (DSA) are being developed for next generation means to achieve single digit nm image features. It has been accepted in the industry that the polymer is one of the most important chemicals in the photoresist and that many important lithographic properties depend on polymer structure to be in specification and reproducible from lot to lot. To achieve and extend such extremely fine resolution, the industry is very actively seeking to understand how specific polymer properties impact lithographic performance. DuPont Electronic Polymers, LP is working closely with its customers and industry consortia to enable this effort.

Currently, RAFT (Reversible Addition Fragmentation Chain Transfer) technology is being used to produce polymers with low polydispersity and high compositional uniformity for a variety of photoresist applications as well as to produce block copolymers in support of DSA development. RAFT polymerization enables the production of these materials provided that careful process monitoring and compositional homogeneity measurement systems are employed. It is uniquely suited to construction of multiblocks with components of widely divergent surface energies and functionality. In view of required levels of construct defectivity, polymer compositional uniformity and reproducibility is under intense scrutiny. Production processes and metrologies are being developed to provide control over long-range order, registered pattern geometries, and pattern perfection commensurate with lithographic needs. Industry R&D programs on Line Edge Roughness (LER) are being supported with polymers made using RAFT technology. More recently, high chi block copolymers synthesized using RAFT technology have been developed specifically for < 10 nm DSA applications. Unique partially fluorinated polymer systems are among those being tested to enable smaller and smaller features using this emerging technology.

This paper will review a brief history of 248 nm and 193 polymer development as well as the current status of RAFT technology used for 193 nm photoresists and DSA applications.
171 - Present and future uses of controlled polymerization techniques in the coatings industry

Kurt G Olson, kgolson@ppg.com, Department of polymer synthesis, PPG Industries, Allison Park, PA 15101, United States

The large scale industrial use of controlled radical polymerization techniques has been elusive to date, but the promise of intelligent surfaces, controlled morphologies, and other important advances in a number of scientific disciplines would suggest that the current state will change significantly in the not too distant future. Commercially successful coatings require control of coating surface energy, rheology, pigment dispersion, layer interactions, adhesion, and morphology. The current uses of controlled radical techniques in various coatings applications will be given, as well as predictions of future impacts that these techniques will have on the coatings industry.

Several reasons for the slow adoption of CRP for industrial applications will be given and possible ways to overcome these paradigms will be discussed. Manufacturing hurdles and mitigation strategies will be considered.

Nanopigments stabilized with a CRP produced polymer is one commercial application to be discussed.

Monday, August 11, 2014 02:15 PM
Controlled Radical Polymerization (01:00 PM - 05:30 PM)
Location: Hilton San Francisco Union Square
Room: Continental Ballroom 4
172 - RAFT: The development of a polymer platform technology for national development and international impact

Gregory W Simpson, greg.simpson@csiro.au, Megan Fisher. Materials Science and Engineering, CSIRO, Clayton, Victoria 3158, Australia

The invention of the RAFT technology by Rizzardo and co-workers in 1998 has transformed the field of radical polymerisation, making available a new process for the synthesis of a wide range of polymers with potential commercial application in diverse fields – from industrial polymers to medical applications, from commodity chemicals to speciality additives.

The technology was developed by CSIRO, Australia's largest publically funded research agency, in partnership with DuPont, one of the world's leading chemical companies. There are significant challenges and issues in commercialising platform technologies such as RAFT where the interests of companies must be balanced with need to deliver benefit to the nation in return for the public investment in CSIRO.
Lubrizol Corporation recently commercialized Asteric® star polymers as rheology modifier for lubricant oil, based on RAFT chemistry invented by CSIRO. The polymers are sold in thousands of tons annually and are well received in the market place. The RAFT agent used in the manufacture process is a novel trithiocarbonate developed at Lubrizol. The Ketoform Reaction, which is a general method for the synthesis of hindered molecules, enables us to make hindered amines, hindered phenols and hindered imines, etc. in high yields. When the methodology is extended to RAFT agents, hindered and mono- and di-carboxyl-terminated trithiocarbonates, dithiocarbamates and xanthates can be obtained practically in large quantities.

These functional RAFT agents have different reactivity toward controlled polymerization and also in esterification of the the carboxyl groups. Although trithiocarbonate as a class is more active as RAFT agent, the carboxyl-terminated dithiocarbamated can be esterified easily with most alcohols. Thus it provides the latter with another route to make unique structures such as block copolymers through esterication, followed by polymerization.

Besides the commercial rheology modifier, we have made other unique polymer compositions for potential industrial applications. Examples include telechelic di-carboxyl-terminated poly(meth)acrylates for toughening epoxy resins, poly(PDMS0-block-pol(meth)acrylate-block-poly(PDMS) as hair spray and polyurethane-block-poly(meth)acrylate-polyurethane dispersion for industrial coatings.
Soft colloid polymeric nanoparticles have many potential applications such as viscosity modifiers, porogens for the generation of porous thin films, drug delivery vehicles, biomedical imaging reagents, antimicrobial agents, nanoreactors, multifunctional reagents for biomedical applications, polymeric coordinating materials for metallic nanoparticles, catalysts for inorganic shell deposition, particulate coating media etc. We have been studying nanogel core-shell polymers for some time using an arm first bottom up approach to synthesis where the arms are generated by controlled polymerization techniques including anionic, controlled free radical and ring opening polymerization using organic catalysts. Using functionalized initiators and orthogonal polymerization techniques, we have produced a variety of multifunctional star polymers with various functionality, controlled molecular weights and low polydispersities. The size of these particles typically ranges from 10-50 nm and it is difficult to make larger particles by the bottom up procedure. Since larger particles were needed for biomedical applications, alternate routes have been explored. We have found that larger structures with similar molecular topologies can be prepared by core crosslinking of assembled block copolymer micelles. The linear components with graded functionality can be prepared using controlled radical polymerization techniques including ATRP and RAFT. I will describe the synthesis, characterization and potential applications of nanogel core crosslinked polymeric nanoparticles.
175 - Block copolymer based acrylics for waterborne coating applications

Mike Schellekens, mike.schellekens@dsm.com, Jens de Bont, Ad Overbeek. DSM Coating Resins, Waalwijk, The Netherlands

In the coatings industry a growing need exists for cost-effective and sustainable waterborne coating binders. These binders are used in a broad variety of end markets where clear trends are found towards enhanced control over polymer microstructure to effectively steer material properties such as coating adhesion. Free-radical emulsion polymerization has for many years been the most widely used industrial process for large scale preparation of waterborne acrylics but lacks the desired level of polymerization control. Many new opportunities in polymer synthesis have emerged with the development of controlled radical polymerization (CRP) technologies. The fundamentals of CRP are well established but the main challenge remains the translation to commercial applications. Implementation of any CRP technology on industrial scale requires consideration of key aspects including ease of implementation in existing processes and costs related to the controlling agent, licensing and post-polymerization purification. This paper highlights the industrial relevance of reversible addition-fragmentation chain transfer (RAFT) polymerization for the development of block copolymer based waterborne acrylic binders offering unique coating performance. The approach relies on the synthesis of water-dispersible block copolymers and their subsequent use as highly effective particle stabilizers in an emulsion polymerization process to produce block copolymer stabilized waterborne binders as shown in Figure 1. Examples will be presented demonstrating that the unique level of control over functional group incorporation effectively allows steering of macroscopic properties such as coating adhesion.

Figure 1. Approach towards block copolymer based waterborne acrylics

Monday, August 11, 2014 04:15 PM
Controlled Radical Polymerization (01:00 PM - 05:30 PM)
Location: Hilton San Francisco Union Square
Room: Continental Ballroom 4
176 - Application of ATRP to the synthesis of nonporous chromatographic media optimized for the separation of proteins

Christopher Pohl, Chris.Pohl@thermofisher.com, Department of R&D, Thermo Fisher Scientific, Sunnyvale, California 94085, United States

The synthetic method used in the preparation of commercially available stationary phases for chromatography is generally a trade secret. As such, the extent to which ATRP is used in the preparation of such stationary phases is not generally known. Even so, we believe that our lab leads the world in the use of ATRP as a synthetic tool for the preparation of engineered stationary phases on nonporous styrenic substrates. Currently we utilize ATRP in the synthesis of four different commercially available stationary phases and we are in the process of developing a fifth stationary phase using this technology. ATRP provides considerable advantages over conventional radical grafting techniques, especially in regard to control of the length of polymer chains attached to the surface of nonporous materials. ATRP also allows for the precision control of three-dimensional architecture required for high resolution separation of intact proteins. I will describe the range of synthetic tools used in the preparation of such materials and demonstrate the advantages that ATRP provides in the preparation of high resolution chromatographic media.
Recent innovation and commercialization in controlled radical polymerization (CRP)

Sebastian T Grajales, sebastian.grajales@sial.com, Yong Zhang, Bryce Nelson. Aldrich Materials Science, Sigma-Aldrich, Inc., Milwaukee, WI 53209, United States

Controlled radical polymerization (CRP) technology enables the production of polymers with a controlled molecular weight, narrow distribution of chain lengths, and highly specific architectures. Polymers generated through controlled radical polymerization (CRP) are broadly used in applications such as biomedical, energy, and electronics materials. The production and commercial availability of RAFT agents is one set of examples of how Aldrich Materials Science is enabling the wider use of RAFT technology.

Aldrich has made a variety of monomers and polymerization tools available for researchers in order to facilitate the greater use of controlled radical polymerization. These efforts help to increase the potential for industrial adoption of CRP techniques in a number of application areas. For example, the ability to produce RAFT agents at appropriate cost still limits widespread industrial adoption. This talk will provide a background on major CRP techniques, the commercially available CRP reagents, and the latest efforts and challenges of scale-up of CRP tools for use in various markets.
178 - Surface and interface engineering with polymer brushes

Harm-Anton Klok, harm-anton.klok@epfl.ch, Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux, Laboratoire des Polymères, Lausanne, Switzerland

Thin polymer coatings are of great importance to control the interactions of synthetic materials with other materials (lubrication, wear), the environment (corrosion) as well as biology (marine antifouling). Modern polymer science offers unprecedented opportunities to chemically engineer the properties of surfaces and interfaces. This presentation will discuss three aspects. The first part of the presentation will introduce modern controlled/“living” radical polymerization techniques and “polymer brushes” (chain-end tethered monomolecular assemblies of densely grafted polymer chains) and present the scope and possibilities of these approaches to chemically modify surfaces and interfaces. The second part of the presentation will address the need for accurate surface chemical characterization and the challenges related to the precise determination of the localization and distribution of functional groups in thin polymer films. The presentation will end with 3 brief showcases that illustrate the use of modern polymer science tools to develop ultrathin polymer films that possess sensory properties, which can be used to control fluid flow or to template the controlled growth of metallic or non-metallic inorganic films on complex, 3D structured substrates.
We designed a class of helical, cationic charged polypeptides via the ring-opening polymerization of vinyl benzyl glutamic acid N-carboxyanhydrides. These materials have unusual helical stability and display excellent cell penetrating property, outperforming TAT peptide. By controlling the chemical, morphological and self-assembly structures of these side chain charged, helical polypeptides, we identified a few materials that showed excellent gene and siRNA delivery efficiency in vitro and in vivo.
180 - Sugar-coated polymer synthesis: From sustainable materials to selective drug delivery

Theresa M. Reineke, treineke@umn.edu, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, United States

The increased demand and environmental impact of petroleum-based chemical feedstocks have spurred a large research push in the area of renewably sourced polymers. Bio-based feedstocks such as carbohydrates offer great promise for materials development due to their rich functionality (high heteroatom content and stereochemistry) and renewable production on an impressive scale. In addition, carbohydrates offer unique properties that are of high interest for biological applications such as the development of selective drug and nucleic acid delivery vehicles. Herein, we present the design and development of a variety of materials derived from carbohydrates and their application in the development of sustainable plastics, thermosets, and drug delivery vehicles. For example, new dimethacrylate feedstocks have been synthesized from glucarodilactone and mannarodilactone (derived from glucose and mannose) that contain rigid core structures. Thermal initiated free radical polymerization of these substrates formed highly cross-linked thermoset materials with mechanical properties comparable to those reported for commercially available stiff poly(dimethacrylates). ADMET polymerization has been used to create linear polymers with interesting and tunable tensile properties. We show that materials derived from these structures, while stable in aqueous neutral and acidic conditions, rapidly degrade in aqueous basic conditions, offering a potential triggered degradation pathway. Further studies exploring the utility of these and related monomers and polymers in clear film, monodisperse microgel particle formation, as well as drug and nucleic acid delivery will be discussed to support this feedstock platform for a variety of sustainable applications.
181 - Bioresponsive degradable polymeric nanocarriers for active intracellular drug and protein delivery

Fenghua Meng, Chao Deng, Ru Cheng, Jan Feijen, Zhiyuan Zhong, zyzhong@suda.edu.cn. College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, China

In the past decade, degradable polymeric nanocarriers such as micelles, polymersomes and nanoparticles have emerged as one of the most promising platforms for targeted and controlled drug and protein delivery. These nanoscale polymeric drug formulations have several advantages including decreased side effects, better pharmacological profiles, and/or improved drug tolerance over the current clinical approaches. It should be noted, however, that these nano drug formulations are plagued with slow and deficient intracellular drug and protein release, which has led to low therapeutic efficacy. In recent years, significant effort has been directed to the development of bioresponsive nanocarriers that are adequately stable under extracellular conditions while rapidly release drugs inside the target cancer cells. In particular, pH and reduction-sensitive nanosystems have received the most attention due to existence of a lower pH in the endo/lysosomal compartments and a high redox potential in the cytosol and cell nucleus. In this presentation, I will discuss about our recent work on design and development of pH- or reduction-sensitive degradable micelles, polymersomes and nanoparticles for active intracellular delivery of poorly soluble anti-cancer drugs, hydrophilic anti-cancer drugs, or proteins. Moreover, I will also present several novel designs of reduction and pH dual-bioresponsive degradable nanocarriers for precision intracellular drug or protein delivery.
Copper mediated living polymerisation remains one of the most widely applied and useful methods of controlling vinyl polymerization. Thus, a greater understanding and development of very well controlled Cu-mediated polymerization in water and other aqueous media is required. All existing protocols are encumbered by important, and often overlooked, competing reactions that can reduce the polymerisation control, broadening PDi values which can generally fall between 1.2->1.4. An observation first seen by Perrier in 2000 has finally been understood and exploited. The prior disproportionation of CuBr/Me₆TREN in water is been exploited for the SET-LRP of hydrophilic monomers. Reactions proceed faster and with no induction periods when compared to SET-LRP mediated by commercial Cu(0) sources without any compromise in polymerization control. Thorough analysis of model and reaction mixtures confirmed complete disproportionation of CuBr/Me₆TREN in the water system. Attempted polymerization with the separated products of disproportionation revealed the synergistic character of the products of the disproportionation reaction.
183 - High-performance thermoplastic elastomers from glucose

Marc A. Hillmyer, hillmyer@umn.edu, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, United States

Sustainable block polymers hold much promise as tomorrow's advanced macromolecular materials. In this presentation I will describe our work aimed at the development of next-generation polymers that (i) can be produced from renewable resources on large scale, (ii) can be incorporated in block polymers with precision control over molar mass and composition, and (iii) exhibit properties that can outperform traditional petroleum derived materials from a combined environmental and mechanical property perspective. Key to the success of this strategy was the development of a biosynthetic pathway to a methyl substituted valerolactone and its subsequent controlled incorporation in triblock polymers. This comprehensive strategy offers an economically viable approach to both sustainable elastomers and plastics for a broad range of applications.
184 - Self-assembly of macromolecular ruthenium drugs into micelles and peptide tubes

Bianca Blunden¹, Sebastien Perrier², Martina H. Stenzel¹, m.stenzel@unsw.edu.au. (1) Centre for Advanced Macromolecular Design, University of New South Wales, Sydney, NSW 2052, Australia, (2) Warwick University, Coventry, CV4 7AL, United Kingdom

Ruthenium complexes are a promising avenue to better, and more selective, chemotherapeutics. They have been shown to have less systemic toxicity and to be more selective towards metastatic cancer. Conjugations of ruthenium complexes to polymers can potentially further enhance the therapeutic effect. We focused our investigations on two ruthenium drugs, coined RAPTA-C and NAMI-A. To enhance the delivery of these drugs, we designed an amphiphilic block copolymer capable of self-assembling into polymeric micelles. The formation of drug loaded micelles enhanced the cellular uptake and biological activity of RAPTA-C [1] and NAMI-A [2] loaded micelles. Furthermore, peptide-polymer conjugates that could self-assemble into polymeric nanotubes were identified as further suitable carriers.
185 - Molecular Lego®s for macromolecular engineering

Sebastien Perrier, s.perrier@warwick.ac.uk, Department of Chemistry, University of Warwick, Coventry, United Kingdom and Faculty of Pharmacy, Monash University, Melbourne, Victoria VIC 3052, Australia

This lecture will present our latest results in the design of macromolecules of controlled functionality and architecture, to engineer nanostructured materials. The combination of precision polymer chemistry, organic synthesis and supramolecular chemistry permits us to design building blocks that can be assembled into materials of controlled structures. The lecture will focus on the design of functional polymeric nanoparticles of varying shapes and sizes, and their applications in the medical and materials fields.

References


Gody, G.; Maschmeyer, T.; Zetterlund, P.B.; Perrier, S. Rapid and Quantitative One-Pot Synthesis of Sequence-Controlled Polymers by Radical Polymerization, Nat. Commun., 2013, 4:2505 DOI: 10.1038/ncomms3505


Dehn, S.; Castelletto, V. ; Hamley, I. W.; Perrier, S. Altering Peptide Fibrillisation by Polymer Conjugation Biomacromolecules, 2012, 13 (9), 2739–2747


186 - Accelerating organic growth by leveraging the lessons from the Tritan™ innovation

Christopher M. Killian, ckillian@eastman.com, Eastman Chemical Company, Kingsport, TN 37662, United States

The successful commercialization of the Tritan™ family of copolyesters represents a major achievement for Eastman Chemical Company, for the polymer industry, and for consumers. This new family of polymers, commercialized in 2007, has opened up a sizeable new addressable market for Eastman's Specialty Plastics business and has exhibited the highest growth rate of any modern engineering polymer introduced in the last 3 decades. The product's success is a testimony to the creativity, expertise, and dedication of hundreds of Eastman team members working together to bring this new product to a competitive market. Today, Tritan is used for diverse applications in several markets including sports water bottles, small appliances and consumer housewares, as well as medical devices and medical packaging. This paper will focus on lessons learned from the Tritan™ innovation and how we might leverage those lessons as we drive organic growth through innovation.

Monday, August 11, 2014 01:05 PM
Industrial Innovations in Polymer Chemistry (01:00 PM - 05:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
187 - Adapting computational methods to polymer research and development at Boeing

Samuel J Tucker, samuel.j.tucker@boeing.com, Polymer Science, Synthesis, and Simulation, Boeing Research & Technology, Seattle, WA 98108, United States

Since 2003, Boeing Research and Technology has been using computational methods such as Quantum Mechanics, Molecular Dynamics, Monte Carlo, Meso-level simulations, and Informatics techniques to increase speed and decrease cost necessary to 1) troubleshoot materials-based problems affecting manufacturing and service of Boeing products and 2) introduce new materials into our manufacturing processes and aerospace products. The majority of this simulation work has been focused on polymers due to their ubiquitous use across aerospace products including composites, interiors, adhesives, paints, coatings, sealants, and hydraulic fluids. This talk will give a number of examples of how computational tools based on polymer physics are helping troubleshoot emergent manufacturing and service problems and direct new polymer research.
WITHDRAWN

188 - WITHDRAWN
This submission will describe the application of Quantum Dot Films in Liquid Crystal Displays (LCD). Quantum Dots (QD) are nanocrystals of semiconductor material that exhibit unique emission properties. Specifically, the excitons are confined with the QD, and therefore the size of the dot determines the energy level of the emission. In fluorescent applications, the frequency of emitted light increases as the size of the quantum dot decreases, allowing the emission to be highly tunable. Based on the tunability and the narrow emission spectra, QDs have been described for use in LCD’s to improve the color gamut.

A color LCD is lit by conventional white LEDs that are color filtered to produce red, green, and blue pixels. However by switching to a blue-emitting LED, a portion of the blue light can be converted into green and red light by the quantum dots. This produces a white backlight for an LCD panel which can provide improved color gamut for the display.

One drawback of QDs is their susceptibility to oxidization and hydrolysis. To maintain their high fluorescence quantum yield, the QDs must be maintained in an air free environment. Therefore to make a commercial LCD application possible, a delivery format that maintains an air free environment and can be easily handled is required. This presentation will explore the application and the polymer properties required to bring this technology to commercial success.
Through varied stereo chemistry, additive formulation and processing, a great variety of structures and properties can be optimized, enabling poly(lactic acid) to be competitive for broad industrial uses. Meeting the high performance materials needs of industry today within both commodity and specialty markets will be discussed. Secondly, now in its first generation of manufacturing technology, the NatureWorks vision for the future direction of feedstock diversity and price competitiveness will be outlined.
Amino acid bearing degradable polyesteramides (PEA) are the next stage of evolution in degradable polymers from aliphatic polyesters to nitrogen bearing polymers such as polyurethanes, polyester amides and polyureas. The pursuit of these changes has been to achieve better control over biocompatibility, degradation and release properties for medical and pharmaceutical applications. Incorporation of amino acid-based building blocks offers not only metabolizable units, but also reactive sites that allow further modification of the polymer to tailor physicochemical properties, tune cellular response and degradation.

PEAs are based on α-amino acids, aliphatic dicarboxylic acids and aliphatic α-ω diols. Among this class of polymers it is the AA-BB hetero-chain polymers that offer the greatest versatility in terms of molecular level design to tailor drug release properties.

Schematic representation of the amino acid based biodegradable polyesteramides for drug delivery and applications as coatings, injectable microspheres and fibrils

These PEAs allow with minimal chemical modification the tailoring of degradation to be either predominantly enzymatic or hydrolytic. Furthermore these polymers degrade without a significant lowering of pH an effect known to aggravate inflammation and foreign body response. In this lecture we will describe how the degradation characteristics are tailored, elaborate on the degradation mechanism and breakdown products as well as present in vitro – in-vivo correlations.

The biocompatibility of these materials and their use as coatings, microparticles and fibres will be presented in applications such as a drug eluting stent where these materials are in a clinical trial and as injectable formulations for osteoarthritis in an orthopedic setting and for treatment of glaucoma in an ocular setting.

References


192 - Role of a polymer scientist at Google? Polymers in advanced technologies

Jeffrey Linhardt\textsuperscript{1}, jglinhardt@google.com, Jay Kunzler\textsuperscript{2}. (1) GoogleX, Google, Mountain View, CA 94043, United States, (2) Kunzler Biomedical, Canandaigua, NY 14424, United States

Polymers have played a ubiquitous role in vision care and medical diagnostics. After the commercialization of the HEMA based soft contact lens by Bausch & Lomb in 1971, decades of research have led to a wide variety of lens materials. This talk will cover the technical challenges that were overcome to produce the highest water content contact lens on the market as well as look at the challenges to producing continuous wear SiHy lenses. In addition, research on several of the world’s first diagnostic lenses will be reviewed with an outlook of what the future holds for contact lenses and diagnostics.

Monday, August 11, 2014 04:25 PM
Industrial Innovations in Polymer Chemistry (01:00 PM - 05:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
Motivated by the need for peptide synthetic methods that would be readily scalable that could provide multi-pound peptide quantities at costs that would allow their use in a wide range of performance materials, our laboratory is exploring protease-catalyzed oligopeptide synthetic routes from amino acid (AA) ethyl ester (OEt) monomers. Although proteases have been successfully used to prepare a range of homo-oligopeptides in aqueous media, problems arise in using the protease approach for co-oligopeptides where sequence control is desired. For example, co-oligomerizations of L-leucine ethyl ester (L-Et-L) and L-glutamic acid diethyl ester (L-Et$_2$-E) catalyzed by different proteases all cases random sequence co-oligopeptides. As a first target, we selected the synthesis of silk inspired (AG)$_x$ sequences. Indeed, even short (AG)$_x$(e.g. $x = 2$) sequences installed in materials as side or main chain groups provide powerful drivers of self-assembly. First, AG-OEt was prepared by standard chemical coupling. Then, AG-OEt was converted by papain-catalysis in 30 s to (AG)$_x$ (80%-yield, $x = 9.4$). Alpha-chymotrypsin catalyzed oligomerization of the "dipeptide lego" KL-ethyl ester (OEt) in aqueous media triggers a rapid sol–gel transition due to formation of alternating (KL)$_x$. Mixed chain oligomers, at alkaline pH, self-assemble into beta-sheets as shown in figure 1. Thereafter, intermolecular backbone hydrogen bonding between peptides causes formation of physically entangled nanofibrillar networks. Finally, this paper will discuss opportunities where random sequenced oligopeptides are useful in bio-based materials applications.
Fatty acid-based polyesters and amphiphilic block copolymers thereof: Compatibilizers for polyethylene-based polymer blends

Rob Duchateau\textsuperscript{1,3}, R.Duchateau@tue.nl, Lidia Jasinska-Walc\textsuperscript{2,3}, Miloud Bouyahyi\textsuperscript{3}, Mark P. F. pepels\textsuperscript{1}. (1) Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands, (2) Department of Polymer Technology, Gdansk University of Technology, Gdansk, Poland, (3) Technology & Innovation, SABIC Europe B.V., Geleen, The Netherlands

Polyethylene is one of the most common and versatile plastic materials in our daily life. However, there are several challenges for polyethylene. Polyethylene is non-degradable, causing major environmental problems in places where waste collection is impossible, for example in the marine environment. While polyethylene has ideal properties for many applications, it is notoriously difficult to modify in a controlled manner because of its inert chemical structure and the sensitivity of Ziegler-Natta catalysts towards functional groups. This creates challenges in areas where adhesion or polymer blending is required.

A new class of polymers with the potential to address these challenges are fatty acid-based polyesters, which can be produced by polycondensation of w-hydroxy fatty acids or by ring-opening polymerization of the corresponding macrolactones.\textsuperscript{1,2} As a consequence of the large number of CH\textsubscript{2}-groups between the ester functionalities, the properties of these polymers resemble those of polyethylene.\textsuperscript{3} The presence of labile ester bonds implies degradability under conditions found in the environment and in recycling processes.

The topic of the current contribution is the marriage of PE-like fatty acid-based polyesters with polymers that are fundamentally different in nature. Based on the concept that such polyesters are miscible with polyethylenes, synthesis of their linear and branched block copolymers via catalytic ring-opening polymerization of macrolactones is relatively easy and ensures control over their molecular weight and molecular weight distribution as well as polymer composition, microstructure and polarity.

We will demonstrate different novel strategies to produce amphiphilic block copolymers by means of catalytic living and immortal ring-opening polymerization. Blending experiments with polyethylenes and polar polymers were successful and will also be discussed.


Monday, August 11, 2014 01:55 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (01:30 PM - 04:40 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
ω-Pentadecalactone (PDL) is a renewable monomer that can produce materials with properties similar to low-density poly(ethylene) as a consequence of a highly hydrophobic, long carbon chain backbone. Most ring-opening polymerizations rely on the positive enthalpy of ring-breaking to drive polymerization, however macrolactones such as PDL do not exhibit high ring-strains and are entropically-driven polymerizations. Catalysts that have been demonstrated to polymerize PDL require rigorously dry and often inert atmospheres in order to avoid initiation from water and ester hydolysis, that lead to large dispersities and low end-group fidelity. Herein, a relatively inexpensive magnesium-based catalyst is demonstrated for the 'immortal' ring-opening polymerization (ROP) of PDL. Successful polymerizations were shown under low catalyst loadings (0.5 mol% with regards to monomer). Furthermore, when reagents were not dried prior to use and ROP conducted under non-inert atmosphere, catalyst deactivation was not observed and polymerization still occurred. Materials produced through this 'benchtop' method displayed no side reactions as a consequence of the presence of water and displayed comparable dispersities and molecular weights to polymers produced in dry, inert conditions. Other solvents and bulk conditions were also shown to be effective in the production of poly(ω-pentadecalactone). In addition to PDL, a range of other lactones were shown to polymerize 'immortally' through use of this catalyst.
Polylactic acid (PLA) is a high-modulus, high-strength polyester derived from renewable resources, and thus serves as a promising alternative for ubiquitous polymers from petroleum feedstocks. However, PLA often fails as a drop-in replacement for its petrochemical-derived counterparts, owing to its brittleness, low thermal tolerance, hydrolytic instability, etc. Rational chemical modification of PLA is a promising approach to impart favorable properties into the polymer, but this is often challenging due to PLA’s lack of synthetic handles and adverse lability in the presence of many useful reagents. Direct and facile approaches to chemical modification of PLA’s monomer, lactide, are presented, which allows for an abundance of chemical moieties to be incorporated directly into the PLA backbone. The resulting modifications of PLA with functional groups and/or grafted polymers permits desired material properties to be engineered directly into PLA. Also, in addition to simply obtaining “functionalized PLA,” lactide is chemically modified to yield fundamentally new polylactide structures through alternate polymerization paradigms (i.e., polylactide formed through chemistry other than typical the ring-opening polymerization) with unique and tunable properties.
A family of renewable macrobis- and trisphenols containing bio-based polyols and ferulic acid, derived respectively from plant polysaccharides and lignocellulose, was prepared through a chemo-enzymatic process under mild conditions. The lipase-catalyzed condensation step can be conducted in bulk as well as in solvent and leads to high purity grade macromonomers in high to excellent yields.

These bio-based macrobisphenols were then used as macromonomers for the preparation of (1) alternating aliphatic/aromatic copolymers, (2) aliphatic/aromatic polyurethanes, and (3) linear homogeneous phenolic homo-oligomers through an oxidase-mediated aryl-aryl coupling.

The newly obtained aliphatic/aromatic homo- and copolymers were characterized by GPC, thermal (DSC) and thermogravimetric analyses (TGA). These analyses revealed not only good thermal stabilities but also a broad range of accessible glass transition temperatures ($T_g$).
198 - Marine-degradable polylactic acid

**Ryan T Martin**, rtmartin@floridasustainables.com, Ludmila P Carmargo, Stephen A Miller. Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

In a future less reliant on fossil fuels, polymeric materials must be realized which, along with being economically advantageous, come from sustainable sources, are at least as useful as fossil fuel plastics, and, when their useful lifetimes are up, be amenable to returning to biological and geological life cycles in reasonable timeframes. In other words, plastics of the future must have a green birth, an effective lifetime, and a green death.

The oxa-lactone 1,3-dioxolan-4-one was prepared from glycolic acid and paraformaldehyde, which in turn can be made from georenewable small molecules such as methanol, carbon monoxide, and formaldehyde. Ring-opening polymerization (ROP) of 1,3-dioxolan-4-one can be accomplished in modest yields using tin octoate/benzyl alcohol co-initiator system affording crystalline, insoluble materials. Melting temperatures of these homopolymers range from 143-217 °C, depending on initiator concentration.

Though of interest as homopolymers, perhaps more commercially attractive is the use of esteracetals as comonomers. When a small amount (app. 4%) of dioxolanone is incorporated in the ROP of lactide, the resulting modified polylactic acid (poly(L-lactide-co-1,3-dioxolan-4-one)) exhibits a small increase in glass transition temperature (a rarity in copolymerizations), while simultaneously enhancing the degradation profile of PLA by around 100-fold.

Utilizing this approach to modifying polyesters can create highly attractive and cost-effective candidates for either enhancing or replacing existing thermoplastic materials coming from non-renewable sources.
199 - Reversible lamellar thickening accompanied with stress induced reversible crystal transition in poly(butylene succinate)

Guoming Liu, Dujin Wang, djwang@iccas.ac.cn. Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

Semi-crystalline polymers, with typical lamellar structure built from alternatively packed crystalline layers and amorphous layers, exhibit a complex behavior during plastic deformation. In general, an isotropic polycrystalline structure gradually transforms to a highly oriented fibrillar structure with the chain axis preferentially aligned along the drawn direction during stretching. It is generally believed that the structure of polymer fibril is very stable. Only inter-fibrillar slip proceeds during further deformation. For polymers with stress induced crystal transition, some open questions still need to be answered, such as on which stage of plastic deformation does the $\alpha-\beta$ transition take place, and more importantly, what happens on the lamellar structure during crystal transition.

In present talk, crystal transition was observed during tensile deformation of poly(butylene succinate) (PBS). An increase of long period was identified during stretching. The step-cycle deformation measurement showed that the long period ($L$) reversibly increased under stress and decreased upon removing stress. The contribution of crystalline layer thickness (lamellar thickness) and amorphous layer thickness to the long spacing was discriminated by correlation function analysis. The variation of the amorphous layer thickness was partially recoverable while the variation of lamellar thickness was nearly fully recoverable. The reversible lamellar thickening was shown to mainly stem from the reversible crystal transition: the repeating length in chain direction in the $\beta$ crystal is 9% longer than that in $\alpha$ form due to the conformation change. Reversible lamellar thickening mechanism was also confirmed in another polymer (polyethylene succinate, PES).

Monday, August 11, 2014 04:00 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (01:30 PM - 04:40 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
The melt polymerization of diglycerol with anhydrides was investigated as a method to provide a high degree of bio-based content, low E factors, and degradable polyesters. This approach satisfied a number of green chemistry principles. For instance, Principle 1 (reduce waste), Principle 2 (atom economy), Principle 4 (less hazardous chemical syntheses), Principle 7 (use of renewable feedstocks), Principle 9 (catalysis), and Principle 10 (design for degradation) were addressed in the synthetic design.
A new architecture, [Ir(phtpy)(ppy)Cl]⁺, for luminescent Ir(III) complexes with diverse applications is explored. Straightforward modification of all three ligand sites in the new architecture has been achieved, and the geometric arrangement of the ligands is unambiguously assigned via X-ray crystallography. The rich electrochemistry of the complexes is presented via cyclic voltammetry and shows that ligand modification affords control of electrochemical behavior and electronic structure. Effects of ligand tuning are also shown in solution-based photophysical measurements. The three-ligand architecture allows the design of luminescent coordination polymers from these tailored monomers. The electronic coupling between the monomeric units can be controlled synthetically. The application of these materials in solar energy conversion, electrochromic devices, oxygen sensors, etc. is highlighted.
The efficient conversion of light into electrochemical energy constitutes a contemporary challenging task. Besides the primary charge separation event after excitation, the cumulative charge transport and the prevention of recombination processes are of key importance. Molecular photo- and/or redox-active units have been studied in a multitude of dyad and triad model systems and demonstrated their versatility to undergo efficient light-induced charge separation. However, the alignment within larger molecular assemblies sets a significant synthetic challenge. Meyer and colleagues demonstrated the efficient energy transfer among embedded Ruthenium-complexes within such assemblies,[1] and recently reported the chain-end decoration with an electron acceptor.[2] Following the same principle, modern polymerization techniques were employed to assemble the electro-chemically active units, e.g. donors (triarylamine, TARAs)[3] or acceptors (naphthalene diimides, NDIs) along a polymer’s backbone, which may further enables to collect the charges within the domains.

In this contribution, the synthesis of selected donor- or acceptor-polymers with and without an terminally attached ruthenium sensitizer is presented, complemented by (time-reesolved) spectroscopy and electrochemical analyses. The results of a systematic bimolecular quenching study showed the lifetime enhancement of the fully charge-separated state by three orders of magnitude in comparison to its low molecular counterparts. In addition, the comparison of emission and transient absorption data shows only marginal recombination within the encounter complex, demonstrating the possibility to achieve long-lived charge-separation within a suitable sensititizer-polymer combination.

Ru(II) polyimine complexes have been widely studied as photosensitizers due to their intense metal-to-ligand charge transfer (MLCT) transition. In contrast, their abundant and environmentally benign congeners, Fe(II), have received little attention. Such a discrepancy lies in the fact that the energy splitting between the $t_{2g}$ and $e_g$ orbitals in Fe(II) is much less than that in Ru(II) when ligated identically. Therefore, the photochemically reactive $^3$MLCT state is usually deactivated in unity yield by low-lying metal-centered states in common Fe(II) polyimine complexes. Recently, we demonstrated effective suppression of such deactivation using strongly donating tridentate N-heterocyclic carbene (NHC) ligands, resulting in elongated $^3$MLCT lifetime from 150 fs to 9 ps. By subtle manipulation of the ligand energy level, the $^3$MLCT lifetime can be further increased to 20 ps. This implies great prospects of sensitizing TiO$_2$ with novel Fe(II) NHC complexes, which is now being actively conducted in our group.

In parallel, we have constructed heteroleptic tris(bidentate) Fe(II) NHC complexes from the perspective of more versatile functionalities. This also delivered an $^3$MLCT lifetime as long as 16 ps. Further chemical modification is now on the way, aiming at fitting the sophisticated Fe NHC chemistry to the earnest expectation for photochemically valuable Fe(II) compounds.

References

3 Y. Liu, et al. To be submitted.
204 - Photofunctional metal-containing conjugated materials

Michael O. Wolf, mwolf@chem.ubc.ca, Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

Conjugated polymers and oligomers are of interest for a broad range of applications including solar cells, chemical sensors, molecular electronics and catalysis. Many of these applications are dependent on the photophysical properties of the materials, including absorption and emission properties, excited state charge separation and photochemistry. Hybrid conjugated materials in which conjugated polymers and oligomers are combined with metal-complexes can give rise to enhanced photofunctional properties. The role of inter- and intramolecular self-assembly in determining the properties of these metal-containing conjugated materials will be discussed.
Our program has developed a series of cyclometalated ruthenium(II) complexes of type [Ru\textsuperscript{II}(N^N)_2(C^N)]\textsuperscript{2+} and [Ru\textsuperscript{II}(N^N^N)_2(N^C^N)]\textsuperscript{2+} to accomplish the requisite light-absorption and charge-separation events in the dye-sensitized solar cell (DSSC). This class of molecules offers a distinct advantage over conventional ruthenium-based dyestuff for DSSC applications because the replacement of the NCS\textsuperscript{−} ligands with aromatic ligands presents the opportunity to manipulate both the ground- and excited-state energy levels. Moreover, these complexes enable the portion of the molecule that is, in the oxidized form, responsible for reacting with the electrolyte to be manipulated. This presentation will detail how the careful design of this class of compounds has yielded unprecedented resolution of key reaction steps in the DSSC, including regeneration of oxidized dyes, and intra- and inter-molecular hole-transfer at the semiconductor interface.
A series of heteroleptic bis(tridentate) ruthenium(II) complexes featuring 1,2,3-triazole-, 1,2,3-triazolylidene-, or 1,2,3-triazolate-containing ligands is presented. The new ligand platforms are readily and modularly functionalized by making use of azide-alkyne cycloaddition reactions. The bis(tridentate) ruthenium(II) complexes of mesoionic carbene ligands exhibit very long excited-state lifetimes suggesting potential applications in photoredox-catalysis, while the ruthenium(II) complexes bearing anionic chelates feature suitable electronic properties for application in dye-sensitized solar cells. The latter was confirmed by achieving power-conversion efficiencies that approach those obtained with thiocyanate-based ruthenium(II) complexes. Additionally, the anodic electropolymerization of thiophene-equipped N^C^N-cyclometalated ruthenium(II) complexes is demonstrated.
207 - Photoswitchable ruthenium-cyanamide/polymer materials

Diane S. Jodoin, Robert J. Crutchley, robert_crutchley@carleton.ca. Department of Chemistry, Carleton University, Ottawa, Ontario K1S5B6, Canada

The synthesis and characterization of photodynamic media composed of spiropyran/polymers will be discussed.

When the complex, \([\text{Ru(NH}_3)_5\text{dicyd}]^{4+}\) is dispersed in these media, the intensity of its Ru(III)-cyanamide NIR absorption band decreases with the photogeneration of merocyanine. Reversibility is only partial and it is suggested that the binding of \([\text{Ru(NH}_3)_5\text{dicyd}]^{4+}\) to merocyanine creates a kinetic barrier to the thermal back reaction. The decrease in NIR absorption can be as great as 76% and is dependent on the nature of the photodynamic media. Polymers and spiropyran derivatives are examined to optimize the photodynamic response in the NIR and the rate of thermal back reaction. Application of these materials to photoswitching devices is highlighted.
**208 - Molecular assemblies for solar fuel applications in dye sensitized photoelectrosynthesis cells**

Dennis Ashford, Michael Coggins, Javier Concepcion, Animesh Nayak, Christopher Glasson, Kenneth Hanson, Yusuke Tamaki, Derek Ryan, Kassio Zanoni, Marcey L. Waters, Neyde Y. Murakami Iha, Thomas J. Meyer, tjmeyer@unc.edu. (1) Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States, (2) Chemistry, University of Sao Paulo, Sao Paulo, Brazil

In a Dye Sensitized Photoelectrosynthesis Cell (DSPEC) a chromophore-catalyst assembly is surface-bound and integrated with a high band gap oxide semiconductor for applications in solar water splitting or CO\textsubscript{2} reduction to CO, formate, or other carbon-based fuels. The assembly shown in the figure, on transparent conducting oxide/TiO\textsubscript{2} core shells, \[((PO\textsubscript{3}H\textsubscript{2})\textsubscript{2}bpy)\textsubscript{2}Ru(bpy-bimpy)Ru(tpy)(OH\textsubscript{2})\]\textsuperscript{4+}, has provided a basis for visible water splitting into hydrogen and oxygen.

![Molecular assembly diagram](image)

The synthetic chemistry and surface characterization of chromophore-catalyst assemblies has advanced rapidly. Examples will be discussed based on: 1) covalent linking; 2) layer-by-layer assembly; 3) co-loaded surfaces; 4) catalyst overlayers; 5) electro-assembly formation; 6) electro-oligomerization; and 7) oligoprolines.
209 - Sensitization and symmetry breaking charge transfer in organic solar cells

Mark Thompson\textsuperscript{1,2}, met@usc.edu, Andrew Bartynski\textsuperscript{2}, Cong Trinh\textsuperscript{1}. (1) Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States, (2) Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California 90089, United States

The exciton is a critical part of each of the processes leading to photocurrents in Organic PhotoVoltaics (OPVs), and being able to control the location, lifetime and energy of the exciton is essential to achieving high efficiency. We have investigated methods for tuning exciton energies and controlling their migration paths, both intramolecularly and within a thin film. I will discuss our most recent work with the efficient use of multiple absorbers to efficiently harvest photons through the entire visible spectrum. In particular, we have used careful control of exciton and carrier energies to design and implement sensitizers that give fullerene films efficient light collection throughout most of the visible spectrum. I will also discuss a new approach to designing materials for OPVs that involves symmetry breaking charge transfer. These materials are symmetric molecules that spontaneously form an intramolecular charge transfer complex, with nearly complete one electron transfer from one part of the molecule to another. This intramolecular CT state readily forms a charge separated state at the D/A interface of the OPV. We have explored these materials as both donors and acceptors in OPVs and found that they give good performance and high $V_{oc}$.

Monday, August 11, 2014 04:10 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (01:00 PM - 04:50 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 1/2
The talk will summarise progress in the development of conjugated donor-acceptor polymers (see Figure 1) for use in blends with solution processable fullerene acceptor derivatives for application as the active layer in bulk heterojunction organic solar cells. In designing these polymers the HOMO-LUMO gap must be optimized for light absorption at the emission maximum of the solar spectrum and the energy difference between the HOMO of the donor polymer and the LUMO of the acceptor fullerene should ideally be of the order of 1 eV. The presentation will summarize progress towards a laboratory-based device exhibiting an energy conversion efficiency in excess of 10%.

Bis-indene adducts of C-70 have been employed as efficient electron accepting components in bulk heterojunction solar cells. The effect on device efficiency of a poly(3-hexylthiophene) acceptor in combination with a single crystalline bis-indene C-70 adduct (compared with a mixture of isomers) will be described.

Finally progress will be presented on the development of fully printed bulk heterojunction solar cell modules.
In this contribution, selected examples of the properties and use of poly(2-oxazoline) (POx) as very promising polymer therapeutics will be presented [1-9]. This will include the use of amphiphilic POx triblock copolymers as high-capacity drug delivery systems (DDS) for hydrophobic drugs such as paclitaxel [7] and others [2], exhibiting synergistic effects for the delivery of multiple chemotherapeutic drugs. The talk will focus on the reasons for the unparalleled high drug-loading capacities of the POx system and outline the consequences of the drug loading on the DDS morphology [9] and anticancer efficaiy found in recent preclinical studies.

Acknowledgement. This work is supported by the National Cancer Institute Alliance for Nanotechnology in Cancer through the National Institutes of Health grant to the Cancer Nanotechnology Platform Partnership (U01 CA116591).


(2) Han, Y. et al. Mol. Pharmaceutics 2012, 9, 2302


(9) Schulz, A. et al. ACS Nano 2014, 8, 2686.
Targeted drug delivery by polymer particles is considered as one of the most promising strategies for improving patients’ recovery and well-being. Poly(2-oxazoline)s have gained considerable attention as material class for the production of such particles. Two strategies can be employed for the synthesis of crosslinked poly(2-oxazoline)-based networks, in-situ crosslinking during the polymerization itself or polymeranalogous crosslinking by click reactions such as the thiol-ene reaction. Correspondingly, poly(2-oxazoline) networks can be synthesized from mono- and bisfunctional 2-oxazolines in one-pot/one-step strategies. Depending on the type of monomers, substitution patterns, and amount of crosslinker, gels with varying swelling degrees and varying hydrophilicity can be synthesized. Those gels can be loaded with small organic compounds such as APIs during the polymerization (covalent attachment) or during swelling/deswelling strategies (physical inclusion). Surface functionalization of ene-bearing gels with cysteine-bearing peptides exhibiting the RGD motif yields microparticles with enhanced recognition of BON cancer cells compared to healthy EA.hy cells.

Tuesday, August 12, 2014 08:30 AM
Poly(2-Oxazoline)s and Polypeptoids (08:00 AM - 11:30 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
Serina Therapeutics, Inc. has developed a patented, proprietary poly(oxazoline) (POZ) polymer platform designed for drug delivery. Drugs are attached to pendant groups along the polymer backbone employing "click chemistry" – a highly reproducible and facile method to generate POZ-conjugates. 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 (which is 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.
Poly(2-alkyl-2-oxazolines) represent nearly ideal building material for diagnostic and drug delivery applications. Radionuclides possess certain advantages compared to chemical drugs as biologically active components in these systems – the weight of the effective dose is orders of magnitude lower than for any chemical drug, it is easier to combine diagnostic and therapeutic approach into theranostics etc.


Hybrid systems composed of two or more different materials may combine advantage of combining advantages and suppressing disadvantages of its components. Therefore, poly(2-methyl-2-oxazoline) – coated fluorescent nanodiamonds combine the properties of a nanodiamond as fluorescent probe and nanoparticle of appropriate size with biocompatibility of poly(2-methyl-2-oxazoline). Another system of this type is glycogen-graft-poly(2-alkyl-2-oxazoline) combining biodegradable polysaccharide nanoparticle core with active component-bearing polymer corona, which also determines degradation rate or may be thermoresponsive (in such case this system may be used as, e.g., scaffold for tissue engineering; see Figure 1).

The authors thank for financial support to the Academy of Sciences of the Czech Republic, grant No. M200501201, Ministry of Industry and Trade of the Czech Republic, grant No. TIP FRTI4/625 and Grant Agency of the Czech Republic, grant No. P304/12/0950.
Meeting the prescription requirements of either abuse-free application or easy-to-use medication in the context of leaving older-aged individuals independent of nursery, novel dosage forms of APIs are under thorough investigation, in particular implantable polymer-based drug depots. Generic approaches, however, symptomatically suffer from degradation rates of the polymers that vary over time. Hence, the release of the drug(s) at constant rates cannot be provided. One strategy to overcome this bottleneck is the employment of copolymers comprising two different polymer classes. Biopolysters and PEG are one type of considerable candidates for that type of application; poly(2-oxazoline)s have been chosen as the counterpart for the production of novel poly(ether/ester amide) networks. These hydrogels act as depots with the ability to overcome the limitations of the individual polymer classes. In order to correlate the networks’ properties with their structures, compound libraries were synthesized and characterized by wettability, swelling degrees, mechanical properties and degradation kinetics.
Polyplex micelles (PMs) prepared from pDNA and block copolymer containing a nonionic hydrophilic segment and a polycation segment through electrostatic interaction is a promising carrier system for non-viral gene delivery. The PMs structure add stealthiness to pDNA in a physiological environment owing to hydrophilic shell. Nevertheless, the harsh environment of in vivo condition limits the practical use of PMs. Among various obstacles, polyanionic compounds that can cause disassembly of PMs by polyanion exchange and abundant nucleases are committing major interfering obstacles. To improve the stability of PMs against them, we demonstrated here the PMs with the hydrophobic protective palisade. The novel triblock copolymer composed of hydrophilic and biocompatible poly(2-ethyl-2-oxazoline) (PEtOx) segment, thermoresponsive poly(2-n-propyl-2-oxazoline) (PnPnPrOx) segment, and DNA binding cationic poly(Lysine) (PLys) segment was designed. The triblock copolymer allowed for obtaining PMs integrating with the protective palisade between hydrophilic outer shell compartment and condensed pDNA core compartment by preparing PMs at 4 °C and subsequent incubation at 37 °C, which is above the LCST of PnPnPrOx segment.

**Figure 1.** Schematic illustration of the PMs with core protective palisades prepared from ABC triblock copolymer containing thermo-responsive middle segment.

With this thermal treatment, the hydrophobized PnPnPrOx segment successfully settled on the interface of the core, providing the tolerability against DNase I attack as well as dissociation triggered by polyanion. Eventually, the PMs demonstrated promoted cellular uptake and thereby increased transfection efficiency, as well as improved blood circulation property, and the appeal of the design concept of thermo-stimulated PMs as smart gene carrier.
The hydrophilic poly(2-oxazoline)s (POx), i.e. poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline), are known to be non-toxic and reveal similar protein-repellent properties as the well-known poly(ethylene oxide). Thus, POx-based materials with amine moieties should represent promising materials for the interaction with genetic material. The amine moieties are cationically charged under physiological conditions and capable to form polyion complexes with the negatively charged DNA, while the PETOx or PMeOx segments of the polymer reduce the cytotoxicity.

Since the cationic ring-opening polymerization of 2-oxazolines prohibits the direct incorporation of amine functionalities, alternative routes were developed comprising the copolymerization of a Boc-protected 2-oxazoline monomer,¹ the post-polymerization modification of double-bond containing POx via thiol-ene chemistry,² and the functionalization of linear poly(ethylene imine) resulting in hydrogels with molecular structures that are analogous to POx (Figure 1).³ The derived materials were either tested regarding their cytotoxicity, pDNA complexation, transfection efficiency and cytotoxicity or cross-linked to yield hydrogels which were used to selectively catch and release genetic material for purification purposes.


Two new methods of using copper complexes at ambient and sub ambient temperature will be presented 1) using visible light with copper(II) complexes and 2) utilising rapid disproportionation of copper(I) in water and aqueous media. Photo-activated living radical polymerization of acrylates, in the absence of conventional photo-initiators or dye sensitizers upon irradiation with UV radiation ($\lambda_{\text{max}}$ 360 nm) will be described. In the presence of low concentrations of copper(II) bromide and an aliphatic tertiary amine ligand (Me$_6$-Tren), near-quantitative monomer conversion (> 95%) is obtained within 80 minutes yielding poly(acrylates) with dispersities as low as 1.05 and excellent end group fidelity (>99%). The control retained during polymerization is confirmed by MALDI-ToF-MS and exemplified by in situ chain extension upon sequential monomer addition furnishing higher molecular weight polymers with an observed reduction in dispersity ($D = 1.03$). Similarly, efficient one-pot block copolymerization by sequential addition of PEGA$_{480}$ to a poly(methyl) acrylate (PMA) macroinitiator without prior work-up or purification is also reported. Minimal polymerisation in the absence of light confers temporal control and alludes to potential application at one of the frontiers of materials chemistry whereby precise spatiotemporal “on/off” control and resolution achieved.

A new approach to perform single-electron transfer living radical polymerization (SET-LRP) in water will be also described. The key step in this process is to allow full disproportionation of CuBr/Me$_6$TREN to Cu(0) powder and CuBr$_2$ in water prior to addition of both monomer and initiator. This provides an extremely powerful tool for the synthesis of functional water-soluble polymers with controlled chain length and narrow molecular weight distributions (PDI approx. 1.10), including poly-NIPAM, DMA, acrylamide, zwiterionic monomers, PEG acrylate, HEA and an acrylamido glyco monomer.
This study was directed to the synthesis of various periodically-functionalized polymers by the transition metal-catalyzed simultaneous chain- and step-growth radical polymerization. The simultaneous polymerization was performed among N-isopropylacrylamide (NIPAM), functional dihalides (1), and dialyl compounds (2) with CuCl/Me$_6$TREN in DMF/H$_2$O = 1/1 at 20 °C. The reaction smoothly proceeded along with consumption of the three monomers. The $M_n$ of the resultant polymers increased in proportion to monomer conversion remaining narrow MWDs in the initial stage, while it progressively increased up to $M_n > 20,000$ with broad MWDs after the complete consumption of NIPAM. These results indicate that the simultaneous polymerization took place to give poly(NIPAM)s with periodical functional groups. The effects of the periodic functional groups were also investigated on the thermoresponsive behavior of the aqueous solution of the obtained poly(NIPAM), in which specific self-aggregation behavior forming micelles was observed for polymers with periodically-sequenced hydrophilic groups.
220 - Aqueous RAFT/MADIX polymerization: Pushing back the limits of control

Mathias Destarac¹, destarac@chimie.ups-tlse.fr, Aymeric Guinaudeau¹, Emmanuelle Read¹, Olivier Coutelier¹, Stéphane Mazières¹, David J Wilson². (1) IMRCP, Université Paul Sabatier, Toulouse, Haute-Garonne 31062, France, (2) Paris Research and Innovation Center, Solvay, Aubervilliers, France

Reversible-deactivation radical polymerization (RDRP) is one of the most convenient approaches for tailor-making various kinds of hydrophilic polymers with complex architectures. Among the RDRP options available, RAFT/MADIX is a method of choice because of its high tolerance to water and ionic monomers. We recently focused our attention on two important challenges, namely the control of N-vinyl pyrrolidone (NVP) polymerization in water and the polymerization of acrylamido monomers with controlled molar masses up to $10^6$ g.mol$^{-1}$.

We recently reported the first example of RDRP of NVP in water by means of a RAFT/MADIX redox-initiated process at room temperature in the presence of an O-ethyl xanthate. The use of the t-butyl hydroperoxide/ascorbic acid initiator allowed a controlled polymerization of NVP polymerization. Later, the initiator system was greatly improved by replacing ascorbic acid with sodium sulfite. In particular, it became possible to polymerize NVP in a dilute aqueous medium without forming monomer-derived by-products. Consequently, several original P(NVP)-based double hydrophilic block copolymers were prepared.

In another project, we pushed back the limits of molar mass control in aqueous RAFT/MADIX polymerization through a fast a quantitative gel polymerization of a series of acrylamido monomers. Unprecendently high $M_n$ up to $10^6$ g.mol$^{-1}$ with low polydispersities ($M_w/M_n<1.2$) were achieved in homopolymerization, statistical and block copolymerization. The reasons for access to abnormally high kinetic chain length in the presence of a RAFT/MADIX agent are discussed.
221 - Structure reactivity studies in ATRA and ATRP reactions catalyzed by copper complexes with substituted tris(2-pyridylmethyl)amine based ligands

Tomislav Pintauer, pintauert@duq.edu, Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania 15282, United States

A series of symmetrical and asymmetrical novel tris(2-pyridylmethyl)amine (TPMA) based ligands implementing electron donating groups were synthesized. The molecular structures of the corresponding copper(I) and copper(II) complexes indicated a wide variety of geometries in the solid state (Figure 1). Variable temperature NMR studies confirmed fluxionality of the substituted pyridine arms and dimerization in the case of copper(I) complexes. Furthermore, the reducing power of the copper complexes increased on the addition of each pyridyl scaffold containing electron donating groups. However, more reducing copper complexes were not found to be more active in ATRA and ATRP reactions when compared to unsubstituted TPMA. This was tentatively attributed side reactions such as radical coordination to the copper(I) centers.
222 - Comproportionation, activation, and termination in SET LRP/SARA ATRP

*Simon Harrisson*¹, polyharrisson@gmail.com, Julien Nicolas². (¹) Université Paul Sabatier, Toulouse, Haute Garonne 31062, France, (²) Faculté de Pharmacie, Université Paris-Sud XI, Chatenay-Malabry, France

Single Electron Transfer Living Radical Polymerization (SET LRP), also known as Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization (SARA ATRP), is a form of controlled radical polymerization which is carried out in the presence of copper metal, a ligand (e.g. Me₆tren), and an activated alkyl halide initiator. The mechanism of the polymerization is contested, with debate focusing in part on the relative importance of comproportionation and disproportionation of copper species. We present here a simple method for the determination of two key rate constants: activation of alkyl halides by copper metal ($k_{a0}$) and comproportionation of copper(0) and copper(II) ($k_{comp}$). This is carried out by following the consumption of an alkyl halide initiator in the presence of copper metal, ligand, and a radical trap such as N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide.

The elementary reactions of comproportionation, disproportionation and activation by copper(0) can be added to the standard reactions of ATRP to form a kinetic model of the polymerization. Observed features such as $\frac{1}{2}$-order dependence on the copper surface area and loss of control in strongly comproportionating solvents arise naturally from this model. Finally, chain length dependence of termination kinetics can be probed by observing the rate of generation of copper(II) species during the reaction. We show that addition of copper(II) halide, while narrowing the molecular weight distribution, can cause a reduction in chain-end functionality due to faster termination of shorter chains.
Over the past two decades, controlled radical polymerization has revolutionized the design and synthesis of new polymer-based materials. This presentation will focus on the exploitation of nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization for the preparation of block copolymer-based materials. We will discuss the use of NMP and RAFT polymerization for the preparation of thermally responsive block copolymer assemblies and the use of NMP, ATRP, and RAFT in the construction of block copolymer/metal hybrid materials.
Organotellurium compounds are activated under photo irradiation generating the corresponding carbon-centered radicals. This photochemical condition was successfully applied to organotellurium-mediated living radical polymerization (TERP) by applying low intensity light source. On the other hand, radical coupling reaction of polymer-end species selectively took place by employing high intensity light source. Synthetic aspects of these conditions as well as their application to elucidate the mechanism of radical polymerization will be discussed.
225 - Photoinduced electron transfer, reversible addition fragmentation chain transfer (PET-RAFT): A robust and versatile photocontrolled polymerization of conjugated and unconjugated monomers and its oxygen tolerance

Cyrille Boyer, cboyer@unsw.edu.au, Jiangtao Xu, Kenward Jung. School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2031, Australia

ABSTRACT: Controlled/living radical polymerization techniques have transformed polymer chemistry in the last few decades, affording the production of polymers with precise control over both molecular weights and architectures. It is now possible to synthesize almost an infinite variety of macromolecules using non-specialized equipment, finding applications in high-tech industry. However, they have several short-comings. The polymerizations cannot be well controlled via an external stimulus, such as light, pH, mechanical, chemical, etc. Moreover, they are usually sensitive to trace amounts of oxygen in the system. In this communication, we report a new photocontrolled polymerization technique based on photoinduced electron transfer between a photoredox catalyst and thiocarbonylthio compounds. This technique is able to polymerize a large range of monomers, including conjugated and unconjugated monomers, using ultra-low concentrations of photoredox catalyst (typically 1ppm to monomers) and a low energy visible LED as the light source (1 W-4.8 W). In this study, different inorganic and organic photocatalysts were successfully employed. The synthesis of homopolymers with molecular weights ranging from 1 000 to 2 000 000 g/mol was successfully achieved with narrow molecular weight distributions ($M_w/M_n < 1.2$) with a very high retention of end group fidelity demonstrated by successive chain extensions of poly(methacrylate)s and poly(acrylate)s to prepare multiblock copolymers. The reusability of the catalyst was demonstrated by the synthesis of decablock polymer by multiple chain extensions. This polymerization can be employed in a large range of solvents, including toluene, acetonitrile, DMSO, DMF and water. The polymerization rate can be manipulated by the light intensity. Most importantly, PET-RAFT process can be employed to prepare well-defined polymers and multiblock copolymers in the presence of air. Finally, we successfully employed this method for the synthesis of bioconjugate macromolecules using a grafting “from” approach in water or in biologic media. In conclusion, this polymerization technique appears to be extremely robust and efficient for the production of well-defined polymers.
Tetradentate amine-bis(phenolate) iron(III) halide complexes containing chloro substituents on the aromatic ring are extremely efficient catalysts for controlled radical polymerization. Molecular weights are in good agreement with theoretical values and dispersities are as low as 1.07 for substituted styrenes and methyl methacrylate polymerizations. Kinetic data reveal activity for styrene polymerization among the fastest reported to date, with the excellent control shown to be electronic rather than steric in origin. Mechanistic studies implicate a multi-mechanism system with cooperation between atom transfer radical polymerization (ATRP) and organometallic mediated radical polymerization (OMRP). The \textit{in situ} reduction of the Fe(III) complex with ascorbic acid or tin octanoate allows polymerizations to be initiated by both 1-phenylethyl chloride (1-PECl, ATRP regime) and azobisisobutyronitrile (AIBN, OMRP regime), to explore the mechanism of control and offer unique initiation pathways. Selected high pressure and computational studies will be presented to support mechanistic conclusions.
227 - Advanced characterization of acrylic polymers by size exclusion chromatography coupled with multi-angle light scattering detection

Hongwei Shen\textsuperscript{1}, hshen@dow.com, Yongfu Li\textsuperscript{2}, Robert Baumann\textsuperscript{3}, Mike Radler\textsuperscript{4}, Wei-Wen Tsai\textsuperscript{1}, Ralph Even\textsuperscript{1}, Sipei Zhang\textsuperscript{5}, Philip Imbesi\textsuperscript{6}.  (1) Core R&D Formulation Sciences, Dow Chemical Company, Spring House, PA 19477, United States, (2) Core R&D Analytical Sciences, Dow Chemical Company, Midland, MI 48667, United States, (3) Dow Advanced Materials, Dow Chemical Company, Horgen, ZH 8810, Switzerland, (4) Dow Advanced Materials, Dow Chemical Company, Midland, MI 48674, United States, (5) Core R&D Analytical Sciences, Dow Chemical Company, Collegeville, PA 19054, United States, (6) Dow Advanced Material, Dow Chemical Company, Collegeville, PA 19054, United States

Water-soluble acrylic polymers are widely used as thickeners, dispersants and flocculants in many applications such as coatings, concrete admixtures and water treatment. The performance of such polymers is significantly influenced by their molecular architectures. Size exclusion chromatography coupled with multi-angle light scattering detection (SEC-MALS) is used to investigate the molecular architecture of water-soluble acrylic comb polymers and traditional acrylic polymers. Figure 1 illustrates the estimation of the polymer persistence length via Kratky-Porod chain model.

![Persistence length estimated from $R_g$ vs. $M$ plot of SEC-MALS](image)

It is found that 1) all polymers investigated have a random coil configuration since the slopes of conformation plots are from 0.5 to 0.6; 2) the estimated apparent persistence length, a measure of polymer chain stiffness, of comb polymers increases with increasing the comb brush length significantly and also increases with increasing absolute molecular weight; 3) with the same molecular weight, poly(acrylic acid) has a larger radius of gyration than acrylic comb polymers but the estimated persistence length can be lower than the comb polymers depending on the comb brush length. The potential reasons for the observed phenomena are discussed in some detail.

Tuesday, August 12, 2014 08:00 AM  
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:20 PM)  
Location: Hilton San Francisco Union Square  
Room: Golden Gate 7
228 - Development of sequence-controlled polymers using a relay metathesis strategy

Will R. Gutekunst, willgute@mrl.ucsb.edu, Craig J. Hawker. Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, CA 93106, United States

Biological polymers, such as proteins and DNA, readily demonstrate how a unique polymer sequence can lead to exquisite function and selectivity in terms of catalysis, molecular recognition and data storage. Likewise, control of primary structure has far reaching implications for the future of synthetic polymers, but methodologies for their preparation remain limited. In this presentation, a new and general strategy for the synthesis of sequence-defined polymers is detailed that employs relay metathesis to promote the polymerization of programmed macrocyclic sequences. A small molecule “polymerization trigger” has been designed that allows for facile sequence incorporation and mediates the controlled, unidirectional polymerization of the macrocyclic monomer. Using this system, a diverse range of sequences can be polymerized with high levels of control over polymer molecular weight and molecular weight distribution.
Robert Tuba¹, robert.tuba@tamu.edu, Robert H Grubbs¹,². (1) Department of Science, Texas A&M University at Qatar, Doha, Qatar P.O.Box 23874, Qatar, (2) Division of Chem and Chem Eng, California Institute of Technology, Pasadena, California CA 91125, United States

The linear trans-polypentenamer has unique relevance among the synthetic rubbers since it has similar physical properties to the natural rubber. One of the most exciting new possibilities is the capability of preparing cyclic polypentenamers. This new type of polymer is of significant theoretical and commercial interest. Since many of the properties of polymers are controlled by end group and the defects they introduce, cyclic polymers that contain no end groups should show new and valuable physical properties. Cyclic polymers can result in unique properties in comparison of linear analogues such as different hydrodynamic radii, functional group density and lower viscosity. Although in the past couple of decades a number of new cycopolymer synthetic techniques have been developed, cyclopolypentenamers have not been synthetized and studied.

New approaches to the synthesis of such materials have been recently developed. Highly pure cyclopolypentenamer (MW: 36 kDa; PDI: 1.3) have been synthetized in equilibrium ring opening metathesis polymerization by silica supported Hoveyda-Grubbs second-generation catalyst systems. The polymer yields are comparable with those of linear analogues synthetized by homogeneous ruthenium and tungsten catalyst systems. The Mark-Houwink “a” parameters show significant difference between the linear (0.59 ± 0.4) and cyclic (0.92 ± 0.05) polypentenamers indicating the formation of high number of double bond containing, rigid cyclic polyolefins. Similar experiments with cyclooctene resulted in the formation of high molecular weight (939 kDa, PDI: 1.6) and highly pure cyclopolyoctenamer. The silica supported catalysts systems could be recycled three times without significant reduction of polymerization yield. The formed cycopolymers can be hydrogenated off by Pd/C resulting in cyclopolyethylene at atmospheric hydrogen pressure and room temperature. The synthetic methodology and analysis of cyclic polyolefins are reported.

Figure 1. Synthesis of linear and cyclic polypentenamers. Toluene solution; room temperature; [cyclopentene] = 2.17 M; 0.01% Ru catalyst loading.
230 - Macromolecular characterization of novel amphiphilic copolymer grafted nanoparticles, as concentration-independent dispersants for improved oil spill remediation

Alina M Alb, aalb@tulane.edu, Department of Physics and Engineering Physics, Tulane University, New Orleans, LA 70118, United States

The effectiveness of complimentary macromolecular materials in encapsulating oils and stabilizing their emulsions is investigated in this study. Since the instability upon surfactant dilution is an unavoidable, a promising approach to accessing long-term stability in emulsions is the use of unimolecular micelles, which, as amphiphilic macromolecules with structure held together by covalent bonds, yield stable emulsions for longer time frames. Therefore, following this rationale, amphiphilic polymers (biocompatible or biodegradable) grafted to well-defined, functionalized silica nanoparticles (10-100 nm) were synthesized in controlled fashion by several routes. Light scattering-based unique methodologies together with traditional methods were used in the characterization studies of SiO₂-GPS-PCL-PEG copolymer grafted particles, with major focus on understanding of how critical structural parameters, such as polymer chain length, hydrophilic/hydrophobic block ratio, size of nanoparticle core, affect their performance as dispersants for remediation. Experiments were designed to monitor stability and dynamics of the nanoparticles in aqueous solutions, to measure kinetics and quantity of entrapment loading of organic components by the novel nanoparticles and unimolecular micelles and measure kinetics and conditions for release. The loading limits of the SiO₂-GPS-PCL-PEG copolymer grafted particles were correlated to the thickness and density of hydrophobic PCL layer in the amphiphilic copolymer nanoparticles and with the concentration and type of the organic component incorporated.

. It is hoped that the knowledge gained from these studies will offer convincing arguments in proving that the novel amphiphilic materials synthesized, represent efficient concentration-independent biocompatible dispersants.
231 - (Meth)acrylates organopolymerization directly induced by N-heterocyclic carbenes (NHCs)

Winnie Nzahou Ottou, nzahou@enscbp.fr, Anne-Laure Wirotius, Joan Vignolle, Daniel Taton. Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux-CNRS, Pessac Cedex, France

In the last decade, N heterocyclic carbenes (NHCs) have emerged as organic mediators to trigger various polymerization reactions.1 This is due to their unique nucleophilic and basic properties that can be finely tuned through their substituent pattern.

In this work, we have investigated the reactivity of both 1,3-bis(tert-butyl)imidazol-2-ylidene (NHCtBu) and 1,3-bis-(isopropyl)imidazol-2-ylidene (NHCiPr) towards MMA. The direct 1:1 1,4-nucleophilic addition (top of Figure 1) between a NHC and MMA as Michael acceptor forms a zwitterionic imidazolium enolate.2 It was already reported that 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4 triazol-5-ylidene(TPT) promotes the dimerization of MMA3 (Figure 1, route A). 1,3 Bis(mesityl)imidazol-2-ylidene (NHCMes) selectively forms a single-addition (1:1) product with MMA, whereas NHCtBu directly polymerizes MMA4 (routes B and C respectively).

In our case, we have observed that NHCiPr yields an unprecedented stable zwitterionic cyclodimer with two molecules of MMA5 (Figure 1, route D). DFT calculations have allowed rationalizing experimental differences between with NHCtBu and NHCiPr. The reactivity of NHCiPr and NHCtBu towards miscellaneous (meth)acrylic monomers has been screened experimentally and supported by theoretical considerations.

References

232 - WITHDRAWN
Bifunctional catalysts that combine a nucleophilic activator with an electrophilic activator have shown a great capacity in enhancing the rate and selectivity of ring-opening polymerizations of lactones in the presence of alcohol initiators. We have extended this strategy for the zwitterionic ring opening polymerization (ZROP) of lactones with amidine or isothiourea nucleophilic initiators. The ZROP of lactide with the amidine DBU (1,8-diazabicyclo[5.4.0] undec-7-ene) generates cyclic polylactides. In the presence of a thiourea cocatalyst, the polymerization rates and molecular weights of the resulting cyclic polylactides were significantly higher than that observed in the absence of cocatalysts. This cocatalysis strategy for ZROP could be potentially used to generate high molecular weight cyclic polymers for the experimental investigation of the physical properties of highly entangled cyclic polymers.
Ferulic acid (FA), a bio-based resource found in cereals, fruits and vegetables, and a hydroxyl-amino acid, have been used to develop a new class of poly(carbonate-amide)s which possess the potential to degrade into natural products under hydrolytic or enzymatic conditions. L-Serine was first envisaged as partner for FA to generate the diol necessary for the condensation polymerization. Unfortunately, the $p$-nitrophenyl carbonate synthesized led systematically to the elimination product. Consequently, the strategy was revised and L-tyrosine ethyl ester, which lacks an acidic proton on the α-position of the ethyl ester, was used. To determine the microstructure importance into the polymer properties, we decided to generate the three regioselective poly(carbonate-amide)s possible: head-to-tail, head-to-head and tail-to-tail. Two AB monomers, activated as $p$-nitrophenyl carbonate and chloroformate, were necessary to reach the high regioselectivity expected for a head-to-tail polymer, whereas the synthesis of the dimer and its polymerization in presence of diphosgene gave access to the head-to-head and tail-to-tail sequences. A more effective way to reach the desired polymer was developed via the straightforward synthesis of a regiorandom poly(carbonate-amide) in only two steps from commercially-available reagents. Moreover, fluorescent studies revealed interesting photophysical properties for the monomers and their corresponding poly(carbonate-amide)s, making these materials potentially viable for sensing and/or imaging applications, in addition to their attractiveness as engineering materials derived from renewable resources.
Thermoplastic elastomers based on polyisoprene, polybutadiene, or polybutylacrylate soft blocks and polymethylmethacrylate or polystyrene hard blocks have been synthesized previously by anionic and living radical polymerizations. This work reports the first synthesis of new thermoplastic elastomers based on polybenzofulvene (PBF) and polyisoprene (PI). In developing these new elastomers, well-defined homopolymers and block copolymers containing PBF blocks were synthesized by living anionic polymerization in benzene at room temperature via high vacuum techniques. NMR Analysis of homo-PBF microstructure indicated there there is 91% 1,4-addition and 9% 1,2-addition, withno 3,4 addition. PI-b-PBF block copolymers were synthesized by sequential anionic polymerization in a quantitative yield with narrow molecular weight distribution (Mw/Mn=1.12). Isoprene cannot be initiated by living polybenzofulvenyl lithium because of its low nucleophilicity. PBF-b-PI-b-PBF triblock copolymer was synthesized using a difunctional lithium-based initiator (1,3-phenylene)-bis-(3-methyl-1-phenylpentylidene), with lithium sec-butoxide as a polar additive in benzene. The pendent vinyl groups of the PI block were hydrosilylized using chlorodimethylsilane in order to attach chlorosilane groups along the backbone. Grafted triblock copolymer PBF-b-(PI-g-PBF)-b-PBF was synthesized by the reaction of living polybenzofulvene with chlorosilane groups on the PI block (Figure 1).
A “Janus polymerization” is defined to include a cationic and an anionic polymerizations on both ends of a single growing polymer chain followed by a self-triggered polycondensation.

We design ring-opening polymerizations (ROPs) of ε-caprolactone (CL) and tetrahydrofuran (THF) using a catalytic system of lutetium triflate/propylene oxide (Lu(OTf)₃/PO) to realize the concept. Lu(OTf)₃ opens PO ring to generate a zwitterion-like intermediate. Its positive-charged end starts a living cationic copolymerization of THF with CL, while a living coordinated anionic ROP of CL performs at the negative-charged end. Kinetic and mechanistic studies demonstrate that the two chain-growth ROPs have no mutual interference up to 90% of CL conversion. Diblock copolymers of PCL-b-P(THF-co-CL) with narrow polydispersities below 1.2 are obtained. The depletion of CL triggers a final step-growth polymerization via intermolecular coupling reaction of cationic and anionic chain ends, developing multiblock polyester–polyether elastomers of [PCL-b-P(THF-co-CL)]ₘ.

Studies on Janus polymerization help us to understand the co-existence of incompatible cationic and anionic polymerizations in a single growing polymer chain, as well as the combination of chain-growth and step-growth polymerizations.
Crotonates are an underexplored class of α, β-unsaturated ester monomers, and can be produced by the selective degradation of poly(3-hydroxy)butyrate.[1] In this talk we will detail our investigations of environmentally benign organocatalytic transformations of crotonates. We have discovered umpolung tail-to-tail dimerizations of crotonates to adipic acid ester analogues and investigated their use in the synthesis of novel poly(ester)s. Our efforts in developing organocatalytic routes to poly(crotonate)s, structural isomers of poly(methacrylate)s, will also be discussed.


Tuesday, August 12, 2014 11:20 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:20 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
The incorporation of reactive functionalities onto polymer backbones has attracted significant attention and has been extensively studied by many researchers to create highly-functionalized polymeric materials. This work involves the development of a facile synthetic method for aldehyde-functional polycarbonates, which could be utilized as reactive platforms to construct a variety of functional dynamic and/or static polymer materials under mild reaction conditions. Versatile allyl-functional polycarbonates were synthesized by ring-opening polymerization of a functionalized cyclic carbonate monomer using 1,8-diazabicyclo[5.4.0]undec-7-ene as an organocatalyst. Pendant alkene groups were efficiently converted into aldehydes by ozonolysis and reductive work-up. We demonstrated that two model aminooxy compounds were efficiently installed onto the well-defined polycarbonate backbones by reactions with aldehydes forming oxime linkages. In addition, alkenes and aldehydes were readily introduced as orthogonal functional groups, by partial ozonolysis and the resulting statistical copolymer was functionalized by stepwise aldehyde-aminooxy and thiol-ene “click” reactions in an orthogonal manner. This efficient approach for the preparation and modification of versatile degradable polymer platforms will be useful to a wide range of research areas due to their capability to form various conjugates via combinations of oxime, hydrazone, and/or Schiff base linkages with aldehydes and also thioether or other linkages to the alkenes.
Polyesters are utilized in biomedical engineering applications such as drug delivery devices and tissue engineering constructs because of their biodegradable and biocompatible properties. The most common polyesters employed for such applications include poly(lactide), poly(lactide-glycolic acid), poly(caprolactone), and poly(hydroxyalkanoates). The ability to synthesize large quantities of polymer with high molecular weights and narrow distributions via the ring-opening polymerization of cyclic esters enables their broad application [figure 1]. Functional diversity within this class of material, however, is difficult to achieve and involves block copolymers or monomer modifications.

An alternative approach to achieving functionally diverse aliphatic polyesters is copolymerization. Important biomedical polyesters are synthesized using the step-growth of diols with diesters. However, to advance applications in biomedical engineering, polyesters must be produced with control over molecular weight and distribution, as well as microstructure and architecture. To date, few methods exist to synthesize functionally diverse polyesters that meet these criteria.

This talk will discuss the evolution of discrete catalysts able to perform the alternating copolymerization of a variety of epoxides with cyclic anhydrides under mild conditions to produce well-defined polyesters [figure 1]. Commodity feedstocks are used to synthesize new polyesters with high molecular weight, diverse compositions, and controlled microstructures such as stereo- and regiochemistry.
A double hydrophobic and amphiphilic block copolymer nanostructured membranes were manufactured by non solvent induced phase inversion (NIPS) technique. The combination of NIPS process and self assembly of block copolymer aids us to produce an isoporous membrane with pores sizes of about 20-30nm. Here we used PS-b-PEO (amphiphilic) and PS-b-PMMA (double hydrophobic) block copolymer for nanostructured membrane formation. The self assembled structures of polymer membranes were tuned using the mixture of different solvent compositions and polymer concentrations. Pure water was used as a phase inversion medium for the nanostructured membrane formation. SEM, AFM and TEM measurements were employed to characterize the self assembled structure of the membranes.

References:
241 - Multi-block copolymers grafted by "click" chemistry: A new strategy for high performance membranes for ethyl tert-butyl (ETBE) bio-fuel purification

Miao Wang¹, miao.wang@univ-lorraine.fr, Carole Arnal-Herault¹, Claire Rousseau¹, Aurélie Palenzuela¹, Jérôme Babin¹, Laurent David², Anne Jonquières¹. (1) Laboratory LCPM FRE 3564, ENSIC, University of Lorraine/CNRS, Nancy, Lorraine 54000, France, (2) Laboratory IMP UMR 5223, University of Lyon/CNRS, Lyon, Rhône-Alpes 69622, France

The conventional purification process of ethyl tert-butyl ether (ETBE), one of the most promising biofuels in Europe, is highly energy intensive. A membrane separation process, such as pervaporation (PV), could be a simple, clean and economical alternative. The main challenge in pervaporation is to develop high performance membranes that are both highly permeable and highly selective. A multi-block poly(urea-imide) (PUI) with outstanding selectivity and excellent film-forming character, was selected as a promising membrane polymer but its permeability had to be improved for this application. In this project, we aim at developing novel membrane materials by plasticizing this promising polymer with selective polymethacrylate soft grafts in order to increase its permeability ideally without interfering with its excellent selectivity. Novel grafted PUIs were obtained by an original synthesis scheme based on 3 orthogonal chemistries: Polycondensation, polymer functionalization and grafting by "click" chemistry. The functional grafts were prepared by controlled radical polymerization (ATRP). Dense membranes were then obtained for the different grafted PUIs. Their sorption and permeability properties were assessed for the purification of ETBE by PV. An analysis in terms of structure-morphology-property relationships showed that membrane permeability increased strongly with the graft content while the excellent selectivity decreased very slightly. This strategy enabled to overcome the common permeability/selectivity trade-off and led to polymer membranes, which are amongst the best ones reported so far for ETBE purification.
242 - Water permeability of polyamide/graphene and polyamide/graphene oxide composites reverse osmosis membrane studied with atomistic simulations

Haiyang Zhao\textsuperscript{1,2}, haiyangzhao@zju.edu.cn, Tao Wei\textsuperscript{2}, Lin Zhang\textsuperscript{1}. (1) Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China, (2) Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United States

Polyamide reverse osmosis (RO) membrane is one of the most successfully commercialized membranes for desalination and water purification. Inorganic nano-particles have been introduced into polyamide thin layer to enhance the separation performance and operation stability of RO membrane. In this work, atomic molecular dynamics simulations and free energy computations were carried out to investigate water permeability of polyamide/graphene sheet (PA/GS) and polyamide/grapheme oxide (PA/GO) composites RO membranes. We compared the free energy barriers for water permeation across polymer bulk phase, polymer-particle interface and nano-channel between graphene (or graphene oxide) sheets. Crosslinked polyamide morphologies on nano-particle surfaces were also investigated. This fundamental study will rationalize PA/GS and PA/GO composites RO membrane design.

Tuesday, August 12, 2014 09:10 AM
Transport in Polymer Membranes (08:30 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 8
243 - Water uptake and swelling of weak polyelectrolyte brushes in a humid environment

Casey Galvin¹, Michael Dimitriou², mdimitriou@exponent.com, Sushil Satija², Jan Genzer¹. (1) Department of Chemical & Biomolecular Engineering, NC State University, Raleigh, NC 27695-7905, United States, (2) Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

Previous work on polyelectrolyte brushes has shown hydration profiles with greater swelling at the polymer-liquid interface than at the polymer-substrate interface. However, swelling behavior for polyelectrolyte brushes has rarely been studied in humid environments. This work utilizes X-ray reflectivity (XRR) and neutron reflectometry (NR) to investigate swelling profiles of the tertiary-amine bearing weak base poly(dimethylaminoethyl methacrylate) (PDMAEMA) after exposure to different relative humidity levels. Ellipsometry and XRR characterize the swelling behavior of the polymer brush while NR was used to assess the distribution of water (D₂O) within the brush. We show that PDMAEMA brushes grown using surface-initiated ATRP swell extensively in humid environments at room temperature (graphic attached). Further work was performed to compare the swelling profile after quaternizing the tertiary amine with deuterated methyl iodide (CD₃I). Utilizing CD₃I in conjunction with NR allowed us to characterize two phenomena: 1) the quaternization profile as a function of depth in the brush and 2) the change in humidity uptake after quaternization. The results indicate a non-linear increase in swelling of the brush with increasing relative humidity before quaternization and an altered swelling character after quaternization. NR also shows a unique quaternization profile along the depth of the brush.
Ionic polymers form structures interfaces where both hydrophilic and hydrophobic segment co-exist. These types of materials are currently used as selective transport membranes ranging from electrolytic membranes and water purification ones, to drug delivery capsules where the nature of the solvent depends on the specific application. To advance the current state of the art to responsive transport, the mechanism of diffusion across dynamic interfaces has to be resolved. In other words, the transport as the chemical composition and the topology of the interfaces are changed as transport takes place has to be elucidated. Here using in situ neutron reflectometry we study the transport of a series of alcohols across an interface of thin of a sulfonated polyphenylene based ionomers, whose highly rigid backbone distinguishes it from it from flexible polymers. The films were exposed to alcohols with varying chain lengths and the reflectometry patterns were recorded as a function of time. We will present the results for different sulfonation levels of the ionomer. At early stages the diffusion was characterized by a linear $t^{1/2}$ mass uptake that crossed over to a slower uptake at later times. Interfacial effects dominate the onset of diffusion resulting in significant slower diffusion in comparison with the bulk polymer. The effects of the hydrophobicity of the alcohols will be discussed following by comparison with the diffusion of water. A schematic representaion of teh overall process is shown in Figure 1 [figure 1].
245 - Transport and material science needs of the future for reverse osmosis membrane technology

Steven Rosenberg, steve.rosenberg1@dow.com, Abhishek Roy, Abhishek Shivastava. Dow Water & Process Solutions, The Dow Chemical Company, Edina, MN 55439, United States

As scientists have continued to improve reverse osmosis (RO) membrane technology, the breadth of application continues to expand. Central to this has been development real world RO system thermodynamic models and then the targeting of practical membrane synthesis to improve desired properties.

However, our scientific understanding is far from complete. Transport models based on a firm knowledge of the detailed morphological and functional group contributions are as yet not available. As a result, practical membranes utilize a relatively narrow group of polymer backbones. This is the challenge for the next 3-5 years. How to design new materials? During this talk, we'll lay out some of the major application challenges, the state of the art in system thermodynamics and membrane synthesis while also suggesting a path forward to advance the state of the art in understanding membrane transport.

Tuesday, August 12, 2014 10:30 AM
Transport in Polymer Membranes (08:30 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 8
246 - Transport and fouling behavior of nanostructured membranes modified with RAFT-synthesized polymer brushes

Kai Gao, gao169@purdue.edu, John A. Howarter. School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States

Polymer membranes, including ultrafiltration (UF) membrane, nanofiltration (NF) membrane and reverse osmosis (RO) membrane, have been widely used in wastewater treatment, biotechnology, and desalination. However, fouling has been a major problem for these membranes' application in reality, due to membrane hydrophobicity. A combination of RAFT polymerization and "grafting to" approach was used to incorporate hydrophilic polymer brushes on polymer membranes, including polysulfone UF membranes with variable pore size and polyamide based reverse osmosis membranes, for anti-fouling enhancement. In this study, we developed a dynamic durability test with the use of quartz crystal microbalance (QCM). Likewise, QCM was used to assess membrane fouling behavior on model surfaces which mimicked the modified membranes. Structure-property relationships were established regarding the chemistry and grafting density of the surface modifying polymers and the macroscale membrane transport behavior.
Gels are ubiquitous in many industrial applications, such as drug delivery, tissue scaffolds, microfluidics, and fuel cell membranes, where controlling selective transport is critical to the performance of the device. In general, the structure of the gel determines its transport properties. However, developing the gel structure-transport-property relationships often requires multiple measurement techniques. In this work, we demonstrate poroelastic relaxation indentation (PRI) as a single measurement tool to establish the relationships between the network structure and the transport properties of model hydrogels with a well-defined homogeneous network structure synthesized via a thiol-norbornene click reaction of poly(ethylene glycol) (PEG) chains. Using PRI, we are able to obtain mechanical properties (Young’s modulus), transport properties (diffusion coefficient), and thermodynamic parameters (Flory-Huggins χ parameter and mesh size) of these “click” hydrogels. Specifically, we systematically vary the network density by changing the molecular weight between crosslinks as well as the crosslinker concentration. First, we validate PRI by comparing the mesh size obtained from this technique with reported data via neutron scattering. We then use the results from PRI to establish network structure-transport-property relationships for these materials.
A predictive model for mass transfer has been formulated based on the multicomponent generalization of the Flory-Rehner theory using the generalized Onsager formalism. Experiments on benzene/cyclohexane permeation through peroxide crosslinked NBR show that the relative permeation of the components can be predicted in a completely a priori manner given data on the network modulus and pure component swelling ratios. A single parameter sets the absolute permeation rates. The formalism is capable of being used for materials design and its application has led to a world record in selectivity for the separation of isobutanol from water. Accordingly, experiments confirm the applicability of the theory to practical problems in multicomponent mass transfer through cross-linked rubbery polymer materials.
The use of cellulose and other precursors for the production of carbon fibres will be reviewed and contrasted. The first part of the talk will focus on work done to convert cellulose fibres spun by electrospinning into nanofibres for the production of medium modulus filaments (100-140 GPa) and for use as electrode materials for supercapacitors. It is shown that the small size of the fibres contributes to the effective graphitization of the fibres\(^1\) and ultimately to the high surface areas required for supercapacitors\(^2\). The incorporation of carbon nanotubes into the spinning dope also enhances the capacitance\(^2\) (see Figure 1).

The second part of the programme will present the concept of spinning fibres from a polyethylene precursor as part of a newly funded European Commission research project NMP3-LA-2013-604168 NEWSPEC; www.newspec.eu). NEWSPEC (New cost-effective and sustainable polyethylene based carbon fibres for volume market applications) aims at the production of Carbon Fibres (CFs) through very promising low-cost sustainable polyethylene (PE) precursors. Published work on this precursor will be reviewed and the overall aims of our project introduced. PE can be derived from three independent sources: bio-ethanol, synthetic oil and recycled plastics. The main attribute of this project is the use of an available pilot scale facility (HPFC) that allows design and optimization of continuous CF processing and, at a later date, easy scale up to a larger industrial size plant. For PE stabilisation an original dry oxidation method, assisted by Electron Beam Curing (EBC), that introduces heteroatoms at the precursor stage is proposed.\[^{[2]}\] Deng, L., Young, R.J., Kinloch, I.A., Zhu, Y.Q., Eichhorn, S.J. 2013. Carbon Nanofibres Produced From Electrospun Cellulose Nanofibres. Carbon, 58, 66-75.\[^{[1]}\] Deng, L., Young, R.J., Kinloch, I.A., Abdelkader, A., Holmes, S.M., De Haro-Del Rio, D.A., Eichhorn, S.J. 2013. Supercapacitance from Cellulose and Carbon Nanotube Nanocomposite Fibers. ACS Applied Materials & Interfaces, 5, 9983-9990.\[^{[2]}\]
250 - Broadening the window of properties of biobased polymers via manipulating the structures of building blocks

Jinwen Zhang, jwzhang@wsu.edu, School of Mechanical and materials Engineering & Composite Materials and Engineering Center, Washington State University, Pullman, WA 99163, United States

Compared with petrochemical polymers, biobased polymers are very scarce in terms of variety and production volume. There are only a few biobased polymers commercially available with relatively small scales of production. Currently biobased polymers only find some niche applications due to limited performance and relatively high production costs. In order for biobased polymers to replace conventional polymers in a broad range of applications, it is necessary to manipulate the monomer and building block structure of the renewable polymers for attaining diverse properties. In this work, we made a series of attempts to explore the use of several renewable feedstocks in developing new thermosetting polymer resins. The renewable feedstocks used include rosin, vegetable oils, lignin, terpenes, etc. Syntheses of epoxies, curing agents, and unsaturated polyesters using these renewable feedstocks were studied. By manipulating the molecular structures of monomers and polymers, the resulting polymers exhibited a broad spectrum of properties.
Organic visible-light photoredox catalysis is a popular 'green' alternative for organic synthesis and functionalization reactions\(^1,2\). Since radicals are readily produced under mild conditions, and even with sunlight-activation, it can also be advantageous in macromolecular synthesis\(^3\). Chromophores are easily tuned to match absorbance to emission. Thus, high quantum-efficiency photopolymerizations are possible at ambient conditions with low intensity visible-light (CFL's or LED's)\(^4\). Nonetheless, detailed understanding of the intertwined initiation/polymerization mechanisms is limited and practical advantages not fully recognized.

We characterized mechanisms of organic visible-light (400-600 nm) photoredox catalysis initiation in bulk and solution polymerization of (meth)acrylates. We monitored millisecond kinetics of photocatalyst and monomer consumption with a real-time UV-Vis/FT-IR/fluorescence set-up. Simultaneously, we used quantum chemistry (TD-DFT) to elucidate the complete initiation mechanism, and monomer/polymer interactions with the photocatalytic initiation process.

We found free-radical photoinitiated systems in which polymerization continues after a brief low-intensity irradiation pulse and beyond the spatial reach of light. This novel light-triggered redox initiation mechanism occurs via the ground-state reaction responsible for catalyst regeneration, and thanks to relatively faster photobleaching of the photocatalyst (only forms closed-shell species), thus, effectively preventing initiation of the polymerization from the photochemical reaction and storing light-energy in an electrochemical potential. This energy-storage scheme for polymer synthesis mimics the NADP\(^+\)/NADPH cycle in photosynthesis. Furthermore, this could lead to more energy-efficient greener photopolymerizations, and ultimately be introduced as an advantageous synthetic approach for 'click' step-growth and controlled living radical polymerizations as well.

---


Fibers that are sustainable and biodegradable are engineered from a combination of cellulose and proteins, such as soy protein, silk fibroin, gelatin, zein, etc. In a binary polymeric blend, the compatibility of cellulose and protein is influenced by the nature and behavior of each polymer in the employed solvent system as well as processing conditions. Therefore, an effective, environmentally friendly solvent system, ethylenediamine and potassium thiocyanate (ED/KSCN), is chosen to directly dissolve cellulose with proteins at optimum conditions. This process ensures fast dissolution at 80 to 90°C within 2-4 hours with no temperature cycling. In addition, the solvent is nondegrading to the polymers and no stabilizer is necessary. By regulating solution and coagulation characteristics of the blends, a variety of novel cellulose - high protein content solutions are converted into fibers to examine the properties of the resultant polymer compositions.

Initially, soy protein is blended with cellulose to form the fiber via ED/KSCN solvent system by dry jet wet spinning technique. In this spinning system, the spin draw ratio is constant for all compositions and only as-spun fibers are produced and characterized. The modulus of the cellulose/soy protein fibers increases gradually from 0 to 40% protein content but strain at break decreases. The morphology of the blend fibers exhibit a round shape and a relatively compact structure. Also, microfibrils are observed.
In the context of sustainable materials, bacterial cellulose (BC) is often regarded as a prime candidate as nano-reinforcement for the production of renewable polymer nanocomposites. However, the mechanical performance of most BC-reinforced polymer nanocomposites is often inferior than commercially available polylactide (PLLA). Approximately 80% of the reported nanocomposites performed worse or only equally well than PLLA. One major reason for this is the loading fraction of nanocellulose ($v_f$) within the composites. In order to achieve or exceed the mechanical performance of PLLA, $v_f > 30$ vol.-% is necessary. This poses a challenge in the manufacturing of the nanocomposites, as conventional polymer extrusion methods cannot be used. Researchers often have to either limit the choice of polymers to water-soluble polymers, using solvent exchange methods if non-water soluble polymers were to be used and for the case of BC, culturing BC in the presence of a polymer to produce high $v_f$ nanocomposites. These extra steps involved will no doubt lead to poor cost-performance ratio of the resulting nanocomposites.

Therefore in this work, we apply the forgotten manufacturing concept of paper-based laminate (i.e: 'papreg') to BC nanopaper, producing BC nanopaper-reinforced PLLA, herein known as 'nano-papreg', with improved cost-performance ratio. We demonstrate that high performance nano-papreg containing 65 vol.-% of BC with tensile modulus and strength of 6.9 ± 0.5 GPa and 125 ± 10 MPa, respectively, can be fabricated without the use of laborious solvent exchange method or the use of water-soluble monomers. In addition to this, we also show that the tensile properties of nano-papreg are predominantly governed by the mechanical performance of BC nanopaper instead of the individual BC nanofibres due to difficulties impregnating the dense nanofibrous BC network. Micromechanical modelling of these BC-reinforced PLLA nanocomposites will also be discussed.
Triazolinediones as a versatile click chemistry platform providing functionalization and cross-linking of unsaturated renewable building blocks

Stijn Billiet, stijn.billiet@ugent.be, Oğuz Türünç, Samira Ouardad, Kevin De Bruycker, Johan Winne, Filip E Du Prez. Department of Organic Chemistry, Ghent University, Ghent, Belgium

Recently, an increasing number of research groups started to concentrate on carbohydrate-, plant oil and terpene-based polymers. Some of them have even been commercialized to some extent. When the chemical structures of these products are evaluated, one realizes that they provide different amounts of double bonds that are available for chemical functionalization. The possibility to use the plant oil directly, without chemical modification or functionalization, most often leads to cross-linked structures. A wide range of polymerization and/or functionalization methods, including, radical and metathesis procedures as well as thiol-ene & yne and azide-alkyne addition reactions have been applied. The scope, limitations, and possibility of utilizing such methods reveal that new robust, non-toxic, atom-efficient, orthogonal and industrially attractive chemical pathways are still needed.

In this presentation, we will highlight a new click chemistry platform based on triazoline diones (TAD), recently developed by our group[1], with the aim to functionalize and crosslink plant oils and renewable ADMET polymers directly in an atom-efficient and additive-free manner. Although TAD is known as an identification tool for GC-MS[2] and as functionalization tool for triglycerides[3], we show here for the first time the synthesis of cross-linked polymeric materials based on pure plant oils, as well as the modification and crosslinking of fatty acid-derived polymers to achieve new renewable polymers with complex macromolecular structures that are not yet easily achievable by any currently known chemical pathways. Within this contribution, the very first examples of the application of TAD chemistry to the renewable ADMET polymers as well as triglycerides will be reported and compared to thiol-ene addition reactions. TAD chemistry overcomes the drawbacks of the thiol-ene addition reactions, and thus appears to be a perfect and powerful complementary tool, enabling the access to new polymers and broadening the synthesis and/or functionalization of fatty acids and fatty acids derived (co-)polymers.

References:

255 - Novel sustainable polymers derived from renewable rosin

**Perry A Wilbon**, wilbon@email.sc.edu, Kejian Yao, Chuanbing Tang. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Rosin is an abundant, hydrocarbon rich renewable resource obtained from pine trees. Several rosin-containing polymers were prepared with the aid of a number of controlled polymerization techniques. These polymers can be divided into two categories: non-degradable polymers and degradable polymers.\(^1\)-\(^5\) The non-degradable polymers were prepared by atom transfer radical polymerization (ATRP), while the degradable polymers were prepared by either ring-opening polymerization or acyclic diene metathesis polymerization (ADMET). The attachment of the rosin moiety onto the polymeric framework led to an increase in the thermal properties of the polymers when compared to their un-substituted counterparts. The use of bi-functional initiators and the retention of end group functionality have led to the production of several novel polymers and have expanded the use of rosin based materials.


Poly(N-isopropylacrylamide) microgel (NMG) has been developed by adding various functional groups to control surface charges, hydrophobicity, pH and protein adsorption capacity. Here, we focused on the protonation/deprotonation of NMG's functional groups and present the NMG in anchoring potential functional groups as a polymeric catalyst, to possess the amidase activity at the optimized conditions. Various concentrations of microgels and functional groups were evaluated for efficient amidase activity on p-nitroaniline-based substrate via the colorimetric assay. At higher functional group concentrations, the distance between functional groups was reduced, consequently increasing the amidase activity of the NMG. The pH of the reaction environment is crucial to create a balance between neutral and deprotonated species of functional group to enhance the catalytic efficiency of NMGs. We proposed the amidase activity mechanism and the theoretical average distance based on the pH and functional group concentration studies, using NMG bearing functional group of 1-vinylimidazole as the study model. The results of substrate specificity evaluation showed that the efficient turnover rate was greatly affected by the factors of substrate bulkiness and electrostatic interaction between NMGs and substrates. Also, amidase activity was inhibited by a transition-state protease inhibitor, which suggested an enzyme-like amidolytic catalysis and confirmed the proposed NMG reaction model. These results provide an insight into the strategies to functionalize hydrogels through an enzyme-mimic approach for future robust bio- and chemical conversions as well as therapeutic utilities.
257 - New polymeric materials based on element-blocks

Yoshiki Chujo, chujo@chujo.synchem.kyoto-u.ac.jp, Department of Polymer Chemistry, Kyoto University, Kyoto, Kyoto 615-8510, Japan

A structural unit consisting of various groups of elements is called an "element-block." The design and synthesis of new element-blocks, polymerization of these blocks, and development of methods of forming higher-order structures and achieving hierarchical interface control in order to yield the desired functions are expected to encourage the creation of new polymeric materials that share, at a high level, electronic, optical, and magnetic properties not achievable with conventional organic polymeric materials as well as forming properties of molding processability and flexible designability that inorganic materials lack.

Tuesday, August 12, 2014 08:00 AM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (08:00 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 1/2
Supramolecular polymers are considered as ideal candidates for the development of intelligent soft materials. Although macrocyclic hosts have been widely exploited for the construction of supramolecular polymers, they suffer from a variety of problems such as poor solubility and tedious synthesis for host–functionalization procedures. In this respect, acyclic receptors such as molecular tweezers, on account of their preorganized yet sufficient flexible properties, could overcome the limitations encountered for their macrocyclic counterparts. Herein, we have successfully constructed novel supramolecular polymers based on the bis-alkynylplatinum(ІІ) terpyridine molecular tweezer/arene recognition motif, which expands the host–guest toolboxes and represents a more versatile strategy for the fabrication of supramolecular polymeric assemblies.

Furthermore, stimuli-responsive properties were assigned to the resulting supramolecular polymers, by taking advantage of the unique tweezer/arene recognition behavior. Up to now, the switching elements in response to external stimuli are predominantly embedded into the supramolecular building blocks themselves. In contrast, employment of a second component as the stimuli responsive auxiliary, which allows for the achievement of programmed supramolecular systems with increasing complexity, has been far-less explored. Herein, with the employment of anthracene derivatives and cyano-functionalized dienophile as the stimuli-responsive auxiliaries, supramolecular polymerization/depolymerization process could be precisely regulated in a facile manner. Such protocol advances the concept of utilizing Diels–Alder chemistry to achieve stimuli-responsive materials in compartmentalized systems.
259 - Tuning optical properties of difluoroboron β-diketonate biomaterials for oxygen sensing

Cassandra L. Fraser1,2, fraser@virginia.edu, Christopher DeRosa1, Jelena Samonina-Kosicka4, William A. Morris1, Ziyi Fan2, J. N. Demas1, Alexander Mathew1, Gregory M. Palmer3, Mark W. Dewhirst3,4, Christina L. Hofmann4, Hansford Hendargo3. (1) Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319, United States, (2) Department of Biomedical Engineering, University of Virginia, Charlottesville, Virginia 22904-4319, United States, (3) Department of Radiation Oncology, Duke University, Durham, NC 27710, United States, (4) Department of Biomedical Engineering, Duke University, Durham, NC 27710, United States

Luminescent materials find wide application in biological imaging applications. Difluoroboron β-diketonate (bdk) complexes have desirable properties for optical imaging. When in a biocompatible, biodegradable polymer matrix such as poly(lactic acid) (PLA), they have strong, even two photon absorption, intense fluorescence and room temperature phosphorescence. That this dual emission is also present at body temperature makes them ideal for applications in biology and medicine. Previously we reported that BF2bdkPLA dye emission properties are tunable through dye molecular structure, heavy atom substitution, and polymer molecular weight (i.e. dye loading). As nanoparticles, these materials have been utilized in cell, tissue and in vivo optical imaging studies. Dynamic oxygen maps of tumor hypoxia, primate brain function and cell-seeded matrices have been demonstrated. Recent studies focus on understanding and further tuning dye optical properties, namely red-shifting absorption and emission, for safer non-UV wavelength excitation and greater tissue penetration of light. Furthermore, for ratiometric imaging it is important to understand factors that control relative fluorescence and phosphorescence wavelengths and intensities. Modulating luminescence lifetimes and thus, oxygen sensitivity is also important to different optical imaging applications and modalities. Progress in the synthesis and characterization of heavy atom-substituted dye-PLA analogues will be discussed. Naphthyl-substituted dyes will be highlighted. Fabrication and use in optical imaging and biological oxygen sensing will be presented.
260 - Enhancing the electron-deficient character of π-conjugated materials by borane functionalization

**Frieder Jaekle**, fjaekle@rutgers.edu, Department of Chemistry, Rutgers University-Newark, Newark, NJ 07102, United States

A promising approach to new π-conjugated materials with enhanced properties is to introduce heteroatoms, either embedded into the conjugated backbone or attached at the periphery. Conjugated organoboranes are known for their desirable optical and electronic properties, which have been exploited, for example, in the development of new linear and non-linear optical materials, emission and electron conduction layers in organic light emitting devices (OLEDs), and new probes and sensors for anions.[1]

In this presentation we will discuss our recent work on oligomers and polymers that contain highly electron-deficient organoborane moieties.[2] Interaction of the empty $p$ orbital on boron with the organic π-system results not only in strongly enhanced electron acceptor properties, but also very interesting optical characteristics. We will also discuss our efforts toward regioregular borane-functionalized polythiophenes and the corresponding conjugated organoboron block copolymers.[3]

![Diagram of borane-functionalized π-conjugated materials](image)


Metallopolymers have been utilized for various applications in past decades, ranging from sensors and magnetic materials to catalysts to biomaterials. Metalloocene-containing polymers with inorganic metal centers and organic framework present unique properties in many aspects. Recently, cationic metalloocene-containing polymers have attracted increasing attention. While the synthetic methodologies have been on the right trajectory to provide polymers with controlled structures, compositions and functionalities. The use of these polymers for biomedical applications is still in their infancy stage. This presentation will cover some of latest discoveries from our group on how to use these polymers as antimicrobial agents against some of most malicious bacteria. In addition, I will also talk about other possibilities in developing these biomaterials for interesting biomedical applications.
262 - Luminescent polymeric nanoparticles for in vitro studies using correlative light and electron microscopy

**Stephanie Schubert**, stephanie.schubert@uni-jena.de, Martin Reifarth²,³, Stephanie Hoeppener², Rainer Heintzmann³, Ulrich S. Schubert². (1) Department of Pharmaceutical Technology, Friedrich-Schiller-University Jena, Jena, Choose a State or Province 07743, Germany, (2) Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena, Choose a State or Province 07743, Germany, (3) Department of Physical Chemistry, Friedrich-Schiller-University Jena, Jena, Choose a State or Province 07743, Germany

High resolution fluorescence microscopic techniques allow the investigation of target objects in the intact biological sample with a resolution better than Abbe's limit without confusing them with the biological matrix. Transmission electron microscopic studies require a sophisticated sample preparation technique (e.g. cryo tomography), but allow the investigation of ultrastructural details including elemental composition. A combination of both techniques will give detailed insights, e.g., in the uptake mechanisms and localization of polymer nanoparticles in human cells. In order to give a high contrast in both techniques, the nanoparticles are supposed to show luminescent properties and to contain heavy elements. Therefore, we aim to synthesize an iridium(III)-based luminescent complex, which is covalently attached to the biocompatible polymer poly(lactic-co-glycolic acid) (PLGA) and formulated into nanoparticles via nanoprecipitation. In another approach, gold cluster containing nanoparticles will be formed using poly(ethylene imine) (PEI) functionalized with fluorescent dyes.

---

Figure 1: An iridium(III) complex is covalently attached to a biocompatible polymer and formulated into nanoparticles.

Figure 2: Gold-PEI clusters gold clusters enhance the contrast in electron microscopy, covalently attached fluorescent dyes make the nanoparticles detectable in fluorescence microscopy.
263 - Phosphorous as a scaffold for transition metals: Synthesis, characterization, and reactivity of organometallic phosphonium salts

Amir Rabiee Kenaree, Paul J. Ragogna, Joe B. Gilroy, joe.gilroy@uwo.ca. Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research (CAMBR), The University of Western Ontario, London, Ontario N6A 5B7, Canada

Metal-containing polymers are a class of macromolecules that possess interesting properties such as semiconductivity, redox activity, and preceramic characteristics due to the incorporation of transition metals into processable polymer chains. 1 Although several classes of metal-containing polymers exist, there remains a need for new synthetic strategies towards the realization of metallopolymers with tunable and well-defined properties. Quaternary phosphonium scaffolds have proven to be powerful tools in the generation of multifunctional polymers due to their versatility and stability. However, to the best of our knowledge, these salts have not previously been employed in the synthesis of metal-containing polymers. Our efforts in this area are focused on the generation of metal-containing quaternary phosphonium salts from phosphine gas and their subsequent polymerization. Recent results in this area will be presented.

264 - Colloidal polymerizations with metallic and semiconductor nanoparticle monomers

Jeffrey Pyun, jpyun@email.arizona.edu, Department of Chemistry & Biochemistry, University of Arizona, Tucson, Arizona 85721, United States

We will discuss our recent efforts on the synthesis of new class of metallopolymers based on self-assembling inorganic nanoparticle monomers to form colloidal polymers. The polymerization of these colloidal monomers is enabled by the synthesis of ferromagnetic dipolar nanoparticles (diameter » 20 nm) that form 1-D assemblies spanning hundreds of nanometers to microns in length. We will discuss our recent efforts to synthesis structurally complex dipolar nanoparticles and their (co)polymerizations with disparate monomers to form novel colloidal copolymers with segmented, or statistical compositions. Furthermore, we will discuss the phase behavior of these colloidal polymers when blended and cast into thin films.
Metal-containing polymers represent an important research field due to their combination of unique and intriguing redox, electronic, magnetic, optical, and catalytic properties and their ability to be easily processed and fabricated into thin films, fibers, and other forms. Modern technology depends on fast, reliable data processing and storage. Hard ferromagnetic (L1₀-phase) FePt alloy nanoparticles (NPs) with extremely high magnetocrystalline anisotropy are considered to be one of the most promising candidates for the next generation of ultrahigh-density data storage systems. The question of how to generate ordered patterns of L1₀-FePt NPs and how to transform the technology to the practical application is challenging. As these metallopolymers can be readily shaped and patterned using various lithographic techniques, they offer a convenient synthetic access to patterned arrays of metal NPs with control of their composition and density per unit area, which are crucial factors for many magnetic and electronic device applications. However, many of the most desirable properties are exhibited by metal alloy NPs rather than single-component metal NPs. In this talk, the recent advance in developing new functional metallopolymers (including bimetallic metallopolymers or blends of Fe and Pt homopolymers) as precursors to magnetic metal alloy nanoparticles and their lithographic patterning studies will be presented. These metallated polymers are promising as building blocks in high-density magnetic data storage media where the convenient and rapid patterning of magnetic NPs is highly desirable.
266 - Cylindrical brushes with azide endfunctionalized polyoxazoline side chains for application in tumor immune therapy

Jasmin Bühler¹, Sabine Gietzen¹, Anika Reuter¹, Karl Fischer¹, Matthias Bros², Stephan Grabbe², Manfred Schmidt¹, mschmidt@uni-mainz.de. (¹) Department of Physical Chemistry, University of Mainz, Mainz, Germany, (²) Department of Dermatology, Medical Center of the University of Mainz, Mainz, Germany

Polymeric nanocarriers constitute a rapidly developing field for various biomedical applications ranging from chemotherapeutics to contrast agents. The ideal nanocarrier is not cytotoxic, has a size between 10 and 100 nm and does not form aggregates in blood serum due to strong interactions with the numerous proteins and enzymes present in the complex biological fluids. In order to achieve specific cell targeting via various receptors for oligosaccharides or antibodies the carrier itself must not be taken up by any of the very many different cells in the body. Being biologically inert, the ideal nanocarrier needs many functional groups prone to clean conjugation chemistry, in order to derive chemically well defined structures with a high biological specificity. Towards these goals, a new nanocarrier is introduced which consists of a cylindrical brush polymer with poly-2-oxazoline side chains carrying an azide functional group on each of the many side chain ends. Utilizing copper-free “click” chemistry fluorescent dyes, anti-DEC205 antibodies and tumor associated antigens were successfully conjugated to the periphery of the cylindrical brush polymer. Selective binding to DEC205⁺ positive mouse bone marrow derived dendritic cells (BMDC) was observed in the presence of DEC205⁻ negative BMDC and non DC both of which did not take up the conjugate to a significant extent.
Poly(2-oxazoline)s are representing an intriguing alternative to PEG. It was found recently that poly(2-methyloxazoline) (PMOx) and poly(2-ethyloxazoline) (PEtOx) are both preserving proteins in their natural folding. Particularly enzymes are highly active in presence of these polymers. Here, we present amphiphilic polymer conetworks based on PMOx and PEtOx that afford entrapped enzymes to be highly active in organic solvents. This is successful, because macromeric crosslinkers based on PMOx and PEtOx act as compatibilizer and protecting agents for rendering enzymes soluble in mixtures containing hydrophobic monomers. After polymerization the obtained conetworks contain intact enzymes, such as lipases, proteases, and peroxidases, which catalyze chemical conversions in organic solvents with high activity. Additionally, PMOx was covalently attached to enzymes rendering them soluble in organic solvents. By using blockcopolymers containing a block of the hydrophobic poly(2-heptyloxazoline) enzymes, such as lipase, can even be solubilized in toluene. In some cases these PMOx-enzyme conjugates are much higher active that the unmodified protein in organic solvents. For example, PMOx-laccase-conjugates dissolved in chloroform show an up to 150,000 times increased bioactivity.
The efficient and reliable closure of internal and external surgical wounds is one of the greatest challenges in surgery. The traditional techniques using sutures and staples have improved, but they have limitations: the most common and serious one is leakage. A number of innovative materials are available to repair and support tissue, but none of them is able to fully replace sutures. We are developing a general adhesive tissue tape (GATT) based on poly(2-oxazolines) (POX) containing NHS esters in the side chain (POX-NHS) as biocompatible scaffold, which will be crosslinked by a multi-amine. In this way a crosslinked tissue adhesive polymer film will be formed.

The material properties and tissue adhesion are tunable by e.g. controlling NHS content and NHS : amine ratio. In this presentation we will present the developed synthesis strategies for POX-NHS and the results on the adhesive polymer films.
Poly(2-oxazolines) are an interesting and upcoming class of polymers as potential alternative to poly(ethylene glycol). While poly(ethylene glycol) has to be prepared using highly reactive oxirane-monomers via anionic polymerization, the living cationic ring-opening polymerization is an easy and experimentally robust method to polymerize 2-substituted 2-oxazolines. It offers the advantage of controlled degree of polymerization and polymer architecture for polymers with low dispersity and broad variability in terms of the chemical functionalization of the polymer side chains. For example, different oxazoline monomers with acrylic or allyl side-chains combine oxazoline-based advantages like biocompatibility with the opportunity of metal salt free "thio-ene-click" reactions [Luxenhofer,2006] that can be exploited for the preparation of cytocOMPATIBLE hydrogels. [Farrugia,2013]

The introduction of thiazolidines (protected cysteines) at the side-chain of polymers would provide water-soluble macromers with cysteine capacity. [Hackenberger,2008] Vicinal amino thiols offer versatile opportunities, for example using the amine for ionic interaction and the thiol for redox sensitive cross-linking. They especially permit chemo-selective coupling using native chemical ligation (NCL) which describes the selective conjugation of cysteine moieties with thioesters via a stable peptide bond. Thioesters rapidly exchange with α-aminothiols yielding thioesters with an adjacent amine. These amine-substituted thioester rearrange fast to the final stable amide.

Here we present an easy route to synthesize water-soluble cysteine functionalized poly(oxazolines) by living cationic ring opening polymerization of the thiazolidine-functionalized monomers 2-(methyl)-2-oxazoline and 2-(butenyl)-2-oxazoline respectively 2-(decenyl)-2-oxazoline and subsequent deprotection to cysteine-residues. The amount of cysteine side-chains were predetermined by the statistical copolymerization of the monomers and confirmed by NMR. We present examples of hydrogel formation using these polymers and show that the functionalization with deprotected thiazolidines enables simple attachment of proteins by NCL and leads to polymer-protein conjugates in a chemically orthogonal and highly selective manner.
270 - Designer hydrogels based on poly(2-oxazoline)s for 3D cell culture systems

Tim R Dargaville1, t.dargaville@qut.edu.au, Jodie Haigh1, Kathleen Lava2, Bart Verbraeken2, Brett Hollier1, Danica Hickey1, Richard Hoogenboom2. (1) Institute of Health and Biomedical Innovation, Queensland University of Technology, Brisbane, Queensland 4000, Australia, (2) Department of Organic Chemistry, Ghent University, Krijgslaan, Ghent B-9000, Belgium

Poly(2-alkyl-2-oxazoline)s (PAOx) are enjoying renewed interest thanks to recent advances in their synthesis and potential as biomaterials. Hydrogels are one of the most important types of biomaterials and have a long and successful history in scientific and medical applications. Many early hydrogels were based on passive, inert materials, but more recently, new hydrogels with function and dynamic features have become possible. Despite these advances, there has been little innovation in the backbone polymers used for such hydrogels, and almost all studies rely on just a select few hydrophilic polymers, hindering further advances. The poly(2-oxazoline)s are a promising alternative to more established hydrogel materials, including poly(ethylene glycol) (PEG), and the range of 2-oxazoline monomers available is ever increasing, which has opened up the possibilities for numerous types of crosslinking reactions. Included in these are very mild and cell-compatible conditions allowing for use with cells. The protein-resistant properties of PAOx, coupled with their ease of functionalization make them ideal candidates for the basis for cell-instructive hydrogels for use in 3D cell culture to study disease.

We have used copolymers of methyl 2-oxazolines with unsaturated alkyl-2-oxazolines to produce hydrophilic networks decorated with peptides consisting of integrin bindings sites and enzyme-degradable sites via simple thiol-ene photochemistry. Crosslinking was achieved using di-thiol functional small molecules, also exploiting photochemistry giving temporal control over the gelation process. The resulting PAOx hydrogels showed good swelling properties with control over adhesion of human fibroblasts on the surface of the gels. When seeded with breast cancer cells, the hydrogels containing matrix metalloproteinase degradable crosslinks became populated with 3D cancer spheroids with morphology similar to that observed in cancerous tissue. As such, these fully synthetic hydrogels can be used to study cancerous and other diseased tissue types in vitro with improved reproducibility and handling over existing 3D cell culture systems.
Poly(2-alkyl-2-oxazolines) have attracted much attention recently. We are interested in exploiting poly(2-oxazoline)s in novel applications particularly in the context of cellular engineering. We report here the development of biologically compatible poly(2-alkyl-2-oxazoline) materials.

We have synthesised different poly(2-alkyl-2-oxazoline) coated cell substrates. These surfaces have been characterised using two types of cell (human bronchial epithelial cells (16HBE) and human fetal lung fibroblast cells (MRC5)). By comparing their adhesion and growth behaviour we have developed a procedure which allows one of our studied cell types to be preferentially grown from a mixture of the two.

We also report the development of poly(2-oxazoline) thermogelling polymers. These consist of a polar carboxymethylcellulose backbone, supporting poly(2-oxazoline) 'arms' which reversibly link the gel together. These materials reversibly gel within a temperature region suitable for biological applications. We have then used this material to support multi-layered cell sheet production. This allows cells of different type to be grown and layered on top of one another.
Design of biocompatible and responsive hydrogels and nanogels made from poly(2-oxazoline)s

Camille Legros\textsuperscript{1,2,3}, camille.legros@enscbp.fr, Daniel Taton\textsuperscript{1}, Sébastien Lecommandoux\textsuperscript{1}, Michael K.C. Tam\textsuperscript{2}, Marie-Claire Gillet de Pauw\textsuperscript{3}. (1) University of Bordeaux - LCPO, France, (2) Chemical engineering, University of Waterloo, Waterloo, Canada, (3) University of Liège, Belgium

Nanogels made from partially hydrolyzed poly(2-ethyl-2-oxazoline) (PEtOx) were prepared first, in dilute aqueous solution in the presence of a di-glycidyl ether cross-linker (1), and by an inverse w/o emulsion process. In the latter case, in addition to 1, the use of a cleavable cross-linker homologue (2), namely 1,6-hydroxyethyl disulfide-bis-di-glycidyl ether, led to cleavable nanogels. The pH-responsiveness of all cross-linked PEtOx derivatives was demonstrated in an acidic environment, owing to the protonation of amino-groups. Nanogels derived from 2 were cleaved under a reductive environment.\textsuperscript{1}

Another series of hydrogels were derived from poly(2-oxazoline)s statistical copolymers bearing pendant aldehydes functionalities, in presence of dihydrazide cross-linkers. These hydrogels were stable for several days at physiological pH but were readily cleaved in acidic environment. Such systems could potentially be used to encapsulate hydrophilic biomacromolecules such as proteins, in situ, thanks to the specificity of the chemistry used.

Finally, some toxicity assays were performed on the nanogels prepared (complement activation and viability tests). We evidenced a non-toxic and stealth behavior that attested their interest in biotechnology and medicine. Such nanogels were made biocompatible and responsive to specific environmental conditions; two key attributes for a smart delivery system for biomedical applications.\textsuperscript{[ol][ii]} C. Legros \textit{et al.}, \textit{Polym. Chem.} \textbf{2013}, \textit{4}, 4801-4808.\textsuperscript{[ii][ol]}

\textbf{Tuesday, August 12, 2014 04:20 PM}
Poly(2-Oxazoline)s and Polypeptoids (01:30 PM - 05:05 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
273 - Synthesis of thermoresponsive poly(2-oxazoline) polymers for biomedical applications

Marcel A Boerman\textsuperscript{1,2,3}, M.Boerman@science.ru.nl, Harry L Van der Laan\textsuperscript{1}, Johan Bender\textsuperscript{3}, Richard Hoogenboom\textsuperscript{4}, Sander C.G. Leeuwenburgh\textsuperscript{2}, John A. Jansen\textsuperscript{2}, Jan C.M. Van Hest\textsuperscript{1}. (1) Radboud University Nijmegen, Institute for Molecules and Materials, Nijmegen, The Netherlands, (2) Radboudumc, Department of Biomaterials, Nijmegen, The Netherlands, (3) GATT Technologies BV, Nijmegen, The Netherlands, (4) Ghent University, Supramolecular Chemistry Group, Ghent, Belgium

Recently, poly(2-alkyl-2-oxazolines) (PAOx) have found their way into biomedical applications. PAOx have PEG-like properties regarding 'stealth' behaviour and biocompatibility. However, in contrast to PEG, PAOx-polymers are free to functionalize in both side chains and end groups which greatly increases the scope of these polymers over PEG. In the current study, PAOx co-polymers were synthesized by living cationic ring opening polymerization (LCROP) using both methylester functionalized monomers (MestOx) and n-propyl functionalized monomers (n-PropOx). The resulting polymers were postmodified towards amine and NHS-ester functional polymers (Figure 1). Interestingly, these nPropOx-based co-polymers exhibit lower critical solution temperature behaviour in water (Figure 2), which is dependent on both the polymer architecture and composition (f.e. the ratio between hydrophobic/hydrophilic groups, Mn) and external factors (concentration, pH, salt). In this work, the synthesis and thermal solution properties of these copolymers is discussed in view of possible biomedical applications.

- Figure 1: Synthesis of nPropOx-based co-polymers

- Figure 2: LCST-behavior of P(nPropOx-COOH) copolymers in MQ (5 mg/mL)
Producing synthetic soft worm and rod structures with multiple chemical functionalities on the surface would provide potential utility in drug delivery, nanoreactors, tissue engineering, diagnostics, rheology modifiers, enzyme mimics and many other applications. Here, we have synthesized multifunctional worms and rods directly in water using a one-step reversible addition-fragmentation chain transfer (RAFT)-mediated dispersion polymerization at high weight fractions of polymer (> 10 wt%). The chain-end functionalities included alkyne, pyridyl disulfide, dopamine, β-thiolactone and biotin groups. These groups could further be converted or coupled with biomolecules or polymers. We further demonstrated a nanorod colorimetric system with good control over the attachment of fluorescent probes. Membranes with various chemical functionality will also be discussed.
275 - Low-catalyst-concentration atom transfer radical polymerization (ATRP) of monomers bearing reactive functional groups and post-polymerization modifications of the produced polymers

Nicolay V. Tsarevsky, nvt@smu.edu, Yannick P. Borguet, David C. McLeod, Shannon R. Woodruff. Department of Chemistry and Center for Drug Discovery, Design and Delivery in Dedman College, Southern Methodist University, United States

The synthesis of polymers with reactive functional groups that can participate in easy to carry out and high-yield post-polymerization modifications, and can therefore serve as precursors of numerous functional materials, is of great importance in materials science. For example, epoxides are very attractive for post-polymerization modifications owing to the ease with which they react with a wide variety of nucleophiles, oxidants, or reducing agents. Likewise, phosphonium and sulfonium salts undergo a number of reactions that are useful for the synthesis of functional polymers. This work will describe the preparation of well-defined linear, star-shaped, and branched epoxide-, phosphonium-, and sulfonium-salt-containing polymers by low-catalyst-concentration ATRP [figure 1], as well as various chemical transformations that these polymers undergo. In addition, general rules for the rational selection of reaction conditions (e.g., selection of the initiators, reducing agents, solvents, etc.) suitable for conducting the polymerization of reactive monomers under low-catalyst-concentration ATRP conditions will be outlined.
Using atom transfer radical coupling (ATRC) on dibrominated polymers prepared by atom transfer radical polymerization (ATRP) can afford macrocyclic polymers. This method is limited to polymeric end groups that undergo bimolecular termination reactions by head-to-head coupling, and also have $K_{ATRP}$ values large enough to make a bimolecular radical-radical reaction feasible. The inclusion of a radical trap in the ATRC phase (RTA-ATRC) allows for more lenient conditions during the ring closure, but more importantly allows for the participation of polymer chains incompatible with coupling by traditional ATRC. Here, we report the use of intramolecular RTA-ATRC towards streamlining the production of macrocycles, and also as a method that allows for the creation of new macrocyclic materials.
Recently, drug delivery systems have begun to utilize membrane-penetrating polymers and peptides to facilitate release of endocytosed therapeutic agents. Nucleic acid-based therapeutics such as siRNA must escape the endosome prior to fusion with lysosomes which contain degradative nucleases. A number of viruses utilize pH-responsive fusogenic peptides to penetrate cellular and endosomal membranes, but the use of viral peptides in drug delivery applications presents immunogenic concerns. This limitation has prompted the investigation of pH-responsive polymers capable of inducing hydrophobic membrane disruption within the pH range typically found in the endosome (pH=5-7).1 Bae and colleagues2 have prepared pH-tunable poly(acryloyl sulfonamide) (PAS) endosomolytic polymers with rapid and adjustable pH response behavior. However, the nature of the uncontrolled polymerization method used by Bae and coworkers limited their preparation of advanced well-defined polymer architectures. In this work, we report on the reversible addition-fragmentation chain transfer (RAFT) polymerization of sulfonamide-containing methacrylamide monomers to yield a library of polymers which undergo rapid and reversible pH-induced solubility changes in aqueous media across a range biologically relevant pH values. Current work entails the study of sulfonamide-substituent effects on solubility behavior of the resulting polymers and their application as potential endosomal membrane disrupters.


278 - Boron polymers as luminescent, sensory, and stimuli-responsive materials

**Frieder Jaekle**, fjaekle@rutgers.edu, Department of Chemistry, Rutgers University-Newark, Newark, NJ 07102, United States

With the advent of controlled polymerization techniques as versatile synthetic tools, the field of amphiphilic block copolymers has experienced tremendous growth. However, while much work has been performed using typical organic monomers, the area of organic-inorganic hybrid systems has only recently seen significant advances.

The combination of the advantageous features of boranes with the assembly behavior or block copolymers has proved to be a promising new direction with numerous potential applications. Among notable recent examples are boronic acid-functionalized stimuli-responsive block copolymers for use as sensory materials, luminescent nanomaterials derived from boron diketonate modified polylactide or bodipy-functionalized polyacrylates for medical imaging, and self-assembled block copolymers that feature pendant carborane moieties for optoelectronic applications.[1]

In this talk we will discuss our recent results on the use of controlled radical polymerization to prepare well-defined organoboron homo, block and star polymers. We will also elaborate on the use of boron polymers in supramolecular chemistry, including the development of new sensory and stimuli-responsive materials.

279 - Multiblock copolymer synthesis by the RAFT process

Sebastien Perrier, s.perrier@warwick.ac.uk, Department of Chemistry, University of Warwick, Coventry, United Kingdom and Faculty of Pharmacy, Monash University, Melbourne, Victoria VIC 3052, Australia

This lecture will present our latest results in the design of multiblock copolymers by the RAFT process. We have designed multiblock copolymers with block number varying from 3 to 20 and degrees of polymerisation varying from 5 to 200 by sequential monomer addition, each step reaching near 100% conversion. The reaction can be undertaken at room temperature or above, in a variety of solvent, including water. The same process also allows to produce polymers of molecular weight up to 1 million g/mol.

References


Gody, G.; Maschmeyer, T.; Zetterlund, P.B.; Perrier, S. Rapid and Quantitative One-Pot Synthesis of Sequence-Controlled Polymers by Radical Polymerization, Nat. Commun., 2013, 4:2505 DOI: 10.1038/ncomms3505
280 - New design of amphiphilic core-shell particles for catalysis: One-pot synthesis in emulsion and application to the rhodium-catalyzed aqueous biphasic olefin hydroformylation

Rinaldo Poli\textsuperscript{1}, rinaldo.poli@lcc-toulouse.fr, Si Chen\textsuperscript{1}, Xuewei Zhang\textsuperscript{2}, Andrès Cardozo\textsuperscript{3}, Muriel Lansalot\textsuperscript{2}, Franck D'Agosto\textsuperscript{2}, Bernadette Charleux\textsuperscript{2}, Eric Manoury\textsuperscript{1}, Florence Gayet\textsuperscript{1}, Carine Julcour\textsuperscript{3}, Jean-François Blanco\textsuperscript{3}, Laurie Barthe\textsuperscript{3}, Henri Delmas\textsuperscript{3}.

\textsuperscript{(1)} Laboratoire de Chimie de Coordination, CNRS, Toulouse, France, \textsuperscript{(2)} Chemistry, Catalysis, Polymers & Processes (C2P2), CNRS, Villeurbanne, France, \textsuperscript{(3)} Laboratoire de Génie Chimie, CNRS, Toulouse, France

RDRP has reached sufficient maturity and flexibility to elaborate complex architectures for specific functions. The recently emerged development of nanoreactors for multiphasic catalysis attracts growing attention. In industrial olefin hydroformylation, the successful aqueous biphasic approach is limited to the lighter olefins (propene, butene) with sufficient solubility in water. Among various solutions for the successful extension to higher olefins, micellar catalysis suffers from loss of the free surfactant at the interface and from stable emulsion formation by micelle swelling.

We have generated unimolecular equivalents of micelles by cross-linking the amphiphilic arms at the core. This was achieved by one-pot RAFT polymerization in water, with successive copolymerizations of a hydrosoluble MAA:PEOMA 50:50 mixture (Step 1), a hydrophobic mixture containing a ligand-functionalized monomer (x:(1-x) 4-diphenylphosphinostyrene:styrene; x=0.05-0.25) (Step 2) and a styrene/diethylene glycol-dimethacrylate mixture (Step 3) for crosslinking the structure. Steps 2 and 3 can also be done simultaneously. The resulting latex consists of monodispersed spheres.

Various solvents can swell the polymer core and coordination of the hydroformylation precatalyst Rh(acac)(CO)\textsubscript{2} is rapid. These nanoreactors have been applied to the aqueous biphasic hydroformylation of 1-octene as a model substrate, leading to fast transformations, rapid and effective reaction product separation and low catalyst leaching. The effect of the nanoreactor structure (shell/core size, phosphine density, cross-linking) and reaction parameters (temperature, pressure, stirring rate) on the catalytic efficiency, selectivity and leaching will be presented and discussed.

Tuesday, August 12, 2014 03:50 PM
Controlled Radical Polymerization (01:00 PM - 05:30 PM)
Location: Hilton San Francisco Union Square
Room: Continental Ballroom 4
281 - Synthesis and properties of block and gradient copolymers made using RAFT polymerization

Kate A. Knapp, Lily A. Dayter, Devon A. Shipp, dshipp@clarkson.edu. Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam, NY 13699-5810, United States

Reversible addition-fragmentation chain transfer (RAFT) polymerization using malonate N,N-diphenyldithiocarbamate (MDP-DTC) controls molecular weight growth in the polymerization of styrene, N-vinyl pyrrolidone (NVP), vinyl laurate (VL), and n-butyl acrylate (nBA), monomers with disparate reactivities. The progress of $M_n$ and dispersity ($D$) with conversion in these reactions indicate that reasonable control is imparted on the growth of all monomers, particularly NVP, VL, but to a lesser extent nBA and styrene. Homopolymers of styrene were isolated and used as the macro-RAFT agent for the synthesis of poly(styrene-block-VAc) copolymers. The GPC data provide evidence of successful block copolymerization. $^1$H nuclear magnetic resonance (NMR) spectroscopic and differential scanning calorimetry (DSC) data also support the formation of block copolymers.
By focusing on synthetic reactions that are highly specific and reliable, the concept of click chemistry has enabled a transfer of the creative power of chemical synthesis to a wide range of scientific research areas and applications. In this contribution, we introduce triazolinedione compounds (TAD), build up from an aza-moiety, as scalable and robust building blocks for click chemistry applications in the area of polymer synthesis. Examples of facile catalyst-free and ultrafast macromolecular functionalization, polymer-polymer linking and polymer cross-linking under ambient conditions, mostly in combination with copper-mediated controlled radical polymerization techniques, will be presented. An added feature to this powerful type of chemistry is the intense colour switch from the TAD compounds (red) to the corresponding adducts (colourless), providing a visual feedback system.

Moreover, triazolinediones, when combined with indole reaction partners, can also be 'unclicked' at elevated temperatures, and furthermore integrally transferred to an alternative reaction partner. This new concept of *transclick* reactions has also been used to introduce thermoreversible links into materials, giving rise to dynamic bulk properties such as polymer network healing, reshaping and recycling.

In conclusion, we think that TAD-based click/transclick reactions, in combination with controlled radical polymerization techniques, can enable an unprecedented advancement in the field of macromolecular engineering.

Incorporation of metal centers into macromolecules has led to materials that combine the catalytic, magnetic, and electronic properties of metals with desirable mechanical and processing properties of polymeric frameworks. Metallocene-containing polymers attract significant attention due to their high thermal stability, fully reversible redox chemistry and many other fascinating properties that arise from their unique sandwich-like structures. Recent advances in polymerization techniques have provided opportunities to prepare polymers with tunable chemistry and compositions with controlled topologies, predetermined molecular weight and narrow molecular weight distribution. In this presentation, we will summarize some of latest development on the use controlled and living polymerization to prepare functional polymers containing metallocenes. One of major focuses in our group is to integrate cationic metallocenes into polymeric frameworks. This presentation will also cover the efforts in preparing cationic metallocene-containing polyelectrolytes.
Polymer brushes as ideal materials to interface with biological systems. They transition from the hard materials to the softer biological world over a distance of a few nanometers, can prevent non-specific binding, and provide additional entities for attachment or functionalization. This presentation will describe the important role polymer brushes play in two types of biosensors. Infectious diseases, such as influenza, present a constant threat of pandemics and increasingly require sensors able to rapidly detect selective antibodies. We present a novel electrochemical detection system based on an antibody catalyzed water oxidation pathway, which takes advantage of the intrinsic ability of the primary antibody to generate H2O2 when in the presence of singlet oxygen and water. The platform incorporates a patterned polymer brush-modified surface where specific antibodies bind to conjugated haptens with high affinity, specificity and sensitivity. In contrast, a second biosensor includes a PEDOT:PSS based microelectrode on polymer substrate to measure neuronal activities in vivo. Here polymer brushes are integrated as soft, biocompatible scaffolding to anchor glucose oxidase for specific charge exchange reactions to occur between the biological media and the conducting polymer sensor. We demonstrate that our method of brush polymerization from the PEDOT:PSS surface does not alter the conductivity of the transistor. Covalent binding of glucose oxidase to the brushes prevents enzyme leakage showing remarkable sensitivity and stability over a time period of 100 days.
285 - Preparation of functional bioconjugates using atom transfer radical polymerization

Saadyah Averick, Saverick@andrew.cmu.edu, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, United States

The properties of bioconjugate materials have inspired the search for advances in polymer and biochemistry. Atom transfer radical polymerization is a popular method for preparing bioconjugates due to its tolerance of functional groups and ambient polymerization conditions. Figure 1 demonstrates the applications of ATRP in the synthesis of bioconjugates and this presentation will expound two examples 1) AGET ATRP was used to grow polymers from a genetically encoded initiator that was expressed at the 134 amino acid residue in the green fluorescent protein while maintaining the protein’s tertiary structure 2) An ATRP initiator phosphoramidite was synthesized and directly incorporated into DNA on a solid phase resin. The DNA macroinitiator was used to grow well defined hydrophilic and hydrophobic polymers. The DNA block copolymers were capable of selectively recognizing their compliment strand thereby demonstrating both the integrity of the DNA during polymerization and their potential usage as sensors.

Figure 1: Application of ATRP to synthesize bioconjugates leading to innovative polymer solutions for biomedical applications
The living cationic ring-opening polymerization of 2-oxazolines has been studied in great detail since its discovery in 1966. The versatility of this living polymerization method allows copolymerization of a variety of 2-oxazoline monomers to give a range of tunable polymer structures and properties, including orthogonal end-group and side-chain modification. However, poly(2-oxazoline)s were almost forgotten in the 1980s and 1990s due to the long reaction times and limited application possibilities. In the new millennium, a revival of poly(2-oxazoline)s has arisen because of their potential use as biomaterials.[1-3]

Recent developments that illustrate this potential of poly(2-oxazoline)s will be discussed in this lecture, including their use as pharmaceutical excipients,[4] evaluation of degradation and toxicity behavior[5] as well as the preparation of various side-chain functionalized polymers and their use for the preparation of hydrogel cell scaffolds.[6]

REFERENCES

287 - Rapid and versatile construction of polyphosphoester-based nanostructures designed for various biomedical applications

Shiyi Zhang\textsuperscript{1,2}, zhangshiyi5@gmail.com, Karen Wooley\textsuperscript{1}. (1) Departments of Chemistry and Chemical Engineering, Texas A&M University, United States, (2) Department of Chemistry, Washington University in St. Louis, United States

The development of synthetic methodologies for the preparation of complex, functional polymer materials by simple strategies has enormous potential for biomedical applications. Here, two degradable nanoparticle systems based on one alkyne-functionalized polyphosphoester and their broad applicability in treating diseases, such as pulmonary cancers, infections and injuries, will be discussed. The highly water-soluble backbone of the polyphosphoester endowed the first system with ultrahigh paclitaxel loading capacity (55 wt%) and a maximum paclitaxel Concentration of 6.2 mg/mL in water, for the treatment of lung cancers. In the second system, the easily functionalizable side-chain of the polyphosphoester allowed for the preparation of a family of nanoparticles with diverse surface charge types, non-ionic, anionic, cationic and zwitterionic, in a rapid and versatile manner. The anionic nanoparticles are designed to load silver ions to treat pulmonary infections, while the cationic nanoparticles are being applied to regulate lung injuries by their degradation products.
Controlled release drug delivery systems have transformed therapeutics used in modern medicine but exhibit limitations for treating various diseases. Biodegradable polymers have been extensively studied to address such challenges. Through chemically incorporating therapeutic bioactives into a polymer backbone via hydrolytically degradable bonds, high drug loading, improved delivery, and enhanced bioactive stability can be achieved. Polymers containing a non-steroidal anti-inflammatory drug, salicylic acid, and antioxidant molecules from the hydroxycinnamic acid class were synthesized into bioactive-based poly(anhydride-esters) as controlled release drug delivery systems. The synthesis, characterization, drug release profiles, formulation methods, and potential applications of bioactive-containing poly(anhydride-esters) were studied.
289 - Biomedical polymers for fun and profit

Joseph P. Kennedy, josep19@uakron.edu, College of Polymer Science and Polymer Engineering, The University of Akron, United States

This session on Innovative Polymer Solutions for Biomedical Application is for young professionals starting in the field of biomaterials. I am certain all had superb technical education in polymer science and are ready to start their career in industry or academia. But they will also need deep appreciation of how to create marketable value with polymer science. To this end, I will briefly present my perception of innovation and entrepreneurship and follow up with a road-map toward innovation in biomaterials. I will illustrate my point by showing how fundamental research in carbocationic polymerizations has led to designed polymers by macromolecular engineering and thence to a wide variety of novel biomaterials designed to improve the human condition. The star of this presentation is polyisobutylene, a beautifully simple highly biocompatible and superbly biostable molecule, which is used as a building block for engineered biomaterials. I will highlight biomaterials research during the past three decades mainly at The University of Akron with PIB-based polymers that became commercial or are close to becoming commercial.
The objective of this presentation is to elucidate the structure-dynamics-property relationships that underpin the performance of ion containing polymers as membranes in electrochemical energy storage and delivery technologies. We leverage quasielastic neutron scattering to quantify the dynamics within the polymeric membrane on the nano- to picosecond time scales over length scales of few angstroms to several nanometers in a series of model single ion conducting polymers, where only the cation is mobile, with systematic variations in the spacing between the ions, degree of ionization, and the type of ion. Variations in the nature of the polymer dynamics on these times and lengths scales are compared with changes in the mobility of the free ions as quantified by impedance spectroscopy. Preliminary measurements show that on the nano- to picosecond time scale the polymer relaxations can often be described by a summation of 3 different relaxation processes. The slowest, least mobile of the 3 processes generally looks purely diffusive and shows a normal thermal activation. An intermediate and more mobile process often shows strong signs of confinement; the relaxation is almost independent of Q, indicated a strongly caged type motion. However, the fastest process usually falls between the extremes of confinement and free diffusion. The motion is characteristic of jump diffusion with a characteristic residence time and jump length. Furthermore, in some cases there is clear evidence of this motion slowing down upon heating, the opposite of normal thermal excitation. In these cases the slowing down with upon heating is correlated with the appearance of ionic aggregates in the temperature dependent X-ray scattering. In this presence the relationship between the nature of these ionic aggregates, the intrinsic mobility of the polymer membrane, and the transport properties will be examined in detail.
291 - Multiscale modeling of ion transport in polymer electrolytes

Stephen J Paddison, spaddison@utk.edu, Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, United States

The utilization of clean energy sources will require the development of advanced materials through an integration of synthesis, characterization, and computations and simulations. Energy storage and conversion systems (i.e., batteries, fuel cells, supercapacitors, etc.) utilize polymeric based electrolytes that must transport ionic charge at high rates and exhibit substantial chemical and mechanical stability. Understanding the connections between the structure of the polymer and its function across multiple spatial and temporal scales remains an important challenge. This talk will present our recent efforts to understand transport in polymer electrolytes which function as the central component in various electrochemical devices. Although the transport mechanisms of cations in bulk media is fairly well understood, presently utilized polymer electrolytes are significantly more complex as the transport is determined by: nanoconfinement, interfacial effects, the dielectric constant of the composite material, and in some cases the acidity. A case will be made for the provocation afforded by experiments to motivate simulations of 'model systems' which in their turn provoke synthesis of novel materials for evaluation and testing, thereby accelerating deployment.
Replacing traditional liquid electrolytes by polymers will significantly improve electrical energy storage technologies. Despite significant advantages for applications in electrochemical devices, the use of solid polymer electrolytes is strongly limited by their poor ionic conductivity. In this talk, several important design principles for polymer electrolytes will be discussed. In particular, we will focus on the fundamental relationship between ionic transport and segmental relaxation in polymers. The classical theory predicts that the ionic transport is controlled by the segmental motion of the polymer matrix. As a result, the low mobility of polymer segments is often regarded as the limiting factor for development of polymers with sufficiently high ionic conductivity.

Using a modified Walden plot analysis, we show that the ionic conductivity in many rigid polymers can be strongly decoupled from their structural dynamics, in terms of both temperature dependence and relative transport rate.

On the other hand, polyether-based solid electrolytes have intrinsic limitations for ionic transport at ambient and low temperatures, due to strongly coupled segmental and ion dynamics. Our analysis emphasizes that decoupling of ionic transport from segmental dynamics is the key for successful design of “superionic” polymers.
Polymerized ionic liquids (PILs) are promising candidates for solid polymer electrolytes applications. They present an opportunity to combine the intrinsic high ionic conductivity of ionic liquids and superior mechanical property of polymers, while keeping the transference number of the untethered ions close to unity. A systematic study has been carried out to provide a better understanding of the ion transport mechanism in PILs. By using broadband dielectric spectroscopy, together with differential scanning calorimetry, our analysis reveals a decoupling of conductivity relaxation from the segmental relaxation in all the PIL samples. This observation stands in stark contrast to the behavior of aprotic ILs, where the ion transport and structural dynamics are closely coupled. Rheological study shows that both samples A and F have extensive aggregates of long lifetime and samples B, C, D and E have identical mechanical spectra. We find that the global chain dynamics and large scale aggregation have little effect on the decoupling phenomena and the ion transport is determined mainly by the local dynamics in our samples. Our study demonstrates that understanding and promoting the decoupling of conductivity from segmental relaxation is the key for designing highly conductive polymerized ionic liquids in electrochemical applications.
Ionomers are attractive as single-ion conducting polymer electrolytes, which would be safer and have higher efficiency than currently-used liquid electrolytes. However, ionomers do not have sufficiently high conductivities for practical application. An understanding of the relationships between ionomer chemistry, morphology, and ion transport is needed to design ionomers with improved conductivity. To investigate the morphology formed by aggregates of the ions, we have performed molecular dynamics simulations of a series of polyethylene-based model ionomer melts, in which the spacing between functional groups is precisely controlled. The simulations provide new insights into the shape, size, and composition of ionic aggregates. In particular, we observe a wide variety of aggregate morphologies, ranging from small spherical aggregates to string-like shapes and large percolated networks. The structure factors calculated from simulation agree well with X-ray scattering data, as shown in the figure.
A series of ion-bearing polymethacrylates and polyacrylamides were synthesized via Atom Transfer Radical Polymerization (ATRP). The polymerization of these molecules was well controlled with PDIs below 1.3. Polymethacrylate-block-polyacrylamide copolymers were synthesized with varying compositions using Azide-Alkyne Cu-catalyzed cycloaddition or chain extension of a macroinitiator. These copolymers served as model structures to examine the dependence of lithium ion transport on conductive domain morphology and size. In these materials, the first block contained polymer-bound lithium sulfonates and acted as a mechanical reinforcer, while the second block acted as the lithium solvating matrix. Our results showed that the ionic conductivity increased as the interfacial surface area between the two blocks increased (i.e. ionic conductivity increased as domain size decreased).

Some of these block copolymers exhibited lithium conductivities within one order of magnitude from Li-doped PEG standards. The methods and results described in this report will help guide the development of new highly conductive, mechanically robust, ion transporting layers for lithium rechargeable batteries.

Tuesday, August 12, 2014 03:55 PM
Transport in Polymer Membranes (01:30 PM - 05:15 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 8
Recent research in Polymer electrolyte membrane fuel cell (PEMFC) has focused on the development of membranes that operate at medium-high temperature (100 – 200 °C). The medium-high temperature PEMFC offer several advantages, such as low CO catalyst poisoning, higher efficiencies, heat management, high fuel diffusion rate and cost. However, relatively low glass transition temperature and poor thermal stability of Nafion® limits operating at high temperature. To replace perfluorosulfonic acid ionomer, sulfonated hydrocarbon membranes, acid-doped PBI membranes, inorganic additive composite membranes, pore-filling reinforced membranes and blend membranes have been studied. In particular, sulfonated hydrocarbon membranes have been studied for medium temperature applications (< 120 °C) to overcome degradation of perfluorosulfonic acid membranes and acid leakage of acid-doped PBI membranes.

In this study, sulfonated poly(sulfide sulfone imide) copolymers were successfully synthesized, and the polymer electrolyte membranes were characterized with physical properties and electrochemical performances. The obtained new polymers containing flexible sulfide bond and six-membered imide ring were synthesized in m-cresol, at 180 °C, by random polycondensation. Two types of membranes were prepared by using different non-sulfonated diamine to verify effects of the hydrophobic component. IEC values were controlled by the degree of sulfonation ranging from 50 to 80 %. All the membranes showed good thermal stability and high mechanical strength. Dimensional stability of membranes exhibits excellent properties. Proton conductivity of two types of membranes composed of different non-sulfonated diamine shows different behavior and displays relatively high correlation with dimensional stability. Furthermore, well separated hydrophilic/hydrophobic membranes morphology was observed and the single cell performance was also tested (at 80 – 120 °C) and reported.
Solid block copolymer electrolytes for lithium batteries, comprising a polyethylene oxide (PEO) ion-conducting block and a polystyrene (PS) structural block mixed with lithium bistrifluoromethanesulfonylimide (LiTFSI) salt have been deeply studied in the past. However, transport of lithium ions in these electrolytes results in concentration over potentials during battery operation due to low cation transference numbers. Following the pioneering work of Armand and coworkers, a series of single-ion conducting block copolymer electrolytes have been synthesized where the TFSI anion is covalently bound to the PS backbone (EOS-LiTFSI). The transport of the lithium ion is studied by ac impedance spectroscopy while the morphology is studied by small angle X-ray scattering. We demonstrate an unexpected relationship between charge transport and morphology in these systems.
Anion exchange membrane fuel cells (AEMFCs) have gained significant attention in recent years because they can efficiently and cleanly convert the chemical energy stored in fuels directly into electrical energy. Since AEMFCs utilize a solid alkaline electrolyte [i.e. anion exchange membrane (AEM)] to transport hydroxide anions, they can avoid issues previously faced with the concentrated aqueous KOH electrolyte in alkaline fuel cells. However, significant shortcomings still remain in AEMFCs such as poor long-term alkaline stability and low hydroxide conductivity. In attempts to improve alkaline stability, we prepared styrene-ethylene/butylene-styrene (SEBS)-based AEM materials bearing various ammonium-cation groups. Utilizing our groups’ recently developed metal-catalyzed synthetic strategy, involving C-H borylation followed by Suzuki coupling, we introduced highly stable ammonium-cation species to the aromatic units of SEBS. We will present the synthesis, hydroxide transport properties, and alkaline stability of these SEBS-based AEMs.
299 - Practical and robust biocatalytic routes to low odor architectural coatings

James Bohling, jbohling@dow.com, Paul Doll, David Frattarelli, Selvanathan Arumugam. The Dow Chemical Company, Collegeville, PA 19426, United States

There are approximately 700 million gallons of house paint sold in the United States each year. From the 1940’s to today the amount of Volatile Organic Compounds (VOC) typically found in an architectural paint (and released into the environment) has been reduced from over 400g/L to often less than 50 or even 5 g/L. The drive for water based “near 0” VOC architectural paints with ever lower odor is driven by both environmentally and health conscious consumers as well businesses that want to minimize down-time. While consumers may correlate reduced VOC levels with a parallel odor reduction this may not be the case. Small quantities of malodorants with a low odor threshold can have a large impact on a paint’s odor profile. One method to address this group of low quantity but high odor impact materials would be to distill them out; however, this would require a large amount of energy to remove the very small amount of contaminate from the huge volumes of paint components in question. A number of the malodorants in the headspace of a typical latex paint have been identified and categorized by odor potency and functional group. The structure of the malodorants often has similar local structure and functional groups as many of the formulation materials which are critical to paint performance. Any method to reduce the undesirable materials must be selective as well as time and cost effective. By employing commercially available biocatalysts the most impactful classes of malodorants were cost (and energy) effectively mitigated without damaging other paint components. The selection of biocatalysts and conditions which achieved this balance will be discussed.

Tuesday, August 12, 2014 01:30 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (01:30 PM - 05:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
Biology is poised to become the underpinning science for materials developments in the 21st century. Since many of biology’s functional materials are built from polymers, biology provides important materials and mechanisms to create structure and function. We will focus on two capabilities that often characterize biological polymers: stimuli-responsive self-assembly and enzymatic functionalization. Many biopolymeric systems can be triggered to self-assemble by modest changes in conditions (e.g., temperature and pH). While self-assembly results from physical interactions that are individually weak, a large number of such interactions may participate in the process - making the self-assembly process appear irreversible and the final structure dependent upon the conditions used to trigger self-assembly. We review recent studies that demonstrate structure and properties can be controlled by the sequence of triggering cues and the conditions that are imposed at the time of self-assembly. Also, biological polymers can be acted-upon by enzymes and this enables biocatalytic mechanisms to be enlisted to create structure and confer function. We describe recent studies with two enzymes that have been shown to confer functionality to biopolymers. We anticipate that the integration of biology into materials science will have important impacts in emerging applications in the medical and life sciences.
301 - Biorefinery technology: Expanding the market for renewables through superior performance in lubricants and other high value applications

Kathleen O'Leary Havelka, kathleen.havelka@elevance.com, Elevance Renewable Sciences, Woodridge, IL 60517, United States

The chemical industry is facing increasing regulations toward more sustainable solutions globally that do not compromise performance. This talk will review the latest advances in design and development of high-performance, bio-based lubricants and other high value products that are based on Elevance's novel and proprietary biorefinery process. The biorefinery is based on Nobel prize winning technology and patented metathesis processes that create unique building block molecules from renewable feedstocks; the unique building blocks enable a higher level of performance than previously obtainable.

This talk will cover the advantages of metathesis technology in preparing these building blocks from renewables. These bio-based building blocks offer significant versatility in the design and development of synthetic pathways to a variety of high-performance synthetic lubricants and other products. Examples of the components that have been developed, and the data indicating significant performance benefits versus conventional technology will be presented. The superior performance demonstrated in lubricants and other high value applications is helping to ensure wide market demand for biobased technology.

Tuesday, August 12, 2014 02:20 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (01:30 PM - 05:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
302 - Vegetable-based building blocks for the synthesis of renewable polyurethanes and polyesters

Henri Cramail, cramail@enscbp.fr, Etienne Grau, Lise Maisonneuve, Carine Alfos. LCPO, University of Bordeaux, Pessac, France

Synthetic polymers (300 Mtons per year) have become an integral part of our modern technological society. They are mainly used in the packaging, textiles, adhesives, coatings, medicine, electronics, cosmetics, etc. As fossil feedstock runs low, the role of chemists is now to develop green chemistry and environmentally friendly alternatives to access bio-sourced polymers. Vegetable oils have a large potential to provide renewable chemicals, thanks to their availability, sustainability and biodegradability. The latter bring different functional groups (esters, unsaturations) that can be derivatized to design novel well-defined functional building blocks for the synthesis of speciality polymers. In this talk, recent investigations performed at the LCPO in the field of bio-based polyurethanes and polyesters will be presented.

Tuesday, August 12, 2014 02:45 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (01:30 PM - 05:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
Despite many significant advancements during past few decades in the field of polymeric materials to improve their performance and environmental footprint, our heavy dependence on petrochemical resources make them unsustainable for future development. Bio-based materials, such as plant oils, are important resources and sustainable alternatives to petroleum-derived materials. Their unique chemical structure and functionality provide opportunities to derive functional building blocks for polymeric materials such as coatings, adhesives and composites. Using principles of green chemistry and engineering, our research group has designed and developed a platform of soybean oil-based functional building blocks for their use in advanced coatings such as water-borne, high-solids and UV-curable systems. These "green" soy-based building blocks promise effective replacement of petro-based products in the current industrial coating formulation, while maintaining equal or better performance attributes.

A family of hyper-branched soy-polyols having different chemical structures, morphology, functionality, and functional group contents has been developed from epoxidized soybean oil. Specifically, soy-oligomers with –hydroxyl, -isocyanate, -acrylic and –silane functionality have been prepared and characterized. UV-curable aqueous polyurethane dispersions with excellent balance of mechanical properties have been derived using soy-polyols and acrylated soy-polyols as primary components. High-solid moisture-cured urethane coatings have been developed from hyper-branched soy-polyols prepared by Michael-addition reaction of acrylated epoxidized soybean oil and N,N-Diethanolamine, showed excellent mechanical and chemical resistance properties suitable for a number of protective coating applications. This study clearly demonstrates that these functional soy-building blocks with high bio-renewable contents have myriads of potential commercial applications.
304 - Nanosurface properties of biopolymer coatings used for oral drug delivery

*Maurice Brogley*, maurice.brogly@uha.fr, Ahmad FAHS, Sophie Bistac. LPIM, Université de Haute Alsace, Mulhouse, France

For pharmaceutical applications such as oral controlled drug delivery systems, Hydroxypropyl methylcellulose (HPMC) is a promising raw material for coatings or films obtained from aqueous systems. Additives are incorporated into biopolymer matrices to produce high quality drug protective films.

The aim of this work is to explore their bulk and surface properties [1]. The influence of additives on HPMC structuration and morphology, permeation, hydrophilic or hydrophobic character as well as surface adhesion and friction are evaluated at nanoscale. Stearic acid additive has a strong influence on HPMC surface properties and morphology due to microphase separation and surface migration of stearic acid molecules. A sharp variation of nano-adhesion and nano-friction forces is observed with addition of fatty acid and thus even for low additive content 1% (w/w HPMC). PEG additives induce an increase of the surface hydrophilicity and affect HPMC morphology by insertion mechanisms. Swelling of HPMC clusters is observed as PEG content increases.

At the nanoscale, the increase of PEG content causes an increase of friction and adhesion forces.

Results underline the strong dependence of surface film properties with additive nature and concentration. formulation is then an original way to tune surface morphology and properties of biopolymer films.

One way to increase the bioavailability and thus the efficiency of an active pharmaceutical ingredient (API) is to appropriately formulate it into a vector. Nowadays challenges in encapsulation technologies for drug delivery applications are the design of nanomatrices that (i) are able to provide sustainable drug release (especially those which has low solubility in the receiving phase) and (ii) respond to changes to external stimuli (i.e. temperature, pH). Here we report an original nanovector for loading and release of curcumin (CU), a hydrophobic API, known for its anti-oxidant or anti-cancer activity. The vector is prepared by combining solid lipid nanoparticles (SLN) with mesostructured silica materials. Indeed, silica is known to be safe, not only for the environment, but also for the human body within a certain range of administrated dose while SLN are promising drug carriers with potential applications in pharmaceutics. Therefore, combining mesoporous silica with solid lipid nanoparticles is a straightforward approach for the design of advanced formulations in drug delivery or food chemistry.

The carrier matrix were prepared by first loading the curcumin into dispersions of solid lipid nanoparticles in a micellar phase, followed by the silicalization of the colloidal system by sol-gel. [1,2]. The dual templating mechanism afforded a compartmentalized nanovector, with both macro and mesostructured domains. The SLN act as a reservoir of curcumin while the surfactant present in mesopores is assisting the release (Fig. 1). Moreover, the sustainability of the release depends on the nature of the solid lipid and on the pH of the receiving phase. Cell viability experiments confirm the potentiality of the designed silica-SLN-CU nanovector for drug delivery formulation.


(2) A. Pasc, J.-L. Blin, M.-J. Stébé, J. Ghanbaja RSC Advances 2011, 1, 1204
Polymeric materials significantly enhance the daily lives of all citizens of the developed world. For most applications these materials must be flame retardant. Organohalogen compounds, particularly brominated aryl ethers, are readily available at moderate cost, may be readily incorporated as additives into polymeric matrices, and are very effective gas-phase flame retardants. However, these are stable compounds which do not readily degrade in the natural environment. Further, they tend to bioaccumulate and may pose health hazards to the human population. For these reasons, effective alternatives are being sought. Organophosphorus compounds can serve as replacements for popular organohalogen flame retardants. Ideally, these compounds should be derived from non-toxic renewable biosources and should be degradable to innocuous products in the environment. A series of such compounds derived from esters of isosorbide (from starch) and 10-undecenoic acid (from castor oil) is being developed.
We report the synthesis of different diblock and triblock metal containing polymers with pendant pyrene and terpyridine units. These polymers may serve as the dispersants for carbon nanotube or graphene due to the strong non-covalent pi-pi interactions. The terpyridine unit may form a variety of metal complexes with interesting optical and electronic properties. As a result, the resulting polymer-carbon nanotube/graphene hybrids may exhibit enhanced photosensitivity. These properties of studied by photoconductive atomic force microscopy. The potentials of employing these hybrid materials for sensing probes have also been investigated.
Regioregular organometallic polymers possessing titanacyclopentadiene-2,5-diyl units in the main chain were converted into new \( \pi \)-conjugated polymers possessing various elements-blocks such as thiophene-1-oxide, selenophene, tellurophene, phosphole, stibole, and bismole. Subsequent chemical modifications of the polymers possessing 1,4-bismercapto-1,3-diene, tellurophene, and phosphole units were also carried out to give \( \pi \)-conjugated polymers that exhibit unique optoelectronic properties. Namely, the polymers obtained in the present studies exhibited both p-type and n-type semiconducting properties depending on the nature of the elements-blocks attached to the \( \pi \)-electronic systems. The narrow band gap materials have also been prepared by the facile molecular design of diynes. For example, a phosphole-containing polymer obtained from diethynyldithienogermole was subjected to the chemical modifications at its phosphorus atom to obtain polymers with band gap \( E_g \) less than 1.3 eV. Some of the polymers were found to be potentially applicable to photovoltaic cells.
 Polyfluorenes, one of the largest and most thoroughly studied families of conjugated polymers, have a wide range of applications. The structure of polyfluorene is such that the 9-carbon can be substituted with a heteroatom without disrupting the underlying conjugated system. We are currently studying poly(9-heterofluorene)s, where the 9-carbon of fluorene is replaced with an inorganic element. We will present our preliminary investigations into the synthesis and characterization of novel poly(9-heterofluorene)s and 9-heterofluorene containing copolymers featuring group 13 and 15 elements.
A variety of metal-based clusters can be incorporated inside carbon cages that vary in size, shape and electronic properties. The most abundant compounds include trimetallic nitrides, with general formula $M_3N@C_{2n}$ ($n$ starting at 34), but dimetallic sulfides have also been prepared and characterized in our research group, $M_2S@C_{2n}$. In the latter series we have fully characterized the compounds with $C_{82}$ cages (two isomers), $C_{72}$ and $C_{70}$, mainly with rare earth metals inside. The compound with the $C_{72}$ cage elegantly exemplifies the principle of shape complementarity between the cluster and the cage and these results will be presented and discussed. The interplay between size and electronic complementarity will be illustrated with the trimetallic nitride series, changing the metal size going from Sc to La. One of the unusual observations in this series, especially for cages smaller than $C_{86}$, is the existence of pentalene units on the surface of the cages, resulting in violations of the Isolated Pentagon Rule (IPR). Electronic factors are involved in these IPR violations. Using sulfides, we recently succeeded in preparing and characterizing a compound containing transition metals only inside, $Ti_2S@C_{78}$, which exhibits very interesting electrochemical properties, see figure.
311 - Hybrid materials containing NHC complexes for catalysis and other applications

Kate F Donnelly, Juan Olguin, Ana Petronilho, Martin Albrecht, martin.albrecht@ucd.ie. School of Chemistry & Chemical Biology, University College Dublin, Dublin, Ireland

The utilization of N-heterocyclic carbenes (NHCs) as ligands has substantially modified the scope and application of transition metals in a variety of areas.\(^1\) Advantageous effects have been, in parts, attributed to the strong metal-carbon bond in NHC complexes, which originate from a relatively high covalent contribution to the overall bonding.\(^2\) In addition, NHC ligand design is most versatile, enabling an enormous synthetic variability. As a consequence, NHCs have been combined with a range of other privileged ligand classes in attempts to foster synergies, including for example bipyridine-type scaffolds, phosphine NHC hybrids, and pincer platforms. We will discuss some of our endeavours in combining versatile NHC metal active sites with orthogonal functionalities, including for example biochemical scaffolds, inorganic and polymeric supports, and photochemically active entities.\(^3\)
Bis-ortho-chelated aryl-metal complexes, the so-called ECE-pincer metal complexes, exist in great varieties. Several novel strategies for anchoring these ECE-pincer metal complexes to soluble and insoluble supports have been developed. Key of this approach are the synthetic routes allowing for the direct introduction of functional para-substituents directly onto the preformed ECE-pincer metal complexes.¹ For example, this allows the introduction of anionic tethers which can non-covalently bind the ECE-pincer metal complex to the core of multicationic core-shell dendrimers. Recently we concentrated on the covalent anchoring of ECE-pincer metal complexes to proteins. This approach, involving the inhibitory activity of nitrophenyl phosphonate esters to the catalytic triad (serine, histidine and asparagine) of lipases, has great potential for future applications in the fields of protein structure elucidation (NMR, X-Ray, mass spectrometry), medicinal chemistry (biomarkers, MRI contrast agents, radiopharmaceuticals), biomaterials and catalysis (enantioselectivity, catalysis in aqueous media). Crystal structures of these novel ECE-pincer metal-lipase hybrids show in detail how the ECE-pincer metal unit is covalently attached to the enzyme.²

The immobilization of such a catalytic hybrid on beads and their use for the dynamic kinetic resolution of a racemic alcohol will be demonstrated.³

Organic light-emitting devices (OLEDs) are on the lips of most electronic manufacturers in the current times. With good progress made in the areas of production cost, efficiency and color output, OLEDs are being utilized in considerably more applications than were possible just a short time ago. In particular, white OLEDs (WOLEDs) hold great promise for applications in flat-panel displays and solid-state lighting. Recently, multilayered WOLEDs based on Ir(III) complexes have shown great improvements on light emission efficiencies and have already surpassed their competitive counterparts, e.g. fluorescent lamps. The use of phosphorescent materials is an effective way to get high efficiency in OLEDs due to their ability to efficiently utilize both singlet and triplet excitons. By incorporating adjacent emitting layers with blue/orange complementary colors or blue/green/red colors in a multilayered structure, stable white emission can be attained. High efficiency and good color rendition of white light emission are important issues for practical use. In this presentation, we highlight our recent progress of metallophosphors based on Ir(III) complexes and their phosphorescent WOLED applications.

References:


For many potential applications of polymer organogels and hydrogels, a high range of motion (i.e., achieving high strains) is desirable, but the maximum strain achievable is limited by the high solvent content and network defects of polymer gels. Here we use a family of organometallic complexes to show that the addition of transient, supramolecular cross-links to a covalent polymer gel can provide dramatic increases in the maximum achievable strain at break, even when the added supramolecular cross-links are so weak and dynamic as to be effectively invisible in terms of their contribution to bulk modulus or energy dissipation in materials.

The results suggest that classes of "very weak" supramolecular interactions might play an important, previously overlooked, role in developing next generation gels.
315 - Transition metals carbon nanotube complexes

Timothy M. Swager, tswager@mit.edu, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

This lecture will detail the use of transition metal complexes of carbon nanotubes for catalytic and sensing applications. Reactions with the sidewalls and termini of carbon nanotubes to install metal binding sites will be detailed. These methods include use of 1,3-dipolar cycloadditions to install functionality and model reactions on fullerenes will be described. The use of transition metals to create selective chemiresistive sensors will also be described. Specifically, we will detail the selective detection of ethylene gas in complex backgrounds by utilizing the specific reactivity of transition metal complexes.
316 - Migratory insertion polymerization (MIP): A newly developed polymerization technique for main chain metal-containing polymers

Xiaosong Wang, xiaosong.wang@uwaterloo.ca, Department of Chemistry and Waterloo Institute of Nanotechnology, University of Waterloo, Waterloo, ON N2L 3G1, Canada

Migration insertion polymerization (MIP) has been developed based on well-studied organometallic migration insertion reaction (MIR). By combing both CpFe(CO)$_2$ (Fp) and phosphine groups via an alkyl spacer, CpFe(CO)$_2$(CH$_2$)$_nP$(Ph)$_2$, FpP, were prepared as A-B type difunctional monomers. Intermolecular MIR of the monomers allows metal complexes to be connected into macromolecular backbone with P-Fe-C bonding, leading to a new group of main chain metal containing polymers. The polymers are soluble in organic solvent and stable enough for GPC analysis. Polymerization behavior and properties of resultant polymers will be presented and discussed.
317 - Novel well-defined vinyl copolymers: Control of sequence and topology by advanced bond design

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

Living polymerization has allowed control of molecular weight (chain length) and terminal groups for synthetic polymers. On the other hand, as found in DNA and peptides, sequence of functional groups or chain topology seems to be rather essential structural factor for functions of the macromolecules in nature. We have been interested in control of sequence\textsuperscript{1-5} and topology\textsuperscript{6} for vinyl polymers with a belief that the control will lead to a new family of carbon-chain with the specific functions. Crucial to realize the control is the advanced "bond design" on living polymerization where initiation (generation of active species) and propagation are basically controlled. This work deals with molecular design of initiator and monomers with such specialized bonds (e.g., cleavable, renewable, reversibly activated, etc.) and control of sequence and topology for novel well-defined copolymers.

Poly(ionic liquid)s (PILs) are polyelectrolytes with ionic liquids incorporated in the polymer backbone. PILs have attracted much attention due to their unique properties such as conductivity, etc. We have developed a new synthetic approach to access well-defined PILs using activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP). Well-controlled polymerization of the ionic liquid monomer, 1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide, was conducted with 50 ppm or lower of a copper catalyst and tris(2-pyridylmethyl)amine (TPMA) as a ligand. The resulting PILs were characterized by gel permeation chromatography (GPC) using salt-containing THF as the eluent. The polymerizations had excellent control over molecular weight and molecular weight distribution ($M_w/M_n = 1.1−1.3$). High chain-end functionality of the synthesized PIL homopolymers was achieved, which was confirmed by chain extensions to further access block copolymers.
Poly(ionic liquid)s block copolymers: Synthesis by ATRP, characterization, and self-assembly

Hongkun He¹, hongkunh@andrew.cmu.edu, Khosrow Rahimi², Mingjiang Mingjiang¹, Ahmed Mourran², Martin Möller², David Luebke³, Hunaid Nulwala³, Krzysztof Matyjaszewski¹. (1) Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States, (2) Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany, (3) National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, Pittsburgh 15236, United States

Poly(ionic liquid)s (PILs) block copolymers with well-defined structures were successfully synthesized by atom transfer radical polymerization (ATRP). Both AB and ABA type PIL block copolymers were obtained using various ATRP macroinitiators, including polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), poly(n-butyl acrylate) (PnBA), poly(t-butyl acrylate) (PtBA), and PIL macroinitiators. The resulting PIL block copolymers were characterized by gel permeation chromatography (GPC) using salt-containing THF as the eluent. The amphiphilic poly(acrylic acid) (PAA)-b-PIL self-assembled in THF/H₂O mixture to form nanoscale particles with internal bicontinuous cubic phase and external cuboidal morphology. The morphologies of the self-assembled aggregates were influenced by the variations in the polymer composition and concentration, temperature, the nature and content of the common solvent and precipitant (water).
320 - ICAR ATRP to synthesize and morphology studies of PAN-b-PSt block copolymers

**Melissa Lamson, mlamson@andrew.cmu.edu, Jake Mohin, Tomasz Kowalewski, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States**

A series of polyacrylonitrile-b-polystyrene (PAN-b-PSt) block copolymers was synthesized via initiators for continuous activator regeneration (ICAR) atom transfer radical polymerization (ATRP) and the morphologies of these polymers in thin film were studied. Appropriate ICAR ATRP conditions, for the synthesis of a PAN-Br macroinitiator, were selected to reduce copper catalyst concentration (<100 ppm) and to preserve chain end functionality. Chain extension with styrene by ICAR ATRP was also accomplished with 100 ppm of copper catalyst. The degree of polymerization (DP) of PAN was constant at 55 and the DP of PSt was varied from 5 to 37 by targeting different conversions of styrene during chain extension. Differential scanning calorimetry (DSC) of the block copolymer powders was performed to determine the onset of PAN cross-linking for all block copolymer samples. Interestingly, with increasing PSt contents the cyclization temperature of PAN increased, which indicates interference by PSt with PAN cyclization. Thin films of all PAN-b-PSt samples were cast and AFM imaging was performed to reveal different morphologies, including lamella and bicontinuous. The films were pyrolyzed to create nitrogen-enriched carbon. Pyrolysis yields ranged from 29 to 60% and surface areas ranged from 300 to 400 m²/g. Additionally, SAXS was used to investigate the morphologies of the PAN-b-PSt samples in thin film and their resulting carbons.
321 - Soft conductive materials based on Polyaniline doped by star block copolymers prepared by ARGET ATRP

Hangjun Ding\textsuperscript{1,2,3}, dinghj@andrew.cmu.edu, Mingjiang Zhong\textsuperscript{2}, Chin Ming Hui\textsuperscript{2}, Sangwoo Park\textsuperscript{2}, Christopher J Bettinger\textsuperscript{3,4}, Krzysztof Matyjaszewski\textsuperscript{2}. (1) Department of Materials Physics and Materials Chemistry, University of Science & Technology Beijing, Beijing, China, (2) Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (3) Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (4) Department of Biomedical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Star polymers with branched molecules containing multiple arms connected at a central core have properties different than their linear analogues. Herein, the linear block copolymers as the precursors of stars arms were synthesized by feeding reducing agent in activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP). Several poly(butyl acrylate)-b-poly(tert-butyl acrylate) diblock copolymer with different DP and different block order were crosslinked with divinylbenzene, using arm first technique. Optimization of ARGET ATRP conditions allowed for the preparation of well-defined star polymers in high yield (> 95%). After hydrolysis, the PtBA segments were converted into poly(acrylic acid) and used as dopant for conducting polyaniline(PANI). The star copolymers composites with PANI resulted in flexible and stretchable electronic materials, which could be suitable for potential use as flexible electronic devices and energy storage. Scheme for synthetic route and GPC traces of star polymer as show in
Control in electrochemically mediated atom transfer radical polymerization (eATRP) with copper catalysts (Cu/L, L = ligand) was achieved with chronoamperometry. The CuI/CuII ratio near the working electrode surface was determined by the applied potential ($E_{app}$) and distributed to the bulk reaction mixture through vigorous stirring. The rate of polymerization ($R_p$) correlated to the established CuI/CuII ratio generated by $E_{app}$, until the diffusion limit of the catalysts was reached. In particular, "on-demand" polymerization was achieved by switching the $E_{app}$ value either to the CuI or CuII dominant range. Removal of the transition metal ($M_t$) was carried out by further reduction of CuI to Cu0. The Cu0 was deposited on to the working electrode surface and reused for the next polymerization once stripped from the surface. Utilizing the control over the CuI/CuII ratio afforded by $E_{app}$, various monomers were polymerized by eATRP including acrylates and methacrylates under organic or aqueous media. Additionally, polymers with precisely controlled architectures, such as block, star, and brush (co)polymers, were prepared by eATRP.
323 - Synthesis of DNA block copolymers using AGET ATRP

Saadyah Averick, saverick@andrew.cmu.edu, Sourav K Dey, Subha R Das, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Functional biohybrid materials have found applications in many diverse fields such as catalysis, drug delivery, imaging and sensing. An interesting class of biohybrid materials are DNA block copolymers (DNABCp) which have been previously synthesized using "grafting-to" methodologies. We recently used a "grafting-from" approach via activators generated by electron transfer atom transfer radical polymerization to grow well-defined polymers from the 5’ end of DNA modified with an ATRP initiator (Figure 1). A potential application of this system was demonstrated by synthesizing DNA latex particles and demonstrating their ability to selectively recognize the compliment DNA strand.

Monday, August 11, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Moscone Center, North Bldg.
Room: Hall D

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
Herein we report the synthesis and characterization of molecular bottlebrushes with bimodal distribution of poly(n-butyl acrylate) (PnBA) side chain length. First, densely grafted copolymers were prepared via the "grafting from" approach using Atom Transfer Radical Polymerization (ATRP), followed by a selective deactivation of a fraction of chain ends, and a subsequent extension of the remaining active groups to form longer grafts. A capping with persistent radical, 4-butoxy-TEMPO, was proved to quickly and quantitatively remove bromine end groups, which was confirmed using a model studies with linear PnBA polymer. Three bottlebrush polymers: 100-0, 20-80 and 50-50, with 0, 20 and 50% of extended (longer) side chains respectively, were synthesized and characterized via AFM. AFM images of macromolecules 20-80 and 50-50 clearly showed a core-shell topology that was not observed for the bottlebrush 100-0, which proved a successful formation of architectures with the bimodal distribution of side chain length.
The synthesis of unique polymers with star-shaped molecular bottlebrush topology is reported. Macromolecules were prepared by the combination of bottlebrush arms with a molecular spoked wheel (MSW) core. A hexahydroxy-functionalized MSW was synthesized and converted into six-fold ATRP initiator (6-Br), from which six backbone arms with HEMA-TMS units were grafted via Atom Transfer Radical Polymerization (ATRP). Post-functionalization of the polymers provided star-shaped ATRP macroinitiators, which were further used to polymerize side chains by ATRP, thus producing star-shaped bottlebrush architectures. Three different hexa-armed brush copolymers with varying lengths of arms and grafts, i.e., MSW$_{420-g-20}$, MSW$_{420-g-40}$ and MSW$_{200-g-60}$, were prepared. GPC confirmed the formation of well-defined structures with narrow molecular weight distributions and AFM allowed for the visualization of individual polymers with unique starfish topology. Additionally, an intriguing aggregation behavior of the star-shaped macroinitiators and cleavage of star arms due to high congestion were observed.
ABA bottlebrush triblock copolymer was synthesized through the combination of Atom Transfer Radical Polymerization (ATRP) and post-modification techniques to mimic lubricin, the lubricating protein. First, block B was prepared by a copolymerization of methyl methacrylate (MMA) and 2-(triethylsiloxyl)ethyl methacrylate (HEMA-TMS) forming a pre-cursor of the brush segment, followed by the extension of the macroinitiator B with copolymers of MMA and 2-(dimethylamino)ethyl methacrylate (DMAEMA). The quaternization of DMAEMA produced a charged block A for high adsorption on negatively charged mica surfaces. HEMA-TMS was then functionalized with ATRP initiating groups to give ABA macroinitiator, followed by the grafting of biocompatible polyzwitterionic branches of poly[2-(methacryloyloxy) ethyl phosphorylcholine] (pMPC). The ABA triblock brush polymer was further assessed as a lubricant using a Surface Forces Apparatus. Interaction forces between two mica surfaces fully covered by the brushes provided a repulsive interaction force between the surfaces. When submitted to shear, the system shows extremely low frictional forces ($\mu=0.0025-0.0115$), much smaller than lubricin and dependent on the salinity of the medium, showing a potential application as biocompatible artificial lubricants.
327 - Synthesis of PEG-based star-like and bottlebrush polymers via a “grafting-through” method by ATRP

Hong Y. Cho, Pawel Krys, pkrys@cmu.edu, Sangwoo Park, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 2080$ or $950$) macromonomer was investigated as a function of monomer concentration and applied pressure in atom transfer radical polymerization (ATRP). The polymerizations were carried out at different [PEGMA]_0 ranging from 50 to 300 mM. Polymerizations were successfully conducted with [PEGMA]_0 ranging from 75 to 300 mM, whereas polymerization with [PEGMA]_0=50 mM showed no monomer conversion, indicating macromonomer concentration below equilibrium monomer concentration ([M]_e). ATRP under high pressure (HP ATRP, 3 k bar) shifts [M]_e to lower level than under ambient pressure, allowing polymerization at [PEGMA]_0 = 50 mM and resulting in high monomer conversion (>99%) and polymers with narrow molecular weight distribution.

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
328 - RDRP in the presence of Cu\(^0\): SARA ATRP vs. SET-LRP

Pawel Krys, pkrys@cmu.edu, Dominik Konkolewicz, Yu Wang, Mingjiang Zhong, Chi-How Peng, Yaozhong Zhang, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Reversible-deactivation radical polymerization (RDRP) in the presence of Cu\(^0\) is a versatile technique allowing for synthesis of well-defined polymers with complex architectures. Since 2006 a vigorous debate has continued in literature on the subject of the mechanism of this process. One proposed model, namely supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP) has Cu\(^I\) as the predominant activator of alkyl halides, and Cu\(^0\) as supplemental activator of alkyl halides and reducing agent of Cu\(^II\) through slow comproportionation process, with negligible contribution of disproportionation. Second model, named single electron transfer living radical polymerization (SET-LRP), has Cu\(^0\) as the major activator of alkyl halides. Cu\(^I\) does not activate alkyl halides but undergoes instantaneous disproportionation. Even though both models are based on the exactly same components (monomer, ligand, solvent), the kinetic contribution of participating reactions is vastly different. The experimental results show that experimental data and theoretical simulations both consistently agree with SARA ATRP and not SET-LRP mechanism in DMSO and also in aqueous media.
Atom transfer radical polymerization (ATRP) is a robust reversible-deactivation radical polymerization (RDRP) technique. ATRP uses transition metal catalysts in a low oxidation state, most commonly Cu I, to reversibly activate an alkyl halide, providing a radical and a deactivator complex in a higher oxidation state. Traditionally, ATRP required high catalyst loadings to prevent the build up of excessive concentrations of the deactivator complex. In recent years there has been a significant interest in developing techniques that allow ATRP to proceed with parts per million catalyst loadings. These low concentrations of catalyst can be used when the excess CuII deactivator in the system is reduced to Cu I. Photochemical regeneration of the activator complex is attractive due to its simplicity and miniscule amount of additives needed. An analysis of the reaction kinetics of photochemical ATRP will be present. Additionally, photochemically mediated ATRP is used to create polymers with complex architectures such as block copolymers and stars.
330 - Atom transfer radical polymerization catalyzed by iron porphyrins

Antonina Simakova, asimakov@andrew.cmu.edu, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Synthetic derivatives of a naturally occurring iron porphyrin, hemin, as catalysts for ATRP were studied. The catalytic activity of PEGylated mesohemin (hydrogenated hemin) for ATRP in aqueous and organic media was previously reported. This work extends this class of catalysts by mimicking axial ligation of iron in heme-containing proteins with histidine or methionine residues. Mesohemin with single PEG chain was modified either with imidazole or thioether moieties through the second available carboxyl group. According to electrochemical measurements, the imidazole modified version of mesohemin has a reduction potential similar to PEGylated mesohemin, but performed significantly better in polymerization. Results of polymerizations suggested a higher activity of the new imidazole modified mesohemin, exhibiting faster kinetics with lower required catalyst loadings for polymerization.
331 - FeX₃(NHC) catalyzed ICAR ATRP of MMA and St

Seiji Okada, sokada@andrew.cmu.edu, Sangwoo Park, Krzysztof Matyjaszewski. Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

N-heterocyclic carbene (NHC) adducts of iron trihalide FeX₃ (X = Cl, Br), FeX₃(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and FeX₃(HIDipp) (HIDipp = 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) were prepared and investigated for catalytic activity in initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP). Cyclic voltammetry (CV) showed a single reversible redox process and a redox potential ($E_{1/2}$) of about -480 mV ($X = Cl$) and -350 mV ($X = Br$), which indicated that FeX₃(NHC)s might be efficient catalysts for ICAR ATRP. All FeX₃(NHC)s were found to be active catalysts for ICAR ATRP of methyl methacrylate (MMA) and styrene (St). While each FeX₃(NHC) showed almost the same activity, using FeBr₃(NHC)s resulted in better controllability. For example, ICAR ATRP of MMA, using 50 ppm of FeCl₃(HIDipp) or FeBr₃(HIDipp) as a catalyst and azobis(isobutyronitrile) (AIBN) as a thermal radical initiator in 50% (v/v) anisole at 60 °C, reached 65% conversion in 24 h and gave poly(MMA) with a molecular weight distribution ($M_w/M_n$) of 1.44 and 1.20 respectively. ICAR ATRP of St was also investigated. The conversion reached 44% in 48 h and the polymerization was well controlled, giving poly(St) with $M_w/M_n = 1.15$, using 50 ppm of FeBr₃(IDipp) and AIBN in 50% (v/v) anisole at 60 °C. The number average molecular weight ($M_n$) corresponded well with theoretical values, as conversion increased in polymerizations of both MMA and St.
332 - Development of highly active copper catalysts for atom transfer radical polymerization (ATRP)

**Thomas Ribelli**, tribelli@andrew.cmu.edu, Callista Jerman, Dominik Konkolewicz, Kristin Schroder, Krzysztof Matyjaszewski. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15203, United States

Atom transfer radical polymerization (ATRP) is a well-known method to synthesize polymers with high chain end functionality and low molecular weight distributions (MWD). To further push the limits of ATRP it is imperative to continually strive towards the synthesis of more active catalysts. The activity of Cu based ATRP catalysts have been shown to correlate very well with the reduction potential \( E_{1/2} \) of the complex. It is now well established that the addition of electron donating groups (EDG) such as amino or ether groups to the ligand significantly decreases the reduction potential and therefore increases activity. Two of the most active ligands commonly utilized in ATRP, tris(pyridin-2-ylmethyl)amine (TPMA) and tris[2-(dimethylamino)ethyl]amine (Me₆TREN), have been used in this study as ligand scaffolds. Substitution of TPMA in the para position with electron donating groups resulted in highly reducing copper complexes with \( E_{1/2} \) values less than -400 mV resulting in the most active catalyst to date. Reaction of tris(2-aminoethyl)amine (TREN) with substituted benzaldehydes, subsequently followed by reduction, resulted in highly active Me₆TREN based complexes which gave linear kinetics and MWD < 1.3 at low ppm amounts of Cu. Various low ppm methods of ATRP were conducted with Me₆TREN and TPMA based ligands which gave polymers with high molecular weight and high chain end functionality. Full characterization of the synthesized ligands and complexes including \(^1\text{H}\) and \(^{13}\text{C}\) NMR, UV-Vis spectroscopy, cyclic voltammetry and X-Ray diffraction (where applicable) were conducted.
Expanding the range of functional polymers prepared using reversible-deactivation radical polymerization is critical to developing advanced materials. Poly(2-(methylthio)ethyl methacrylate) and poly(2-(methylthio)ethyl acrylate) and their respective tertiary sulfonium derivatives were synthesized using activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP). Optimization of ARGET ATRP conditions allowed for the preparation of well-defined polymers with high conversions and low molecular weight distributions (conversions >80% & $M_w/M_n < 1.2$). The stability and rate of sulfonium de-alkylation by halide anions was determined by $^1$H NMR analysis. It was found that with decreasing solvent polarity the rate of de-alkylation increased. These studies show the preparation of new functional and responsive polymers.
Embedding nanofillers into plastics and polymeric materials has enhanced many properties of composites. Nanofillers improve control of light scattering in diverse optical media and create mechanically robust self-healing materials. The control of nanocomposite properties can be programmed via a desired polymer architecture with a specific functionality and nanostructure, uniquely suited to the application. Preparation and characterization of well-defined nanocomposites synthesized using ATRP methods with ppm amounts of catalyst will be presented.
The robustness of commercial plastic materials can be enhanced by embedding nanoparticles (NPs). Interfacial area plays a very important role and affects the materials' mechanical and optical properties. Polymers grafted from/onto NPs increase their dispersability and stability of resulting nanocomposites. There are several parameters affecting the interactions of polymers with matrices, including structure and composition of polymer chains, graft density, molecular weight, and molecular weight distribution. Longer chains can entangle and improve mechanical properties, whereas shorter ones prevent particle aggregation. Thus, we will present several methods of grafting polymer brushes from surfaces of NPs with bimodal molecular weight distribution using surface-initiated atom transfer radical polymer (SI-ATRP).
Polymers have greatly enhanced the quality of life. Through them, new medical devices, protective equipment, comfort items, and safe food containers have been engineered and constructed. Yet, there are many more advances to be made with polymers. Conductive polymers are plastics (which are organic polymers) and therefore can combine the mechanical properties (processibility, flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. Their properties can be fine-tuned using the exquisite methods of organic synthesis. Polythiophenes is one of the conductive polymers that has less conductive than many other conductive polymers such as polyaniline, but has desirable mechanical properties that make it more valuable in the production of micro robotics and sensors. Specifically, its high boiling point and insolvency make it stand out from other conductive polymers. In this research unmodified and modified polythiophenes (i.e. polythiophene and 2-benzoyl polythiophene) were synthesized by radical electropolymerization strategy. The conductivity of modified polymer was determined using an IDA electrode and compared with control unmodified polymer. In conclusion 2-benzoyl substituted polythiophene showed higher conductivity possibly due to expansion in resonance system of the polymer.
337 - High pressure and temperature investigation of copper catalyzed atom transfer radical addition (ATRA) utilizing monohalogenated alkyl halides

Allison Jansto, janstoa@duq.edu, Carolynne Ricardo, Tomislav Pintauer. Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15219, United States

By the addition of a reducing agent, catalyst regeneration in atom transfer radical addition (ATRA) and cyclization (ATRC) has significantly reduced the amount of catalyst, thus creating a “greener” process. This method was first applied in the addition of polyhalogenated alkyl halides to various alkenes, and was extended to the utilization of monohalogenated substrates such as bromoacetonitrile (BrACN), 2-bromopropionitrile (BrPN), and 2-ethylbromophenylacetate (EBrP). The single carbon-halogen bond formed from the monohalogenated alkyl halides is more expedient for further organic transformations. After optimizing the reactions in NMR tubes, significantly higher yields were achieved when performed in pressure tubes with BrACN, BrPN, and EBrP, allowing increase in the reaction temperature regardless of the solvent. Copper catalyzed ATRA reactions were generally much faster when conducted in pressure tubes.

The reactions were performed with BrACN, BrPN, and EBrP with alkenes such as 1-octene, styrene, methyl acrylate, and methyl methacrylate.

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
338 - Kinetic and catalytic studies of modified copper-based tris(2-pyridylmethyl)amine (TPMA) complexes in atom transfer radical addition (ATRA)

Gabrielle Pros, prosg@duq.edu, Aman Kaur, Evan Perez, Tomislav Pintauer. Department of Chemistry, Duquesne University, Pittsburgh, PA 15282, United States

Atom transfer radical addition (ATRA) is a synthetically useful tool which adds an alkyl halide across a double bond of a terminal alkene, creating both a carbon-carbon bond and a carbon-halogen bond. TPMA, or tris-(2-pyridylmethyl)amine, when coordinated to copper, has been a successful catalyst in ATRA at very low concentrations. Much of its success is due to the electronically rich environment that the ligand provides. Cyclic voltammetry studies have shown that adding methyl and methoxy groups to the 3, 4, and 5 positions of the pyridine rings of TPMA increases the electron density around the copper, which theoretically should increase the catalytic activity. Experimental data have shown the opposite trend, where copper complexes with altered TPMA ligands with the most electron density were in fact much less active than the unsubstituted TPMA complex. Activation rate constants and equilibrium constants for ATRA were also determined for all complexes and were correlated with both electrochemical and ATRA studies.

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
339 - Ligand design based on tetradeionate tris(2-pyridylmethyl)amine (TPMA) skeleton for copper catalyzed atom transfer radical addition (ATRA)

Aman Kaur1, kaurr@duq.edu, Kristen Schröder2, Krystof Matyjaszewski2, Tomislav Pintauer1. (1) Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania 15282, United States, (2) Department of Chemistry and Biochemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

Tetradeionate ligand, Tris(2-pyridylmethyl)amine (TPMA) has resulted in the formation of highly active and stable copper complexes used for catalyzing various radical processes such as atom transfer radical addition (ATRA), cyclization (ATRC) and polymerization (ATRP). ATRA and ATRC are the fundamental organic transformations used to generate C-C bond via addition of the alkyl halides across alkene in the presence of the reducing agents. In pursuit to design even more active catalytic system to activate C-X (X= Cl, Br) bond of less active alkyl halides, we tailored three new ligands 1-(5-methoxy-4,6-dimethylpyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine (TPMA*), bis(5-methoxy-4,6-dimethylpyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine(TPMA2*), tris((5-methoxy-4,6-dimethylpyridin-2-yl)methyl)amine (TPMA 3*) with TPMA backbone in which the electron-donating groups such as methyl and methoxy are attached at 3,4,5 position on the pyridine rings. Using these ligands, new novel copper based catalytic systems were synthesized and characterized using IR, UV-Vis spectroscopy, cyclic voltammetry and single X-ray crystallography.
Novel thermoresponsive double-hydrophilic fluorinated block copolymers were successfully synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Poly[N-(2,2-difluoroethyl)acrylamide] (P2F) was synthesized via RAFT polymerization of N-(2,2-difluoroethyl)acrylamide (M2F) using 2-dodecylsulfanylthiocarbo-nylsulfanyl-2-methylpropionic acid (DMP) as the chain transfer agent (CTA) and 2,2'-azobisisobutyronitrile (AIBN) as the initiator.

The resulting P2F macroCTA was further chain extended with N-(2-fluoroethyl)acrylamide (M1F) to yield poly{[N-(2,2-difluoroethyl)acrylamide]-b-[N-(2-fluoroethyl)acrylamide]} (P2F-b-P1F) block copolymers with different lengths of the P1F block. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC). The average molecular weight (Mₙ) of the resulting polymers ranged from 2.9 x 10⁴ to 5.8 x 10⁴ depending on the length of the P1F block. The molecular weight distribution was low (Mₙ / Mₚ = 1.11 – 1.19). Turbidimetry by UV-vis spectroscopy, dynamic light scattering (DLS), and in situ temperature-dependent ¹H-NMR measurements demonstrated that the P2F block underwent a thermal transition from hydrophilic to hydrophobic, which in turn induced self-assembly from unimers to aggregates. Transmission electron microscopy (TEM) studies demonstrated that polymeric aggregates formed from an aqueous solution of P2F-b-P1F at 60 °C were disrupted by cooling down to 20 °C and regenerated by heating to 60 °C. Temperature-triggered release of a model hydrophobic drug, coumarin 102, was also demonstrated.
A series of thermoresponsive ureido-derivatized polymers were synthesized via atom transfer radical polymerization (ATRP) and a post-modification process. All of the polymers were designed to exhibit an upper critical solution temperature (UCST) in aqueous solution, which was mainly dependent on (i) the presence of ureido moieties, (ii) the chain length of the side groups, and (iii) the degree of quaternization (DQ) on a triazole ring. Side group modification of PHEMA was carried out by DCC coupling with 4-pentynoic acid to prepare PHEMA-alkyne (PHA). 2-Azidoethylurea and 2-azidopropylurea were combined with the PHA backbone via a click reaction, resulting in triazole-ring containing ureido-derivatized polymers. Quaternization reactions with methyl iodide were conducted on the triazole-ring of each polymer to further control the UCSTs. Results showed that the UCST could be precisely tuned by the level of DQ.
The network structure of polymer gels to induce rapid thermoresponse was designed by post-crosslinking of controlled ABA triblock polymers with hydrophilic and thermoresponsive blocks. The triblock prepolymer was prepared by RAFT polymerization of hydrophilic $N,N$-dimethylacrylamide (DMAAm) and the monomer carrying activated ester as a reactive site with bifunctional macro-RAFT agent of poly($N$-isopropylacrylamide) (PNIPAAm). Then, gelation was performed by post-crosslinking reaction of the triblock polymers by diamine crosslinkers. The obtained gel showed rapid shrinking against temperature change compared to conventional copolymer gels prepared by random copolymerization of DMAAm and NIPAAm in the presence of divinyl compound. This rapid shrinking property of the triblock polymer gels is probably due to hydrophilic blocks in the network working as water pathway through which the dehydrated water effectively spilled out from the inside of the gel during shrinking.
Nitrooxide-mediated radical ring-opening copolymerization: Towards the design of block copolymers comprising a degradable block

Vianney Delplace¹, vianney.delplace@gmail.com, Antoine Tardy², Yohann Guillaneuf², Didier Gigmes², Patrick Couvreur¹, Julien Nicolas¹. (1) Univ Paris-Sud, Institut Galien Paris-Sud, UMR CNRS 8612, Châtenay-Malabry, France, (2) Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire UMR 7273, Marseille cedex 20, France

Controlled/living radical polymerization (CLRP) techniques enable the synthesis of well-defined and functionalizable macromolecular architectures, which are essential features for potential biomedical applications. But the non-degradability of such vinyl (co)polymers remains a main obstacle for further developments.

Among the few strategies allowing the insertion of degradable units in the backbone of a radical polymer, radical ring-opening polymerization (rROP) is one of the most promising approaches.

In this project, taking advantage of both a CLRP technique such as nitrooxide-mediated living radical polymerization (NMP) and the rROP of cyclic ketene acetals (CKAs), oligo(ethylene glycol) methyl ether methacrylate OEGMA has been copolymerized with 2-methylene-4-phenyl-1,3-dioxolane (MPDL), aiming to obtain new biocompatible and biodegradable structures.

Chemical hydrolysis showed predictable molar mass reductions, from 25% to 90%, as a function of the chosen amount of MPDL in the monomer feed, with dispersities as low as 1,25. Livingness was confirmed by 31P NMR, with living fraction up to 75%, allowing the synthesis of a library of block copolymers containing a degradable block. The innocuousness of the obtained copolymers was also confirmed on three different cell lines (NIH/3T3, HUVEC and J774 cells), thus representing a promising approach for new tailor-made biodegradable and biocompatible polymers in the biomedical field.
344 - Bespoke poly(ethylene glycol)-based diblock copolymer nano-objects via polymerization-induced self-assembly

Nicholas J Warren, n.warren@shef.ac.uk, Oleksandr O Mykhaylyk, Daniel Mahmood, Anthony J Ryan, Steven P Armes. Department of Chemistry, University of Sheffield, Sheffield, United Kingdom

A well-defined PEG$_{113}$-dithiobenzoate is used for the reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA). Systematic variation of the mean degree of polymerization of the core-forming PHPMA block allowed PEG$_{113}$-PHPMA$_x$ diblock copolymer spheres, worms or vesicles to be prepared at up to 17.5% w/w solids, as judged by dynamic light scattering and transmission electron microscopy studies. Small-angle X-ray scattering (SAXS) analysis revealed that more exotic oligolamellar vesicles were observed at 20% w/w solids when targeting highly asymmetric diblock compositions. A PEG$_{113}$-PHPMA$_x$ phase diagram was constructed to enable the reproducible targeting of pure phases, as opposed to mixed morphologies (e.g. spheres plus worms or worms plus vesicles). Moreover, the thermo-responsive nature of the PHPMA block gives rise to order-order morphological transitions, hence this new RAFT PISA formulation is expected to be important for the rational synthesis of a wide range of biocompatible, thermo-responsive PEGylated diblock copolymer nano-objects for various biomedical applications.
We describe the facile atom-efficient synthesis of diblock copolymer nano-objects via a one-pot RAFT aqueous dispersion polymerization protocol starting from the water-immiscible glycidyl methacrylate (GlyMA). GlyMA is completely hydrolyzed to produce a 10% w/w aqueous solution of glycerol monomethacrylate (GMA) at 80°C in air within 9 h in deionized water. Kinetic analysis indicates that a significant rate acceleration occurs as the reaction mixture switches from a two-phase emulsion to a single aqueous phase. The 10% w/w aqueous solution of GMA can be polymerized using RAFT chemistry to produce a near-monodisperse PGMA macromolecular chain-transfer agent (macro-CTA), which can be subsequently chain-extended using 2-hydroxypropyl methacrylate (HPMA) via RAFT resulting in diblock copolymers which can form well-defined spheres, worms or vesicles depending on the relative block compositions. The worm phase forms free-standing aqueous gels which are soft, shear-thinning, highly biocompatible and thermo-responsive. This unusual behavior allows facile sterilization via cold ultra-filtration.
A series of poly(glycerol monomethacrylate-block-2-hydroxypropyl methacrylate-block-benzyl methacrylate) framboidal triblock copolymer vesicles (denoted as G\textsubscript{63}-H\textsubscript{350}-B\textsubscript{z} for brevity; where the mean degree of polymerization of the third block, z, is systematically varied from 21 to 373) were prepared via RAFT seeded emulsion polymerization of benzyl methacrylate using a linear G\textsubscript{58}-H\textsubscript{300} vesicle precursor. These framboidal vesicles were characterized using TEM, DLS and small-angle x-ray scattering (SAXS) and then evaluated as Pickering emulsifiers for the stabilization of \textit{n}-dodecane droplets in water. When z exceeds 125, increasing the aqueous vesicle concentration led to a monotonic reduction in the mean droplet diameter until a limiting value of 60 µm was attained at 2.0% w/v. This concentration dependence indicates that the additional hydrophobic character conferred by the poly(benzyl methacrylate) block is sufficient to stabilize the vesicles during high shear, allowing adsorption at the oil/water interface as intact vesicles. A turbidimetry assay was used to determine the vesicle adsorption efficiency as a function of increasing surface roughness. The adsorption efficiency increased from 17% up to 90% when z was increased from 21 to 125, but remained relatively constant at higher z values. Hence there is a strong positive correlation between surface roughness and Pickering adsorption efficiency. Moreover, this represents a significant improvement in Pickering emulsifier efficiency compared to that reported previously for non-framboidal cross-linked copolymer vesicles [\textit{J. Am. Chem. Soc.}, 2012, 134, 12450].
347 - Addition of water to an alcoholic RAFT PISA formulation affects both polymerization kinetics and copolymer morphology

Elizabeth R Jones, cha07erj@sheffield.ac.uk, Steven P Armes. Chemistry, The University of Sheffield, Sheffield, South Yorkshire S3 7HF, United Kingdom

The efficient synthesis of amine-functional diblock copolymer nano-objects via RAFT alcoholic dispersion polymerization has been recently reported. Benzyl methacrylate (BzMA) is polymerized in ethanol using a poly(2-(dimethylamino)ethyl methacrylate) (PDMA) chain transfer agent at 70°C. Depending on the packing parameter, p, polymerization-induced self-assembly (PISA) can produce spherical micelles, worm-like micelles or vesicles. High monomer conversions (> 99% by 1H NMR) are achieved within 24 h, while THF GPC studies indicate low copolymer polydispersities (M_w/M_n < 1.30), suggesting good pseudo-living character. When transferred from ethanol to water, the nanoparticles remain colloidally stable and acquire appreciable cationic character, as judged by DLS and aqueous electrophoresis studies respectively. Utilising an ethanol/water mixture leads to a significantly faster rate of BzMA polymerization, with 80% conversion being achieved at 70°C within 7 h. This is presumably because water is a poor solvent for the BzMA monomer, which partitions into the growing micelles; thus enhancing the local monomer concentration and increasing the polymerization rate. Moreover, the addition of water also affects the final copolymer morphology, with only kinetically-trapped spherical micelles being obtained when targeting diblock compositions that produce well-defined vesicles when utilizing pure ethanol. This suggests possible protonation of the PDMA stabilizer chains in the presence of water. The resulting charge repulsion between neighbouring chains means that more asymmetric diblocks (i.e. longer PBzMA blocks for a fixed PDMA block) are needed to achieve non-spherical morphologies.
348 - Quantum dots-glycopolymer conjugates (QD-GPs): An imaging tool for the study of polysaccharide-cell interactions

Chongyu Zhu, Chongyu.Zhu@warwick.ac.uk, Muxiu Li, Qiang Zhang, David M Haddleton. Department of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom

Polysaccharides, one of the abundant biomacromolecules in nature, have much potential in diverse applications. They have bio applications as both energy sources and as important information coding in living systems, including cell differentiation, cell–cell recognition, pathogen identification, etc. However, many issues remain unresolved because the study of the interaction between polysaccharides and proteins/cells is challenging to study.

The fluorescent imaging of polysaccharides can provide a direct-vision of the function of polysaccharides and its interaction with cells. However, the direct labeling of natural polysaccharides is not easy since the complexity of their structures. Conversely, a synthetic glycopolymer is an ideal model for mimicking polysaccharides and can be easily modified with fluorescent tags for imaging. So far, some synthetic glycopolymers with fluorescent monomers have already been made to tracking the polysaccharide-protein interaction in vitro and in vivo.

In this current work, we present the synthesis of quantum dots-glycopolymer conjugates (QD-GPs, Figure 1). Compared with normal fluorescent dyes, quantum dots (QDs) provide higher photo-luminescence for sharp and tunable excitation spectra, and offer suitable scaffolds for glycopolymer to achieve long-term colloidal stability in aqueous system. We hope this type of conjugates can become a convenient imaging tool for study polysaccharide-cell interaction.

Monday, August 11, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Moscone Center, North Bldg.
Room: Hall D

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
Within the past year Single Electron Transfer – Living Radical Polymerization (SET-LRP) has been extended to include reactions in aqueous media with low dispersities ($\bar{D} < 1.2$). This novel development has allowed for the ultrafast polymerization of water soluble monomers, particularly acrylamides, which have previously been challenging and problematic via ATRP, with unprecedented control.

The crucial step to this approach is to allow for the full disproportionation of Cu(I)X/L and Cu(0) in water prior to the addition of monomer and initiator. Disproportionation is highly dependent upon the geometry of the ligand, which if sterically hindered, can lead to co-ordination with monomer and water or ligation. Thus, the main focus of this work will be a detailed investigation into the disproportionation of various ligands in water and their subsequent use in polymerizations.

With the choice of ligand being important to the mediation of living/controlled radical polymerization, optimization of reaction conditions for the polymerization of water soluble monomers is essential. By utilizing a wide range of initiators and ligands, and allowing for full disproportionation, this work will demonstrate ultrafast living radical polymerizations with excellent levels of control.
350 - Synthesis and reactivity of telechelics by Cu(0)-mediated LRP in aqueous and non-aqueous media

Alexandre Simula, a.simula@warwick.ac.uk, David M Haddleton. Department of Chemistry, The University of Warwick, Coventry, United Kingdom

Homo and hetero-telechelic polymers provide access to a large range of architectures, from simple block copolymers to cross-linked co-network structures or self-assembled structures\(^1\). Recent advances in Cu(0)-mediated controlled/living radical polymerization (CLRP) provide the necessary control required to design such complex architectures, resulting in predictable molecular weights (\(M_w\)), narrow distributions (\(D = M_w/M_n\)) and unprecedented end group fidelity for a wide range of monomers\(^2\),\(^3\),\(^4\) (Scheme 1).

Scheme 1. Representative scheme of the synthesis and reactivity of homotelechelic polymer chains.

This presentation will show the results of an investigation into the synthesis and reactivity of \(\alpha,\omega\)-halide terminated polymer chains using two types of Cu(0) catalyst. The polymerization of hydrophobic and hydrophilic monomers is conducted in DMSO or 2-isopropanol using Cu(0) wire as a catalyst. Alternatively, water-soluble polyelectrolytes, polyzwitterionics, poly(meth)acrylates and poly(acryl amides) are obtained in aqueous media. Functional monomers can be combined to yield copolymers with tailor-made properties (\(T_g\), LCST, stimuli-response). Rapid disproportionation of Cu(I)Br in a polar medium is used in the presence of aliphatic ligands prior to polymerization to yield well defined structures. Functionalization of the halogen chain ends post-polymerization via nucleophilic substitution or ‘end-capping’ strategies are conducted to yield unique polymeric diols, diamines, ABA triblock copolymers and nanostructures.

Oxytocin, a particularly important nine residue peptide, is currently used as a therapeutic for a variety of reasons, one of the most important being in the prevention of post-partum haemorrhages. A big problem arises with access to oxytocin in low resource settings, due to having a limited stability in aqueous solutions particularly above refrigeration temperatures; therefore methods to enhance the stability are being required.

Bioconjugates, consisting of a protein covalently attached to a polymer are an area of increasing interest within the polymer field due to the important materials they provide for a range of different fields by enhancing or giving new characteristics to existing biomolecules. Controlled/living radical polymerisation techniques have been particularly important for the successful synthesis of highly defined conjugates with a high level of structural control.

This work will present some different approaches being taken for the synthesis of oxytocin-polymer conjugates utilising SET-LRP in aqueous media. For a grafting from approach well-defined polymers can be synthesised via initiator with conjugating groups attached and post polymerisation grafted. The synthesis of an Oxytocin macroinitiator is particularly useful for a grafting from approach at specific sites on the peptide.
352 - One pot synthesis of sequence-controlled polymers via photoinduced living radical polymerization

Vasiliki Nikolaou, V.Nikolaou@warwick.ac.uk, David M Haddleton. Department of Chemistry, The University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom

Biopolymers, such as DNA, peptides and proteins, present a well-defined sequence regulation of repeat units which confers remarkable properties. However, nature’s precision in regulating the molecular weight of these polymers has not been yet realized in synthetic chemistry. Herein, we report for the first time the synthesis of well-controlled multiblock copolymers of acrylates at room temperature via photoinduced living radical polymerization. The synthesis of a well-defined dodeca (12) block copolymer has been achieved, presenting quantitative yields and very narrow dispersities.

Minimal polymerization in the absence of light illustrates temporal control and alludes to potential application, one of the frontiers of materials chemistry, whereby precise spatiotemporal “on/off” control and resolution is desirable.
353 - Synthesis of hyperbranched polymers using microwave assisted CCTP

Samuel R Lowe, s.r.lowe@warwick.ac.uk, David M Haddleton. Department of Chemistry, The University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom

The synthesis of hyperbranched polymers through the use of microwave assisted reactions of both methyl methacrylate and methacrylic acid using ethylene glycol dimethacrylate as a branching point will be described. Catalytic Chain Transfer Polymerisation (CCTP) is a well-established technique with numerous industrial applications, due to its ability to effectively limit the molecular weight of methacrylate based polymers and so form low molecular weight polymers/oligomers. Hyperbranched polymers have recently become of increasing interest due to their applications in the formation of aqueous nano-structures. CCTP is particularly interesting in this regard due to the peculiarities of its mechanism which leaves a vinyl end group terminating the polymers which can be exploited by further polymerization reactions and/or ene reactions rendering the polymer as a macromonomer. Microwave assisted reactions are an appealing route for small scale synthesis and synthesis of polymers because of the high conversions that the reactions run to and the very short reaction times they require, an added benefit to this is the control that can be exerted over the reactions through the use of IR sensors and software that allows for very close control of both the temperature and the pressure of the reaction through power input.
The Reversible Deactivation Radical Polymerization (RDRP) of hydrophilic monomers in water and aqueous media has presented a challenge with respect to the control of polymerisation.\(^1\)

Single-Electron Transfer Living Radical Polymerisation (SET-LRP) is one of the RDRP techniques which allows for the synthesis of polymers with exceptionally high end-group functionality. The disproportionation of Cu(I)Br in the presence of a ligand is the key step in the SET-LRP mechanism as it generates both the activator Cu(0) and the deactivating Cu(ΙΙ)Br\(_2\) species.\(^2,3,4,5\)

This study will report on the synthesis of "block" homopolymers and multiblock copolymers of acrylamides via an iterative sequential monomer addition method using SET-LRP in water/aqueous solvents. The polymerisations are performed at or below ambient temperature without any purification steps throughout the monomer additions. Functional water-soluble polymers such as poly(\(N\)-isopropyl acrylamide), 2-hydroxyethyl acrylamide were synthesised to give unprecedentedly controlled chain length and extremely narrow molecular weight distributions (dispersity <1.10). Full disproportionation in water prior to addition of both monomer and initiator is a new approach and this order is shown to be very important\(^5\) and has been exploited in order to obtain near quantitative conversions in minutes. Moreover, the hydrolysis reaction effect on the chain end of different polyacrylamides will be discussed.

References

355 - Effect of the confined space within a protein nanoreactor on atom transfer radical polymerization

Kasper Renggli\textsuperscript{1,2}, renggli@mit.edu, Martin G Nussbaumer\textsuperscript{2}, Raphael Urbani\textsuperscript{2}, Thomas Pfohl\textsuperscript{2}, Nico Bruns\textsuperscript{2,3}. (1) Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States, (2) Department of Chemistry, University of Basel, Basel, Switzerland, (3) Adolphe Merkle Institute, University of Fribourg, Marly, Switzerland

Thermosome (THS), a group II chaperonin from the archaea Thermoplasma acidophilum, is described as nanoreactor for controlled/living radical polymerization. THS is a protein cage approx. 15.8 nm in size that displays two hemispheres with cavities of approx. 130 nm\textsuperscript{3} each (Figure A). The cavities of THS possess large pores that allow for macromolecules to enter and leave the reaction space.

A copper catalyst was engineered into the cavities of the THS using bis-aryl hydrazone chemistry. The confined space of the nanoscale volume in the nanoreactor favorably influenced the atom transfer radical polymerization (ATRP) of N-isopropyl acrylamide and poly(ethylene glycol)methylether acrylate (Figure B). Reactions in the THS resulted in polymers with lower polydispersity indices in comparison to polymerizations that were catalyzed by globular protein-catalyst conjugates. This effect results most likely from a closer proximity of the reaction partners within the confined space of the protein nanoreactor.
356 - Protein cage-polymer conjugates for drug-delivery applications synthesized by atom transfer radical polymerization

Martin Rother¹, martin.rother@unibas.ch, Martin G. Nussbaumer¹, Nico Bruns². (1) Department of Chemistry, University of Basel, Basel, Basel-Town 4056, Switzerland, (2) Adolph Merkle Institute, University of Fribourg, Marly, Fribourg 1723, Switzerland

The chaperonin thermosome (THS) from Thermoplasma acidophilum is a hollow protein complex with a diameter of approx. 15.8 nm. It has large gated pores that allow macromolecules to enter and leave the cavities of the cage. Polymers were synthesized inside of the protein cage by a grafting-from approach using atom transfer radical polymerization (ATRP). The polymers were then used as anchors to entrap therapeutic payload into the THS in order to create drug delivery systems (Figure 1). A genetically engineered variant of THS that features cysteines inside of its cavities was used for thiol-specific attachment of ATRP-initiators. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was polymerized under ARGET ATRP-conditions. Poly(DMAEMA) is a cationic polymer that allowed to enclose siRNA and DNA in the cage via ionic interactions. The protein cage-polymer hybrid was explored for siRNA and gene delivery to cells. The THS-Poly(DMAEMA) conjugates protected the oligonucleotides from degradation by RNAses. Furthermore, the protein cage shields the cationic charges of poly(DMAEMA), which reduces the toxicity of the polymer.
We have synthesized well-defined poly (butyl methacrylate (BMA)), poly (butyl acrylate (BA)) and BMA/BA copolymers using Activators ReGenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) with parts per million (ppm) levels of copper (Cu) catalyst in less than six hours under a broad range of conditions. The observed polymerization rate and initiator efficiency decrease significantly with decreasing amounts of initial Cu added. At the lower copper levels (35 ppm), only a large increase in the reducing agent concentration results in a sufficiently high polymerization rate. As a result, a semi-batch feed of reducing agent was implemented (see Figure 1). In addition, increasing BA content led to a significant increase in the initiator efficiency of the copolymerization of BMA and BA.

Kinetic modeling with Predici and Monte Carlo methods attributed the decreased polymerization rate to slow initiation, a finding subsequently confirmed experimentally. This study is expanded to the copolymerization of BA/BMA to gain further understanding through kinetic modeling. Slow initiation is also present in the model, with the increase in initiator efficiency with increasing BA content attributed to the significant difference in activation/deactivation rate coefficients for the two monomers.
We synthesized three Pluronic-based cationic pentablock copolymers with different hydrophilic/lipophilic balance (HLB) values using atom transfer radical polymerization (ATRP), including PF127-\textit{block}-poly(N,N-dimethylamino-2-ethyl methacrylate) (PF127-\textit{b-pDMAEMA}), Pluronic P123-\textit{block}-poly(N,N-dimethylamino-2-ethyl methacrylate) (PP123-\textit{b-pDMAEMA}), and PL121-\textit{block}-poly(N,N-dimethylamino-2-ethyl methacrylate) (PL121-\textit{b-pDMAEMA}). The copolymers self-assembled into core–shell structures, which could be used to co-deliver a plasmid DNA (pEGFP) and a hydrophobic drug (epirubicin, EPI). The physicochemical properties of the copolymers and drug-loaded micelles were thoroughly characterized. The micelles had a high EPI encapsulation efficiency, ~6%, and the EPI-loaded micelles exhibited a similarly cytotoxic effect to free EPI. Among the three copolymers, the gene transfection efficiency of PL121-\textit{b-pDMAEMA} was the highest, indicating the greater the hydrophobic effect the greater cellular internalization was. The co-delivery effect of pEGFP and EPI using PL121-\textit{b-pDMAEMA} as a vector was directly visualized using a confocal laser scanning microscope. The PL121-\textit{b-pDMAEMA} is a promising co-delivery system for therapeutic pDNA and hydrophobic anticancer drugs.
359 - Introducing new mediators for controlled radical polymerizations: Triazine-based unimolecular initiators

Kaila M. Mattson2,1, kailamattson@gmail.com, Jetsuda Areephong1,3, Nicolas J. Treat1,4, Saemi Oh2,1, John W. Kramer5, Hazel A. Sprafke1, Javier Read de Alaniz1,2, Craig J. Hawker1,2,4, (1) Materials Research Laboratory, University of California Santa Barbara, Santa Barbara, CA 93106, United States, (2) Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106, United States, (3) Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4R2, Canada, (4) Materials Department, University of California Santa Barbara, Santa Barbara, CA 93106, United States, (5) The Dow Chemical Company, Midland, MI 48667, United States

Controlled radical polymerizations (CRP) are of paramount importance to the field of polymer chemistry. Nitroxide mediated polymerization (NMP) is arguably the most mechanistically simple and elegant of the CRP methods. Key to the mechanism of NMP is a persistent nitroxide radical that reversibly caps the growing polymer chain-end.1 In addition to nitroxides, a number of other radicals have been employed as mediating species for polymerizations, including (arylazo)oxy, borinate, triazolinyl, and verdazyl. In seeking new persistent radicals, we identified the benzo-1,2,4-triazinyl (triazine) radical, which is highly stable in air.2 The modular synthesis of triazine-based unimolecular initiators and their utility in controlling radical polymerizations will be presented.


Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
360 - Functionalization of polyacrylamide-based materials by atom transfer radical polymerization

Vincent Beaugeard, vincent.beaugeard@etud.univ-montp2.fr, Sophie Monge, Jean-Jacques Robin. Equipe Ingénierie et Architectures Macromoléculaires, Institut Charles Gerhardt de Montpellier, UMR 5253 CNRS, Montpellier, LR 34095, France

Atom transfer radical polymerization (ATRP)\(^1\) is known as particularly interesting method to functionalize insoluble materials such as membranes, beads, fibers, etc. For such purpose, valuable groups present at the surface are converted to ATRP initiators which are then used to achieve polymerization of an appropriate monomer.

In this contribution, we report on the synthesis of an original polyacrylamide-based material using surface initiated atom transfer radical polymerization (SI-ATRP). The first step consisted in reducing some nitrile functions at the surface into primary amine. After functionalization, the SI-ATRP of acrylamide was carried out in water at room temperature. Grafting proved to be effective as notably shown by thermal gravimetric analysis, Infra-Red spectroscopy or X-ray photoelectron spectrometry. Influence of polymerization time and initial monomer concentration on the quantity of polyacrylamide (PAM) grafted on the surface were investigated.

Such material could find applications for water treatment where polyacrylamide is known to be outstanding. The interest of grafting PAM onto solid supports consists in making the separation step easier after wastewater purification. Some preliminarily results dealing with this use will be reported.

Figure 1. Synthetic pathway for the functionalization of insoluble polyacrylamide-based materials by ATRP

361 - WITHDRAWN
362 - Fluorous microgel star and single-chain folding polymers via living radical polymerization: From design to functions

Yuta Koda, koda@living.polym.kyoto-u.ac.jp, Takaya Terashima, Mitsuo Sawamoto. Department of Polymer Chemistry, Kyoto University, Graduate School of Engineering, Kyoto, Kyoto 615-8510, Japan

Perfluorinated microgel-core star and single-chain folding polymers were designed and synthesized by the Ru-catalyzed living radical polymerization to create unique fluorous functions (ref 1). With their fluorous core compartments, the core-fluorinated star polymers selectively recognized polyfluorinated amphiphilic compounds (PFCs) in water.

![Fluorous Core Star](image)

These star polymers (S1: fluorine core with 13FOMA; S2: fluorine/amine core with 13FOMA/DMAEMA; S3: fluorine/ion core with 13FOMA/METMAC) were obtained by the Ru-mediated linking reaction of PEG-Cl arms with a fluorinated monomer (13FOMA), a divinyl compound (EGDMA), and amine- or quaternary ammonium-bearing methacrylates (DMAEMA or METMAC) (e.g., S2: \( M_w = 957,000; 77 \text{ PEG-arms}; 10,000 \text{ F atom/core}; 600 \text{ N atom/core} \)). As confirmed by \(^{19}\text{F NMR}, S_1 \) and \( S_2 \) interacted with perfluorooctanoic acid (PFOA) in water, and \( S_2 \) captured PFOA more efficiently than \( S_1 \) by the in-core fluorous and acid/base cooperative interactions. The multi-functionalized star polymers (\( S_2 \) and \( S_3 \)) further achieved stepwise and selective release of encapsulated PFCs. Particularly important, \( S_1 - S_3 \) were effectively recognize, capture, and then remove PFOA and related PFCs from water even at ppm contamination level.

Amphiphilic and perfluorinated random copolymers were designed as a new class of single-chain folding polymers (ref 2). The conformation of these polymers dynamically and reversibly changes, while responding to water and fluorinated solvents, thus undergoing single-chain folding into unimer micelles. The details of the synthesis, characterization, and functions are presented in our poster session.

Transition metal-catalyzed living radical polymerization (Mt-LRP) is now a very convenient tool for precise syntheses of "well-defined" polymers. Among them, we have targeted very active catalytic systems in water, and highly robust systems with Fe (iron), abundant and safe (ref 1). Crucial is decoration of ligand under steric and electronic viewpoints.

For iron, we designed an hydrophilic phosphine ligand, P(PhOPEG)_3, with PEG chains in all three para positions. This ligand led to robust iron-catalyzed systems. For example, in contrast to most of the conventional iron catalysts that are poorly tolerant to the hydroxy group, the iron complex from FeBr₂ and P(PhOPEG)_3 enabled a random living copolymerization of 2-hydroxyethyl methacrylate and three other methacrylates, where all the monomers randomly copolymerized into statistical copolymers of controlled molecular weights. For ruthenium, P(PhOPEG)_3 also allowed aqueous controlled radical polymerizations, when combined with a precursor of Cp*Ru catalyst ([Cp*Ru(µ₃-Cl)]₄) to in-situ give an active catalyst for aqueous polymerization of PEGMA at 40 °C. The polymerization was remarkably fast and well controlled (completion in 1 h; Mₘ/Mₙ < 1.2).

References: 1) Macromolecules 2013, 46, 3342.
364 - Ferrocene-assisted "concerted redox" in living radical polymerization: Active, versatile, and sustainable catalysis

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

We developed the highly active catalysis for metal-catalyzed living radical polymerization (Mt-LRP) using ferrocene (FeCp₂) as the cocatalyst via "concerted redox" catalysis in conjunction with Ru main catalyst that is responsible for generating growing radicals. FeCp₂ promotes the following key catalytic steps (See the attached illustration): the regeneration of the Ru catalyst through reduction of trivalent forms (XRu³⁺ → Ru²⁺; X: halogen) and the halogen-capping reaction by the resultant trivalent ferrocenium halide (FeCp₂⁺X⁻).

The ferrocene-concerted catalysis allowed the synthesis of high MW polymers even with a small amount of a Ru main catalyst (50 ppm for monomer) without any loss of controllability (ref 1). In addition, ferrocene and its derivatives effectively work as cocatalysts for iron (Fe) main catalysts to realize "all-iron" catalysis. In particular, decamethylferrocene (FeCp*₂) in conjunction with FeBr₂/n-Bu₄NBr led to controlled polymerizations of polar functional methacrylates, such as polyethylene glycol methacrylate (PEGMA), 2-hydroxyethyl methacrylate (HEMA), and methacrylic acid (MAA).

365 - Ring-expansion living cationic polymerization: Precision syntheses of ring-based architectures

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

An effective route to cycopolymers has been developed via the Lewis acid-assisted “ring-expansion” living cationic polymerization of vinyl ethers, directly from a simple “cyclic initiator” with a hemiacetal ester for dynamic and reversible initiation and propagation (ref 1).

The built-in hemiacetal ester, or a carboxylic acid–vinyl ether adduct, is a key to control the ring-expansion polymerization: as the leaving group, the activated carboxylate is well-suited for retaining the ring structure, differing from monovalent halogens often employed in carbocationic initiation. The choice of a Lewis acid catalyst (SnBr4) is equally crucial, to form a reversibly dissociable but relatively strong ester bond not only during propagation but also even after quenching. The formation of cyclic polymers was proved by irreversibly cleaving the hemiacetal ester linkage of the product via acidic hydrolysis into an open-chain structure, as shown by an increase in SEC molecular weight (hydrodynamic radius), along with the clean transformation of the endocyclic hemiacetal ester into an α-carboxylic acid and ω-aldehyde terminals (by NMR). Importantly, the propagation is well-controlled to prepare ring block copolymers by sequential addition of another monomer.

Reference: 1) ACS Macro Lett. 2013, 2, 531.
366 - Functional star and single-chain polymers via living radical polymerization: From precision space/chain design to functions

Takaya Terashima, terashima@living.polym.kyoto-u.ac.jp, Mitsuo Sawamoto. Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Kyoto 615-8510, Japan

We report recent advances in the synthesis, characterization, and functions of functional star and single-chain polymers via living radical polymerization, especially focusing on the precision space/chain design for unique functions.

(A) Functional microgel star polymers were synthesized by arm-linking reactions with functional linkers and monomers: 1) star polymers with multi-functional (fluorous/amine) microgels for selective/efficient capture and stimuli-responsive release of polyfluorinated surfactants via cooperative recognition in water; 2) star polymers with self-assembly linkers for the creation of higher-order supramolecular structures within microgels; 3) arm-cleavable star polymers for the isolation and characterization of microgels.

Macromolecules 2011, 44, 4574; ACS symposium series 2012, 1101, 65

(B) Single-chain folding polymers were obtained from amphiphilic random copolymers that undergo self-folding in water via intramolecular hydrophobic/hydrogen-bonding interaction. Similarly, single-chain patched polymers were obtained from these random copolymers but with pendent olefins by crosslinking on self-folded precursors. Folding properties and structures were investigated in detail to create precision functional spaces.

J. Am. Chem. Soc. 2011, 133, 4742; Macromolecules 2014, 47, 589

(C) Functional gradient copolymers were obtained in one-pot via a tandem catalysis that synchronized ruthenium-catalyzed living radical polymerization and metal alkoxide-mediated transesterification of methacrylates with alcohols. The high controllability and versatility of the catalysis led to functionalized gradient copolymers of complex sequence (random gradient, gradient block) exhibiting unique physical properties.

Efficient, modular approaches to functional gradient copolymers and end-functional polymers were developed in metal-mediated living radical polymerization coupled with selective transesterification. Taking advantage of the high versatility of alcohols and methacrylates in transesterification, gradient copolymers are directly obtained from concurrent tandem catalysis of metal-catalyzed living radical polymerization and in situ transesterification of methacrylates with alcohols (ref. 1,2). Typically, methyl methacrylate (MMA) was polymerized with a ruthenium catalyst in the presence of a chloride initiator R–Cl (1), titanium isopropoxide, 1-dodecanol, and molecular sieves 4A. MMA was transesterified into dodecyl methacrylate (DMA), concurrently with living copolymerization of both monomers, to afford MMA/DMA gradient copolymers in one pot (ref. 2), where gradient sequence is catalytically controllable by the Ti concentration. Interestingly, gradient copolymers with a linearly shifting sequence distribution from MMA to DMA showed an extremely broad range of glass transition temperature. The tandem catalysis is further applicable to various functional gradient copolymers with unique physical properties: amphiphilic MMA/PEGMA gradient copolymers with MMA and poly(ethylene glycol); fluorous 13FOMA/DMA gradient copolymers with a perfluorinated methacrylate (13FOMA) and 1-dodecanol; MMA/RMA “bidirectional” gradient copolymers with a bifunctional chloride initiator (2). Additionally, end-functional polymers were obtained by the selective transesterification of the w-end methacrylate.

368 - Protein-reactive RAFT agents for the design of polymer-protein conjugates

Nane Vanparijs¹, nane.vanparijs@ugent.be, Benoit Louage¹, Samarendra Maji², Qilu Zhang², Lenny Voorhaar², Richard Hoogenboom², Bruno De Geest¹. (1) Department of Pharmaceutics, Ghent University, Ghent, Oost-vlaanderen 9000, Belgium, (2) Department of Organic Chemistry, Ghent University, Ghent, Oost-vlaanderen 9000, Belgium

Polymer-protein conjugation is attractive for a large number of therapeutic and diagnostic applications. Controlled radical polymerization offers a unique tool to design well defined polymers with functional end-groups that could be used for protein conjugation. Here we compare head-to-head different RAFT based approaches to design polymers with a protein-reactive end-group. For this purpose, a series of functional chain transfer agents were synthesized. 2-propionic acidyl butyl trithiocarbonate was modified with either a NHS (N-hydroxysuccinimide) or a PFP (pentafluorophenyl) ester as lysine-reactive moiety, and either a furan-protected MAL (maleimide) or PDS (pyridyl disulfide) as cysteine-reactive moiety. These functional CTAs were used for RAFT polymerization of 2-hydroxyethylacrylate. Polymerization with NHS, PFP and PDS CTAs provided well defined polymers with low dispersity. The maleimide CTA however, was prone to side-reaction above 50% conversion. This is probably due to early deprotection of the maleimide during polymerization. Additionally, further side-reactions were observed upon final deprotection of the maleimide, even after end-capping of the trithiocarbonate group. Protein conjugation was performed in aqueous buffer using bovine serum albumin and ovalbumin as model proteins, and evaluated by SDS-PAGE. PFP-functionalized polymers were found to outperform NHS-polymers, likely owing to the higher hydrolytic stability of the PFP group. PDS-functionalized polymers outperformed the MAL-polymers, likely due to the higher end-group fidelity obtained via the PDS route. Additionally, the disulfide bond between formed with the PDS-strategy can be cleaved in reductive medium, which could offer particular advantages.
369 - Synthesis of cyclic poly(methyl methacrylate) homopolymers and diblock copolymers using radical trap-assisted atom transfer radical coupling

Scott C Blackburn, scb026@bucknell.edu, Eric S Tillman. Department of Chemistry, Bucknell University, LEWISBURG, Pennsylvania 17837, United States

Despite showing promise in such widespread applications as artificial photosynthesis and drug delivery vessels due to the difference in properties found with comparison to the linear chain precursors, macrocyclic polymers remain synthetically difficult and tedious to produce. Dibrominated poly(methyl methacrylate) (BrPMMABr) chains were produced by atom transfer radical polymerization (ATRP), and were added dropwise into a redox active solution to activate the dormant chain ends. In the presence of specific radical traps, intramolecular radical trap-assisted atom transfer radical coupling (RTA-ATRC) was the major pathway, creating cyclic PMMA. Evidence of macrocyclic formation was obtained by size exclusion chromatography, mass spectrometry, and also by thermolysis of the alkoxyamine bond contained within the cycle. The BrPMMABr was used as a bifunctional initiator to subsequent ATRP reactions creating BAB triblocks which, upon ring closure by RTA-ATRC, generated macrocyclic diblock copolymers.
As is the case in all areas of organic chemistry, the simplification of any synthetic process is a goal of chemists in order to obtain the product as easily and efficiently as possible. It is of special interest to polymer chemists to be able to make cyclic polymers in high yields under lenient conditions, as achieving this specific polymeric architecture is generally a tedious process. Typically, linear polymers are synthesized, isolated, end-functionalized, and then finally employed in a cyclization reaction. An approach reported by our group involves atom transfer radical polymerization (ATRP) to synthesize the linear polymers that are then directly used in an atom transfer radical coupling (ATRC) type reaction, where the same steps of purification and isolation are required in between each phase. Our research group has shown that the ATRP reaction can be directly crossed over to an ATRC type reaction without the purification step that would have previously removed any excess monomer, catalyst, and ligand. Here, we show that cyclic polymers are produced by converting an ATRP reaction of styrene into an intramolecular radical trap-assisted ATRC (RTA-ATRC) reaction by manipulating the reaction conditions.
371 - Investigation on the homogeneity of RAFT polymerized PMMA gels using dynamic light scattering and rheology

Robert Scherf¹, robert.scherf@tu-clausthal.de, Lisa S. Müller¹, Daniel Grosch¹, Eike G. Hübner², Wilhelm Oppermann¹. (1) Department of Physical Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld, Germany, (2) Department of Organic Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld, Germany

Generally, polymer networks created by controlled radical polymerization techniques (CRP) such as RAFT copolymerization of monomers with a suitable cross-linker are assumed to be more homogeneous than those made by free radical copolymerization (FRP). Our dynamic light scattering studies of PMMA gels in γ-Butyrolactone cast some doubt on this perception.

Inhomogeneity was quantified as the static fraction of the total ensemble-averaged scattering intensity. This quantity does not differ strongly between RAFT and FRP gels, when gels with identical macroscopic properties (moduli) are compared (Figure 1).

![Graph](image)

Figure 1. Plot of the static fraction of the total ensemble-averaged scattering intensity $\langle f(q) \rangle / \langle f(q) \rangle_0$ obtained at a scattering angle of 90° vs the effective density of network strands $r_{ef}$. Closed symbols refer to RAFT gels and open symbols to FRP gels.

Furthermore, rheological and swelling experiments revealed that the cross-linking efficiency of RAFT gels decreases appreciably with increasing amount of RAFT agent and is significantly lower than that of FRP gels. This indicates a larger fraction of loops, dangling chains and possibly other imperfections in RAFT gels.

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
372 - Hyperbranched modular polymers by RAFT polymerization

Patricia R Bachler, pbachler0220@chem.ufl.edu, Brent S Sumerlin, Kenneth B Wagener. Department of Chemistry, University of Florida, Gainesville, FL 32611, United States

With increasing interest in functional polymers for various applications, modular or tunable polymers have become a growing research area. A modular or tunable polymer is a polymer that serves as a platform for many different post-polymerization functionalizations. Controlling the structure of such polymers is essential since the structure directly affects the function. Hyperbranched polymers show interesting physical properties that differentiate them from their linear analogs. Many of these properties are similar to dendrimers, whose biomedical applications have been extensively studied. In this work, we describe the synthesis of modular hyperbranched RAFT polymers via two different polymerization methods to obtain polymers with predetermined branching frequencies and varying molecular weights. These polymers readily react with nucleophiles, such as amines, and therefore can be easily functionalized with many different reagents. Attachment of drugs or therapeutic agents will allow for these polymers to be used in biomedical applications, providing an alternative to dendrimers, which require a tedious step-by-step synthesis.
The effect of reaction parameters (solvent, temperature, Cu-ATRP method) and reagents (initiators, ligands) were evaluated towards optimizing the ATRP of butadiene. The polymerizations were conducted at 90 C-150 °C in a wide variety of solvent/ligand combinations (toluene, dioxane, anisole, THF, DMF, DMAC, DMSO etc. and bpy, diNbpyp, TREN, Me₆TREN etc.) using either reverse ATRP, conventional ATRP, ARGET, SARA or ICAR methods. However, while initiation was demonstrated (NMR) from a wide variety of alkyl halides (bromoester, sulfonyl, allyl, benzyl etc.), the chain end halide functionality was rather poor. Nonetheless, block copolymers could be synthesized from samples prepared at low conversions.
A series of transition metal carbonyls (Re$_2$(CO)$_{10}$, Mn$_2$(CO)$_{10}$, Cp$_2$W$_2$(CO)$_6$, Cp$_2$Mo$_2$(CO)$_6$, Cp$^*$$_2$Cr$_2$(CO)$_4$, Cp$_2$Fe$_2$(CO)$_4$, Co$_2$(CO)$_8$, Mo(CO)$_6$, Cr(CO)$_6$, Fe(CO)$_5$) in conjunction with alkyl (CH$_3$(CH$_2$)$_5$Cl, CH$_3$(CH$_2$)$_5$Br, CH$_3$(CH$_2$)$_5$I, CH$_3$I, CCl$_4$, CCl$_3$Br) or perfluoroalkyl halides (CF$_3$(CF$_2$)$_3$I, Cl(CF$_2$)$_8$Cl, Br(CF$_2$)$_6$Br, and I(CF$_2$)$_6$I) were evaluated in the initiation and control (CRP) of vinylidene fluoride (VDF) photopolymerizations and for PVDF block copolymerizations under visible light. While initiation occurred for all halides except CH$_3$(CH$_2$)$_5$Cl, and Cp$^*$$_2$Cr$_2$(CO)$_4$, Cp$_2$Fe$_2$(CO)$_4$, Co$_2$(CO)$_8$, Mo(CO)$_6$, Cr(CO)$_6$ and Fe(CO)$_5$, did not afford PVDF regardless of conditions, a free radical polymerization was observed for CH$_3$(CH$_2$)$_5$Br, CH$_3$(CH$_2$)$_5$I, CH$_3$I, CCl$_4$, CCl$_3$Br, Br(CF$_2$)$_6$Br, whereas perfluoroalkyl iodides (R$_2$I = CF$_3$(CF$_2$)$_3$I, I(CF$_2$)$_6$I) additionally mediated VDF-CRP via iodine degenerative transfer (IDT) in the presence of Re$_2$(CO)$_{10}$, Mn$_2$(CO)$_{10}$, Cp$_2$W$_2$(CO)$_6$, Cp$_2$Mo$_2$(CO)$_6$, Cp$^*$$_2$Cr$_2$(CO)$_4$, and Cp$_2$Fe$_2$(CO)$_4$. Finally, Re$_2$(CO)$_{10}$, Mn$_2$(CO)$_{10}$, Cp$_2$W$_2$(CO)$_6$, Cp$_2$Mo$_2$(CO)$_6$, and Cp$_2$Fe$_2$(CO)$_4$ also provided complete activation of both PVDF-CH$_2$-CF$_2$-I and PVDF-CF$_2$-CH$_2$-I chain ends, and were subsequently used in the synthesis of well-defined PVDF block copolymers with vinyl acetate, t-butyl acrylate, methyl methacrylate, isoprene, styrene, and acrylonitrile.
375 - Iodo(trifluoro)methylations and controlled radical polymerization of vinylidene fluoride with hypervalent iodide carboxylates under visible light

**Alexandru Asandei**, asandei@ims.uconn.edu, Christopher P. Simpson, Olumide Adebolu, Joon-Sung Kim. University of Connecticut, Storrs, CT 06269, United States

Commercially available hypervalent iodide carboxylates such as (CX$_3$COO)$_2$III$\text{Ph}$ ($X = F, H$) and (CH$_3$COO)$_3$IV(C$_6$H$_4$COO) are introduced as a new class of free radical, visible light photoinitiators for the metal-free polymerization of vinylidene fluoride (VDF) initiated by the CX$_3$ radical. Moreover, in the presence of I$_2$, a controlled radical, iodine degenerative transfer (IDT) process is mediated by the in situ generated CF$_3$I.

The iodine chain ends are further exploited in the synthesis of novel CF$_3$-decorated block copolymers with 2,2,2-trifluoroethyl methacrylate and methyl 2-(trifluoromethyl)acrylate, using Mn$_2$(CO)$_{10}$ for the activation of CF$_3$-PVDF-I.

**Tuesday, August 12, 2014 06:00 PM**
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a unique compound that consists of fused cyclohexane rings with a fixed, highly symmetric, and thermodynamically stable structure same as the diamond lattice, leading to characteristics such as a high melting point, less intermolecular interaction, a low friction coefficient, and highly hydrophobicity. A large variety of adamantane-containing polymers have been synthesized for the uses as the thermoresistant polymers, rigid-chain polymers, high-performance membranes, photoresists, photoswitchable supramolecular hydrogels, unimolecular polymer micelles, and host-guest materials. Poly(1-adamantyl acrylate) (PAdA) exhibits a high glass transition temperature (T_g), which is enough to be used as thermoplastic material with excellent thermal stability, while polyacrylates have been used as adhesives, paints, sealants, rubbers, and UV-curable resins. Thermally stable and transparent polymers are important for optical disk, fiber, lens, displays, digital signage, and lighting in the modern information and electronics technology fields.

In this study, we prepared the sequence-controlled block copolymers consisting of PAdA and poly(n-butyl acrylate) block sequences as the hard and soft segments, respectively, including polar repeating units by the organotellurium-mediated living radical polymerization (TERP). The TERP technique is one of the most powerful method of the controlled radical polymerizations for the synthesis of high-molecular-weight polyacrylates including polar and functional side groups. We investigated the thermal, optical, and mechanical properties of the acrylate block copolymers including an adamantyl moiety as the new transparent acrylic polymers with a high T_g (Figure 1). The microphase-separated structures were confirmed by the DSC and AFM observations as well as dynamic mechanical measurements. The molecular motions of the hard and soft segments were observed and the transition temperatures and activation energies increased by the introduction of the polar hydroxy and carboxy moieties in the side groups of the soft segments due to the formation of intermolecular hydrogen bonding. The effects of the hydrogen bonding and the cross-linking of the polymers on their tensile elasticity, strength, and strain were also evaluated.
Sequence-controlled polymerization is one of the most challenging topics for polymer synthesis during recent years because a polymer with well-defined sequences exhibits smart performance. The N-substituted maleimides (RMIs) polymerize in the presence of a radical initiator to give a polymer with excellent thermal stability. The RMIs and maleic anhydride (MAn) as the electron-accepting monomers react with linear and cyclic 1,3-diene compounds, such as butadiene, isoprene, cyclopentadiene, and furans, to mainly provide Diels-Alder adducts, but not alternating copolymers. This is contrast to the easy formation of high-molecular-weight and alternating copolymers with olefins and styrenes in a high yield during a free-radical copolymerization process. Recently, we found that some methyl-substituted diene monomers provided the alternating copolymers with MAn and the RMIs in a high yield because of effectively suppressed Diels-Alder reaction (Scheme 1, Figure 1). The obtained copolymers included the anhydride group and the unsaturated carbon-to-carbon double bond in the main chain and they were used for the post polymerization reactions, such as cross-linking and oxidative ozonolysis (Scheme 2). We proposed a new method for the design of reworkable resins with excellent heat-resistance using controlled radical polymerization process.
378 - Using and modeling a radical scavenger to improve the resolution in one photon direct laser writing lithography

**Shuyi Weng**¹,², sw5198@bard.edu, Christopher N. LaFratta¹, Csilla Szabo². (1) Department of Chemistry, Bard College, Annandale-on-Hudson, NY 12504, United States, (2) Department of Mathematics, Bard College, Annandale-on-Hudson, NY 12504, United States

Direct laser writing (DLW) lithography is a useful way to generate microscopic patterns for lab-on-a-chip devices. We have developed a simple and inexpensive platform for the creation of these initial patterns using a homemade acrylic resin, a 405 nm laser diode, and a fluorescence microscope. To create sub-micrometer linewidths, we included a radical scavenger into the photoresist to quench excessive amounts of radicals generated from the laser exposure. In this poster we compare various formulations of the resin and we present a model for the radical polymerization in our photoresist. The model utilizes the method of finite differences to numerically solve a system of parabolic partial differential equations that describes the diffusive behaviors of particles in the photoresist. The model also makes use of Markov chains to simulate the step-wise polymerization of the photoresist. The parameters in the model were determined by fitting the model on experimentally-obtained data.
Well-defined star shaped and linear block copolymers were synthesized to study the dispersion stability of copper phthalocyanine (CuPc). Poly (2-dimethylamino) ethyl methacrylate (PDMAEMA) and poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA) were synthesized by activators generated by electron transfer (AGET) atom transfer radical polymerization (ATRP). PDMAEMA-b-PPEGMA copolymers were characterized by GPC and NMR. Furthermore, we study the effect of the dispersion stability of copper phthalocyanine by controlling degree of polymerization of PEGMA as a stabilizing group. 4-arm star shaped polymeric dispersant showed better dispersion stability of CuPc at 25 °C for 7 days.

Figure 1. TEM images from pigment dispersed:

(a) with linear dispersant (b) with star shaped dispersant after 7 days

**Tuesday, August 12, 2014 06:00 PM**
*Controlled Radical Polymerization (06:00 PM - 08:00 PM)*
*Location: Moscone Center, West Bldg.*
*Room: Exhibit Hall*
Bicyclic polystyrene was prepared by combining atom transfer radical polymerization (ATRP) and click chemistry. The bicyclic polymer was separated from concurrently produced acyclic (branched) polymers through fractional precipitation and its purity was quantified by two-dimensional liquid chromatography (2D-LC) analysis. The structure of bicyclic polymer was characterized by SEC, MALDI-TOF MS, \(^1\)H NMR and FT-IR.

Figure 1. Preparation of bicyclic polystyrenes by combining ATRP and click chemistry and their facial separation.
There are only a few reports on the polymerization of isoprene in a controlled manner and even less work has been done on the surface polymerization of isoprene. In this work, we report the surface-initiated RAFT polymerization of isoprene on silica nanoparticle surfaces. The first step in this process is to prepare RAFT agent anchored nanoparticles. Normal RAFT agents cannot be employed for the polymerization of isoprene ascribed to the high reaction temperature (above 100°C). Thus, a high temperature stable trithiocarbonate RAFT agent, 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDSS), was anchored onto nanoparticles [Figure 1, (a) and (b)]. The amount of CDSS covalently bound to the nanoparticles surface (0.17 to 0.61 chains/nm²) was determined quantitatively by comparing the absorbance (at 299 nm) for the CDSS modified particles to a standard UV-vis absorption curve prepared from known amounts of free CDSS. Surface-initiated polymerization from modified nanoparticle surfaces was performed at 120°C in THF in a Parr reactor at different pressures [Figure 1, (c)]. GPC analysis revealed molecular weights of grafted polyisoprene ranging from 7 to 38 kg/mol with polydispersities of 1.24 to 1.9. The resulting polyisoprene grafted silica nanoparticles were mixed with polyolefin (polyethylene and polypropylene) matrices to investigate their dispersion and miscibility behavior.
Controlled radical polymerizations have significantly impacted the field of polymer science by facilitating the synthesis of polymers with greater control over molecular weight and polydispersity. Furthermore, the ease of execution, functional group tolerance and access to complex molecular architectures, have contributed to their widespread adoption. As these synthetic techniques continue to evolve, more degrees of control over the synthesis of polymeric materials are realized. Recently, external regulation of the polymerization process by various stimuli has gained attention as a way to increase the scope of polymer synthesis. To this end, our group has demonstrated external regulation of a controlled radical polymerization process with light using a photoredox catalyst. While light offers many advantages as a stimulus for polymerization, scaling up presents unique challenges such as shallow and uneven penetration of light through the reaction medium, thus negatively impacting the rate of polymerization. In this work, we address some of the challenges associated with scaling up light-mediated controlled radical polymerizations by employing a continuous flow microreactor.
It has been demonstrated that an Iridium-based photoredox catalyst can polymerize methacrylates with targeted molecular weights and low molecular weight distributions. Furthermore, light was used to mediate this process and could efficiently deactivate and activate the polymer chain end throughout the polymerization. This presentation discloses the further development of this system and its modularity in polymerization processes.

Scaffolds for tissue engineering function as an artificial extracellular matrix and play a vital role in cell adhesion, proliferation, differentiation and new tissue formation. Polymeric materials like poly(lactide) (PLA) and other polyesters have been widely used due to their favorable properties such as biodegradability, biocompatibility, low immunogenicity and good mechanical properties. However, the main disadvantage lies in the inherent hydrophobicity, which affects important factors such as circulation time in the body, cell adhesion and proliferation rates.

We thus report the development, synthesis and characterization of PLA-based amphiphilic block copolymers for the preparation of biodegradable and biofunctionalized polymer scaffolds with improved hydrophilicity and biocompatibility. The use of a unique hydroxyl-functionalized trithiocarbonate chain transfer agent allows for subsequent synthesis of these block copolymers via combination of ring opening polymerization (ROP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. In this way, poly(ethylene glycol)-block-poly(lactide) (PEG-b-PLA), poly(lactide)-block-poly(ethylene glycol ethyl ether methacrylate) (PLA-b-PPEGEEMA), and poly(lactide)-block-poly(N-(2-hydroxypropyl) methacrylamide) PLA-b-PHPMA were prepared and characterized. Furthermore, the incorporation of poly(N-methacryloxysuccinimide) (PmNAOS) via copolymerization of mNAOS with either PEGEEMA or HPMA allows for biofunctionalization of the block copolymers with bioactive agents like RGD peptide or growth factors like rh-BMP-2. Lastly, electrospinning and thermal phase separation techniques were employed to transform these novel amphiphilic block copolymers into core-shell type fiber scaffolds with potential applications in bone tissue engineering.
385 - Living cationic RAFT polymerization: Development of new chain-transfer agent and synthesis of novel block copolymer via transformation from cationic into radical RAFT polymerization

Mineto Uchiyama, uchiyama@chiral.apchem.nagoya-u.ac.jp, Kotaro SATOH, Masami KAMIGAITO. Department of Applied Chemistry, Nagoya University, Nagoya, Aichi 464-8603, Japan

Recently, we found a new metal-free initiating system for living cationic polymerization via reversible addition-fragmentation chain transfer (RAFT) mechanism using thioester in the presence of a trace amount of super acid catalyst. This work was directed to development of new chain transfer agents and synthesis of novel block copolymer. We carried out cationic polymerization of isobutyl vinyl ether (IBVE) using various transfer agents. The living cationic polymerization of IBVE proceeded with dithioesters, in which especially dithiocarbamate gave very narrow molecular weight distribution ($M_w/M_n < 1.1$). Furthermore, novel block copolymers consisting of cationically and radically polymerized segments, such as vinyl ether and vinyl ester, respectively, were synthesized via transformation from cationic into radical RAFT polymerization (scheme1).

![Scheme 1](image)

Scheme 1. Transformation from Cationic into Radical RAFT Polymerization

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
This study was directed to the synthesis of novel sequence-specific vinyl copolymers via radical alternating copolymerization between styrene and maleimide, of which the latter possesses organized sequence of two acrylate and one styrene monomer units as the building blocks.

The maleimide-functionalized oligomers were prepared by sequential Kharasch radical addition of vinyl monomers to halogen compounds, followed by SN2 reaction with furan-masked maleimide and its deprotection. The copolymerization of the maleimide-functionalized oligomers and styrene was investigated in toluene using AIBN as the initiator. Both monomers were smoothly consumed at almost the same rate and gave alternating copolymers. Although the sequence of the side chain showed small effects on the thermal properties, such as glass transition and degradation temperatures, the solubility of the copolymers significantly depended on the side-chain sequences. To clarify the effect of the sequences, the alternating copolymers with various functional groups on the side-chain sequences were also examined.
A well-defined oligo(2-ethyl-2-oxazoline)acrylate (OEtOxA) macromonomer was obtained by direct end functionalization of the living cationic oxazolinium species from the cationic ring-opening polymerization of EtOx with in situ deprotonated acrylic acid. Kinetic studies during subsequent reversible addition–fragmentation chain transfer (RAFT) polymerization as well as nitroxide mediated polymerization (NMP) experiments revealed proceeding monomer consumption but no increase of the molar mass of the resulting comb polymers. The chain transfer during the radical polymerizations is proposed to result from backbiting and subsequent b-scission of the formed mid-chain radical and took place in a well-defined manner, so that POEtOxA could also be obtained by free radical polymerization with a PDI value below 1.2. A series of POEtOxA was synthesized by RAFT polymerization with varying [monomer]/[chain transfer agent] (M/CTA) ratios and analyzed in detail by means of analytical ultracentrifugation (AUC) and small angle neutron scattering (SANS), indicating that the backbone DP does not exceed 25, which is in accordance with the thermal polymer properties in bulk and in aqueous solution (Tg = 32 °C, Tcp = 73 °C).

388 - Nitroxide-mediated polymerization of styrenic triarylamines and naphthalene diimide: Synthesis and end-functionalization of hierarchical redox-active macromolecules

Michael Jäger\textsuperscript{1,2}, michael.jager.iomc@uni-jena.de, Robert Schroot\textsuperscript{1}, Ulrich S Schubert\textsuperscript{1,2}. (1) Organic and Macromolecular Chemistry, Friedrich-Schiller-University, Jena, Germany, (2) Jena Center for Soft Matter (JCSM), Jena, Germany

The nitroxide-mediated polymerization of various styrenic triarylamines (TARA) and naphthalene diimide (NDI) employing commercially available initiators is detailed. The monomers are readily prepared by Pd-catalysed Hartwig-Buchwald coupling (TARA) or a step-wise condensation route (NDI). The kinetics of the polymerization was followed by NMR, MS and SEC analysis and confirmed the “living character” up to 50% conversion, supported by the steady molar mass increase over time and a low dispersity. Subsequent re-initiation furnished the preparation of block-copolymers with an internal redox cascade, tuned by the substituent of the triarylamine monomer (X = F, Me, OMe). The precise decoration of the chain-end by a photo-redox active ruthenium complex was achieved by simple nucleophilic substitution at the terminal benzyl chloride moiety of the initiator fragment. This methodology was readily applied to prepare the naphthalene diimides congeners. The detailed NMR and electrochemical analysis showed only marginal influence on the chemical shifts and redox-properties of the TARA units, while in case of NDI a mutual interaction of the planar pi-systems was observed. In summary, hierarchical macromolecules with tailored redox-properties can be prepared in only a few synthetic steps, which are attractive candidates as electron relays in light-driven charge separation devices.
Developments in surface-initiated controlled radical polymerization have led to the ability to precisely control the characteristics of polymer chains grafted from particle surfaces. In this presentation we systematically analyze the role of polymer graft modification on the mechanical properties and structure (order parameter) of assemblies formed by polymer-grafted nanoparticles (also called particle brushes). Using surface-initiated atom transfer radical polymerization methods, silica nanoparticles were surface grafted at high grafting densities with low dispersities over a wide range of chain molecular weights. Order formation and mechanical properties of assemblies of these particle brush systems will be interpreted on the basis of a scaling model and an inverse relationship between mechanical robustness (i.e. fracture toughness) and high degrees of order will be demonstrated. Conditions to realize concurrent order formation and toughness using SI-ATRP will be discussed.
390 - Elucidation of the governing parameters that dictate thermal transport in polymer nanocomposites

Clare Mahoney¹, clarem@andrew.cmu.edu, Benjamin Hui², Zongyu Wang¹, Shubhaditya Majumdar³, Maxim Tchoul⁴, Jonathan Malen³, Krzysztof Matyjaszewski², Michael Bockstaller¹. (1) Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (2) Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (3) Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (4) Central Research and Services Lab, OSRAM-SYLVANIA, Beverly, MA 01915, United States

Increasing the thermal conductivity of polymer nanocomposites is a prerequisite for the application of polymers in a wide range of technologies, such as electronic packaging. A key challenge in designing polymer nanocomposites with high thermal conductivity is in the thermal boundary resistance present at the particle matrix interface and subsequent reduction in efficiency of thermal conductivity enhancement from embedding inorganics. This presentation will highlight the opportunity to use Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP) to control, tailor, and minimize thermal boundary resistance in polymer nanocomposites. Through the use of SI-ATRP, it is shown that it is possible to isolate specific parameters such as nature of interfacial interactions or structural confinement of polymer graft, and evaluate the overall influence of each parameter on contributing to the overall thermal transport seen in polymer particle blends. It will be demonstrated that polymer graft modification of inorganics that introduce enthalpically favorable interactions at the interface and induce chain confinement (or extension) in the polymer grafts facilitate increases in thermal conductivity values of polymer nanocomposites that significantly exceed conventional binary nanocomposite systems. The figure below displays enthalpically favorably interacting and extended polymer chains (red) compared to conventional binary composites (blue).
Asteric polymers are currently used at The Lubrizol Corporation to provide performance advantages that enable the next generation of fuel and energy efficient lubricants. In lubricating fluids, star-shaped poly(alkyl)methacrylates (PMAs) exhibit improved viscosity index and shear stability at comparable thickening versus linear PMAs. It is now possible to prepare star-shaped PMAs on an industrial scale by utilizing a Reversible Addition Fragmentation chain Transfer agent (RAFT CTA) with processing conditions similar to a conventional radical polymerization. Until recently, the RAFT chain transfer agent S-1-dodecyl-S'-(a,a'-dimethyl-a'-acetic acid)trithiocarbonate (RAFT TTC-acid) was not commercially available in bulk quantities. The Lubrizol Corporation put forth a process development plan that has allowed for the large scale production of star-shaped PMAs. The numerous steps taken to overcome significant challenges to produce high purity RAFT TTC-ester, shown below in figure 1, on a multi-ton scale and the use of purified and technical grade RAFT TTC-ester in the preparation of PMAs will be discussed.

[figure 1]
Despite the RAFT process being well-established, little attention has been given to RAFT polymerizations in inverse microemulsion systems; two manuscripts have been published to date. In this research, we report the RAFT inverse microemulsion polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA). The inverse microemulsion system was first optimized by generating a pseudo-three-component phase diagram using cyclohexane as oil phase, a non-ionic surfactant, and an aqueous phase containing DMAEMA. The polymerization reactions were conducted at a fixed temperature while varying the CTA content, the radical source, and the pH of the aqueous phase. Based on our initial results, monomer partitioning between the dispersed aqueous phase and the continuous oil phase of the inverse microemulsion plays an important role on the polymerization kinetics, droplet/particle size, and polymer properties. Depending on the monomer/CTA ratio, only partial control over molecular weight \(M_n\) and molecular weight distributions is obtained. This suggests that the RAFT mechanism in inverse microemulsion needs further investigation.
Thiol-isocyanate “click” reactions have been used to synthesize complex polymer architectures, otherwise difficult or impossible to achieve, in a facile way due to their high efficiency and versatility. Direct polymerization of isocyanate-functional monomers has been achieved with controlled radical polymerizations (CRP), both in solution and on surfaces, 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 thereby limiting the usefulness and lifetime isocyanate functional polymers.

Herein, we use blocked isocyanate-functional monomers for polymerization by reversible addition-fragmentation chain transfer (RAFT) polymerization in solution. 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 further investigate the range of blocking agents used and the impact of the blocking agent’s structure on deblocking conditions such that stable polymers that can react efficiently with various thiols at room temperature are obtained.
Several symmetric viologen-containing crosslinkers (compounds I, II, and III) were synthesized. The copolymerization of these crosslinkers with various monomers under conventional radical polymerization (Conv. RP) conditions yielded electrochromic crosslinked polymers. When the polymerizations were carried out in the presence of carbon tetrabromide (an efficient chain transfer agent) or when atom transfer radical polymerization (ATRP) was used as the synthetic method, hyperbranched polymers containing viologen groups at the branch points and alkyl bromide functionalities at the chain ends were formed. Asymmetric viologen (compound IV) containing both a polymerizable (methacrylate) and ATRP initiating (2-bromoisobutyrate) group was also synthesized. When compound IV was polymerized under ATRP conditions, it served as an inimer, affording hyperbranched polymers. Alternatively, the compound could be homo- or copolymerized under conventional radical polymerization conditions, yielding linear polymers with multiple pendant initiating units, which could be employed as a macroinitiator for ATRP to produce brush copolymers. All synthetic procedures as well as the redox activity of the formed polymers will be described.
395 - Polyacrylate based block copolymers with well-defined end groups via radical polymerization: Synthesis and applications

Kaushik Mishra, km75@zips.uakron.edu, Abraham Joy. Department of Polymer Science, The University of Akron, Akron, Ohio 44325, United States

The importance of drug delivery systems has increased exponentially in the last decade. With advancements in polymer science and the fundamental theories behind drug delivery systems today there is a huge scope for advancement. Our aim is to investigate di-block copolymer micelles synthesized from acrylates and acrylamides. Emphasis is on both active and passive targeting via Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization with a drug of choice. Passive targeting is achieved by getting control over specific block lengths and molecular weights. Active targeting is achieved by attaching receptor molecules which are overexpressed in tumors. In the di-block copolymer structure the receptor is chemically conjugated to the α end of the RAFT agent while the drug is conjugated with the ω end. It is expected that receptor moieties are exposed on the micellar surface; while the drug is chemically entrapped in the core of micelles. This is in line with Helmut Ringsdorf’s model of a drug carrier.

We use this chemistry to show effective end functionalization on both ends of the polymeric system. Having two ends functionalized along with scope for chemical modifications on the side chains of the blocks would enable the next generation of drug delivery systems.
396 - Trithioperesters and trithiocarbonates as control agents in RDRP initiated thermally

*Ramiro Guerrerao-Santos, ramiro.guerrero@ciqa.edu.mx, Habram Leon-Gasca, Miguel A. Macias-Contreras, Hortensia Maldonado-Textle. Polymer Chemistry, Centro de Investigacion en Quimica Aplicada, Saltillo, Coahuila 25294, Mexico*

Trithioperesters (Z-C(=S)S-SR) were used as control agents in polymerizations carried out in absence of free radical initiator at T=110 °C. In the case of styrene, narrow polymers (Ð = 1.1) were obtained which were excellent precursors of block copolymers prepared through RAFT polymerization initiated with AIBN. Trithiocarbonates (R-SC(=S)S-R) were also used in thermal polymerizations of methacrylic monomers yielding polymers with Ð = 1.4 but, a complicated behavior was encountered. In this case the experimental molecular weight differs from that estimated (Mn_{th}) from the molar ratio [M]/[R-SC(=S)S-R]. Nevertheless, some block copolymers were successfully prepared. The alternated use of thermal and RAFT polymerizations was explored as a new pathway to form multiblock copolymers.

*Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall*
397 - Synthesis of antimicrobial latexes

*Ramiro Guerrero-Santos*, ramiro.guerrero@ciqa.edu.mx, Roberto Yañez, Jaime Gonzalez Villa, Antonio S. Ledezma Perez, Jorge Romero-Garcia. *Polymer Chemistry, Centro de Investigación en Química Aplicada, Saltillo, Coahuila 25296, Mexico*

In this contribution, we describe the preparation of antimicrobial latexes via *ab initio* surfactant-free emulsion polymerization induced by RAFT using monomers as: 3-(trimethylammonium) propyl methacrylamide chloride (MAPTAC), 2-(dimethylamino) ethyl methacrylate chloride (MADQUAT), quaternized dimethylamino propyl methacrylamide (DMAPMA) and quaternized 2-(dimethylamino) ethyl methacrylate. First, a stabilizing block was formed from one of these water-soluble monomers in aqueous media. Then, the butyl acrylate was introduced to form a block copolymer which self-assembled forming nanoparticles holding the quaternary ammonium cations in the hydrophilic corona. The molecular weight of block copolymers was estimated from their UV spectra (Mn = 6,000 – 15,000 g/mol) and the minimum inhibitory concentration (MIC) of latexes was evaluated against *Staphylococcus aureus* (Gram +), *Escherichia coli* (Gram -).
398 - Electrophoretic vinyl polymers via atom transfer radical polymerization of a methacrylate containing sulfide

Tomomi Kameyama, kame0422@gmail.com, Akinori Takasu. Department of Frontier Materials, Nagoya Institution of Technology, Nagoya-shi, Gokiso-cho, Aichi 466-8555, Japan

We have targeted on new synthetic procedure and polyester design using low temperature polycondensation or click polymerization of ester-containing monomers. Recently, we found non-ionic poly(ester-sulfone) showed anode-selective electrophoresis under the electrophoretic deposition (EPD) condition. In this presentation, we investigated an electrophoretic behavior of polymethacrylate having a sulfonyl group in the side chains and compared with the main chain type of poly(ester-sulfone) we already reported. First, we prepared a new vinyl monomer having a pendent sulfide [2-(ethylthio)ethyl methacrylate (ETEMA)] using esterification of methacryloyl chloride by 2-(ethylthio)ethanol. Subsequently, we carried out conventional radical polymerization of ETEMA but gelation occurred, in which we speculated that the gelation is ascribed to chain transfer to carbon-sulfur during the radical polymerization. Therefore, we applied copper-catalyzed "atom transfer radical polymerization (ATRP)" of ETEMA to control the reactivity of the propagating center as well as the molecular weight. As an example, when we used copper(I) bromide/1,1,4,7,10,10-hexamethyltriethylenetetramine as the catalyst and ethyl 2-bromoisobutyrate as the initiator, expected molecular weight control was attained ($M_n=8.3\times10^3, M_w/M_n=1.3$). Next, we tried to Oxone® oxidation of poly(ETEMA) to synthesize vinyl polymers containing pendent sulfones. To demonstrate the electrophoretic behavior, anode-selective EPD on stainless steel was investigated from the $N,N$-dimethylformamide/n-butanol suspension. Coated film using this polymer was transparent, although that using poly(ester-sulfone) was turbid. These fundamental results provide new guideline to fabricate titanium(IV) oxide (TiO$_2$)-based electronic papers as well as self-cleaning materials.

![Figure 1. Polymerization of 2-(ethylthio)ethyl methacrylate (ETEMA) and subsequent oxidation.](image-url)
399 - Application of organotellurium mediated living radical polymerization (TERP) to pigment dispersant for inkjet ink

Hikaru Umemoto\textsuperscript{1}, humemoto@otsukac.co.jp, Kazuhiro Kawano\textsuperscript{1}, Shigeru Yamago\textsuperscript{2}. (1) Department of Central R&D, Otsuka Chemical Co., Ltd., Tokushima, Japan, (2) Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Block copolymers synthesized with TERP were utilized as pigment dispersants for inkjet ink. The dispersants gave better dispersion stability compared with a commercial dispersant especially in case of magenta, which is generally difficult to be dispersed (Figure 1). Moreover much better redispersibility of the dried ink was observed, which leads to keeping ink from blocking a nozzle of inkjet print head (Figure 2). Its printed ink was also improved in terms of stability against friction (no data here). It is likely that the above features come from the block structure of the polymers. Further detailed data will be shown on the meeting.
400 - Immobilization of 1,5,7-triazabicyclo[4.4.0]dec-5-ene onto an amphiphilic block copolymer for catalysis of Michael additions in an aqueous system

Katherine Farrance, K.Farrance@warwick.ac.uk, Rachel K O'Reilly, Ezat Khoshdel. (1) Department of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom, (2) Unilever Research & Development Port Sunlight, Unilever, Bebington, Wirral CH63 3JW, United Kingdom

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is a widely studied superbase that catalyzes many organic reactions such as Michael additions. Previous immobilizations of the catalyst TBD onto polymeric scaffolds has resulted in reduced activity due to inaccessibility of the catalytic site – which consequently resembles the less active catalyst – methylated TBD (MTBD). This work will show how the catalytic activity of the immobilized TBD has been increased through the use of the concentrator effect. Reversible deactivation radical polymerization (RDRP) permits the synthesis of complex architectures such as amphiphilic block copolymers. Upon self-assembly, these block co-polymers offer access to a wide range of polymeric assemblies including polymer micelles, which provide a unique hydrophobic environment in an otherwise aqueous system. Through immobilization of TBD onto the hydrophobic block of an amphiphilic polymer, synthesized via nitroxide mediated polymerization (NMP), it has been possible to assemble micelle constructs that place the catalyst in the hydrophobic interior. These micelle nanoreactors have been used to carry out Michael additions using hydrophobic substrates, such as the Michael acceptor trans-chalcone and Michael donor dimethyl malonate, in an aqueous system. This has given much improved reaction rates due to the concentrator effect bringing the catalyst and substrates into close proximity.
401 - Effect of complementary nucleobase interactions on the copolymer composition of RAFT copolymerization and self-assembly

Yan Kang, Y.Kang@warwick.ac.uk, Rachel K. O’Reilly. Department of Chemistry, University of Warwick, Coventry, United Kingdom

The specific hydrogen bonding interactions between nucleobase pairs play a key role in nature for precise biosynthesis and stereospecific molecular assembly. Inspired by nature, nucleobases have been employed as building blocks in synthetic polymer chemistry. However, to date, there has been very little research into the effect of nucleobase interactions on the resultant copolymer composition using RAFT polymerization methods.

Methacryloyl-type monomers containing adenine and thymine were synthesized in a good yield. RAFT polymerizations using these two monomers were carried out with a good control. In addition, the copolymerization behaviour of the nucleobase functionalized monomers was studied. These results indicate that the presence or absence of hydrogen bonding interactions between two monomers (Figure 1) can be used to access the copolymers with different monomer sequences. Moderate alternating copolymers had a tendency to be formed in chloroform, while in DMF statistical copolymers were formed. Moreover, nucleobase containing polymers were self-assembled in both organic solvents and water, with the effect of solvent and temperature on self-assembly investigated.

Figure 1. (A) The expected hydrogen bonding interactions of the adenine-thymine pair is shown where the key down signal used in the 1H NMR spectra of the AHMA and TMAH mixtures with varying concentrations of AHMA (TMAH = 10 mM). [AHMA] = 0.25, 0.1, 0.15, 0.20 mM. (B) Plot of $f_1$ vs $f_2$ for the copolymerization of TMA and AHMA using 2-cyano-2-propyl maleimide thiol and chloroform as chain transfer agents (1) in DCM (2) in CHCl3 (the red line is the plot of $f_1$, vs $f_2$, for an ideal polymerization, where $f_1 = f_2 = 1$).

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
RAFT polymerization for imidazole-containing ABA block copolymers: From electro-active membranes to nucleic acid delivery vehicles

Asem I. Abdulahad¹, aabdula6@vt.edu, Michael H. Allen², Sean T. Hemp³, Chainika Jangu¹, Keren Zhang¹, Timothy E. Long¹.
(¹ Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States, (² Adhesives Research, Glen Rock, Pennsylvania 17327, United States, (³ Michelin, Greenville, South Carolina 29602, United States

Block copolymers enable the design of well-defined supramolecular structures for engineering and biological applications. Controlled radical polymerization (CRP) techniques enabled the synthesis of well-defined macromolecules with molecular weight control and narrow polydispersity (PDI). Reversible addition-fragmentation chain transfer (RAFT) polymerization is currently one of the most versatile CRP techniques to afford complex macromolecules with highly controlled architecture leading to block copolymers with tailorable properties. The introduction of electrostatic interactions as well as hydrogen bonding enhances the microphase separation in chain-growth polymers. Control over block composition enables tailored charge content, tunable thermomechanical properties, and nanoscale morphology. This presentation will describe efforts with different classes of tailored copolymers that impart a specific functionality tailored mechanical, rheological, and ion-transport properties. These copolymer architectures represent various synthetic approaches towards designing functional macromolecules for broad range of applications with a focus on electro-active membranes and switchable adhesives.
Despite over 40 years of study, the underlying mechanisms which govern the action of biological antifreezes is still poorly understood, which is in part due to their limited availability and challenging synthesis. This lack of understanding has also prevented their application for biological cryopreservation. Poly(vinyl alcohol) has been shown to display remarkable ice recrystallisation inhibition activity despite its major structural differences to native antifreeze proteins. Here controlled radical polymerization is used to obtain the first quantitative structure-activity relationships, to probe the role of molecular weight and comonomers on IRI activity. Crucially, it was found that IRI activity is 'switched on' when the polymer chain length increases from 10 and 20 repeat units. Substitution of the side chain with hydrophilic or hydrophobic units was found to diminish activity when incorporated above 20 mol %, but hydrophobic modifications to the backbone were slightly more tolerated, implying unbroken sequence of hydroxyl groups are necessary for activity. These results show the role of hydrophobicity on IRI is important, but not a guarantee of activity.

Figure 1. Ice recrystallization inhibition activity of PVA homopolymers as measured by the splat assay. (A) Example micrographs showing ice crystals grown in PBS alone (upper) and with PVA$_{351}$, 1 mg.mL$^{-1}$; (B) IRI activity as a function of polymer concentration. MLGS = mean largest grain size relative to a PBS control, expressed as %.
404 - Potential curves of selected radical thiol double additions to alkynes

Kyle Throssell, ktthross@gmail.com, Brian Northrop. Department of Chemistry, Wesleyan University, Middletown, CT 06457, United States

In the pursuit of characterizing and elucidating click chemistry thiol additions to hydrocarbons, we studied a set of sequential radical additions to the terminal and four different substituted alkynes. Using Gaussian09, we characterized the transition states with CBS-QB3 and used the relevant thermochemistry to determine the barrier heights and rates of reaction. The result agrees with accepted ideas of chemical intuition about stabilization of radicals as well as entropy in transition states.
405 - Synthesis of polymer with perylene diimide pendant side chains and characterization of its higher order structure

Tomoyasu Hirai¹,², t-hirai@cstf.kyushu-u.ac.jp, Makoto Kido², Takamichi Shinohara², Shiki Nojima², Jungeun Kim³, Noboru Ota³, Ryohei Ishige², Kevin White¹, Yuji Higaki¹,², Atsushi Takahara¹,². (1) Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan, (2) Graduate School of Engineering, Kyushu University, Fukuoka, Japan, (3) JASRI/SPring-8, Hyogo, Japan

Perylene diimde (PDI) derivatives are a promising class of electron-donating semiconducting materials that show excellent electronic and optical properties when assembled in ordered crystalline domains. Integrating PDI moieties in a polymeric structure is desired to improve film forming properties and mechanical stability, but is typically associated with an increase in disorder of the PDI phase that limits electronic properties. Here, we have synthesized polyacrylate containing PDI side chains (PAc12PDI) using nitroxide mediated radical polymerization (NMRP) method, which shows well-ordered crystalline structure in bulk and thin film state. The thermal behavior and crystal structure of the monomer and polymer in thin film are studied on the basis of temperature-dependent grazing incidence wide-angle X-ray diffraction measurement (GIWAXD). Figure 1 shows the GIWAXD results. Sharp and regular diffraction spots that correspond to a monoclinic lattice were observed. We found that the PAc12PDI thin films crystallize in a monoclinic lattice with two populations of ordered domains. The ratio of lattice orientation in parallel and perpendicular directions with respect to the substrate was 97 to 3. The PDI-containing polymers containing crystalline structure in thin film have significant potential for use as n-type semiconductors in solar cells.

Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
406 - Understanding the copolymerization behavior under controlled radical surface-initiated polymerization using XPS

Chaitra Deodhar¹, chaitra.deodhar@nist.gov, Sara Orski¹, Derek Patton², Kathryn Beers¹. (1) Material Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States, (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS, United States

In this work we investigate the copolymerization behavior in synthesis of statistical copolymer brushes under controlled radical conditions. In statistical copolymer brushes monomer sequence within the chains is dictated by monomer reactivities. Therefore, knowledge of monomer reactivity ratios is necessary so that polymer brushes can be tailored to the exact needs of a particular application. A new approach to measure the reactivity ratios from surface-initiated copolymerization using X-ray photoelectron spectroscopy (XPS) was demonstrated previously under conventional, photoinitiated free radical conditions. To address the question of factors influencing the observed “reactivity” of a chain end, particularly where interfacial diffusion and effective activation/deactivation processes are likely to influence the copolymerization behavior, we employed a controlled radical grafting mechanism and compared several monomer pairs (n-butyl methacrylate/N,N-dimethylaminoethyl methacrylate (BMA/DMAEMA) and 2-hydroxyethyl methacrylate/N,N-dimethylaminoethyl (HEMA/DMAEMA)) for potential discrepancies in monomer reactivity ratios under controlled and conventional radical surface-initiated polymerization conditions using XPS. Statistical copolymer brushes are synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP) and free radical photo-polymerization representing controlled and conventional radical conditions, respectively.
407 - Synthesis and properties of mixed bimodal brush grafted nanoparticles

Tony Neely¹, neelytl@email.sc.edu, Brian Benicewicz¹, Ying Li², Linda Schadler². (1) Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States, (2) Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States

Reversible addition-fragmentation chain transfer (RAFT) polymerization has been widely used for the synthesis of varying polymer architectures, including polymer brushes on nanoparticles for incorporation into polymer nanocomposites. Surface modification of nanoparticles allows for control of the surface properties and therefore the interface between a nanoparticle and the polymer matrix. Adverse interactions between the nanoparticles, grafted polymer, and polymer matrix can lead to aggregation and autophobic de-wetting. This can be suppressed when the enthalpic and entropic effects are decoupled for their independent study, using a bimodal system containing a small number of long polymer chains on a surface that primarily consists of a short dense brush. Here we demonstrate a sequential RAFT polymerization process for the synthesis of bimodal polymer brush anchored nanoparticles. This process allows for the control of brush parameters such as composition, graft density, and molecular weight for both populations separately and independently. The bimodal brush grafted silica nanoparticles show superior dispersion and thermomechanical properties over monomodal brush grafted particles in polymer nanocomposites. In addition, the synthesis and properties of mixed bimodal brushes (brushes of mixed chemical composition) will be discussed. With mixed bimodal, short brushes offer an enhancement in properties while long brushes help retain matrix compatibility. Analogous to block copolymers, the addition of a polymer chain population with different chemical composition can lead to materials with added and differing properties compared to materials with only a single chemical composition.
Continuous flow chemical processing provides a simple means of synthesizing RAFT polymers followed by the subsequent removal of the thiocarbonylthio end-group via thermolysis. Styrene, acrylates, methacrylates, and acrylamides were tested for end-group removal by thermolysis between 220 and 250 °C in a stainless steel tube flow reactor, without the use of additional reagents. MA and MMA were polymerized and the RAFT end-group removed by thermolysis in a two-step flow process, with no need for isolation of intermediates (See Figure 1).

Figure 1. Sequential two-step continuous flow process consisting of polymerization followed by end-group removal by thermolysis.


Tuesday, August 12, 2014 06:00 PM
Controlled Radical Polymerization (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
409 - WITHDRAWN
Block copolymers have known applications as dispersing agents, with research traditionally focusing on composition, molecular weight, and topology of the copolymer; the molecular weight dispersity is not typically studied as a design parameter, but its effects on overall performance may be significant. An important industrial concern is that achieving very low dispersity will add cost, but it is not known to what extent it will deliver enhanced performance. This research investigates poly(styrene)-b-poly(acrylic acid) block copolymers, synthesized by nitroxide-mediated radical polymerization, as protective colloids in the emulsion polymerization of styrene. The effect of molecular weight dispersity of the stabilizing block on stabilization behaviour is studied, independent of molecular weight and composition, using a series of copolymer blends with variable dispersity (Figure 1). Stabilization behaviour is evaluated by the size, distribution, and nucleation of particles, as well as self-assembly properties including critical micelle concentration and aggregation number.
411 - Controlling sequence in step-growth polymerizations: Role of sequence on rheological and thermal properties of segmented polyesters

Joseph M. Dennis¹, jmden88@vt.edu, Ashley M. Nelson¹, Musan Zhang², Daniel J. Buckwalter³, Timothy E. Long¹. (1) Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States, (2) Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States, (3) Owens Corning, Granville, Ohio 43023, United States

Segmented copolymers have provided a wide array of applications beyond the physical constraints of their composing homopolymers. Recently, research has been primarily focused on the design of well-defined di- and triblock copolymers using anionic and controlled free radical polymerization methods. However, these techniques typically require the use of solvents during polymerization and purification. Utilizing bulk transesterification techniques to ascertain segmented block copolymers proves advantageous. Segmented polysulfones, polyesters, and polysiloxanes enable compositions with enhanced mechanical properties over their predecessors. Their properties will be discussed relative to the need for advanced membranes for emerging technologies.
A series of poly(vinylbenzyl chloride)-grafted fluoropolymer films with various degrees of grafting were prepared using a pre-irradiation method, and the effect of degree of grafting on the thermal decomposition behavior of the grafted films was evaluated using DMA, FT-IR, and TGA instruments. The DMA and TGA results indicate that a crosslinking reaction of PVBC-grafted fluoropolymer film occurs at high temperature (over 250 °C). Since the crosslinking reaction becomes more severe as the degree of grafting increases, the crosslinking is considered to be due to the poly(vinylbenzyl chloride) graft chains. The FT-IR spectrum of the thermally treated sample showed a decrease of the –C-Cl peak, and indicated that the observed thermal crosslinking reaction at high temperature occurred owing to the graft chain. The DSC and XRD instruments were used to observe the effect of the degree of grafting on the crystallinity of the grafted film.
Sheet Molding Compound (SMC) is a ready to mold fiber-reinforced polyester material, molded by heating compression. The polymer matrix is an unsaturated polyester (UP) resin which reacts with styrene to form a crosslinked polymer. SMC is currently molded at 150°C under 60-100 bars. The aim of this project is to develop new SMC formulations to lower the molding temperature and pressure at respectively 100°C and 5 bars with cure time below 10 minutes. The SMC must exhibit a high reactivity at 100°C but also a high storage stability before molding. The aim of this study is to adjust the reactivity of the UP resin with initiators and inhibitors. Peroxides initiate the radical copolymerization of the UP resin with styrene. The reactivity of the resin is influenced by the quantity of peroxide, as shown on figure 1 which presents the gel time of the resin as a function of dibenzoyl peroxide (PBO) concentration, measured at 100°C with a rheometer.

Inhibitors allow to stabilize the SMC during storage (before molding) and to adjust the resin reactivity during the curing. In this study, the UP resin reactivity in presence of several inhibitors was studied by Differential Scanning Calorimetry (DSC) and rheological measurements. The influences of the inhibitor nature and concentration on the inhibition time, gel time and conversion of UP resin are investigated.
414 - Tertiary amine-functional poly(ethylene glycols): Thermo- and pH-responsive behavior in aqueous solution

**Jana Herzberger**¹,³, janaherz@students.uni-mainz.de, Dennis Kurzbach², Mathias Werre², Holger Frey¹. (1) Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany, (2) Max Planck Institute for Polymer Research, Mainz, Germany, (3) Graduate School Materials Science in Mainz (MAINZ), Mainz, Rhineland-Palatinate 55128, Germany

The outstanding properties of poly(ethylene glycol) (PEG) like its remarkably water solubility, high chain flexibility and biocompatibility, can be selectively manipulated and expanded by the incorporation of epoxide-based comonomers into the polyether backbone. For example, thermo-responsive PEG derivatives can be synthesized by anionic ring opening polymerization (AROP) of ethylene oxide (EO) and various comonomers, like allyl glycidyl ether (AGE) or isopropylidene glyceryl glycidyl ether (IGG).[1]

We present three \(N,N\) -dialkyl glycidyl amines (DXGA) as novel building blocks in the AROP with EO: \(N,N\) -Dibutyl glycidyl amine (DBuGA), \(N,N\) -dihexyl glycidyl amine (DHeGA) and \(N,N\) -dioctyl glycidyl amine (DOcGA). Well-defined (\(M_w/M_n = 1.05-1.13\)), water-soluble gradient and block copolymers with different comonomer fractions ranging from 4 to 18 mol% can be obtained. The microstructures of these unique copolymers and the relative reactivity of the novel DXGA were elucidated by \(^1H\) NMR kinetic studies and \(^{13}\)C NMR triad analysis. \(^1H\) NMR, turbidimetry and electron paramagnetic resonance (EPR) studies confirmed that thermo- and pH-responsive behavior of these copolymers is precisely adjustable by the incorporated comonomer ratio and structure. Transition temperatures at human body temperature are easily accessible, without distinctly changing PEG’s unique properties. This feature is essential for future biomedical applications.

![Figure 1](image1.jpg)

**Figure 1.** Polymerization strategy for the block and concurrent copolymerization of EO and the respective DXGA.

Surface eroding materials are increasingly sought after in the biomedical area as a consequence of their potential application in drug delivery or tissue engineering. Poly(orthoester)s (POEs) are an ideal example of polymers that exhibit surface erosion with relatively mild degradation products compared to those of other surface erodible polymers, for example, poly(anhydride)s. However, POEs have previously proven difficult to synthesize, with general techniques for POE production involving the polymerization of highly unstable diketene acetal monomers, that are highly sensitive to air and moisture. Herein, an alternate method for the production of POEs via the use of air- and moisture-stable vinyl acetal monomers is discussed. POEs were successfully produced using a ruthenium-based catalyst through the 1,3-dihydride shift of the vinyl acetal monomers. A range of vinyl acetal monomers, including hetero- and homo-difunctional monomers, are readily shown to polymerize via this method. Furthermore, the technique was expanded to produce a range of POEs that have previously proven challenging to obtain. The efficient installation of functional groups via an ortho ester linkage to a degradable aliphatic poly(carbonate) backbone is also realized.
The concept of click chemistry was introduced by Sharpless et al. not much more than a decade ago, and the reactions it advocates have rapidly found their way into the standard toolbox of many research disciplines, also outside of the chemical sciences. The search for suitable combinations of modular reagents (and catalysts) that can result in a very efficient and reliable covalent coupling is an important objective of ongoing fundamental chemical research. Some subdivisions have even become more strict with regard to which reaction characteristics are desirable for click chemistry applications, as was recently proposed for the polymer community. Many alternative systems for the archetypical copper-catalyzed azide-alkyne cycloaddition have been suggested in recent years each with their advantages and disadvantages. However, the quest for a truly versatile system is still continuing. In the ideal case, such a system, besides having all characteristics associated with the click concept, should also offer a choice between irreversible and reversible connections. For example, in the case of polymer chemistry applications, dynamic or reversible covalent bonds are highly desired nowadays as these can be used to elicit unique material properties such as self-healing, recycling and network malleability.

Here, we introduce the use of triazolinedione compounds as scalable and robust building blocks for click chemistry applications, by presenting examples of facile and ultrafast macromolecular functionalization, polymer-polymer linking and polymer cross-linking under ambient conditions without the need for a catalyst. Moreover, triazolinediones, when combined with indole reaction partners, can also be ‘unclicked’ at elevated temperatures, and furthermore integrally transferred to an alternative reaction partner. This new concept of ‘transclick’ reactions has also been used to introduce thermoreversible links into materials, giving rise to dynamic bulk properties such as polymer network healing, reshaping and recycling.

References:
2. (a) Moses, J. E.; Moorhouse, A. D., The growing applications of click chemistry. *Chemical Society Reviews* 2007, 36 (8), 1249-1262; (b) Xi, W.; Scott, T. F.; Kloxin, C. J.; Bowman, C. N., Click Chemistry in Materials Science. *Advanced Functional Materials* 2014, n/a-n/a.
417 - Ruthenium catalyzed synthesis of functionalized polypentenamers

Robert Tuba¹, robert.tuba@tamu.edu, Robert H. Grubbs¹,². (1) Department of Science, Texas A&M University at Qatar, Doha, Qatar P.O.Box 23874, Qatar, (2) Division of Chem and Chem Eng, California Institute of Technology, Pasadena, California CA 91125, United States

Polypentenamers and their functionalized derivatives are synthetized by equilibrium ring-opening metathesis polymerization (ROMP) using well-defined ruthenium catalyst systems. The unique feature of the equilibrium polymerization opens a way for the synthesis of durable, environmentally friendly and recyclable materials.

The ruthenium catalyzed polymerization and co-polymerization of cyclopentene (2.17 M) at low catalyst loading (0.01%) in toluene solution were investigated. The monomer-polymer equilibrium concentration (45 - 55%) was achieved within one hour at room temperature (MW: 129 kDa; PDI: 1.64). The molecular weight of the polypentenamers gradually decreased as the reaction time was prolonged up to 16h (MW: 76kDa) meanwhile the PDI values gradually increased (up to 1.84) and the isolated polymer yields remained comparable. The co-polymerization of cyclopentene with 0.5 % 2,5-norbornadiene at 0 ºC in toluene results in the formation of cross-linked polypentenamers. The gradual addition of diluted 2,5-norbornadiene solution over the cyclopentene equilibrium ROMP resulted in significant polymer molecular weight increase (MW: 3220 kDa; PDI: 1.5) and shorter gelation time comparing to the polymers obtained in the absence of 2,5-norbornadiene at the same condition (MW: 408 kDa; PDI : 1.32).

Highly polar polyhydroxy polypentenamers (MW: 16.6 kDa; PDI: 1.5) have been synthetized by equilibrium ROMP of 3-cyclopentene-1-ol or acyclic diene metathesis polymerization (ADMET) of 1,6-heptadien-4-ol in THF. The thermodynamics of 3-cyclopentene-1-ol ROMP was investigated. Equilibrium of growing chain and monomer was observed and the thermodynamic parameters were determined as: \( \Delta H = -6.4 \text{ kcal} \cdot \text{mol}^{-1} \); \( \Delta S = -21.4 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \). The co-polymerization of 1,6-heptadien-4-ol with cyclopentene (1 : 1) resulted in a polymer containing block-polymer (65%) and alternating polymer (35%) units, respectively. The synthesis of cross-linked polypentenamers, polyhydroxy polypentenamers and the thermodynamic investigation of their equilibrium polymerization are reported.

Figure 1. Synthesis of polyhydroxy polypentenamers with ruthenium catalyzed acyclic diene metathesis polymerization (ADMET) and equilibrium ring opening metathesis polymerization (ROMP).

Monday, August 11, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Moscone Center, North Bldg.
Room: Hall D

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
We have reported the influence of primary structure of the main chain on backbone stiffness of the cylindrical rod brushes. Interestingly, the rod brushes consisting of polymethacrylate main and poly(n-hexyl isocyanate) (PHIC) rodlike side chains were much stiffer than that of polystyrene main and same PHIC side chains. Figure shows the double logarithmic plots of $z$-averaged mean-square radius of gyration ($<S^2>_z^{1/2}$) versus the weight averaged degree of polymerization of the main chain for poly(MA-EO1-HIC-63-Ac) and poly(VB-HIC-62-H) in THF at 25 °C. The present study is aimed to clarify why chain stiffness of polymethacrylate main chain is much higher than that of polystyrene, in spite of having the same side chains. Conformational properties of cylindrical rod brushes having a flexible spacer between main and side rod have thoroughly been studied by static light and small-angle X-ray scatterings in THF at 25 °C. These rod brushes were prepared by radical homopolymerization of PHIC macromonomer (MA-EO$^m$-HIC-$N_s$-Ac, where $N_s$ is the weight-averaged degree of HIC). EO is an oxyethylene between the main and PHIC side chains ($m = 1, 2, 4.5, 8$). The molecular weight dependence of $<S^2>_z^{1/2}$ of the brush is determined and analyzed in terms of the wormlike cylinder model. The backbone stiffness of poly(MA-EO$_2$-HIC-$N_s$-Ac) is larger than that of the poly(MA-EO$_1$-HIC-$N_s$-Ac) with the corresponding contour length, implying the effects of the flexible spacer on the conformation of the rod brushes.

![Figure](image.png)
419 - Catch and release of a metallic payload in amphiphilic block copolymer micelles

Johannes Elbert¹, J.Elbert@mc.tu-darmstadt.de, Cristina Mari², Gilles Gasser², Markus Gallei¹. (1) Department of Chemistry, Technische Universität Darmstadt, Darmstadt, Germany, (2) Department of Chemistry, University of Zurich, Zurich, Switzerland

Amphiphilic block copolymers feature the intrinsic capability to self-assemble into well-defined micellar structures.¹⁻³ The formation of block copolymer micelles in polar solvents with core-shell-type or patchy architectures with a hydrophobic core segregated from its hydrophilic exterior, allows for the selective incorporation of hydrophobic molecules while the outer polar polymers chains shield the payload from the polar environment. Block copolymer micelles are excellent drug delivery systems due to their adjustable drug-loading capacity and their unique distribution characteristics in the body.⁴ Furthermore block copolymer have a size in the range of several tens of nanometers, causing an accumulation of the micelles in tumor tissue by the “enhanced permeation and retention” (EPR) effect.⁵

A promising technique in cancer treatment is the use of photodynamic therapy (PDT).⁶ In this technique, a photosensitizer is used to generate reactive oxygen species (ROS) upon light irradiation. ROS are extremely toxic and can engender cell death.

In order to study the catch and release of novel amphiphilic micelles based on different methacrylate monomers, poly(methyl methacrylate-b-dimethylamino methacrylate) (PMMA-b-PDMAEMA) block copolymers with a narrow molecular weight distribution were synthesized by using sequential anionic polymerization protocols. These block copolymers form micelles in water as confirmed by TEM and DLS measurements. Our potential photosensitizer, a ruthenium(II) polypyridyl complex, was encapsulated in the micelles and the amount quantified by UV/Vis and atomic absorption spectroscopy (AAS).

420 - Using crystallization-driven self-assembly to probe poly(lactide)-containing cylindrical micelles

Liang Sun¹, Liang.Sun@warwick.ac.uk, Anaïs Pitto-Barry¹, Nikos Petzetakis¹, Tara L Schiller²,³, Nigel Kirby³, Daniel J Keddie⁴, Ben J Boyd⁵, Rachel K O’Reilly¹, Andrew P Dove¹,². (1) Department of Chemistry, University of Warwick, Coventry, Warwickshire CV4 7AL, United Kingdom, (2) Department of Materials Engineering, Monash University, Clayton, Victoria Victoria 3800, Australia, (3) Australian Synchrotron, Clayton, Victoria Victoria 3168, Australia, (4) Chemistry, School of Science and Technology, University of New England, Armidale, New South Wales NSW 2351, Australia, (5) Monash Institute of Pharmaceutical Sciences, Parkville, Victoria Victoria 3052, Australia

Cylindrical or worm-like micelles from the self-assembly of amphiphilic block copolymers in selective solvents were early reported in 1990s. However, as a consequence of the narrow compositional window in which they can be accessed, they have not been as widely studied as spherical and vesicular structures. Living crystallization-driven self-assembly (CDSA) of crystalline or semi-crystalline block containing polymers, has emerged as a powerful method to realize cylindrical micelles across a wide range of block copolymer compositions. Recently, we have explored the use of semi-crystalline poly(L-lactide)-containing cylinders using CDSA approach in aqueous media.

In the present study, we demonstrate the control over the cylinder size by changing the composition of PLLA-b-PAA diblock copolymers using CDSA. All of the resultant cylinders showed narrow size distributions from transmission electron microscopy analysis and the crystalline core nature of these cylinders was revealed by wide angle X-ray diffraction with further evidence of the relationship between crystallinity and cylinder formation through synchrotron small-angle X-ray scattering studies. We have also explored PLLA core- containing cylindrical micelles with different hydrophilic coronas such as poly(4-acryloyl morpholine), poly(ethylene oxide) and poly(N,N-dimethylacrylamide) via CDSA. The hydrophilic characters of the polymers have been shown to direct the length of the cylinders, with the most hydrophilic corona block leading to the shortest cylinders.

Figure 1. Various PLLA core containing cylindrical micelles with controllable dimensions via Crystallization-driven self-assembly.
421 - Tailoring the properties of polysaccharides for functional encapsulation

Soohwan Ahn, double2706@gmail.com, Jonghwi Lee. Department of chemical engineering and material science, Chung-Ang university, Seoul, Republic of Korea

Polysaccharides play an important role in the pharmaceutical, food, and cosmetics areas which have useful properties for skin such as moisturizing, antioxidant ability, and improvement of elasticity. Among these properties, antioxidant activity was focused in this work. The accelerated ageing process through the free radicals generated by UV radiation could make serious damages on skin. Antioxidants are able to inhibit this process through oxidizing themselves, but unfortunately they are intrinsically highly unstable. Herein, the antioxidants were stabilized via chemical coupling with polysaccharides using epichlorohydrin as a coupling agent. The derivatives were purified through repeated precipitation, followed by dialysis against water and freeze drying. 1H-NMR and FT-IR characterizations confirmed that polyphenols were covalently bonded to polysaccharide backbone. The modified polysaccharides showed the same absorbance characteristics of UV-visible spectra as the raw antioxidants. Furthermore, its 2,2-diphenyl-1-picrylhydrazyl scavenging assay confirmed the polyphenols had antioxidant activity. The 3,4-dihydroxyphenylalanine structure presented in the antioxidants was found to improve the adhesion property of neat polysaccharide in shear and tensile direction, which is similar to the adhesive functional group of mussel adhesive proteins. The modified polysaccharides have better solubility in water and lower viscosity than the pure polysaccharides. These unique properties could make the modified polysaccharides useful for functional encapsulation in the drug delivery, cosmetic active ingredient, and other related areas.
As one of the most powerful tools, the application of light to control the formation and structure of polymeric materials has been intensively studied in the past decades. However, the disassembly of current nanocarriers for drug delivery always involves UV or visible light, which to some extent limited their in vivo and clinical trials because the light used are also highly absorbed by human body. In this poster we report a new and general strategy for preparing photo-induced nanogels using photoreleasable thiol chemistry, where the crosslinking reaction is photo-triggered but the disassembly is redox responsive. This is achieved by designing a random copolymer that contains oligoethyleneglycol (OEG), pyridyl-disulfide (PDS) and o-nitrobenzyl (NB) protected thiol groups. Deprotection under UV light (λ=365 nm) at room temperature is followed by the free thiol groups attacking PDS groups, which causes the formation of intra-/intermolecular disulfide bond. We show that the nanogel size could be easily tuned by varying the concentration of polymer solution. Guest molecules can be successfully encapsulated inside of the nanogels and then be released in response to a redox trigger, glutathione (GSH). We further demonstrate that the guest encapsulation stability inside the nanogels can be tuned by the radiation time through in vitro fluorescence resonance energy transfer (FRET) experiments.
423 - Synthesis, self-assembly, and photophysical properties of oligo(2,5-dihexyloxy-1,4-phenylene vinylene)-block-poly(ethylene glycol)

Maria Jose Gonzalez-Alvarez\textsuperscript{1}, mgonzale@chem.utoronto.ca, Chun Feng\textsuperscript{1}, Yin Song Song\textsuperscript{1}, Isaac Li Li\textsuperscript{1}, Guangyao Zhao\textsuperscript{1}, Gregory Molev\textsuperscript{1}, Gerald Guerin\textsuperscript{1}, Gilbert Walker\textsuperscript{1}, Gregory D. Scholes\textsuperscript{1}, Ian Manners\textsuperscript{2}, Mitchell A. Winnik A. Winnik\textsuperscript{1}. (1) Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada, (2) School of Chemistry, University of Bristol, Bristol, United Kingdom BS8 1TS, United Kingdom

Rod-coil block copolymers form an important class of molecules for the self-assembly of functional polymer systems. The incorporation of a conjugated rigid polymer into a block copolymers results in extremely rich self-assembly. The π-π interaction between the conjugated rods not only provides additional structural control factors and functionality, which differ from conventional block copolymers, but also bring electroactive and optical properties for photonic and electronic applications.

We describe the synthesis and characterization of a family of diblock copolymers with a dihexyloxy-phenylenevinylene pentamer (OHPV\textsubscript{5}) connected to a series of poly(ethylene glycol) (PEG) blocks of different average lengths (12, 45 and 115 ethylene glycol units). We investigated the self-assembly of these block copolymers in ethanol, which is a good solvent for the PEG units, but poor for the OHPV segment. The structures obtained were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC). In addition, their photophysical properties were examined by UV-vis, steady state fluorescence and fluorescence decay measurements. The results of these experiments indicate that OHPV\textsubscript{5}-PEG\textsubscript{115} formed long fiber-like micelles of uniform width, whereas OHPV\textsubscript{5}-PEG\textsubscript{45} formed fragile broad ribbons. We also obtained disordered lamellar structures with OHPV\textsubscript{5}-PEG\textsubscript{12}. 
A new symmetrically substituted cationic monomer bis[3-(diethoxyphosphoryl)propyl]diallylammonium chloride has been synthesized and cyclopolymerized to give the corresponding cationic polyelectrolyte (+) (CPE) bearing two identical (diethoxyphosphoryl)propyl penedents on the pyrrolidinium repeating units. The hydrolysis of the phosphonate ester in (+) (CPE) gave a pH-responsive cationic polyacid (+) (CPA) bearing the motifs of a tetrabasic acid. The (+) (CPA) under pH-induced transformation was converted into a water-insoluble polyzwitterion acid (±) (PZA) or water-soluble polyzwitterion/monoanion (± −) (PZMAN) or polyzwitterion/dianion (± ≡) (PZDAN) or polyzwitterion/trianion (± ≡) (PZTAN), all having identical degree of polymerization. The interesting solubility and viscosity behaviors of the polymers have been investigated in some detail. The apparent protonation constants of the anionic centers in (± ≡) (PZTAN) and its corresponding monomer (± ≡) (ZTAN) have been determined. Evaluation of antiscaling properties of the PZA using supersaturated solutions of CaSO₄ revealed 100% scale inhibition efficiency at a meager concentration of 10 ppm for a duration over 71 h at 40°C. The PZA has the potential to be an effective antiscalant in Reverse Osmosis plants.
425 - Novel copolymers of styrene and halogen ring-disubstituted methyl 2-cyano-3-phenyl-2-propenoates

Gregory B Kharas, gkharas@depaul.edu, Sonia E Chavez, Harrison S Browning, Jennifer A Sepe, Mario E Romanelli, Melissa K Susnis, Gonzalo Choque-Gonzales, Kevin N Fuentes. Department of Chemistry, DePaul University, Chicago, IL 60614, United States

Electrophilic trisubstituted ethylenes, halogen ring-disubstituted methyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)CO₂CH₃ (where R is 2,5-dichloro, 3,5-dichloro, 2,3-difluoro, 3-chloro-2-fluoro, 3-chloro-4-fluoro, 4-chloro-3-fluoro) were prepared and copolymerized with styrene.

The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and methyl cyanoacetate, and characterized by CHN analysis, IR, ¹H and ¹³C-NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ¹H and ¹³C-NMR.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
426 - Mechanical and electrical properties of carbon nanotube-grafted polyimide nanocomposites

Nam-ho You, polymer@kist.re.kr, Jun Lim, Bon-Cheol Ku, Munju Goh, Dong Geun Shin, Hyeonuk Yeo, Cheol-Min Yang, Dong Su Lee, Jun-Yeon Hwang. Department of Carbon Convergence Materials Research Center, Korea Institute of Science and Technology (KIST), Jeonbuk, Republic of Korea

Polyimide (PI)-based nanocomposites containing aminophenyl functionalized multi-walled carbon nanotubes (AP-MWCNTs) obtained through a diazonium salt reaction was successfully prepared by in situ polymerization. PI composites with different loadings of AP-MWCNTs were fabricated by the thermal conversion of polyamic acid (PAA)/ AP-MWCNTs. The mechanical and electrical properties of the AP-MWCNTs/PI composites were improved compared with those of pure PI due to the homogeneous dispersion of AP-MWCNTs and the strong interfacial covalent bonds between APMWNT and the PI matrix. The conductivity of APMWNT/PI composites (5:95 w/w) was $9.32 \times 10^{-1}$ S/cm which was about $10^{15}$ times higher than that of Pure PI. The tensile strength and tensile modulus of the AP-MWCNTs/PI composites with 0.5 wt% of AP-MWCNTs were increased by about 77% (316.9 ± 10.5 MPa) and 25% (8.30 ± 1.10 GPa) compared to those of pure PI, respectively.
Micelles assembled from amphiphilic copolymers have garnered interest for their potential application in targeted drug delivery. To probe the effects of chirality on the micelle stability, chiral amino acids were incorporated into either the hydrophobic or hydrophilic block of an amphiphilic copolymer that was polymerized using controlled radical techniques. For a hydrophilic monomer, Boc-amino acids were functionalized at the C-terminus with a methacrylate handle. Polymerization with MMA and deprotection of the Boc group afforded the cationic copolymer. Polymers exhibited either no or enhanced chirality depending on the side chain identity, as analyzed by optical rotation and circular dichroism. As the basis for a hydrophobic monomer, amino acids were functionalized with alkyl groups at the C-terminus and with an acrylamide handle at the N-terminus (see figure 1). After polymerization and deprotection, the copolymer was anionic and readily self-assembled to micelles ~65 nm in diameter (DLS). These copolymers were thermally stable at pH 7.4.
428 - Synthesis and applications of alkyl-functionalized graphene oxide/polyimide nanocomposites

Hyeonuk Yeo1, yeo@kist.re.kr, Do-Hoon Lee1,2, Seokhoon Ahn3, Nam-Ho You1. (1) Carbon Convergence Materials Research Center, Korea Institute of Science and Technology (KIST), Eunha-ri San 101, Bongdong-eup, Wanju, Jeonbuk 565-905, Republic of Korea, (2) Department of BIN fusion Technology & Department of Polymer and Nano Science and Technology, Chonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea, (3) Soft Innovative Materials Research Center, Korea Institute of Science and Technology (KIST), Wanju, Jeonbuk 565-905, Republic of Korea

Polyimide (PI) nanocomposites containing alkyl functionalized graphene oxide (A-GO) were successfully fabricated by in situ polymerization. The A-GO was synthesized through reaction with alkyl bromide and commercial graphene oxide (n-GO) and investigated by XPS spectra, FT-IR spectra and TGA analysis. PI composites with various loadings of the fillers were prepared by the gradual thermal imidization of polyamic acid (PAA) precursor containing A-GO.

The mechanical properties of the A-GO/PI composites were improved compared with those of pure PI and n-GO/PI composites because of the homogeneous dispersion of A-GO by the interfacial non-covalent interaction (van der Waals force) between A-GO and the PI matrix. The tensile strength of the A-GO/PI composites with 0.5wt% of A-GO was increased by about 18% (121.0 ± 10.9 MPa) improvement compared to that of pure PI. Tensile modulus of the A-GO/PI composites with 0.5wt% of APMWNT was improved by 45% (3.24 ± 0.15 GPa) compared to that of pure PI.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
429 - High temperature gel permeation chromatography using dual flow refractive index detection

Amandaa K. Brewer, amandaa.brewer@tosoh.com, Tosoh Bioscience LLC, King of Prussia, PA 19406, United States

Single detector high temperature gel permeation chromatography (GPC) is used 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 in the EcoSEC® High Temperature GPC System for the determination of molar mass averages via peak position calibration at temperatures up to 220 °C. The dual flow RI detector 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. Additionally, we will demonstrate how single detector high temperature GPC can be used for the characterization of polyolefins, polyethylenes of varying density, and polyphenylene sulfide (PPS) compounds. Finally we will show the coupling of a dual flow refractive index detector to a multi-angle light scattering detector for the determination of absolute molar mass and polymeric size of synthetic polymers.

Figure: A: Depiction of a dual flow refractive index detector cell. B: High temperature GPC elution profile and molar mass averages of low density polyethylene.

Monday, August 11, 2014 08:00 PM
Sci-Mix (08:00 PM - 10:00 PM)
Location: Moscone Center, North Bldg.
Room: Hall D

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
430 - Synthesis and characterization of kinase inhibitors encapsulated in mPEG-PLGA NPs for anticancer drug delivery

Carolyn Kan, ckan2@calstatela.edu, Department of Chemistry and Biochemistry, California State University, Los Angeles, Los Angeles, CA 90032, United States

mPEG-PLGA (methoxy poly(ethylene glycol)- poly(lactic-co-glycolic acid) is an amphiphilic biocompatible polymer which can form nano-scale micelles, or nanoparticles (NPs), in aqueous environment. Hence, hydrophobic drugs are readily encapsulated within the hydrophobic cores of the NPs. In cancer therapies, NPs are found to passively accumulate at solid tumor sites by the enhanced permeability and retention (EPR) effect. This is because angiogenesis generates vessels with fenestrations of 600-800 nm in diameter, and tumors also have an impaired drainage system. Therefore, mPEG-PLGA NPs are promising for targeted delivery of potent hydrophobic anticancer drugs. One hydrophobic kinase inhibitor drug Sorafenib, used to treat renal cancer carcinoma, was chosen for this study. The objective is to find the experimental methods and conditions to encapsulate Sorafenib in mPEG-PLGA NPs with the most optimal sizes, drug loading levels, and drug release profiles. The drug delivery efficacies of these nanoparticles will be further tested in mouse models with the collaboration with City of Hope Cancer Center.
431 - Position-controlled functionalization of hyperbranched polyglycerol: The modification site controls melt rheology and thermal behavior

Christian Schubert¹, christian.schubert@uni-mainz.de, Carina Gillig², Christian Friedrich², Holger Frey¹. (1) Institute of Organic Chemistry, Johannes Gutenberg-University, Mainz, Rhineland-Palatinate 55128, Germany, (2) Freiburg Materials Research Center (FMF), Albert-Ludwig-University, Freiburg, Baden-Württemberg 79104, Germany

Thermo rheological properties and the dependence of the glass transition temperature ($T_g$) on site-selective functionalization of hyperbranched polyglycerols (hbPG) are presented in this work. DbPG exhibits a highly flexible aliphatic polyether backbone, multiple hydroxyl groups with a well-defined degree of branching (DB) and narrow polydispersity (PDI). In order to tailor functionality, we employed a synthetic strategy permitting selective modification of linear and terminal units of hbPG.¹ This approach can be viewed as a tuning of the polarity and associative interactions in two different localities. We investigated the linear viscoelastic properties and the $T_g$ of several protected hyperbranched polyglycerols with respect to the locality and type of protection group (benzyl, methyl and acetonide). The results show that the trend of the $T_g$ is particularly remarkable. In dependency of their interactions and steric demand, the different protection groups show a significant effect on the $T_g$. Moreover, the linear units mainly affect the flexibility of the polymer, although hbPG exhibits clearly fewer linear than terminal OH-groups.

The zero shear viscosity is not as strongly affected by the type of protection groups as the amount and locality of the OH-groups. For the first time, this work provides elementary insights in the influence of linear and terminal OH-groups on thermo rheological properties of a hyperbranched polymer and correlates them with locality and type of modification.


Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
432 - Preparation of polyols and diols by chopping high-molecular-weight aliphatic polycarbonates

Jong Yeob Jeon, jjy023@gmail.com, Bun Yeoul Lee, bunyeoul@ajou.ac.kr. Department of Molecular Science and Technology, Ajou university, Suwon, Gyeonggi-do 443-749, Republic of Korea

High-molecular-weight poly(1,4-butylene carbonate) (PBC) (Mₙ: 40,000-90,000) was prepared through the condensation polymerization of dimethyl carbonate (DMC) and 1,4-butanediol (BD) in the presence of 0.05 mol % sodium alkoxide catalyst. The subsequent feeding of 15 mol % HOAOH, such as 1,6-hexanediol, 1,5-pentanediol, 1,4-cyclohexanediethanol, or 1,4-benzenediethanol and stirring at 190–150 ºC converted the extremely thick high-molecular-weight polymer to low-molecular-weight macrodiols with GPC-measured Mₙ 2000. The analysis of the ¹H NMR spectra indicated that the –A– units and 1,4-butylene units were randomly distributed in the resulting oligomers. The chopping of the high-molecular-weight PBC using either triols or tetraols such as glycerol propoxylate, 1,1,1-tris(hydroxymethyl)ethane, or pentaerythritol also afforded macropolyols containing branched chains with GPC measured Mₙ 2000. When the chopped polymers were genuine PBCs, the resulting macrodiols or polyols were in a waxy state at room temperature. However, permanently oily compounds were obtained when the chopped polymers were prepared using 0.90 mole fraction of BD admixed with various other diols. The macrodiols and polyols synthesized in this study may have potential applications in the polyurethane industry.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
433 - Synthesis of polyolefins strictly spaced with aryl ether via ADMET polymerization: Effect of aryl ether on crystallization and thermal properties

Dirong Gong\textsuperscript{1,2}, gongdirong@nbu.edu.cn, Shaofei Song\textsuperscript{1,2}, Zhong-ren Chen\textsuperscript{1,2}. (1) Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, China, (2) Key Laboratory of Specialty Polymers, Grubbs Institute, Ningbo University, Ningbo, Zhejiang 315211, China

Dirong Gong\textsuperscript{1,2*}, Shaofei Song\textsuperscript{1,2} and Zhong-Ren Chen\textsuperscript{1,2*}

1. Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P.R.China

2. Key Laboratory of Specialty Polymers, Grubbs Institute, Ningbo University, Ningbo 315211, P. R. China

Corresponding to: Chenzhongren@nbu.edu.cn and gongdirong@nbu.edu.cn

Abstract: A series of aryl ether-containing polyolefins (5a-5f) were prepared by acyclic diene metathesis (ADMET) polymerization of the corresponding diene monomers (3a-3f) followed by the hydrogenation. The well-defined structures of the polymers were confirmed by \textsuperscript{1}H, \textsuperscript{13}C NMR and FTIR. Thermal properties of the unsaturated (4a-4f) and saturated polymers were investigated via differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The crystallizing behaviors of the polymers are largely affected by the structure of aryl ethers, with bulky aryl ether distracting the crystallization. TGA results show that the thermal stability is also enhanced probably due to the aryl ether.

Figure 1 The synthetic scheme of well-defined polyolefins strictly spaced with aryl ether

References


434 - Cationic amphiphiles as disruptive antimicrobial agents

Allison M. Faig1, allison.faig@rutgers.edu, Susan Skelly2, Kathryn E. Uhrich1. (1) Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, United States, (2) Division of Life Sciences, Rutgers University, Piscataway, NJ 08854, United States

The development of multidrug-resistant (MDR) bacteria is a global healthcare concern that has led researchers to investigate new antimicrobial agents. Naturally occurring antimicrobial peptides (AMPs) have demonstrated promise in antimicrobial applications, often through disrupting bacterial cell membranes. AMPs’ net cationic charge and amphiphilicity, respectively, enable them to electrostatically interact with negatively charged bacterial cell membranes and subsequently associate with the membrane interior via hydrophobic interactions, ultimately disrupting membrane integrity. Given that this mechanism-of-action is driven by charge and amphiphilicity, we hypothesized that through mimicking AMPs’ physicochemical properties, novel antimicrobial materials could be designed to combat MDR bacteria. To this end, a series of cationic amphiphiles was developed, comprised of tartaric acid-based backbones and branched aliphatic arms containing terminal amine moieties, which could be further functionalized with poly(ethylene glycol) to improve amphiphiles’ solubility and stability under physiological conditions. The chemical structures of all amphiphiles and their precursors were confirmed by nuclear magnetic resonance spectroscopy, while mass spectrometry or gel permeation chromatography served to verify compounds’ molecular weights. Upon complete physicochemical characterization, amphiphiles’ bioactivities were assessed to measure their potential as antimicrobial agents.
435 - Study on synthesis, self-assembly behavior, and mutiple stimuli-responsive property of POSS-based block or random copolymer in solutions

Yiting Xu¹, xyting@xmu.edu.cn, Jianjie Xie¹, Min Chen¹, Ying Cao¹, Chang Feng-Chih², Lizong Dai¹. (1) Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, Fujian 361005, China, (2) Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung, Taiwan, China

Incorporating inorganic or organometallic moieties into organic polymers to obtain organic-inorganic hybrid with new properties has attracted considerable interest. Polyhedral oligomeric silsesquioxane (POSS), a hybrid molecule with nanoscale dimension, is emerging as new chemical feedstock for preparing organic-inorganic nanocomposites. However, little attention has been focused on the synthesis and self-assembly behaviors of block/random copolymers containing POSS with novel architectures, especially these hybrid assemblies that can respond to multiple external stimuli. Our work aims at synthesizing well-defined POSS based amphiphilic block/random copolymers via living radical polymerization, preparing nano-hybrid materials with novel topological structure by utilizing self-assembly technology in solutions, and further tuning parameters to explore the stimuli-responsive property. We have found different polymeric units that have distinct responsive moieties are incorporated into one copolymer system, which will display multiple responsive mechanisms. The introduction of MAPOSS domain makes it possible for these novel hybrid copolymers to self-assemble into aggregates owing to the strongly hydrophobic nature of the silicon-containing moieties. More importantly, the incorporation of other hydrophilic monomers in these copolymers is proposed to be capable of displaying temperature-responsive, pH-responsive, metal ions-responsive and so on, see Figure 1(a, b, c). More recently, we have prepared a novel hybrid micelle self-assembled from interpolyelectrolyte complexation based on random POSS-containing copolymers. Study on hybrid micelle reveals that electrostatic interaction has a tremendous effect of on thermo-responsive, see Figure 1d.
We present a novel way to generate AgNPs without adding additional reducing agents. In this method we reduced the silver nitrate by utilizing the epoxy group on the polymer (glycidyl methacrylate) (PGMA) sub-microspheres, which upon ring opening become hydroxyl group enabling polymer itself to act as reducing agent. The AgNPs formed by the polymer are successfully coated on the polymer spheres, see the HRTEM image.

Size of the AgNPs is controllable by optimizing time and concentration of the silver nitrate solution.

Production of AgNPs without adding additional reducing agent, can transform the production of AgNPs saving time and cost along with reducing toxic metabolites. Furthermore we tested antibacterial and anticancer properties of AgNPs coated PGMA composite produced by this method using E.Coli and cancer cell line KB-31 & HepG2. These AgNPs polymer composite successfully kill both bacteria and cancer cells confirming the active biological properties of the AgNPs produced by auto-reduction. Also the biological activities of the AgNPs was found to better against both the cancer cells lines KB-31 and HepG2 cells with a concentration of 9.9 μg/mL comparing to the pure AgNPs without composite of 20μg/mL.
**437 - Synthesis and characterization of a new polymer of star-shaped poly(N-vinylpyrrolidone) with a β-cyclodextrin core via xanthate-mediated RAFT polymerization**

**Jiang Jianwei, jiangsheng310@163.com, Piao Longhai. Department of Chemistry, Kongju National University, Unaffiliated, Kongju, Chungnam 314-701, Republic of Korea**

The β-cyclodextrin (β-CD) derivative with an average degree of substitution of 4(4Br-β-CD) was synthesized by treating β-CD with 4 equivalents of 2-bromo propionyl bromide. It was then reacted with potassium ethyl xanthate to produce β-cyclodextrin xanthate derivative as the chain transfer agent (CTA) in reversible addition-fragmentation chain transfer polymerization (RAFT). The star-shaped β-CD-(PVP)_4 (Poly(N-vinylpyrrolidone)) was prepared. The structures of 4Br-β-CD, CTA and star-shaped polymers were characterized with NMR spectra, and the molecular weight distribution of the polymers was measured by GPC.

![Synthesis diagram](image)

**Figure 1.** Synthesis of star-shaped PVP with β-cyclodextrin core

<table>
<thead>
<tr>
<th>[AIBN]₀:[CTA]₀:[NVP]₀</th>
<th>Mn,thᵃ</th>
<th>Mn,NMRᵇ</th>
<th>Mn,GPCᶜ</th>
<th>Mw/Mnᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial molar ratio</td>
<td>g/mol</td>
<td>g/mol</td>
<td>g/mol</td>
<td></td>
</tr>
<tr>
<td>1 : 5 : 50</td>
<td>6,280</td>
<td>5,340</td>
<td>2,332</td>
<td>1.91</td>
</tr>
<tr>
<td>1 : 5 : 100</td>
<td>10,720</td>
<td>8,862</td>
<td>3,861</td>
<td>2.05</td>
</tr>
<tr>
<td>1 : 5 : 200</td>
<td>19,600</td>
<td>12,631</td>
<td>6,325</td>
<td>3.00</td>
</tr>
<tr>
<td>1 : 5 : 400</td>
<td>37,360</td>
<td>29,654</td>
<td>12,023</td>
<td>3.57</td>
</tr>
</tbody>
</table>

ᵃ Mn,th: theory molecular weight of polymer. ᵇ Determined by ¹H NMR. ᶜ Determined by GPC in water with PEG standards.
438 - Heterogenous nucleation in the polymer melting kinetics

**Benjamin Yancey**, bjyancey@uab.edu, Kahleah Walker, Sergey Vyazovkin. Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294, United States

The kinetics of poly(ethylene terephthalate) and poly(e-caprolactone) melting is studied by means of differential scanning calorimetry and treated in the frameworks of a nucleation kinetic model. The study focuses on the temperature dependence of the effective activation energy of melting. A theoretical dependence is derived from the nucleation model and an experimental dependence from the Kissinger plot. Although the theoretical dependence fits accurately, the experimental dependence has some deviations from what is expected based on homogenous nucleation. The fit of the experimental data gives rise to the surface free energy that is significantly smaller than that obtained from crystallization data. A similar result is reported in other publications that make use of a homogeneous nucleation model for polymer melting. We demonstrate that a heterogeneous nucleation model is a more appropriate representation of the melting process and that its use resolves the problem of estimating the unusually small surface free energies.
439 - Kinetics of the coil-to-globule transition in aqueous solution of poly (N-isopropylacrylamide)

Reza Farasat, rfarasat@uab.edu, Sergey Vyazovkin. Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294, United States

In an aqueous solution, poly (N-isopropylacrylamide) (PNIPAM) undergoes a reversible coil-to-globule phase transition that occurs above the lower critical solution temperature (LCST). The transition is driven by temperature-dependent molecular interactions that include hydrogen bonding and hydrophobic association. By increasing the temperature above LCST, the PNIPAM-water bonds break, and the polymer coils collapse to globules.

The process is accompanied by an endothermic thermal effect which is detectable by Differential Scanning Calorimetry (DSC). A 10 wt. % solution of PNIPAM in water was prepared and subjected to DSC experiments under different heating rates (from 0.5 to 16°Cmin⁻¹). With increasing the heating rate, the transition temperature as well as the DSC peak shift to higher temperature. The DSC data have been analyzed by an isoconversional method to evaluate the temperature dependence of the effective activation energy of the process. The resulting dependencies have been interpreted in terms of a nucleation kinetics model. The process has also been studied under nanoconfinement by introducing the PNIPAM solution into the silica nanopores. The results obtained under nanoconfinement are compared to those obtained for the bulk solution.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
440 - Facile method to prepare polyphosphines from environment–friendly chemical

Zhi-Wei Tan¹, Min Zhang¹, Jin-Jun Qiu¹, Zhude Tu², tuz@mir.wustl.edu, Cheng-Mei Liu¹, liukui@mail.hust.edu.cn. (1) Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China, (2) Department of Radiology, Washington University School of Medicine, St. Louis, United States

Phosphorus is one of the most abundant elements on earth and introducing this elements into polymer bankbone is clearly of both fundamental and applied interest[1] . Small amounts of phosphorus in a polymer can be greatly advantageous, imparting flame retardancy[2–4], adhesion to metals[5], ion-exchange characteristics[6] and biodegradable and blood compatible characteristics[1]. Normal two kinds of phosphorus-containing polymers have been widely studied: polyphosphoester (P-O bond linkage) and polyphosphines (P-C bond linkage). Polyphosphoesters are of commercial interest because of their biodegradable characteristics, but obvious disadvantage is the lack of long-term hydrolytic stability. This problem has been partially overcome by elimination of the phosphorus-oxygen bonds in the backbone of polymers. For the past years, polyphosphines with structure [-P(R)-CR′]n have been the subject of extensive research. Polyphosphines with long-term hydrolytic stability obtained from polymerization of phosphaalkenes (P(R)=CR′)=CR′[7–10], copolymerization of olefinic monomers with small phosphorus heterocycle compounds[11] and via the polycondensation of functional phoshine monomer[12–15].

Probing into present research results in phosphorus chemistry, it is found that most phosphorus-containing polymers were synthesized from hazardous starting chemicals, such as white phosphorus, PCl_3 and POCl_3. Exploring the possibility to prepare polyphosphines from less hazardous chemicals is the current topics.

Tetrakis(hydroxymethyl)phosphonium sulfate (THPS) is one of environment–friendly chemicals which is readily biodegradable and has no potential to bioaccumulate. It passed an environmental attestation in America and was awarded the American Green Chemicals Award in 1997[16]. THPS originally used as a biocide, effective against micropests in industrial cooling systems, oil field operations, and the paper-making industry[17]. THPS is also a reactive intermediate for some fine phosphorus compounds. Based on these research results, we recently focus on the design and synthesis of polyphosphines from THPS. Here we report our progresses in this filed.

References


Tuesday, August 12, 2014 06:00 PM

General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)

Location: Moscone Center, West Bldg.

Room: Exhibit Hall
In literature, polymers including N-methylol acrylamide (NMA) are synthesized by emulsion copolymerization method and these polymers are used in so many applications such as adhesives, protective coatings, binders for nonwoven fabrics and latex paints. Self-cross-linkable monomers increase tensile strength, impact resistance, abrasion resistance of the latexes. These latexes are produced in industry by using NMA in small amounts (3−7 wt % of the copolymer). However, NMA has a disadvantage of generating and releasing formaldehyde.

because of its toxicity, efforts have been focused on other alternative self-crosslinking monomers to lower the level of formaldehyde. In this project, the aim is to synthesize a novel formaldehyde-free crosslinker for binders polymers, which will eliminate the side effects of binders caused from formaldehyde.

**Figure 1.** The self crosslinking mechanisms of N-methylol acrylamide
442 - Novel melt processible technology platform for polar functionalization of polyolefins

Do Eui Lee, doeunice@naver.com, Sung Chul Hong. Faculty of Nanotechnology and Advanced Materials Engineering, Sejong Polymer Research Center, Sejong University, Seoul, Gwangjin-gu/Gunja-dong 143-747, Republic of Korea

Polar functionalization of non-polar polyolefins has become increasingly important. Incorporations of polar units in polyolefins render functionality to polyolefins and enable them to be used in many value-added applications. In this presentation, a novel polar functionalization strategy for polyolefin is introduced. HDPE, iPP and EPDM are employed as model non-polar polyolefins, while radically polymerizable copolymers with various functionalities are adopted as polar polymer chains. The modified polyolefins are prepared in two-step reaction: i) preparation of polar functional copolymers by reversible addition and fragmentation chain transfer (RAFT) technique; ii) chain transfer reaction of polyolefin macro-radicals to the polar functional copolymers in melt-mixing process. The molecular weights, compositions and architectures of the polar functional copolymers are easily controlled through the RAFT process. This technology platform builds up scalable and various functionalization choices for polyolefins by using all commercially available resources, affording broadened application fields of already industrially important polyolefins.

Acknowledgements: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012R1A1A2005345).
443 - Synthesis and characterization of oligostyrene-b-polyisobutylene block copolymer via oligostyrene macroinitiator

Adekunle A. Olubummo, adekunle.olubummo@usm.edu, C. Garrett Campbell, Robson F. Storey. Department of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States

Synthesis of oligostyrene-b-polyisobutylene via cationic polymerization with sequential monomer addition, starting either from isobutylene and switching to styrene or vice versa becomes increasingly difficult as the degree of polymerization of the styrene block decreases. Difficulties include the unfavourable crossover rate relative to the polymerization rate of the styrenic monomer when starting from isobutylene and crossing over to styrene and decomposition of the polystyrene living centers at high styrene conversion when starting from styrene and crossing over to isobutylene.

We therefore have developed a new synthetic method toward oligostyrene-b-polyisobutylene (OS-b-PIB) as follows. Oligostyrene (M_n = 600 g/mol, PDI = 1.1) was synthesized first via living carbocationic polymerization (LCCP) using n-hexane/methyl chloride (50:50 v/v) solvent mixtures at -70°C using 1-chloro-1-(p-methylphenyl)ethane as initiator and TiCl_4 as co-initiator. The oligostyrene was then used as a macroinitiator for the polymerization of isobutylene to generate the OS-b-PIB block copolymer. Block copolymers created by this method have been extensively characterized via GPC, NMR, and MALDI-TOF spectroscopy. This proposed method can also be used for longer polystyrene chains.
Recently, there has been increasing interest in physically crosslinked hydrogels due to their ability to gel under mild, aqueous conditions in the absence of chemical crosslinkers. Although chemically crosslinked gels tend to have better mechanical properties than their physically crosslinked counterparts, the toxicity associated with residual chemical crosslinkers and organic solvents is highly undesirable for biomedical applications. Some of the most robust physical hydrogels have been achieved by introducing stereocomplexed domains into the hydrogel network. The stereocomplexation between poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) is one such example. Double-crystalline PDLA-b-PEO-b-PDLA triblock copolymers served as our inspiration to synthesize a new material with potential applications in hydrogel drug delivery. The synthesis and characterization of this new double-crystalline material will be presented.

Surface-initiated controlled radical polymerizations (SI-CRP) have enabled the facile preparation of well-defined polymer brushes. The ability to control the chemical identity, polymer architecture and molecular weight of the surface-grafted chains allows for a variety of surface properties to be controlled for applications ranging from antifouling to nanostructured surfaces. The density of grafted chains, and therefore surface coverage, is also an important parameter which can greatly affect surface properties. Current strategies for modulating the density of grafted chains are limited due to tedious synthetic procedures. Furthermore, spatial control over grafting density is limited to length scales of millimeters to centimeters. In this study, we demonstrate a general method for tuning the grafting density of polymer brushes using visible light. Light as an external stimulus for controlling grafted chain density also enables spatial control over the surface properties and the opportunity for the fabrication of nanostructures.
Verdazyl molecules are a class of stable free radicals. Substituting polyaniline with verdazyls has the potential to modify the charge transport properties of the polyaniline by changing the redox potential of the polymer. Such polymers have the potential to be used in spintronic devices. There are two possible substituted polyanilines that can be created, N-substituted and C-substituted. We are developing the synthesis of an N-substituted verdazyl oligoaniline through the Buchwald-Hartwig amination.

We report the synthesis of monomers and oligomers and characterization by UV-vis, ESR, and electrochemistry.
Conjugated polymers offer the opportunity for the solution-based fabrication of low-cost optoelectronic devices. There is considerable interest in understanding structure-function-property relationships and expanding the scope of these materials to achieve complementary functionality in the near-infrared. Here, we explore donor-acceptor (DA) copolymers employing bridgehead imine substituted 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) donors appended with increasingly bulky substituents. This affords the capability to influence the degree of intermolecular coupling in the solid-state and ascertain the effect on the optoelectronic properties. Grazing incidence wide-angle x-ray scattering (GIWAXS) shows that systematic increases in steric bulk increase both π-π stacking, from 3.6 Å to 4.2 Å, and spacing in a semi-crystalline face-on morphology until an amorphous packing is reached. This correlates with a progressive blue shift in the absorption maxima, increase in the onset of oxidation, and widening of electrochemical bandgap. Furthermore, we demonstrate that cross-conjugated structural motifs in combination with highly electronegative acceptors with progressively delocalized n-systems affords DA copolymers with broad absorption profiles that span technologically relevant wavelength (λ) ranges from 0.7 < λ < 3.2 µm.

The presence of the cross-conjugated substituent at the donor bridgehead position results in the capability to fine-tune structural and electronic properties and overcome conjugation saturation behavior to achieve very narrow optical bands (E_{g,opt} < 0.5 eV). This strategy affords modular DA copolymers with absorption in the infrared, and solution processable materials with the narrowest band gaps reported to date.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
Polyacrylonitrile copolymer is one of the most important precursors for the production of high performance carbon materials. The architecture of the precursor has significant influences on the properties of the resulting carbon materials. In this study, various poly(acrylonitrile-co-itaconic acid)s (PAIs) are prepared by free radical polymerization and controlled/living radical polymerization technique. The structural evolution of PAI during its thermal oxidative stabilization (TOS) processes was investigated through Fourier transform infrared spectroscopy (FT-IR) analysis. The TOS process includes cyclization, oxidation and tautomerization, as characterized by the evolution of the overlapping peaks of cyclic C=C, C=N, N-H and C=O vibrations in FT-IR. An investigation of the evolution of the copolymer architectures determines the optimal structural characteristics of the precursors for high performance carbon materials. Acknowledgements: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012R1A1A2005345).
449 - Synthesis of poly(methylidene-co-ethylidene) with a new secondary ylide monomer via C1 polymerization

Ruobing Zhao, ruobingz@uci.edu, Kenneth J. Shea. Department of Chemistry, University of California, Irvine, Irvine, CA 92697, United States

The living C1 polymerization of ylides allows for the production of linear hydrocarbon polymers with controlled molecular weight, polydispersity and well-defined topology. Sulfoxide ylides are the most common C1 monomers. For example, dimethylsulfoxonium methyldene is used to produce low molecular weight linear, highly crystalline polymethylene with a narrow molecular weight distribution. Secondary ylides such as (dimethylamino)phenyloxosulfonium ethylide have been employed to synthesize substituted carbon backbones. In this work we report a new, convenient source of the ethylidene monomer for the introduction of branched groups in the carbon backbone. The monomer precursor, triethylsulfoxonium chloride (Et₃SOCl), was synthesized in 74% overall yield in 3 steps. Copolymers of dimethylsulfoxonium methyldene and diethylsulfoxonium ethylide yield materials with the same composition as an ethylene-propylene copolymer. The copolymers were synthesized with control of molecular weight, monomer composition and narrow polydispersity.
Azobenzene Compounds(AC) have attracted more and more attention due to their unique photoisomerization properties. Trans-structure with rodlike shape could be changed into cis-structure with bent shape under irradiating with ultraviolet light of 360nm and reverse transfer from cis to trans isomer can occur thermally or photochemically under visible light. These geometrical change could yield a concomitant change in chemical and physical properties in the environment around them. For example, when mixture of Azeobenzene with Cholesteric Liquid Crystal(CLC, composed of Nematic Liquid Crystal(NLC) and chiral molecule), the trans-structure of Azobenzene compound stabilize the phase structures of CLCs while cis-structure tends to destabilize the phase structure of the mixture due to its bent shape. Therefore, controlling of the orientation of liquid crystal molecules could be achieved by Azobenzene photoisomerization in this way.

In this paper, a new kind of functional Azobenzene Compound with chiral moieties has been synthesized. IR and ¹H-NMR has confirmed the presence of mesomorphic phase. It shows trans-cis photoisomerization under UV irradiation. The synthesized chiral azobenzene was doped into SLC1717. Under UV irradiation, trans isomers of chiral azobenzene change to cis, which disrupt LC molecules alignment resulting in the appearance of planar and fingerprint texture of CLCs.
Poly(ethylene oxide) (PEO), having the same repeat units as poly(ethylene glycol) (PEG), is a nonionic hydrophilic polymer. It is of great interest in both biology and materials science as it demonstrates a unique lack of adhesion to proteins, and amphiphilic block copolymers containing PEO are widely used in biological applications such as drug delivery. The synthesis of PEO homopolymers and block copolymers can be experimentally challenging, however, with the typical method involving a hydroxyl-terminated polymer reacted with an air sensitive potassium naphthalenide to form a potassium alkoxide. This method requires removal of naphthalene from the final product and undesirable reactions with water impurities in the reaction. We report a synthetic route that avoids these limitations by driving off water, through azeotropic distillation, of the alcohol + potassium hydroxide / water + alkoxide equilibrium. This pushes the equilibrium towards the formation of the alkoxide while avoiding the use of naphthalene and removing any water impurities. GPC and NMR are used to characterize the polydispersity and molecular weight of polymers made from various alcohols or the extension of premade PEO polymers.
Gertjan Vancoillie, gertjan.vancoillie@ugent.be, Richard Hoogenboom. Department of Organic Chemistry, Ghent University, Gent, Belgium

Size-exclusion chromatography is amongst the most widely used polymer characterisation methods in both academic and industrial polymer synthesis research. This technique is used for the determination of molecular weight parameters and dispersity of unknown polymers using a relative calibration on polymer standards including polystyrene and poly(methyl methacrylate). The many advantages, including high accuracy, reproducibility and low sample consumption, have contributed to the worldwide success of this analytical technique. The current generation SEC systems have a stationary phase mostly containing highly porous, styrene-divinylbenzene particles allowing for a size-based separation of different polymers in solution but limiting the flow rate and solvent compatibility. Recently, sub-2µm ethylene-bridged hybrid (BEH) packing materials have become available for SEC analysis. These packing materials not only can withstand pressure up to 15000 psi but also show high spatial stability towards different solvents. Combining these BEH columns with the ultra-high performance LC (UPLC) technology opens up new UHP-SEC analysis, showing strongly reduced runtimes and unseen solvent compatibility.

This poster will present an overview of the analysis of different polymers using UHP-SEC on a wide range of solvents. After the initial Van Deemter optimization and calibration using PMMA or PS standards, different polymers were analysed using the optimized conditions and compared to previously obtained SEC results. To evaluate the scope of the UHP-SEC, the choice of mobile phases was focussed on commonly used solvents in SEC with a wide polarity range namely tetrahydrofuran, N,N-dimethylacetamide and methanol. In order to evaluate the suitability of the equipment in a research environment, a large variety of functional polymers including polyoxazolines (see figure), poly(oligo ethylene acrylate)’s and boronic acid containing polymers were injected in order to identify possible undesirable column interactions.
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, thermomechanical, mechanical, and adhesive properties of the catechol modified thiol–ene networks.
454 - Nitrosocarbonyl hetero-Diels–Alder cycloaddition: A versatile new tool for conjugate formation

Andrey V. Samoshin\textsuperscript{1}, asamoshin@umail.ucsb.edu, Javier Read de Alaniz\textsuperscript{1}, Craig Hawker\textsuperscript{2}. (1) Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106, United States, (2) Materials Research Laboratory, University of California Santa Barbara, Santa Barbara, CA 93106, United States

It is demonstrated that nitrosocarbonyl Diels–Alder chemistry can be applied in macromolecular synthesis. Polyethylene glycol functionalized with a hydroxamic acid moiety, can be coupled to cyclopentadiene terminated polystyrene, through a copper catalyzed, as well as thermal hetero Diels–Alder reaction.

The mild and orthogonal methods used to carry out this reaction make it an attractive method for the synthesis of block copolymers. Using GPC and NMR, the resulting block copolymers were analyzed and characterized. The product materials were subjected to thermal retro [4+2] cycloaddition, allowing for the liberation of the individual polymer chains, and subsequent recycling of the diene terminated polymers.

\textbf{Tuesday, August 12, 2014 06:00 PM}
\textbf{General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)}
\textbf{Location: Moscone Center, West Bldg.}
\textbf{Room: Exhibit Hall}
The development of functional polymers is central to advancement in fields such as drug delivery, complex sensors, and microelectronics. Unfortunately, current polyester syntheses possess several disadvantages: the step-growth copolymerization of diols and diesters requires high heat and vacuum removal of small molecule byproducts, and the ring opening polymerization of lactones is limited in scope due to a lack of monomer diversity. An alternative route that has received little attention is the copolymerization of lactones and epoxides. Previous examples show that this reaction gives either homopolymers or low molecular weight copolymers. We report the alternating ring-opening copolymerization of epoxides with lactones using metal-based catalysts. This process represents a significant advance over previously reported processes, as it gives access to a variety of highly alternating polyesters with high molecular weights and low molecular weight distributions.
456 - WITHDRAWN
Organic photovoltaics (OPVs), in contrast to conventional silicon-based solar cells, have the potential to be mass produced at much lower costs through facile methods like spin coating and inkjet printing onto flexible substrates. However, they exhibit lower efficiency than the conventional cells. Present high-efficiency OPV devices utilize fullerene derivatives as the electron accepting and transport material, which give good performance but have many drawbacks as well, including high cost, narrow light absorption in the visible spectrum, environmental instability, and poor processability. This research focuses on the synthesis of novel electron acceptor materials, tri-(perylene bisimides) (tri-PBIs)—derivatives of inexpensive industrially available dyes, and have the potential to increase the efficiencies of polymer solar cells through increased light absorbance, morphology and phase control through tunability of solubilizing groups, as well as greater photochemical stability and increased device lifetimes. The tri-PBIs were synthesized according to established procedure, and characterized through $^1$H NMR, MALDI-TOF mass spectrometry, and UV-VIS spectroscopy. Tri-PBIs were blended with poly(3-hexyl thiophene), spin cast into thin films, and incorporated into OPV devices. Morphology and phase of the thin films were characterized using atomic force microscopy, and photovoltaic performance was analyzed.
Microwave assisted synthesis and electrochemical characterization of phosphole containing conjugated oligomers

Robert M Pankow, robert.pankow.107@my.csun.edu, Kenneth F Cooper, Katsu Ogawa. Department of Chemistry & Biochemistry, California State University Northridge, Northridge, California 91330-8262, United States

The orbital energies of phosphole containing conjugated systems can be tuned through synthetic modification at the phosphorous center, such as oxidation. Existing synthetic methods for 1,2,5-triphenylphosphole require refluxing at elevated temperature (>170°C) for a prolonged time, resulting in decomposition of the phosphole product to form large amounts of oligomeric byproduct. Using microwave heating, phosphole oligomers with phenyl, p-methoxyphenyl, p-fluorophenyl, or thienyl groups were prepared. This method shortens reaction times and lowers the amount of oligomeric byproduct formation. The prepared phosphole containing oligomers were modified at the phosphorus center to provide the corresponding sulfides and oxides. The oxidized phospholes substituted with thienyl groups can be polymerized electrochemically to yield the corresponding conjugated polymer. When the aryl group of the butadiene is phenyl or thienyl, electrochemical data shows either stabilization or a destabilization of the HOMO after annulation to form the phosphole, respectively. After oxidation of the phosphorous center of the phosphole, we observe a stabilization of the LUMO and destabilization of the HOMO. New phosphole oligomers can be tailored based on these electrochemical properties, along with an optimized synthetic procedure for each step of the preparation.
In order to investigate structure-property relationships of phosphole containing organic π-conjugated oligomers, derivatives of 1-phenyl-2,5-biaryl phospholes were synthesized using biarylbutadienes as precursors, and steady-state photophysical characterizations of the compounds were performed. Spectroscopic data shows that annulation of the butadiene moiety with a phosphorous atom increases the π-conjugation, causing bathochromic shifts in the absorption/emission maxima. Oxidation at the phosphorous by oxygen or sulfur also results in a bathochromic shift in the absorption/emission maxima. In addition, introduction of a heavy atom such as sulfur promotes intersystem crossing to the triplet excited state resulting in phosphorescence. To explore the electronic effects of the aryl groups, p-fluorophenyl, p-methoxyphenyl, and 2-thienyl analogues were investigated. Spectroscopic analyses show bathochromic shifts in the absorption/emission maxima in case of p-methoxyphenyl and thienyl derivatives, while no such shifts are seen in the case of the p-fluorophenyl analogue. Absorption/emission maxima proved to be relatively independent of solvent, while quantum efficiencies are shown to be highly dependent on solvent polarity.
460 - WITHDRAWN
461 - Synthesis of a new perfluorocyclopentene-derived bisphenol for multi-functional step-growth polymers

Cynthia A Corley, cynthia.corley@usafa.edu, Derek B Barbee, Scott T Iacono. Department of Chemistry and Chemistry Research Center, US Air Force Academy, USAF Academy, CO 80840, United States

There has been much interest in recent years in the development of fluorinated monomers due to their increased chemical and thermal stability and low dielectric loss as compared to hydrocarbon analogs. A new bisphenol monomer has been prepared containing a perfluorocyclopentene (PFCP) unit via aryl ether linkages. Bisphenol A (BPA) was initially mono-protected using chlorotrimethylsilane followed by addition of perfluorocyclopentene and finally deprotected with tetrabutilammonium fluoride to afford the desired compound, denoted PFCP BPA. This work will highlight the versatility of the PFCP BPA monomer in step-growth polymerizations in multi-functional, high performance fluorinated polymers including polyurethanes, polyethers, polycarbonates, and epoxide resins.
462 - Olefin-bearing polymethacrylates and polymethacrylamides as solid-solid phase change materials: Effect of spacer length on heat storage capacity

Kelli A. Stockmal, kstockmal@clarku.edu, Sergio Granados-Focil. Department of Chemistry and Biochemistry, Clark University, Worcester, MA 01610, United States

A series of new solid-solid phase change materials (PCMs) have been synthesized via radical and RAFT polymerization to evaluate the effect of the pendant chain chemical structure on latent heat. Flexible, non-crystallizable spacers were added between the polymer backbone and the crystallizing olefin. The structure of the spacers was modified to evaluate the effect of chain length and hydrogen bonding ability on phase change behavior. The spacer increased the conformational freedom of the olefin chains and produced polymethacrylates and polyacrylamides with latent heats higher or comparable to those of commercially available encapsulated PCMs. Our results indicate that a 4-6 atom spacer maximized the heat storage capacity. Furthermore, introduction of hydrogen bonding motifs increased the latent heats of the polymers by up to 50% without significantly altering their melting temperature. We expect that these trends can be used to guide the design of more efficient solid-solid PCMs for a wide range of applications.
463 - Side-chain conducting polymers: Application for various anode materials as polymeric binders for lithium-ion batteries

Sang-Jae Park, sangjae@sas.upenn.edu, Vince S Battaglia, Gao Liu. Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

New polymeric binder materials are required for the practical development for lithium-ion batteries with high power and energy densities. Pyrene-based polymers consisting of side-chain electron conducting moieties yield a battery anode with the good cycling performances when they are used as polymeric binders for silicon nanoparticles without additional conductive carbon additive. Furthermore, the polymer properties can be easily tuned through facile incorporation of certain functional groups in order to increase the binding force toward the active materials and enhance the ion transport. Herein, we exhibit that the polymers can be applied to various anode materials as binders and could be further tailored for the silicon nanoparticles possessing higher tap density and bigger particle diameter.

Figure 1. (a) Cycling performance (C/10 cycling rate: charging or discharging a cell in 10 hours) of a coin cell consisting of silicon nanoparticle/graphite/polymer and (b) scanning electron microscopy (SEM) of the electrode.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
464 - Synthesis of two highly fluorinated dendrimer hypercores for $^{19}$F MRI

Adria A Lombardo, adria.lombardo@gmail.com, Xi Zeng, Douglas B Grotjahn, Eric C Wiener. (1) Department of Chemistry and Biochemistry, San Diego State University, SAN DIEGO, California 92182, United States, (2) Hillman Cancer Center, University of Pittsburgh Cancer Institute, Pittsburgh, Pennsylvania 15213, United States

Dendrimers are uniquely suited for utilization as MRI contrast agents. The syntheses of two cores are described in an effort to develop novel imaging agents for $^{19}$F MRI. The first is based on the highly fluorinated, achiral, hindered amino acid α, α'-bis-[3,5 bis(trifluoromethyl)phenylmethyl]glycine, and the other consisting of a fluorinated, rigid seven aromatic ring system.

Synthetic methodology for click chemistry and peptide coupling conditions has been investigated for dendrimer formation.
Structure-kinetics-properties relationships in polymerization reactions have slowly been gathered over the past century. Thanks to ever-improving optoelectronic devices, kinetic analysis has dramatically improved in precision, sensitivity and performance, while becoming increasingly accessible. Hence, real-time infrared spectroscopy for polymerization monitoring (RTIR), introduced in 1988, is now commonly preferred over discrete FT-IR, NMR and photoacoustic spectroscopy techniques; as well as over time-response-limited tools, such as calorimetry, dilatometry and IR-radiometry. Moreover, RTIR allows correlation of kinetics to mechanical properties during and after polymerization. However, RTIR-integration into a versatile, robust, one-sample technique has not been fully exploited.

We designed a robust high-throughput set-up incorporating real-time UV-Vis and fluorescence spectroscopy to RTIR with millisecond resolution, which permits post-polymerization analysis. Experiments run parallel to RTIR/rheometry and prior to GPC, DMA or TGA characterization; thus, kinetics can be directly correlated to polymer structure. Thermal, redox or photo-initiation schemes can be studied, time-resolved reactions performed and a variety of conditions and synthetic approaches tested.

We have quantified photopolymerization quantum-inefficacies due to mobility restrictions in bulk polymerization of (meth)acrylate networks, linked fluorescence of molecular rotors to polymer micro-environment and elucidated complex photocatalysis-based initiation schemes. We aim at targeting partially resolved mechanisms, e.g. photo-CuAAC “click” or light-activated living radical (ATRP) polymerizations. Our ultimate goal is to refine fundamental understanding of the intricate connections between monomer structure, polymer growth and final properties to aid rational design of smarter and greener materials.

---

Blending of different types of polymers offers a cost-effective way to develop high performance materials. However, when the polymers are miscible, determination of each polymer's molecular weight can be challenging. The 2D-GPC method is a versatile technique for the separation and analysis of polymer blend’s molecular weight. Using Liquid Adsorption Chromatography (LAC) the blend is first separated by polarity. A second separation using Gel Permeation Chromatography (GPC) provides molecular weight information for fractions eluted from the LAC separation. Examples of analysis using the 2D-GPC system are discussed.
467 - Characterization of poly N-isopropyl acrylamide particles for optical sensing

Nuwan T Perera¹, undugodage.perera@okstate.edu, Sandhya Pampati¹, Leah Oxenford², Barry K Lavine¹. (1) Department of Chemistry, Oklahoma State University, Stillwater, OKLAHOMA 74075, United States, (2) University of Science and Arts of Oklahoma, United States

Swellable pH sensitive polymer particles prepared by free radical dispersion polymerization using N-isopropyl acrylamide (transduction monomer), methylene bisacrylamide (crosslinker), 2-dimethoxy-2 phenyl-acetophenone (radical initiator), N-tert-butylacrylamide, and methacrylic acid, ethacrylic acid or propacrylic acid and respond to pH have been incorporated into hydrogel membranes. When the polymer particles are dispersed in a hydrogel, there are large changes in the turbidity of the membrane as the pH of the buffer solution in contact with the membrane is varied. These polymer particles show a larger response over a narrower pH range than predicted by the Henderson-Hasselbach equation. The apparent pKa of the swellable polymer particles and their response to the ionic strength of the solution can be tuned by varying the composition of the formulation used. Proposed applications of these polymer particles include gastric pH measurements that require indwelling pH electrode systems to continuously monitor ruminal acidosis in dairy cows (pH 4 thru 7), continuous in vivo measurement of pH sensing of blood in arteries and muscles for patients suffering from tissue ischemia, and pH sensing to study gastro-esophageal reflux disease, a digestive disorder related to the retrograde movement of gastric acid into the esophagus.
468 - Synthesis and applications of carbon materials converted from PIM-1

Byoung Gak Kim, bgkim@kRICT.re.kr, Changsuk Bok, Young Seok Kim, Jong Chan Won. Division of Advanced Materials, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Republic of Korea

As an effort to prepare carbon nanosheet and carbon film through catalyst- and transfer free process, several research groups have reported carbonization of polymers and small molecules such as polyacrylonitrile (PAN) and a small molecular pitch extracted from petroleum. Carbon nanosheets converted from PAN or pitch were obtained through two steps: cyclization and carbonization. Because the quality of the carbon materials sensitively depends on the cyclization conditions such as temperature, ramping rate, and oxygen contents, there is a great need for a cyclization-free process. Recently, we developed a cyclization-free carbonization process using PIM-1 (polymer of intrinsic microporosity). In this presentation, shape and dimension control of carbon materials and direct use as electrodes of organic solar cells or supercapacitors will be discussed.
469 - TMAFM inspection of the fibrous aggregated morphologies and other complex architectures self-assembled from helical (R)-and (S)-triazolepolycarbodiimides

Oleg V. Kulikov¹, oleg.kulikov.chem@gmail.com, James F. Reuther¹,², Gregory McCandless¹, Bruce M. Novak¹. (1) Chemistry, University of Texas at Dallas, Richardson, TX 75080, United States, (2) Chemistry, North Carolina State University, Raleigh, NC 27695, United States

Functionalization of (R)- and (S)-polycarbodiimides of different composition bearing active ethynyl groups was accomplished thru standard CuAAC "click"-chemistry protocol leading to cross-linked products. Morphology characterization (SEM, TMAFM) revealed the formation of fiber-like aggregates assembled from the bundles of individual helices. It seemed likely that behavior observed is a result of extensive hydrophobic interactions of the singular polycarbodiimide chains. Model proposed is originated from the analysis of single crystal X-ray data of multiple aliphatic ureas showed interdigitation pattern in a crystal lattice that possibly mimics the organization of macromolecules in fibrous aggregated morphologies.
470 - Fluctuation-induced dynamics of monodisperse capsules and multi layer polyelectrolyte capsules assembly in microfluidic device

Liyuan Zhang, liyuanzhang@seas.harvard.edu, Esther Amstad, Ingmar Polenz, David A Weitz. Harvard University, United States

Droplet-based microfluidics which involves the generation of producing high mono-dispersity drops offers a platform for miniaturizing LbL technique by imparting benefits of time and reagent reduction. In the classical lay-by-layer technique, polyelectrolyte multi-layer capsules are fabricated by alternatively deposited charged polyelectrolytes onto an oppositely charged colloidal template followed by dissolved the template which is high consuming. We present a novel deposition method by designing a new microfluidic coating device which utilizes "Z" shape channel to guide discrete templates. Similar to the game of pinball in which the templates guided and diverted to the downstream direction smoothly by repeated unit rows of fabricated channels. Shorter fabrication time of multilayer capsules can be achieved regarding to the number of layer in this kind of microfluidic device.
471 - Rheological properties of fumed silica in organic suspensions: A new route to polymer pore size control

Mariana Duarte$^{1,2}$, mariana.duarte@biotage.com, Johan Billing$^2$, Ecevit Yilmaz$^2$. (1) Department of Biomedical Engineering, Lund University, Lund, Sweden, (2) Biotage AB, Lund, Sweden

The pore control method developed in this work relies on silica nanoparticles with a methylated surface used as solid porogen in polymer synthesis. In the present investigation, the nanometer size and rheological properties of fumed silica in organic media are explored a new route to create a uniform porosity in highly crosslinked polymeric materials.

The resulting polymers are mesoporous materials, exhibiting an extremely narrow pore size distribution with an average pore size of about 100 Å (BET) and surface areas up to 350 m$^2$/g. The average pore size value by inverse size-exclusion chromatography is 94 Å which correlates with values obtained by N$_2$ adsorption. The development of the pore network is influenced by the concentration of fumed silica. At concentrations of filler higher than 20 wt.%, the particles create a stable suspension which, after polymerization and etching, results in a polymer with a well-connected and uniform porosity.

Figure 1. Schematic process of pore network development.

Figure 2: Pore-size distribution of polymers produced with different concentrations of fumed silica, obtained by N$_2$ adsorption and calculated by the BJH method applied to the desorption branch of the isotherm.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
472 - Preparation of uniform sized chitosan and QDs-chitosan microcapsules by gas-liquid microfluidic technique

Rongyi Yao, Yanjun Chen, yifengwang@whut.edu.cn, Yifeng Wang, Ming Chen. School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, China

Chitosan microcapsules have been considered for various biomedical and pharmaceutical applications due to their non-toxicity, biocompatibility, mucus-adhesion and biodegradation. However, many traditional methods to prepare microcapsules are unable to control the size and size distribution, and this would limit its application. We recently describe a convenient microfluidic approach based on gas-liquid shear to generate monodisperse chitosan microcapsules. Using home-made capillary microfluidic device, monodisperse chitosan droplets are first generated by the shearing force of N₂, and then the electrostatic interaction between chitosan and sodium dodecyl sulfate (SDS) leads to the formation of monodisperse microcapsules.

The size of microcapsules is in hundreds of microns and can be conveniently changed by changing the flow rate of N₂. In addition, quantum dots (QDs) are packaged in the chitosan microcapsules by using the mixed solution of chitosan and CdS QDs as inner phase. Due to potential toxicity and bio-incompatibility, incorporation of the metallic QDs into chitosan microcapsules is attractive in biological research. The obtained CdS quantum dots-chitosan (QDs-chitosan) microcapsules keep monodispersed and retain the fluorescence features of CdS QDs, which give their potential applications as fluorescent labels.
473 - Isothermally responsive polymers for therapeutic delivery and diagnostics

Daniel J Phillips, daniel.phillips@warwick.ac.uk, Matthew I Gibson. Department of Chemistry, University of Warwick, Coventry, United Kingdom

Inspired by Nature, the ability to prepare and apply synthetic materials capable of responding specifically to one or multiple stimuli, either externally-applied or naturally occurring, has increasingly found itself at the forefront of scientific and technological innovation. Many stimuli such as pH and light have been investigated yet arguably the most commonly studied trigger is that of temperature. So called “thermo-responsive” polymers are typically characterised by a critical solution temperature in which a polymer in aqueous solution either dissolves (UCST) or, more commonly, phase separates (LCST).¹ The ability to manipulate this transition without the need for an external temperature change (i.e. isothermally) holds promise in applications such as drug delivery, where patient compliance is of critical importance. Furthermore, isothermally responsive polymers hold far broader application as a generic scaffold upon which “smart” polymers can be developed. Considering this, we will present new methodologies for the incorporation of biochemically (e.g. redox- and enzymatic-) responsive units into thermo-responsive templates as a means of targeting specific intracellular degradation, cargo release and as a switch to control lipophilicity.²⁻⁶

² Phillips, D. J.; Gibson, M. I. Chemical Communications 2012, 48, 1054.
⁴ Summers, M. J.; Phillips, D. J.; Gibson, M. I. Chemical Communications 2013, 49, 4923.
⁵ Phillips, D. J.; Patterson, J.; O'Reilly, R. K.; Gibson, M. I. Polymer Chemistry 2014, 5, 126.
⁶ Phillips, D. J.; Gibson, M. I. Antioxidants and Redox Signalling 2014. DOI: 10.1089/ars.2013.5728
Hiroyuki Koide, hkoide@u-shizuoka-ken.ac.jp, Yu Hoshino, Yuri Nishimura, Yoshiko Miura, Naoto Oku, Kenneth J Shea. (1) Department of Medical Biochemistry, University of Shizuoka, Shizuoka, Shizuoka 422-8526, Japan, (2) Department of Chemical Engineering, Kyushu University, Motooka, Fukuoka 819-0395, Japan, (3) Department of Chemistry, University of California Irvine, Irvine, CA 92697, United States

Synthetic polymer hydrogel nanoparticles (NPs) capable of capturing and/or releasing target biomacromolecules are of interest as alternative bioaffinity ligands. Recently, poly-N-isopropylacrylamide (pNIPAm) based NPs have been prepared with the capacity to bind and neutralize the hemolytic toxin melittin. These NPs were found to neutralize the toxicity of melittin in vivo. In the present study, we focused on developing a synthetic NP for anticancer therapy by capturing and inhibiting the vascular endothelial growth factor (VEGF). Cancer cells secrete a number of growth factors to create new blood vessels in a process known as “angiogenesis”. VEGF_{165} is the most important angiogenesis growth factor. Polymer NPs were prepared by precipitation polymerization from solutions of monomers containing complementary functional groups that included sulfated N-acetylglucosamine monomers in addition to NIPAm, N-tert-butylacrylamide (TBAm, a hydrophobic monomer), and N,N'-methylenebisacrylamide (Bis, a crosslinker)

Figure 1. (a) The functional monomers used for nanoparticle synthesis (b) Schematic illustration of the QCM experiments. NPs of various compositions were injected onto VEGF_{165} immobilized QCM cells. (c) Langmuir isotherm of NP-VEGF_{165} interactions. The isotherms represent various monomer compositions in the NPs.

(Fig. 1a). A quartz crystal microbalance (QCM) sensor functionalized with VEGF_{165} was used to screen the NP library for protein binding (Fig. 1b). Interestingly, the NP affinity for VEGF_{165} was found to be very sensitive to the relative amounts of functional monomers (Fig. 1c). An optimized NP containing sulfated N-acetylglucosamine monomers strongly inhibited the phosphorylation (Tyr951) of VEGF receptor in vitro. This biologically inspired nanoparticle may very well point the way to a novel and cost effective cancer therapeutic agent.

Tuesday, August 12, 2014 06:00 PM
General Topics: New Synthesis and Characterization of Polymers (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
475 - Correlation between protein binding process of nanogel particles and facilitation of protein refolding

Masahiko Nakamoto, m.nakamoto@kyudai.jp, Yu Hoshino, Yoshiko Miura. Department of chemical engineering, Kyushu university, Fukuoka, Fukuoka 8190395, Japan

In nature system, protein called “molecular chaperone” assist the folding of denatured and nascent proteins by inhibiting irreversible aggregation. GroEL, known as the typical chaperone, interacts with nonnative protein far stronger than with native protein. Recently, nanogels that could facilitate the protein folding are of significant interest as artificial chaperone. However, contribution of protein recognition process on its function of artificial chaperone is unclear. In this study, lysozyme was selected as a model target protein. Poly-N-isopropyl acrylamide based nanogel particles (NPs), which recognize protein via combination of electrostatic and hydrophobic interaction, were prepared by incorporating acrylic acid (AAc) and N-tert-butylacrylamide (TBAm) with various feed ratios. Binding process of lysozyme to NPs was analyzed by quartz crystal microbalance (QCM). Lysozyme denatured by 6 M guanidine hydrochloride was 100 times diluted in NPs solution (100 mM phosphate buffer (pH 7.4)) and incubated for 30 minute at 25°C. The formation of aggregation was effectively inhibited with increasing of feed ratios of TBAm and AAc.

![Graph showing the correlation between remaining activity (%) and AAc (%) for 0% TBAm (opened) and 50% TBAm (closed) PNIPAn NPs as a function of feed ratio of AAc, without NP as a control (dashed line).](image)

In this presentation, correlation between protein-binding process of NPs and facilitation of protein refolding by NPs will be discussed.
A novel polymer that is sensitive to reactive oxygen species (ROS) has been developed and incorporated into a lab-on-a-chip sensor for the detection of lipid hydroperoxides in blood. Lipid hydroperoxides, which are the biomarkers and primary product of lipid oxidation, are formed from ROS reacting with lipid containing structures, which leads to the formation of more ROS-containing lipids and propagation of free-radical chain reactions. This results in cellular damage, inflammation, and the accumulation of lipid-loaded macrophages which are key mediators in development of atherosclerosis. Currently, assays have been developed to quantify the amount of hydroperoxides in blood; however they require advanced instrumentation and have low sensitivity. Here we report a portable lab-on-a-chip sensor, termed ROC, which is highly sensitive to ROS generated from the decomposition of lipid hydroperoxides in presence of iron. The ROC is composed of interdigitated electrodes (IDE) coated with a thin layer of an ROS responsive polymer. ROS formation in the sample leads to cleavage of the cross-linking moiety and degradation of the polymer from the surface of the IDE, which generates a measurable electrical signal that correlates with the amount of hydroperoxides present. Preliminary experiments of the ROC sensor to detect the amount of hydroperoxides in vitro indicated an electrical response which linearly increased with the concentration of hydroperoxide. Further evaluation using blood samples revealed a similar trend. These results suggest that the ROC sensor can serve as an instrument-free and sensitive platform for lipid hydroperoxide detection for routine clinical monitoring and in effort to prevent developing atherosclerosis.
Bacterial cellulose (BC) has been reported as the ideal material in the tissue repair fields, such as skin, bone, vascular and cartilage tissue regeneration [1-4]. Exploitation of the skin substitutes and modern wound dressings by using BC has attracted much attention [5]. The skin tissue repair materials based on BC have been biosynthesized, characterized and evaluated by *Gluconacetobacter xylinus* [6, 7]. Chitosan has excellent antimicrobial property and only one natural alkali polysaccharide. Thus chitosan is used in many applications, e.g., food, cosmetics, biomedical and pharmaceutical fields [8]. To develop an antimicrobial BC-based materials, BC/chitosan *in-situ* composites were produced by adding chitosan at different concentrations in the culture medium. Chitosan could be wrapped in the network of BC during its biosynthesis (Figure.1). XRD results indicated that the highest degree of crystallinity occurred when the medium contained 2% chitosan. The nanocomposites formed cohesive gel structures in SEM images. The results demonstrated that *in-situ* BC/chitosan nanocomposites have great promise and potential for skin tissue repair and wound healing.

Figure.1 Images of *in-situ* BC/CS nanocomposites. A & B: BC/1% CS, BC/2% CS, BC/ 3% CS and BC (left to right). Scale bar=5 cm. SEM: BC/1% CS, BC/2% CS and BC/ 3% CS (left to right). Scale bar=1 μm.

References

478 - Development of polymeric prodrug of a Janus kinase (JAK) inhibitor for the improved treatment of particle-induced osteolysis associated with orthopaedic implant

Jianbo Wu¹, jianbo.wu@unmc.edu, Xin Wei¹, Zhenshan Jia¹, P. Edward Purdue², Ted R Mikuls¹, Kevin L Garvin¹, Steven R Goldring², Dong Wang¹. (1) Department of Pharmaceutical Sciences, University of Nebraska Medical Center, Omaha, NE 68198, United States, (2) Hospital for Special Surgery, New York, NY, United States

Wear particle-induced osteolysis is considered to be the major cause of aseptic implant loosening and clinical failure after total joint replacement. There is no FDA approved treatment for this devastating medical condition at present. Tofacitinib, a novel JAK inhibitor has already been proved by the FDA for adult patients with moderately to severely active RA who have had an inadequate response or intolerance to methotrexate. Recently, it was found that Tofacitinib could ameliorate wear particle-induced osteolysis when given orally in animal model. Its systemic side effects, however, may hamper the potential clinical translation of this novel therapy. To address this issue, Tofacitinib was conjugated to N-(2-hydroxypropyl) methacrylamide (HPMA) copolymer via a carbamate bond to form a macromolecular prodrug. We hypothesize that after endocytosis by inflammatory infiltrates at the lesion associated with wear particles, the prodrug will reside in the endosomal/lysosomal compartments, providing sustained-release of Tofacitinib as a drug depot. The free drug will then act in an autocrine/paracrine fashion to regulate the local inflammatory processes. The preliminary in vivo experiment showed that polymeric Tofacitinib prodrug could produce sustained inhibitory activity in the mouse calvarial osteolysis model, preventing wear particle induced osteolysis. This result suggests that the polymeric Tofacitinib prodrug we developed may have the potential to become a novel therapeutic intervention of peri-implant osteolysis and subsequent orthopaedic implant failure.
In situ transformation of injected polymeric biomaterials in vivo has become a desired feature for many clinical applications. For example, polymers are rendered sensitive to environmental conditions (e.g. temperature, light or pH changes), which can convert materials from one form to another (e.g. liquid to gel or solid) to allow easy transplantation and to provide better material-tissue contact. Aside from these material-therapeutics matrices, which can be injected locally to known disease sites, systemically injected smart materials that can be activated upon physiochemical changes at diseased sites can offer unique opportunities in the generation of new diagnostics and therapeutics. However strategies allowing in situ transformation of systemically administered materials at desired sites are scarce, due to the lack of suitable bioorthogonal chemistries that allow stimuli activation in deep tissues. We have developed a condensation reaction between 2-cyanobenzothiazole and 1,2-aminothiol (second-order rate constant of 9.19 M$^{-1}$ s$^{-1}$), which allow installation of stimuli activatable handles. Using this chemistry, we have designed a small molecule-based system that can be selectively activated by physiochemical changes (such as reducing conditions or overexpressed enzymes) at the target site to form water-soluble polymers (MW up to 40 kDa, as determined by MALS), which has the potential to be used in diagnostics and therapeutics. Dual-modality optical imaging, fluorescence and photoacoustics, revealed the formation of polymers in living animals.
Affinity-based controlled release is an innovative method used to sustain protein release from drug delivery vehicles. These systems are primarily used to deliver therapeutic protein growth factors to sites of injury to promote tissue regeneration, but may also be used in combination with cell delivery. Building upon previous work in the Shoichet lab [1], we have developed a new affinity-based controlled release technology capable of delivering two (2) or more therapeutic proteins at independent rates from an injectable hydrogel. The delivery vehicle is comprised of an injectable hydrogel scaffold, modified with the Src homology 3 domain (SH3), and two therapeutic proteins, epidermal growth factor (EGF) and basic fibroblast growth factor (FGF2), each modified with a unique SH3-binding peptide (Figure 1). A mathematical model was applied to gain further insight on the mechanisms controlling protein release from the affinity-based system. Protein release can be tuned by varying either the strength ($K_D$) of the affinity interaction or the ratio of protein to binding ligand in the system. This versatile system provides concomitant and tunable protein delivery at independent rates.

481 - Synthesis of sequence-controlled brominated PLA and its copolymers by protection/deprotection methods

Xianglin Yin, xy15@zips.uakron.edu, Abhishek Banerjee, Coleen Pugh. Department of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH 44304, United States

We previously copolymerized 2-bromo-3-hydroxypropionic acid (BrH) with glycolic acid (GA) and lactic acid (LA) by acid-catalyzed polyesterifications of the comonomer mixtures to produce a functional group on the backbone of poly(lactic acid-co-glycolic acid). However, the molecular weight of the copolymers were less than those of the PLA homopolymers, and the molecular weight of the copolymers decreased with increasing amounts of BrH and GA. This paper will compare the polymerizations of trimers of BrH and GA end-capped with LA units, to that of the corresponding 2:1 comonomer mixtures in order to study the comonomers' relative reactivities, as well as the properties of the resulting sequence-controlled vs. random copolymers. The LA-capped trimers were prepared in analogy to the protection/deprotection routes of Meyer, et al., although not exactly the same. As outlined in Scheme 1, the LA-capped trimers were polymerized at both room temperature using carbodiimide coupling, and at elevated temperature by acid-catalyzed polyesterification. We will also present the synthesis and polymerization of two brominated dimers (BrH-LA and LA-BrH).

Scheme 1. Synthesis of sequence-controlled brominated PLA.

References


482 - Reactive extrusion compatibilization of PLA with poly(ω-hydroxytetradecanoic) results in important improvements in PLA properties

Stephen M Spinella¹,²,³, sgaluf@gmail.com, Jiali Cai², Cédric Samuel³, Jianhui Zhu¹,², Youssef Habibi³, Jean-Marie Raquez³, Phillipe Dubois³, Richard A Gross¹. (1) Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180, United States, (2) Department of Materials Chemistry, NYU Polytechnic School of Engineering, Brooklyn, NY 11201, United States, (3) Service des Matériaux Polymères et Composites, University of Mons, Mons, Wallonie B-7000, Belgium

One potential way to overcome the poor toughness and low ductility of poly(lactic acid), PLA, is to blend it with more ductile components that may or may not be biobased and biodegradable. Our lab has developed a mild and efficient biotechnological route to convert fatty acids such as tetradecanoic acid to ω-hydroxytetradecanoic acid. This monomer is then chemically converted by conventional condensation polymerizations to prepare poly(ω-hydroxytetradecanoic acid) (PC14). This new-to-the-world bioplastic has an elongation at break of 700% and true tensile strength of 50 MPa resembling some properties of medium density polyethylene (PE).

In this presentation we describe a reactive processing method that results in compatibilized PLA/PC14 blends that offer attractive properties. Processing parameters such as residence time in the extruder, reaction temperature and screw speed were investigated, and it was found that a reaction time of 15 min, screw speed of 150 RPM, temperature of 200 °C in the presence of 200 ppm of Ti(OBu)₄ gave optimal results in terms of mechanical properties and control of depolymerization. With just 5% PC14 (95% PLA) the blend elongation at break relative to pure PLA increased from 3% to 150% with a small decrease in the tensile modulus (3200 MPa to 2900 MPa). Without catalyst, a typical morphology showed pullout which is typical of immiscible polymer blends. However, with the addition of catalyst, an increased compatibility between the two phases was achieved as shown in figure 1.

Figure 1: Morphology of PLA/PC14 Binary blend (a) without Ti(OBu)₄ and (b) with Ti(OBu)₄

Tuesday, August 12, 2014 06:00 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
Cellulose is one of the most abundant macromolecules on the planet found in plants, sea creatures and some species of bacteria. By using controlled acid hydrolysis it is possible to isolate highly crystalline rod like crystals or Cellulose Nanocrystals (CNs). They possess many desirable characteristics for nano-fillers such as being non-toxic, biodegradable, low density, and a highly reactive surface.

The most common method to make CNs uses either sulfuric acid or hydrochloric acid hydrolysis. Use of the latter results in CNs that when dried are irreversibly aggregated due to formation of a strong hydrogen bonding network. Surface modification of CNs can prevent this aggregation phenomenon upon drying.

Recently, a green one-step approach based on concurrent Fischer Esterification with an organic acid and acid hydrolysis occur resulting in functionalized ready-to-use CNs. This presentation reports the development of one-step methods to prepare CNs decorated with free carboxylic acid moieties by esterification with citric, malonic and malic acids as shown in figure 1. The concentration of hydrochloric acid in mixtures with the above organic acids was varied and optimal amounts of hydrochloric acid were determined. Residual unhydrolyzed cellulose was then subjected to further hydrolysis reactions to generate additional CNs to increase the yield. The modified CNs were characterized by FTIR, NMR, contact angle, SEM, and XRD.
484 - Novel family of biobased polysophorolipids used as scaffolds for tissue engineering

Yifeng Peng¹, yp415@nyu.edu, Dany Munoz Pinto², Mariah Hahn², Richard Gross³, grossr@rpi.edu. (1) CBE, NYU Polytechnic School of Engineering, Brooklyn, NY 11201, United States, (2) Department of Biomedical Engineering, Rensselaer Polytechnic Institute, Troy, 110 8th street 12180, United States, (3) Department of Chemistry and Biology, Rensselaer Polytechnic Institute, Troy, 110 8th street 12180, United States

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(2Ac)) 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(2Ac) into P(LSL(2Ac)) (\(M_n>100,000\), \(T_g \approx 61^\circ C\), \(T_m 123^\circ C\), semi-crystalline).

To extend our understanding of LSL(2Ac) ROMP polymerizations, studies were conducted using Grubbs 2nd (G2) and 3rd (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([M]₀/[M]ₜ) versus reaction time for G2 are linear, suggesting apparent first-order kinetic behavior. In G2 catalyzed LSL(2Ac) 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(2Ac) was regioselectively modified at its two primary -OH positions, including deacetylation to prepare P(LSL(OH,Ac)) and esterification with various vinyl esters (e.g. vinyl butyrate to prepare LSL(Bu,Ac)). Clickable groups including methacrylate and azide were also selectively introduced into LSL monomers. These monomers were successfully converted into new SL (co)polymers with tailored properties and potential to conjugate bioactive groups. P(LSL(2Ac)), P(LSL(OH,Ac)), P(LSL(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. In addition, measurement of level of RUNX2 and alkaline phosphatase suggested the osteogenesis was upregulated on the polysophorolipid substrates.
485 - Biobased anionic polymerizable surfactants from ω-hydroxyfatty acids

Jing Hu1, Zhennan Jin1, Tzu-Yin Chen1, Jennifer D Polley1, Michael F Cunningham2, Richard A Gross1, grossr@rpi.edu. (1) Department of Chemistry and Biology, Rensselaer Polytechnic Institute, Troy, New York 12180, United States, (2) Department of Chemical Engineering, Queen’s University, Kingston, Ontario K7L 3N6, Canada

Two biobased polymerizable surfactants ω-acryltetradecanoic acid (MA-1) and ω-maleate tetradecanoic acid (MA-2) were synthesized from ω-hydroxytetradecanoic acid, which was prepared via an efficient yeast catalyzed ω-hydroxylation reaction. MA-1 is a single polar-headed surfactant whereas MA-2 is a bolaamphiphile with carboxylic acid polar groups at both chain ends. The surface tension test of surfactant solutions and experimental determination of the reactivity ratios for surfactants with styrene were conducted. Emulsion polymerizations with varying amounts of MA-1 and MA-2 (1-10 wt% with respect to styrene) gave colloidally stable latexes with particle sizes ranging from 52 nm to 155 nm. 1H-NMR and potentiometric titration were used to measure MA-1 and MA-2 polymerization conversions, as well as how the surfactants were distributed on the particle surface. Observed differences were rationalized based on the comparative structures of MA-1 and MA-2 and their corresponding partitioning behavior.
486 - Improving thermoplastic polyurethane performance by building polyols from bio-derived w-hydroxyfatty acid units

Jianhui Zhu1,2, Pei Pei2, Jiali Cai2, Wenchun Xie2, Richard A Gross1, grossr@rpi.edu. (1) Department of Chemistry and Biology, Rensselaer Polytechnic Institute, Troy, NY 12180, United States, (2) Department of Chemical and Biological Engineering, NYU POLY, Brooklyn, New York 11201, United States

Thermoplastic polyurethanes (TPU) are a broad class of macromolecules composed of chemically dissimilar units commonly denoted as hard and soft segments. Due to the extensive diversification of possible chemical constituents, a rather wide variety of mechanical properties are accessible from these materials. In a recent report by our laboratory and collaborators, a biotechnological route to w-hydroxytetradecanoic acid (w-HOC14) was disclosed. An engineered strain of the diploid yeast Candida tropicalis was developed that produces commercially viable yields of w-OHC14. In this work, w-HOC14 was converted by a condensation polymerization catalyzed by titanium tetraisopropoxide (Ti[OiPr]4) to a series of polyester polyols with variable quantities of w-HOC14, 1,4-butanediol (BD) and adipic acid (AA) units. High hydroxyl end group fidelity was achieved allowing the successful synthesis of a series of thermoplastic polyurethanes (TPU) with $M_w$ values of about 100K. Two-series of TPU’s were prepared: i) with copolyester polyols having with varied contents of w-HOC14, BD and AA units and ii) varied ratios of BD-capped w-HOC14 and AA-BD polyols. Studies will be reported on the thermo-mechanical properties of the resulting polyols that present in different ways variable contents of w-HOC14 units. With increasing w-HOC14 content in the polyols of corresponding TPU’s, the tensile strength increased from 30 MPa to 470 MPa while the %-elongation decreased from 900 to 300%. Thus, by increasing the w-HOC14 content in TPU’s their mechanical properties shifted from elastomeric to semi-crystalline thermoplastics. In summary, benefits achieved by incorporating an w-hydroxylated fatty acid include: i) increasing the bio-content of TPUs, ii) at moderate w-HOC14 contents elastomeric TPU’s were obtained that have increased tensile strength and stress at break, iii) based on structure we anticipate that the introduction of w-hydroxylated fatty acid units in TPU’s will also increase the materials resistance to hydrolysis and microbial mediated erosion.
This work describes the synthesis, structure and physico-mechanical properties of a bio-based polyester PBF prepared from 1,4-butanediol and 2,5-furandicarboxylic acid. Melt-polycondensation experiments were conducted using titanium tetraisopropoxide (Ti[OiPr]4) as catalyst. M_w and polydispersity were determined by GPC. Studies of a series of PBF samples varying in molecular weight, %-elongation at break does not increase beyond 1000% observed at M_w = 38K, however, further increases in M_w led to higher values in Young's Modulus and stress at break. Work will be reported on how variation in the quench rate of molded PBF molded bars allows variation in PBF crystallinity and, correspondingly, changes in PBF tensile properties. Furthermore, the crystal structure of PBF will be discussed. Relative to PBT at similar crystallinity values, the mechanical properties of PBF are similar.
488 - Renewable polyester based on hydrophobic monomer derived from monoterpene

**Dakshinamoorthy Deivasagayam, dakshing80@gmail.com, Robert T Mathers. Department of Chemistry, Pennsylvania State University, New Kensington, New Kensington, Pennsylvania 15068, United States**

This report details the synthesis of renewable hydrophobic polyester by melt polymerization of diglycerol and a new bicyclic anhydride monomer based on α-phellandrene. This method satisfied a number of green chemistry principles.

![Reaction Scheme]

**Figure**: Melt polymerization of diglycerol and bicyclic anhydride with para-toluene sulfonic acid.

---

**Tuesday, August 12, 2014 06:00 PM**
**Green Polymer Chemistry: Biobased Materials and Biocatalysis (06:00 PM - 08:00 PM)**
**Location**: Moscone Center, West Bldg.
**Room**: Exhibit Hall
489 - Exploring green methods through a one-pot salicylic acid-based poly(anhydride-ester) synthesis

Jonathan J Faig, jfaig@eden.rutgers.edu, Kervin Smith, Kathryn E. Uhrich. Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States

Green chemistry aims to mitigate the environmental, health, and economic concerns associated with traditional chemical processes by increasing reaction efficiencies, reducing waste, using innocuous materials, and developing biodegradable products. Poly(anhydride-esters) (PAEs) are biodegradable surface-eroding polymers that represent such products, exhibiting a controlled, near-zero-order release of naturally occurring bioactives, including salicylic acid (SA) and ferulic acid (FA), which are used in biomedical and personal care applications. Currently, the synthesis of bioactive-based PAEs uses excessive solvents, hazardous purification chemicals, and multistep reactions, all of which can be improved upon using green chemistry principles. To improve upon this, SA- and FA-based PAE monomers were synthesized via a one-pot methodology that requires minimal purification and drastically reduces reaction time. For instance, SA-based PAEs were synthesized via solvent free methods by linking two SA moieties with an acyl chloride to form an SA diacid within minutes, which can be activated and subsequently polymerized under high vacuum and heat to form product. Products were then purified using nontoxic and environmentally safe solvents. Polymers and their precursors were then characterized to ensure the greener methodology did not have a detrimental influence on physiochemical and thermal properties. Similar methodologies were explored to synthesize and characterize FA-based PAEs. Through our green synthetic methods we hope to reduce PAEs' environmental impact and move towards a more economical and sustainable future.
490 - Preparation and characterization of nanoparticles from fatty acid modified polyesters

Muhammad Bilal, Muhammad Haris Samiullah, muhammad.samiullah@chemie.uni-halle.de, Joerg Kressler. Institute of Chemistry, Martin-Luther-University Halle-Wittenberg, Halle, Sachsen Anhalt 06120, Germany

By using materials from renewable resources such as glycerol and sugar alcohols (D-sorbitol, meso-erythritol and D-xylitol), biocompatible and biodegradable polyesters were enzymatically synthesized by using Candida Antarctica type B (CAL-B) lipase. Due to regioselectivity of lipase enzyme, these multiple hydroxyl containing structures along with divinyladipate, produce linear polyesters possessing unreacted hydroxyl groups on their backbone. These aliphatic functional polyesters were hydrophilic in nature but only poly(xylitol adipate) and poly(sorbitol adipate) were water soluble.

Modification of pendent hydroxyl groups with saturated and unsaturated fatty acids was carried out with different degree of substitution by using both bio and chemical catalysts. Poly(glycerol adipate) was enzymatically modified with oleic and linoleic acid however, poly(sorbitol adipate) was modified with stearoyl chain using chemical catalysis. Nanoparticles of these grafted polyesters were prepared by using interfacial deposition method. Dynamic light scattering measurements revealed nanoparticles with relatively narrow size distributions and with an average hydrodynamic radius of around 40 nm. All the synthesized products were characterized by NMR- and IR-spectroscopy and their thermal behavior was analyzed by DSC.
**491 - Chemo-enzymatic synthesis and characterization of polyester-urethanes bearing amino-acids moieties**

Karla A Barrera-Rivera¹, Angel Marcos-Fernández², **Antonio Martinez-Richa**¹, richa@ugto.mx. (1) Department of Chemistry, Universidad de Guanajuato, Guanajuato, GTO 36050, Mexico, (2) Departamento de Química y Tecnología de Elastómeros, Instituto de Ciencia y Tecnología de Polímeros (CSIC), Madrid 28006, Spain

Yarrowia lipolytica lipase (YLL) has demonstrated to be efficient in the synthesis of different biodegradable polyesters, obtained by ring-opening polymerization of cyclic esters. Using biocatalysis with immobilized YLL, oligomeric PCL diols can be efficiently produced using diethyleneglycol as initiator. Linear poly ester-urethanes were prepared from synthesized PCL diols, hexamethylenediisocianate (HDI) and L-lysine ethyl ester dihydrochloride, L-cysteine hydrochloride, L-histidine monohydrochloride monohydrate and L-ornitine hydrochloride

---

**Tuesday, August 12, 2014 06:00 PM**  
Green Polymer Chemistry: Biobased Materials and Biocatalysis (06:00 PM - 08:00 PM)  
**Location:** Moscone Center, West Bldg.  
**Room:** Exhibit Hall
492 - Ultra-fine soy protein hybrid fibers by aqueous electrospinning and genipin crosslinking

Xingchen Liu, xcliu@ucdavis.edu, You-Lo Hsieh. Fiber and Polymer Science, University of California, Davis, Davis, California 95616, United States

Soy protein is a valuable plant biopolymer resource for environmentally friendly materials and fibers because of its similarly high molecular weight as animal fibrous proteins such as silk and collagen and abundant availability as a by-product of biodiesel. This study explored the denaturation and aqueous dispersion of soy protein isolate (SPI) for improved fiber spinnability. Heat denaturation (90 °C, 45 min) of aqueous SPI under basic condition (pH 12) enabled extended electrospinning (1.5 mL/h, 5 hr) of SPI mixture with as little as a quarter by mass of poly vinyl alcohol (PVA, 124-186 kDa) into ca. 200 nm wide fibers. The electrospun SPI/PVA hybrid fibers could be rendered insoluble in water and more thermally stable by reacting with a natural crosslinker genipin (11 mM in 1:1 ethanol/water, pH 7, 5 hr). These biocompatibly crosslinked soy protein hybrid fibers may find use for controlled release of chemicals and as scaffold.
A covalently crosslinked hydrogel was prepared by radical co-polymerization of vinyl-functionalized soy protein (SP) macromer and acrylic acid (AA) in aqueous media. After drying, the gel absorbs 100–500 times distilled water of its own weight, and is categorized as a superabsorbent polymer (SAP). The SP macromer was prepared using an unsaturated anhydride, methacrylic anhydride (MAh), via the reaction between the anhydride functionality and the amino groups in protein. Prior to turning into macromer, the SP was hydrolyzed under alkaline condition to various degrees. The present method for the preparation of bio-based SAPs is much more efficient, controllable and produces hydrogels with much higher mechanical properties as compared to the conventional grafting method. Several factors including the degree of hydrolysis (DH) of SP, degree of substitution (DS) of amino groups in SP, initiator amount etc., were systematically investigated. The structure-property relationship of the hydrogel was established.
494 - Ligand effects on metal catalysts for copolymerization of epoxides and CO₂

Masato Mizutani, mm2445@cornell.edu, Geoffrey W Coates. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, United States

CO₂ is an ideal synthetic C₁ feedstock because it is abundant, safe, nonflammable, and inexpensive. A topic of current interest is the development of catalysts for the organic synthesis from CO₂. One growing area in CO₂ chemistry is the development of transition metal catalysts for the alternating copolymerization of CO₂ with epoxides to form aliphatic polycarbonates. In this work, we report highly active derivatives of metal catalysts for the copolymerization of epoxide/CO₂ at low CO₂ pressure and at ambient temperature. We varied systematically the substituents on the ligand in the metal catalysts to optimize catalyst activity and selectivity for formation of alternating copolymer.
Wood cellulose cannot be easily dissolved in water or any common organic solvent, which largely limits its applications. In this work, spruce cellulose was hydrolyzed by diluted sulfuric acid of various concentrations and hydrolysis times. The dissolution of these partially degraded samples was investigated in a NaOH/urea aqueous solution system considered environmentally "green". The effects of acid hydrolysis on the structure and properties of subsequent thermally induced gels were examined using scanning electron microscopy, swelling and re-swelling experiments, and mechanical testing. The molecular weight of spruce cellulose was significantly reduced by acid hydrolysis, whereas its crystallinity slightly increased. All samples could be partially dissolved in the NaOH/urea aqueous solution and formed stable suspensions. Hydrolyzed cellulose samples with lower molecular weight exhibited a higher solubility. Rheological experiments showed these cellulose suspensions could form gels easily upon heating. A porous network structure was observed in which dissolved cellulose was physically crosslinked upon heating and then regenerated to form a three-dimensional network, where the dispersed swollen cellulose fibers filled spaces to reinforce the structure.

The swelling behavior and mechanical properties of these ‘matrix-filler’ gels could be controlled by varying the mild acid hydrolysis conditions, which adjusts their degree of solubility. This research provides several opportunities for manufacturing wood cellulose based materials.
496 - Electrospun biomimetic synthetic polymer for templated ceramic condensation

Garrett M. Kraft¹, garrett.kraft@uconn.edu, Ashley Santiago², Chetan C. Hire¹, Douglas H. Adamson¹,². (1) Polymer Program, Institute of Material Science, University of Connecticut, Storrs, CT 06269, United States, (2) Department of Chemistry, University of Connecticut, Storrs, CT 06269, United States

In biological systems there are many examples of organic macromolecules templating inorganic structures. By necessity the inorganic structures are formed under mild conditions, in stark contrast with sol-gel and sintering processes currently in use. Previous work in our group developed a polymer modeled after the enzyme Silicatein a that has been shown to template and catalyze the formation of silica spicules in marine sponges. By mimicking this enzyme, ceramic coatings can be made with precise control and in an environmentally friendly way. Herein we report the formation of ceramics from the condensation of metal alkoxides onto an electrospun mat of poly(hydroxylated isoprene-b-2-vinylpyridine) under mild conditions. The use of electrospinning techniques with ceramic condensation allows for the straightforward synthesis of novel porous functional materials with high surface area, ideal for applications in catalysis and membrane separation.

Figure 1: (Left) Electrospun poly(hydroxylated isoprene-b-2-vinylpyridine) fibers. (Right) Electrospun fibers with condensed TiO₂.
497 - Effect of temperature on the gelation and structural characteristics of silk sericin

Yoon Nam Jo, timidyn@naver.com, In Chul Um. Department of Bio-fibers and Materials Science, Kyungpook National University, Daegu, Daegu 702701, Republic of Korea

Silk is bio-based material consisting of fibroin and sericin. Recently, silk sericin is reported to have various function including biocompatibility, high water retention, gelation and wound healing properties as a biomaterial. In this study, silk sericin gel and film are fabricated at various storage temperatures. Effect of temperature on the gelation behavior of silk sericin solution and structural characteristics of sericin film was examined. As the storage temperature for sericin solution was increased, the gelation of sericin was retarded and the strength of resultant gel was decreased. The rheological properties and structural characteristics of sericin did not change depending on the cycle number of cooling and heating. β-sheet crystallization of sericin film occurred less resulting in a decrease of crystallinity index by increasing the drying temperature.

![Graph showing gelation behavior of silk sericin solution at different storage temperatures.](image)

Figure 1. Gelation behavior of silk sericin solution at different storage temperatures.
Effect of silkworm variety on the electro-spinning of silk fibroin

Bo Kyung Park, qhrid1004@naver.com, In Chul Um. Department of Bio-fibers and Materials Science, Kyungpook National University, Daegu, Daegu 702701, Republic of Korea

Electro-spun silk fibroin (SF) has attracted researcher's attentions due to its good cyto-compatibility and excellent performance as a tissue engineering scaffold. Although it was reported silkworm variety affected molecular weight (MW) and solution viscosity of silk fibroin, the effect of silkworm variety on the electro-spinning performance of silk fibroin has not been studied, yet. In the present study, the regenerated SF with five different silkworm varieties was used in electro-spinning and the effect of silkworm variety on the electro-spinning of silk fibroin performance was examined. It was turned out that silkworm variety strongly influenced electro-spinning rate and diameter of electro-spun fiber. Geumgwangju and Wonwon126 showed the highest and the lowest electro-spinning rate and fiber diameter. β-sheet crystallization of electro-spun SF fibers took place partially and silkworm variety almost did not effect crystallization of SF.
Silk is naturally occurring material consisting of two polymers: fibroin and sericin. Regenerated silk film has attracted the researcher's attentions because of its good biocompatibility and excellent cyto-compatibility. Although sericin has been removed from silk to produce regenerated silk film, recently it was reported residual sericin in silk can improve crystallinity, mechanical properties, electro-spinning performance of regenerated silk, etc. In this study, the effect of residual sericin content on structural characteristics and mechanical properties of regenerated silk film were examined. FTIR results showed that the crystallinity index was increased with increasing sericin contents to 0.6% and after that, the crystallinity index was decreased. Also, the breaking strength of regenerated silk film showed similar trend to that of crystallinity index indicating proper amount of sericin can increase breaking strength of regenerated silk film.

Figure 1. Tensile strength of regenerated silk film with different residual sericin contents.
500 - Mechanical properties and structural characteristics of wet spun silk fibroin fiber with different silkworm varieties

Mi Jin Jang, mngu1004@naver.com, In Chul Um. Department of Bio-fibers and Materials Science, Kyungpook National University, Daegu, Daegu 702701, Republic of Korea

Regenerated silk fiber, one of bio-based fiber, has attracted researcher’s attention because of its good blood compatibility, excellent cell attachment and minimal inflammatory reaction in the body. Recently, it was reported that silk fibroin obtained from different bombyx mori silkworm varieties showed different molecular weight (MW) and rheological properties. In this study, regenerated silk fibroin filaments were fabricated by using wet spinning, and the molecular conformation and mechanical properties of wet spun silk fibroin fiber from different silkworm varieties were examined. Post drawing performance, molecular conformation and mechanical properties of the wet spun silk fibroin fiber were not affected significantly by silkworm variety, although the dope solution viscosity of silk fibroin and mechanical properties of regenerated silk fibroin film depended on silkworm varieties.
501 - WITHDRAWN
Vegetable oils are sustainable and environmentally benign sources. More and more chemicals and polymeric materials are developed from vegetable oil. Here we report polyacids derived from corn oil. First, epoxidized corn oil (ECO) was polymerized by ring-opening polymerization in the presence of boron trifluoride diethyl etherate as catalyst. The effect of catalyst concentration, from 1 mol% to 4 mol%, was studied. Soluble fraction and thermal analysis shows with 2 mol %, the product has the highest crosslink density. Second, by hydrolysis, polymerized ECO was converted to a polyacid with acid value of 158 g KOH/g. The epoxy resin cured with this polyacid has T_g in the range of 12-19 °C, and exhibits good thermal stability, the temperature of 5 % weight loss up to 334 °C.
Currently there is a strong trend establishing materials from renewable resources to traditional polymer systems. Lignin obtained as a by-product in the paper making process has been used in past decades as a source of energy. Only 2% of the obtained lignin is up to now used as a chemical commodity.\[1\] With the aim to widen up the scope using lignin as potential candidate for an additive in epoxy curing, we used efficient Mannich-reaction route to obtain highly substituted amino-functionalized Kraft Lignin (KL) based on the synthetic protocol described by Yue et al.\[2\] Modification and up-scaling enabled us to synthesize amino-functionalized lignin in kilogram-scale. Introducing amino-groups at lignin moieties permits the possibility to incorporate the amino-functionalized KL in epoxy resin by taking advantage of the ability of the amino-function to crosslink with the epoxy groups. This opens up the possibility to reduce the amount of hardener or using amino-functionalized KL as an additional crosslinking-agent as demonstrated in figure 1.\[3\]

Thermal characterization shows that the curing kinetics of amino-functionalized KL differs from non-functionalized lignin.\[4\]

Different types of lignin were tested and compared to amino-functionalized lignin. The modification of lignin with amino-functions opens up several possibilities to introduce a former waste material to epoxy-based applications like composite materials and structural adhesives.

504 - Synthesis of monomers from biomass

Gaoyuan Ma, Gaoyuan.Ma@ndsu.edu, Ramkumar Moorthy, Mukund P Sibi. Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, United States

Currently, fossil fuels such as oil, coal and natural gas represent the prime energy sources in the world. However, it is anticipated that these sources of energy will be depleted within the next 40–50 years. Monomers and other chemical intermediates are typically obtained from non-renewable resources, specifically fossil fuels. Renewable resources, such as plant-derived biomass, may become a significant source of these critical materials. Benzene, toluene, xylenes and phenolics from biomass are potential precursors for valuable monomer synthesis. We will present efficient methods for the synthesis of diacids as well as diols from biomass.
A novel diblock copolymer consisting of poly(vinylferrocene) (PVFc) and poly(\(N, N\)-diethylacrylamide) (PDEA) is synthesized via a combination of anionic and RAFT polymerization.

The utilization of a novel route to hydroxyl-end-functionalized metallopolymers in anionic polymerization and subsequent esterification with a RAFT agent leads to a PVFc macro-CTA (\(M_n = 3800 \text{ g mol}^{-1}; \ D = 1.17\)). RAFT polymerization with DEA affords block copolymers as evidenced by \(^1\text{H} \text{NMR spectroscopy as well as size exclusion chromatography (6400} \leq M_n \leq 33700 \text{ g}\) mol\(^{-1}\); 1.31 \leq D \leq 1.28\)). Self-assembly of the amphiphilic block copolymers in aqueous solution leads to micelles as shown via TEM. Importantly, the distinct thermo-responsive and redox-responsive character of the blocks is probed via dynamic light scattering and found to be individually and repeatedly addressable.
506 - Supramolecular polymerization promoted and controlled through self-sorting

Zehuan Huang, huangzh13@mails.tsinghua.edu.cn, Liulin Yang, Yiliu Liu, Oren A. Scherman, Zhiqiang Wang, Xi Zhang.
Department of Chemistry, Tsinghua University, Beijing, Beijing 100084, China

In this poster, a new method of supramolecular polymerization promoted and controlled through self-sorting is reported. The bifunctional monomer containing p-phenylene and naphthalene moieties is prepared. Supramolecular polymerization is promoted by selective recognition between the p-phenylene group with cucurbit[7]uril (CB[7]) and 2:1 complexation of the naphthalene groups with cucurbit[8]uril (CB[8]), and can be controlled by tuning the content of CB[7]. Additionally, Asymmetric Flow Field Flow Fractionation is firstly introduced to characterize the supramolecular polymers to obtain specific information about molecular weight and polydispersity. This research will enrich the field of supramolecular polymers with important advances towards the realization of molecular weight and structural control.

Tuesday, August 12, 2014 06:00 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
507 - Incorporating photosensitive organometallics into non-linear polymers using an asymmetric dimer

**Justin T Barry**, jbarry2@uoregon.edu, David R Tyler. Department of Chemistry, University of Oregon, Eugene, Oregon 97403, United States

Kinetic investigations of light degradation can be effectively conducted on photochemically reactive polymers. By varying the location of photoactive sites or the frequency of their occurrence within a polymer, insight into structural effects on polymer degradation can be determined. The photoactive molybdenum dimer $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}_2(\text{CO})_6$ is an ideal candidate for a photoactive site as it contains a well characterized Mo-Mo bond that homolyzes under visible light. The two molybdenum radicals produced can subsequently be trapped with halides. The degradation of the molybdenum dimer can be followed by the carbonyl stretches using IR spectroscopy. Although having one degradation pathway simplifies analysis, the molybdenum dimer functionalization is difficult when producing non-linear polymers. This is because non-linear polymers require an asymmetric dimer to act as a building block in their synthesis. Manipulations with protecting groups as well as different synthetic schemes have allowed for the construction of non-linear polymers containing photosensitive bonds.
Nanocomposite materials consisting of polyaniline (PANI) and WS$_2$ were synthesized. The WS$_2$ was prepared by reacting tungstic acid with thiourea at 500°C under nitrogen flow. Our research showed that WS$_2$ can be used as a filler to improve the activation energy of decomposition of PANI. By using the Ozawa method, we have studied the decomposition kinetics for the nanocomposites, as well as for the pure polymer. The activation energy for the decomposition of pure PANI was found to be 131 kJ/mol. Increasing the amount of WS$_2$ to 20% in the PANI did not change the activation energy of decomposition. However, the activation energy of the decomposition increased to 153 kJ/mol when WS$_2$ was present at 64% by weight, an enhancement of 22 kJ/mol over the pure polymer. Furthermore, an improvement in the electronic conductivity of PANI was observed through the incorporation WS$_2$. For instance, the electronic conductivity of PANI-WS$_2$ at 20% by weight was 9 S/cm, a three-fold increase when compared to pure PANI. Powder X-ray diffraction (XRD) and electron paramagnetic resonance (EPR) provided evidence that the nanocomposites are exfoliated (Figure 1). The diffractograms of the nanocomposites were completely amorphous, suggesting lack of structural order in these materials, while their EPR signals were considerably narrower compared to pure PANI, indicating the formation of genuine exfoliated systems.
509 - Coordination polymer of perylene bisimide directed by metal-halogen interactions

Mei-Jin Lin¹, Krzysztof Radacki², David Schmidt¹, david.schmidt@uni-wuerzburg.de, Frank Wuerthner¹. (1) Institute of Organic Chemistry, University of Wuerzburg, Wuerzburg, Bavaria 97074, Germany, (2) Institute of Inorganic Chemistry, University of Wuerzburg, Wuerzburg, Bavaria 97074, Germany

The field of coordination polymers containing cationic metal centers connected by organic linkers has grown tremendously during the last decade and encompasses metallosupramolecular architectures with different dimensionalities such as one-dimensional polymers, two-dimensional sheets and three-dimensional solid state materials (also called metal-organic frameworks, MOFs). Depending on the choice of the metal ion and/or the organic ligands such coordination polymers are useful materials in a variety of applications such as gas storage, catalysis, electrochromism, luminescence or electrical conductivity. Remarkably, for one of the most outstanding multifunctional organic molecules, perylene bisimide (PBI), only few coordination polymers are known to date that are all of polydisperse nature and accordingly none of them could be characterized by single crystal X-ray analysis.

In this contribution we report on the metallosupramolecular self-assembly of an almost planar bay-substituted perylene bisimide dye bearing two divergent pyridyl coordinating sites with the soft Lewis acid HgCl₂. The resulting one-dimensional coordination polymer features an interesting packing in the solid state that is characterized by weak intermolecular Hg···Cl interactions along the metallosupramolecular chain and slipped p-p-stacking arrangement with J-type excitonic coupling among the dyes.
Electroplastic elastomer hydrogels (EPEHs) are a class of materials whose mechanical properties can be switched reversibly between hard and soft states with the application of an electric potential. Previously, we reported on our first-generation EPEH which utilized the Fe(II)/Fe(III) redox couple to reversibly tune mechanical properties by electrochemically switching iron oxidation states between the strongly-crosslinking Fe(III) and weakly-crosslinking Fe(II). In an effort to better understand the crosslinking mechanism and conversion between hard and soft states, quantitative analysis of iron and carboxylate content was performed. Mechanical properties measurements of the EPEHs as a function of the Fe(II)/Fe(III) ratio were determined. Magnetic susceptibility measurements were consistent with the formation of iron clusters within the hydrogel. Potentiometric titrations provided additional information about iron coordination. Incorporation of graphene oxide (GO) as a filler enhanced the mechanical properties of the material and decreased the conversion time between hard and soft states.
Modification of surfaces by means of polymer brushes has become an active area of research during the past few years due to numerous potential applications of such systems in nano- and biotechnology. Polymer brushes can be used as 3D matrices for immobilization of nanoparticles. In this study, responsive brushes are used as a matrix for the attachment of negatively charged, citrate-coated gold nanoparticles (AuNPs). This hybrid system exhibits intriguing optical properties due to the surface plasmon resonance of the AuNPs. Two different kinds of brushes are employed: (1) neutral polymer poly-(N-isopropylacrylamide) (PNIPAM) which shows an LCST in water at 30°C and (2) poly-(N,N-(dimethylaminoethyl)methacrylate) (PDMAEMA), a weak polyelectrolyte with an LCST in water at 55°C. Experiments are reported in which brush/particle hybrids (15 nm diameter AuNPs) were prepared by attaching the particles at room temperature where the brush is swollen. Neutron reflectivity (NR) was used to study the structure of the pure brushes and brush/particle hybrids and to monitor changes in particle distribution upon increasing the temperature above the respective LCST of the brush. Additionally, experiments were carried out in which brush/particle hybrids were fabricated by impregnating the brushes with AuNPs (4 and 18 nm diameter) at temperatures below and above the LCST. The particle uptake at these different temperatures was studied using UV/VIS spectroscopy.
Macrocyclic arrays which are composed of highly organized chromophores play a unique role in chemistry and biology. One of the most exceptional examples in this regard is given by the light-harvesting system of the purple bacteria, in which numerous chlorophyll and bacteriochlorophyll chromophores are arranged in macrocyclic assemblies by non-covalent interactions. As a consequence of the intriguing functional properties of those dye arrays the interest in the development of artificial counterparts has grown tremendously.

Here we present the synthesis of a series of covalent bonded perylene bisimide (PBI) macrocycles with ring sizes of two up to nine PBI dyes which exhibit a well-defined electronic coupling among the dye molecules due to the rigidity of the cyclic systems. These supramolecular macrocycles were self-assembled on a highly ordered pyrolytic graphite surface in a two-dimensional manner which could be confirmed by atomic force microscopy. Furthermore these compounds were used to investigate host-guest phenomena by encapsulating fullerene and perylene.
513 - CNT loaded mediator gels for enzymatic biofuel cells

Samar Kazan, samar.kazan@imtek.uni-freiburg.de, Oswald Prucker, Jürgen Rühe. Department of Microsystem Engineering, University of Freiburg, Freiburg, Baden Württemberg 79110, Germany

Enzymatic biofuel cells have emerged as an interesting candidate as power source for implantable biomedical applications (Figure 1-a). A key step for the function of such cells is the electron transfer, from the active site of the enzyme to the electrode surface, which in our case is aided by a mediator for shuttling the electrons. The mediator gel we use is a copolymer consisting of N,N-dimethyl acrylamide (DMAA) with hydrophilic backbone, methacryloyloxy benzophenone (MABP) as crosslinking agent and a ferrocene based electron transfer agent. This gel immobilizes the enzyme within the redox polymer network by a mixture of covalent links and entrapment within the hydrogel. The redox hydrogel swells in water and is capable of charge transport. One of the main challenges for enzymatic biofuel cell systems is to increase the output power. Integration of multi-walled carbon nanotubes (MWCNT) into the mediator gel enhances the conductivity of the gel, increases the surface area of the electrode and fastens the electron transfer rate of the redox reaction. This results in 12 times faster diffusion of charges to the electrode surface and thus a higher output current. The presence of CNTs also improves the stability of the enzyme and allows for higher loading of the enzyme in the film, again leading to an enhanced output current up to a factor of 20 compared to a non-modified mediator gel (Figure 1-b).

![Figure 1: (a) A schematic drawing of an enzymatic biofuel cell (EBFC). The enzyme [] at the anode are immobilized with the MWCNT-modified mediator gel p(DMAA-MABP-Ferrocene). The chemical structure of the mediator gel is shown in the left of the EBFC. Part (b) shows the electrochemical response at the anode for the MWCNT-modified p(DMAA-MABP-Ferrocene) electrodes of the EBFC. The output current at a certain voltage range for different electrode coatings is shown: no glucose oxidase (black), 25% (dark blue), 60% (orange), and 75% (blue). Measured at 10 mM/s, 1000 rpm RDE in 5 a mM glucose, pH 7.4 buffer solution, nitrogen atmosphere, 37°C.](image)
Polyoxometalates (POMs) as "soluble molecular metal oxides" feature a remarkable stability and, even more interesting, a distinct redox behavior. Therefore, such clusters are highly suitable for an implementation into photophysical or electrochemical systems. Their appropriate chemical modification enables the preparation of inorganic-organic hybrids combining the properties of both subunits: The ability of POMs to serve as an electron reservoir and the opto-electronic behavior of the attached organic/organometallic part. The covalent (or electrostatic) binding of opto-electronically active transition metal complexes, based on metal centers such as Ru(II) or Ir(III), to a POM might allow photo-induced electron-transfer (PET) processes.

Various strategies to covalently combine POM units with terpyridine-containing organic ligands (as well as their transition metal complexes) have been employed. The hybrid ligands have been fully characterized and investigated with respect to their electrochemical properties. First examples for dyads comprising a terpyridine complex, as donor part, and a POM unit, as acceptor, have also been obtained.
Fabrication of vesicles made from synthetic phospholipids and block copolymers has been attracting much attention for potential applications in microreactors, drug delivery systems, and as a model system for living organisms. Although a large variety of synthetic vesicles were created, it is still a major challenge to mimic dynamic behaviors which appear in living vesicles such as a nuclear envelope and synaptic vesicles. Herein, we demonstrated a totally synthetic vesicle which can afford to show periodic structure oscillations by incorporating transition metal complex (Ru(bpy)$_3$) catalyzing an oscillatory chemical reaction (Belousov-Zhabotinsky (BZ) reaction) into a thermo-responsive diblock copolymer. Self-regulated formation and fragmentation cycles of the artificial vesicles are investigated in terms of time-resolved dynamic light scattering measurements as well as direct observations of oscillating behavior by using an optical microscope.
516 - Synthesis and characterization of 1D coordination polymer of tin and 4-aminothiophenol

Eon S Burkett, eburkett@my.tnstate.edu, Tasneem A Siddiquee. Chemistry, Tennessee State University, Nashville, TN 37209, United States

Tin and its compounds have found uses in many different branches of chemistry: catalysis, redox chemistry and medicinal chemistry to name a few. Coordination polymers of tin and sulfur containing ligands are known. One such ligand is 4-aminothiophenol (4-ATP). The reported compound is a three dimensional polymer with tin at oxidation state +4 from a non aqueous medium. Here we report the synthesis and characterization of a one dimensional coordination polymer with tin at oxidation state +2. Unlike the previous reports this compound was synthesized from aqueous medium. Structural characterization was achieved by single crystal X-ray diffraction studies.
517 - Molecular metallohydrogels based on Cu pincer complexes

Weiwei Fang, Tao Tu, taotu@fudan.edu.cn. Department of Chemistry, Fudan University, Shanghai, China

Based on visual discrimination of 2,2'-bipyridine out of its positional isomers via selective thixotropic metallo-hydrogel collapsing, a novel photo-switchable two-component metallo-hydrogel system was fabricated with pincer type Cu(II) complex 1 and photo-responsive 2,2'-azopyridine.

In assistance with SEM, HR-MS, UV and crystal analysis, the mechanism of gel collapse by addition of 1,10-phenanthroline, 2,2'-bipyridine and cis-azopyridine was explained, which not only further demonstrated that π-stacking and metal-metal interaction between molecular 1 are responsible for the gel formation, but also indicated the molecular assembly blocking strategy is a good approach to fabricate a new platform for visual discrimination and photo-responsive soft materials.
Metal containing polymers are materials of high interest because they combine the unique properties of organic polymer scaffolds with the magnetic or redox properties of metallic materials. Incorporation of ferrocene groups into a polymer material introduces an efficient electron-transfer relay system, which can be hardly realized with a fully organic material. However, the synthesis of such compounds still presents challenges, if narrow molecular weight distributions, complete functionalization and high stability of the resulting products are targeted.

We present an approach for the synthesis of block copolymer architectures containing poly(vinylferrocene) (PVFc) via an epoxide termination strategy. PVFc can be synthesized via living carbanionic polymerization, and quantitative functionalization is possible using epoxides as termination reagents. The resulting hydroxyl-functionalized macroinitiators are suitable for several subsequent polymerization methods. We were able to synthesize AB block copolymers and AB₂ miktoarm star polymers containing PVFc (A) and either poly(lactide) (PLA) (via catalytic ring opening polymerization) or poly(ethylene glycol) PEG (via oxyanionic ring opening polymerization) as a second block (B). A series of polymers with molecular weights in the range of 8,000 to 42,000 g mol⁻¹ and narrow size distributions (PDI = 1.21 – 1.36) were obtained. Additionally, we studied the self-assembly behavior of the obtained polymers in solution with transmission electron microscopy (TEM), dynamic light scattering (DLS) measurements and their redox activity via cyclovoltammetry (CV).
Developing materials that can catalytically decontaminate chemical warfare agents (CWAs) under ambient conditions continues to be a significant goal in the scientific community. Due to its relatively slow rates of degradation in the environment, sulfur mustard (HD) remains a challenge to decontaminate under such conditions. We report a hybrid organic/inorganic nanomaterial based on organically-functionalized hexavanadate (V6) building blocks linked by 1,3,5-benzenetricarboxamide, $N,N',N''$-tris[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]- (9CI) molecules in a polymer-like network, capable of catalyzing the aerobic oxidation of sulfides and exhibiting gelating properties in polar aprotic solvents. The gel swells instantaneously in polar aprotic solvents as well as the HD analog 2-chloroethyl ethyl sulfide (CEES), demonstrating sequestration ability of the gel network for CWA agents. Reoxidation of the V6 units by ambient O2 is the rate-limiting step in the catalytic cycle, and thus oxidation of CWA substrates is accompanied by a change in color from red to green as the V(V) centers are reduced, offering a method for detection of CWAs during the degradation process in addition to the sequestration and decontamination abilities. We thank the ARO (grant W911NF-12-1-0136) for support.
520 - Designing cyclometalated ruthenium(II) complexes for anodic electropolymerization

Benjamin Schulze\textsuperscript{1,2}, benjamin.schulze@uni-jena.de, Christian Friebe\textsuperscript{1,2}, Michael Jaeger\textsuperscript{1,2}, Ulrich S. Schubert\textsuperscript{1,2}. (1) Laboratory of Organic and Macromolecular Chemistry, Friedrich Schiller University Jena, Jena, Germany, (2) Jena Center for Soft Matter, Friedrich Schiller University Jena, Jena, Germany

The anodic electropolymerization of thiophene-functionalized cyclometalated ruthenium(II) complexes is shown for the first time. It is demonstrated that the electron-rich complexes tolerate the highly positive potentials that are required for the thiophene oxidation if electron-withdrawing groups are installed at the cyclometalating phenyl ring. Thus, conductive polymer films featuring a broad UV−vis absorption as well as reversible redox-switchability can be prepared. The employed cyclometalated ruthenium(II) complexes are promising candidates for future photovoltaic applications based on photo-redox-active films.

Tuesday, August 12, 2014 06:00 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
Metal-organic supramolecular systems have been extensively studied for their numerous fields of application, from catalysis to sensors, to luminescent and magnetic materials.

Our work focuses on metallacrowns (MCs), a family of metallomacrocycles analog of crown ethers, that exhibit widely variable topologies and high stability in solution, and that can be used as supramolecular synths. Few examples in literature report the use of MCs as building blocks for supramolecular networks in the solid state.\textsuperscript{1,2}

The aim of our work is to control MCs assembly through optimization of the supramolecular interactions occurring between MC scaffolds. A few hydroxamic acids ligands have been designed to allow MCs to interact with specific simple connecting units. Great attention has been directed to finding connecting units that could limit the formation of undesired interactions and thus of alternative crystalline packing.

In order to enhance the control over tridimensional arrangement of the metallacycles over structural variability, the main challenge lies in optimizing both axial and equatorial interactions with respect of the MC scaffold, since both interactions would be fundamental for ultimately exploiting MC as MOF building blocks.

\textsuperscript{1} C. McDonald \textit{et al.}, \textit{CrystEngComm}. (2013) 15, 6672

522 - Energy transfer and oxygen sensing range modulation in luminescent boron \( \beta \)-diketonate-PLA hybrid nanoparticles

**Jelena Samonina-Kosicka**\(^1\), jskosicka@virginia.edu, Cassandra L. Fraser\(^{1,2}\). (1) Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States, (2) Department of Biomedical Engineering, University of Virginia, Charlottesville, VA 22904, United States

Fluorescence imaging is a powerful tool for understanding fundamental processes in cellular biology. Materials used in imaging range from small organic molecules to proteins and nanoparticles (NPs). Polymeric nanoparticles with embedded dyes benefit from easy fabrication, high biocompatibility and design versatility. Light-emitting dyes integrated into the scaffolds by covalent attachment help to prevent dye leaching. A dual emissive iodide-substituted difluoroboron \( \beta \)-diketonate dye with covalently attached poly(lactic acid) (PLA), BF\(_2\)b(I)bmPLA, has been being used for tumor hypoxia imaging. Both fluorescence (\( \lambda_F = 425 \) nm) and phosphorescence (\( \lambda_P = 525 \) nm) were exploited in ratiometric imaging. Recently a more redshifted naphthyl-substituted material, BF\(_2\)n(Br)bmPLA, was prepared. Emission wavelengths (\( \lambda_F = 480 \) nm, \( \lambda_P = 565 \) nm) are well aligned with the blue and green channels of a CCD camera for inexpensive and convenient imaging. By combining these two dyes via co-precipitation (i.e. one solution containing both polymers), energy transfer to and emission from the redshifted naphthyl dye is observed and the intensity of naphthyl dye phosphorescence relative to fluorescence increases. Though the dynamic range for oxygen sensing is only 0-3% for NPs made from BF\(_2\)n(Br)bmPLA alone, when NPs were formed from the co-precipitation of BF\(_2\)n(Br)bmPLA and BF\(_2\)b(I)bmPLA, a 0-21% (i.e. air; ambient) oxygen range was observed. On the other hand, when these two dye-polymers are nanoprecipitated sequentially, one after another from separate solutions, core-shell materials may result. There is no evidence of energy transfer in this case. Instead, the observed optical properties are additive. The luminescence and oxygen sensing properties of the respective boron NPs and their admixtures fabricated in these different ways will be discussed.
523 - Synthesis of polyisobutylene-attached metallophthalocyanines as homogeneous catalysts in reduction and oxidation reactions

Chih-Gang Chao, chih-gang.chao@chem.tamu.edu, David E Bergbreiter. Department of Chemistry, Texas A&M University, College Station, TX 77840, United States

Phase selective polymer-supported catalysis has been extensively studied by our group in recent years with schemes that enable facile separation of the catalyst, simplify purification of products, and allow for recycling of the catalyst after a reaction. Our group has reported a number of examples of functionalized polyisobutynes (PIBs) that can be utilized in various catalytic applications and shown that PIB serves as a heptane selectively soluble phase anchor. This talk will show how introducing polyisobutylene onto metallophthalocyanines can greatly increase the solubility of metallophthalocyanines in non- and modestly polar solvents producing potential homogeneous Lewis acid, oxidation, and reduction catalysts that are soluble at concentrations of 20 wt%. Using such functional MPCs either in heptane or in a mixed solvent systems allows for recycling of these catalysts. In the work discussed in this talk, two new polyisobutylene-supported metallophthalocyanines were prepared. PIB-bound MPC incorporating Co(II) and Fe(II) were both studied as catalysts. Reduction of nitrobenzene by hydrazine in the presence of the PIB-bound Co(II) phthalocyanine and aerobic oxidation of hydrazinecarboxylate derivatives catalyzed by PIB-bound Fe(II) phthalocyanine will be discussed.
524 - Supramolecular assemblies of block copolymer and small molecules using solvent evaporation method

Eunhye Kim¹, eunhye2001035@nate.com, Tae-Hwan Kim¹, Young-Soo Han¹, Du Yeol Ryu². (¹) neutron science division, Korean Atomic Energy Research Institute, Daejeon, Republic of Korea, (²) department of chemical and biomolecular engineering, Yonsei University, seoul, Republic of Korea

Block copolymer self-assembly in thin films is currently of great interest as a bottom-up approach for generating templates and scaffolds with well-defined periodic nanostructures of spherical, cylindrical, and lamellar morphologies. In addition, adding small molecules into the block copolymer which has strong interaction with one of the component of block copolymer can have great advantages of well-ordered particle arrangement and different nanostructures from neat block copolymer itself. We investigated supramolecular assembly in thin film via strong hydrogen bonding between small molecule including ferrocene and block copolymer. Taking advantage of a solvent annealing process, we obtained different nanostructures and surface morphology of supramolecular assembly. Distribution of small molecules was confirmed by atomic force microscope (AFM) and grazing incidence small angle x-ray scattering (GISAXS). Finally, when solvent annealing, the effect of solvent mixing ratio on the structures was also investigated by small angle neutron scattering (SANS) measurement.
525 - Suprametallogels based on Fujita sphere self-assembly

Aleksandr V Zhukovitskiy, alexzhuk@mit.edu, Jeremiah A Johnson. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Hydrogels derived from metal-ligand association have shown promise as biomimetic self-healing materials. Current limitations of these systems include their relatively poor mechanical properties and narrow functional scope. We wondered if it would be possible to combine metal-ligand association with metallosupramolecular self-assembly to induce a hierarchical gelation process that would lead to novel materials with enhanced properties and well-defined porous structures for encapsulation of small molecules. This talk will discuss a novel class of hydrogels prepared via coordination-based self-assembly of Pd(II) ions with dipyridine-terminated poly(ethylene glycol) (PEG) macromers (1). These materials lead to hydrogels wherein the junctions are uniform hollow nanoscopic "Fujita spheres" (Figure 1). The dynamic nature of the self-assembly derived from the relatively weak pyridine-Pd(II) coordination bonds was expected to allow the network to flow under high rates of shear stress and subsequently to heal. Meanwhile, the large number of coordination bonds formed at each junction makes the network mechanically robust.

The chemical, structural, rheological, and thermodynamic characterization of our novel suprametallogels and the mechanism through which they form will be described. Control over macroscopic gel properties (e.g., storage modulus) through variation parameters including gel concentration, length of PEG chains, and source of Pd(II) ions will be discussed. Lastly, the network spheres can be employed as vectors for delivery of biologically-relevant materials. For instance, the spheres can encapsulate and then steadily release doxorubicin, a widely used chemotherapeutic agent.
Metallosomes as bioactive polymersomes formed by supramolecular assembly of block copolymer-metal complexation

Kensuke Osada¹,², osada@bmw.t.u-tokyo.ac.jp, Horacio Cabral¹, Yuki Mochida¹, Yasutaka Anraku³, Akihiro Kishimura⁶, Nobuhiro Nishiyama⁵, Kazunori Kataoka³,⁴. (¹) Department of Bioengineering Graduate Schools of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan, (²) JST-PRESTO, Japan, (³) Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan, (⁴) Department of Clinical Biotechnology, Center for Disease Biology and Integrative Medicine, Graduate School of Medicine, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan, (⁵) Department of Polymer Chemistry, Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama Midori-ku, Kanagawa 226-8503, Japan, (⁶) Department of applied molecular science division, Kyushu University, Higashi-ku Fukuoka-shi, Fukuoka 812-8581, Japan

Supramolecular architectures constructed through a self-assembly of block copolymers are attracting much interest due to their various morphologies. In particular, polymersomes have emerged as a key area of focus because of interest in the study of their formation mechanisms, morphology tuning and their potential as delivery carriers. Among various interactions utilized in constructing polymersomes, we focused on metal coordination bond because the membrane properties of polymersomes can be changed within water by a ligand exchange reaction, allowing controlled release of loaded materials in the polymersomes. Spontaneous polymersome formation with uniform size (~100 nm) triggered by metal coordination bond, namely metallosomes, were found to occur in aqueous medium through the reaction of an anticancer agent, DACHPt, with a Y-shaped block copolymer of omega-cholesteroyl-poly(L-glutamic acid) and two-armed poly(ethylene glycol) (PEGasus-PLGA-Chole).

Circular dichroism spectrum measurements revealed that the PLGA segment forms an alpha-helix structure within the metallosomes, suggesting that secondary-structure formation of metallo-complexed PLGA segment may drive the self-assembly of the system into vesicular structure. These metallosomes can encapsulate water-soluble fluorescent macromolecules into their inner aqueous phase, and eventually deliver them selectively into tumor tissues in mice owing to the prolonged blood circulation. Accordingly, fluorescent imaging of the tumor was successfully demonstrated along with an appreciable antitumor activity by DACHPt retained in the vesicular wall of the metallosomes, indicating the potential of metallosomes as multifunctional drug carriers.
527 - Electrochemical and fluorescence studies of η⁶-dichlorobenzene-η⁵-cyclopentadienyliiron-based, β-naphthol-labeled dendrimers

Christian Agatemor, cagatemor@upei.ca, Nola Etkin, Rabin Bissessur, Alaa S Abd-El-Aziz. Department of Chemistry, University of Prince Edward Island, Charlottetown, PEI C1A 4P3, Canada

Arene-cyclopentadienyliiron complexes form the basis of a number of polyaromatic ethers, thioles and amines. We exploited its versatility in the design of three generations of multifunctional dendrimers with a pentaerythritol core, a pendent cyclopentadienyliiron, and peripheral β-naphthol. Functionally, redox and optical activities were induced by the η⁶-dichlorobenzene-η⁵-cyclopentadienyliiron and β-naphthol moieties, respectively. UV-visible light absorption as well as steady-state and time-resolved fluorescence spectroscopies provided information on the optical properties of these dendrimers. The redox activity of this series of dendrimers was probed with cyclic voltammetry. Scanning electron microscopy offered information on the surface morphology of these dendrimers.
528 - Synthesis and spectroscopic studies of organoiron complexes containing novel porphyrin dendrimers and polymers

Inan Kucukkaya, ikucukkaya@upei.ca, Brian D Wagner, Rabin Bissessur, Alaa S Abd-El-Aziz. Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island C1A 4P3, Canada

Porphyrins are highly interesting compounds with potential applications in a wide range of fields, including light-energy conversion, fluorescence switches, fluorescent sensors, organic light-emitting diode (OLED) devices, photodynamic therapy (PDT), third-order non-linear optical materials and molecular wires. Cationic η6-chloroarene-η5-cyclopentadienyliron(II) complexes containing novel porphyrin and metalloporphyrin dendrimers were synthesized and their spectroscopic properties were studied. Divergent approaches were applied to give highly symmetrical branched dendritic compounds. Metal-mediated nucleophilic aromatic substitution and Steglich esterification were used to prepare these dendrimers. Furthermore, the synthesis and spectroscopic properties of a series of porphyrin-based polymers prepared via condensation polymerization of disubstituted porphyrins with cationic η6-chloroarene-η5-cyclopentadienyliron(II) complexes will be described. The incorporation of cationic η6-chloroarene-η5-cyclopentadienyliron moieties into both polymer and dendritic systems enhance solubility, and also facilitate the synthetic nucleophilic aromatic substitution, addition and condensation reactions, due to the intense electron-withdrawing ability of the iron center. This incorporation resulted in improved polymerization and dendrimer formation reactions, with greatly reduced reaction times in mild conditions. In addition, demetallation of the resulting polymers and dendrimers by photolysis resulted in the formation of novel, entirely organic materials, with unique structures, properties, and applications. For example, the linear polyether porphyrin polymers prepared in this way have potential applications in the purification of natural waters, due to their selective coordination with heavy metals. The spectroscopic properties of the porphyrin polymers, dendrimers and their precursors have been characterized using nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), ultraviolet-visible absorption and fluorescence spectroscopy. Redox and conductivity studies of these materials will also be discussed.
529 - Polymer brush/gold particle hybrids: Mutual structural (and dynamic) effects on the particle distribution

Stephanie M.E. Christau, stchristau@gmail.com, Regine von Klitzing. Department of Physical Chemistry, Technical University Berlin, Berlin, Germany

The modification of surfaces by coating with polymer brushes has attracted much interest in the past few years due to numerous potential applications in material and life science for the development of smart surfaces. They can be used as 3D matrices for the immobilization of nanoparticles, resulting in nanocomposite materials with interesting mechanical, optical, or catalytic properties with tailored functions. Using stimuli sensitive polymers allows controlling the distribution of the particles during and after particle loading. This is of high impact for optics, sensorics and for drug delivery systems. Regarding these purposes, it is essential to understand the mutual effect of polymer brushes and particles on the particle distribution.

In this study, responsive poly-(N,N-dimethylamino)ethyl methacrylate (PDMAEMA) brushes with a LCST at 55 °C and a pKa 7.5 are used as a matrix for the attachment of gold nanoparticles (AuNPs). The plasmon coupling between the AuNPs is controlled by external parameters (T, pH). By tuning the synthesis parameters, polymer brushes of different thicknesses (molecular weights) or grafting densities are produced using a new type of sealed reactor. This reactor allows the preparation of brush samples where only one single parameter of the system is varying while keeping all the other parameters constant. The effect of brush thickness and brush grafting density on the particle loading within the brush matrix is investigated by ellipsometry, X-ray reflectometry and high resolution cross section scanning electron microscopy. The structure (and dynamics) of the resulting hybrids in dependence of brush thickness and grafting density is discussed.
530 - In-situ liquid transmission electron microscopy (ISL-TEM) for the analysis of metal containing polymer nanoparticles

Joseph P Patterson¹, jppatterson@ucsd.edu, Nathan C Gianneschi¹, Patricia Abellan², James E Evans², Seth Cohen¹, Michael Denny Jr.¹. (1) Chemistry and Biochemistry, UCSD, San Diego, CA 92093, United States, (2) Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, United States

Transmission Electron Microscopy (TEM) and Scanning TEM (STEM) are extremely powerful techniques for characterizing nanomaterials in due to the high spatial resolution, the ability to determine internal and 3D structures and the possibility of obtaining elemental information through the use of energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Due to the high vacuum requirement of the microscope column, nanoparticles in solution are typically imaged through one of two techniques a) dehydration onto a TEM grid (dry state TEM) or b) vitrification of thin films of solution on a TEM grid (cryo-TEM).

Recent developments in microchip fabrication have allowed for the commercialization of vacuum tight flow cells with 'electron transparent' silicon nitride windows. This technology permits TEM of nanoparticles in liquids at ambient temperatures and pressures and has been used to observe inorganic nanoparticle motion and growth. The ability to image metal containing polymer colloids/nanoparticles in liquids at high magnification promises to be an exciting avenue of research.

Here we show that metal containing polymer nanoparticles can be imaged in liquids, allowing their motion and growth to be observed in-situ. We also investigate damage mechanisms under different imaging conditions and discuss the difficulties and limitations of observing particle formation in-situ. Prior to any quantitative analysis of these systems, the optimal conditions, free of artifacts must be found.

Tuesday, August 12, 2014 06:00 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
531 - Light-emitting metallo-conjugated polymers: Synthesis and characterization

Yemineni S L V Narayana, slvnarayanay@gmail.com, School of Chemistry, University of Hyderabad, Hyderabad/Gachibowli, Andhra Pradesh 5000 46, India

The design and synthesis of light-emitting polymer materials have attracted much attention because of their direct applications in display and lighting devices. In my presentation, the synthesis and characterization of few color displaying high molecular weight 2,6 (bis(pyrazole) pyridine and thiophene, 2,6(bispyrazolyl)pyridine and 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-ethynyl-2-methylthiophene), 2,6 (bis(pyrazole) pyridine and 4,7-di(thiophen-2-yl)-4,5,6,7-tetrahydrobenzo[1,2,5] thiadiazole based conjugated copolymers (CPs) will be presented. The conjugated polymers were solution-processed to prepare thin films which exhibited colors under UV. The photophysical properties of the polymers were also studied, both in solution and in thin-films. The self-assembly studies of the polymers will be discussed during the presentation.

REFERENCES


We designed and produced soft nanocomposites for electrical applications. Poly(n-butyl methacrylate) (PBMA) or poly(n-butyl acrylate) (PBA) were grafted from commercial ZnO and Al₂O₃ nanoparticles (NPs) produced by flame spray pyrolysis - using surface initiated atom transfer radical polymerization. Initially, the NPs were modified by silane multilayers from which the PBMA or PBA were subsequently grafted. Different chain lengths were grafted from the NPs, while the graft density and the thickness of the silane coating were kept constant. After cleavage, the graft lengths were determined by SEC and compared to the length of free polymer chains (initiated simultaneously from a free initiator) as well as theoretical calculations of the graft length based on data from TG and UV-Vis. The surface chemistry of the modified NPs was further characterized by IR-spectroscopy and STEM. The modified NPs were mixed with two soft polymer matrices: poly(ethylene-co-butyl acrylate) (EBA) and PDMS with different volume fractions of NPs. The films were allowed to thermodynamically stabilize before curing. Variations in surface morphology of the nanocomposite films were characterized by AFM and confirmed by a novel simulation method. Homogeneous dispersions of NPs could be explained by the shielding of the core-core attraction by the silane multilayer in combination with dominating enthalpic contributions of the polymer grafts to the rubber-NPs system – similar to a bimodal graft system. Finally, the electrical properties of the nanocomposite films were evaluated.

(2) Malmström, E. et al., Polymer, 2014, http://dx.doi.org/10.1016/j.polymer.2014.03.005
533 - Electrografting of redox active organometallic poly(ionic liquids) from ionic liquid by cathodic reduction: Synthesis and applications

**Xueling Feng**, x.feng-1@utwente.nl, Xiaofeng Sui, Mark Hempenius, Julius Vancso. Department of Materials Science and Technology of Polymers, University of Twente, Enschede, The Netherlands

Redox responsive poly(ferrocenylsilane) (PFS) films have great potential for electrode modifications in electrochemical sensing. Robust, dense PFS layers, featuring imidazolium side groups were successfully electrografted to Au substrate from ionic liquid (IL) 1-ethyl-3-methylimidazolium ethyl sulfate. We will discuss the electrografting process in detail. Films with thickness in the 10 nm range were obtained and characterized by electrochemistry, AFM, XPS, contact angle, and FTIR for the reduced and oxidized PFS, respectively. An ascorbic acid sensor based on surface-anchored electrografted PFS exhibits a high sensitivity, stability and reproducibility.
534 - Proton conducting membranes formed by networks of Al\(^{3+}\) and phosphorylated monomers and polymers

Markus Klapper, klapper@mpip-mainz.mpg.de, Jennifer Wegener, Robert Graf, Anke Kaltbeitzel, Klaus Müllen. Max Planck Institute for Polymer Research, Mainz, Rhino-Palatia 55128, Germany

Various combinations of phosphorylated molecules and metal ions are used to build up stable porous networks. Depending on the composition the pore sizes can be altered and with small proton conducting molecules as ionomers filled. The networks are stable under aqueous and acidic conditions and show an strongly improved retention behavior for the small ionomers due to hydrogen bonding in comparison to other membranes.

The resulting materials can be incorporated in polyimides or polysulfones and show excellent film-forming properties. By solid-state NMR, TEM and SEM the structure is elucidated. The proton conductivity of the polymer/ metal networks are in the range of 10\(^{-1}\) to 10\(^{-2}\)S/cm. In particular at higher temperature the values are higher than for Nafion, and therefore matching the requirements for fuel cell membranes in automotive industries defined by the DOE.

535 - WITHDRAWN
We report the development of electronically-varied polystyrene-based polymers as supporting ligands for homogenous nanoparticle catalysts. The supporting polymer has the potential to control not only the growth and aggregation of nanoparticle catalysts during synthesis, but also to influence the reactivity of the incorporated nanoparticles in catalytic transformations. In this manner, our polymer-ligand approach to nanoparticle catalysis could mimic standard ligand screening studies performed on homogeneous transition metal catalysts that aim at optimizing catalytic efficiency. We have synthesized a series of polystyrene-based polymers containing both electron rich and electron poor arenes and studied both the impact of polymer electronics on nanoparticle size (TEM) and catalytic efficiency (aerobic oxidation reactions). In this report, we will describe our efforts to study the impact of polymer electronics on the catalytic efficiency of aerobic oxidation reaction performed with transition metal (Au, Ru, etc) nanoparticle catalysts.
Metallopolymers consisting of semiconducting polymers have been designed to combine the optoelectronic and processing properties of the polymeric component with the tunable optical, redox, and catalytic properties of the metal center. These types of metallopolymers can be used in sensing, switching, or memory devices as well as in solar photovoltaics/catalysis. By using Grignard Metathesis (GRIM) polymerization, we have synthesized ligand-functionalized poly(3-hexylthiophene) derivatives where the ligands are multidentate polypyridyl species. The introduction of ligand functionalization on the polymer is to enable the formation of different supramolecular structures by metal complexation. Heteroleptic complexes formed by metal coordination to different ligand-functionalized polymers/biopolymers result in integrated assemblies featuring multiple components such as a primary semiconducting polymer, metal center, ligand units, and a secondary (bio)polymer. These polymer assemblies with increased supramolecular complexity can integrate the characteristic properties of each individual component. The coordination-based "plug and play" nature of this approach allows for the facile synthesis of libraries of metallopolymer assemblies with tunable functionalities.
Wetting-resistant surfaces are useful in a variety of applications, where low surface energy fluoropolymers have been used to reduce liquid wetting on surfaces for some time. While it is understood that surface roughness also contributes to reduced wetting, more recent work has demonstrated that surface structure also contributes to wetting-resistance, enabling the repulsion of low surface tension liquids, such as oils and alcohols, which previously was not possible. Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS) are useful in a variety of military, industrial, and commercial wetting-resistant surface applications. This is partially due to their microcrystalline structure created during surface preparation. The low surface energy values of F-POSS also contribute to their usefulness, with one variety possessing the lowest solid surface energy value of any known crystalline solid. Many different types of F-POSS compounds have been prepared. These include octahedral, unsymmetrical, ionic, and mixtures of polyhedral compounds, in addition to SF₅- and silanol-functional materials, many of which can be used in copolymerization reactions. This presentation will discuss past and present materials research performed at the Air Force Research Laboratory, Rocket Propulsion Division, located at Edwards Air Force Base and applications of these useful compounds.
Coordinative assembly allows organic-inorganic coordination polymer, metal ion and metallopolymer to be built up as the supramolecular functional assemblies. The polyelectrolyte, made by conjugated polymer with ionic moieties, quenches in luminescence when met with metal ion. Nonconjugated polyelectrolyte, however, cannot emit light. Here, we reported a nonconjugated polyelectrolyte-ion complex system, which shows the fluorescence "turn-on" gelation. The complex film was prepared via layer-by-layer assembly by sequential dipping in the polycations and polyanions solutions. Ag⁺ was introduced by forming the stable complex with either branched polyethylenimine (BPEI) or poly(acrylic acid)(PAA) solution during assembly. During assembly, each layer captures Ag⁺ into multilayer through both chelate with the amine groups of BPEI and carboxylic acid groups of PAA. The multilayer film without Ag⁺ was barely fluorescent. Once Ag⁺ was participated in the assembly process—in either the polycations or polyanions solution, an orange emission color would be generated from the multilayer film. This fluorescent polyelectrolyte-Ag⁺ complex film would quench when met with formaldehyde vapor due to the reduction of Ag⁺ in the complex film.
540 - Poly(vinyl alcohol) organogels containing Pd porphyrins for sensitized low-power light upconversion

Roberto Vadrucci, Christoph Weder, Yoan C. Simon, yoan.simon@unifr.ch. Adolphe Merkle Institute, University of Fribourg, Marly, FR 1723, Switzerland

Light upconversion via triplet-triplet annihilation (TTA-UC) allows the combination of two low-energy photons with power densities below 0.1 W.cm\(^{-2}\) to produce blue-shifted light. TTA-UC systems typically consist of two dyes: a metal sensitizer, harvesting incoming light, and an emitter, required for the TTA-step. Originally reported in solution, TTA-UC was recently implemented in efficient solid-state materials using new strategies, such as dye-blending in rubbery polymers or encapsulation in hard-shell soft-core systems to overcome solid-state related problems, such as oxygen exposure and low molecular mobility. Here, we present poly(vinyl alcohol)-based DMF/DMSO organogels as an innovative for easy production of transparent and efficient upconverting self-standing gels. The dispersed phase (DMF/DMSO) serves as a solvent providing high molecular mobility and oxygen shielding for both dyes: palladium(II)-mesoporphyrin IX (Pd-MesoIX) and 9,10-diphenylanthracene. Upconverting organogels are expected to broaden the scope of TTA-UC materials by accessing novel gel-related applications/functionalities.

Tuesday, August 12, 2014 06:00 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
541 - Lanthanide-containing biomaterials and solution assemblies

Gina L Fiore, gina.fiore@unifr.ch, David Thevenaz. Polymer Chemistry and Materials, Adolphe Merkle Institute, Fribourg, Switzerland

[figure 1] The incorporation of lanthanide complexes into polymer matrices is attractive due to the unique luminescence properties of the lanthanide series, such as long excited state lifetimes, sharp emission lines, insensitivity to oxygen quenching, and two-photon absorbance. Biocompatible and biodegradable polymers prepared by ring opening polymerization (ROP) such as hydrophobic poly(lactic acid) (PLA), poly(e-caprolactone) (PCL), and more elaborate block copolymer hybrids (e.g. with hydrophilic poly(ethylene glycol) (PEG)) have been combined with lanthanide complexes to create a series of inorganic-organic hybrid materials. Solution assemblies of these materials were prepared and the assembled structures were tuned by varying the preparation method. The luminescence analysis of the resulting nanoparticles confirmed the incorporation of lanthanide complexes into the polymer matrix and solution assembled structures. The preparation and characterization of lanthanide-containing biomaterials, along with the solution assemblies and optical characterization will be presented.
Metallopolymers based on metal polypyridyl complexes can feature interesting photocatalytic properties. The light absorption of these polymers, which is caused by the MLCT in the wave-length range, can be extended by the introduction of additional dyes. As a consequence light of a wide spectral range can be absorbed by these systems. The energy can be transferred from the dye molecules to the metal complexes.

In this context different metallopolymers featuring metal complexes (e.g., Ru(II)tpy$_2^{2+}$, Os(II)(dmbpy)$_2$(trz-py)$_2^{2+}$), comonomers to tune the solubility as well as dye molecules for light harvesting (e.g., thiadiazole dyes) have been synthesized via a controlled radical polymerization – namely the RAFT polymerization. Well-defined metallopolymers with adjustable molar mass as well as composition could be obtained (Figure 1).

![Figure 1](image.png)

**Figure 1:** Schematic representation of photoactive metallopolymers with light-harvesting dyes.

The optical properties of the polymers have been characterized in detail. Energy transfer between the different dye molecules (up to three different thiadiazole dyes) as well as the metal complex could be observed.

These metallopolymers are interesting materials for light harvesting and hydrogen generation/photocatalysis.
Our research group has developed a series of novel electropolymerizable monomers that incorporate well-defined metal complexes directly into conducting polymer backbones. These hybrid electroactive materials known as conducting metallopolymer materials have a variety of applications including light-emitting devices, sensors, separation materials, and catalytically-active polymers. This unique class of materials exploits the properties of both the conducting polymers and the metal centers in a cooperative fashion. For example, in the development of electrocatalysts the redox-active polymer backbone can serve as an effective way to shuttle charge to the catalytically-active metal center. In another embodiment of these materials, the conducting polymer backbone can be used as a redox-attenuated ligand to precisely and directly tune the activity of a catalytically active metal center. Through the use of specifically-designed ligands that possess both a binding site for a catalytic metal center and functional groups that undergo electropolymerization, the highly-controlled growth of conducting metallopolymer materials has been accomplished. The catalytically-active metal centers have been judiciously chosen for activity in either important electrocatalytic transformations or chemical catalysis that would benefit from on/off attenuation. Our results concerning the design, synthesis, characterization, electrochemistry, and catalytic properties of a new class of conducting metallopolymer hybrid materials containing catalytically-active metal centers will be discussed in detail.
Block copolymers (BCPs) are ideal building blocks for a variety of nanoscale objects due to their ability to undergo spontaneous phase separation in selective solvents. Our group has previously shown that BCPs with a metal-containing poly(ferrocenyldimethylsilane) (PFS) core-forming block can be used to prepare well-defined nanostructures via a crystallization-driven self-assembly (CDSA) process in solution that resembles a living covalent polymerisation. The self-assembly of crystalline-coil BCPs in thin films and the bulk phase has been exploited for the fabrication of nanoscale domains with a diverse range of patterns. However, examples of cylindrical micelles with coronas that undergo spontaneous phase segregation during solution CDSA are rare. We report studies of the CDSA of a series of crystalline-brush BCPs with \(n\)-alkyl branches. When co-crystallized with a linear BCP, the resulting micelles displayed chemically nanosegregated coronas where the size and frequency of compartmentalisation could be controlled by the ratio of linear to brush BCP. Furthermore, the co-crystallisation occurred in a gradient, with an initial bias for the growth of the linear BCP over that of the more sterically demanding brush BCP. This result represents the first example of living gradient CDSA, an analogous process to a covalent gradient copolymerisation.

\[\text{Figure 1. Schematic representation of the transformation from linear to brush BCP.}\]

545 - Dehydration and phase-separation behaviors of poly(2-oxazoline) containing block copolymers in solution

Rintaro Takahashi\textsuperscript{1}, takahashi-rintaro@nexyxbb.ne.jp, Xing-Ping Qiu\textsuperscript{2}, Takahiro Sato\textsuperscript{1}, Ken Terao\textsuperscript{1}, Françoise M Winnik\textsuperscript{2}. \textsuperscript{(1)} Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, \textsuperscript{(2)} Chemistry, University of Montreal, Montreal, Quebec H3C 3J7, Canada

We have investigated the heat-induced self-association of block copolymers poly(2-isopropyl-2-oxazoline)-b-poly(2-ethyl-2-oxazoline) (PIPOZ-b-PEOZ) in water and poly(2-isopropyl-2-oxazoline)-b-poly(N-isopropylacrylamide) (PIPOZ-b-PNIPAM) in water-methanol (MeOH) mixtures using differential scanning calorimetry, light scattering and small-angle X-ray scattering (SAXS) together with visual observation. The dehydration temperatures of the PIPOZ and PEOZ blocks in water are 43 and 54 °C, respectively. When heated abruptly to 50 °C where PIPOZ-b-PEOZ is amphiphilic, the copolymer first forms star micelles that further aggregate to form large concentrated phase droplets, and finally the droplets coalesce into a bulk liquid phase. When heated abruptly to 70 °C, where both blocks are hydrophobic, the copolymer solution also separates into two liquid phases, consisting of phase-separated polymer-rich droplets dispersed in a polymer-poor phase, but the droplets do not coalesce into a liquid bulk phase.

Although the difference in the phase-separation temperature between solutions of the PIPOZ and PNIPAM homopolymers is enlarged with increasing the MeOH content, the dehydration occurs almost simultaneously on both block copolymer chains in most solvent conditions, and the solutions undergo a liquid-liquid phase separation. The copolymer chain in the coexisting dilute phase was mostly molecularly dispersed, having more compact conformation with increasing temperature, without forming micelles. Although PIPOZ-b-PNIPAM behaved like a homopolymer in water and water-MeOH mixtures, the amphiphilicity of the block copolymer affects the colloidal stability of concentrated-phase droplets in the phase separating solutions in a complex manner.
546 - UV-induced self-assembly of amphiphilic polyoxazolines

Laetitia Korchia, Vincent Lapinte, vincent.lapinte@univ-montp2.fr, Cécile Bouilhac, Jean Jacques Robin. Institut Charles Gerhardt de Montpellier UMR 5253, FRANCE, Montpellier, France

The importance of amphiphilic block copolymers is undeniable, this being largely associated to their outstanding self-organizing in solution giving rise to different soft materials such as micelles, vesicles, polymersomes and gels. The peculiar behavior of these copolymers in solution allows their use as surfactants, emulsifiers, drug carriers, etc. Some of them reversibly be assembled and disassembled upon ultraviolet exposure. The concept needs the incorporation of chromophores into the amphiphilic copolymer structure in terminal position or in pendant chain. The "decorvation" of polyoxazoline (POx) as well as the elaboration of POx macromolecular architectures have extensively been described.

In this study we investigated the synthesis of amphiphilic diblock copolymers based on polyoxazoline bearing photo-sensitive group (coumarin). The dimerization of this photochromic moiety was then undertaken after the self-organization into micelle to stabilize the core of the nanoobject. Alternatively, the amphiphilic copolymers have been dimerized into amphiphilic A-B-A triblock copolymers before being self-organized into liposome. According to another route, the photo-cross-linking of amphiphilic grafted copolymers has been studied for the preparation of core-cross-linked micelles.


Poly(2-oxazoline)s and copoly(2-oxazoline)s reproduce the versatility introduced by the substitution pattern of the repetition units, paving the way for various applications of the derived materials. Benefiting from their susceptibility to microwave-supported cationic ring-opening polymerizations, reaction times for the polymerization are significantly decreased, while the structural properties of the polymers can be well controlled. For the application of poly(2-oxazoline)s as photoresist, chemical functionalities allowing for UV-induced polymeranalogous crosslinking and the fine-tuning of the surface energy play a key role. In order to expand the toolbox of stimuli-responsive crosslinkable copoly(2-oxazoline)s on the one hand and to further develop the strategies for polymeranalogous modifications, norbornenyl- and thiophenyl-substituted 2-oxazoline monomers were synthesized due to the high reactivity of the constrained double bond in thiol-ene click reactions and the possibility to perform Friedel-Crafts reactions, respectively. These monomers can preferably be polymerized using oxazolinium-based macroinitiators, and copolymers of 2-norbornenyl-2-oxazoline can be used in highly reactive photoresists.

**Tuesday, August 12, 2014 06:00 PM**

**Poly(2-Oxazoline)s and Polypeptoids (06:00 PM - 08:00 PM)**

**Location:** Moscone Center, West Bldg.

**Room:** Exhibit Hall
2-Oxazoline monomers can undergo cationic ring-opening polymerizations if certain criteria are met, in particular the absence of certain functional groups: Only non-nucleophilic functional groups do not inherently disturb the polymerization. Hence, XH groups such as alcohols, amines and thiols must either be protected during the polymerization or be introduced in polymeranalogous fashion. Click reactions are a set of key reactions for the post-synthetic strategy due to their high yield, and as such the UV-induced thiol-ene reaction plays a prominent role: 2-Oxazoline monomers bearing unsaturated double bonds can be easily synthesized from compounds from renewable resources such as undecenoic acid, and be reacted with (commercially available) thiols. While non-conjugated double bonds do not interfere with the polymerization itself, these click reactions can be applied to the monomers and polymers, respectively, ranging from the derivation of 2-oxazoline monomers and poly(2-oxazoline)s with functional groups as well as the crosslinking of the corresponding (co-)polymers.
Biocidal polymers such as the antimicrobial active telechelic Poly(2-alkyloxazoline) (POx) with one quaternary N,N-dimethyldodecylammonium (DDA) end group, were found to be greatly controlled by the non-bioactive distal end group, the so-called satellite group. The introduction of these SG either in the initiation or termination step of the reaction, reveals the possibility to control the antimicrobial activity of the resulting polymers. The biocidal group was attached to the polymer in the reaction-step vice versa. In particular, either the biocidal DDA-group was introduced via termination of the PMOx in the last step of the polymerization or by the antimicrobial initiator 4-(bromomethyl)-N-dodecyl-N,N-dimethylbenzen Ammonium Bromide (DDA-X), a DDA derivative, in the initiation step. It was found that the antimicrobial inactive endgroup of telechelic biocidal PMOx has an activating/deactivating effect on the biocidal activity of the whole macromolecule. This satellite group effect controls the antimicrobial activity over two orders of magnitude and it can be used to switch the antimicrobial activity of PMOx in polymer-analogous reactions.
550 - Synthesis of polyisobutylene-poly(2-phenyl-2-oxazoline) block copolymers via macroinitiator and click chemistry approaches

C. Garrett Campbell, christopher.g.campbell@eagles.usm.edu, Robson F Storey. Department of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi 39401, United States

We have synthesized poly(isobutylene-b-2-alkyl-2-oxazoline) PIB-POX block copolymers from primary bromide-terminated PIB (PIB-Br) obtained by quenching living polymerization of isobutylene with 3-bromopropanoxybenzene. Two approaches were used. In the first, PIB-bromide was converted to PIB-hydroxyl and then to PIB-triflate and used as a macroinitiator to initiate the cationic ring opening polymerization of 2-alkyl-2-oxazoline using toluene/DMF solvent system (product A). In the second approach, PIB-Br was converted to PIB-N3 using KN3, and POX homopolymer was polymerized using propargyl tosylate as the initiator. The resulting alkyne functional POX was reacted with PIB-N3 via the copper catalyzed azide/alkyne cycloaddition (CuAAC) click reaction (product B). In both approaches, the target DP of the PIB and POX blocks were 60 and 5-10, respectively. PIB and POX precursor blocks and final block copolymers were analyzed using nuclear magnetic resonance (NMR) spectrometry to determine structure and gel permeation chromatography (GPC) to determine molecular weight.

Figure 1. Graphical abstract depicting the two synthetic methods used to synthesize PIB-POX block copolymers.
Amino acid N-thiocarboxy-anhydride (NTA), the thio-analog of N-carboxyanhydride (NCA), is much more stable than NCA against moisture and heat. The convenient monomer synthesis without rigorous anhydrous requirements makes the ring-opening polymerization of NTA a competitive alternative to prepare polypeptide- or polypeptoid-containing materials with potential of large-scale production.

Water-soluble polysarcosines (PSars) with high yields (>90%) and low polydispersities (<1.2) are synthesized from sarcosine N-thiocarboxy-anhydride (Sar-NTA) at 60 °C initiated by poly(ethylene glycol) amine (PEG-NH₂). The lengths of PSar segments are controlled by various feed ratios of Sar-NTA to PEG. PEG-b-PSar products are a class of novel double-hydrophilic diblock copolymers. Due to the different solubility of PEG and PSar blocks, PEG-b-PSar polymers stabilize oil-in-water emulsions at nano- and micro-scale, which exhibits promising encapsulation applications in food, cosmetics and drug delivery. They also self-assemble to micelles in organic solvents and demonstrate the potential to carry water-soluble cargos.
552 - PEG-polypeptide dual brush block copolymers

Yanfeng Zhang, yfzhang@illinois.edu, Jianjun Cheng. Department of Materials Science and Engineering, University of Illinois at Urbana, Champaign, Urbana, ILLINOIS 61801, United States

We designed and synthesized a series of amphiphilic polypeptide-containing hybrid dual brush block copolymers with controlled molecular weights and narrow molecular weight distributions in one pot via sequentially ring-opening metathesis polymerization of norbornyl-PEG and \(N-(2-((\text{trimethylsilyl})\text{amino})\text{ethyl})-5\)-norbornene-endo-2,3-dicarboximide (M1), followed by ring-opening polymerization of amino acid \(N\)-carboxyanhydrides (figure1). Polylactide (PLLA) nanoparticles coated with these amphiphilic dual brush block copolymers showed significantly improved stability in PBS solution compared to those coated with amphiphilic linear block copolymers such as PEG-polylactide and PEG-polypeptides.
Nature uses a broad range of structures and assemblies to perform its tasks within a living environment. Amongst them, the vesicle is of our interest, e.g. the formation of polymersomes by amphiphilic block-copolymers. Whilst polymersomes are now known to contain a large variety of functionalities, a lack of biodegradable polymers used can be observed. This feature is aimed for in this study making use of poly-beta-peptoids in a solid-state approach.

Figure 1: Solid-State / ATRP Synthesis of a Poly-beta-Peptoids – methacrylate copolymers for Polymersomes

Solid State Synthesis for alpha peptoids is already well studied by the Zuckermann group. In our studies, we deploy their sub monomer approach towards beta peptoids. As previously mentioned, vesicles will only from if the polymer used is of amphiphilic nature. Since betapeptoids are generally insoluble in water, they are to be converted into an ATRP initiator to grow something the hydrophilic part in a consecutive reaction. In intial studies, we managed to create a fully hydrophobic beta-peptoid using this approach Methoxy-Ethylamine and Amylamine as a side chain but aim to accomplish the conjugation soon. The choice for ATRP monomers will be the cell-targeting phosphoryl choline derivative PMPC and a methacrylic version of the immunogenic PEO are to be used. Once conjugated, the self-assembly of these polymers will be studied using DLS and TEM as a verification for vesicle formation.
554 - One-pot synthesis of cyclopentadienyl endcapped poly(2-ethyl-2-oxazoline) and subsequent ambient temperature Diels–Alder conjugations

Mathias Glassner¹, mathias.glassner@ugent.be, Kristian Kempe², Ulrich S Schubert², Christopher Barner-Kowollik³, Richard Hoogenboom¹. (1) Department of Organic Chemistry, Ghent University, Ghent, Belgium, (2) Department of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena, Germany, (3) Department of Technical and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

Diels-Alder reactions represent an efficient and metal free strategy for polymer post-functionalization and polymer-polymer coupling reactions.¹ Employing cyclopentadiene (Cp) end-capped polymers enables conjugation under very mild conditions.² The fact that Cp-moieties are highly reactive functional groups has prevented the synthesis of Cp-functional initiators or chain-transfer agents. An emerging class of polymers providing a promising platform for the synthesis of highly functional materials are poly(2-alkyl-oxazoline)s which have received considerable attention for, amongst others, biomedical applications.³

In the present contribution we present an efficient strategy for the one-pot synthesis of poly(2-ethyl-2-oxazoline) bearing a highly reactive Cp end-group via living cationic ring opening polymerization (CROP) employing sodium cyclopentadienide as termination agent.⁴ We further demonstrate the potential of PEtOx-Cp to undergo quantitative Diels–Alder reactions with various N-substituted maleimides including the formation of a block copolymer.


Tuesday, August 12, 2014 06:00 PM
Poly(2-Oxazoline)s and Polypeptoids (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
The specific sequence of monomers make proteins have amazingly precise 3D structures and special functions. Scientists have been trying to synthesize polymers with similar level of order and precision for application in medicine, catalysis and material sciences. Polypeptoids are structural mimics of polypeptides, and can be synthesized from diversified monomers with specific sequence. Originated for studying proteins, HP lattice model, in which only hydrophobic (H) and polar (P) monomers are considered, has been employed to predict folding behaviors of heteropolymer chains. We believe that hydrophobic sequence patterning in polymer chains is one of the most predominant determinants of folding a heteropolymer into a defined structure. Carrying this idea and based on HP model, we prepared polypeptoids with defined sequence by solid-phase synthesis from two monomers, hydrophobic N-isobutylglycine and polar N-(2-hydroxyethyl)glycine or N-(2-carboxyethyl)glycine monomers. Here we systematically evaluate the ability of HP peptoid 40-50mers of varying composition and sequence to fold into compact single-chain globular structures, and to catalyze simple chemical transformations.
Poly(2-oxazoline)s are an interesting class of polymers. Their properties can be tuned by varying the R group on the monomer and in this way functional groups can also be introduced. Methyl ester functionalized side chains are especially interesting as it can be hydrolysed to the carboxylic acid, a versatile functionality for conjugation of peptides and proteins. Moreover, the methyl ester group can undergo a transamidation reaction to easily introduce a wide variety of side chain amide moieties. Even though the synthesis and copolymerization of 2-methoxycarbonylethyl-2-oxazoline has been reported, the (co)polymerization kinetics are yet unknown. In this poster we present detailed studies on the homo- and copolymerisation kinetics of two methyl ester functionalized 2-oxazoline monomers with 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline and 2-n-propyl-2-oxazoline, unexpectedly revealing that the methyl ester containing monomers significantly accelerate the polymerization.
Fine-tuning the lower critical solution temperature (LCST) of aqueous polymer solutions via simple mixing of polymers with different cloud point temperatures (Tcp's) is an attractive strategy since re-synthesis or copolymerization can be avoided. To obtain controlled intermediate Tcp's via mixing of two polymers can be referred to as cooperative LCST behavior. It has been suggested that polymers with molecular weight dependent Tcp's are essential to obtain such cooperative behavior based on screening of mixtures poly(N-vinyl pyrrolidone), poly(N-isopropylacrylamide), poly(N-vinylcaprolactam) and poly(oligo(ethylene glycol) methacrylate). However, poly(2-oxazoline)s, as a highly tunable family of thermoresponsive copolymers, were not included in this work. In this contribution, we will report a systematical study on the cooperative LCST behavior of copoly(2-oxazoline)s with various Tcp's ranging from 25 to 90 °C. The results suggested that hydrophilicity is a key factor to control the cooperative behavior of poly(2-oxazoline)s as only mixtures of the most hydrophilic copolymers revealed cooperative behavior as shown in the Fig.1.

Fig.1 Cooperative behavior of copoly(2-oxazoline)s, P70 represent copoly(2-oxazoline) with Tcp=70 °C, while P90 is copoly(2-oxazoline) with Tcp=90 °C

In recent years 2-oxazolines have received considerable attention as ligands for asymmetric catalysis,\cite{1} and as monomers for living cationic ring opening polymerization (CROP; see figure) leading to poly(2-oxazoline)s - regarded to be pseudo-polypeptides.\cite{2} The living nature of the CROP of 2-oxazolines leads to good control over dispersity, very high end group fidelity while variation of the monomer structures provides straightforward access to a broad range of polymer structures and properties. This synthetic versatility in combination with good biocompatibility make poly(2-oxazoline)s very interesting materials for, amongst others, biomedical applications.\cite{3}

In this study, amphiphilic gradient and block copolymers were synthesized with different ratios of poly(2-methyl-2-oxazoline)s (n) and poly(2-phenyl-2-oxazoline)s (x). The micellization behavior of these polymers was studied with dynamic light scattering (DLS), small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) in water and water-ethanol mixtures. To perform SANS contrast variation measurements, $d_{2}$-2-methyl-2-oxazoline was synthesized and used to make similar partially deuterated amphiphilic block and gradient copolymers.

559 - Sweet polymers by combination of carbohydrates and poly(2-ethyl-2-oxazoline)s

Maarten A Mees¹, maarten.mees@ugent.be, Richard Hoogenboom¹, Dietmar Appelhans². (1) Department of Organic chemistry supramolecular chemistry, Ugent, Ghent, Oost-Vlaanderen 9000, Belgium, (2) Department of Polymer Research, Leibniz institute Dresden, Dresden, Germany

The role of carbohydrates in biochemical processes is essential for living matter, because of their importance in signaling, energy (storage) and metabolism. Depending on their function, carbohydrates are included into larger constructs, such as proteins (glycoproteins), lipids (glycolipids) or other functionalities (glycoside). By mimicking these natural products based on synthetic constructs decorated with carbohydrates, it is possible to control biological interactions, such as cell uptake, specific interactions or interference with biochemical processes. To this end, one can use polymers that act as a carrier for the carbohydrate and in this work we have chosen poly(2-ethyl-2-oxazoline) (PEtOx). Such poly(2-alkyl-2-oxazoline)s (PAOx) are regarded as pseudo peptides because of their structural similarity to peptides. Moreover these polymers are invisible for the immune system, the so-called stealth effect, which is an important asset if they are used in the body. PAOx can be prepared by living cationic ring opening polymerization (CROP) of the 2-oxazoline monomer yielding well-defined polymers. Via partial hydrolysis of PEtOx, a copolymer of PEtOx and poly (ethylene imine) PEI is obtained. In the current work, we have exploited these PEtOx-PEI copolymers for the preparation of glycopolymers by reductive amination with the open forms of glucose and mannose. The aldehyde of the open for carbohydrates can attach to the secondary amines of PEI by imine formation, which is subsequently reduced to a stable tertiary amine. The ratio of PEtOx and carbohydrates is systematically varied and the glycoconjugates solution behavior is examined in detail by dynamic light scattering (DLS) revealing polymers that are present as unimers, polymers that exhibit lower critical solution temperature behavior and polymers that always agglomerate into microparticles.

Tuesday, August 12, 2014 06:00 PM
Poly(2-Oxazoline)s and Polypeptoids (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
The first reports on the synthesis of end-functionalized polyoxazolines appeared approximately twenty five years ago when matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectroscopy was not widely available for polymer characterization. For example, titration of amino- and carboxy-functional polyoxazolines was commonly used for end-group characterization, but this method is known to be susceptible to errors and cannot take into account for possible side reactions that occur during the termination of the living polyoxazoline with nucleophiles.

In the present contribution hydroxy-, carboxy-, and amine-functional polyoxazolines were synthesized by living cationic polymerization of oxazolines by termination of the living polymer with functionalized nucleophiles.

Unprecedented side reactions were observed during the synthesis of amino-terminated polyoxazolines. The reaction products were quantified and possible termination mechanism was constructed with the help of $^1$H and 2D NMR analyses and MALDI-TOF spectroscopy of oligomeric model polyoxazoline derivatives.
561 - Nanocomposite hydrogels with tunable rheological properties: Polyoxazoline/laponite hydrogels

Clémence Le Coeur¹, Gisèle Volet¹, volet@icmpe.cnrs.fr, Catherine Amiel¹,², Cédric Lorthioir⁴. (1) SPC (SYstème Polymère Complexe), ICMPE (Institut Chimie Matériaux Paris Est), Thiais, FRANCE 94, France, (2) UPEC (Université Paris Est Créteil), Créteil, FRANCE 94, France

Nanocomposite gels constituted of nanoclays and polymers are solutions which have many interests as material in fields such as painting. In order to optimize these mechanical properties, the control of nanoclay dispersion and polymer structure seems important. Among nanoclay hydrogels, we chose to use laponite, synthetic monodisperse nanoclay which is known to form a gel phase at low concentration and whose understanding is still a theoretical challenge.

Several studies have been carried out on laponite/PEO systems. In water PEO has a gaussian chain conformation. The addition of PEO in PEO/laponite hydrogel has been observed by rheology and SANS and it seems that the polymer chains "break" its structure.

We performed polymer/nonoclays based hydrogel which shows really interesting properties. We add to laponite solution another hydrophilic polymer synthesized in our lab by G. Volet and L. Marx which conformation is really different from the one of PEO, Polyoxazoline (POXAZ). NMR measurements have shown that this polymer adsorbs more intensively on laponite than PEO. This different conformation and adsorption on laponite of the added polymer would change structural such as rheological properties of the hydrogels.

Whereas the increase in concentration of a polymer such has PEO seems to "break" laponite gels, the increase of concentration of POXAZ seems to display a different behavior. At fixed laponite concentration and at low POXAZ concentration (below 0.63%), the addition of polymer decreases G' modulus and seems to break laponite hydrogel like PEO. Over this value, it seems to increase G'.
562 - Bromomaleimide as a basis for polymersomes forming copolymer conjugation for both cell imaging and lineactant purposes

Jens Gaitzsch¹,², j.gaitzsch@ucl.ac.uk, Eloise Morecroft¹, Lea Messager¹,², Monika Magon¹,², Guiseppe Battaglia¹,². (1) Department of Chemistry, University College London, London, United Kingdom, (2) MRC/UCL Centre for Medical Molecular Virology, University College London, London, United Kingdom

Nature uses a broad range of structures and assemblies to perform its tasks within a living environment. Amongst them, the vesicle is of our interest which can be mimicked using amphiphilic block-copolymers forming polymer vesicles, or polymersomes. Besides other challenges, the synthesis of complex polymer structures, such as multi block-copolymers or fluorescently labelled polymers are of major interest in this field.

**Figure 1**: (A) Monomers used, (B) Bromomaleides applied to synthesise (C1) PEG/PMPC/PDPA miktoarm stars acting as (D) lineactant for domains as well as (C2) dye labelled PMPC-PDPA block-copolymer chains enabling (E) cell imaging.

Interesting enough, both objectives can be reached using the same bromomaleimide chemistry as a basis (B). Essentially, the bromine atoms can be substituted by thiols in a controlled and quanititative fashion as reported by the Caddick group. In our case, we substituted hydrophilic (PMPC) and hydrophobic (PDPA) polymers onto the maleimide core. Another core feature of the bromomaleimides used in this study is their activated imide site, which can be substituted by amines – in our case PEG-NH₂. Using these three simple steps, a highly functional PEG/PMPC/PDPA (C1) mikto arm star block-copolymer was created and proved to act as lineactant to stabilise domains in patchy polymersomes. (D)

Similarly we show that a suitable linker molecule between a thiol functionalised PMPC-PDPA block-copolymer and a dye molecule carrying an amine functionality enabling cell imaging. (C2, E)
563 - On bead combinatorial DOTA modifications for molecular imaging tool development

Jaspal Singh, jaspal.singh@utsouthwestern.edu, Roberta Napolitano, Todd Soesbe, Dean Sherry, Gomika Udugamasooriya. 
Department of Advanced Imaging Research center, University of Texas Southwestern Medical Center, Dallas, Texas 75390, United States

Magnetic Resonance Imaging (MRI) is one of the most important diagnostic tools in clinical medicine today; and DOTA is an enormously applied contrast agent in the imaging arena. Sensitivity of an MRI agent is highly dependent on the rate of water exchange between the inner sphere of a paramagnetic ion and bulk water, which is predominantly controlled by the physio-chemical environment around the DOTA-metal complex. We report here a rapid and economical on-bead combinatorial synthesis methodology to couple peptoid units onto three side arms of DOTA (the other arm is used to attach DOTA onto the resin), in order to introduce these various physio-chemical characteristics such as electronic effects, hydrophobicity, polarity and steric bulkiness, examining how these modifications influenced the rate of water exchange between bulk water and Ln(III)-DOTA.

In our first approach, peptoid modifications onto three free DOTA side arms were probed for CEST-MR imaging using the synthesized 80 compound peptoid-DOTA library. The whole library was imaged by placing it inside a 63 mm diameter quadrature volume coil of Varian 9.4 T animal imaging system. Interestingly, the single CEST image of the on-bead library allowed describing the chemical features of a ligand that most influence water exchange rates. In the second approach, a unique strategy was developed to couple variable peptoid units onto all four arms of DOTA (or Cyclen) while those holding the DOTA onto the resin. In addition, various peptoids with different linker lengths were scrutinized under different reaction conditions to selectively obtain one and two DOTA-arms modifications as well. Eventually, desired peptoid modifications onto DOTA arms were synthesized on-bead and probed to compare the CEST imaging with the previous approach in order to obtain a better MRI agent.
564 - Biodegradable polyoxazoline based nanoparticles as a drug carrier

**Mengmeng Zong**, mengmeng.zong@dsm.com, **Aylvin Dias**, Vanessa Andrés Guerrero, Rocio Herrero Vanrell, Beatriz de las Heras. (1) DSM, Geleen, The Netherlands, (2) Department of Pharmaceutical Technology, Universidad Complutense de Madrid, Madrid, Spain, (3) Department of Pharmacology, Universidad Complutense de Madrid, Madrid, Spain

**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). Micelle 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(caprolactone)-b-poly(2-ethyl-2-oxazoline)-b-poly(caprolactone) (PCL-PEtOz-PCL) for intravitreal injection. The potential of PCL-PEtOz-PCL micelles as carriers for dexamethasone was evaluated by estimating the loading efficiency. A the end, to ensure that the materials studied are appropriate for biomedical application, the cell cytotoxicity of the micelle was evaluated using macrophages cell RAW 264.7.

**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 of acrylic acid after polymerization. Secondly, mono thionic acid PCL block were synthesized by ring opening polymerization and termination group was modified 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 solution 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>
<tr>
<th>MW (NMR)</th>
<th>MW (GPC)</th>
<th>PDI (GPC)</th>
<th>Particle size (DLS) nm</th>
<th>PDI (DLS)</th>
<th>CMC (mole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1K-2.1K-1K</td>
<td>3720</td>
<td>1.3</td>
<td>61.4</td>
<td>0.18</td>
<td>1,25×10-7</td>
</tr>
</tbody>
</table>

Dexamethasone loading into PCL-PEtOz-PCL micelles occurred simultaneously with self-assembly of block copolymers into micelles. Polymer micelles of PCL-PEtOz-PCL block copolymer exhibited a remarkable capability for carrying dexamethasone. Up to 14.86 wt% of drug was successfully loaded into nanoparticles. No precipitated drug crystals were observed and a clear aqueous solution was obtained, and the particle sizes were in a range of 86 nm with a narrow size distribution (PDI = 0.12). In addition, the biocompatibility of the micelles was investigated macrophages cell RAW 264.7. Study of the MTT assays showed that PCL-PEtOz-PCL micelles were quite biocompatible because they showed minimal influence on cell viability in a concentration of up to 1 mg mL⁻¹.

**CONCLUSION**

In conclusion, we have successfully synthesized a block copolymer micelle system that are show good biocompatibility as drug delivery vehicles. Dexamethasone was successfully loaded into PCL-PEtOz-PCL micelles up to 14.86 wt%. These results suggest that PCL-PEtOz-PCL micelles can be regarded as promising carriers for dexamethasone.

**REFERENCES**

1. C. Gómez-Gaete et al., Int. J. Pharm. 331 (2007), 153-159
2. R. Luxenhofer et al., Biomaterals, 2010 (31), 4972-4979
3.a) WO2007/028612 (b) WO2010/ 070132 A.A. Dias et al.
4.US201110223206A1, J. Lebouille et al.

**ACKNOWLEDGMENTS**

The authors acknowledge European Union (7th Research Framework Programme: PANOPTES/246180) for providing financial support to this project.
565 - Thermal and mechanical analysis of anthracene-filled epoxy nanocomposites

Jamie M Messman, jmessman@kcp.com, Sabrina M Wells, Somnath Sarkar, Daniel E Bowen, Theresa Morris. Materials Engineering, Honeywell FM&T, Kansas City, MO 64147, United States

Due to a combination of high strength and lightweight, epoxy nanocomposites are exceedingly useful in aerospace, automobile, electronic and sporting equipment applications. These materials are increasingly important for mesoscale requirements in order to manage discrepancies between the thermal expansion coefficient and reinforcement and macroscale requirements to alleviate residual stresses resulting from volume changes in real-life materials used. Favorable interactions between the matrix and filler generally lead to enhanced physical (thermal and mechanical) properties, which can be further tailored by the shape and size of the nanofiller and the quality of the dispersion. In general, mixing of components is unfavourable due to the loss of entropy; however, entropy loss can be overcome by making one (or both) of the components more similar to each other. In this case, an epoxy matrix (Epon 828) is cured with a multi-functional amine (EPICURE 3270). To generate the nanofilled composites, we use anthracene, a polycyclic aromatic hydrocarbon (PAH), to tailor physical properties. PAH incorporation is achieved by physical blending or through reactive mixtures. For reactive mixtures, Epon 828 is modified with 2-aminoanthracene and subsequently cured with the un-bound PAH. In this vein, 2-aminoanthracene reacts with some of the epoxy groups, which in turn, chemically modifies the matrix and subsequently provides interactive sites for the nanofiller to form stronger physical interactions with the matrix. Our results show strong reinforcement through the enhancement of the glass transition temperature (Tg) and degradation temperature at a critical volume of anthracene/2-aminoanthracene incorporation. We also observe varying thermal expansion and contraction by Thermomechanical Analysis (TMA).
Polypropylene (PP) based materials is one of the most versatile plastics with wide applications in various aspects of daily life because of lower production cost and environmental impact. Polymer/inorganic nanocomposites have opened new application areas of polymer material. However, low light and thermal stability is the problems for the long-term usage of PP. PP composite promotes volatilization of the antioxidant from the filler/matrix interface. Therefore, the addition of various antioxidants is essential in order to obtain practical lifetime. The efficiency and the reduction of physical loss of antioxidants, such as volatilization and leaching from PP matrix are important. This study focused on a long-term stability of PP materials, which strongly depends on the lifetime of antioxidants. It was found that the lifetime of the PP and PP nanocomposites (PP/SiO$_2$) is greatly elongated by the addition of hyperbranched bis-MPA polyester-16-hydroxyl, generation 2 (G2-HBP) or hyperbranched bis-MPA polyester-64-hydroxyl, generation 4 (G4-HBP) as a molecular capsule of antioxidants.

HBP significantly suppressed the volatilization of the antioxidants without compromising the mobility of antioxidant. This efficiency strongly depends on the generation of HBP. The addition of HBP in the presence of SiO$_2$ elongated the oxidation induction time (OIT) more than that in the absence of SiO$_2$, indicating the high efficiency for PP nanocomposites. HBP might be grafted to SiO$_2$ surfaces and highly dispersed in PP matrix. The merit of this method is to improve the efficiency of the conventional antioxidants, which makes the synthesis new antioxidants unnecessary.
Polypropylene (PP) has been widely used in various industrial fields because of its wide variety of characteristics. However, the oxidative degradation of PP easily proceeds, which leads to poor mechanical properties. Generally, the degradation starts from the reaction by alkyl radical, and proceeds according to the 'auto-oxidation mechanism'. Once radical is formed, it reacts with oxygen to make peroxide radical and re-generate new radicals. The oxidative degradation mechanism of PP has been studied by many researchers. However, the mechanism of initial radical formation still remains unclear. If it becomes clear, it can be expected to get quite effective information on PP stabilization. The objective of this study is about the initial radical formation. Propylene polymerization was carried out using industrial Ziegler-Natta catalyst under various conditions to find the possibility. The oxidation induction time (OIT) of PP was evaluated by chemiluminescence (CL) analysis because CL analysis is one of the most sensitive techniques to detect the initial stage of the oxidative degradation. Increased concentration of cocatalyst causes decrease of OIT.

In addition, triethylaluminum (TEA) having short alkyl groups compared with triisobutylaluminium (TIBA) and tri(n-octyl)aluminium (TNOA) showed the lowest OIT due to high reactivity of TEA for the catalyst. It is highly possible that the initial radical formation is caused by the reaction of catalyst and cocatalyst during polymerization.
568 - WITHDRAWN
The emphasis on sustainable energy has brought with it challenges associated with materials performance. In particular, geothermal wells push the boundaries of elastomer stability due to harsh environmental conditions, where temperatures around 300°C and pressures of 5000 psi or greater are not uncommon. Additionally, well brines and drilling fluids subject these materials to very severe chemical environments which also impacts elastomer degradation and stability. The aim of this study is to understand how commercially available elastomers perform under geothermal well-like conditions and make recommendations to the community based on these results. This poster will highlight the mechanical performance of several elastomers after aging at elevated temperature, pressure, and in well brine solution.

O-rings of various material types subjected to a “drilling fluid” mimic with pH 9–10 for 7 days at 300°C.
570 - Crack growth mechanism of natural rubber under fatigue loading studied by a real-time crack tip morphology monitoring method

Gengsheng Weng$^{1,2}$, wenggengsheng@nbu.edu.cn, Hong Yao$^{1,2}$, Aijun Chang$^{1,2}$, Kun Fu$^{1,2}$, Yanpeng Liu$^{1,2}$, Zhong-Ren Chen$^{1,2}$. (1) Department of Polymer Science and Engineering, Ningbo University, Ningbo, Zhejiang 315211, China, (2) Key Laboratory of Specialty Polymers, Grubbs Institute, Ningbo University, Ningbo, Zhejiang 315211, China

The present paper presents the crack growth behavior of vulcanized natural rubber under fatigue loading. Our research focuses on the crack tip morphology evolution and its relationship with crack growth rate. For this purpose, an original real-time monitoring apparatus is employed to capture the crack tip morphology during standard fatigue testing. This method involves the use of a high speed microscopic camera and a dynamic mechanical analyzer with crack growth testing function. The tear energy ($T$) dependence of crack tip morphology is analyzed. It reveals that there are two characteristic cracking morphologies: at $T < 600$ J/m$^2$, the power law slope of crack growth rate ($dc/dn$) versus $T$ is 6. Surface peeling at the crack-front surface occur, which result in the appearance of secondary cracks; at $T > 600$ J/m$^2$, the power law slope of $dc/dn$ versus $T$ is 2. The breaking-up of ligaments seems to be the mechanism of crack propagation. The result can be seen in Figure 1.

This work gives us new opportunities to study the crack growth mechanism of rubbers in the viewpoint of real-time crack tip morphology investigation.
571 - Stability towards γ-radiation of nanoscale enrichment polymer layers

Nikolay Borodinov\textsuperscript{1}, nikolab@g.clemson.edu, James Giammarco\textsuperscript{1}, Neil Patel\textsuperscript{2}, Igor Luzinov\textsuperscript{1}. (1) Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, United States, (2) Microphotonics Center, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Enrichment polymer layers (EPLs), which are capable of absorbing a number of chemical substances from the environment, are known to significantly increase the sensitivity of chemical sensors. For a certain applications those devices have to retain their analytical performance under aggressive environment including different types of radiation. To this end, we studied stability towards γ-radiation of nanometer-scale enrichment layers based on polyglycidyl methacrylate (PGMA). Specifically, radiation stability of PGMA and PGMA grafted with polystyrene (PS) EPLs was evaluated. The samples were subjected to doses of 1, 5, and 15 Mrad of 60\textsuperscript{Co} γ-radiation. It was demonstrated that all of the films studied retained their swelling (enrichment) ability even after 15 Mrad irradiation. Thus, the layers are sufficiently stable for operating as an active EPL in harsh environment such as Van Allen belt exposure for orbiting satellites or in the vicinity of high radiation nuclear facilities. However, increasing dose of radiation led to cross-linking of PGMA, elimination of carbonyl groups, and creation of carbon-carbon double bonds/hydroxyl groups. Comparison of FTIR spectra of PGMA/PS and PGMA films demonstrated better resistance towards γ-radiation for PGMA/PS films.
572 - Modeling of spatially dependent oxidative degradation

Adam Quintana, adaquin@sandia.gov, Nicholas Giron, Mathew Celina. Materials Characterization and Performance, Sandia National Laboratories, Albuquerque, NM 87185-1411, United States

For improved polymer lifetime predictions it is necessary to establish relevant correlations between physical property changes and oxidative chemistry as well as to extrapolate relatively slow oxidative reactions to lower temperatures. Significant challenges in lifetime extrapolations to lower temperatures, such as in mechanical strength or bulk modulus, also exist because oxidative reactions are spatially variant, and thus lower temperature behavior may exhibit dissimilar thermal dependence in specific polymer property changes as a function of sample geometry and material transitions.

Simple 1D localized oxidative degradation models have been available via kinetic or DLO models for many years. As an extension of this work, we have succeeded to predict spatially resolved degradation processes for layered materials in 2-dimensions, and 3D where symmetry is valid, using Galerkin FEM approaches to accommodate boundaries or material transitions, i.e. step changes in oxygen permeation and similar parameters. Elastic modulus can then be spatially predicted when oxidative correlations from non-DLO conditions exist. Oxidation rate pressure dependence also affects permeation experiments, which have been demonstrated as a method for deducing the rate-pressure dependence through spatially resolved simulation. Analytical treatment of the spatial differential equation is shown to yield a solution for the total O2 flux as a function of oxidation rate and oxygen permeation, which has not been previously demonstrated.
573 - Phosphorous-filled nanobrick wall multilayer thin film eliminates polyurethane melt dripping and reduces heat release associated with fire

Tyler Guin\(^1\), tylerguin@tamu.edu, Amanda Cain\(^1\), Craig Nolen\(^1\), Yu-Chin Li\(^2\), Rick Davis\(^2\), Jaime Grunlan\(^1\), jgrunlan@tamu.edu. 
(1) Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States, (2) Flammability Reduction Group, National Institute of Standards & Technology, Gaithersburg, Maryland 20899, United States

Unique trilayer (TL) thin films of sodium montmorillonite (MMT), poly(allylamine hydrochloride) (PAH) and poly(sodium phosphate) (PSP) are prepared via layer-by-layer (LbL) assembly. This three-component nanocoating completely shuts down melt dripping and reduces heat release of open-celled flexible polyurethane (PU) foam when exposed to direct flame due to a synergistic interaction between PSP and the thermally shielding clay platelets in the condensed phase. Post burn scanning electron microscopy reveals the nanocoating's swollen morphology is able to maintain foam shape, cellular structure, and porosity. Cone calorimetry reveals that 4 TL coated foams

---

**Monday, August 11, 2014 08:00 PM**
Sci-Mix (08:00 PM - 10:00 PM)
Location: Moscone Center, North Bldg.
Room: Hall D

---

**Tuesday, August 12, 2014 06:00 PM**
Polymer Degradation, Performance and Ultimate Stability (06:00 PM - 08:00 PM)
Location: Moscone Center, West Bldg.
Room: Exhibit Hall
574 - Synthesis of silica dispersant through combination of living anionic polymerization and controlled radical polymerization

Taeheon Lee¹, taeheon.lee@pusan.ac.kr, Jong-yeop Lee¹,³, Kihyun Kim², Byunghee Kim¹, Gwanghoon Kwag³, Jae-yun Kim³, Sangchul Ji³, Wonho Kim², Hyun-jon Paik¹. (1) Department of Polymer Science and Engineering, Pusan National University, Busan, Korea ASI KR KS012, Republic of Korea, (2) Department of Chemical Engineering, Pusan National University, Busan, Korea ASI KR KS012, Republic of Korea, (3) R&B Center, Kumho Petrochemical, Daejeon, Korea ASI KR KS015, Republic of Korea

As filler, silica particles are used to reduce rolling resistance of tire with SBR matrix which not only enhances fuel efficiency but also improves tire physical properties such as traction and abrasion. However, silica dispersion within SBR is hampered by polarity difference. To overcome this problem, silica dispersants such as an amphiphilic block copolymer were added to the SBR/silica compound.

Therefore we synthesized \( p(\text{styrene-r-butadiene})-b-p(\text{poly(ethylene glycol) methyl ether methacrylate}) \) \( (p(\text{SB-b-PEGMA})) \). And the improved properties induced by the improved silica dispersion were verified by applying the method to SBR/silica compounds. Prepared \( p(\text{SB-b-PEGMA}) \) were characterized by GPC and \(^1\)H NMR. The SBR 1739/silica compounds with the applied silica dispersant exhibited higher moduli at 100% and 300% elongation, higher degrees of cross-linking density, and better wear resistances than the SBR/silica compounds without any silica dispersant. From the Payne effect analyses, we determined that the SBR 1739/silica compounds with the applied silica dispersant had lower \( \Delta G' \) compared to the SBR 1739/silica compounds without any silica dispersant. The TEM measurements also indicated that the SBR/silica compounds containing the silica dispersant showed better dispersion. Therefore, we could confirm that the silica dispersant assisted in the reduction of silica flocculation in the silica-filled SBR compounds.

synthesis of \( p(\text{SB-b-PEGMA}) \)
575 - Grafting multi-block copolymers by "click" chemistry for overcoming the membrane permeability/selectivity trade-off: Application to butanol biofuel recovery from dilute aqueous solution

Vijay Kumar, Carole Arnal-Herault, Miao Wang, miao.wang@univ-lorraine.fr, Jérôme Babin, Anne Jonquières. Laboratory LCPM FRE 3564, ENSIC, University of Lorraine/CNRS, Nancy, Lorraine 54000, France

Butanol is an attractive renewable biofuel offering several specific advantages compared to bioethanol such as higher energy content, lower vapor pressure and lower hydrophilicity for fuel formulations. Nevertheless, in the related Acetone-Butanol-Ethanol (ABE) fermentation process, the butanol content is limited to ca. 2 wt% to avoid cytotoxicity for the bacteria. With this respect, the recovery of butanol from fermentation broth is a real challenge for the bioindustry. Membrane processes including pervaporation have been identified as key technologies for this application. In this work, grafted multi-block copolymer membranes were developed for the continuous extraction of butanol from dilute aqueous solution. The "click" grafting of alkyne-functionalized poly(siloxane-urethane-urea) copolymers with azido-polydimethylsiloxane (N3-PDMS) led to different membranes with increasing PDMS contents. The membrane properties were assessed for butanol recovery during sorption and pervaporation experiments with dilute aqueous solution at 50°C. An analysis in terms of structure-property relationships showed that PDMS grafting enabled to increase both membrane permeability and selectivity at the same time. These grafted multi-block materials thus overcame the usual permeability/selectivity trade-off. In addition to being amongst the best polymer membranes reported for this application, these copolymers have the advantages of physical cross-linking and improved processability compared to chemically cross-linked PDMS. Therefore, their unique membrane properties offer great potential for butanol recovery by fermentation/pervaporation coupling in the biofuel industry.
576 - Influence of polymer interdiffusion and clay concentration on gas barrier of polyelectrolyte/clay nanobrick wall quadlayer assemblies

Ping Tzeng\(^1\), pingtzengg@gmail.com, Cale R Maupin\(^2\), Jaime C Grunlan\(^2\). (1) Chemical Engineering, Texas A&M University, College Station, TX 77843, United States, (2) Mechanical Engineering, Texas A&M University, College Station, TX 77843, United States

Thin film assemblies of polyvinylamine (PVAm), branched polyethylenimine (PEI), poly(acrylic acid) (PAA) and sodium montmorillonite (MMT) clay, created using the layer-by-layer assembly technique, demonstrate the influence of polymer interdiffusion and clay concentration on oxygen barrier behavior. These quadlayer (QL) assemblies can be switched from linear to exponential growth by varying the placement of PVAm and PEI layers. PEI has a much lower T\(_g\) and is better able to interdiffuse with PAA, resulting in exponential growth and greater clay deposition in each layer. When deposited on 179 \(\mu\)m poly(ethylene terephthalate) (PET), these 'nanobrick wall' thin films only decreased visible light transmission by 2% as the thickness increased by a factor of 10, indicating that clay platelets are highly oriented and well separated. Atomic force and transmission electron microscope images also reveal this high level of clay orientation that creates an extended gas diffusion pathway that dramatically reduces oxygen transmission rate (OTR). A 6QL PVAm-based assembly, with a thickness of 175nm, has an OTR of 0.009 cm\(^3\)/(m\(^2\)×day×atm). OTR was found to be linked to both the degree of polymer interaction and clay concentration in these thin films. The desired barrier can be obtained by substituting PVAm layers for PEI. This study demonstrates a promising technique for tailoring the gas barrier of polymer/clay composite thin films that could find use in flexible electronics and food packaging.
Ultrafiltration of surface water by poly(vinylidene fluoride) (PVDF)/TiO₂ mixed matrix hollow fiber membranes (HFM) with advanced antifouling properties under ultraviolet (UV) light irradiation

Xiaofeng Wang¹, xiaofengwang666@gmail.com, Jun Yin², Baolin Deng¹,², dengb@missouri.edu. (1) Department of Chemical Engineering, University of Missouri-Columbia, Columbia, Missouri 65211, United States, (2) Department of Civil & Environmental Engineering, University of Missouri-Columbia, Columbia, Missouri 65211, United States

TiO₂, a hydrophilic and ultraviolet (UV) light-active photocatalyst, was applied to prepare poly(vinylidene fluoride) (PVDF)/TiO₂ mixed matrix hollow fiber membranes (HFM) by the phase inversion method. The membranes were characterized by scanning electron microscopy (SEM), attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy, contact angle measurement, and UV-Vis absorbance. The membranes' performances for treating surface water were evaluated based on the water flux, humic acid (HA) rejection and total organic carbon (TOC) rejection in surface water. The results showed the hydrophilicity as well as water flux of the mixed matrix membranes was significantly improved under UV light irradiation when compared to original PVDF membranes. The as-prepared PVDF/TiO₂ mixed matrix membranes rejected over 40% of humic acid and 20% of TOC in a surface water sample, which were comparable to conventional PVDF membranes, but had much better antifouling properties.
This communication is concerned with the optimization of the neutralization dialysis process. This process is used for salt removal from a NaCl model solution, and a three-compartment membrane stack is typically used (acid, salt, and alkali compartments) with a cation-exchange membrane and an anion-exchange one, i.e. Neosepta® CMX and AMX respectively.

The desalination process has been investigated as a function of three main parameters, namely the initial concentration and the flux rate of acidic and alkaline solutions as well as the saline solution volume. A fractional factorial design, $2^{5-1}$, has been employed to assess the parameters affecting the desalination efficiency, and specifically to study the ion-exchange of $H^+$ and $Na^+$ through CMX and that of $OH^-$ and $Cl^-$ through AMX. A linear theoretical model based on the experimental results has been carried out to account for the influence of the different parameters investigated and their relative interactions. Variance Analysis (ANOVA), the F-test, and Student's test have shown that the interaction between acidic and alkaline initial concentration is the most statistically significant parameter affecting the ion transport through CMX and AMX.
579 - End group cross-linking of sulfonated polymer electrolyte membranes via click reaction

Na Rae Kang¹, cutedevilkin@hanmail.net, So Young Lee², Dong Won Shin³, Young Moo Lee¹. (1) Department of energy engineering, Hanyang University, Seoul, Republic of Korea, (2) Korea Institute of Science and Technology (KIST), Seoul, Republic of Korea

The development of novel polymer electrolyte membranes (PEMs) with high proton conductivity, good mechanical flexibility and less humidity dependence remains an important challenge to the realization of practical PEM fuel cells and other alternative energy applications. For this reason, various researches of hydrocarbon polymer membranes have been investigated as alternative PEM materials due to their excellent mechanical, thermal stability and high proton conductivity. However, their major problem, such as excessive water swelling and weak durability, are unsuitable to satisfy practical operations. Cross-linking is a simple and efficient method to reducing water uptake and also enhancing mechanical properties and dimensional stability.

In this study, end group cross-linking via 'click' reaction were introduced to highly sulfonated PEMs. Click reaction has the advantages such as short reaction time, a high yield and superior region selectivity. Thus, the method has been used to synthesize a wide variety of linear, branched and cross-linked polymer. Here we have focused on developing new materials that are capable of conducting protons under low RH conditions and show excellent long term stability. This method is one of the effective methods for highly sulfonated PEMs because end group cross-linking improves mechanical and chemical stabilities without loss of acid sites or chemical structure change of the polymer main chain. The click reaction functionalized end group cross-linked membranes are expected to be promising materials for various alternative energy applications.
580 - Morphological characterization of \((PS-PIB)_{2-s}-PAA_{x}\) miktoarm star polymers

Katrina M Knauer, katrina.knauer@eagles.usm.edu, Yaling Zhu, Robson F Storey, Sarah E Morgan. School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States

Miktoarm star polymers are a relatively new and unique class of macromolecules, which possess linear polymer chains of two or more different compositions radiating outward from a central branch point. Much emphasis has been recently placed in developing synthetic methodologies to these star polymers and examining their properties and phase-separated morphology as a function of arm composition and length. Morphology of miktoarm polymers has been shown to have a profound effect on their physical properties including mechanical, thermal, and diffusion. This work reports the morphologies of poly\([(styrene-b-isobutylene)_{2-s}-acrylic acid_{x}]\) \((PS-PIB)_{2-s}-PAA_{x}\) miktoarm star polymers with varying PAA content. Phase separation was characterized directly by transmission electron microscopy, quantum nanomechanical mapping via atomic force microscopy, and indirectly by dynamic mechanical analysis. These materials possess varying degrees of order within three-phase morphologies that contain elements of rods and lamellae that are arranged as a function of polyacrylic acid block composition in continuous polyisobutylene phases.
581 - Aging properties of polymers in support of through life assessment programs

Mogon Patel, mogon.patel@awe.co.uk, Anna Walmsley, Terrence Smith, Mathew Robinson. Materials Science, AWE, Aldermaston, Reading RG7 4PR, United Kingdom

Polysiloxanes, Polyurethanes and poly (ethylene-co-vinyl acetate) based materials are currently used for stress absorbing and alignment applications, as well as adhesive binders for specific filler particles. When used in specialised multi-material assemblies, these materials experience a complex ageing regime with potential for significant age related changes. A key objective of our studies is to understand the link between age related changes to the individual material and the potential impact on the assembly as a whole.

This paper reports on our ageing and life assessment strategy. Our testing for zero time properties and quantifying age related changes of critical properties, together with sensitivity studies, will be reported. Figure 1 shows a typical example of changes in material performance with storage age where the black line is the zero time response and the arrow/box the manufacturing specification limits.

The green line represents behaviour outside the specification limits with potential for significant impact on the system performance. This paper also details options to mitigate against age related change and extend life.
582 - Predicting multi-material aging and degradation using reactive transport modeling

Elizabeth A Glascoe, glascoe2@llnl.gov, Stephen J. Harley, Yunwei Sun. Chemistry Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, United States

Predicting the aging and degradation of polymeric materials is important to almost every industry (e.g. automobile, food packaging, defense applications, satellites, biomedical, etc.). One key challenge with many prediction methods is the fact that materials are usually assembled and used as multi-material assemblies. Hence, we need a tool sophisticated enough to predict the aging of the assembly, and, specifically, long term compatibility issues of multiple materials in contact with each other and with the surrounding environment. We are developing a computational tool for simulating the aging and chemical compatibility of multiple material assemblies. Our model includes (1) a triple-mode sorption model that includes absorption, adsorption, and pooling of species, (2) molecular diffusion, and (3) chemical reaction kinetics. Using a 1D or 3D mesh we can simultaneously simulate the transport and chemical reactions of mobile species through polymeric materials. This talk will discuss our approach and our progress to date, which will include, model development and experimental work using polymeric systems to parameterize and validate the model.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Wednesday, August 13, 2014 09:00 AM
Polymer Degradation, Performance and Ultimate Stability (08:30 AM - 12:05 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
583 - Assessment of electrical cable condition monitoring methods

Stephanie Watson, stephanie.watson@nist.gov, Deborah Stanley, Neil Redeker. Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

Premature electrical cable failures in nuclear power plants (NPPs) have been observed which have raised questions about long-term performance of electrical cables and renewed interest in investigating the service life of electrical cables. For new NPPs, assessing the integrity of electrical cables generates new concerns, which arise from the global nature of the cable market and from changes taking place in new construction of NPPs. From these studies, it has been concluded that for both new and existing NPPs, research is lacking for determining aging mechanisms of low voltage cables exposed to high RH and wet (submerged) conditions and for high voltage cables and new electrical cables subjected to temperature/radiation/wet conditions and validating methodologies for predicting the service life of electrical cable. In this paper, we will describe our research program on cable condition monitoring and discuss results from a set of condition monitoring methods as a function of degradation on polymer cable insulation.

EXPERIMENTAL DESIGN

CONDITION-BASED QUALIFICATION METHODOLOGY
A high-throughput chemiluminescence instrument was developed, which enables the in-situ observation of oxidative degradation for 100 samples under controlled circumstances. The instrument was employed to study relationships between molecular structures of various anti-oxidants and their performances in stabilizing polypropylene.
585 - Challenges in lifetime control of oxo-degradable polyolefins and oxo-biodegradable blends

Graeme A George¹, g.george@qut.edu.au, Melissa Nikolic¹, John Colwell¹, Chun-Liang Yeh¹, Steven Bottle¹, Bronwyn Laycock², Gregory Cash², Emilie Gauthier², Peter Halley². (1) School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, Queensland 4000, Australia, (2) School of Chemical Engineering, The University of Queensland, St Lucia, Queensland 4072, Australia

There is dispute over the relative merits of oxo-degradable and biodegradable polymers in applications where lifetime control is required. While considerable attention has been paid to litter and the ultimate degradability of plastic items, precise control of the time taken to degrade and lose mechanical properties has been considered of less importance than biodegradability as given by the rate of production of carbon dioxide. One of the more challenging applications for controlled lifetime degradable polymers is thin, transparent agricultural crop propagation films which are partly buried and stretched to form a mini-greenhouse and so enable early germination and growth. Degradation must be synchronized with the emerging crop as shown below for the ideal case (a) compared to where degradation has occurred either too slowly (b) or too quickly (c):

Oxo-degradable polyolefins based on photo-initiation and accelerated hydroperoxide decomposition through transition metals fatty acid additives provide the best control of above-ground degradation. Biodegradable polymers such as aliphatic (PHA and PLA) and mixed aliphatic-aromatic (PBAT) polyesters offer superior below-ground degradation but the two systems are often antagonistic and do not form compatible blends. Furthermore the photochemistry of humic acids in the soil may accelerate photo-oxidation of the polyolefins so that the photodegradation may not be simply modelled. This application is one where the best attributes of both oxo-and bio-degradable polymers are required and the challenges in meeting this are considerable.

Wednesday, August 13, 2014 10:00 AM
Polymer Degradation, Performance and Ultimate Stability (08:30 AM - 12:05 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
586 - Effects of highly structured low density carbon nanotube networks on the thermal degradation behavior of polysiloxanes

James P. lewicki, lewicki1@llnl.gov, Marcus A. Worsley, Theodore F Baumann, Harris E. Mason, Robert s. Maxwell. Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, United States

Carbon nanotube-carbon aerogel (CNT-CA) networks are a member of a novel class of ultra-low density, high surface area, carbon-based materials possessing unique physical properties. Through the incorporation of a polymer matrix into these aerogel systems it is possible to form intercalated polymeric hybrid CNT-CA composite materials with polymer to carbon surface internal contact areas in the order of 600 m²g⁻¹ at carbon loadings as low as 1.5 wt %. Reported here is the synthesis of a series of well-defined poly(dimethylsiloxane) (PDMS)/CNT-CA composite systems, their characterization and the in-depth analysis of the effects of the carbon architecture on the thermal stability and degradation behaviour of the PDMS matrix.

The results of degradative thermal analysis clearly demonstrate that the presence of the CNT-CA scaffold within the PDMS matrix greatly increases the thermal stability of the system and drives the matrix towards calcination at temperatures above 600°C. Subsequent characterization of the residual materials using a combination of nuclear magnetic resonance, energy dispersive X-ray spectroscopy (EDAX) and electron microscopy have demonstrated that the improvements in thermal stability are concurrent with the relative loading of carbon nanotubes within the aerogel matrix, that the PDMS matrix is being driven towards the formation of increased levels of SiO₂ on degradation and that the preferential calcination effect is a function of the unique high surface area fibular network structure of the CNT-CA monoliths.
587 - Heterogeneous oxidation of PDMS fluids at metal surfaces

**Todd M. Alam**, tmalam@sandia.gov, M. Kathleen Alam, Mathew Celina, Bredan L. Nation, Michael T. Dugger.

(1) Department of Electronic, Optical and Nano Materials, Sandia National Laboratories, Albuquerque, NM 87185, United States, (2) Department of Energetics Characterization, Sandia National Laboratories, Albuquerque, NM 87185, United States, (3) Department of Material Science, Sandia National Laboratories, Albuquerque, NM 87185, United States, (4) Department of Materials Reliability, Sandia National Laboratories, Albuquerque, NM 87123, United States

PDMS fluids and polymer are generally very stable and resistant to degradation. While oxidative degradation of PDMS materials is commonly observed at higher temperatures and under oxidative conditions, we have recently characterized accelerated degradation occurring at metal surfaces under vibrational or sliding contact conditions. While frictional degradation/polymerization of organic gases, solvents, fluids and lubricants has been known for over half a century, examples of frictional degradation in PDMS systems are rare. In this presentation we explore the oxidative degradation of PDMS fluids at different metal oxide surfaces in electrical contact alloys using NMR, IR and GPC. It is argued that the degradation is very heterogeneous in nature, and can occur rapidly in localized regions, and is impacted by the frictional/vibrational environments, the specific contact metals present, and the concentration of dissolved oxygen in the PDMS fluid. Different molecular level degradation mechanisms are explored, with spectroscopic evaluation of the different degradation species produced.
588 - Effects of nanofillers on polyurethane-polybutadiene multiblock copolymers and epoxy resins: Thermal, mechanical, and dielectric properties

Dan E Bowen¹, dbowen@kcp.com, Jamie M Messman¹, Eric A Eastwood¹, Sabrina M Wells¹, Somnath Sarkar², Nicola Bowler³.
(¹) Department of Materials Engineering, Honeywell FM&T, Kansas City, MO 64147, United States, (²) Department of Biochemistry, Chemistry & Physics, University of Central Missouri, Warrensburg, MO 64093, United States, (³) Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, United States

In order to impart utility to polymeric materials particularly in high performance applications, polymers are oftentimes compounded with particles that reinforce and improve properties. These particles include fibers, metal oxides, and engineered nanoparticles to name a few. Arguably the most important thermal property of a polymer is the glass transition temperature, which can be tailored through the incorporation of nanofillers that reinforce polymer chains at the molecular scale. Here we present two methods to enhance thermal properties of two different types of nanocomposites. In the first system, we use boron cage compounds to tailor rheology, thermal properties, and the dielectric spectrum of segmented polybutadiene/polyurethane-based multi-block copolymers. Upon incorporation of $n$-hexylcarborane, we observe plasticization of PU hard segments and reinforcement of PBD soft segments. Broadband dielectric spectroscopy reveals multiple relaxations consistent with glass transition measurements made via DSC and DMA.

In the second system, we evaluate the influence of small molecule nanofillers on thermal properties of an epoxy matrix. Here we observe that chemical modification of the epoxy matrix with an anthracene moiety combined with the inclusion of anthracene as nanofiller results in a substantial enhancement of thermal properties. The combination of matrix modification and nanofiller synergistically imparts increased degradation and glass transition temperatures, and interesting thermomechanical response. This cooperative effect manifests itself in distinct irreversible contraction upon thermal cycling even though the system is fully cured.

Wednesday, August 13, 2014 11:20 AM
Polymer Degradation, Performance and Ultimate Stability (08:30 AM - 12:05 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 6
589 - Oxygen diffusion through polymers at elevated temperature

Mathew C Celina, mccelin@sandia.gov, Adam Quintana, Nicholas Giron. Sandia National Laboratories, Albuquerque, NM 87185-1411, United States

Thermal performance of polymers and degradation under oxidative conditions depends on oxygen permeation. Prediction of spatially dependent polymer degradation with DLO models or related degradation mechanistic kinetic models for lifetime extrapolations, require input of oxygen diffusivity, solubility, or overall permeability at elevated temperature. Unfortunately, such data are not always available and basic physical transport measurements can be convoluted by 'reactive chemistry' loss of oxygen. Often estimations are made from indirect measurements or theoretical approaches. This presentation will focus on the optimization of experimental approaches and data extraction, which can now be applied to characterize thin films of low permeable polymers. Checks and corrections for oxidative chemistry during the experiment can be accommodated. The O₂ permeation features of a few epoxy thermo-set materials, Kapton, and polypropylene between 25 and 140°C were investigated with time-dependent flux measurements and are being compared to offer data, which so far have not been available in the literature. Interestingly, the glass transition of Epon 828/D230 epoxy at 95°C has a significant effect on the permeability, but not the diffusion constant in an Arrhenius plot.
This talk will focus on various routes towards cyclic and catenated polymers by ATRP. The eventual goal is to develop a series of chemistry toolboxes that is useful for the synthesis of even complex and knotted polymers. The use of living free radical methods such as ATRP is useful for making monodispersed chains and block copolymer routes towards functional materials. Specifically, the challenge is to observe high yield synthesis methods with architecture and composition control. By modification of ATRP in to atom transfer radical cyclization (ATRC), it is possible to obtain cyclic and catenated polymer architectures and compositions. Reversible addition fragmentation chain transfer (RAFT) is also a viable approach towards this topologically interesting macromolecules. The utility of cyclic and catenated polymer structures have yet to be fully exploited because of lack of samples in terms of their physical properties. This talk will also summarize some of the future possibilities.
591 - Amphiphilic block copolymers prepared using two controlled radical polymerization methodologies and click coupling

Tsung-han Tsai¹, Huseyin Tas¹, Eiji Nakamura², Kikuo Arimoto², Toshio Suzuki², E. Bryan Coughlin¹, 
Coughlin@mail.pse.umass.edu. (1) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01002, United States, (2) Research and Technical Center, Kuraray America, INC, Pasadena, TX 77507, United States

Controlled radical polymerization methodologies provide both a means to prepare targeted molecular polymers with narrow dispersity as well as specifically designed end-groups as a consequence of the initiator, or chain-transfer agent, employed for the synthesis. Atom-Transfer Radical Polymerization (ATRP) of styrene, followed by the nucleophilic substitution of the benzyl bromide end-group with an azide anion gave PS-N₃ samples. A novel alkyne functionalized xanthate has been used in the Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization of vinyl acetate to prepare poly(vinyl acetate) end functionalized with an alkyne, PVAc-CCH. Azide alkyne Huisgen cycloaddition reactions were used to efficiently couple PS-N₃ with PVAc-CCH. The 1,2,3-triazole junction between the PS and the PVAc segments was found to be robust to hydrolysis under the alkaline conditions required to effect the conversion of PS-b-PVAc to the corresponding amphiphilic polystyrene-b-poly(vinyl alchohol). The copolymers PS-b-PVAc and PS-b-PVOH form well-ordered bulk and thin film morphologies. The preparative and characterization aspects of these copolymers will be discussed.
A new type of supramolecular thermoplastic elastomer is reported, consisting of oppositely charged oligomeric ABA-type triblock copolymers with an uncharged hydrophobic middle block and charged outer segments. The polymers were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization using a bifunctional chain transfer agent. Separately these polymers behave as viscous liquids, but when mixed together a supramolecular network is formed through electrostatic interaction between the oppositely charged segments. The charged blocks are phase-separated from the uncharged block in a cylindrical structure that was observed by Transmission Electron Microscopy (TEM). Thermal and mechanical analysis of the material using Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and rheology shows that the charged sections have a glass transition temperature ($T_g$) close to room temperature, but that the material has elastomeric properties at temperatures far above this $T_g$. 

Figure 1: Mixing of oppositely charged triblock copolymers causes the charged segments to associate and form supramolecular cross-links in the material. This results in a phase-separated thermoplastic elastomer.
Pentafluorostyrene (PFS) is an intriguing monomer and has turned out to be an indispensable tool in the architecture of various functional materials. The ATRP merits with pentafluorostyrene were revealed a decade ago and since then especially the lability of the para-fluorine of pentafluorostyrene has been exploited by the nucleophilic substitution methodology to create numerous other monomers. Two very recent applications have exploited short alkyne initiated poly(pentafluorostyrene)s.

The first example is development of polyelectrolyte materials comparable to the industrial fuel cells standard Nafion®. Our solution to this polyelectrolyte challenge is the combination of a thermally and chemically very stable backbone PSU ($M_n \approx 40,000$ Da), which is also an excellent film forming material, with poly(pentafluorostyrene) grafts that additionally ensures high thermal stability as a very promising scaffold for phosphonates for polymer electrolyte membranes. This design idea was executed by use of CuAAC, where clickable azides were fabricated on the PSU (7 mol%) through lithiation chemistry at low temperature introducing first chloromethyl followed by conventional conversion of chloro groups to azides by sodium azide treatment. After clicking the two components together the poly(pentafluorostyrene) grafts were phosphonated. Graft copolymer (PSU-g-PhPFS) membranes could be cast that showed high thermal stability and proton conductivity. Soft silicone elastomers are materials in demand for actuators or energy production e.g. through wave harvesting. Functionality can be introduced to the commercially available silicone formulations by use of functional cross-linkers. In this particular case a short PFS-A was “clicked” to the cross-linker. A poly(pentafluorostyrene) enrichment of the surface of the cured silicone elastomer was observed by a water contact angle (WCA) of 116° as opposed to a plane silicone elastomer with a WCA of 108°. This is in contrast to other applied functionalities that was shown by confocal microscopy to be evenly distributed throughout the elastomer matrix.
594 - Synthesis of star polymers by combination of controlled radical polymerization and sequential post-polymerization modification

Fenja Moldenhauer, Ryohei Kakuchi, Patrick Theato, theato@chemie.uni-hamburg.de. Institute for Technical and Macromolecular Chemistry, University of Hamburg, Hamburg, Hamburg 20146, Germany

We present a new synthetic route for the synthesis of miktoarm star polymers. Placing a single reactive maleimide unit in the middle or at the end of a polymer chain under nitroxide-mediate polymerization conditions allows a subsequent sequential post-polymerization modification with two end-functionalized polymers. This arm-first approach takes advantage of the defined sequence of conjugation chemistries comprised of an ester-amine conjugation and a Mitsunobu reaction.

This new route enables the linkage of amino-terminated and hydroxyl-terminated polymers onto a polymer chain that has been equipped with a single reactive moiety. Examples of stars along with the control of the arm-length and its chemistry will be discussed.
Polymerization-induced self-assembly (PISA) enables the direct synthesis of a range of well-defined block copolymer nano-objects in concentrated solution, without requiring any post-polymerization processing. PISA syntheses are conducted via dispersion polymerization: a soluble RAFT macro-CTA (e.g. based on water-soluble poly(glycerol monomethacrylate) or PGMA; see part (a) in the schematic cartoon shown below) is chain-extended using a second monomer (e.g. 2-hydroxypropyl methacrylate or HPMA; see part (b) shown below) that is miscible with the continuous phase but forms an insoluble second block. Microphase separation of this growing second block drives in situ self-assembly, while the soluble first block confers steric stabilization (see part (c) shown below). This approach is highly versatile; it can be conducted in water, alcohol or n-alkanes at up to 50 % solids and is applicable to a wide palette of (meth)acrylic monomers. Copolymer morphologies include spheres, worms, vesicles, frambooidal vesicles and lamellae. Phase diagrams can be constructed that serve as 'road maps' to enable the reproducible synthesis of the desired pure phase morphology. Selected PISA formulations will be presented and potential technological applications for this platform technology will be discussed.
596 - Controlled synthesis of tetra-arm star–block copolymers and fabrication of gel with homogeneous network structure

Katsuya Kida, Ryohei Ishige, Keita Sakakibara, Kohji Ohno, Yoshinobu Tsujii, tsujii@scl.kyoto-u.ac.jp. Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

"Tetra Gels" have been attracting much attention in the field of functional gel materials. These gels are synthesized from two different tetra-arm star polymers with cross-reacting functional group at the end of each arm, giving favorable properties, like high transparency, high mechanical-strength, bio-compatibility and so on, because tetrahedral geometry of the arms enable the cross-linking point to distribute homogeneously. In this study, tetra-arm star-block copolymer was designed to prepare physically crosslinked gels, where the microphase-segregated domains are crosslinking points. Therefore, the crosslinking domains can be visualized, enabling us to discuss, in more details, the relationships between the network structure and mechanical properties. Firstly, high-molecular-weight tetra-arm star-block copolymers were prepared by living radical polymerization in an ionic liquid and/or under high pressure condition. The molecular weight distribution was still narrow up to high molecular weight (10^6 g mol\(^{-1}\)). The transesterification reaction enabled us to cut the obtained these block copolymers into four segments and hence to precisely characterize the initiation efficiency of block copolymers. They were swollen with ionic liquids to form ionic gels. Finally, the mechanical properties and network structures were investigated by dynamic viscoelasticity and small-angle x-ray scattering (SAXS) measurements, respectively.
597 - Twisting RAFT polymerization to prepare functional polymers and materials

Renaud Nicolay, renaud.nicolay@espci.fr, Matière Molle et Chimie, ESPCI ParisTech, Paris, Paris 75005, France

Reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the most effective methods to control radical polymerization. The RAFT process relies on degenerative chain transfer between growing and dormant polymer chains, the latter containing a dithiocarbonyl moiety at one of their extremity at least. Structural parameters of the chain transfer agents (CTA) and experimental conditions that provide the best control for RAFT polymerization of a given monomer are now well known. However, by playing on those conditions and parameters, it is possible to extend the range of macromolecular architectures and functional materials accessible by RAFT polymerization. For example, addition of a metal catalyst to the system allows generating the active radicals directly from dormant species, thereby suppressing the need for an additional source of radical, such as AIBN. This feature is of great interest for the synthesis of very high molecular weight polymers. By adjusting the structure of dithiocarbonyl moieties usually employed in RAFT polymerization, it is possible to completely suppress their reactivity towards carbon radicals and thereby to use them as thiol protecting groups instead of CTAs. This approach was recently used to prepare polythiols. The dynamic covalent nature of dithiocarbonyl compounds can also be used to design responsive materials. Self-healing materials prepared with crosslinkers containing a group capable of RAFT will be presented to illustrate this concept.
Core-shell cylindrical polymer brushes (CPBs) with a PDMAEMA shell block were synthesized via a grafting-from process using ATRP. The polymer backbone was ruptured upon drying on solid surfaces, due to Coulombic interactions with the surface. Tuning the surface nature or pH controls this scission behavior. Thus, core-shell CPBs serve as a tool to directly compare the weak intermolecular forces with the strong carbon-carbon covalent bonds.

These brushes were employed as templates for the preparation of various rare-earth metal cations (Ln$^{3+}$) incorporated silica hybrid nanoparticles (NPs). The silica hybrid NPs obtain unique and diverse properties from the incorporated Ln$^{3+}$ ions, such as visible photoluminescence, paramagnetic behavior, and a longitudinal relaxation time ($T_1$) shortening effect. They can be applied as multimodal bioimaging probes.

Imitating the natural "energy cascade" architecture, we developed single-molecular, rod-like nano-light harvesters (NLHs) on the basis of CPBs. Herein, a number of block copolymer side chains carrying light absorbing antennae groups (9,9-diethylfluorene, energy donors) were tethered to a linear polymer backbone containing emitting groups (anthracene, energy acceptors). These NLHs provide very efficient energy transfer from antennae to energy acceptors. We manipulate the efficiency of energy transfer by tuning the distance between energy donors and energy acceptors in physical and/or chemical ways.
Cyclobutenes containing pendant groups of varying sizes were polymerized via ROMP using Grubbs catalyst 2nd generation. The polymerization of these new molecules proceeded with first order kinetics, consistent with a living, well-controlled reaction. The “living” nature of the polymerization was confirmed by chain extension experiments and by the synthesis of diblock copolymers with PDIs below 1.4. This is the first report of the synthesis of diblock copolymers using Grubbs catalysts and cyclobutene monomers. The rate of polymerization depended on the size of the pendant groups in the cyclobutene rings and it decreased as the pendant group size increased. Diblock copolymers of the new cyclobutene monomers and norbornene analogs were prepared with low PDIs. The synthetic methods in this report will allow access to new complex polymeric architectures with a higher density of pendant groups than those possible when using norbornene and cyclooctene derivatives as the starting materials.
Block copolymers have attracted much attention for use in a variety of applications over the last few decades. Choice of monomer and composition ratio of each block are known to influence resulting material properties. We engineered an ABC main-chain triblock copolymer, based on poly(styrene)-b-poly(norbornene)-b-poly(methyl methacrylate), polymerized via ring-opening metathesis polymerization and atom transfer radical polymerization; their morphology was also studied. In addition, we installed supramolecular end-groups via functionalized initiators during polymerization, imbuing complexity in the design of our multiblock copolymers.
601 - Iodinated polyesters as a versatile platform for radiopaque biomaterials and nanoparticles

Katelyn R Houston¹, houstkr@live.unc.edu, Valerie Sheares Ashby¹, Yueh Z Lee²,³,⁴, (1) Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (2) Department of Radiology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (3) Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States, (4) Biomedical Research Imaging Center, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States

Radiopaque polymeric biomaterials that maintain their thermal and mechanical properties are critical for the ever-expanding scope of implantable biomaterials. We have developed a platform of highly iodinated polyesters based on a stable iodinated, aliphatic monomer. These polyesters have high radiopacity, low cost and low cytotoxicity with tunable thermal and mechanical properties. The resulting biomaterials are ideal for applications such as radiopaque implants and meshes, as well as computed tomography (CT) nanoparticle contrast agents. Traditional CT contrast agents suffer from limitations including rapid excretion, unspecific biodistribution, and, most critically, renal toxicity. Nanoparticles have been shown to have longer circulation times as well as controlled biodistribution and extravasation. We can formulate iodinated nanoparticles using a modified nanoprecipitation method exploiting the polyesters described above. These nanoparticles are unique in that they are much cheaper than currently developed gold or bismuth nanoparticles, and that they are completely nonaromatic. Figure 1 displays CT images, which show the high radiopacity of an iodinated polyester film implanted in porcine liver (A) and nanoparticles of multiple concentrations dispersed in water in Eppendorf tubes (B) with corresponding Hounsfield unit (HU) values for each of the nanoparticle suspensions (C). The HU values were higher than the expected attenuation of bone for all three suspensions.
Over-the-counter non-steroidal anti-inflammatory drugs (NSAIDs) such as aspirin and ibuprofen are commonly used for reducing pain and fever owing to their distinct anti-inflammatory, analgesic, and antipyretic functions. However, NSAIDs normally have low water-solubility, which leads to a large dosage in medication. After a long-term use, they often develop side effects like gastrointestinal bleeding and ulcers. NSAIDs also need to be taken daily, even for multiple times a day, to maintain the therapeutic level of the drugs inside the body. This work develops a novel strategy enhancing the solubility of NSAIDs and reducing their dependence on patient's compliance in treatment. Multiple NSAIDs are incorporated via biocompatible and biodegradable links into different layers (or generations) of a dendrimer structure to form a drug-tree, which can potentially release the drugs in a sustained manner. To make the dendrimer more water-soluble, hydrophilic carbohydrates are covalently attached to the surface of the dendrimer. This research specifically incorporates salicylic acid into a poly(glycerol-succinic acid) (PGLSA) dendrimer, and sugars including glucose, galactose, and mannose are conjugated onto the termini of the dendrimer to increase the solubility. Such 'sweet' salicylic acid drugtrees can have a well-defined drug capacity, which depends on the generation of the dendrimer, or drugtree, to be synthesized thus the delivery of the drugs can be more controllable for future applications. This novel synthetic strategy can also be applied to make drugtrees from other drugs.
603 - Modulation of copolymer microstructure by micellar MADIX

Sylvia Stoilova¹, Viviane Le Drogo¹, Remi Giordanengo¹, Mathias Destarac², Simon Harrisson², polyharrisson@gmail.com, D. James Wilson¹. (1) Paris Research and Innovation Center, Solvay, Aubervilliers, France, (2) IMRCP, Université Paul Sabatier, Toulouse, Haute Garonne 31062, France

Developed in the 1980s, micellar polymerization allows the copolymerization of hydrophobic and hydrophilic monomers in aqueous solution. Hydrophobic monomers are dispersed using a surfactant in the form of monomer-loaded micelles, with the average number of monomers per micelle dependent on the ratio of surfactant to hydrophobic monomer. The resulting polymers have a multi-block structure, as the growing chain alternates between the aqueous phase, rich in hydrophilic monomer, and the dispersed phase, rich in hydrophobic monomer. Until now, however, confirmation of this structure has relied on indirect methods, as the low concentrations of hydrophobic monomer typically used (< 2%) make direct observation of the microstructure by 13C NMR impossible.

We report the preparation of copolymers containing up to 50% hydrophobic monomer using the micellar MADIX polymerization technique. In this process, a xanthate RAFT agent provides molecular weight control as well as the possibility to form block copolymers. The high concentration of hydrophobic monomer allowed direct observation of the copolymer microstructure using 13C NMR. The polymers exhibited a blocky structure which could be modified by changing the surfactant:hydrophobic monomer ratio. Average block lengths were much smaller than expected, however, indicating the presence of hydrophobic monomer in the aqueous phase and hydrophilic monomer in the dispersed phase.
604 - Tunable network properties based on dual cure hybrid (meth)acrylate and benzoxazine polymer networks

Jananee Narayanan, nsjananee@gmail.com, Derek L. Patton. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States

Hybrid dual curable cross-linked polymer network has been developed by incorporating both orthogonal acrylate and benzoxazine chemistries with the aim of attaining a wide array of tunable thermo-mechanical properties. This approach allows an ease of handling of the otherwise brittle polybenzoxazine films via the incorporation of covalently bonded and stable intermediate networks. Moreover, the sequential nature of network synthesis offers systematic study of network formation and properties of the individual polymer networks. With the advantages of photopolymerization combined with catalyst free thermal polymerization, the meth(acrylate) and benzoxazine chemistries offers enormous molecular design flexibility.

For this study, a methacrylate functional bis-benzoxazine was synthesized. A series of structurally distinct acrylates were employed as co-monomers using varying mole ratios and functionality. Dual hybrid network films were prepared by sequential bulk meth(acrylate) photopolymerization followed by thermal polymerization of benzoxazines. Real-time FTIR studies were conducted to determine the conversions of acrylate functional groups after the photopolymerization event. The curing processes for the formation of hybrid networks were systematically monitored by FT-IR analysis and differential scanning calorimetry (DSC). To understand and evaluate the structure-mechanical property relationships of dual polymer networks, dynamic mechanical analysis (DMA) was used. Thermal stability studies were performed using thermogravimetric analysis (TGA) to determine initial weight loss temperature and char yield values. A systematic trend was observed between network structures, composition, glass transition temperature and rubbery modulus. This approach offers a facile route to attain a broad horizon of desirable thermo-mechanical properties within one system by appropriate selection of meth(acrylate) monomers and varying the co-monomer composition.
Interest in thiol click chemistry continues to grow as more uses for the simple synthetic platform are explored. Recently we reported the fabrication of nanocomposites containing gold and silver nanospheres using photoinitiated thiol-ene and thiol-yne chemistry. The resulting films and fibers exhibited unique optical and mechanical (e.g. Young’s modulus, glass transition temperature) properties that could be tuned based on the type of brush ligand used to functionalize the nanoparticles that they contained, or by the concentration of nanoparticles that were within the polymer. The possibility of using thiol click nanocomposites as unique surface enhanced Raman spectroscopy (SERS) conduits was also explored yielding promising results. The value of fabricating high-performance nanocomposites spans numerous research areas including surface chemistry, smart textiles, optically active materials and sensors. The ease with which such materials can be fabricated using thiol click chemistry makes this work of great value to the polymer science community.
606 - Thiolene polymers for biomedical devices

**Benjamin R. Lund**\(^1,2\), benjamin.lund@utdallas.edu, Radu Reit\(^3\), Dustin Simon\(^2\), Taylor Ware\(^2\), Walter E. Voit\(^{1,2,3,4}\). \(^{(1)}\) Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75080, United States, \(^{(2)}\) Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, United States, \(^{(3)}\) Department of Bioengineering, The University of Texas at Dallas, Richardson, TX 75080, United States, \(^{(4)}\) Department of Mechanical Engineering, The University of Texas at Dallas, Richardson, TX 75080, United States

Chronically implantable neural devices (>1 year) remain elusive despite significant advances in biomedical engineering and materials science. Loss of signal fidelity, a significant challenge to the field, is caused by a scaring response around device due to a modulus mismatch between the tissue and the device. This modulus mismatch can be mitigated through the use of clever polymer chemistry to develop substrates which possess excellent geometric and thermal properties (necessary for device fabrication) and soften in vivo to possess moduli at or near that of body tissue. Thiol-ene “click” polymers offer an excellent array of properties for these applications, however, these polymers often suffer from low glass transition temperatures, necessitating highly cross-linked systems and leading to high rubbery modulus. To circumvent these issues, the development of monomers which are rigid and will allow for a decrease in crosslink density (and thus rubbery modulus) while maintaining a high glass transition (necessary for device insertion). In this paper we discuss the design and synthesis of new class of thiol-ene polymers based around rigid aliphatic thiols and their application in biomedical devices.

![Figure 1. Comparison of the mechanical properties of a rigid dithiol (TCDDT) to a “floppy” trithiol (TMICN) with a common tri-ene (TATATO).](image)

**Wednesday, August 13, 2014 10:20 AM**

**General Topics:** New Synthesis and Characterization of Polymers (08:00 AM - 11:40 AM)

**Location:** Hilton San Francisco Union Square

**Room:** Golden Gate 7
607 - Porous poly(styrene-b-isoprene-b-dimethylsiloxane) triblock copolymer membranes

Sri Harsha Kalluru, skalluru@iastate.edu, Eric Cochran. Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States

We report a new method of membrane design consisting of percolating networks of pores in a triblock copolymer matrix, fabricated through self-assembly. We probed the phase diagram of this triblock copolymer system to locate the double gyroid morphology (with Ia3d space group symmetry) rich region. This morphology should have core-shell gyroid structure with continuous poly(dimethylsiloxane) (red color in figure 1) networks inside of poly(isoprene) (green color in figure 1) shells in continuous poly(styrene) (blue color in figure 1) matrix. Circular membranes are cast from bulk polymers, poly(isoprene) is lightly cross-linked for structural integrity, and finally D- channels are quantitatively etched. Selective chemical etching of D channels leaves a network of pores lined with poly(isoprene), which can then be functionalized to enhance membrane selectivity. Apart from this, we also wish to change the pore diameter by changing the volume fraction of poly(dimethylsiloxane) channel. We wish to test these various types of membranes for basic separations in a stirred cell reactor. Characterization of block copolymer samples to determine morphology is accomplished by dynamic shear rheology, SAXS (Small angle X-ray scattering) and TEM (transmission Electron microscope) measurements.

Wednesday, August 13, 2014 10:40 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 11:40 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
Autonomic material regeneration following catastrophic damage requires a versatile chemistry capable of complex demands in material properties and fluid transport. We present a two-stage polymer chemistry which undergoes tunable transitions from sol-to-gel and gel-to-polymer at ambient temperatures. The regenerative chemistry incorporates a crosslinked polymer gel within a monomeric liquid. The gel scaffold supports deposition of additional fluids until the entire damage region is filled. A subsequent bulk polymerization to structural solid recovers the mechanical properties of the virgin substrate. Timing of each stage is controlled by reaction triggers – an acid catalyst for gelation and initiator-promoter system for polymerization. This two-stage chemistry can be combined with numerous vinyl monomers yielding a broad selection of final mechanical and chemical performance; example monomers are shown in the figure. We investigated the gelation and polymerization kinetics by varying trigger concentrations and monomer solvent. Furthermore, cooperative gelation and polymerization reactions are necessary for solution stability and orthogonality of the two stages. These challenges are addressed by varying the initiation technique and rate of the monomer polymerization. By splitting the chemistry into two low viscosity fluids, we demonstrate regeneration of millimeter-sized gaps of material and introduce a general chemistry with adaptable material properties.
Hyperbranched polyglycerol (hbPG) is synthesized via anionic ring-opening multi-branching polymerization (ROMBP) of glycidol, a latent AB₂ oxirane. It is a highly versatile polymer due to its excellent water-solubility and biocompatibility, enabling its use in biomedical applications. Additionally, the high number of hydroxyl groups allows for further functionalization and derivatization of the polymers. However, the direct introduction of additional functionalities into the polymer is rather difficult, because it requires carefully chosen comonomers with (protected) functional groups that withstand the harsh, basic polymerization conditions. Additionally, reaction conditions need to be adjusted for every single copolymer system resulting in considerable synthetic effort.

Here, we present a platform-based approach to overcome these problems using furfuryl glycidyl ether (FGE) as a comonomer. Subsequent Diels-Alder "click" reaction with functional maleimide derivatives allows for reversible introduction of functional groups that can be controlled by temperature. We were able to reversibly introduce allyl, alkyne, catechol, amine and acid groups. These functionalities enable post-polymerization modifications orthogonal to the hydroxyl groups and demonstrate the high versatility of the concept.

HbPGs with molecular weights between 2000 and 7000 g mol⁻¹ and different comonomer contents (4 to 18 mol%) were obtained. Polydispersity indices (PDI) are moderate to narrow (1.34 to 1.81). Quantitative Diels-Alder reaction of furfuryl groups with functional maleimides was proven by 2D NMR experiments and SEC measurements.

In conclusion, we have introduced a novel construction kit for the reversible temperature-controlled functionalization of hbPG which may open pathways to a plethora of further applications in different areas.

Owing to their high CO₂ flux, membranes made from thermally rearranged (TR) polymers are under active investigation for several applications involving CO₂ removal. TR polymers are thermally stable up to 300 °C and are resistant to hydrolysis. For these reasons, they are strong candidates for CO₂ capture from flue gas sources. Because water vapor is a major constituent of flue gas, a thorough understanding its influence on gas transport in these materials is important.

In this work, results of permeation experiments are presented for mixtures of CO₂, N₂, and water vapor in TR polymers derived from 3,3’-dihydroxy-4,4’-diamino-biphenyl (HAB) and 2,2’-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). HAB-6FDA polyimide films were converted to polybenzoxazole (PBO) by heating to 350-450 °C under flowing nitrogen. Permeation tests were conducted using converted PBO films for pure CO₂, N₂, and H₂O, for binary CO₂/N₂ mixtures, and for ternary CO₂/N₂/H₂O mixtures. It was found that the permeabilities of both CO₂ and N₂ in these PBOs are depressed strongly in the presence of water vapor. For example, for a 50% CO₂/N₂ mixture at 10 bar and 35 °C in a PBO film, both CO₂ and N₂ permeabilities decreased by more than half at 50% relative humidity from their values for dry gas; CO₂/N₂ selectivity increased by about 10% for the wet gas versus the dry gas. These experimental results are discussed within the framework of the dual-mode sorption and permeation model.
Ultrathin (< 100 nm) and transparent composite films created by the alternate layering of water-soluble polymers and clay platelets (1 nm thick and 200 nm diameter) are useful for a variety of packaging applications, such as the protection of food and flexible electronics (e.g., displays). Inorganic oxides or bulk polymer composites, suffer from cracking when flexed and poor transparency, respectively. Layer-by-layer (LbL) assembly of polyethylenimine (PEI), poly(acrylic acid) (PAA), PEI, montromillonite (MMT) clay quadlayers (QL) produces a nanobrick wall structure (with clay as impermeable bricks and the polymer as mortar). Flexible and transparent films as thin as 51 nm require only 4 clay layers (12 total layers) to achieve an oxygen permeability below that of SiOx or metalized plastic film. These extremely low oxygen permeability films could improve the shelf life of food products and operational lifetime of flexible organic light-emitting diodes (FOLEDs). Additionally, these films exhibit size selective behavior that suggests they could be used to purify hydrogen or helium. Thicker versions of these films actually exhibit some barrier to these very light gases, reducing the helium transmission rate by 100X relative to uncoated PET film.
Thermally rearranged (TR) polymers are a family of emerging materials used for membrane based separations. These polymers are formed by thermally treating polyimides or polyamides that contain reactive functional groups ortho-position to their diamine at temperatures typically between 350 and 450°C. Upon thermal treatment, these polymers often show increases in permeability of several hundred percent and a resistance to plasticization.

The thrust of this presentation is to investigate the chemical structure of TR polymers and to compare differences in transport properties that arise as a result of their synthetic pathways. For comparison, we have synthesized two TR polymers: one from a polyimide (PI) precursor and one from a polyamide (PA) precursor. These polymers have nearly identical proposed chemical structures. Typically, TR polymers are highly insoluble in common organic solvents, which precludes analyzing their chemical structures with NMR; however, the PA-TR polymer is partially soluble in chloroform. Therefore, we have investigated the chemical structure of this TR polymer with proton, carbon, and 2-D solution NMR experiments. Our results suggest that the PA-TR polymer has a polybenzoxazole chemical structure. The PI-TR polymer, however, was insoluble in NMR solvents, so its structure was investigated in comparison with the PA-TR polymer using solid-state NMR. Solid-state results suggest that both samples have a polybenzoxazole structure.

Pure gas permeabilities up to 50 bar were determined for the PI-TR and PA-TR polymers for H₂, N₂, O₂, CH₄, and CO₂, and these results show that the PI-TR polymer has better separation performance than the PA-TR polymer, despite both samples having nearly identical structure. The difference in these transport properties relates to morphology and a meta/para isomer effect for the PI-TR polymer.
613 - Synthesis, characterization, and gas transport properties of isomeric thermal rearranged (TR) polymer for gas separation membranes

Hailun Borjigin\textsuperscript{1}, hailun@vt.edu, Qiang Liu\textsuperscript{2}, Kyle Gaines\textsuperscript{1}, Wenrui Zhang\textsuperscript{1}, Sue Mecham\textsuperscript{1}, James E. McGrath\textsuperscript{1}, Benny D. Freeman\textsuperscript{2}. (1) Virginia Tech, Blacksburg, Virginia 24061, United States, (2) University of Texas, Austin, Austin, Texas 78758, United States

Two Soluble Isomeric aromatic polyimides containing ortho-positioned functional groups (hydroxyl or acetate groups) were synthesized for thermal rearrangement (TR) processing to complex partially crosslinked polybenzoxazoles (PBOs). The latter have been shown to have great potential for highly selective CO\textsubscript{2}/CH\textsubscript{4} separation membranes applications. Fully imidized film forming polyimides with high-molecular-weight were afforded via a 'one-pot' solution imidization technique utilizing the ester-acid (EA) method starting from 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) with two isomeric monomers, 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) and 3,3'-diamino-4,4'-dihydroxybiphenyl (AHB). The two isomeric polyimides were comprehensively characterized with respect to chemical structure, molecular weight, thermal and mechanical properties by SEC, NMR, DSC, TGA and stress-strain testing. The synthesis, characterization, film casting, thermal treatment, gas transport properties of high molecular weight polyimides and the isomeric effect on the properties of the polymers will be discussed.
614 - Super stretchy multilayer thin film gas barrier

Fangming Xiang¹, edwardxfm@tamu.edu, Sarah Ward², Jaime Grunlan¹. (1) Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States, (2) Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

A super stretchy hydrogen-bonded gas barrier coating was fabricated using layer-by-layer (LbL) assembly. Unlike ionically bonded gas barrier coatings that exhibit mud-cracking after 10% strain, hydrogen-bonded polyethylene oxide (PEO) and polyacrylic acid (PAA) multilayer thin films show no cracking after 100% strain (Fig. 1) due to low modulus. It is proposed that the exceptional elasticity of this coating originates from the intrinsic elasticity of PEO, the moderate bond strength and the breaking-reforming capability of hydrogen bonding. The oxygen transmission rate of a 1 mm thick carcass rubber can be reduced by half with a 500-nm-thick PAA/PEO coating. More importantly, the reduced oxygen transmission rate can be retained even after 100% strain. This finding marks the first super stretchy gas barrier thin film, which is useful for elastomeric substrates designed to hold air pressure.
Polymer-derived materials allow optimizing selectivity performance vs. processing costs

A = traditional polymers
B = crosslinked polymers
C = hybrid polymer-inorganic mat’ls
D = carbon molecular sieve mat’ls

Polymeric membranes are an important class of materials in the separation of gas mixtures, where crosslinked polymers tend to exhibit desired performance. I will discuss work in our laboratory that demonstrates that “polymer-derived” membranes such as hybrid materials and carbon molecular sieve materials, as well as crosslinked polymers, are important materials when optimizing performance and processing cost.
The production of inexpensive, high purity hydrogen remains a critical challenge to improving the sustainability of fossil fuels and for realizing renewable and clean energy sources capable of displacing fossil fuels. Polymeric gas separation membranes combining low production costs with robust mechanical properties have found broad industrial application for O₂ and N₂ enrichment of air, upgrading of natural gas and hydrogen recovery from ammonia. In the absence of structure (i.e. in amorphous glassy or rubbery films), increasing the free volume of size-selective polymer membranes improves the permeability at the cost of reducing the permselectivity. This translates to an upper bound in separation performance achievable by dense, homogeneous and amorphous polymeric films [1,2] (Figure 1). The authors have recently demonstrated that layer-by-layer (LbL) deposition techniques provide a robust, low-cost means to introduce size-selective functionality via manipulation of polymer processing conditions.[3]

Extension of the LbL assembly technique to gas purification membranes promises the ability to tune overall gas permeabilities and permselectivities through manipulation of film nanostructure by varying deposition conditions. In this presentation, the authors report the use of a branched polyethylenimine (PEI) / poly (acrylic acid) (PAA) system is used for achieving breakthroughs in light gas separations (Figure 1). This PEI/PAA assembly appears to have a “scrambled salt” structure, resulting in a highly interpenetrating network of high density which demonstrates size-selective gas separations in excess of Robeson’s 'upper boundary,' [1,2] which we attribute to the structure imparted by a high degree of 'ionic-crosslinking.' Details of materials analysis and separation measurements will be presented. The potential of the LbL approach to gas separation coatings to impact to several other significant applications of social and industrial importance will also be discussed.

617 - High gas barrier polymer films using oxygen scavenging palladium nanoparticles

Matthew M Herbert, herbs0812@gmail.com, David A Schiraldi. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States

Polymers are currently used in a wide variety of liquid and gas barrier applications, ranging from food and beverage packaging to construction materials. Organic light emitting diodes (OLEDs) using plastic substrates are expected to provide a means of producing next-generation displays that are thin, lightweight, and flexible. The use of transparent polymer films for encapsulating such displays is limited due to their unacceptably high permeation rates for oxygen and water vapor. Few thin films that possess the combination of flexibility, transparency, gas barrier, thermal stability and mechanical strength have been reported to date.

Incorporation of platinum group metals, such as Palladium, Platinum or Rhodium, have seen widespread use for their catalytic properties in applications such as catalytic converters, groundwater treatment and fuel cells. In this project, palladium nanoparticles will be utilized as oxygen scavengers in order to enhance the barrier properties of selected polymer films. Palladium particles acts as catalysts for the reaction of oxygen with hydrogen to form water molecules, based on the Langmuir-Hinshelwood Mechanism. A dispersion of palladium nanoparticles within the selected polymer films can be realized using an infusion technique, where the polymer is evacuated under high vacuum and palladium is subsequently infused into its free volume via thermal degradation. This has the benefits of creating palladium nanoparticles on the scale of the polymer’s free volume, creating a higher reactive surface area than through techniques such as surface coating or solution dispersion, which typically results in micron-sized particles due to agglomeration. The combination of inherent high gas barrier properties in the selected polymers, with the incorporation of oxygen scavenging effects of infused palladium nanoparticles, is expected to yield flexible and transparent films which can provide oxygen barrier properties similar to that of glass or metal.

Wednesday, August 13, 2014 11:20 AM
Transport in Polymer Membranes (08:30 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 8
Artificial photosynthesis seeks to provide simultaneous solution to renewable energy generation and storage. Polymeric membranes developed for solar fuel cells often possess non-optimal combination of properties for artificial photosynthesis. Herein we report ionic polymer membranes designed from the ground up for solar water splitting. Poly(phenylene oxide) (PPO) and poly(epichlorohydrin) (PECH) were functionalized by a variety of quaternized ammonium and imidazolium groups to provide functional, conductive units to the membrane. Structure property relationships were established for these materials by varying ion identity and charge density. The ionomers exhibited conductivity of 10 mS/cm with hydroxide as the mobile ion. Gas permeability and chemical stability were also measured and we found that the PPO and PECH ionic membranes exhibit balanced ion conductivity, gas transport, and chemical stability for water splitting devices used in artificial photosynthesis.
619 - Air-filled emulsions and oil foam templates for renewable macroporous polymers

Koon Yang Lee¹, Ling L.C. Wong², Alexander Bismarck²,³, alexander.bismarck@univie.ac.at. (1) Department of Chemical Engineering, University College London, London, United Kingdom, (2) Department of Chemical Engineering, Imperial College London, London, United Kingdom, (3) Faculty of Chemistry, University of Vienna, Vienna, Austria

Emulsion templating is an effective method to synthesise macroporous polymers with tailored pore morphology and physical properties. High or Medium Internal Phase Emulsions (HIPEs or MIPEs) with a continuous phase consisting of monomers are used as templates for the preparation of high porosity macroporous polymers, called poly(merized)M/HIPEs. A limitation of emulsion templating for the synthesis of polyHIPEs is that large amounts of water need to be removed by energy intensive drying to obtain the polymer foam. As an alternative method for producing very high porosity polymer foams we created polymerisable air filled MIPE templates by mechanical frothing particle stabilised water-in-acrylated epoxidized soybean oil (AESO) emulsions. However, polyAESO has a relatively low glass transition temperature and poor mechanical properties. Therefore, to produce even higher performance macroporous polymers we used a renewable 2 component epoxy system in to which we introduced air by mechanical frothing. This epoxy foams can be cured into high porosity (75 - 80%) renewable macroporous polymers with excellent compression strengths and moduli. The key to foam templating to utilise the very viscous nature and very short working time of a biobased epoxy resin. We will show that the properties of the macroporous polymer can be tailored by increasing the frothing time of the epoxy resin. Unlike emulsion templating, which uses HIPEs to produce macroporous polymers the mechanical frothing technique has the advantage of creating macroporous polymers from monomers, which cannot be easily emulsified.
620 - Phosphonium ionic liquids in the design of novel high performance membranes

Timothy E. Long¹, telong@vt.edu, Alison R. Schultz¹, Sean T. Hemp², Asem I. Abdulahad¹, Ryan J. Mondschein¹. (1) Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States, (2) Michelin, Greenville, South Carolina 29602, United States

Phosphonium ionic liquids offer an ensemble of advantages for the preparation of novel polymer compositions and the design of functional membranes. Phosphonium ionic liquids offer enhanced chemical stability, thermal stability, and ion conductivity, coupled with their lack of volatility in many emerging applications ensure their potential impact. The phosphonium cation is relatively unexplored compared to ammonium analogs, and hence this lecture will focus on the design of novel phosphonium cation containing monomers and polymers. The ionic liquid motivation also has resulted in the preparation of novel polyelectrolytes and ion-containing polymers, wherein the ionic sites impart enhanced mechanical properties and conductivity in membranes and drug delivery systems. Phosphonium ionenes allow the preparation of unprecedented melt processable polyelectrolytes and ion-containing polymers, removing the requirement of volatile organic solvents in many membrane fabrication technologies.
Polymer aerogels can be produced using an environmentally-friendly freeze drying process which converts 100% of solids to products. By using bio-based polymers, and either clay or even renewable cellulose as the inorganic phase, the aerogel itself can be produced with a very small carbon footprint. Recent work also examines the use of renewable materials as flame retardants in these materials.
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 will describe our recent efforts to employ vanillin, ferulic acid, and other bio-aromatics for the synthesis of thermally robust polyesters. Efficient, commercial pathways for synthesizing these polymers from inexpensive agricultural waste will be proposed. These novel thermoplastics have improved thermal properties and degradation behaviors compared to specific fossil fuel-based plastics—in particular polyethylene terephthalate (PET) and polystyrene (PS).
623 - Novel hyaluronic acid derivatives as bioadhesive encapsulation materials

Kantappa Halake, ks.halake@gmail.com, Jonghwi Lee. Department of Chemical Engineering and Material Science, Chung-Ang University, Seoul, Republic of Korea

Nature provides broad examples of functional materials like polyphenols often found in various fruits. Polyphenols are bulky biopolymers having the unique chemical structures of multiple hydroxyl groups similar to DOPA, and are useful for adsorbing proteins. Herein, we have developed chemical modification and its stabilization method for the preparation of HA-polyphenol derivatives. Four different polyphenols were successfully attached to hyaluronic acid (HA) using epichlorohydrin (ECH) chemistry. $^1$H NMR, and FT-IR confirms the covalent bonding, whereas UV assay highlights the substitution rate increased with polyphenols. However the higher substituted derivative has enhanced degradation as seen in its intrinsic viscosity data. The DPPH scavenging assay confirmed that the antioxidant activities remained intact even after the chemical modification. The adhesion strength of HA derivative under uniaxial tensile strain mode was much higher than that of the neat HA macromolecules.

This improved adhesion and antioxidant behavior of these derivatives possibly came from the introduced multiple hydroxyl groups of polyphenols.

Wednesday, August 13, 2014 10:25 AM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (08:30 AM - 11:45 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
624 - New hierarchical nanocomposite blends incorporating stereocomplexation

John R Dorgan¹, jdorgan@mines.edu, Laura O Hollingsworth², Bo Liu², Rodolfo Sosa². (1) Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States, (2) PolyNew Inc., Aurora, CO 80045, United States

Polylactide (PLA) is the leading bioplastic in production volume. To overcome its heat resistance limitations a novel hierarchical strategy has been developed. In this unique approach DD-lactide is grafted onto various nanoparticles (including degradable fillers like nanocellulose and non-degradable like fumed silica) and then embedded in commercially available poly(LL-lactide). The resulting high temperature use materials are relatively brittle with low extension to break.[figure 1]

To overcome this limitation, blending with renewable poly(butylene succinate) is conducted. The full property suite of these unique biobased nanocomposite blends incorporating stereocomplexation is reported on. It is shown that the materials are suitable for a wide variety of uses requiring degradability.

Wednesday, August 13, 2014 10:45 AM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (08:30 AM - 11:45 AM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 3
625 - “Grafting from” approach: A tool to improve properties of clay-based stereo-complexed PLA nanocomposites

Giada Lo Re¹, giada.lore@umons.ac.be, Stephen Spinella¹,²,³, Samira Benali¹, Youssef Habibi¹, Jean-Marie Raquez¹, Richard Alan Gross², Philippe Dubois¹. (¹) Centre d’Innovation et de Recherche en Matériaux Polymères CIRMAP, Service des Matériaux Polymères et Composites, UMONS University of Mons, Mons, Belgium, (²) Center for Biotechnology and Interdisciplinary Studies, Department of Chemistry and Biology, Rensselaer Polytechnic Institute (RPI), Troy, N.Y. 12180, United States, (³) PNYU Polytechnic School of Engineering, Brooklyn, New York, N.Y. 11201, United States

Polylactide (PLA) is considered as one of the most industrially relevant bio-based polymers because of many desirable characteristics such as that it is completely bio-based and is biodegradable. Despite these advantages, PLA has suffers from several drawbacks which impede its industrial implementation such as slow crystallization. These drawbacks limit its use particularly in long-lasting applications like automotive, electronics and food packaging. PLA stereocomplexation and the addition of nanoclay are two strategies often used to overcome this drawback.

In this work, we propose the use of the “grafting from” approach, via in situ intercalative and metal-free ring-opening polymerization of L-lactide and D-lactide from the surface of a hydroxyl-functionalized organomodified montmorillonite (i.e., Cloisite 30B) to enhance the dispersion of nanoclay. This approach is combined with the stereocomplexation to enhance the rigidity, thermal and gas-barrier properties of the polyester matrix. In particular, the nanohybrids obtained by "grafting from" approach were subsequently melt-blended with commercial PLA in order to obtain stereocomplexed PL-based nanocomposites upon the stereocomplexing of the nanohybrids, which were compared with materials without stereocomplexation.

By using this approach, an increase of more than 60 % was observed in the Storage modulus of the bio-PDLA nanohybrid with commercial PLLA, as compared with the neat PLA. Moreover, an increase of 40°C was seen in the melting temperature of the nanocomposites. These nanocomposites also showed a significant improvement in oxygen-barrier properties. These results indicate that these new bio-based materials can find applications in long term packaging applications.

Figure 1 - WAXD patterns of melt blended materials and pristine Cloisite30B with d-spacing.
In this presentation, an overview will be presented of recent research into sustainable nanocomposites, with specific focus given to Cellulose Nanotechnology. Cellulose Nanocrystals (CNCs) and Cellulose Nanofibrils (CNF) are attractive materials for possible applications in nanocomposites reinforcement, nanomaterials and biomedicine as they have high strength and stiffness, yet are renewable, biodegradable, non-toxic, cheap, and optically transparent. Here, we will detail efforts to utilize these materials in composites, both as nanoreinforcements and as a neat material for both structural materials and consumer applications with discussion of the resultant mechanical and thermal properties. Thus, we provide new elements to understand the interconnection among preparation variables towards an optimal CNC or CNF materials design. Additionally, we will detail recent efforts at sustainable resins for in an effort to "green" composite materials.
Hierarchical fabrication of colloidal hybrid mesostructures based on core-crystalline block copolymer micelles

Mitchell A. Winnik\textsuperscript{1}, mwinnik@chem.utoronto.ca, Lin Jia\textsuperscript{1}, Gerald Guerin\textsuperscript{1}, Ian Manners\textsuperscript{2}. (1) Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada, (2) School of Chemistry, University of Bristol, Bristol, United Kingdom

The creation of hybrid hierarchical structures by combining colloidal organic and inorganic building blocks remains a challenge due to the difficulty of preparing organic structural units of precise size and shape. Here we describe a design strategy to generate controlled hierarchical organic-inorganic hybrid architectures by multistep bottom-up self-assembly. Starting with a suspension of large inorganic nanoparticles (silica nanoparticles or silica-coated nanorods), we anchor uniform block copolymer micelle crystallites onto the nanoparticle, taking advantage of the interactions between repeat units in the micelle corona and the nanoparticle surface. These colloidally stable multi-component particles can initiate the living growth of uniform cylindrical micelles from their surface, leading to three-dimensional architectures. Structures of greater complexity can be obtained by extending the micelles via addition of a second core-crystalline block copolymer. In Figure 1A we show a TEM image of an example in which poly(ferrocenylsilane-\textit{block}-2-vinylpyridine) (PFS\textsubscript{30-b-P2VP\textsubscript{300}}) micelle crystallites have been adsorbed to the surface of silica-coated nickel hydrazine nanorods. When a colloidal suspension of the seed-coated nanorods in 2-propanol is treated with a solution of additional block copolymer in THF, the butterfly structures shown in Figure 1B are formed. This controlled growth of polymer micelles from the surface of inorganic particles opens the door to the construction of previously inaccessible colloidal organic-inorganic hybrid structures.
Advances in the synthesis of coordination polymers will be described. Dynamic ring-opening polymerization of chelate or macrocyclic complexes may give selective formation of crystalline polymers. Examples with bis(amidophosphine) ligands will be featured in this paper, including self-recognition or self-discrimination and the use of the amide groups for secondary coordination or to increase dimensionality through hydrogen bonding.
The design of structurally well-defined peptide motifs has been an active area of research aimed at generating models of biological systems, or to develop novel biomaterials. Peptide structural motifs such as α-helices and β-sheets have been designed de novo using non-proteinogenic amino acids. In this context, disubstituted ferrocenes are becoming popular scaffolds, which are known to induce turn-like structures that enable efficient hydrogen bonding interactions between peptide chains.

Work in the Kraatz group focuses on the design of ferrocene-peptide derivatives for the structural mimicry of β-sheets and helices and on molecules that can recognize ions, small molecules, or even proteins. Here, a summary is presented of the synthesis and use of some ferrocene-peptide conjugates. Examples are discussed of their properties as gelators forming organogels that are responsive to external stimuli [1]. For example, ferrocenoyl-Val-Phe-Phe-OMe undergoes a redox and ultrasound directed self-assembly and displays a redox-controlled reorganization between gel nanofibers and spherical micelles [2].

630 - Micronanoporous redox responsive "smart" films from poly(ferrocenylsilane) polyionic liquids: Preparation, characterization, and applications in filtration and catalysis

Julius G. Vancso, g.j.vancso@utwente.nl, Kaihuan Zhang, Xueling Feng, Xiaofeng Sui, Mark Hempenius. Materials Science and Technology of Polymers, University of Twente, MESA+, Enschede, The Netherlands

Thin, micro-nanoporous polyelectrolyte membranes consisting of poly(ferrocenylsilane) featuring imidazolium side groups were obtained in different morphologies by an electrostatic complexation approach employing poly(acrylic acid) anions. The films were characterized by AFM, electron microscopy, FT-IR, electrochemistry, and water permeability experiments. Film thickness, pore size and cell morphology can be controlled by molecular structure, composition, and preparation conditions. The porous structure featured open cells, with cell wall openings that have diameters depending on the oxidation state of the matrix PFS polymer. Due to redox responsive properties of PFS, cell size of the micro/nanopores, matrix charge, and permeability can be switched by controlling the redox state of the matrix either electrochemically, or by oxidizing/reducing agents. Ag nanoparticles in the porous matrix were formed via reduction of Ag nitrate solutions in contact with the redox active polymer. Applications in micro-nanofiltration and catalysis of these smart porous membranes are discussed.

Figure 1. (a) Structure of PFS-VImTf2N and PAA; (b) Chemically induced redox switching process of the PFS based porous membrane.
631 - Recent developments with self-assembled polyferrocenylsilane block copolymers in thin films and solution

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

Metal-containing block copolymers (BCPs) offer fascinating opportunities for the development of self-assembled functional nanomaterials.1,2 In this talk recent developments concerning the use of polyferrocenylsilane (PFS) BCPs as phase-separated thin films and as self-assembled nanoparticles will be described.3-6

Collaborations: Caroline Ross (MIT), Rick Register (Princeton), Mitch Winnik (Toronto), and Rob Richardson, and Charl Faul (Bristol).

632 - Insights into polymer photochemical degradation from the study of metal-containing polymers

David R. Tyler, dtyler@uoregon.edu, Justin T. Barry. Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States

The rates of polymer photodegradation are dependent on the molecular weight of the polymer, the morphology of the polymer, the intensity and wavelength of the light, the temperature, the chromophore concentration within the polymer, the stresses on the polymer sample, and on a host of other environmental and molecular parameters. As such, mechanistic studies of how and why these parameters affect photodegradation rates can be difficult to interpret. To facilitate our mechanistic studies of polymer photodegradation, we synthesize and study polymers with metal-metal bonds along their backbones. These polymers are photochemically reactive, and the relative simplicity of their degradation reactions allows insights into how the parameters listed above affect degradation rates. This talk will specifically report on how temperature, oxygen diffusion rates, and polymer morphology affect the degradation rates of polymers with metal-metal bonds along their backbones. The implications of these results for the degradation of commodity polymers and plastics will then be discussed.
Reversible addition fragmentation transfer (RAFT) polymerization of a $\eta^5$-cyclopentadienyl-cobalt-$\eta^4$-cyclobutadiene (CpCoCb) containing monomer under a variety of experimental conditions was examined (e.g. different solvents, temperatures, RAFT agents, concentrations, and [RAFT agent]/[initiator] ratios). In all cases the results revealed that although the monomer was being consumed over the course of the reaction (determined by $^1$H NMR spectroscopy), there was no increase in the polymer's molecular weight (determined by GPC analysis). As the polymers chain grow to an oligomeric stage ($D_{Pn} \approx 10$), they take on tight coil morphology hindering the approach of the sterically demanding CpCoCb containing monomer, resulting in premature termination/chain transfer reactions instead of increase in the polymers' chain length. To address this problem a smaller monomer, methyl acrylate (MA), was copolymerized along with the bulky monomer to act as a spacer providing the necessary space for the approach of another Co-containing monomer. This copolymerization results in a random copolymer with drastic improvement in the polydispersity and the molecular weight of the end material. Furthermore, the random copolymer was used as a macro-RAFT agent to prepare block copolymers, with excellent control over the polymers' molecular weight allowing for an examination of their solid-state self-assembly.
Stimuli-responsive polymers have been in the focus of intensive research over the last decade. The vast majority of reports deal with temperature, light or pH changes, as external triggers. In recent years, the redox stimulus has gained significant attention for switching polymer conformation or the polarity of surfaces. Within this field, ferrocene-containing polymers are excellent stimuli-responsive materials due to their highly reversible and fast switching behaviour of the ferrocene moieties between two oxidation states. While oxidizing the ferrocenes units, both the local polarity of the polymer chain environment and the solubility of the polymers can be varied and adjusted.

The combination of anionic polymerization of vinylferrocene with different polymerization methods allows access to a wide variety of amphiphilic block copolymers. Furthermore, the formation of micelles in selective solvents and their structural change upon oxidation was investigated.  

Immobilized ferrocene-containing polymers on silica surfaces were accessible by a grafting to protocol of endfunctionalized polyvinylferrocene (PVFc) and surface-initiated ATRP of poly(2-(methacryloyloxy)ethyl ferrocenecarboxylate) (PFcMA). The polarity change and swelling of these polymers were used for the modulation of the activity of surface bound catalysts, switching the wettability of flat surfaces and changing the permeability of mesoporous silica membranes.


Over the last two decades, ring-opening polymerization of silicon-bridged [1]ferrocenophanes ([1]FCPs) was developed into an elegant route to metallopolymers with well-defined molecular weights and narrow weight distributions. Even though many other strained sandwich compounds can be polymerized, often their polymer chemistry could not be developed further due to a variety of problems, including low solubility of resulting metallopolymers in organic solvents.

Recently, we developed a flexible approach to a new class of [1]FCPs (1; R = Me; E = B, Ga, In, Si, Sn). These species were equipped with two alkyl groups adjacent to the bridging moiety in order to provide steric protection of a bridging moiety and to act as solubilizing groups. We now expanded this chemistry by preparing a family of boron- as well as phosphorus-bridged [1]FCPs (1), equipped with two different alkyl groups on the Cp moieties (CHR₂ = CHMe₂ or CHEt₂). The synthesis and characterization of these enantiomerically pure monomers (1) as well as our first results of ring-opening polymerizations will be discussed.


636 - Kinetics of the oxidation of polyamide 11

Emmanuel Richaud¹, emmanuel.richaud@ensam.eu, Octavie Okamba Diogo¹, Brivo Fayolle¹, Jean Guilmant², François Fernagut², Jacques Verdu¹. (1) Procédés et Ingénierie en Mécanique et Matériaux, Arts et Métiers ParisTech, Paris, France, (2) Cerdato, Arkema, Serquigny, France

Oxidation of polyamides differs from polyolefins one in several aspects:

- The presence of a nitrogen attractive heteroatom on the main chain changes the chemistry of oxidation, as for example the rate at which radicals combine and hence the ratio chain scission over crosslink,

- The nature of end groups implies post condensation reactions that counterbalance chain scission effects. For the different phenomena can overlap with opposite influences, it is compulsory to have at our disposal a reliable model predicting degradation kinetics in the use conditions different from accelerated ageing and a kinetic model gives better insights in the experimental data. Literature on amide model compounds was first reviewed in order to extract a suitable set of rate constants to incorporate in a classical model describing auto-oxidation of polymers. When compared to polyolefin rate constants, it was shown that polyamide oxidation is characterized by:

  - a lower chain scission over carbonyl ratio,

  - a weaker stability of the hydroperoxydes formed,

  - a higher propagation rate constant.

These data were used as constraints in order to limit the number of adjustable parameters in the model. The rate constants remaining unknown were estimated from hydroperoxide kinetics and carbonyl build up curves. Thus, a scheme was elaborated for pure polyamide:

- able to simulate the changes in molar mass,

- easily adapted to describe the even most complex case of phenols stabilized polyamides. The heuristic properties of this model were compared with other data (hydroperoxides titrations, carbonyl build up and chains scissions) of ageing of pure PA11 thermally oxidized at several temperatures under various oxygen pressures.
The understanding and the simulation of stabilized polyamide oxidation is a significant stake for users and producers. The present work aims at proposing the first kinetic model for thermal oxidation of polyamide 11 films stabilized by phenols.

Three hindered phenols are investigated: Irganox 1098, 1010 and 245 at concentration range between 0.05 and 0.5 % wt., and the thickness of the corresponding polyamide 11 films is about 100 µm. Accelerated agings are performed between 90 and 165 °C. Carbonyl build-up, investigated by FTIR, do not bring out induction period as usually observed for stabilized PE, but the curves display a complex shape: after a fast increase, the carbonyl build-up reaches a plateau of which level and length depend on phenol concentration before another increase (figure 1a). Phenols reduce yellowing kinetics, determined by UV-Vis spectroscopy. However, the relationship between carbonyl concentration and the absorbance at 280 nm (which is our discoloration index) remains similar for stabilized and unstabilized PA11. The investigation of molar mass changes by size exclusion chromatography points out an increase of molar weight during the plateau assigned to a post-polycondensation process (figure 1b). These results will be discussed in the light of a PA11 kinetic model in which phenol stabilization mechanism is implemented.
638 - Investigations of the factors that trigger thermal degradation during the processing of polymers

Ya-Ting Su, ysu5@ncsu.edu, Russell E. Gorga, Melissa A. Pasquinelli. North Carolina State University, Raleigh, NC 27514, United States

During the formation of polymer products, thermal degradation has been an issue, which is also affected by the presence of oxygen and other impurities as well as the processing conditions. Thermal degradation not only impacts the physical and mechanical properties of the products, but also often leads to the failure of production lines. An understanding of the molecular mechanisms that underlie thermal degradation can thus lead to the production of polymer materials with enhanced properties and can minimize waste during production. The goal of this work is to utilize both experiments and simulations to investigate the effects on polymer thermal degradation of its processing conditions (residence time, temperature, pressure) and the local environment (the presence of oxygen, water, additives, crystal domains, or impurities). We studied two model systems, polypropylene (PP) and polyethylene (PE). From both simulations and experiments, the processing conditions including temperature and the residence time during the melt processing phase of extrusion were identified to be critical factors. Both PP and PE were observed to have their own mechanisms for thermal degradation. Other interesting observations from both the simulations and the experiments will also be discussed.
We have demonstrated that aqueous hydrogen peroxide is an effective reagent for chain scissioning or vis-breaking of polypropylene (PP) to produce a controlled rheology product. Our process involves direct injection of aqueous hydrogen peroxide into the polypropylene melt under pressure in a melt extrusion process. The PP produced has reduced molecular weight, narrowed molecular weight distribution, and is indistinguishable in terms of melt flow rate, molecular weight distribution, crystallinity and melt rheology from a conventionally vis-broken PP produced using an organic peroxide (2,5-dimethyl-2,5-di-tert-butylperoxyhexane). However, the PP produced in the current process is notably free of the organic volatiles formed as byproducts from the organic peroxide.

Figure. Comparison of the dependence of vis-breaking of commercial polypropylenes LyondelBasell HP400N and HP555G (throughput 20 kg/h) on peroxide addition rate for 60% aqueous hydrogen peroxide (H2O2) and 2,5-dimethyl-2,5-di-tert-butylperoxyhexane (DHBP).
640 - Thermal measurements in assessing the performance of poly(lactic acid)/natural fibre composites for food packaging applications

Stephen W Bigger\textsuperscript{1}, stephen.bigger@vu.edu.au, Intan S M A Tawakkal\textsuperscript{2}, Marlene J Cran\textsuperscript{3}. (1) Centre for Environmental Safety and Risk Engineering, Victoria University, Melbourne, Victoria 8001, Australia, (2) College of Engineering and Science, Victoria University, Melbourne, Victoria 8001, Australia, (3) Institute for Sustainability and Innovation, Victoria University, Melbourne, Victoria 8001, Australia

The performance of composites comprised of renewable biopolymers such as poly(lactic acid) (PLA) with natural fibres such as kenaf is currently being assessed in the context of their potential use as antimicrobial (AM) food packaging materials [1]. The incorporation of fibres enhances the physico-mechanical properties of the PLA and its presence as a filler also reduces the cost of the material. The formulation of an AM packaging system comprised of PLA/kenaf and the natural AM agent thymol along with steps taken to optimize performance are discussed. Thermogravimetric (TG) and DSC measurements were made to assess the interaction between the composite matrix and the AM agent and hence the release of the AM agent.

The application of non-isothermal TG kinetic analysis [2,3] is re-visited in the form of a seemingly novel computer-based iterative numerical method that was developed to execute an integral approach to the processing of experimental data (see above Figure). The method delivers the kinetic activation energy and Arrhenius factor parameters without having to invoke the usual simplifying assumptions. The program incorporates an algorithm that enables the goodness of fit of the TG data across the range of many of the known kinetic models to be determined. This algorithm is based on the characteristics criteria of various models derived from a theoretical study [4].

References

Hydrogen-blown polysiloxane foams are used in applications requiring prolonged service lives. These foams are often used to fill gaps and to absorb stress between surrounding components. Over the lifetime of the foam, they are required to maintain specified shape and elasticity. These properties are known to degrade over time due to continued chemical reactions such as cross-linking and chain scission in the polymer network. Within the DOE complex, extensive field data is available for a discontinued Dow-Corning formulation, S5370. There is, however, comparatively little laboratory data. For recent alternatives to S5370, the opposite is true. Various in-house formulations have undergone numerous accelerated aging trials, but have yet to provide significant field data. Laboratory data is analyzed through time-temperature superposition as illustrated by the compression set master curves at 30°C for three polysiloxane foam formulations.

Field data is analyzed by measuring variability in the material. Both laboratory and field data are confounded by numerous factors besides formulation, including density, thickness, and degree of strain while in storage. By comparing field and laboratory results, the ability to predict performance in this family of heterogeneous materials is assessed (LA-UR-14-21488).
To study the thermal stability of nitroplasticizer (NP), vinyl copolymer elastomer (VCE), and VCE composites, we conduct systematic TGA characterizations in non-isothermal and isothermal modes. We investigate the effects of NP concentration, filler concentration, and time on the aging behaviors of VCE polymer in its composites. We probe the structural changes in the VCE samples before and after thermal treatments with FTIR characterization. The results suggest that the thermal stability of NP decreases as the filler concentration and temperature increase. The deteriorated NP greatly degrades the stability of the VCE polymer. Through the isothermal TGA study, we also estimate the NP transport properties to migrate through the VCE/filler composites.

LA-UR-14-21494

Figure 1. Effect of heating rate on DT$_{pp}$ and DT$_{KC}$ of the 20% VCE/filler/NP composites (DT is referred to as decomposition temperature).
Polyolefin geosynthetics have to be stabilized by antioxidants (AO) to achieve life-times as required for geotechnical application. Two classes of AO packages are typically used for geosynthetics: (1) a combination of steric hindered phenols and phosphites, (2) hindered amines in combination with a marginal process stabilization. Depletion of the AO and degradation of plastic products show specific features. We argue that the exudation of the antioxidants is of paramount importance. This is discussed within the framework of a three processes model. Process A: AO deplete. Process B: induction period of the depleted material. Process C: degradation impairs properties of the product. In case of package (1) the processes follow each other consecutively. In case of package (2) process A overlaps with process B and C. Estimates of life-times are given for HDPE geomembranes (package (1)) and PP geotextiles (package (2)). Against this background high pressure autoclave testing is evaluated.
Among thermosetting resins, polycyanurate networks (derived from cyanate ester monomers) offer excellent flame, smoke, and toxicity characteristics along with enhanced thermo-oxidative stability compared to epoxy resins. Recent structure-property investigations in polycyanurate networks have revealed new insights into the relationship between the chemical moieties found in the networks and the corresponding levels of thermo-oxidative resistance. In particular, it appears that the presence of methyl groups next to tertiary or quaternary carbons has a decidedly negative impact on thermo-oxidative stability during TGA heating ramp tests. In the case of silicon-containing cyanate esters, thermo-oxidative stability can be improved significantly by the incorporation of silicon only in cases where either a large portion of the chemical repeat unit is formed from inorganic groups, or the thermo-oxidative stability of the carbon-containing analog is relatively poor compared to other organic polycyanurate networks.
645 - Thermo-oxidative profiling of EPDM seals used in nuclear power plants

Payam Pourmand, pourmand@kth.se, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, School of Chemical Science and Engineering, Stockholm, Stockholm SE-100 44, Sweden

In nuclear power plants there is a vast number of polymeric materials used with important functional requirements related to the safety during normal operation and accidental events. A common polymer utilised in reactor containments is ethylene-propylene diene (EPDM) rubber. There is a need to understand how these polymers are affected over a longer operation e.g. 10 years. Knowledge of possible degradation mechanisms and predictability is an important foundation and basis for proper management of the aging issue. The so-called NMR-MOUSE (NMR mobile universal surface explorer) is a mobile instrument initially designed for analysis of polymer materials. It is portable and can be carried to the object of interest. The objects can be investigated entirely non-destructively up to several millimetres in depth by placing the NMR-MOUSE in the spot to be measured. NMR measurements with the NMR-MOUSE can help to investigate the heterogeneity of rubber induced by thermal oxidative aging by depth-selective measurements. The thermal degradation of EPDM rubber material was investigated at temperatures in the range 170-120°C. We intend to show the applicability of the NMR-MOUSE for investigations of the heterogeneity in depth, complemented with infrared microscopy and indenter modulus profiling of sample cross-sections. IR spectroscopy of the sample cross-section is anticipated to result in degradation-related spectral changes primarily in the carbonyl region. These chemical oxidation profiles will be correlated with mechanical indenter modulus and NMR T2 relaxation data up to 4 mm in depth.
Dithiomaleimides (DTMs) with alkyl substituents are shown to be a novel class of highly emissive and stable fluorophores. Variable solubility and further functionalization of this unit can easily be tailored through the choice of N and S substituents. Furthermore, inclusion of a DTM unit into a polymerization initiator or insertion into the disulfide bond of proteins demonstrates the utility for fluorescent labelling. A key advantage of this new reporter group is its versatile chemistry and its notably small size, which allows for ready incorporation without affecting or disrupting the self-assembly process. This is critical to the formation of core-shell polymeric contrast and drug delivery agents and enables the facile tracking of the nanostructure. We demonstrate the potential of this functionality through incorporation into a ring opening polymerization (ROP)/reversible addition-fragmentation chain transfer (RAFT) polymerization diblock system which has been shown to be appropriate for micellization and, when in the micellar state, does not self-quench. The further exploration of this functional group as a handle in a range of polymeric materials will be discussed.
Multi-functional carriers for intracellular protein drugs have been developed that enhance endosomal release and cytosolic delivery to disease targets. The carrier systems are designed to mechanistically mimic pathogenic delivery systems that have evolved remarkably efficient cytosolic delivery capabilities. After internalization into vesicular compartments, the pH drops during endosomal-lysosomal development, triggering exposure of a membrane-destabilizing domain in viral proteins such as hemagglutinin or pathogenic proteins such as diphtheria toxin. The ampholytic carriers are designed like these pathogens to activate via protonation events triggered in the endosome. This endosomal-releasing activity is then built into a multi-functional polymer platform that incorporates targeting elements, conjugation or complexation elements, and a “stealth” component to optimize safety and pharmaco-kinetic properties. Initial studies have shown these carriers can suppress tumor growth and prolong survival in human lymphoma disease models.
648 - Using CRP to translate bioinspired sequences toward synthetic polymers to explore sequence specific interactions

**Hans Boerner**, h.boerner@HU-berlin.de, Niels ten Brummelhuis, Thorsten Schwemmer. Department of Chemistry, Humboldt-University Berlin, Berlin, Berlin 12489, Germany

Recently enormous efforts have been spend to advance polymer synthesis methods, enabling monomer sequence control.\(^1\),\(^2\),\(^3\) Methods of controlled radical polymerization played one major role to precisely position functionalities in synthetic polymers.\(^4\) After principles of advanced synthesis routes have been established, one of the upcoming challenges will be finding applicable sequences to demonstrate the potentials of fully synthetic polymers, which exhibit a defined monomer sequence. Here we summarize recent advances and present our approach to extract interesting minimal sequences from biological sources to design precision polymers. Those polymers mimic aspects of functional biomacromolecules with non-biological monomer building blocks and might enlarge the functional space available for polymers useful for drug delivery,\(^5\) adhesives\(^6\) or nanoengineering of surfaces.\(^7\)

Figure. Extracting minimal sequences from biological macromolecules to be mimicked with fully synthetic precision polymers.

---

649 - Surface initiated polymerization and its applications in medicine

Ashutosh Chilkoti, chilkoti@duke.edu, Biomedical Engineering, Duke University, Durham, NC 27708, United States

This talk will illustrate how surface initiated polymerization can generate new and interesting applications in medicine. In the first example, I will describe the *in situ* fabrication of brushes of a a PEG-like polymer, poly(oligo(ethylene glycol) methyl ether methacrylate) (poly(OEGMA)), from a planar surface by atom-transfer radical polymerization (ATRP), and the extension of this methodology to the microscale by soft lithography and to the nanoscale by dip-pen nanolithography and interference lithography. These nanometer thick polymer brushes show extraordinary resistance to protein adsorption and the adhesion of cells, an attribute that we have exploited for the development of a point-of-care diagnostic assay in which all components required to complete a sandwich immunoassay are inkjet printed on a poly(OEGMA) brush, and which allow a multiplexed sandwich fluoroimmunoassay to be completed in minutes from a single drop of blood, simply by the diffusion of analytes and reagents across the polymer brush. In a second example, I will describe the application of surface initiated ATRP under aqueous conditions to grow a single chain of poly(OEGMA) from a defined site on the “molecular” surface –the N-terminus or C-terminus– of a protein to yield site-specific and stoichiometric conjugates (1:1) with relatively low polydispersity and high yield. These protein-poly(OEGMA) conjugates show a 20-50 fold increase in their blood exposure compared to unmodified protein upon intravenous administration to mice. This methodology for the *in situ* synthesis of N/C-terminal protein conjugates of poly(OEGMA) is applicable to a large subset of protein and peptide drugs, and is likely to provide a general methodology for improvement of their pharmacological profiles.

Wednesday, August 13, 2014 02:15 PM
Controlled Radical Polymerization (01:00 PM - 05:30 PM)
Location: Hilton San Francisco Union Square
Room: Continental Ballroom 4
In order to overcome the limiting features generally encountered with drug-loaded nanoparticles for drug delivery (e.g., burst release, poor drug loading, etc), the design and the evaluation of novel nanoparticulate systems based on macromolecular prodrug amphiphiles are reported.

The strategy relies on the controlled growth of a hydrophobic and biocompatible polymer from an anticancer drug-bearing initiator, in order to position one chemotherapeutic at the extremity of each polymer chain (Fig. 1). Polyisoprene (PI) has been chosen as hydrophobic polymer due to its biocompatibility whereas we selected gemcitabine (Gem) as a drug, because of its demonstrated activity against a wide range of solid tumors.

Due to the amphiphilic nature of the resulting Gem-PI conjugates, they spontaneously self-assembled in aqueous solution to form stable, narrowly-dispersed nanoparticles of 130-160 nm in diameter. These nanoconstructs exhibited efficient anticancer activities both in vitro on various cancer cell lines as well as in vivo on human pancreatic carcinoma-bearing mice, while suppressing the inherent toxicity of the Gem. The accurate control of the polymer chain length also led to preliminary structure-activity relationships.

This new methodology tends to be universal and versatile as it is virtually applicable to multiple hydrophobic polymers (this was illustrated with the use of a polymer based on squalene, a natural lipid) and multiple drugs, and consequently to different pathologies.
651 - Boronic esters as a tool for bioconjugation to deliver platinum drug loaded micelles

Wei Scarano, Martina Stenzel, M.Stenzel@unsw.edu.au. Centre for Advanced Macromolecular Design, University of New South Wales, Australia

The conjugation of proteins, peptides or other biomolecules to polymers has been an active research field for many years now. An alternative pathway could be the reaction between boronic acids and alcohols. Boronic acids can undergo reactions with a range of compounds, most notably with 1, 2-dihydroxyl functionalities, with high affinity via reversible boronate esters formation. It is possibly one of the strongest single-pair reversible functional group interactions in an aqueous environment and it has already been utilised for various biomedical applications. These encouraging results inspired us to test this chemistry for conjugation of biomolecules to the surface of micelles. Particularly appealing is the potentially reversible nature of the boronic acid ester as a tool to detect pH changes. Aim is to explore borate esters as an efficient tool for bioconjugation, but also to investigate the stability of the complex at various pH values. We therefore developed a RAFT (reversible addition fragmentation chain transfer) agent based on dopamine, which is known to have a high affinity towards boronic acid. Subsequent polymerization led to blockcopolymer that were conjugated to platinum drugs in the core. Folic acid was attached to the surface by boronic acids. Although the complex is pH-responsive, it is reasonably stable under physiological condition. However, the susceptibility of the catechol functionality to oxidation and complex formation result in the disassociation of the boronic complex during apoptosis where increased oxidation and Ca²⁺ influx could potentially lead to the liberation of the boronic acid, thus it can be used to monitor the onset of apoptosis.

652 - Nucleobase-containing block copolymer synthesis via RAFT polymerization: From actuators to thermoplastic elastomers

Timothy E. Long, telong@vt.edu, Chainika Jangu, Keren Zhang. Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States

Nature broadly employs complementary hydrogen bonding of purine and pyrimidine rings to encode our genetic profiles. Our recent studies have demonstrated the effect of nucleobase incorporation on synthetic polymers through probing their physical crosslinking mechanisms and self-assembled morphologies. We designed acrylic nucleobase-functionalized ABC triblock thermoplastic elastomers with extended plateau regions and constant base pair melting temperature. Michael addition reactions readily provide nucleobase acrylic monomers. The robust complementary hydrogen bonding of nucleobase shows potential in solving the paradox of enhanced mechanical strength with solvent-free processibility. Special attention is devoted to the elucidation of the thermomechanical response using a complement of dynamic mechanical analysis, melt rheology, and in situ FTIR spectroscopy as a function of temperature. ABC triblock copolymers and complementary blends demonstrate the role of the complementary hydrogen bonding, and RAFT polymerization is a critical advance to permit the synthesis of a wide range of macromolecular architectures. A difunctional chain transfer agent provides tailored compositions in two steps for the preparation of ABA compositions.
Polymer-bioconjugates have recently received significant attention in the polymer community. This interest is largely sparked by the developments in site-specific conjugation and the ability to target unique features within the body, by exploiting target-directing ligands. Many previous studies focused on increasing the drugs half-life, through poly(ethylene glycol) (PEG) conjugation, PEGylation. This study makes use of polyvinylpyrrolidone (PVP), as an alternative to PEG, because it has been shown to provide a longer plasma half-life and favorable tissue distribution. In earlier work from our group we have shown that xanthate-based Reversible Addition-Fragmentation Chain Transfer (RAFT) agents, with triazole-based leaving groups, yield well-controlled PVP. This allows the introduction of a variety of functionalities via Huisgen click-chemistry. It is also well known that xanthate end-groups can be manipulated, post-polymerization, into various functionalities. Thus, bi-functional PVP can suitably be tailored for both the introduction of polypeptides, as well as target-directing ligands. Nano-vehicles, capable of target-specific delivery of therapeutic polypeptides, can be induced via self-assembly. The most recent developments in this work will be discussed.
In recent years the studies of biodegradable polymers have largely increased as a consequence of the wide range of properties and applications available (e.g. biomedical, pharmaceutical). Poly(ε-caprolactone) (PCL) is a poly(ester) which has been intensively investigated as it presents both biodegradable and mechanical properties to be used in drug delivery devices and engineering scaffolds. Nevertheless introduction of functionality into the PCL backbone is synthetically challenging. While several routes are possible to achieve such polymers, one in which the such polymers could be accessed by simple radical copolymerisation strategies would be attractive.

The use of ketene acetal monomers, specifically 2-methylene-1,3-dioxepane (MDO), represents an alternative route for the synthesis of functionalised and copolymers poly(ester)s as, after polymerisation, a similar structure to PCL results. The copolymerisation of MDO with vinyl ester comonomers provides a route to random copolyesters and offers exciting opportunities in the synthesis of biodegradable polymers with functional side chain groups. Herein, the synthesis of linear and hyperbranched degradable PCL-like copolymers will be reported using MADIX (Macromolecular Design via Interchange of Xanthates) will be reported to yield polymers of controlled molecular weight and with a range of side chain functionalities.
Well-defined high molecular weight polymers have become essential in biomedicine, and such polymers are readily accessible via polymerization of olefinic monomers. Poly(N,N-dimethylaminoethyl methacrylate) (DMAEMA) for example, has found widespread application as a non-viral gene delivery vehicle. Unfortunately, the carbon-based backbone of these polymers is not easily degraded, while incorporation of functional groups along the polymer backbone is far from trivial. Radical ring opening polymerization of cyclic vinyl monomers provides for an elegant, broadly applicable way of incorporating degradable and responsive linkages into the backbone of polymers. We have investigated the use of cyclic vinyl monomers containing allylic sulfides, in the copolymerization with DMAEMA. Copolymers were prepared, containing varying amounts of degradable linkages and their toxicity was evaluated through in vitro cell studies. These studies revealed increases in toxicity as molecular weight of the non-degradable polymers increased, while toxicity of the degradable, disulfide-containing, copolymers remained comparatively low. Our current efforts focus on the application of main-chain functional vinyl polymers in drug and gene delivery.
656 - Synthesis and ring opening polymerization of functionalized lactones

Timothy R Blake, tblake@stanford.edu, Robert M Waymouth. Chemistry, Stanford University, Stanford, California 94306, United States

The aerobic oxidative lactonization of substituted diethanol compounds provides an expedient synthesis of functionalized lactones. Organocatalytic ROP of these lactones yields functionalized polyesters with tunable molecular weights and narrow molecular weight distributions. Thermodynamic and theoretical studies reveal that the thermodynamics of ring opening depend sensitively on the nature of the endocyclic functional group.
Polymers that can undergo continuous head-to-tail depolymerization in response to a specific signal show promise as stimuli responsive materials for use in medical, environmental, and industrial settings. In this presentation, we describe a new class of depolymerizable poly(benzyl ethers) from stabilized quinone methides. These polymers can be synthesized to give high degrees of polymerization and can be end-capped with a variety of reaction-based detection units. Upon application of the appropriate stimulus and exposure to basic conditions, the poly(benzyl ethers) undergo an anionic elimination cascade to release their constituent monomers within minutes. While some current examples of depolymerizable polymers show significant levels of background degradation, these poly(benzyl ethers) remain stable against non-selective degradation from acid, base, or heat while end-capped. Furthermore, a current challenge with depolymerizable polymers is creating polymers that respond in the solid state, due to the low polarity environment within the polymer matrix and conformational restriction of the polymer chains. We have addressed this issue by creating functionalized monomers with pendant reaction-based detection units. These modified units allow for increased interaction with the solution phase, enabling depolymerization of the solid state polymer. This presentation will focus on these results, as well as current efforts that are aimed at making derivatives of the poly(benzyl ethers) with diverse physical and chemical properties to be used as stimuli responsive materials.

Wednesday, August 13, 2014 01:20 PM
General Topics: New Synthesis and Characterization of Polymers (01:00 PM - 05:00 PM)
Location: Hilton San Francisco Union Square
Room: Golden Gate 7
658 - An aza-Diels–Alder approach to polyquinolines

David J Dibble, ddibble@uci.edu, Alon A. Gorodetsky. Department of Chemical Engineering and Material Science, University of California, Irvine, Irvine, CA 92697, United States

Polyquinolines are an important class of materials for applications in electroluminescent devices and n-type organic transistors. To date, polyquinolines have been prepared through a limited number of synthetic routes, including the Friedländer reaction and palladium catalyzed cross coupling methods. We report a novel strategy for the preparation of polyquinolines through the aza-Diels Alder reaction of bifunctional building blocks. The resulting materials have been characterized with spectroscopic, chromatographic, and electrochemical techniques. Moreover, we have synthesized a diverse library of bifunctional monomers, enabling the preparation of polyquinolines with excellent solubility and processability. Our findings hold implications for the development of novel polyquinoline-based organic electronic materials.
659 - Understanding and improvement of the cyclopolymerization of 1,6-heptadiynes using Grubbs catalysts

Eun-Hye Kang, jeanne0821@gmail.com, Soyoung Yu, In Sun Lee, Tae-Lim Choi. Department of Chemistry, Seoul National University, Seoul, Republic of Korea

For preparing soluble conjugated polyenes, the cyclopolymerization (CP) of 1,6-heptadiyne derivatives is an useful method based on the metathesis reaction. While several metathesis catalysts of Mo and W showed reliable activity for CP of 1,6-heptadiynes, CPs using Ru catalysts have been challenging due to the low polymerization efficiency. Recently, we reported the efficient CP based on Grubbs catalysts by using THF as a reaction solvent rather than DCM,\textsuperscript{1} and related works as further applications.\textsuperscript{2,3} The important effect of weakly coordinating solvent was investigated furthermore, and we discovered the reason why Ru-based Grubbs catalysts didn't worked on the CP of 1,6-heptadiynes in DCM, which is a common solvent for metathesis polymerizations. First, by replacing the THF into weakly coordinating additive, the polymerization efficiency was greatly improved in DCM. We found this weak-coordination dramatically increased the life time of the propagating carbene by \textsuperscript{1}H NMR studies. As a result, various monomers were well polymerized with controlled $M_n$ and narrow PDIs in DCM with an additive. Additionally, the reaction temperature effect was also figured out by the same analysis. From these results, we could understand how Grubbs catalyst-based CPs became living system by improved reaction conditions.


A new class of monomers that contain both strained heterocycles and reactive nucleophiles has been synthesized without the use of protecting groups using ring-expansive carbonylation catalysts. We found that these monomers are stable and undergo self-polymerization without the need for a catalyst, resulting in degradable polymers with pendant functional groups. In this presentation, the synthesis, polymerization, and detailed structure-activity study of a broad range of substrates will be discussed.
661 - Synthesis of BPA-polysulfate: Tolerance toward stoichiometric imbalance leads to end-cap-functionalizable fluorosulfate groups

James S Oakdale, joakdale@scripps.edu, Luke Kwisnek, Valery V Fokin, Jiajia Dong, Barry K Sharpless. Department of Chemistry, The Scripps Research Institute, La Jolla, California 92037, United States

The SuFEx (sulfonyl fluoride exchange reaction) mediated synthesis of BPA-polysulfate from bisphenol A-bis(fluorosulfate) ('AA') and bis(silylether) ('BB') monomers is a step-growth polymerization method capable of tolerating stoichiometric imbalance. In addition to the primary reaction of AA + BB, fluorosulfates were observed to undergo homocoupling thereby leading to additional reactivity of AA + AA. High molecular weight polysulfate can thus be obtained in three ways; A) 1:1 equivalents AA:BB, B) excess AA relative to BB, or C) solely from the AA monomer. Methods B) and C) thereby ensure the resulting polysulfate polymer is end-capped with reactive fluorosulfate groups. The ability to manipulate these functional handles is demonstrated through the attachment of a UV-traceable, OTBS-substituted nile red dye using post-polymerization SuFEx reactivity.
662 - Controlling surface composition and properties of polyethersulfone films through chain-end chemistry

Katrina M Knauer, katrina.knauer@eagles.usm.edu, Sarah E. Morgan. School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406, United States

The surface composition of polymer films plays a pivotal role in tailoring surface properties such as wettability, adhesion, friction, and biocompatibility. Surface composition of polymeric systems can be controlled via the segregation of low energy components to the polymer surface. Several flexible polymer systems exhibit segmental density distribution due to the localization of functional chain-ends to the polymer-air interface. This chain-end behavior can be used to dictate surface properties of polymer films but has yet to be investigated in rigid-rod polymer systems. This work investigates the surface and interfacial chain-end behavior in rigid rod polyethersulfone (PESU) films with different functional chain ends: hydroxy and fluorescein isothiocyanate (FITC).

Commercial PESU was fractionated and characterized via static and dynamic light scattering. Depth profiles of chain-end distribution in solution cast films was investigated using grazing angle ATR-FTIR, X-ray photoelectron spectroscopy (XPS) with ion gun etching (see figure), and fluorescent labeling. Finally the resulting surface properties were studied using contact angle and atomic force microscopy in both lateral force mode and quantum nanomechanical mapping mode. Experimental results were combined with molecular dynamics simulations to construct an overall model of chain-end distribution in rigid rod systems.
663 - Utilizing exchange reaction at hypervalent iodine center in one-step synthesis of azide containing hyperbranched polymer at ambient temperature

Hongzhang Han, hhan@smu.edu, Nicolay V Tsarevsky. Department of Chemistry and Center for Drug Discovery, Design, and Delivery, Southern Methodist University, Dallas, Texas 75275, United States

Copper-catalyzed azide-alkyne cycloaddition (CuAAC) “click” chemistry has attracted great attention during the past decades due to its efficiency and the simple access to various functional group-containing materials that can be prepared by it. However, the preparation of the needed azide-containing building blocks is often difficult and requires several steps, which limits the broad applications of CuAAC in industry. Sodium azide is a common inexpensive azide source with relatively good stability at ambient temperature. It is often used in nucleophilic substitution reactions to prepare azide-containing organic compounds. Recently our group developed a novel single-step method to prepare azide-containing polymers that utilizes hypervalent iodine(III) compounds, such as (diacyloxyiodo)arenes, and sodium azide. The reaction yields azide radicals that can initiate polymerization of various vinyl monomers at low temperatures, and can also serve as additional azidating agent. When the polymerizations are carried out in the presence of di- or multivinyl crosslinkers, branched polymers are produced prior to gelation, which only occurs at high monomer conversions. The high azide radical concentration is the key factor in producing hyperbranched polymers instead of gels even at high cross-linker ratio to monomer, up to relatively high conversions. The new method provides an efficient one-step route to multiazidated hyperbranched polymeric materials with a number of potential applications.

Acknowledgement. This research was supported by the Petroleum Research Fund of the ACS (PRF# 51030-DNI7).
664 - WITHDRAWN
An understanding of the bulk and surface properties of polyurethane based binder systems are critical to the manipulation of favorable interactions between a given binder system and particulates within a composite material. Inverse gas chromatography was utilized to provide the surface [total surface energy ($\gamma_s$), dispersive ($\gamma_{sd}$) and specific or polar ($\gamma_{ssp}$) components, work of cohesion and adhesion, chemisorption and physisorption affinity] and bulk [glass transition temperature ($T_g$), solubility parameters, polymer cross-linking and diffusion coefficient] characteristics of solid binder samples in comparison to a series of well understood gas phase molecules. Contact angle goniometer measurements were utilized for comparison of the surface free energy of the solid binder sample and the interfacial tension (surface tension) between a liquid probe material and the solid binder surface. Primary outcomes include an increased understanding of the differences in the bulk and surface properties of polyurethane based binder systems with different constituents, development of methods to characterize and evaluate new binder systems and increased wettability of particulates in basic binder systems. Final success and progress was measured by the ability to reproducibly measure surface and bulk energies, interactions and other properties of a series of increasingly complex binder systems and correlate these findings with constituents contained within the binder system.
Development of new process to optimize the performance of methylcellulose

Methylcellulose chemistries are used in variety of applications in the Food & Nutrition markets. The key barriers to the wider use of methylcellulose as a food additive is the requirement to be dissolved / hydrated at low temperatures for long times in order to deliver necessary gel strength properties for the final application. A new method has been developed to overcome the above barrier by improving the hydration efficiency and gel strength of methylcellulose in much shorter period of time to meet the commercial process conditions.

In this study, the focus is to understand the hydration process of methylcellulose in water and its optimization. The new hydration process led to significant reduction of hydration time and improvement of gel strength. The new process led to development of a very different network structure results in the improvement of the methylcellulose performance. Analytical results are going to presented demonstrating the presence of different network structure when the methylcellulose is prepared with the new process.

The schematic diagram for the methylcellulose reaction process is illustrated below.

![Figure 1: Schematic diagram for the methylcellulose reaction process](image)
The direct observation of individual polymer chains would provide valuable information to understand the fundamental properties of polymer materials. Fluorescence imaging is the most effective method to detect a single molecule embedded in a bulk medium; however, the imaging of the conformation of a single chain has been impossible because of the diffraction-limited spatial resolution (\( \lambda/2 \)). In the current study, we developed a super-resolution fluorescence microscopy technique, photo-activated localization microscopy (PALM), for the direct observation of the conformation of a single polymer chain. Figure 1a shows PALM images of single poly(butyl methacrylate) (PBMA) chains in a film with thickness of 210 nm, which corresponds to the projection images onto the xy- and yz-planes. This indicates that PALM can observe the chain conformation in three dimensions with the resolution of 20 \( \times \) 20 \( \times \) 50 nm\(^3\). The analysis of the image of individual chains provides the information that has been unavailable by other methods, such as distribution function of the radius of gyration shown in Figure 1b.

The super-resolution technique would be a powerful tool to discuss the fundamental process of single chains in various phenomena of polymeric materials.
668 - Water hydrogen bonding in functionalized membranes

Michael A. Hickner, mah49@psu.edu, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

FTIR spectroscopy was used to measure the hydrogen-bonding environment of water sorbed into functional polymer membranes. By monitoring of the OD stretch of 10 mol % HOD in H₂O, the populations of water bound to the polymer, in the bulk liquid state, and in intermediate states could be deconvoluted rigorously based on their distinct vibrational frequencies. In a series of sulfonated membranes, the negative charge on the sulfonate group computed from density functional theory corresponded with the observed OD frequency for water hydrating the ionic group. Stronger acids, with a lower negative charge on the sulfonate group, displayed a higher frequency OD stretch indicating a weaker hydrogen between water and the acidic headgroup. This FTIR method has been extended to observing how water is bound within the structure of anion exchange membranes and also polyamide reverse osmosis active layers. In addition to directly observing the hydrogen-bonding environment in the OD stretch region, the polymer fingerprint can be examined for changes in vibrational frequency and peak shape of specific functional groups as they are hydrated. Computing difference spectra and the center of mass of key peaks has revealed the important functional groups of the polymer backbone that induce interactions with water. This talk will discuss details of how water interacts with polymer membranes with a variety of chemistries and how these interactions help determine the water transport properties of the materials.
Methods toward understanding reverse osmosis membrane structure

Robert C Cieslinski1, rccieslinski@dow.com, Abhishek Roy1, Sam Qiu1, Bruce Gerhart1, Mark Rickard1, David Hawn1, Chengli Zu1, Mou Paul2, Steve Rosenberg2. (1) Department of Analytical Sciences, The Dow Chemical Company, Midland, Michigan 48667, United States, (2) Dow Water & Process Solutions, The Dow Chemical Company, Edina, Mn., United States

Since the development of FT30-interfacial polyamide chemistry by the late John Cadotte in the early 70's, efforts have been made to modified the polyamide chemistries to improve both energy and separation efficiency for reverse osmosis membrane. However owing to the complex crosslinked nano scale morphological structure of polyamide, development of structure-property relationships has been a challenge. In the last few years, leveraging Dow's strong analytical capabilities and blending with Dow Water& Process Solution expertise, for the first time, it has been possible to achieve a true fundamental structure-property relationship of polyamide RO membrane. In depth characterization of polymer composition, morphology, topology and post gel properties coupled with fundamental transport and structural modeling led to a breakthrough in membrane chemistry innovation to lower energy requirements for brackish water low energy applications by 35% and at the same time to maintain the state of the art rejection standards.

The research led to several fundamental understandings of how "polymer structure controls membrane performance". For example, it was possible to design FT30 polyamide from a molecular level with systematic incorporation of carboxyl group moieties to understand the role of Donnan exclusion principle in controlling membrane performance. The paper will highlight the analytical characterization perform to understand the network structure and morphology with performance, with an objective to communicate broadly to the scientific community in designing novel and differentiated RO membranes for addressing today’s energy crisis.
670 - Water transport in Nafion thin film membranes using time-resolved polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS)

Eric M. Davis, eric.davis@nist.gov, Christopher M. Stafford, Kirt A. Page. Materials Science and Engineering Division, The National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

Perfluorinated ionomers, specifically Nafion, are the most widely used ion exchange membranes for fuel cell applications. Nafion is typically incorporated into the catalyst ink layer as a binder and proton conductor, where it is confined to films on the nanometer size-scale. Therefore, developing a deeper understanding of the fundamental water transport mechanisms in thin films is critical. In this study, the diffusion of water vapor into Nafion thin films was measured using time-resolved, in situ polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS). Specifically, diffusion of both H$_2$O and D$_2$O in dry and hydrated Nafion films was captured by obtaining molecular-level resolution of the water adsorbed in the thin film in real time. The effective diffusion coefficient of water in the Nafion thin films was many orders of magnitude less than those reported in bulk films and was dependent on the initial hydration state. However, little difference was observed between the diffusion coefficient for H$_2$O and D$_2$O. Moreover, our results indicate that water-induced swelling (polymer relaxation) of the Nafion films was orders of magnitude slower than those calculated for bulk films.
A series of triazole-containing polymers were synthesized to evaluate the effect of polymer matrix dielectric constant on proton transport ability. For polymers with similar triazole contents, the observed proton conductivities increased by as much as 4 orders of magnitude when shifting from the low dielectric constant, polymethacrylate-based, materials to the high dielectric constant, polyethyleneimine-based analogs. The PEI-based materials showed excellent thermal and electrochemical stability between room temperature and 140 °C, and can be incorporated into mechanically robust diblock and triblock copolymer architectures. Extensions of this approach could be used to produce a new generation of highly conductive, mechanically robust, proton exchange membranes for water-free hydrogen fuel cell operation.
Relatively thick nanobrick wall multilayer films were prepared with cationic chitosan (CH), buffered with Trizma base (tris), and vermiculite clay (VMT). This layer-by-layer (LbL) assembly reduced the transmission of oxygen of polyethylene terephthalate (PET) film by three orders of magnitude with just six bilayers (BL). Buffering the cationic and rinse solutions with only 50 mM of tris increased the thickness of the resulting films by an order of magnitude relative to the same recipe prepared without tris buffer. At only eight bilayers (BL), this recipe achieves a thickness of 3.7 μm and a dry mass of 1.2 mg/cm², which is among the highest reported for a layer-by-layer (LbL) system. The oxygen transmission rate (OTR) of coated PET films was 0.009 cc/m²·day·atm with only six bilayers (BL) deposited, and was below the commercial detection limit (< 0.005 cc/m²·day·atm) with eight BL deposited.
Self-organized polymer membranes conduct mobile species (ions, water, alcohols, gases) according to a hierarchy of structural morphologies that span sub-nm to > 10 micron in length scale. Our group combines multi-modal NMR measurements (spectroscopy, diffusometry, relaxometry, imaging) with structural information from scattering and microscopy as well as theories of porous media, electrolytic transport, and oriented matter. Such comprehensive dynamical and structural studies allow for unprecedented understanding of polymer membranes as used in molecular separations, including water purification, fuel cells, and batteries. Using pulsed-field-gradient (PFG) NMR, one can track each chemically distinct mobile species inside a polymer, and can do so over a range of length and time scales. Recently, we have recognized how the activation energy ($E_a$) of diffusion probes 1 nm-scale molecular forces and 1 ps dynamics (M.D. Lingwood et al, *Chemical Communications*, 2013). Combining this knowledge with detailed information on > 100 nm scales (J. Li et al, *Nature Materials*, 2011), we are able to quantitatively separate the two major effects that govern transport in polymer membranes: 1) local intermolecular interactions and 2) polymer morphology. We will discuss example ion conducting polymeric systems and explain strategies for making these observations. Finally, we will discuss broad implications for design of polymeric materials for tailored transport applications.
Polymer electrolyte membrane fuel cells (PEMFCs) are a common type of fuel cell, generally used for relatively low temperature or portable applications. Traditional membranes used in these fuel cells are hydrated, which results in connected water channels that are believed to enhance the transport of protons across the membrane. However, it is often difficult to keep the membrane sufficiently hydrated, resulting in poor performance that necessitates the use of complicated rehydrating systems. Therefore, a membrane that provides high conductivity at low hydration levels is needed. Presented here are experimental data (e.g., SAXs, conductivity, and NMR) and molecular dynamics simulation results of a novel organic aromatic polymer (random and block) that possesses enhanced proton conducting characteristics at low hydration levels as compared to Nafion. The structural and morphological analysis of the random and ordered block polymer reveal the hydrophobic/hydrophilic interactions that favor connected water clusters at low hydration levels, which may be responsible for the membrane's enhanced conductivity.
675 - Precise control of structure and performance in conjugated polymer/fullerene organic photovoltaics with solvent annealing

Mark Dadmun¹, dad@utk.edu, Huipeng Chen¹, Yu-Che Hsiao², Bin Hu². (1) Chemistry, The University of Tennessee, Knoxville, TN 37996, United States, (2) Materials Science, The University of Tennessee, Knoxville, TN 37996, United States

One of the most important challenges facing our society is the development of technologies for renewable energy conversion. Polymeric bulk-heterojunction (BHJ) photovoltaics, based on conjugated polymers and fullerenes, are an economically viable option for low cost renewable power generation. The most promising conjugated polymer:fullerene active layers in organic photovoltaics now utilize low band-gap (LBG) copolymers. Unfortunately, for most of these LBG devices, there is no further treatment available after film deposition to optimize the morphology. We have exploited the selective solubility of the LBG:fullerene nanocomposite components to direct the assembly of these mixtures by annealing in the vapor of a selective solvent. Our recent work demonstrates that annealing in a solvent that is selective to the fullerene forms a sample with fullerene aggregation, while annealing in a solvent vapor that is selective to the polymer forms a thin film with polymer precipitation. There is also a direct correlation between the resultant morphology and OPV performance, increasing PCE by 190%. Further work in this arena has clearly shown that solvent annealing and solvent choice provides a unique tool to precisely tune the morphology of a broad range of CP:Fullerene BHJ systems, optimizing the morphology and performance of the active layer.
Polymer membranes are a vital component of solar-fuel generators. For this application requirements for the membranes include low permeability of the gaseous or liquid products, mechanical strength, and moderate proton or hydroxide conductivity. The relative importance of these factors in the context of artificial photosynthesis are distinct from the requirements of fuel cell membranes, and present unique design opportunities. Current synthetic efforts in the group represent a multifaceted approach of incorporating new conductive motifs, novel structural elements, and exploring innovative concepts in membrane materials. In order to incorporate all of the necessary properties for a solar fuel membrane our attention has been concentrated around synthesizing block co-polymer membranes, which satisfy different requirements with chemically distinct blocks. We used a combination of ring opening metathesis polymerization (ROMP) and anionic ring opening polymerization (AROP) to synthesize triblock copolymers consisting of a semi-crystalline poly(ethylene) (PE) midblock for low gas crossover and good mechanical properties and explored amine and imidazolium based ion-conducting polyether end-blocks due to their versatile chemical functionality and flexibility. The use of AROP allowed us to grow our conductive end blocks of various lengths with optimal control. The conductivity and gas permeability of these membranes have been studied relative to the mole fraction of the functional end blocks.
677 - Improving biomaterials through polymer processing technologies

James H. Wang, jhwang0001@gmail.com, Corporate Research and Engineering, Kimberly-Clark Corporation, Neenah, WI 54956, United States

The presentation covers the concept of sustainability based on the three pillars and global drivers of sustainability, as well as industry's perspective on sustainable development and WBCSD's 2050 vision for sustainability. The perspectives on desired attributes of successful bioplastics as well as the challenges of current bioplastics will be discussed.

Physical, chemical, and biochemical modification technologies were developed to transform various types of biomass accumulated in nature including cellulose, starch, plant proteins into usable thermoplastic materials. However, the thermoplastic natural polymers have deficiencies such as lacking performance, limited melt processability, and high costs, the thermoplastic biopolymers had to be further improved by processing with other polymers and modifiers to make them suitable for real-world applications. Biodegradable aliphatic polyesters such as polylactic acid (PLA), polybutylene succinate (PBS), polybutylene adipate terephthalate (PBAT), and polypropylene carbonate (PPC) were also modified by chemical and physical methods to improve processability and/or performance.
Micromidas has developed a process to convert carbohydrate raw materials such as corn stover, cardboard and starch, into higher value chemicals with the goal of producing biobased chemicals cost-competitively with those of fossil fuel origin. The Micromidas process produces a series of furan intermediates from the conversion of the polysaccharide feedstocks to p-xylene (pX). The feedstock is simultaneously saccharified and dehydrated to 5-chloromethylfurfural (CMF) using hydrochloric acid. CMF is then hydrogenolyzed and reduced to 2,5-dimethylfuran (DMF). The Micromidas team has demonstrated that DMF can be converted to pX with yields greater than 90% by the Diels-Alder reaction of DMF with ethylene (Figure 1). Pilot scale samples show that the p-xylene produced from this process meets the same specifications for terephthalic acid production as p-xylene from petrochemical sources. Process economics demonstrate that, with optimization of intermediate process steps, p-xylene can be made from cellulosic feedstocks at costs competitive with the petrochemical route.
679 - Green-chemistry synthesis of cellulosic derivatives

H.N. Cheng¹, hn.cheng@ars.usda.gov, Atanu Biswas². (1) Southern Regional Research Center, U.S. Department of Agriculture, New Orleans, LA 70124, United States, (2) National Center for Agricultural Utilization Research, U.S. Department of Agriculture, Peoria, IL 61604, United States

A large number of cellulose derivatives are known and commercially available, e.g., cellulose acetate, methyl cellulose, carboxymethyl cellulose, and hydroxyethylcellulose. In this work, two sets of reactions will be described that can potentially enhance the value of these cellulosic derivatives. As an example, these reactions have been applied to methyl cellulose, an industrial polymer used in adhesives, protective coatings, personal care, and agriculture. In the first case, it has been shown that agricultural residues such as wheat straw, barley straw, and rice hull can be converted to methyl cellulose. Weight yields range from 30 to 70%; the degree of substitution (DS) varies from 0.8 - 2.8. In addition, the methyl cellulose can be further converted to acetylated methyl cellulose, with the possibility for additional uses. In the second case, an alternative, simplified synthesis of methyl cellulose is reported, using microwave irradiation and aqueous alkaline medium. No alcohol is needed during the reaction and the reaction time is less than 30 minutes. The resulting polymers have been fully characterized by NMR.

Figure 1. Simplified scheme for the product development of cellulosic derivatives
Chitin is the second most abundant biopolymer on earth after cellulose and serves as building blocks inside crustacean exoskeleton, insect cuticles, and fungal cell wall. Similar to cellulose, chitin semi-crystalline domain can be further nanofibrillated, hence, offer new possibilities towards novel nanotechnology-derived application due to its nitrogen-rich structure. Most of the literature reported the use of crustacean chitin as raw material due to their high yield per dry weight and readily available resources compared to fungal chitin. However, the existence of covalent linkage between chitin and glucan in native fungal cell wall resulted in “soft” and less crystalline biopolymer that set them apart from crustacean chitin. The possibility of finding ductile, flexible, and other interesting properties inherent in fungal cell walls coupled with the ability of controlling their growth behaviour and life cycle motivate our current study. In this study, chitinious material (chitin-glucan) was extracted from common mushroom cell wall (Agaricus bisporus) and defibrillated to nano-level followed by thin film sheet production. Their morphological, mechanical, chemical, and surface properties were compared with crustacean (Cancer pagurus) chitin film. This study also investigates different properties that contributed by different part of mushroom fruiting body, i.e stipe and pileus towards overall characteristic and performance of resulted film. In addition, separate study on chitin-glucan from tree fungus (Daedaleopsis confragosa) was carried out to investigate the effect of matrix-free biopolymer towards its mechanical strength.
681 - WITHDRAWN
Holocellulose nanocrystals (holoCNC) with surface active properties were derived from sulfuric acid hydrolysis (64% H$_2$SO$_4$, 45 °C, 45 min) of holocellulose from rice straw to exhibit similar dimensions as their pure cellulose nanocrystal (CNC) counterparts, but in nearly doubled yield. The holoCNCs were more thermally stable at up to ca. 250 °C, but less charged and crystalline. The presence of hemicellulose on the holoCNCs demonstrated surface active properties, which was not observed on CNCs, to enable stabilization oil-in-water emulsions, forming emulsion droplets with size ranging from 1-2 μm with good stability. Such surface active properties were confirmed by fluorescence spectroscopy and surface tension measurement. The holoCNCs cellulose self-assembled upon by freeze-drying and oven drying to different morphologies and porous structures than those from CNC. The streamlined isolation method in generating holoCNCs presents a more efficient process as well as additional unique characteristics and properties for new applications.
A new heterogeneous synthesis process, which achieves a significant energy reduction, has been developed for a novel cellulose-based bioplastic for durable products using non-food plant resources. The bioplastic is a cellulose ester synthesized by bonding a short side chain (acetic acid) and a long one (3-pentadecylphenoxy acetic acid (PAA): a derivative of cardanol, extracted from cashew nut shells). In conventional homogeneous processes, cellulose esters are recovered by precipitations using large quantities of poor solvents, which require much energy consumption for their distillation.

In the new process, firstly, limited amounts of these chains were bonded in a heterogeneous system to achieve efficient product recovery (high productivity). Secondly, the short-chain acid was additionally bonded to attain good thermoplasticity of the final product, which was recovered by distilling the reaction solvent and the remaining short-chain acid. The solvent usage was reduced by approximately 90% compared to the homogeneous processes, which leads to about 90% reduction in energy. The thermoplasticity of the resulting resin was comparable to that of homogeneous ones.

Furthermore, the mechanical and thermal characteristics of the resin were greatly improved by adding a specific linear polyester, such as poly(butylene succinate adipate), and a glass fiber, reaching high target levels for durable products.

A novel renewable thermoplastic polyacetal was prepared via a catalytic and green polymerization process where the catalyst and solvent can be recycled. The monomer can be obtained in high purity and large quantities from the fast pyrolysis of cellulosic feedstock. The production of the monomer does not use food crops, therefore does not compete with the food supply chain. This novel polyacetal is not only renewable, but potentially biodegradable and therefore compostable. The monomer, which is also expected to be the ultimate product of degradation, is a non-toxic metabolite. The polyacetal will fill the need for renewable and biodegradable plastics as shown in the figure below. The thermal and mechanical properties of this novel renewable polyacetal are comparable to those of LDPE that is used in food packaging applications.
Organometallic polymers, enjoying both advantages of the organic and metallic components, have drawn much attention in the past decades due to their unique electrical, magnetic, optical, sensing and catalytic properties. Among the organometallic polymers, ferrocene-based ones have been widely investigated because they possess the unique redox properties and structure variation. There are many polymerizations to prepare the ferrocene-based linear and branched polymers. Most of these polymerizations, however, must be performed under harsh reaction conditions, which normally require careful exclusion of moisture and oxygen, and greatly limit their further applications.

In this talk, we will present our recent effects on preparation of ferrocene-containing polymers via our established metal-free click polymerization (MFCP) of activated alkyne of propiolates and azide. The MFCPs of dipropiolates and ferrocene-containing diazide carried out in DMF at 80 °C for 24 h without taking caution to exclude moisture and oxygen, readily produced soluble polytriazoles with high molecular weights (up to 13400) and regioregularities (the fraction of 1,4-disubstituted 1,2,3-triazole isomer in the polymers up to 93%) were obtained in high yields (up to 97%) (Figure 1). The resultant polytriazoles are thermally stable and redox active, and the pyrolysis of these polymers readily generates ceramics with high magnetizability and low coercivity.
Photocatalytic reduction of CO$_2$ to CO with [Re(CO)$_3$(bpy)L]$^+$ complexes and triethanolamine requires blue or UV radiation. These reactions may be sensitised to long-wavelengths by the use of ruthenium bipyridine complexes [1] or zinc porphyrins in combination with the rhenium complexes, thereby making them suitable for use with solar radiation [2]. We compare the photocatalytic activity of three dyads with different spacers between zinc porphyrin and rhenium (Scheme 1). We also compare complexes with L = Br$^-$ with those with L = 3-methylpyridine. The dyad with a saturated linker exhibits the highest turnover number in keeping with results on Ru-Re dyads. Bromide complexes give similar turnover numbers to complexes with methylpyridine. The activity of combinations of separate zinc porphyrin and Re components has also been examined with various L substituents. The reactions are sensitive to the nature of L and substituents on the bipyridine. The turnover numbers of the most effective two-component systems are only exceeded by the dyad with the saturated linker. It should therefore be possible to improve the design of dyads by applying design criteria for the two component systems that are more easily synthesised than the dyads.


687 - Taking advantage of imidazole and imidazolium in block copolymer design

Timothy E. Long¹, telong@vt.edu, Alison R. Schultz¹, Chainika Jangu¹, John H. Herlihy¹, Keren Zhang¹, Michael H. Allen². (1) Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United States, (2) Adhesives Research, Glen Rock, Pennsylvania 17327, United States

The imidazole ring offers synthetic versatility with the opportunity to alkylate in a non-symmetrical fashion for the subsequent formation of the imidazolium cation. These ion-containing polymers and polyelectrolytes offer many advantages in the design of metal-containing multiphase systems and ionic liquid monomers play a critical role in these technologies. In addition, the imidazole ring enables coordination with various metals to offer the synthesis of metal-containing polymers with particular emphasis on the design of block copolymers. This lecture describes the formation of ABA triblock copolymers wherein the imidazole ring is located in the central block with comonomers to ensure a low glass transition temperature phase. The presence of the interactive imidazole ring in the low glass transition phase ensures adequate mobility for the design of functional materials. RAFT polymerization using a novel difunctional chain transfer agent ensures the design of pH and ion sensitive polymeric membranes for many applications including electro-active devices and salt-responsive adhesive applications.
688 - Biomolecule sensing using nanoparticle-polymer supramolecular complexes

Vincent M. Rotello, rotello@chem.umass.edu, Department of Chemistry, University of Massachusetts, Amherst, MA 01003, United States

Our research program focuses on the functionalization of metal nanoparticles surfaces for a variety of applications, coupling the control provided by organic synthesis with the versatility of supramolecular chemistry. Through engineering of polymer- and protein-nanoparticle interactions, we have developed array-based sensors to sense and identify of proteins in sera, cell surfaces, and cell lysates. Recent advances in the development and application of these systems to both tissue sensing and high throughput screening will be discussed.
689 - Probing the Pt-organometallic versions of polyaniline: Surprising insights on the electronic communication in PANI

Pierre D. Harvey, Pierre.Harvey@USherbrooke.ca, Département de chimie, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada

Polyaniline (PANI) exists under 4 forms: eucoemaraldine, perigraniline, emaraldine and protonated emaraldine (Figure 1). The latter is conducting and their derivatives exhibit interesting features for the design of electrochemical sensors, rechargeable batteries, organic light emitting diodes (OLED) and solar cells. Recently, PANI received substantial attention as an "ingredient" for the design of photovoltaic cells, notably dye sensitized solar cells (DSSCs). We recently explored the effect of replacing a fragment of PANI by the trans-Pt(C≡C)(PR3)2 unit (ChemComm, 2014, 50, 350-352; Macromol. Rapid Comm. 2013, 34, 511-515; Inorg. Chem., 2012, 51, 13081-13095; ChemComm, 2012, 48, 11542-11545) to form polymers P1a-e, P2 and P3a-e. These materials were fully characterized by means of GPC and SAXS, and model compounds (X-ray structure determination, DFT computations). Their properties were addressed using electrochemistry, photophysics, UV-vis and luminescence spectroscopy. Clear evidence for electronic communication along the backbone of the polymers are detected, even in the reduced form, a communication secured by the N lone pair. Tautomeric forms were also detected in some cases when using amino-substituted anthraquinone diimine units.

---

Wednesday, August 13, 2014 03:00 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (01:00 PM - 05:05 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 1/2
**690 - Non-conjugated polymer with iridium(III) complexes for nonvolatile rewritable memory devices**

Wenpeng Lin, Shujuan Liu, Qiang Zhao, iamqzhao@njupt.edu.cn, Wei Huang. Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing, Jiangsu 210023, China

Recently, polymer memories have attracted a great amount of attention. Herein, two non-conjugated polymers (P1 and P2), containing Ir(III) complex unit and carbazole unit have been designed and synthesized. For them, electroactive carbazole acts as an electron-donor moiety and Ir(III) complex serves as an electron-acceptor moiety. A sandwich-type device with the structure of Al/P1 or P2/ITO is fabricated.

The device exhibits two accessible conductivity states, that is, the low-conductivity (OFF) state and the high-conductivity (ON) state. The OFF state can be switched to the ON state under a negative electrical sweep, which can be reset to the initial OFF state by a reverse electrical sweep. The ON state is nonvolatile and can withstand a constant voltage stress of -0.5 V for 10^4 s under ambient conditions. The nonvolatile nature of the ON state and the ability to write, read and erase the electrical states, fulfill the functionality of a rewritable memory. The devices based on the two polymers show the similar “writing” voltage of below -1 V. However, the device based on P1 exhibits low erasing voltage of 2.4 V, which is lower than the device based on P2 (2.9 V). The ON/OFF current ratio of the device based on P1 (10^3) is larger than that of the P2 (10^2). The memory mechanism can be attributed to the formation and dissociation of a charge-transfer state under the applied voltage.
Iridium(III) complexes have been widely investigated as organic light-emitting materials. However, studies on their application as nonlinear optical materials have been quite limited. Due to the large triplet quantum yield, long triplet lifetime and broad triplet excited-state absorption of many Ir(III) complexes, Ir(III) complexes could be good candidates as nonlinear absorbing materials. Our group has designed and synthesized a variety of cationic or neutral Ir(III) complexes with different degrees of π-conjugation on the diimine ligand and/or on the cyclometalating ligands to understand the structure-property correlations for developing broadband nonlinear absorbing materials. The photophysical properties of the Ir(III) complexes that are closely related to the nonlinear absorption, such as the ground-state absorption spectrum, excited-state lifetime and quantum yield, and excited-state absorption, have been systematically investigated via UV-vis absorption, emission, and transient absorption spectroscopies. DFT calculations were also performed to understand the nature of the excited states. To demonstrate the reverse saturable absorption (RSA) at 532 nm, nonlinear transmission experiments were carried out using 4.1 ns laser pulses. It was found that extending the π-conjugation on the diimine ligand or on the cyclometalating ligands can influence the excited-state characteristics dramatically, which subsequently change the RSA of the Ir(III) complexes drastically.
The generation of renewable fuels by artificial photosynthesis may hold the key to global energy sustainability and has been a major area of recent research. Three important characteristics of working electrodes for an artificial photosynthetic system are strong light absorption, efficient charge transport, and catalysis for fuel formation. To tackle the first two of these, we employ surface plasmon resonance using metallic core-shell nanostructures to concentrate light into thin nanostructured working electrodes. Our initial proof of concept uses hierarchical multi-shelled metal nanoparticles, and introduces the concept of working electrodes incorporating larger core-shell metallic aggregates. These materials possess broadband surface plasmon resonance throughout the visible light region of the solar spectrum, enabling plasmonic light concentration over a wide frequency range. Our current studies using this material show significant enhancement of light absorption in dye-sensitized solar cells, and our future studies incorporate water oxidation catalysts to use this plasmonic architecture in an artificial photosynthetic scheme as well.
Metallopolymers from metallocene derivatives: Controlled synthesis, self-assembly, and applications

Yi Yan, yan9@mailbox.sc.edu, Jiuyang Zhang, Yali Qiao, Perry Wilbon, Chuanbing Tang. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

Metallopolymer is one of the most important functional materials and receives increasing attention during last several decades.\(^1\) One facile method to prepare metallopolymers starts from metallocenes and their derivatives.\(^2\) We are interested in polymers containing metallocenes such as ruthenocene, cobaltocene/cobaltocenium, rhodocene/rhodocenium, which are less studied. In this presentation, we will present our recent work on polymerization of cobaltocenium-, ruthenocene-, cobalt(I)- and rhodium(I)-containing monomers through controlled polymerization methods, such as ATRP, RAFT and ROMP. Furthermore, self-assembly and some interesting properties will be discussed.\(^3\), \(^4\)

Wednesday, August 13, 2014 04:15 PM
Metal-Containing and Metallo-Supramolecular Polymers and Materials (01:00 PM - 05:05 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 1/2
Polymers via ring-opening metathesis polymerization

Elizabeth Elacqua, elizabeth.elacqua@nyu.edu, Marcus Weck. Department of Chemistry and Molecular Design Institute, New York University, New York, NY 10003, United States

The integration of supramolecular chemistry with materials science has resulted in the synthesis of polymers, with a focus on subsequent self-assembly. Owing to the ability of Nature to engineer macromolecules utilizing noncovalent interactions, supramolecular polymers have emerged as attractive modules that sustain a precise assembly, while providing access to functional building blocks. The field of supramolecular polymer science can be divided into two categories: side-chain and main-chain functionalized polymers, both of which require highly-controlled polymerization methods, such as ring-opening metathesis polymerization (ROMP), to design well-defined architectures that can mirror the precision and fidelity demonstrated by Nature. This presentation will focus on design principles of metal-containing supramolecular polymers synthesized via ROMP and their potential applications.
Polycarbosilanes are flexible metal-containing polymers with high thermal and chemical stability. We consider that polycarbosilanes can be key polymers to develop new functional materials. Silacyclobutanes are known as good monomers to prepare polycarbosilanes by various ring-opening polymerizations.

Here, we synthesized a silacyclobutane having an epoxy functional group, 1-(3,4-epoxybutyl)-1-methylsilacyclobutane (OBMSB), and examined its transition-metal-catalyzed ring-opening polymerization. As a result, we found that a polysilacyclobutane having an epoxy pendant group (polyOBMSB) was obtained by heating the monomer in toluene at 70 °C for 1 h in the presence of platinum vinyldimethyldisiloxane catalyst (Figure 1). Ring-opening polymerization of the four-membered silacarbocycle proceeded with keeping the epoxy ring without side reactions in this condition. Copolymerization of OBMSB and 1,1-diethylsilacyclobutane (DESB) also proceeded in the same polymerization condition (Figure 2).

The obtained polyOBMSB homopolymer and poly(DESB-co-OBMSB) copolymers could be transformed to networked polymers through post-crosslinking of the epoxy groups by heating the polymer at 80 °C for 2 h in the presence of catalytic amount of benzylmethylnaphthylsulfonium hexafluoroantimonate (SI-60), a thermally latent cationic polymerization initiator.
696 - Organocatalytic routes to advanced materials: From semiconductors, green chemistry to nanomedicine

James L Hedrick, hedrick@us.ibm.com, Advanced Materials, IBM Research, San Jose, CA 94588, United States

Wednesday, August 13, 2014 06:45 PM
POLY/PMSE Plenary Lecture and Awards Reception (06:00 PM - 08:30 PM)
Location: Hilton San Francisco Union Square
Room: Grand Ballroom B
697 - Surface degradation and nanoparticle release of nano-SiO₂ coatings under UV radiation

Li-Piin Sung¹, lipin@nist.gov, Deborah Stanley¹, Savelas Rabb², Chun-Chieh Tien¹, Tinh Nguyen¹, Lee Yu². (1) Engineering Lab, National Institute of Standards and Technology, United States, (2) Materials Measurement Lab, National Institute of Standards and Technology, United States

Polymer nanocoatings have been observed to exhibit enhanced mechanical properties, and increasingly used to improve performance of traditional coatings. However, because polymer matrices undergo a significant degradation by weathering elements, nanoparticles in nanocoatings may be released into the environments during the life cycle of a coating. Such release potentially poses an environmental health and safety concern and may hinder commercialization of these advanced coatings. The main objective of this study is to develop protocols and methodologies for characterizing surface damage and measuring the amount of nanoparticles released during the exposure of polymer nanocoatings to an UV environment. Specimens of an epoxy coating containing silica nanoparticles were exposed to a well-controlled, accelerated UV environment, and the amount of nanosilica release as a function of UV exposure was measured by inductively-coupled plasma optical emission spectroscopy (ICP-OES). Chemical degradation, mass loss, and nanocoating surface morphological changes were also tracked. The same experiment procedure was adapted to four different temperatures during UV radiation exposure. Effect of temperature on surface degradation and nanoparticle release of nano-SiO₂ epoxy coatings as a function of UV radiation dose will be reported.

a) AFM height and phase images (20 μm x 20 μm scan size) of SiO₂ nanocoating at UV exposure dose of 192 MJ/m²; (b) nanoparticles on coatings surface - SEM image; (c) amount of Si released, measuring using ICP-OES technique, as a function of UV dose.

Thursday, August 14, 2014 08:00 AM
Polymer Degradation, Performance and Ultimate Stability (08:00 AM - 11:50 AM)
Location: Hilton San Francisco Union Square
Room: Imperial Ballroom B
Intumescent coatings are widely used in the field of fire protection. Their performances can be affected by various weathering causes such as UV exposure, moisture, temperature or immersion in corrosive environment such as seawater. This study investigates the weathering of a model epoxy based intumescent thick coating, containing ammonium polyphosphate (APP), melamine and titanium dioxide, designed to improve the fire resistance of steel in case of hydrocarbon fires. The coating was exposed to accelerated UV-light exposure, to humidity combined with heating and to immersion tests in distilled and salted water. UV-light, humidity and temperature only slightly affect the protective efficiency of the coating. Immersion in distilled water for one month however shows a slight decrease of the protective properties. This was explained by the fact that, on coating extreme surface, APP turns into polyphosphoric acid, which, combined with the mechanical erosion effect of water, is dissolved in water. When immersed one month in the salt water bath, the fire protection was totally lost and intumescence was not observed. The mechanisms involved in the loss of fire protection by the salt water, investigated using Electron Probe MicroAnalysis (EPMA) X-Ray mappings as shown in the Figure1, will be further discussed during the conference.

Figure1: EPMA X-ray mappings of (a) phosphorus, (b) sodium, and (c) chlorine of the cross section of the epoxy based intumescent coating after immersion in salt water.
699 - How FTIR measurements of polymer UV photodegradation correlate with changes in the molar mass distribution

Nicholas D Carbone¹, nicholas.carbone@nist.gov, Sara V Orski², Kathryn L Beers², Christopher C White¹. (1) Materials and Structural Systems Division, National Institute of Standards and Technology, Gaithersburg, MD 20794, United States, (2) Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20794, United States

FTIR is the technique most frequently used to examine the chemical changes that occur in polymers during UV photodegradation. Carbonyl and other indices are used in most studies to quantify the degradation of polymers using FTIR data. These indices have not been correlated with molar mass distribution (MMD) changes as degradation proceeds. This work presents the results of a study that links FTIR index changes to MMD changes in PE, PMMA, and PIB under accelerated weathering conditions at the NIST SPHERE facility. Thin film samples of PE, PMMA, and PIB on CaF₂ were irradiated in the NIST SPHERE for 4 weeks at 35 °C and 0 % relative humidity. Three replicates of each polymer were removed each week and analyzed using HPLC-GPC after FTIR spectra of every sample were taken. Each studied polymer degrades through a unique ratio of scission to recombination reactions and through different reaction networks which combined generate unique MMDs. The evolution of those MMDs with UV photodegradation time is compared across polymers and the universalities and differences enumerated. The sensitivity of various FTIR indices to these MMD differences is quantified and the implications of the results are discussed.

Thursday, August 14, 2014 08:40 AM
Polymer Degradation, Performance and Ultimate Stability (08:00 AM - 11:50 AM)
Location: Hilton San Francisco Union Square
Room: Imperial Ballroom B
Determining the molecular effects of short wave UV light on bis-2-ethylhexyl phthalate (DEHP) plasticized poly(vinyl chloride) (PVC) is vital for both green chemistry and environmental purposes. The effects of energy-efficient light treatments for removing toxic plasticizer from plastic films and/or clear plastics after disposal were studied using a variety of analytical techniques including sum frequency generation vibrational spectroscopy and secondary ion mass spectrometry. The surface and bulk of pure PVC and 25 wt% DEHP-plasticized PVC were analyzed before and after a variety of short wave UV treatments from 30min to 8h in length.

It was determined that 254 nm UV exposure at 53 W/m² yielded products phthalic acid, mono-ethylhexyl phthalate and phenyl ring hydroxylated DEHP as well as smaller molecules in the bulk and surface after only 1h exposure time. For pure PVC after 1h exposure, only a minor amount of bulk and surface changes occurred; after 5h exposure increases in polymer conjugation from chlorine removal and dramatic surface CH group reordering were observed. When hydroxide radicals from 35 wt% H₂O₂ solution were added with the intention of increasing DEHP degradation rates, fewer bulk DEHP molecules were removed up to 8h due to competing radical-polymer reactions. Our results indicate a simple exposure to short wave UV is more effective at eliminating bulk DEHP while H₂O₂/UV combination should be used only if accelerated PVC degradation is desired.
701 - Influence of phosphors on the photostability of polymer: Applications for eco-energetic lighting devices (LEDs)

Sandrine Therias, sandrine.therias@univ-bpclermont.fr, Anthony Chapel, Nathalie Pradal, Pierre-Olivier Bussiere, Rachid Mahiou, Genevieve Chadeyron. Photochemistry team, ICCF, AUBIERE, France

Phosphor-converted white light-emitting diodes (LEDs) are emerging as an essential solid-state light source for the next generation of lighting industry and display systems. Recently, research arose on phosphors embedded in a polymer matrix to achieve a composite film suitable with blue (460 nm) or near-UV (380 nm) LEDs. Preserving the properties of phosphors/polymer composite is a major issue for these applications, in order to integrate as soon as the conception, the durability of these devices.

Luminescent oxides such as yttrium garnet (YAG:Ce³⁺) or Y₃BO₆:Eu³⁺ particles as phosphors were mixed with polymers (figure 1) and associated with blue or UV LEDs in order to produce eco-energetic light devices. This process was applied to different polymer matrices. Luminescent composites were obtained with poly(methylmethacrylate) (PMMA), poly(vinylacetate) (PVAc) and poly(ethylene vinyl acetate) (EVA) as polymers.

Depending on their functionality, particles can impact the durability of the composite materials under UV-light exposure. In the case of luminescent particles such as phosphors, one has to face two major questions: i) what is the influence of the polymer degradation on the optical properties of the composite ii) do the particles impact the photostability of the polymer?

The influence of the phosphors on the mechanism of polymer photooxidation, and the impact of the photodegradation on the optical properties of the composites will be presented.
702 - Prediction of the changes in polymers due to outdoor weathering

Christopher White, christopher.white@nist.gov, Kar Tean Tan, Don Hunston, Adam Pintar, James Filliben. Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20816, United States

An empirically-based model has been created to predict the change in modulus for polymers exposed to outdoor weathering. The underlying high precision data supporting this model was obtained using the NIST SPHERE (Simulated Photo degradation by High Energy Radiant Exposure). The NIST SPHERE can independently precisely control each of the four primary components of the outdoor exposure: Temperature, Humidity, Ultraviolet Radiation and Mechanical Loading. The properties of the polymers were measured before and after each exposure period. The resulting empirically-based model produces two major results: the statistical significance of each of the weathering components and a prediction of property change for any location, provided a historical weather file is available. This model has shown that all four weathering factors, listed above, are significant contributors to change in properties of polymers. Additionally, the geographical predictions allow for independent verification of these models.
The accelerated laboratory testing under simultaneous multiple stresses (temperature, moisture, UV radiation) is critical to the development of test methods that correlate to field performance. In this study, the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) was used for accelerated laboratory tests of a number of polymeric materials used in photovoltaics, such as ethylene vinyl acetate (EVA), polyvinyl fluoride/Polyester/EVA (EVA/PET/PVF) backsheet and polyester backsheet materials. Multiscale chemical, optical, mechanical and morphological measurements were carried out to follow changes during accelerated exposures. The effects of the UV irradiance, relative humidity, oxygen and wavelength on degradation mechanisms of these materials were investigated. The results indicated that the UV radiation was the most important factor for the degradation of all studied materials. A synergistic effect between UV and relative humidity was observed for EVA, and PET based backsheet materials. The role of oxygen in the degradation process of UV-stabilized EVA was complex and affected degradation behaviors of the EVA during UV exposure. In addition, advanced cross-sectional characterization techniques combining confocal Raman, atomic force microscopy, and nanoindentation were used to examine chemical, mechanical and structural changes of a multilayered PET-based backsheet before and after exposure. New insights into the effects of accelerated UV and humidity on the innerlayer structures and the properties of PV backsheets will be presented. The implication of this work on the current test standards will be discussed.
The most commonly used photovoltaic (PV) encapsulant material is ethylene-vinyl acetate (EVA) co-polymer. To provide the mechanical and electrical protection to the brittle solar cells from different external stresses, the encapsulants need to meet a number of requirements including: adhesion and UV stability, resistance to water/humidity absorption, and high electrical insulation. As an encapsulant, the EVA can be exposed to internal stresses resulting from environmental stresses such as UV exposure, thermal cycles, temperature gradient between the glass side and the silicon wafer side, and moisture ingress. These stresses can degrade the performance of EVA leading to a reduced adhesion which will eventually lead to failure of the encapsulation. Measuring the EVA internal stresses can help to understand the failure mechanism of PV modules. In this work, we suggest a novel and non-destructive way to measure the encapsulate materials internal stresses during UV degradation by using Raman spectroscopy. Samples were exposed to NIST SPHERE with UV irradiation, moisture, and elevated temperatures. The internal stresses were monitored by Raman spectroscopy, and the corresponding Raman peak shifts were analyzed. The results have indicated that Raman scattering is sensitive to internal stress state of EVA material. As shown in Figure 1, when EVA was under tensional stresses, the Raman peaks shifted downward; while under compressional stresses, the peaks shifted upward. Aging induced internal stresses will be further discussed.
Photodegradation (PD) in polymers occurs through a series of photochemical reactions: oxidation, chain scission, and crosslinking. The PD mechanisms in phenolic thermoset polymers were poorly comprehended owing to the heterogeneity in photochemical reactions created by decay of the radiation intensity as well as reactant concentration with depth. We overcome these limitations by characterizing the photochemical reactions in thin Epoxy Polymer (EP) films (750 nm thick) coated on quartz substrates. Further, a fundamental kinetics model has been developed in terms of coupled and nonlinear differential equations to elucidate the complex sequence of associated photochemical reactions. This model shows an excellent agreement with data systematically recorded by UV-Vis as well as FTIR spectrosopies. Additionally, one of the model parameters, namely crosslinking density, again shows excellent agreement with elastic modulus acquired by nanoindentation. Our analysis establishes that the PD is mainly driven by UVA excitation of the carbonyl groups in the EP network (i.e., n→π* transitions). Carbonyl excitation results in either carbonyl dissociation or energy transfer to O2/H2O for the creation of reactive oxygen species (ROS). Subsequently, radicals from dissociation reactions as well as ROS induce a second round of PD reactions including oxidation (e.g., H-abstraction and creation of new carbonyls), crosslinking and chain scission.

Figure 1: a) Time series absorbance spectra (in solid black) of EP in 1h intervals under UVA irradiation. Decrease in absorbance after 30 h is shown in dashed red line. b) Kinetics of PD in terms of Y and X, which are defined as follows. Y is the integrated optical absorbance of the EP film associated with carbonyl groups. Integration is performed in the wavenumber (1/ wavelength) domain and hence the unit is 1/cm. Y directly quantifies the total number of carbonyl groups in the thin film. Similarly, X quantifies the total number of carbonyls dissociated up to given time (cumulative dissociation).
There is a real need for understanding the mechanisms responsible for the changes in polymer performance associated with specific physical properties. The results presented here show how the photochemically induced oxidation of PET provokes a decrease of the oxygen permeability coefficient of the material. This effect is shown to result from crosslinking by recombination of macroradicals formed by the photooxidation of PET. This effect increases with time, restricting the diffusion of oxygen in the polymer and therefore leading to a decrease in permeability.

The global effect that is observed is thickness-dependent. This is corroborated by measurements of the variations of permeability for films with different thicknesses, as shown in Table 1. Monitoring the distribution of the oxidation photoproducts by cross-sectional infrared analysis of irradiated films shows that the photochemical oxidation of PET only occurs in the first 35 microns from the exposed surface. This is a consequence of the attenuation of the UV light that penetrates the sample. For samples with a thickness larger than that of the oxidised layer, the permeability decreases at the surface, whereas that of the core of the sample is not modified.

<table>
<thead>
<tr>
<th>Exposure time (hours)</th>
<th>OTR (cm³ m⁻² day⁻¹) 23 microns</th>
<th>OTR (cm³ m⁻² day⁻¹) 125 microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62.1</td>
<td>11.4</td>
</tr>
<tr>
<td>150</td>
<td>47.6</td>
<td>11.4</td>
</tr>
<tr>
<td>300</td>
<td>44.0</td>
<td>10.7</td>
</tr>
<tr>
<td>450</td>
<td>35.6</td>
<td>9.8</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 1 Oxygen transmission rate with exposure time (SUNTEST unit - temperature of 70°C for a black standard - irradiance of 650 W cm⁻²).

Acknowledgements: the authors wish to thank Serge Trivis and Serge German (ESEPAC – 43700 St-Germain Laprade-France) for the permeability measurements.
707 - Application of RAFT and ATRP for polymers with biomedical applications: Responsive glycopolymers and amino-functional PMMA

Ulrich S Schubert, ulrich.schubert@uni-jena.de, Christian von der Ehe, Christine Weber, Turgay Yildirim. Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena, Germany

Since sugar units display a strong influence on cellular uptake, their combination with a thermoresponsive polymer such as poly(N-iso-propylacrylamide) (PNiPAm) could provide materials that bind selectively to specific types of cells while the effectiveness of the binding could be controlled by the applied temperature. Thereby, the post-polymerization modification of NiPAm copolymers with suitable functional monomers is advantageous because different sugar units can be bound to the same polymeric precursor. Suitable functional moieties that are reactive towards thiosugars are pendant double bonds or 2-oxazoline rings. The advantages and disadvantages of both methods are discussed in detail based on kinetic studies of the respective controlled radical polymerization technique (RAFT and ATRP) and state-of-the-art characterization methods with a focus on mass spectrometry. Subsequently, suitable glycopolymers were immobilized on solid supports to enable an application as solid phases in chromatography for separation of cells or pathogens.

For the delivery of sensitive drugs to the “place of action”, polymeric carrier materials are highly potent with regard to protection of the active substances from degradation in the human body. In particular polymeric nanoparticles represent a suitable platform that can be designed according to each specific need. In this contribution, the utilization of nanoparticles composed of amine-functional poly(methyl methacrylate) that was obtained by RAFT copolymerization of MMA with three different amine-containing monomers (primary, secondary and tertiary) for the delivery of anionically charged drugs or genetic material is presented.


We report the unique thermoresponsive properties of fluorinated polyacrylamides, poly[N-(2,2-difluoroethyl)acrylamide] (P2F). The solubility of fluorinated polyacrylamides in water can be easily controlled by changing the number of fluorine atoms in N-ethyl groups. We demonstrate that the thermosensitivity of fluorinated polyacrylamides can be easily controlled by changing the number of fluorine atoms in the terminal alkyl group of N-ethyl moiety. Mono-fluorine substituted poly[N-(2-fluoroethyl)acrylamide] (P1F) is water-soluble while tri-fluorine substituted poly[N-(2,2,2-trifluoro-ethyl)acrylamide] (P3F) is water-insoluble. Interestingly, di-fluorine substituted poly[N-(2,2-difluoroethyl)acrylamide] (P2F) exhibits a LCST in water of around 26–28 °C, which is comparable to that of poly-(N-isopropylacrylamide) (PNIPAM). Moreover, we demonstrate that fluorinated polyacrylamides are less cytotoxic than poly(N-isopropylacrylamide) (PNIPAM).
Stimuli-responsive degradation (SRD) or cleavage of dynamic covalent bonds in response to external stimuli is a promising property in the development of polymer-based multifunctional self-assembled nanocarriers as a broad choice of materials for targeted drug delivery. Exploring disulfide-thiol chemistry as an initial thrust, various strategies have been explored to synthesize novel micelles with disulfide linkages positioned at different single locations, as in the micellar core, in the interlayered corona, or at the interface between the hydrophobic core and corona. Recently, we have focused on an effective SRD strategy that centers on the development of new intracellular nanocarriers having multiple stimuli-responsive cleavable linkages at multiple locations (denoted as ML-MSRD strategy). This new strategy offers versatility in that the multi-stimuli responses to each stimulus can independently and precisely regulate drug release at multiple locations. Overall, the developed strategies enable the investigation of structure-property relationship between morphological variance and stimuli-responsive degradation. Ultimately, the results enable the optimization of degradable micelles offering enhanced release inside diseased cells, particularly targeted cancer cells.
Polymers with pendant trehaloses were synthesized by controlled radical polymerization. Styrene and methacrylate monomers functionalized with the disaccharide were synthesized in one to two steps. The monomers were then polymerized with either reversible addition-fragmentation chain transfer (RAFT) polymerization or atom transfer radical polymerization (ATRP). In this manner polymers were prepared with narrow molecular weight distributions and if so desired, functional end groups (Figure 1). The resulting polymers were found to be highly hydrated and soluble in water. The trehalose glycopolymers were then utilized to stabilize proteins to a wide variety of stressors such as temperature. The polymers could be added or covalently attached to the proteins. It was determined that the stabilization imparted by the polymer was a unique result of a combination of the osmolyte and nonionic surfactant character of the molecule. The synthesis and application of these polymers will be discussed.
Atom transfer radical polymerization (ATRP) is a versatile reversible-deactivation radical polymerization (RDRP) method. ATRP employs transition metal catalysts, often Cu, to create precisely controlled polymers with various architectures including block, star and branched architectures. However, aqueous media have traditionally presented a significant challenge to ATRP, especially using low catalyst concentrations, due to the high activity of Cu(I) in aqueous media leading to a high termination rate; potential disproportionation of Cu(I); the loss of the deactivator complex due to the dissociation of the Cu(II)-halide deactivator complex in water, and also loss of chain ends by hydrolysis/elimination. A strategy for overcoming these challenges will be discussed, by using highly active Cu complexes, slowly regenerating the activating species and adding an excess of halide salt to minimize the dissociation of the deactivator complex. Various techniques that allow polymerizations with parts per million catalyst loadings will be presented, by using an excess of halide salts, regenerating the activator complexes using either conventional radical initiators, reducing agents such as ascorbic acid, or Cu(0) that acts as a supplemental activator and reducing agent. These techniques allow the direct synthesis of bioconjugates.
712 - Design a well-defined hyper-star polymer using controlled radical polymerization and explore its application for siRNA delivery

Haifeng Gao, hgao@nd.edu, Robert Graff, Xiaofeng Wang. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, United States

Functional polymers with well-defined nanostructures have been explored for various future applications although facile syntheses of these materials are never easy. Recently, our group applies controlled radical polymerizations in a nanometer-sized confine space and produces a core-shell structured hyper-star polymer with uniform size and tunable core composition for labile degradation. The developed facile synthesis allows us to access large-scale (10 g) uniform hyper-star polymers and explore their properties in siRNA delivery.
Zwitter ionic polymer is a unique class polyelectrolyte which has not been studied systematically because of the difficulty in controlled synthesis and precise physicochemical characterization. In this study, homopolymers and polymer brushes of poly(2-methacryloyloxyethylphosphorylcholine) (PMPC) and poly[3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammoniopropanesulfonate] (PMAPS) were prepared by ATRP. The salt-concentration dependences of the chain dimensions and swollen brush structures of PMPC and PMAPS in aqueous solutions of various ionic strengths were characterized by static light scattering, dynamic light scattering, atomic force microscopy (AFM), neutron reflectivity (NR), contact angle measurements, and macroscopic friction tests by sliding a glass ball under a load of 0.49 N. The hydrodynamic radius $R_H$ of PMPC in aqueous salt solution was independent of NaCl concentration, whereas $R_H$ of PMAPS strongly increased with the ionic strength due to the screening of attractive interaction between sulfobetaines. Similar behaviors were also observed on the PMPC and PMAPS polymer brushes on silica nano particle in water. AFM and NR measurements also showed the independence of NaCl concentration of the swollen thickness of the PMPC brush on flat silicon substrate in aqueous solution, and significant changes in the swollen thickness of the PMAPS brush in aqueous NaCl solution. PMPC and PMAPS brushes both showed oil detachment behavior in water and aqueous NaCl solutions, indicating the super hydrophilic property of both zwitter ionic polymer brushes. The PMPC brush in water had a significantly low friction coefficient (0.02–0.05) at a sliding velocity of $10^{-2} – 10^{-1}$ m/s even under a high normal pressure of 139 MPa.
Controlled/living radical polymerizations enable the synthesis of well-defined functional polymers with complex architectures and predetermined molecular weights, as well as narrow molecular weight distributions. Atom transfer radical polymerization (ATRP) has become one of the most widely used polymerization techniques due to its versatility: it can be applied using the majority of common monomers, it allows the addition of functional groups and it is compatible with numerous biomolecules. However, the transition metal catalysts required for ATRP can represent a challenge, as they can be toxic and potentially harmful to the environment. Moreover, the catalysts can have a negative impact on the polymer properties if not fully removed from the product. A “greener” approach involves the use of enzymes as catalysts, so-called “ATRPases”, rather than transition metals. We have discovered that metalloproteins such as horseradish peroxidase (HRP) and hemoglobin catalyze ATRP under activators regenerated by electron transfer (ARGET) conditions.

We will present results on biocatalytic ATRP of N-isopropyl acrylamide, poly(ethylene glycol) methacrylate and poly(ethylene glycol) acrylate. Moreover, mechanistic insights into this novel enzymatic activity will be reported. Last but not least, we will show how ATRPases can be used to conduct ATRP of vinylimidazoles that cannot be polymerized by conventional ATRP.
Arsenic compounds have been employed as therapeutics for centuries as treatments for diseases such as psoriasis, syphilis, rheumatosis and more recently leukaemia. Arsenic can exist in a number of oxidation states including biologically relevant As(V) and As(III), with As(III) exhibiting high cytotoxicity. In the 1980’s arsenic trioxide (As$_2$O$_3$) was found to induced complete remission in sufferers of acute promyelocytic leukaemia (APL) and has since been exploited to selectively target the adenine nucleotide translocator (ANT) in the mitochondrial membrane of proliferating cells (e.g. tumours) by altering the porosity of the mitochondrial membrane leading to apoptosis. Consequently, a number of small molecule (in)organic arsenicals have been developed and investigated to establish their therapeutic efficacy. On the macromolecular scale, research has focused on the development of arsenolipids which have been assembled into arsenoliposomes for encapsulation and targeted drug delivery applications against a variety of cancer cell lines. However, little is known about the efficacy of polymeric arsenicals either in the guise of protein/peptide-polymer conjugates or polymer nanoparticle therapeutics. Herein we discuss the synthesis of novel arsenical initiators and monomers and the subsequent application to the synthesis of a library of polymeric arsenicals, via controlled radical polymerisation. Present as either As(V) or As(III), varying degrees of arsenic has been incorporated into the polymer composition. The resulting polymers have been screened against both healthy and cancerous cells to assess their cytotoxicity and therapeutic potential.
A series of poly(phenylene ether)-b-poly(hydroxy ether) (PPE-b-PHE) block copolymers were synthesized using hydroxyl-functionalized polyphenylene ether (PPE) macromonomers and diglycidyl ethers of bisphenol A. The PPE content was varied from 24 to 80wt%. These unique block copolymers exhibited broad property enhancements over conventional polyhydroxy ethers including higher glass transition temperatures, significant reductions in moisture absorption, better dimensional stability and greater retention of flexural properties. These amphiphilic block copolymers have segments with affinity for two different types of environments. The PPE segments would be “PPE-philic” and the PHE segments would be “polyester-philic”. Their utility as compatibilizers in blends of thermoplastic polyester with PPE was examined. Compared to un-compatibilized blends, the (PPE-b-PHE) containing blends exhibited stable morphology and notable performance enhancements.
717 - Synthesis and characterization of bipolar redox-active 6-oxoverdazyl polymers

Jacquelyn T. Price, Joseph A. Paquette, Christopher S. Harrison, Joe B. Gilroy, joe.gilroy@uwo.ca. Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research (CAMBR), The University of Western Ontario, London, Ontario N6A 5B7, Canada

The stable radical polymer field has grown rapidly over the past decade, primarily due to the utility of many examples in organic radical batteries.\(^1\),\(^2\) Although advances have been significant, there remains a need for new families of stable radicals to be incorporated into polymer scaffolds in order to take full advantage of their properties. 6-Oxoverdazyl radicals are amongst the most stable classes of organic radicals, and offer unique and tunable (through substituent variation) bipolar redox properties. Our initial work in this area has focused on the incorporation of 6-oxoverdazyl radicals into polymers with phenylmethacrylate backbones. The synthesis and characterization of these polymers and closely related model complexes will be presented.

718 - Biohybrid matrices: Hydrogels formed by composite thiol click chemistries and microflow synthesis

Michael A. Daniele¹, michael.daniele.ctr@nrl.navy.mil, Stella H. North¹, Jawad Naciri¹, Kathryn Radom³, Frances S. Ligler², Andre A. Adams¹. (1) Center for Bio/Molecular Science & Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia 20375, United States, (2) UNC/NCSU Joint Department of Biomedical Engineering, North Carolina State University, Raleigh, NC, United States, (3) U.S. Naval Research Laboratory, Naval Research Enterprise Internship Program, Washington, District of Columbia 20375, United States

Integration of functionalized biomacromolecules and synthetic hydrogels generate biomimetic, mechanically robust and cytocompatible tissue scaffolds. With the use of concurrent photoinitiated thiol-ene and thiol-yne click chemistries form a covalently-crosslinked network of gelatin methacrylamide and multi-arm poly(ethylene glycol).

Compared to physically incorporated gelatin, the covalent networks retain a higher protein content providing superior physical properties and bioactivity. The bioactive hydrogel supports both endothelial cell adherence and smooth muscle cell encapsulation; moreover, the improved mechanical properties were exploited in fabricating cell-encapsulating microfibers. We employed a microfluidic method for the production of microscale fibers and tubes from macromer solutions. By inducing spatial control of material and cellular composition by hydrodynamic focusing, the macromer precursor fluids can be arranged into complex patterns at the microscale. Microtubes have been fabricated on the scale of the arterioles and venules; “capillary-sized” fibers can also be achieved with this method. Microfluidic production of individual blood vessels will provide the necessary level of architectural and cellular control at the microscale for building a tissue model with a complex vascular network.

Thursday, August 14, 2014 08:40 AM
General Topics: New Synthesis and Characterization of Polymers (08:00 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 7
719 - WITHDRAWN
Segmented thermoplastic polyurethanes (TPU), which are composed of alternating hard and soft segments covalently linked together display unique combination of morphological, thermal and mechanical properties depending on the type and nature of the hard and soft segments and their compositions. One of the most critical factors that influence the chemical structure, topology, microphase morphology and properties of TPUs is the synthetic procedure followed and the reaction conditions employed. Unfortunately, this point is generally overlooked, most probably since the majority of the fundamental kinetic studies on polyurethane formation reactions performed in 1960s. This study focuses on the kinetic analysis of polyurethane formation reactions, where the effect of the type and structure of the diisocyanate, solvent, reactant concentrations, reaction temperature and catalysts were investigated. Special emphasis was given to the investigation of reactions between aromatic diisocyanate MDI and poly(tetramethylene oxide)glycol (PTMO-1000). It was demonstrated that when used as a reaction solvent or co-solvent, dimethylformamide (DMF) dramatically increases the reaction rates of both the urethane formation (alcohol-isocyanate reactions), but also the side reactions which lead to allophanate and biuret formation.

Optimum reaction conditions were determined to minimize the side reactions, when DMF is used as a solvent in MDI based urethane formation reactions.
721 - Force interactions of grafted polylactide particles

Robertus Wahyu N. Nugroho, rnugroho@kth.se, Torbjörn Pettersson, Karin Odellius, Anders Höglund, Ann-Christine Albertsson. Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Stockholm 10044, Sweden

One of the primary issues of small particles in the range from tenths of nanometers to hundreds of micrometers is particles agglomeration in aqueous media. This agglomeration may be prevented by introducing tethered chains of hydrophilic polymers covalently anchored on the surface which leads to sterically stable particles. We have previously developed a nondestructive surface modification technique for small polylactide (PLA) particles with different geometries by means of a 'grafting-from' technique. Three hydrophilic monomers: acrylic acid (AA), acrylamide (AAm), and maleic anhydride (MAH) were photopolymerized onto particle surfaces initially activated by benzophenone (BP). Successful surface grafting was verified by analyzing the surface chemistry with X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infra-Red Spectroscopy (FTIR). The force interactions between grafted PLA substrates were assessed via colloidal probe AFM (Atomic Force Microscopy) technique in salt solutions of different concentrations. The AFM force curves were related to two models for colloidal stabilization Alexander de Gennes (AdG) and Derjaguin-Landau-Verwey-Overbeek (DLVO) in order to detect either steric repulsive forces or attractive forces driving the physical interaction. Repulsive forces were primarily detected when two grafted surfaces approached each other, whereas attractive forces dominated when two nongrafted surfaces (neat PLA particles) were brought into contact. The attractive forces were detected at a small separation distance. The surface grafted particles can be used for drug delivery applications where particle agglomeration needs to be avoided.
722 - Functional degradable polymers – simplified

Peter Olsén, polsen@kth.se, Jenny Undin, Karin Odelius, Ann-Christine Albertsson. Department of Fibre and Polymer Technology, KTH, Royal Institute of Technology, Stockholm, Sweden

Bestowing function to a degradable polymer backbone enables the creation of materials with almost endless possibilities. Of particular interest to us is to develop synthetic routes to combine radical graft-polymerization with a living characteristic with ring-opening polymerization, thereby producing an acrylic polymer with a degradable backbone. Traditionally, this task is often a product of tedious lab work with many-steps, low yields, and as a consequence high cost and a large carbon foot-print. In order to overcome these shortcomings we have turned our attention towards an unexploited, α-bromine functional and also commercially available member of the lactone monomer family, α-Bromo-γ-buryrolactone (αBrγBL). The class of γ-lactones monomers is extremely thermodynamically stable, which hinder them from being homopolymerized at conventional temperatures and pressures; however, they can be copolymerized. We therefore explored this ability in copolymers with both ε-caprolactone and L-lactide. This allowed us to generate an easy and straight forward route to a degradable macro-initiator susceptible for further grafting reactions. Our grafting was performed under SET-LRP conditions and realized with the aid of the fluorinated alcohol, 2,2,2-trifloroethanol, that acted as a universal solvent for the hydrophobic polymer backbone, together with a wide range of different acrylates with varying polarity.¹

723 - Functionalization of poly(2-oxazoline)s by post-polymerization modification of side chains and end-groups

Maarten A Mees, maarten.mees@ugent.be, Richard Hoogenboom. Department of Organic chemistry supramolecular chemistry, Gent, Ghent, Oost-Vlaanderen 9000, Belgium

Poly(2-oxazoline)s (PAOx) are readily made by the cationic ring opening polymerization (CROP) providing direct access to well defined polymers with a broad range of architectures. Not only the structure can be tuned, but more importantly, also the polymer properties, such as thermostressive lower critical solution temperature (LCST) behavior. For further applications the introduction of functionalities is important. The functionalisation of PAOx can be achieved via four different pathways, namely through initiation, termination, functional monomers and post-polymerization modification. In this work, we will discuss our endeavors to functionalize PAOx via termination as well as side chain post-modification. The functionalization of PAOx via termination is based on the efficient end-capping of the living PAOx chains with deprotonated carboxylic acids, thiolates and amines that act as nucleophilic terminating agents. In this way different functionalities have been introduced, such as reactive groups for further (click) modification, including thiols and amines and reactive dyes. The second developed method for side-chain post-modification of PAOx is based on the introduction of methyl ester groups in the side chain, either via copolymerization of a methyl ester containing 2-oxazoline monomer or by partial hydrolysis of the PAOx followed by modification of the resulting secondary amine groups with different linkers such as bromo acetate, methyl-chlorosuccinate and methoxycarbonylethyliso(thio)cyanate. It will be demonstrated that these side chain methyl ester groups can be easily reacted with amines in a transamidation step to introduce a wide variety of functional groups such as acid, amine, alcohol, hydrazide and propargyl groups. Finally, the secondary amine groups in the main chain of partially hydrolyzed PAOx are also utilized for the introduction of side chain sugars by reductive amination.
724 - Effects of linear side-chains on 2,5-bis-(3-alkylthiophen-2-yl) thienothiophene semiconductors for organic electronics

Benjamin Peter Cherniawski, bchernia@mail.pse.umass.edu, Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Ma 01003, United States

Effects of linear side-chain length on the properties and performance of short 2,5-Bis(3-alkylthiophen-2-yl)thienothiophene (BTTT) oligomers are studied. Monomers and Dimers with side-chains of lengths (6, 7, 9, 11, 12, and 16) were synthesized using Stille cross coupling. This study aims to validate any performance-related trends with the molecular packing and thin film characteristics of these oligomer systems. Single-crystal X-Ray Diffraction in conjunction with data from DFT Calculations, GIXD, DSC, AFM, and device performance will confirm the shifts in packing habit and provide a geometric rational to bulk property trends. The proposed research provides a transformative approach to understanding the structure-property relations of side-chains in semiconductor materials through the use of crystallizable oligomers. In addition to understanding the BTTT system, this study represents a fundamental contribution to the field as a whole. The results can be applied to other systems and will aid researchers in designing new semiconductors and better the understanding of those already in use.
725 - WITHDRAWN
726 - WITHDRAWN
In this study, one-step enzyme-mediated preparation of a multi-functional injectable hyaluronic-acid-based hydrogel system is reported. Hydrogel was formed through the in situ coupling of phenol moieties by horseradish peroxidase (HRP) and hydrogen peroxide (H$_2$O$_2$) and bioactive peptides were simultaneously conjugated into the hydrogel during the gel formation process. The preparation of this multi-functional hydrogel was made possible by synthesizing peptides containing phenols which could couple with the phenol moieties of hyaluronic-acid-Tyramine (HA-Tyr) during the HRP-mediated crosslinking reaction. Preliminary study demonstrated that two phenol moieties per molecule resulted in consistently high conjugation degree into the HA-Tyr hydrogel network, unlike the one modified with one phenol moiety per molecule. Therefore, an Arg-Gly-Asp (RGD) peptide bearing two phenol moieties (Phenol$_2$-PEG-RGD) was designed for conjugation to endow HA-Tyr hydrogel with adhesion signals and enhance its bioactivities. Human umbilical vein endothelial cells (HUVEC) cultured on or within the RGD-modified hydrogels showed significantly different adhesion behavior from non-adherent on HA-Tyr hydrogel to strong adhesion on hydrogels modified with Phenol$_2$-PEG-RGD. This altered cell adhesion behavior led to improved cell proliferation, migration and formation of capillary-like network in the hydrogel in vitro. More importantly, when HUVEC and human fibroblasts (HFF1) were encapsulated together in the RGD-modified HA-Tyr hydrogel, functional vasculature was observed inside the cell-laden gel after two weeks in the subcutaneous tissue.

Taken together, the in situ conjugation of Phenol$_2$-PEG-RGD into HA-Tyr hydrogel system, coupled with the ease of incorporating cells, offers a simple and effective means to introduce biological signals for preparation of multi-functional injectable hydrogels for tissue engineering application.
728 - Novel polybenzimidazole (PBI) membranes for high temperature H$_2$/CO$_2$ separation

Xin Li$^1$, li46@email.sc.edu, Rajinder P Singh$^2$, Kevin W Dudeck$^2$, Kathryn A Berchtold$^2$, Brian C Benicewicz$^1$. (1) Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States, (2) Materials Physics and Applications Division, Los Alamos National laboratory, Los Alamos, New Mexico 87545, United States

Polybenzimidazole (PBI) membrane materials are promising candidates for H$_2$/CO$_2$ separation at elevated temperatures (>150 °C) with industrially attractive permselectivity behavior. Commercially available PBI (m-PBI, Celazole®) offers advantages such as very high Tg (425 °C), excellent membrane mechanical property, good chemical resistance, and more importantly, very attractive H$_2$/CO$_2$ selectivity at high temperatures (>20 at 250 °C); however, its H$_2$ permeability are low, which mandates ultrathin selective layers to achieve industrially attractive H$_2$ flux. Our work has been focused on using chemical modification methods to manipulate PBI morphology (free volume), in order to achieve a better performance combination (gas permeability & selectivity). In this talk, different synthetic strategies such as PBI backbone modification and random copolymerization as well as the corresponding gas permeation results of new PBI derivatives will be discussed.
The vast majority of the world's energy is presently derived from the burning of fossil fuels, which releases vast quantities of carbon dioxide (CO$_2$) into the environment and results in undesirable climate change. Practical and cost efficient methods of CO$_2$ separation and capture would thus solve one of the most challenging problems facing humanity today. This presentation summarizes our effort on the development of novel polymer membranes for CO$_2$ separation and the investigation of the fundamental understanding in its molecular transport through the polymer membranes. Our strategy focuses on tuning solubility selectivity in addition to diffusion selectivity for achieving high permeability membranes combined with good selectivity. Various synthetic techniques including, ROMP, olefin polymerization, free radical polymerization, step growth polymerization, and post functionalization were used and the combination of these various synthetic methods permits to prepare well-defined novel high permeable polymers containing CO$_2$-philic groups. The structure-property relationships including CO$_2$ uptake, CO$_2$ and N$_2$ permeability, CO$_2$/N$_2$ selectivity to the polymer structure will be discussed.
730 - Gas separation membranes derived from immiscible polymer blends compatibilized with small molecules

Kenneth J. Balkus, Jr., balkus@utdallas.edu, Nimanka P. Panapitiya, Sumudu N. Wijenayake, Cindy N. Nguyen, Inga H. Musselman, John P. Ferraris. Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75080, United States

Polymer blends can synergistically combine the superior properties of different polymers such as high gas permeability and high gas selectivity. However, the complete miscibility of high performance polymers is limited, due to the unfavorable thermodynamics of mixing. The use of compatibilized immiscible polymer blends can relax this limitation. Herein, membranes of derived from blends of immiscible, high performance polymers compatibilized by commercially available small molecules (SM) are described. The membrane microstructure was investigated with SEM imaging and all membranes demonstrated a matrix-droplet type microstructure, in which highly permeable polymer (P1) is the dispersed phase, while the highly selective polymer (P2) is the continuous phase. Membranes with SM compatibilizers demonstrated a microstructure with small and similarly-sized dispersed domains, in contrast to their pure blend counterparts. As the SM loading was increased from 5 to 9 wt%, the size of the dispersed phase became even smaller and more uniform, suggesting even better compatibility between the polymers.

This compatibilization effect of SM was attributed to the interfacial localization of SM, which lowered the interfacial tension similar to a surfactant. Further characterization of the membranes and their gas separation properties will be presented. This approach could afford a novel class of membranes in which immiscible polymer blends can be compatibilized in an economical and convenient fashion.
731 - WITHDRAWN
732 - Modeling of sorption, diffusion, and chemical reactions in polymeric materials

Stephen J Harley, harley2@llnl.gov, Yunwei Sun, Elizabeth A Glascoe. Lawrence Livermore National Laboratory, Livermore, CA 94550, United States

Characterizing and quantifying the transport of volatile species through polymeric materials is important in predicting the aging and compatibility of complex, multi-material systems. We are developing a joint experimental and modeling capability to characterize and quantify sorption and diffusion of volatile species through polymeric materials. The experiments measure the uptake or outgassing response of materials, via gravimetric analysis, as a function of vapor activity (i.e. relative humidity) and temperature. Our high-fidelity transport model includes (1) a triple-mode sorption model that includes Henry's law absorption, Langmuir adsorption, and molecular pooling of volatile-molecules, and (2) molecular diffusion. Using a 1D or 3D mesh we can simultaneously simulate the transport of mobile species through complex geometries and multi-material assemblies. Work is underway to include chemical reaction kinetics in the model, which will allow for a full reactive transport modeling capability that can be used to predict material aging and degradation in complex, multi-material systems. This talk will discuss our approach and our progress to date, which will include, model development and experimental work using on a variety of polymeric materials (e.g. polydimethsiloxanes, polyurethanes, perflorinated polymers, etc) to parameterize and validate the model.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
733 - Role of interfaces, chemistry, and morphology on the structure, water distribution/transport, and physical properties of multicomponent polyelectrolyte membranes for fuel cell applications

Kirt A Page¹, kirt.page@nist.gov, Eric M Davis¹, Christopher M Stafford¹, Jospeh Dura², Kevin Yager³, Ahmet Kusoglu⁴, Jenny Kim¹, Christopher L Soles¹. (1) Materials Science and Engineering Division, The National Institute of Standards and Technology, Gaithersburg, MD 20899, United States, (2) Center for Neutron Research, The National Institute of Standards and Technology, Gaithersburg, MD 20899, United States, (3) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, United States, (4) Electrochemical Technologies Group, Lawrence Berkeley National Laboratory, United States

Since the 1950s polymeric materials have been pursued as electrolytes in fuel cell applications. While a wide variety of polyelectrolytes have been developed and studied (including, but not limited to, poly(perfluorosulfonic acid)s, polystyrene derivatives, polysulfones, polyimides, and engineered block copolymer electrolytes) there still remain many unanswered question about the structure-property relationships of these varied materials. Devices are assembled with multiple heterogeneous materials and failure, or performance losses, can largely occur at the interfaces between these materials. While the structure and transport of bulk PEMs for fuel cell applications have been studied extensively, there has been little effort focused on these materials at interfaces and under confinement as they exist within the membrane electrode assembly (MEA) of a working PEM fuel cell. This talk will cover research investigating two aspects of polyelectrolyte confinement. First, we will present our comprehensive work using a variety of measurement techniques on the effects of geometric/substrate confinement on the properties of Nafion thin films. Second, we will explore the effects of chemistry and structure on the confinement and distribution of water in alkaline, anion exchange block copolymer materials using small-angle neutron scattering.
734 - Critical role of the interface in controlling transport in PFSA membranes

Ahmet Kusoglu, akusoglu@lbl.gov, Adam Z Weber. Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

Perfluoro-sulfonic acid (PFSA) polymers are used as the electrolyte and separator in most solid-state energy-conversion and storage devices. These materials must conduct the ions in a mechanically robust matrix that simultaneously inhibit reactant and product crossover. The performance and durability of the membranes are related to their properties governed by the physiochemical interactions between chemical structure, water uptake, and morphology. The transport of water and ions of these membranes is critical for their operation in various electrochemical technologies. In this talk, the structure/function relationships of these membranes will be examined with a focus on the interface, which is thought to control the transport. Through a combination of time-resolved SAXS, dynamic vapor uptake, computed x-ray tomography, conductive AFM, and dynamic and steady-state transport-property measurements, a theory and data for the transport of ions and water have evolved. It will be shown how the interface and particularly its resistance is critical for controlling water movement into the polymer, which subsequently determines the membrane's structure. For example, Figure 1 shows how the mass-transfer coefficient measured for steady-state transport correlates to the membrane surface's conductive-area fraction as measured by AFM. This relationship shows that the interface and accessibility to water is what is causing the transport resistance (inverse of the mass-transport coefficient). In addition, ways to alter the nature of the interface including polymer moieties, environmental conditions, etc. will be discussed.

Acknowledgement

This work was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Fuel Cell Technologies, of the U. S. Department of Energy under contract number DE-AC02-05CH11231

Thursday, August 14, 2014 11:00 AM

Transport in Polymer Membranes (08:30 AM - 12:00 PM)

Location: Hilton San Francisco Union Square

Room: Continental Parlor 8
 Controlled radical polymerization (CRP) facilitated the synthesis of a broad range of triblock copolymers with well-defined architecture and controlled molecular weights. The block copolymers offer immense potential as sensors and actuators, energy-harvesting devices, and biomimetic materials. Microphase separated block copolymers synthesized using CRP techniques present a facile strategy to mimic morphology of Nafion® through the inclusion of hard domains for mechanical reinforcement and ion-rich soft phases that facilitate ion migration. Control over block composition enables tailored charge content, tune thermomechanical properties, and morphology. The self-assembled, nanostructured morphologies of block copolymers enable their use as solid-state polyelectrolytes, specifically tuning morphology to benefit ion-transport. Dielectric relaxation spectroscopy (DRS) determined ion-transport properties of charged ABA triblock copolymers with different compositions. The electrode polarization (EP) model provided ionic mobility, dielectric constant, and mobile ion concentration for these triblock copolymer systems. This presentation will introduce the efforts with imidazolium triblock copolymers that offer the opportunity to fine tune mechanical and ion-transport properties of electroactive device.
A correct water management is at the basis of the design of more performing PEM fuel cells, especially by avoiding the flooding of cathode and minimizing mass transfer limitations. Gas diffusion layer (GDL) results as critical component for reaching this target and the most effective approaches are actually based on dual-layer GDLs, i.e. a carbon black (CB) layer on a sheet of macroporous carbon cloth (CC) or carbon paper (CP). The wettability of these carbon-based materials is modified by hydrophobic treatments: e.g. CCs or CPs are usually hydrophobized with fluoropolymers such as polytetrafluoroethylene (PTFE) and CB powder is mixed with aqueous dispersion of colloidal PTFE particles. However, the use of solid fluoropolymers causes poor gas transport and high electric resistance.

Gas permeability as well as thermooxidative stability represents the main characteristic of perfluoropolyethers (PFPEs) and highly hydrophobic PFPE chains can be covalently bonded to carbon-based materials by the thermal decomposition of PFPE peroxides.\[1\]

The functionalization of CC and conductive CB with PFPE moieties was performed without any molecular spacer that could decrease both thermal and chemical stabilities of the resulting materials and, as a result, the carbon-based materials became superhydrophobic, maintaining their electrical conductivity.\[2\]

GDLs were prepared with PFPE-modified carbon-based materials and they were tested in a fuel cell at two operating temperatures, 60°C and 80°C, with 80/60% and 80/100% relative humidity (RH) of the inlet gases. The tests revealed that GDLs based on PFPE-modified materials overall performed better than standard PTFE-hydrophobized GDLs.

References


Thursday, August 14, 2014 11:40 AM
Transport in Polymer Membranes (08:30 AM - 12:00 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 8
737 - Vegetable-oil-based pressure sensitive adhesives

Kaichang Li, kaichang.li@oregonstate.edu, Anlong Li. Wood Science and Engineering, Oregon State University, Corvallis, Oregon 97331, United States

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. We have invented novel vegetable-oil-based PSAs and one of the PSAs has been licensed by a big PSA company. In this presentation, we will disclose our new discoveries that superior PSAs can be prepared solely from vegetable oils, especially soybean oil. No petrochemicals are needed for the PSAs. The preparation process is very simple and very environmentally friendly. No organic solvents and toxic chemicals are required for the preparation of the PSAs. Formulations that can lead to superior PSAs will be presented. The novel process for preparation of the PSAs will be discussed. The PSAs have been characterized for their molecular structures, thermal stabilities, and viscoelastic properties. The peel strength, shear strength, tack, and aging stability of the PSAs have also been evaluated and will be discussed in detail in this presentation.
Carbon nanotubes (CNTs) are potentially the ultimate filler for high-performance composite materials due to their exceptional intrinsic properties such as Young's modulus up to 1TPa, tensile strengths of up to 300 GPa and high electrical and thermal conductivity. Recently, biobased cellulose nanowhiskers (CNWs) have attracted lots of interest due to their mechanical properties, such as elastic modulus up to 220GPa and tensile strengths up to 17GPa, as well as the abundance and renewable resource for the raw material. In this study, we explore the potential of partially or totally replacing CNTs with CNWs in advanced composite materials. Specifically, CNTs and CNWs are compared in terms of their mechanical reinforcing capacity for epoxy composites. CNWs, prepared via TEMPO oxidation, were dispersed in the epoxy by a solvent exchange method and a similar procedure was employed for dispersing CNTs in the resin. We determined the percolation threshold for these fillers in the epoxy resin using small amplitude oscillatory rheology. Due to the difference in the aspect ratio (~160 for CNTs versus ~50 for CNWs), the percolation threshold for CNTs at 0.1-0.2 vol. % is lower than that for CNWs at 0.3-0.4 vol. %. Interestingly, DMA measurements show higher storage modulus at temperatures beyond the glass transition temperature for the epoxy composites with CNWs at concentrations around the percolation threshold by comparison with the composites containing CNTs around the percolation threshold (Figure 1).
739 - Tough films made of cellulose nanowhiskers and carbon nanotubes with tailorable electrical conductivity

Qingkai Meng, qxm20@case.edu, Ica Manas-Zloczower. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, United States

Among the most promising candidates for mechanical reinforcement of polymeric systems are carbon nanotubes (CNTs), exhibiting exceptional intrinsic properties such as Young’s moduli exceeding 1TPa and tensile strengths of up to 200GPa. Nevertheless, transfer of such outstanding properties to the polymer composites has been less than satisfactory and has been asserted to difficulties in mixing and the relatively low filler-filler interactions in CNT networks. Recently, bio-based cellulose nanowhiskers (CNWs) have been thought as potential reinforcing nanofillers in polymeric systems, primarily due to their suitable mechanical properties and rich surface functionality. In this study, hybrid films containing CNWs and CNTs were prepared at various CNW/CNT ratios with the purpose of studying the potential replacement of CNTs with CNWs and to probe the hybrid filler network properties. For the hybrid films, prepared by vacuum filtration of aqueous suspensions, with increasing the weight percentage of CNWs, the tensile properties improve above the CNT films. In particular, hybrid films with around 2 wt. % CNTs show tensile properties exceeding those of both CNT and CNW pristine films. The hybrid films show a broad range of surface electrical conductivity by varying the ratio of CNW/CNT and the environmental humidity, which opens the way for wide electronic applications of the films. The morphology and porosity of the films are also presented as well as possible mechanisms for synergistic behavior.
740 - Layered nanofibrillated cellulose/graphene oxide films for reinforcement in advanced composite materials

Liang Yue, lxy129@case.edu, Qingkai Meng, Ica Manas-Zloczower. Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OHIO 44106, United States

Traditional polymer composites used for high-performance applications such as wind turbine blades are usually reinforced with glass fiber mats. We look at the potential of replacing glass fibers with cellulose based reinforcing films. Specifically, films composed of nanofibrillated cellulose (NFC) and graphene oxide nanoplatelets (GONP) are prepared by an evaporation-induced layer-by-layer assembly method. The NFC is synthesized by TEMPO-mediated oxidation of bleached hardwood pulp and the GONP are obtained from graphite powder by the Hummers method. The thin films produced are transparent and exhibit a layered structure as shown in the SEM image in figure 1. These films show improved mechanical properties by comparison with the NFC pristine ones: with the incorporation of 5 wt. % GONP, the tensile strength and Young`s modulus are dramatically improved by about 60% and 120%, respectively. The enhancement in the mechanical properties may result from a synergistic effect when mixing one-dimensional NFC with two-dimensional GONP. Benefiting from the extraordinary mechanical and thermal performance of GONP and the multifunctional properties of environmentally friendly NFC, these layered films hold great potential to be a cheap and sustainable alternative for preparing biobased polymer composites in the future.
Replacement of bisphenol A (BPA) due to its potential as an endocrine disruptor is an important challenge for the chemical industry. Epoxy resins account for about 70% of the thermoset polymer market with a large portion being based on BPA. Cumene is derived from steam cracking of petroleum and is the starting material for production of BPA.

Levulinic acid is a biobased monomer derived from the degradation of cellulose. The US Department of Energy cited levulinic acid as one of the “Top Value Added Chemicals from Biomass,” due to its feasibility of production and ability to be converted into a broad variety of chemicals. A condensation of levulinic acid with phenol yields diphenolic acid, a potential replacement of BPA for use in polycarbonates and epoxy resins.

Herein we report the synthesis of biobased epoxy monomers from esters of diphenolic acid. Similar synthetic conditions pioneered by Shell and Dow were used to produce the biobased epoxy monomers in order to show compatibility with existing processes allowing for a potential drop-in replacement. The diglycidal ethers of diphenolic esters (DGEDPE) were cured utilizing isophorone diamine (IPDA), a widely used industrial hardener of epoxy resins. The results obtained were compared to the diglycidal ether of bisphenol A (DGEBA) under similar curing conditions. Evaluations of the thermal and mechanical properties of these two systems were performed using dynamic mechanical analysis and tensile testing. We found that DGEDPE has similar mechanical and thermal properties as DGEBA. The thermal and mechanical properties of DGEDPE can be controlled through manipulation of the ester. Further investigations are being conducted to confirm if this monomer can replace DGEBA for structural applications.
Renewable alternatives to petroleum-based thermosetting polymers have drawn significant attention due to potential positive economic and ecological impact. New materials should mimic the rigid, phenylic structure of incumbent high-performance thermoset monomers. Furans derived from cellulose and hemicellulose, are promising candidates for phenyl replacement. The synthesis of furan-based di-epoxies is challenging, and direct property comparisons of thermosets prepared using furanyl and phenyl-based epoxy monomer analogs are required. In this work, analogous furanyl-based and phenyl-based di-epoxy monomers were synthesized, and thermosets were prepared using amine curing agents. A structure-property study showed that furan-based polymers possess improved $T_g$ ($\Delta = 8-16 \, ^\circ C$) and improved glassy modulus ($\Delta = 0.1-0.6 \, \text{GPa}$) relative to their phenylic analogs. The furan ring has thus been demonstrated to be a viable building block for renewable high-performance epoxies, with potential for application in other thermosetting polymers.
Polycyanurate thermosetting networks, polycarbonate thermoplastics, and homogenous polycarbonate/polycyanurate network blends have been prepared from a bio-derived bisphenol. The bisphenol was prepared via a solvent-free, ruthenium-catalyzed olefin metathesis coupling reaction of eugenol followed by hydrogenation. The pure polycyanurate network exhibited a glass transition temperature (Tg) of 186 degrees Celsius and a 5% weight loss temperature above 350 degrees Celsius under nitrogen. The pure polycarbonate exhibited a Tg of 71 degrees Celsius, Mn = 8360, and a polydispersity of 1.88. No phase separation was observed in an 80:20 blend of cyanate ester: polycarbonate during or after cure; the resulting homogeneous system showed a single Tg of 132 degrees Celsius. End-group analysis of the polycarbonate provided no evidence of residual phenols, and the polycarbonate fraction was readily extracted from the polycyanurate network, suggesting that no chemical grafting occurred. These new polymer systems represent promising potential alternatives to similar systems derived from Bisphenol A.
Wood and more particularly its principal components: hemicellulose, lignin and cellulose, have been used as renewable raw materials for the fabrication of numerous products during decades. A forth component from the tree that has obtained less focus previously is the bark.

Outer bark of the birch tree, e.g., has traditionally been used for energy recovery as a raw material[1] although its rich structure gives us the possibility to use it as feedstock for raw materials[2].

One of the major components in outer birch bark is called suberin. Through a mild alkaline hydrolysis it is possible to obtain a large variety of omega-hydroxy fatty acids[3] from suberin. One of those compounds is the cis-9,10-epoxy-18-hydroxyoctadecanoic acid (EFA).

In the present study we have prepared polymer thermoset resins[4] using EFA as monomer and utilizing CalB as catalyst. Combining EFA with suitable end-cappers will allow methacrylate end capped oligoesters to be formed in a "one-pot synthesis".

By reacting the epoxy group through cationic polymerization, the methacrylate through radical polymerization or reacting both, we will form polyester resins with different mechanical and thermal properties.

[1] Ekman, R. Holzforschung, 1983 , 37, 205-211
745 - Metal and morphology: Structured hybrid materials from block copolymers

Robert B Grubbs, Jr., robert.grubbs@stonybrook.edu, Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States and Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

Controlled and living polymerization techniques have proven indispensable for the synthesis of new block copolymers and copolymer-based materials. We have used nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation-chain transfer (RAFT) polymerization for the preparation of a range of copolymer architectures, including block copolymer/metal nanoparticle hybrids. Block copolymers with alkyne-functional blocks for the preparation of cobalt nanoparticles have been synthesized by the direct polymerization of alkyne-functional monomers from both molecular initiators and macrorinitiators. The design, synthesis, and characterization of these and other hybrid materials will be discussed.
746 - Synthesis of metal complex π-nanoparticle and their redox and electronic properties

Hiroshi Nishihara, nishihara@chem.s.u-tokyo.ac.jp, Department of Chemistry, School of Science, The University of Tokyo, Tokyo, Japan

Single-layer π-nanoparticle materials have attracted much attention because of their unique physical and chemical properties, which derive from their two-dimensional (2D) nature. We are interested in using coordination reactions to synthesize π-nanoparticle because there are numerous combinations of metal and ligand, so that various chemical structures with unique electronic properties. Also, most coordination reactions proceed in solution under ambient conditions, leading to easy and inexpensive bottom-up synthesis.

We recently synthesized π-conjugated nanoparticle comprising bis(dithiolatonicel) nickel units [1,2].

A liquid−liquid interfacial reaction using benzenehexathiol in the organic phase and nickel(II) acetate in the aqueous phase produced a semiconducting bulk material with a thickness of several micrometers. A single-layer nanoparticle was successfully realized using a gas−liquid interfacial reaction. Modulation of the oxidation state and the electronic conductivity of the nanoparticle was achieved using redox reactions.


747 - Crosslinked inorganic-polymer hybrids as tunable bi-functional catalysts

Oz M Gazit, ozg@technion.ac.il, Chemical Engineering, Israel Institute of Technology - Technion, Haifa, Israel

The reactivity obtained using weakly acidic surface hydroxyls on silica and alumina for polyglucan hydrolysis, typically catalyzed by strong acid sites, highlights the sensitivity for precise positioning in facilitating catalytic reactivity by weak acid sites. Precise positioning of weak acid sites has an even greater role in inducing bifunctional catalytic reactivity on oxide surfaces. This has been achieved by chemical grafting of amine function adjacent to a hydroxyl function. However, the rigid nature of the metal oxide surface hinders the ability to align the active sites in a manner that juxtaposes the acid and base in an optimal form. Conversely, the use of an amine containing polyhydroxylated polymer such as chitosan offers both the high density of hydroxyls juxtaposed next to an amine function and the processing flexibility of a polymeric system. In this case it is imperative to prevent collapse of the pore system, driven by the tendency to form multiple inter- and intra-molecular hydrogen bonds, limiting accessibility to the active site.

Herein we use surface grafting techniques to form inter- and intra-molecular metal oxide crosslinks as mediators between the chitosan chains. The crosslinking in this inorganic-chitosan hybrid material is designed to resist the chain collapse and maintaining accessibility to the bifunctional active sites. The thermal stability of these metal-crosslinked chitosan materials is discussed. Polymer stretching is used as means to macroscopically orient the position and direction of the molecular functions (amine and hydroxy) on the polymer backbone. Finally the performance of these hybrid materials is assessed for catalytic aldol condensation reactions with respect to the degree of crosslinking and the type of metal crosslinker.
748 - Functional (photonic and magnetic) nano/micro scale polymer solids

Rajadurai Chandrasekar, rcsc@uohyd.ernet.in, School of Chemistry, University of Hyderabad, Hyderabad, AP 500046, India

Bottom-up and top-down fabrication of multidimensional (0-2D) nano/micro scale solids, patterns and arrays from tailor made metal containing conjugated polymers and supramolecular polymers possessing specific (photonic and magnetic) properties are at the centre stage of nanoscience and technology. In the beginning of talk, I will discuss the synthesis of coordination polymers and their characterization details. Then, I will discuss several nano/micro fabrication methods useful for polymers. For example, by following a top-down approach, soft lithographic patterning of spin crossover coordination polymers into a highly ordered and spin-state switchable nano/micro scale patterns/arrays and a method to implant the patterns within an optically transparent polymer film will also be discussed.\(^1\)\(^-\)\(^3\) Adopting bottom-up technique fabrication of white emitting metal containing conjugated polymer spheres also will be presented.\(^4\)\(^-\)\(^5\) Finally I will also discuss some of strategy to combine spin crossover coordination polymer nanoparticles with organic optical waveguides.\(^6\)

Although the photophysical properties of lanthanide complexes have been widely exploited in various biotechnology and materials science applications, the development of luminescent metallopolymers has been relatively limited. The unique photophysical properties of the lanthanide ions result from shielding of the f-orbitals by the 5s² and 5p⁶ shells causing narrow line-like emissions of optically pure colors and long radiative lifetimes. Unfortunately, direct excitation of these f-f transitions displaying emission in the visible and near-infrared (NIR) regions of the spectrum are spin- and parity-forbidden, which necessitates the use of organic antenna chromophore molecules to indirectly excite the metal center through energy transfer processes. Antenna ligands for lanthanide emission are typically effective at sensitizing emission from either visible or near-IR emitting Ln(III) ions depending on the position of the ligand triplet excited state energy level relative to the emissive excited state of the Ln metal ion. In the present work, highly conjugated ligands were produced by appending polymerizable groups such as 3,4-(ethylenedioxy)thienyl (EDOT) or bithiophene (BT) onto ligands with suitable binding pockets for lanthanide ions. In this way, electropolymerizable antenna ligands (L) were synthesized, exhibiting triplet excited state energy levels appropriate for possible lanthanide sensitization. A series of (β-diketonate)₃LLn(III) complexes were produced to probe the potential of the ligands to sensitize Ln(III) emission. The metal complex monomers were readily electropolymerized producing luminescent lanthanide-containing conducting metallopolymers. Some of our latest results pertaining to the design, synthesis, characterization, and study of luminescent lanthanide complexes and the corresponding conducting metallopolymers will be discussed.
750 - Supramolecular assemblies comprising anion-binding and metal-coordinating n-conjugated ionic building units

Hiromitsu Maeda, maedahir@ph.ritsumei.ac.jp, College of Pharmaceutical Sciences, Ritsumeikan University, Kusatsu, Japan

Arrangement of well-designed n-systems, especially those responsive to metal ions and anions, in ordered structures is highly important for exhibiting electronic and electrooptical properties. That is, apart from ion sensing and transporting, ion binding enables the control of the states of n-systems as observed in supramolecular assemblies. In fact, anion complexes of the anion-responsive n-systems have been found to provide ion-based assembled structures as thermotropic liquid crystals by combination with appropriate cationic species. In contrast to charge-by-charge assemblies with alternately stacking oppositely charged species, it is challenging to fabricate charge-segregated assemblies, with stacking identical charged species, due to their electrostatic repulsion.

A promising strategy to induce charge-segregated mode is the use of preferable metal···metal interactions worked in cationic metal complexes. Derived from favorable overlap of charged n-planes, ion-based materials with the contribution of charge-segregated arrangements provided charge carrier mobilities, which are often larger than corresponding charge-by-charge-based materials, showing superior semi-conductive properties. Highly ordered arrangement of charged species has been found to be a key factor to exhibit the enhanced performance as fascinating electronic materials.
751 - Tuning the LCST and UCST thermoresponsive behavior of Poly(N,N-dimethylaminoethyl methacrylate) by electrostatic interactions with multivalent metal ions

Qilu Zhang, Richard Hoogenboom, richard.hoogenboom@ugent.be. Supramolecular Chemistry Group, Department of Organic Chemistry, Ghent University, Ghent, Belgium

Poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) has been reported to show not only a lower critical solution temperature (LCST) transition around 60 °C, but also an upper critical solution temperature (UCST) transition when a trivalent anionic hexacyanatocobaltate metal salt is added.¹ This UCST behavior can be ascribed to the electrostatic interactions between the protonated PDMAEMA units and the trivalent metal salt (see Figure). In this contribution, we will report the influence of trivalent metal ion salts and PDMAEMA copolymer structure on the thermoresponsive behavior of PDMAEMA. Furthermore, a triple-thermoresponsive diblock copolymer will be demonstrated based on the combination of PDMAEMA and poly(methoxydiethylene glycol methacrylate).²

² Q. Zhang, J.-D. Hong and R. Hoogenboom, Polymer Chemistry, 2013, 4, 4322-4325.
752 - Stimuli-responsive iron crosslinked hydrogels and hydrogel graphene composites

Tara Y. Meyer1, tmeyer@pitt.edu, Jeffrey T. Auletta1, Gregory J. LeDonne1, Colin D. Ladd1, Kai C. Gronborg1, Hang T. Nguyen2, Anna A. Vainchtein2, David Swigon2, Haitao Liu1, William W. Clark3. (1) Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States, (2) Department of Mathematics, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States, (3) Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

Metals offer unique opportunities for electrical control of polymeric materials properties as their coordination behavior depends on oxidation state. An electroresponsive hydrogel whose mechanical stiffness depends on the redox state of embedded iron crosslinks has been prepared and shown to switch reversibly between hard and soft states electrochemically. The moduli accessed depend on the doping levels, the ratio of Fe(II)/Fe(III), and pH. The addition of graphene oxide/reduced graphene oxide filler shifts the range of moduli by a factor of ca. 2 and decreases the transition times. Quantitative analysis of coordination numbers and the measurement of magnetic susceptibility implicate iron clusters as mediators of the crosslinking.
Chiral metallopolymers: Introduction of chirality in poly(cobaltoceniumethylene) via chiral counter anions

Huibin Qiu, huibin.qiu@gmail.com, Ian Manners. School of Chemistry, University of Bristol, Bristol, Somerset BS8 1TS, United Kingdom

Metallopolymers with transition metals in the main chain are of growing interest due to their useful functionalities that arise from the presence of metal centers. On the other hand, chiral polymers are emerging as promising materials with vast potential applications in chiral recognition, asymmetric catalysis, enantioselective discrimination, etc. However, the combination of these two research areas yet remains virtually unexplored. Here we report the introduction of chirality in a metallopolymers polyelectrolyte, polycobaltoceniumethylene (PCE), through the combination with chiral counter anions. Chiral structure of PCE was firstly achieved by electrostatic complexation with DNA templates, a right-handed double helical anionic polyelectrolyte, in aqueous solutions (Figure 1, left), which generated relatively monodisperse insoluble nanoparticles. To prepare soluble complexes, we subsequently employed amino acid-derived chiral anionic surfactants as the counter anions to neutralize the PCE mainchain and simultaneously drive the formation of chiral structures. This has led to the formation of brush-like chiral PCE complexes (Figure 1, right), which are well soluble in organic solvents and can further self-assemble into long fibers and twisted ribbons in selective solvents.

Figure 1. Schematic representations of (left) [PCE][DNA] and (right) [PCE][chiral anionic surfactant] complexes.

References

Poly(3-hydroxyalkanoate)s PHAs form an enlarged family of biopolymesters, which are biocompatible, biodegradable and non toxic. PHAs biodegradation corresponds to a hydrolysis involving endo- or exo-enzymatic systems in the breaking cleavage of esters bonds. This type of degradation is needed for environmental applications. In the case of therapeutic and biomedical uses, a simple hydrolysis is required. All polyesters are susceptible to degrade by hydrolysis, but under normal conditions PHAs are water stable.

The hydrolytic degradation rate of these polyesters is very dependent on the chemical structure and material crystallinity. Controlled simple hydrolysis is not evident and in many cases, it is necessary to use functionalized PHAs, block copolymers, graft copolymers or blends with hydrophilic or hydrolyzable polymers. Different architectures of functionalized polyesters based on natural PHAs were prepared and their properties of water stability or hydrolysis are presented.

Carboxylic pendant groups constitute, at present time, the most promising functions, necessary to increase polymer hydrolysis degradation. According to the required system, the percentage of carboxyl groups has to be adjusted by varying the percentage of double bonds in the polymer precursor in the perspective of biomedical or environmental applications.
755 - WITHDRAWN
Recent advances in the processing and understanding of neural data has led to a pressure for improvements in materials that are able to interface with soft neural tissue chronically. Traditional electrodes, including those patterned on silicon or polyimide, rely on stiff materials for insertion. However, these materials are grossly mismatched in terms of modulus when compared to the tissues they stimulate and record from. Shape memory polymers (SMPs) have proven a more compatible substrate, leading to neural prosthetics that can both insert reliably while softening considerably after some time in vivo. A challenge with these systems however is the chronic lifespan of these devices due to the hydrolytic instability of traditionally used constituent monomers. Now using a rigid aliphatic dithiol, a chronically stable substrate that exhibits the shape memory effect is described for use as an ultrasoft long-term or permanent platform for neural electrodes. In this study, tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (TMICN) is substituted for a similarly rigid tricyclodecane dithiol (TCDDT) (Fig. 1A) to investigate the effects on water uptake and degradation, as well as the final modulus of the material at relevant physiological temperatures. Using this system, a further order of magnitude drop in modulus is shown (Fig. 1B-C) when compared to previous studies, allowing for substrates which more closely resemble the stiffness of the penetrated tissue. These polymers show promise as a reliable substrate for neural interfaces which can maximize insertion success while minimizing scar-formation in vivo long-term.
Tailoring new materials with a perspective of eco-design drive the use of degradable polymers as environmental-safe alternatives. Though, their effective use is facilitated by controlling its degradation process. PLLA is a hydrophobic biodegradable polyester with a relatively slow degradation rate. Consequently, research has focused substantially on the acceleration of this process. Nevertheless, controlling the polymer stability rather than accelerating its degradation process is usually required. Blending is an industrially attractive method to alter PLLA properties including degradability. Research on degradation of PLLA-based blends has mainly focused on the structural changes upon hydrolysis. Yet, adjusting their degradation profiles without altering the overall degradation time still remains unresolved. Herein, we tune the PLLA-based blends degradation profiles by means of miscibility. Extruded blending systems of PLLA with polypropylene adipate (PPA) and poly[(R,S)-3-hydroxybutyrate] (a-PHB) with differences in molar masses were used. Miscible (PLLA/a-PHB-low-molar-mass; PLLA/a-PHB-high-molar-mass), partially-miscible (PLLA/PPA-low-molar-mass/compatibilizer; PLLA/PPA-high-molar-mass /compatibilizer) and immiscible (PLLA/PPA-low-molar-mass; PLLA/PPA-high-molar-mass) blends were hydrolyzed in water at 37 °C under one year. The blends displayed diverse degradation profiles with no variance in the total times of degradation. Pure PLLA and the miscible blends, presented one and two-stage degradation profiles respectively. The immiscible blends exhibited opposite degradation profiles to pure PLLA. The partially-miscible blends presented degradation profiles within the miscible and immiscible blends. The hydrolytic endurance of degradable polyester-based systems is customized to achieve specific controlled degradation profiles to meet commodity and advanced applications.
Renewable resource based polymers are biodegradable, biocompatible and eco-friendly in nature. Starch, Cellulose, Chitin, Chitosan, Poly(3-hydroxybutyrate) and Poly(lactic acid) are mainly used in biomedical field and for food packaging purposes. However, due to limited thermal stability, these polymers undergo significant degradation when exposed for long time during melt processing. Therefore, understanding of thermal behaviour of these polymers and their composites need to be investigated towards their applications. In the current research work, thermal properties of pure polyactic acid (PLA) along with various bio-fillers combinations like starch, cellulose, chitosan and, also inorganic fillers such as TiO$_2$ & cationic clay (Cloisite®) are studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. The TGA data obtained from several isothermal & non-isothermal experiments are used to determine the thermal degradation behaviour and associated kinetics. Various kinetic models have been reported in the literature for the determination of kinetic triplet. Theoretical equations are developed to study the thermal degradation behaviour of such polymers using isoconversional, maximum rate and model fitting methods. The preliminary classification has been carried out under isoconversional and model fitting methods. Further, efforts are made on the applicability of these models to experimental data. The value of 'E' for pure PLA lies in the range of 140-177 kJ/mole by OFW method while Kissinger and Augis & Bennett produce around 171 kJ/mole. Based on the kinetic data obtained from different models, reconstruction of the conversion profiles for different thermal history was performed and compared with experimental data.

A choice of a model for a specific material, pure & composites biopolymers considered has been proposed.
Comparing ex situ and in situ fragmentation of sulfonated poly(ether ether ketone) (SPEEK) membranes

Shulamith Schlick1, schlicks@udmercy.edu, Mariana Pinteala2, Marek Danilczuk1, Frank D. Coms3. (1) Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan 48221, United States, (2) Institute of Macromolecular Chemistry, Petru Poni, Iasi, Romania, (3) Department of Global Fuel Cell Activities, General Motors, Pontiac, Michigan 48340, United States

Perfluorinated ionomers such as Nafion, Aquивion and 3M membranes exhibit excellent mechanical, chemical, and thermal stability in both oxidative and reductive media, and their fuel cell (FC) performance is close to current DOE requirements for automotive applications. However, some problems remain, among them high cost, low oxygen reduction rate at the low pH, and high gas crossover, hydrogen to the cathode and oxygen to the anode. These drawbacks led to intense activity in the research and development of alternative, nonfluorinated, proton-exchange membranes (PEMs). Due to their properties and low cost, poly(arylene ether)-based sulfonated polymers have been considered as potential candidates for FC applications [1]. We present a study of the chemical stability of sulfonated poly(ether ether ketone) (SPEEK) deduced by a comparison of ex situ experiments under Fenton conditions [2], and in situ experiments in a fuel cell inserted in the resonator of the electron spin resonance (ESR) spectrometer [3,4]. The formation of radicals was monitored by spin trapping ESR, with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap. The magnetic parameters and the relative intensities of DMPO-adducts were determined by simulation of the ESR spectra. The major adducts detected in the in situ experiment were DMPO/OOH and DMPO/H [4]. The generation of the DMPO/OOH adduct at the anode was explained by reaction of crossover oxygen with hydrogen atoms formed at the Pt catalyst; at the cathode this adduct can be generated by hydrogen crossover to the cathode, reaction at the Pt catalyst, and reaction with oxygen. No membrane-derived carbon-centered or oxygen-centered radical adducts were detected in the in situ FC. However, in SPEEK membranes directly exposed to hydroxyl radicals in the presence of the spin trap DMPO, the DMPO/Ph and DMPO/OPh adducts were detected [2], indicating poor chemical stability of SPEEK in the ex situ Fenton test; here Ph and OPh are, respectively, phenyl and phenoxyl radicals. The results presented in these studies indicated that hydrocarbon membranes such as SPEEK demonstrate different chemical stabilities in the two types of experiments.

(a) The repeat unit of sulfonated poly(ether ether ketone) (SPEEK)

(b) Spin trapping with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap

The present study aims at cross-relating the different scales of analysis of polypropylene properties under photoaging.

A conventional approach for studying polypropylene photoaging consists in measuring the carbonyl products by infrared spectroscopic analysis of UV-light exposed samples. Monitoring chemiluminescence has been also proposed many times to perform the analysis of oxidation. However, it is known [1] that a non-negligible amount of photo-products migrate to the gas phase, and are not taken into account by this kind of analysis. Moreover, chemical changes occur before the detection of carbonyl products can be detected [2]. Our investigations show that chemiluminescence has not proven to be a more sensitive technique than FTIR spectroscopy in the early stages of photo-oxidation. Those observations drove us to reconsider the relevancy of the experimental approach of photoaging only based on these measurements.

We will present a critical review of the results that we obtained on the basis of a multi-scale approach, including SAXS, DSC, AFM, micro-hardness and rheology analyses, to describe phenomenon governing the loss of functional properties, such as the gloss loss. A particular attention is given to AFM experiments such as AFM Nanoscale Thermal Analysis Module (VITA) and nano-indentation.

Our results indicate that oxidation provokes an increase of crystallinity, which can be detected very early. This plays a major role in the apperarition of cracks (Figure 1) and results in a dramatic loss of gloss.


761 - Maintaining hand and improving fire resistance of cotton fabric through ultrasonication rinsing of multilayer nanocoating

Tyler Guin, tylerguin@tamu.edu, Aaron Milhorn, Michelle Krecker, Jaime Grunlan, jgrunlan@tamu.edu. Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States

Thin films of environmentally benign polyelectrolytes, cationic chitosan (CH) and anionic poly(sodium phosphate) (PSP), were deposited on cotton fabric via layer-by-layer (LbL) assembly to reduce flammability. This CH-PSP nanocoating promotes charring of the cotton, rendering the fabric self-extinguishing. The coated fabric was rinsed in an ultrasonication bath between deposition steps to improve the softness (i.e., hand) of the coated fabric. Ultrasonication is believed to remove weakly adhered polyelectrolyte, preventing the fabric from becoming stiff, while improving anti-flammable behavior at a given coating weight. At 17 bilayers (BL), only 9.1 wt% was added to the cotton, yet the coated cotton consistently passed vertical flame testing. Electron microscopy provides evidence of intumescence and confirms the cleaner deposition afforded by ultrasonication. The reduction in peak heat release rate and total heat release, as measured by micro cone calorimetry (MCC), were 73% and 81% respectively, which is a new benchmark in LbL FR coating on cotton. The mechanical properties of the fabric were measured using the Kawabata Evaluation System (KES), which showed that ultrasonication rinsing significantly improved the hand. The ability to render cotton fabric self-extinguishing, while maintaining a soft hand, marks a major milestone in the development of these environmentally-benign nanocoatings.
Dendrimers have the capacity for a number of applications that take advantage of their highly uniform architecture and the large number of terminal groups that can be functionalized. Dendrimers with functional terminal groups have been proposed for use in electrophoretic separations, fuel cells, lithium ion batteries and therapeutic agent delivery. In spite of the large body of literature exploring these potential uses of functional dendrimers, very few have been realized. One area of research that has not been extensively explored is the effect of typical use conditions (i.e., in a given application) on the dendrimer structure. For example, do the charging / discharging cycles experienced in a lithium ion battery cause degradation of the dendrimer's uniform architecture? If so, how does this affect the molecule's effectiveness as an electrolyte?

In particular we are interested in understanding the effect on cycling electric fields and varying field strength on dendrimers in aqueous and methanol solvents. To monitor the degradation, the size of the dendrimers was studied by gel permeation chromatography (GPC) and small-angle neutron scattering (SANS), which excels at probing molecules containing light atoms. Additionally, electron paramagnetic spectroscopy (EPR) at X-band frequencies was performed on samples that were exposed to electric fields in situ. EPR spectroscopy allowed us to monitor any radical species that were formed.

Figure 1. SANS of dendrimers (G = generation) in a methanol solution.
The ability to measure the nanoscale contributions of material morphology and interface chemistry to the chemical and mechanical stability of polymeric thin film materials is critically important for the design of new materials. In this study, we systematically expose a polyamide network polymers with a range of interfacial chemistries to hypochlorite solutions and observe the effects of chlorine concentration and exposure time on the film structure and degradation behavior. Quartz crystal microbalance with dissipation monitoring (QCM-D) is a high throughput analysis tool for thin films, which forms the evaluative basis for the study. The QCM operating mechanism allows for nanogram level sensitivity, enabling direct observation of film character changes in real time and is commonly used to assess kinetic processes at surfaces. The polyamide films were chemically and structurally characterized ex situ. Together this data was used to develop a kinetic model and morphological description of chlorine induced degradation of polyamide films. The model and experimental approach is relevant for probing polymer degradation under environmental conditions for polymers used in aqueous environments (membrane materials for example). The work here represents enhanced measurement capabilities for the rapid assessment of nanoscale degradation of material lifetime performance for polymer thin films and related technologies.
764 - WITHDRAWN
765 - Melt processible polyacrylonitrile/methyl acrylate (PAN/MA) statistical copolymers and plasticized blends as polymers for carbon fiber precursors

Padmapriya Pisipati, priyap@vt.edu, Michael Bortner, Sue Mecham, Susan Beck, Jianhua Huang, Donald Baird, James McGrath. Macromolecules Interfaces Institute and Department of Chemistry, Virginia Polytechnic Institute and State University, blacksburg, VA 24060, United States

Abstract: High performance carbon fibers for polymer matrix composites are currently derived from Polyacrylonitrile (PAN) copolymer fiber precursors via careful “stabilization” and carbonization. Polyacrylonitrile homopolymer degrades before it melts and is hence copolymerized with a small amount of comonomer to aid in depression of its melting point. All commercial PAN precursor fibers are presently wet or dry spun using expensive and environmentally harmful solvents and at slower rates than melt processed fibers could be produced. Melt-spun fibers have been successfully generated when the copolymers were plasticized with water. The water plasticized systems however require high pressures for extrusion, since the boiling point of water is below the extrusion temperature. Glycerin, a high boiling non-toxic plasticizer was discovered to have somewhat similar plasticizing effects to water. Glycerin, ethylene glycol, glycerin/water combinations and high molecular weight ethylene-vinyl alcohol copolymers have been investigated as potential plasticizers for high molecular weight (240,000 g/mol), high acrylonitrile (93-96 wt%) content poly(acrylonitrile-co-methylacrylate) random copolymers. Equal weight mixtures of water and glycerin have been successfully extruded into fibers. Pure glycerin (25 wt %) induces an apparent crystallization followed by a reduced “Tm” of about 213 °C via DSC. However, this composition did not process well. A lower MW (100K) copolymer was extruded with no apparent degradation. Our hypothesis is that the hydroxyl groups in glycerin (or water) disrupt the strong dipole-dipole interactions between the chains enabling the copolymer endothermic transition ("Tm") to be reduced and melt before it degrades. Evidence for this is seen in the FT-IR which confirms specific interaction between the hydroxyl group of glycerin and the copolymer.

References:
[2] James E. McGrath, Donald G. Baird, Sue J. Mecham, Susan Beck, Priya Pisipati, Jianhua Huang, Melt Processible Acrylonitrile Copolymers Via Free Radical or RAFT Controlled Radical Copolymerization and Processing Aids Based on Water and/or Glycerin, SAMPE Preprints, May 7,2013
The alarming phenomenon of bacterial resistance to antibiotics causes high morbidity and mortality, which is an extremely critical problem in the healthcare area. A variety of polymer grafted nanoparticles were designed and synthesized for enhancing the bioactivities of bacterial resistant antibiotics. A range of substrate nanoparticles were employed such as fluorescent dye labeled silica, europium doped luminescent silica and Fe$_3$O$_4$/SiO$_2$ core-shell superparamagnetic nanoparticles. A variety of water soluble polymers, such as poly(methacrylic acid), poly(vinylpyrrolidone), poly(ethylene glycol) and poly(N-isopropylacrylamide) were grafted on nanoparticles with a monomodal or bimodal distribution via surface-initiated reversible addition fragmentation chain transfer (RAFT) polymerizations.

These water soluble polymer grafted nanoparticles demonstrated nice dispersion in aqueous environment with diameters of the individual nanoparticles 30 - 50 nm. These polymer grafted nanoparticles can greatly enhance the bioactivity of antibiotics (Penicillin G and oxytetracycline) over a wide range of bacteria (11 bacterial strains of Gram negative or Gram positive) including the very dangerous Methicillin-resistant Staphylococcus aureus (MRSA) when conjugating with these antibiotics.
Cellulose is highly interesting from a material point of view due to its physical and chemical properties. The modification of cellulose has intrigued researchers for centuries and in recent years most of the focus has been into the modification of the nanostructural components of cellulose [1].

Controlled radical polymerization has proven to be a very useful route to control the surface properties of various cellulose substrates [2]. However, this requires the use of organic solvents which is a big disadvantage. Therefore, as an alternative to covalent grafting, we have synthesized a library of cationically charged block-copolymers which can simply be physisorbed onto cellulose under aqueous conditions. Multifunctional di-and tri-block copolymers were synthesized by ATRP or a combination of ATRP and ROP, where one block was composed of an anchoring block and one block of a functional polymer. Quaternized poly(dimethylaminoethyl methacrylate) (PDMAEMA) has been utilized as the anchoring block and either a hydrophobic polymer (polystyrene or polycaprolactone) or a thermoresponsive polymer (poly(di(ethylene glycol) methyl ether methacrylate) as functional blocks. The tailored block-copolymers were adsorbed onto cellulose nanofibrils or cellulose model surfaces. Furthermore, by RAFT-mediated emulsion polymerization, latex particles were produced composed of cationic PDMAEMA and PMMA, with varying length of the PMMA-block. These were subsequently adsorbed onto cellulose surfaces, exhibiting exceptional adsorption capacity.

A. Carlmark, E. Malmström Polymer Chemistry 2012, 3, 1702
Gold nanoparticles and polymers from RAFT polymerization form various types of self-assembled nanostructures, depending on the surface reactivity of the gold particles as well as on the microstructure and topology of the RAFT polymer. When using linear polyNIPAM and gold particles from citrate reduction, perfectly hexagonal lattices of gold cores are formed. The inter-particle distances increased strictly correlated with growing molar masses of the coating polymer, allowing for a reference curve to be found. When using polymers containing multiple RAFT groups along their backbone, the spacing between the gold cores are much lower and remain constant, independent of the polymers’ chain lengths, showing that these macromolecules are wrapped around the nanoparticles. Absolutely no crosslinking is observed for this case. However, when increasing the surface reactivity of the gold particles by generating them via the Brust-Schiffrin method, a self-assembly of RAFT multi-block polymers with gold particles into dispersed three-dimensional superstructures occurs (see figure).

TEM analysis revealed that the inter-particle distances in these superstructures can again be tuned over an unprecedented wide range by employing multi-block polymers with adjusted degree of polymerization and thus tailored RAFT group distances. Crosslinking of the gold nanoparticles in the assemblies was proven by AFM showing partly preserved globular shape after deposition on a solid substrate.
Water-soluble oligomers bearing complexing groups have been synthesized by RAFT copolymerization using various combinations of monomers such as butyl acrylate or styrene as hydrophobic monomers and acrylic acid and/or 2-acrylamido-2-methyl propane sulfonic acid or vinyl benzyl phosphonic diacid as functional hydrophilic ionogenic monomers. Then, these oligo RAFT agents have been used to modify aqueous dispersions of CeO₂ nanoparticles. The adsorption of the oligomers at the surface of the CeO₂ nanoparticles has been characterized by several complementary techniques such as UV-vis spectroscopy, taking advantage of the chromophore RAFT moiety. Finally, the living CeO₂ nanoparticles have been involved in emulsion copolymerization of styrene/methyl acrylate or vinylidene chloride/methyl acrylate. This strategy led to a very efficient formation of CeO₂/polymer hybrid latexes, as evidenced by cryo-TEM microscopy. The correlation between the morphology of the hybrid latex particles and the composition of the oligo RAFT agents allowed us to propose mechanisms for the growth of the polymer particles. Such hybrid latexes may find applications in many areas, for instance in the elaboration of high performance coatings but also as templates for the preparation of functional organic or inorganic porous materials with CeO₂ or other nanoparticles evenly distributed in the porous matrix.
Surface-initiated atom transfer radical polymerization (SI-ATRP) has become an indispensable tool for engineering the structure and properties of polymer/inorganic and polymer/organic interfaces. This presentation will review the progress and challenges that are associated with the application of SI-ATRP to precisely control the molecular characteristics of polymer chains tethered to nanoparticle surfaces as well as the opportunities that are afforded by controlling the architecture of polymer-grafted particles to engineer the properties of novel functional hybrid materials. Of central importance is the concept of chemical confinement in tethered polymer systems. In particular, tethering of polymers imparts constraints on the static and dynamic properties of polymer chains that expand the range of accessible properties in polymer-based materials. Even for the conceptually most 'simple' particle brush systems – that is spherical particles uniformly grafted with amorphous non-polar polymers – the complex superposition of interactions as well as time- and length-scales related to particle core and tethered chains will be shown provides a rich and largely unexplored parameter space for the design of novel functional materials (see Figure 1).

The application of SI-ATRP to the development of materials for applications ranging from photonic inks and paints to advanced high 'k' dielectrics for energy storage and advanced nanocomposite materials with improved optical, mechanical or thermal transport characteristics is discussed.
771 - AGET ATRP of elastomeric polyacrylate and biodegradable polymethacrylate porous polymers within high internal phase emulsions

Inna Gurevitch¹, Melissa Lamson², Dikla Cohen Samoocha¹, Krzysztof Matyjaszewski², Michael S. Silverstein¹,
Michaels@tx.technion.ac.il. (1) Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, NA 32000, Israel, (2) Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213-3890, United States

PolyHIPEs are porous highly interconnected emulsion-templated polymers typically synthesized within surfactant-stabilized water-in-oil high internal phase emulsions (HIPEs). Surfactant-free polyHIPEs can be synthesized in nanoparticle-stabilized Pickering HIPEs. The effects of polymerization mechanism and locus/nature of initiation were investigated.

Elastomeric polyacrylate (PA) polyHIPEs, usually synthesized using conventional free radical polymerization (organic-phase initiation or interfacial initiation), were synthesized using activators generated by electron transfer for atom-transfer radical polymerization (AGET ATRP), Figure 1a. Two different AGET ATRP systems were used, an organic-soluble initiator or an initiator anchored to nanoparticles (NP), either silica or polymer. These NPs could perform 3 functions, stabilizing the HIPEs, initiating the polymerization, and crosslinking the polymer. PolyHIPEs containing around 85% individually encapsulated micrometer-scale water droplets with enhanced resistance to compressive deformation and to ignition upon direct exposure to a flame were synthesized. The polymerization mechanism and locus of initiation had profound effects upon the molecular structures, porous structures, and properties.

A degradable polymethacrylate polyHIPE crosslinked using bis(2-methacryloyloxyethyl) disulfide (DSDMA) was synthesized using AGET ATRP with two different CuBr₂ catalyst systems, a highly hydrophobic N,N-bis(2-pyridylmethyl)octadecylamine (BPMODA) ligand (Figure 1b) or a less hydrophobic 2,2'-bipyridine (bpy) ligand. The BPMODA-based system produced polyHIPEs with more uniform crosslinked networks which degraded into polymer chains with a relatively low dispersity. The bpy-based catalyst exerted less control over the polymerization and produced a non-degradable polymer.
While the grafting of well-defined polymer brushes has become a common approach for the functionalization of flat solid surfaces as well as surfaces of nanoparticles and macropores (pores of diameter above 50 nm), much less attention has been directed towards a similar functionalization of surfaces of mesopores (pores of diameter 2 - 50 nm). Mesoporous materials constitute a very interesting class of solid supports, because they commonly exhibit high surface areas (100-1000 m²/g), and may exhibit mesopores of very uniform and readily adjustable size and well-defined geometry (for instance spherical or cylindrical). The mesopores may also feature quite uniform entrances, whose size can be controlled. Well-defined mesoporous solids can be composed of particles with periodic arrays of pores or with single voids accessible through porous walls. The above structural features make mesoporous materials an attractive platform for functionalization with polymer brushes. Recent work demonstrated that atom transfer radical polymerization (ATRP) is a robust platform for grafting from surfaces of mesopores. If the mesopores are sufficiently large (above 10 nm) and the surface is suitably functionalized with initiator groups, normal ATRP renders layers of controlled thickness composed of polymer chains of low polydispersity (1.05-1.1). Surface-initiated ATRP with activators regenerated by electron transfer (ARGET) can be readily employed, allowing one to functionalize the surfaces of mesoporous particles with polymer brushes of quite low polydispersity (1.2-1.3) without using air-tight glassware and vacuum lines.
773 - Designing electrocatalytically active nanocarbons based on well-defined block copolymers prepared by controlled radical polymerization

Tomasz Kowalewski¹, tomek@andrew.cmu.edu, Krzysztof Matyjaszewski¹, Mingjiang Zhong², Jacob Mohin¹, Eric Gottlieb¹. (1) Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States, (2) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, United States

In past years our groups have developed a versatile approach to the preparation of electrocatalytically active, heteroatom enriched porous nanocarbons from block copolymer precursors obtained by controlled radical polymerization. Precursors need to be comprised at least two immiscible blocks: (i) heteroatom rich carbon source (e.g., polyacrylonitrile), and (ii) sacrificial porogenic block. Upon thermal treatment and pyrolysis block (i) is converted to nanocarbon while block (ii) is decomposed rendering material nanoporous. More recently we have reported high electrocatalytic activity of such prepared materials, in particular in metal-free catalysis of oxygen reduction reaction. This presentation will present our view on the source of electrocatalytic activity of heteroatom enriched nanocarbons, and will discuss the design criteria which need to be considered in order to optimize it.
774 - Simple and versatile preparation of hybrid nanomaterials using controlled radical polymerization

Jerome P. Claverie, claverie.jerome@uqam.ca, Chemistry - Nanoqam - Québec Center for Functional Materials, Université du Québec à Montréal, Montréal, Qc H3C3P8, Canada

We have been interested in the preparation of well-defined dispersants by Reversible Addition-Fragmentation chain Transfer polymerization. We first demonstrated that poly(acrylic acid) prepared by RAFT polymerization was efficient for the dispersion in water of a variety of nanoparticles, mostly metallic oxides. Over the years, the structure of the dispersants was refined so as to provide irreversible adsorption onto the nanoparticle. Then, the resulting dispersion was engaged in an emulsion polymerization process to yield core-shell nanoparticles, where the core is an inorganic particle and the shell a thin polymeric layer. This process was extended to a large variety of nanoparticles (oxides, metals, nitrides, carbides, quantum dots, upconverting nanoparticles) and nanotubes either in water or in organic solvents. In this communication, we will show several of examples of dispersants and encapsulants, as well as some of their applications.
775 - WITHDRAWN
Due to the vast worldwide usage of synthetic polymers in industrial applications (such as wastewater treatment, oil recovery, erosion control and ore processing) concerns have been raised regarding the impact of the release of polymer particles on aquatic life forms. However current methods of tracking the spread of water soluble polymers through the environment have the drawback of being either chemically complex or they are not applicable to contaminants found in fresh water. Here a new detection method is outlined for the detection of specific polymer contaminants in fresh water systems using interpolymer complexation with a specifically synthesised poly(acrylic acid) fluorescence probe.

Time resolved anisotropy shows clear evidence for interpolymer complex formation between poly(acrylamide) and the probe, detectible in concentrations as low as the 10⁻⁵wt% scale.

Figure 1 – The restricted rotation of the polymer probe (\( \tau_0 \) measured in nanoseconds) shows a clear linear response to the presence of poly(acrylamide) at ppm concentrations. The lower limit of detection is dependent on the concentration of polymer probe (PAA conc. 0.3 mg ml⁻¹)

This detection method was tested in a variety of fresh water situations and found to be useful against a range of other polymers, as well as poly(acrylamide). This method is remarkably fast and requires little sample modification compared to existing fluorescence methods of detection.
Novel high performance thermo– and photo–reversible networks utilizing both a Diels-Alder reaction and photo–dimerization of crosslinkable anthracene groups were investigated. Well–defined copolymers with 9–anthrylmethyl methacrylate (AMMA) and other alkyl methacrylates such as methyl methacrylate (MMA) and 2–ethylhexyl methacrylate (EHMA) having different AMMA compositions were synthesized using RAFT techniques. Well–controlled block copolymerization of AMMA and alkyl methacrylates was also successfully accomplished by using a thiolcarbonate–terminated poly(alkyl methacrylate) macroCTA at 80 °C.

According to AFM analysis, lamellar microphase separation was observed in PMMA–bock–PAMMA (PMMA/PAMMA = 50/50 (wt/wt)) films prepared by solvent cast from chloroform (Figure 2). Thermo– and photo-reversibility studies of the copolymers from Diels-Alder modification and photo-dimerization will be also discussed.
We recently and unexpectedly discovered that the cationic polymerization of o-phthalaldehyde generates cyclic poly(phthalaldehyde) in high yield, high molecular weight, and high cyclic purity. Given this surprising result, we pursued the cationic polymerization of ethyl glyoxylate to determine if the macrocyclization phenomenon is, in fact, a general trend in low ceiling temperature polyacetals. Using NMR spectroscopy, MALDI-TOF mass spectrometry, and triple detection GPC, we have uncovered divergent macrocyclization mechanisms in the cationic polymerization of ethyl glyoxylate. Back-biting is observed either via the main-chain acetal backbone or via the pendant ester to give disparate polymer products with differing physical properties. Our recent findings in primary structural characterization of the polymers and elucidation of the polymerization mechanism will be discussed. Understanding the underlying mechanisms of polymerization and the ability to rigorously control polymer structure has profound implications towards the design of new materials.
779 - Radical copolymerization of hydroxy-functional monomers: Kinetic and semibatch studies

Jan ES Schier, jan.schier@chee.queensu.ca, Robin A Hutchinson. Department of Chemical Engineering, Queen's University, Kingston, Ontario K7L 2N6, Canada

Solvent-borne acrylic resins used as polymeric binders in automotive coatings or matrices for contact lenses are complex copolymers containing reactive functional (often hydroxyl) groups. A better understanding of the copolymerization kinetics of these monomers is required in order to ensure uniform distribution of the functional groups among the polymer chains over the course of production. Radical copolymerization propagation kinetics of 2-hydroxyethyl acrylate (HEA) with other acrylates and methacrylates are investigated both in bulk and solution, using high frequency (up to 500 Hz) pulsed-laser polymerization (PLP) combined with size exclusion chromatography (SEC) and proton NMR, with typical SEC output shown in Figure 1.

The experiments show that copolymer composition and averaged propagation rate coefficients are affected by solvent choice relative to bulk polymerization due to hydrogen bonding interactions. In addition, it was found that H-bonding, caused by solvent choice or monomer functionalities significantly affects the backbiting mechanism of acrylates. These kinetic effects influence polymer molecular mass distributions and structure of hydroxy-functional acrylate copolymers formed by higher temperature starved-feed semibatch reactions under industrially-relevant conditions.
New electrophilic sulfur(VI) functional styrenic monomers allowed multiple orthogonal post-functionalization reactions of styrene copolymers. Styrene monomers containing fluorosulfate and catechol cyclic sulfate functional handles were synthesized and copolymerized with styrene, as well as vinylbenzyl azide and silyl ether protected vinylphenol. The copolymers were sequentially functionalized with fluorescent dyes at room temperature without deprotection. Covalent attachment of dyes to the polymers was verified by GPC UV-Vis detection.
781 - Natural polymers use to manufacture “green” membranes and surfaces

Norma A. Alcantar1, norma@usf.edu, Sylvia W. Thomas2, Fei Guo1, Samuel Perez2, Ryan G. Toomey1, Rana Falahat1, Delcie R. Durham3, Brian Bell3, Rasudha Muppaneni2. (1) Department of Chemical and Biomedical Engineering, University of South Florida, Tampa, Florida 33620, United States, (2) Department of Electrical Engineering, University of South Florida, Tampa, Florida 33620, United States, (3) Department of Mechanical Engineering, University of South Florida, Tampa, Florida 33620, United States

The effective preparation of membranes using natural polymeric materials has a positive effect in ‘green’ and sustainable manufacturing. We have successfully synthesized functional membranes and surfaces for water treatment and as raw materials with natural materials extracted from cactus plants (cactus mucilage) and from the waste of shells of crustacean such as crab and shrimp. Such bioinspired membranes and surfaces have been chemically characterized with attenuated total reflection Fourier transform infrared spectroscopy, tested mechanically to determine their strength and elasticity, and evaluated electrically to determine their resistivity. We have found that the strength depends on the concentration of natural polymers versus the amount of crosslinker. We have also determined that depending on the natural extraction process, the physical and chemical characteristics vary internal structure and processing methodologies. The chemical conformation of the membranes was determined to help understanding the effectiveness of the different synthetic methodologies to prepare these membranes and surfaces. The transparency of such surfaces is related to their structure and processing. We have found that crystal like membranes and surfaces led to surfaces that are translucent and conductive, whereas membranes and surfaces with amorphous structure are opaque and non-conductive. A life cycle assessment was made for the bioinspired membranes and surfaces and it was determined that their scalability is feasible, sustainable, and cost-effective. Other applications such as drug delivery, tissue scaffolds and innovating textiles have also been studied.

Figure illustrates the nanoscaled structure of two of the extracts from the cactus plant (A, gelling extract, and B, non-gelling extract) used to produce “green” membranes and surfaces.
782 - Synthesis and post-modification of low cytotoxicity active ester polymers based on salicylic acid and methyl salicylate

Lirong He¹, Lirong.He@chemie.uni-hamburg.de, Hui Zhao¹, Kristina Szameit², Ulrich Hahn², Patrick Theato¹. (1) Department of Chemistry, Institute for Technical and Macromolecular Chemistry, University of Hamburg, Hamburg, Germany, (2) Department of Chemistry, Institute for biochemistry and molecular biology, University of Hamburg, Hamburg, Germany

Activate ester polymers, pioneered by Ferruti and Ringsdorf in the 1970s, are attractive polymeric materials because they can easily be converted into functional polymers by reacting with amine nucleophiles. In the present study, methyl salicylate acrylic ester and salicyl acrylate based polymers were polymerized yielding novel reactive precursors for the post-polymerization modification with primary and secondary amines. The reactivity of poly(pentafluorophenyl acrylate), poly(methyl salicylate acrylic ester) and poly(salicyl acrylate) towards amines were compared by kinetic studies and revealed the practical applicability of salicylic acid based derivatives for efficient post-polymerization modifications. In addition, in vitro cytotoxicity of water-soluble leaving groups, pentafluorophenol and salicylic acid, as well as water-soluble polymers containing these active ester groups were investigated using HeLa cells.

In brief, compared with frequently used pentafluorophenyl esters, poly(methyl salicylate acrylic ester) and poly(salicyl acrylate) active esters have slightly lower reactivity, but exhibit less cytotoxicity. In this respect, poly(methyl salicylate acrylic ester) and poly(salicyl acrylate) as reactive precursor polymers may become alternative routes for the synthesis of functional polyacrylamides for advanced applications in vivo.
783 - Mercapto functional sol-gel coating for copper protection

He Li\textsuperscript{1,2}, lihe@nimte.ac.cn, Shusen Peng\textsuperscript{1,2}, Zhixiang Zeng\textsuperscript{1,2}, Wenjie Zhao\textsuperscript{1,2}, Jin Han\textsuperscript{1,2}, Xuedong Wu\textsuperscript{1,2}. (1) Key Laboratory of Marine Materials and Related Technologies, Ningbo Industrial Technology Research Institute, Ningbo, Zhejiang 315201, China, (2) Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Industrial Technology Research Institute, Ningbo, Zhejiang 315201, China

Copper is very easy to be corroded when exposed in a moist environment. In this presentation, we are going to demonstrate a mercapto functional sol-gel coating which performs an excellent anticorrosion ability to copper. The coating overcomes the drawbacks of the use of bad odor and poor water solubility of thiol functionalized silane, and forms much denser physical barrier than a regular epoxy functionalized sol-gel coating. The protection and degradation behaviors of this coating are also discussed in this presentation. We expect to use the coating to protect copper devices in harsh marine environment.

salt spray test: (a) bare copper, (b) ESol, (c) ESol+DETA, and (d) ESol+TUA coated copper substrates.
784 - Novel polymers for 3D printing with improved interlayer adhesion by reversible Diels-Alder reactions

Kejia Yang\textsuperscript{1}, kejia.yang@utdallas.edu, Gayan Kavinda Siriwardana Adikari Appuhamillage\textsuperscript{1}, Steven Shaffer\textsuperscript{3}, Benjamin Lund\textsuperscript{1,2}, Ronald Smaldone\textsuperscript{1}, Walter Voit\textsuperscript{1,2,3}. (1) Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United States, (2) Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 75080, United States, (3) Department of Mechanical Engineering, The University of Texas at Dallas, Richardson, Texas 75080, United States

3D printing technology has been of growing interest and is becoming an important tool in many industries especially for biomedical applications. In 3D printing, the polymer is melted then extruded through the print head and deposited to a substrate layer by layer. However, 3D printed parts are not as reliable as traditional manufactured parts because of its poor interlayer adhesion. The fact that the materials need to be melt processed during printing make it difficult to use crosslinked polymers directly for 3D printing. This presentation will discuss novel polymers for 3D printing, which, by employing reversible Diels-Alder reactions between polymer chains, possess improved adhesion between interlayers but also allow for melt processing.
785 - Curing behavior and structural characterization of functionalized polysiloxanes blended with diglycidyl ether of bisphenol-A

Wenjun Gan¹, wjgan@sues.edu.cn, Weizhen Li¹, Qiangi Zhang¹, Xiaodan Gu², Chenhui Zhu², Cheng Wang². (1) College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, SHANGHAI, China, (2) Advanced Light Source, Lawrence Berkeley National Lab, Berkeley, California 94720, United States

Functionalized polysiloxanes were used as modifier and blended with a commercial epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) at various ratios. The co-curing behaviors were studied by differential scanning calorimetry (DSC) and curing kinetic parameters were calculated by Kissinger and Ozawa methods. Their morphology, the thermal and surface characteristic of the cured blends were investigated by means of scanning electron microscopy (SEM), small-angle and wide-angle X-ray scattering (SAXS and WAXS), thermogravimetric analysis (TGA) and contact angle measurements.
New low band gap polymers P1, P2, P3 and P4 containing thieno[2',3':5,6']pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (TPTI) and fluorenedicyclopentathiophene dimalononitrile (FDCPT-CN) units were synthesized and tested for their kinetic and two-photon absorption capabilities and their performance were compared with that of PTB7 which has been shown to offer excellent solar cell efficiency.

P3 and P4 showed broad absorption, though negligible, into the near-IR region. P1 and P2 showed good absorption in the visible region up to 700 nm. The polymers had good low-lying HOMO with the HOMO-LUMO gap of P3 and P4, being lower than that of PTB7. Fluorescence emission studies on the polymers showed long-lived excited states of 1.6 and 2.4 ns for P1 and P2 respectively while P3 and P4 showed very fast decay within 353 fs and 120 fs.

Two-photon absorption investigation of the polymers showed that the absorption cross section may be in the region of 4500 – 20000 GM per conjugating unit and this shows the promise they hold as possible two-photon absorbing and photovoltaic materials.
787 - Improving the thermal properties of highly tactic semi-crystalline aliphatic polyesters

Julie Longo, jul.longo@gmail.com, Geoff Coates. Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14850, United States

Polyesters are promising alternatives to polyolefins because of their biodegradability, biocompatibility and functional diversity. Of the methods used for polyester synthesis, the ring-opening alternating copolymerization of cyclic anhydrides and epoxides combines wide substrate scope with the control of microstructure afforded by chain-growth polymerization. In this lecture, a method for synthesizing highly tactic polyesters with improved properties will be presented.
788 - Robust and dynamic polymer membranes for anion transport

Andrew Herring¹, Daniel Knauss², Matthew Liberatore¹, E. Bryan Coughlin³, Coughlin@mail.pse.umass.edu. (1) Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, United States, (2) Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States, (3) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States

The ability of anion exchange membrane (AEM) fuel cells to provide inexpensive compact power from a wider variety of fuels than is possible with a proton exchange membrane (PEM) fuel cell, has continued to drive research interest in this area. Alkaline catalysis in fuel cells has been demonstrated with non-precious metal catalysts, and with a variety of fuels beyond hydrogen and methanol. Alkaline fuel cells (AFCs) based on aqueous solutions of KOH, have serious drawbacks associated with system complexity and carbonate formation. Anion exchange membrane (AEMs) fuel cells have a number of advantages over both PEM fuel cells and traditional AFCs. However, ionic conductivity in AEMs is still lower than ionic conductivity in PEMs, and the chemical stability of membrane attached cations in hydroxide solutions is still not sufficient for practical applications. The goal is to synthesize an AEM with excellent anion transport properties that can be fabricated into a thin robust film suitable for fuel cell applications. To achieve this goal we have started with polymer architectures based on homo- and co-polymers of vinylbenzyltrimethylammonium, PVBTMA, as these are readily synthesized as either ordered diblock or random copolymers. We fully characterize these materials using a variety of techniques to probe anion transport. Of course, while the BTMA cation is stable enough for study in the hydroxide form, it may not have adequate stability for use in practical fuel cells and so other efforts are dedicated to the discovery of novel cations that will have adequate stability. The processing of these compositions into uniform large area thin sheets is also being investigated to understand the conditions required for a particular AEM to be generated as a fuel cell ready membrane.
789 - Anisotropic ion transport in solid polymer electrolytes

Derrick Smith, dms348@drexel.edu, Shan Cheng, Shijun Wang, Brittany Gallagher, Christopher Li. Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, United States

Polymer electrolyte membranes (PEMs) with high ionic conductivity are important for energy-related applications, such as solid state batteries and fuel cells. In order to achieve improved performance and longevity of the device, mechanical properties of the membrane must be promoted to the highest critical factor without sacrificing its ion conductivity, particularly in solid-state lithium ion batteries. In this talk, I will discuss our two new approaches of guiding ion transport in PEMs. The first one is to use holographic photopolymerization to fabricate long-range, defect-free, ordered PEMs with tunable ion conducting pathways. We introduce the name holographic PEM (hPEM) for these unique membranes. By incorporating polymer electrolytes into the carefully selected HP system, electrolyte layers/ion channels with length scales of a few tens of nanometers to micrometers can be formed. The second approach involves re-examining the effect of crystalline lamellae on PEM ion conductivity. By controlling the polymer crystal orientation, we discovered that crystal lamellae can guide ion transport. We believe this finding can lead to new design strategies for manufacturing next generation PEMs.

Thursday, August 14, 2014 02:00 PM
Transport in Polymer Membranes (01:30 PM - 03:05 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 8
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. The key supramolecular unit for these novel materials is based on terpyridine-metal cation complexes. These novel polymer cations have been fabricated into membranes and characterized for their transport of various anions including hydroxide, bicarbonate, and chloride. Their conductivity for hydroxide is 29 mS/cm at 30 °C. Their hydration numbers have also been characterized.
Anion-exchange membranes are used in a variety of energy and separations applications that need to operate under neutral, basic or acidic conditions. In artificial photosynthesis devices, these materials can serve as scaffolds for the light absorbing/catalytic components, which maintain a barrier between the oxidation and reduction sites and thereby separate the generated fuel from oxidation products. In addition, these membranes have to conduct ions efficiently, remain insoluble in the electrolyte and be impermeable to various gases (H₂, O₂).

Block copolymers are good candidates for this purpose because of their ability to self-assemble into ordered bi-continuous phases, wherein one phase imparts mechanical stability to the system, while the other phase allows for the conduction of ions. A range of novel phosphonium-based diblock copolymers were synthesized by reversible addition fragmentation chain transfer polymerization. The relationship between water uptake and anion conductivity of the ion-containing block copolymers is investigated as a function of molecular weight.
792 - Siloxane and biosiloxane bonds

Stephen J Clarson, stephen.clarson@uc.edu, Mechanical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio 45221, United States

The siloxane bond occurs in a wide variety of environments that are in engineering materials systems and in biological materials systems. Given that silicon (Si) and oxygen (O) make up approximately 74% of the Earth's crust, one can make the argument that siloxane bonds are the most "sustainable" chemical links available to mankind. In this oral presentation we shall discuss how siloxane bonds are transformed into biosiloxane bonds (and vice versa). Some aspects of the geobio cycle of "silicon" and its compounds will also be addressed.

Thursday, August 14, 2014 01:30 PM
Green Polymer Chemistry: Biobased Materials and Biocatalysis (01:30 PM - 04:20 PM)
Location: Hilton San Francisco Union Square
Room: Continental Parlor 9
In this work we investigated the kinetics of the transesterification of divinyl adipate (DVA) with tetaethylene glycol (TEG) using *Candida antarctica* lipase B (CALB) as a biocatalyst at 50 °C under solventless conditions. We examined the time-dependence of the reactions with various DVA/TEG ratios. Samples were taken at the specified times, and then the composition and end group structures were analyzed by MALDI-ToF. We found conditions under which polycondensation was minimized and symmetric and asymmetric telechelic TEGs were obtained. Specifically, at DVA/TEG 20/1 molar ratio 82% of the product was Vinyl-TEG-Vinyl after 30 minutes. HO-TEG-Vinyl was maximized at 70% at TEG/DVA 1.5/1 molar ratio at 10 minutes reaction time.
One of our patented formaldehyde-free wood adhesives (a combination of soy flour and a petrochemical-based curing agent) has been commercialized for replacement of carcinogenic urea-formaldehyde resins in the production of plywood since 2004. We have recently developed and commercialized a second generation of formaldehyde-free novel adhesive that is a blend of defatted soy flour and a natural mineral. Both materials are GRAS (generally recognized as safe) materials by the US Food and Drug Administration, and are very abundant, inexpensive, and readily available. This adhesive is solely based on natural materials, i.e., does not contain any petrochemicals and petrochemical-based products. The adhesive is environmentally safe, is cost-competitive to all wood adhesives and is superior to the urea-formaldehyde resins in terms of strengths and water resistance of plywood. In this presentation, we will discuss how the blend of the natural materials can serve as a strong and water-resistant adhesive for bonding wood. The presentation will focus on interactions between the mineral and different components of soy flour that are responsible for the superior bonding. The adhesion mechanism will be proposed and discussed in detail.

Yonghwan Jang, yonghwan.jang@oregonstate.edu, Kaichang Li. Wood Science and Engineering, Oregon State University, Corvallis, OR 97331, United States
This contribution gives an overview of our recent work with the application of controlled free radical polymerization chemistries to produce hyper-branched thermoplastic elastomers from triglycerides. Atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT) both use the free radical propagation mechanism to produce homopolymers, statistical copolymers, and block copolymers with tailored architectures. This is made possible — through two very different chemical mechanisms — by the limitation of the free radical concentration to the picomolar range. We have tailored these two chemistries to copolymerize multifunctional acrylated epoxidized triglycerides (from various vegetable oils) into either statistical or block architectures with styrene as the hard segment to form economical thermoplastic elastomers up to 750 kDa in molar mass. In this talk we will explore the role of the number of functional groups per triglyceride molecule and the resultant properties in both homopolymer and block copolymer chain architectures.
Styrenic block copolymers (BCPs) commonly are employed as commercial thermoplastic elastomers, pressure-sensitive adhesives, and blend compatibilizers. However, styrene is a nonrenewable, carcinogenic, and volatile organic compound, so developing green and inexpensive alternatives to styrene is desirable. Pyrolysis of lignin, a renewable waste stream from pulp and paper manufacturing, yields a suite of phenolic lignin model compounds (LMCs), which are attractive alternatives to styrene due to their abundance, relatively low toxicity, and aromaticity. We have taken LMCs, such as vanillin, and incorporated their methacrylate derivatives into controlled reversible addition–fragmentation chain-transfer (RAFT) polymerizations for BCP syntheses. The polymers containing vanillin methacrylate units have an aldehyde functionality that offers a unique handle for post-polymerization property adjustment. This work highlights both the facile method toward BCP syntheses from LMCs and select property manipulations enabled by vanillin’s aldehyde. Eventually, this work will segue into the de novo design and generation of libraries of renewable polymers with on-demand properties.
Highly porous activated carbon fibers (ACFs) were prepared via simultaneous carbonization and alkali hydroxide activation of fibers electrospun from aqueous alkali lignin (low sulfonate) solutions. The ACFs were >96 wt% carbon and had surface area and pore volume as high as 1400 m$^2$/g and 0.9 cm$^3$/g, respectively. The ACFs were sulfonated by reacting with concentrated sulfuric acid to yield high amount of acid sites and only slightly decreased porosity. The sulfonated ACFs were used as solid acid catalysts to hydrolyze the pure cellulose isolated from rice straw under hydrothermal conditions. The effects of cellulose crystallinity, catalysts to celluloses ratio, and the hydrolysis conditions on the yields and compositions of products including nanocellulose and sugars will be presented.
Worldwide capacity and consumption of polyamides are growing, and a new class of polyamides with a sustainable plasticizer solution is of interest to industry in order to develop low-cost alternative products with properties matching that of expensive long-chain polyamides used in automotive applications. Bio-PDO(TM) has been successfully used as a precursor to many commodity products. We have discovered that Bio-PDO(TM) based oligomers (polypropanediol) and their benzoate derivatives are promising candidates for nylon polymers. These plasticizers successfully reduce the flex modulus of nylon, while maintaining compatibility with the polymer.

In this work, we explore a high-throughput virtual approach towards screening new plasticizers for polyamides that employs condensed-phase molecular dynamics. According to theory, plasticizers interfere with intermolecular bonding between polymer chains. Within the simulations, we use a radial distribution function to quantify the degree of hydrogen bonding between the plasticizer and polymer, and correlate it to the reduction in flex modulus. Hildebrand and Hansen solubility parameters are obtained from the simulations to ensure that plasticizer and polymer are compatible. We focused on the two extremes of the nylon property scale, hydrophilic rigid nylon 6 and hydrophobic nylon 12, in order to propose a plasticizer with broad applicability to polyamides.

We predict that poly(1,3-propanediol) is effective at reducing the flex modulus in nylon 6, but not as effective as the incumbent N-butylbenzenesulphonamide in nylon 12. The large difference in polar-electrostatics between nylon 12 and poly(1,3-propanediol) further limits its performance; the use of the polypropanediol benzoate ester increases polymer compatibility, but at the expense of reducing the flex modulus. The virtual screening approach is found to be effective, and provides physical insight into dynamic polymer properties.
An electrochemical biosensor for the enzymatic sensing of glucose was constructed from poly(ferrocenylsilane) (PFS) polycations and glucose oxidase (GOx). PFS polycations and the negatively charged GOx were deposited layer–by–layer on an electrode surface, making use of electrostatic interactions between these components. In the resulting layer–by–layer structures, the PFS chains served as redox mediator and GOx as biorecognition element. Multilayer fabrication, including the exploration of crosslinking methods to enhance the stability of these multilayers, and sensing characteristics of the layers will be discussed.
The Verani group is interested in the use of metallosurfactants for applications in molecular electronics. This interest arises from the notable behavior of earth-abundant transition metal complexes on molecular wires, transistors and logic gates. Our preferred method for surface deposition of the metallosurfactants is Langmuir-Blodgett physisorption as to minimize the viability of Schottky barriers. In this symposium we will focus on current efforts to understand the mechanisms of rectification—as characterized by an asymmetric I/V curve associated with unidirectional current transport—on (i) iron(III) and manganese(III) complexes with an asymmetric \([\text{N}_2\text{O}_3]\) phenolate-rich ligand and (ii) iron(III) and copper(II) complexes coordinated to saloph (salicylphenylenediimine) ligands. In both cases the metallosurfactants containing a \(3d^{5}\text{HSFe(III)}\) ion display rectifying behavior whereas the species with \(3d^{4}\text{HSMn(III)}\) and \(3d^{9}\text{Cu(II)}\) do not show such behavior. Based on experimental redox potentials, the Fe(III) systems seem to have the metal-centered SOMOs (singly-occupied MOs) matching the Fermi level energies of the Au electrodes, thus suggesting that rectification proceeds via an asymmetric molecular mechanism.

Funding NSF-CHE 1012413
Sequential infiltration synthesis (SIS) has been recently demonstrated to increase the etch resistance of optical, e-beam, and block copolymer lithography resists for sub-50 nm pattern transfer. Although SIS can dramatically enhance pattern transfer relevant to device applications, the complex processes involved in SIS are still not clearly understood. Fundamental knowledge of the underlying chemistry of SIS is necessary to ensure a high degree of perfection in large-scale lithography. To this end, we performed in situ Fourier transform infrared (FTIR) spectroscopic measurements during the SIS of Al₂O₃ using trimethylaluminum (TMA) and H₂O into poly(methyl methacrylate) (PMMA). The FTIR results show that TMA forms an unstable complex with the PMMA, rather than a permanent, covalent bond as previously reported.

As a consequence, the TMA can desorb slowly with time, and the detailed history of the TMA exposure becomes critical to the outcome. This better understanding of the SIS reaction dynamics should improve reliability in SIS lithography as well as other SIS applications.
802 - PTA (3,5,7-triaza-phosphaadamantane): An excellent ligand for the synthesis of water soluble organo-heterometallic polymeric complexes

Antonio Romerosa, romerosa@ual.es, Franco Scalambra, Manuel Serrano-Ruiz. Department of Chemistry and Physics-CIESOL-Section of Inorganic Chemistry, University of Almeria, Almeria, Almeria 04120, Spain

Water is the global solvent, being also an excellent solvent for stoichiometric and catalytic chemical synthesis. For this reason we are interested in the synthesis of organometallic complexes soluble in water. As a consequence of our research activity in this area we obtained the first example of a water-soluble air-stable heterometallic-polymeric complex \( [(\text{PTA}_2\text{CpRuDMSO})\mu-\text{AgCl}_2]_n \) [1] constituted by organometallic-metal-complex moieties. Some year later, we also presented the second example of an air stable hetero-poly-metallic polymer, the \( \{[(\text{PTA}_2\text{CpRu}−\mu-\text{CN}−\text{RuCp(PTA)}_2\mu-\text{Au(CN)}_4]\}_n \) [2]. These new complexes display novel properties never found for organometallic complexes such as gel behavior in water. In the last years other research teams have presented new examples of polymers containing the ligand PTA [3] some of them with interesting properties such as catalytic and bactericide activity. We have extended the synthesis of this kind of backbone-organometallic-polymers to the new polymer complexes \( \{[(\text{PTA}_2\text{CpRu}−\mu-\text{CN}−\text{RuCp(PTA)}_2\mu-\text{MCl}_3]\}_n(M=\text{transition metals}) \). Most of the new polymers are water-soluble and display catalytic, biological, optical and gel properties in water.

Crystal Structure of \( \{[(\text{PTA}_2\text{CpRu}−\text{CN}−\text{RuCp(PTA)}_2\mu-\text{CdCl}_3]\}_n \)

Dendrimers are highly branched organic macromolecules with successive layers or “generations” of branch units surrounding a central core. Organic inorganic hybrid versions have also been produced, by trapping metal ions or metal clusters within the voids of the dendrimers. Their unusual, tree-like topology endows these nanometre-sized macromolecules with a gradient in branch density from the interior to the exterior, which can be exploited to direct the transfer of charge and energy from the dendrimer periphery to its core.

Here we show that tin ions, Sn^{2+}, complex to the imines groups of a spherical polyphenylazomethine dendrimer in a stepwise fashion according to an electron gradient, with complexation in a more peripheral generation proceeding only after complexation in generations closer to the core has been completed. By attaching an electron-withdrawing group to the dendrimer core, we are able to change the complexation pattern, so that the core imines are complexed last. By further extending this strategy, it should be possible to control the number and location of metal ions incorporated into dendrimer structures, which might and uses as tailored catalysts, building blocks, or fine-controlled clusters for advanced materials.
Cyclic, catenated, and knotty polymers have fascinated not only mathematicians and topologists but synthetic chemists alike due to their controlled entanglement and predictable topological structures. However, their synthesis remains a challenge with the limitations of cyclization chemistry and the entropic and enthalpic limited chemistry of reactive end-group chemistry. It is possible to use ring opening polymerization (ROP) and ring expansion polymerization (REP) to an advantage in synthesizing new polymer compositions including block copolymers. While monocyclic systems are accessible through this route, catenated polymers are mostly made possible through controlled associations and most effectively with metal-ligand interactions. This talk will emphasize the use of organometallic supramolecularly assembled complexes to access homopolymer and copolymer catenated polymer compositions. This is done in combination with living polymerization methods with ATRP, RAFT, or polycaprolactones. A more challenging aspect is the demonstration of knotty polymer systems through the use of controlled complex dimetallic and supramolecularly assembled macroinitiators. Control with this route will enable a sure path towards high yield synthesis of mathematically interesting knotted polymer systems.
805 - Arene-cyclopentadienyliron complexes in the design of coordination and organometallic macromolecules

Alaa S Abd-El-Aziz, abdelaziz@upei.ca, Jessica L Pilfold, Inan Kucukkaya, Christian Agatemor, Brian D Wagner, Nola Etkin, Rabin Bissessur. Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island C1A 4P3, Canada

This presentation is focused on the design of a number of classes of coordination and organometallic polymers and dendrimers utilizing arene-cyclopentadienyliron complexes.

Reactions of substituted arene complexes containing terminal carboxylic groups with hexanediolterpyridine led to the formation of the precursors of monomers that were then polymerized to give novel coordination polymers with 4′-substituted functionalized terpyridyls in the backbone and pendent cyclopentadienyliron moieties.

Synthesis and spectroscopic properties of novel porphyrin and metalloporphyrin dendrimers, also containing cationic arene-cyclopentadienyliron complexes, and functionalized with naphthalene and/or capped with ferrocene, will also be described. Divergent approaches were employed to give highly symmetrical branched dendritic materials. The incorporation of these cationic complexes into both the polymeric and dendritic materials resulted in enhanced solubility and ease of synthesis. The divergent synthetic methodology was also used to prepare a new family of organometallic dendrimers that features a pentaerythritol core, redox-active $\eta^5$-aryl-$\eta^5$-cyclopentadienyliron complexes' inner frameworks, and peripheral naphthyl fluorophores. Synthesis, spectroscopic and electrochemical studies of the new materials will be presented.
Poly(ionic liquid)s (PILs), also called polymerized ionic liquids, refer to a subset of polyelectrolytes which feature an ionic liquid (IL) species in each monomer repeating unit, connected through a polymeric backbone to form a macromolecular architecture. In the past few years PILs as an emerging interdisciplinary topic have attracted rapidly expanding interest and take an enabling role in the fields of polymer chemistry and material science. Generally PILs combine some unique properties of ionic liquids with the flexibility and processability of macromolecular architectures. This further broadens the function and application spectrum of ILs and traditional polyelectrolytes in the fields of separation and gas sorption, analytic chemistry, catalysis, sensing, etc.

In this lecture, I will talk about the different types of interactions of metal species with PILs, such as anion exchange, complexation and nanoparticle formation.[1-3] Their function as catalyst will be detailed in the lecture. It will be shown that the catalytic function of metal species and the unique physical properties of PILs are seamlessly combined in catalytic applications.

![Image](image.png)

**Figure 1.** Left: Preparation of PS-PIL-Pt nanocomposite brush particles. Right: The apparent rate constant $k_{app}$ as a function of NaBr salt concentration measured in the presence of PS-PIL-Au composite particles. $T = 20^\circ$C; $[4$-nitrophenol$] = 0.1$ mM, $[\text{NaBH}_4] = 10$ mM.

**Reference**


807 - Influence of molecular connectivity and nearest neighbor interactions on the charge transport properties of porphyrin assemblies on Au surfaces

James Batteas¹, batteas@chem.tamu.edu, Alison Pawlicki¹, Bradley Ewers¹, Charles Drain². (1) Department of Chemistry, Texas A&M University, College Station, Texas 77845, United States, (2) Department of Chemistry and Biochemistry, Hunter College of CUNY, New York, NY 10021, United States

The transport properties of a series of free-base and zinc coordinated tri-pyridyl and tri-phenyl porphyrin thiols inserted into a dodecanethiol matrix on Au(111) were investigated using scanning tunneling microscopy (STM). For single molecules, the tunneling efficiency and I-V behaviour was found to be dominated by tunneling through the hydrocarbon tether used to bind the molecules to the surface. However, when the porphyrin thiols were driven to aggregate into islands on the surface (e.g. through pi-stacking), distinct changes in their charge transport were observed, suggesting that molecular aggregation results in sufficiently reduced charge confinement energy to facilitate a transition from a purely tunneling mechanism to a charge-hopping mechanism. These results illustrate the impact of molecular aggregation and nearest neighbor interactions on charge transport of molecular assemblies, and demonstrate the effectiveness of using such aggregates to achieve single-electron transport characteristics from relatively simple, tunable subunits.
808 - WITHDRAWN
### Sci-Mix - EVE Session

**Location:** Moscone Center, North Bldg.

**Room:** Hall D

**Organizers:** Malika Jeffries-El, Scott Iacono, Dylan Boday

**Duration:** 8:00 pm - 10:00 pm

<table>
<thead>
<tr>
<th>Pub #</th>
<th>Presentation Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>159</td>
<td>Synthesis and applications of metal organic framework nanopillars&lt;br&gt;Arben Kojtari, Jacob Babinec, Dominique Gnatowski, Wenli Ruan, Chris Shindler, Hai-Feng Ji.</td>
</tr>
<tr>
<td>323</td>
<td>Synthesis of DNA block copolymers using AGET ATRP&lt;br&gt;Saadah Averick, Sourav K Dey, Subha R Das, Krzysztof Matyjaszewski.</td>
</tr>
<tr>
<td>348</td>
<td>Quantum dots-glycopolymer conjugates (QD-GPs): An imaging tool for the study of polysaccharide-cell interactions&lt;br&gt;Chongyu Zhu, Muxiu Li, Qiang Zhang, David M Haddleton.</td>
</tr>
<tr>
<td>368</td>
<td>Protein-reactive RAFT agents for the design of polymer-protein conjugates&lt;br&gt;Nane Vanparijs, Benoit Louage, Samarendra Maji, Qilu Zhang, Lenny Voorhaar, Richard Hoogenboom, Bruno De Geest.</td>
</tr>
<tr>
<td>384</td>
<td>Poly(lactide)-based block copolymers as biofunctional scaffolds for bone tissue engineering applications&lt;br&gt;Patrizia P Smith, Melissa K Tran, Stephen G Boyes, Sven O Streubel, Brook K McConnell.</td>
</tr>
<tr>
<td>397</td>
<td>Synthesis of antimicrobial latexes&lt;br&gt;Ramiro Guerrero-Santos, Roberto Yañez, Jaime Gonzalez Villa, Antonio S. Ledezma Perez, Jorge Romero-Garcia.</td>
</tr>
<tr>
<td>407</td>
<td>Synthesis and properties of mixed bimodal brush grafted nanoparticles&lt;br&gt;Tony Neely, Brian Benicewicz, Ying Li, Linda Schadler.</td>
</tr>
<tr>
<td>411</td>
<td>Controlling sequence in step-growth polymerizations: Role of sequence on rheological and thermal properties of segmented polyesters&lt;br&gt;Joseph M. Dennis, Ashley M. Nelson, Musan Zhang, Daniel J. Buckwalter, Timothy E. Long.</td>
</tr>
<tr>
<td>417</td>
<td>Ruthenium catalyzed synthesis of functionalized polypentenamers&lt;br&gt;Robert Tuba, Robert H. Grubbs.</td>
</tr>
<tr>
<td>422</td>
<td>Photoreleasable thiol chemistry for nanogel preparation&lt;br&gt;Longyu Li, Priyaa Prasad, Sankaran Thayumanavan.</td>
</tr>
<tr>
<td>429</td>
<td>High temperature gel permeation chromatography using dual flow refractive index detection&lt;br&gt;Amandaa K. Brewer</td>
</tr>
<tr>
<td>445</td>
<td>Spatial control over polymer brush grafting density using visible light&lt;br&gt;Benjaporn Narupai, Anna Melker, Justin E. Poelma, Brett P. Fors, Craig J. Hawker.</td>
</tr>
<tr>
<td>451</td>
<td>Azeotrope enabled polymerization of ethylene oxide&lt;br&gt;Jennifer L. Bento, Chetan C Hire, Douglas H Adamson.</td>
</tr>
<tr>
<td>484</td>
<td>Novel family of biobased polysorholipids used as scaffolds for tissue engineering&lt;br&gt;Yifeng Peng, Dany Munoz Pinto, Mariah Hahn, Richard Gross.</td>
</tr>
<tr>
<td>494</td>
<td>Ligand effects on metal catalysts for copolymerization of epoxides and CO2&lt;br&gt;Masato Mizutani, Geoffrey W Coates.</td>
</tr>
<tr>
<td>496</td>
<td>Electrospun biomimetic synthetic polymer for templated ceramic condensation&lt;br&gt;Garrett M. Kraft, Ashley Santiago, Chetan C. Hire, Douglas H. Adamson.</td>
</tr>
<tr>
<td>541</td>
<td>Lathanide-containing biomaterials and solution assemblies&lt;br&gt;Gina L Fiore, David Thevenaz.</td>
</tr>
<tr>
<td>542</td>
<td>Photoactive metallolpolymers with light-harvesting dyes&lt;br&gt;Martin D. Hager, Alexander M. Breul, Bobby Happ, Andreas Winter, Ulrich S. Schubert.</td>
</tr>
<tr>
<td>546</td>
<td>UV-induced self-assembly of amphiphilic polyoxazolines</td>
</tr>
</tbody>
</table>
Laetitia Korchia, Vincent Lapinte, Cécile Bouilhac, Jean Jacques Robin.

563 On bead combinatorial DOTA modifications for molecular imaging tool development

Jaspal Singh, Roberta Napolitano, Todd Soesbe, Dean Sherry, Gomika Udugamasooriya.

565 Thermal and mechanical analysis of anthracene-filled epoxy nanocomposites

Jamie M Messman, Sabrina M Wells, Somnath Sarkar, Daniel E Bowen, Theresa Morris.

571 Stability towards γ-radiation of nanoscale enrichment polymer layers

Nikolay Borodinov, James Giammarco, Neil Patel, Igor Luzinov.

572 Modeling of spatially dependent oxidative degradation

Adam Quintana, Nicholas Giron, Mathew Celina.

573 Phosphorous-filled nanobrick wall multilayer thin film eliminates polyurethane melt dripping and reduces heat release associated with fire

Tyler Guin, Amanda Cain, Craig Nolen, Yu-Chin Li, Rick Davis, Jaime Grunlan.

575 Grafting multi-block copolymers by "click" chemistry for overcoming the membrane permeability/selectivity trade-off: Application to butanol biofuel recovery from dilute aqueous solution

Vijay Kumar, Carole Arnal-Herault, Miao Wang, Jérôme Babin, Anne Jonquières.

580 Morphological characterization of (PS-PIB)_2-s-PAA_x miktoarm star polymers

Katrina M Knauer, Yaling Zhu, Robson F Storey, Sarah E Morgan.
Workshops and POLY Sponsored Meetings

Workshop Committee Reports

Complete details on upcoming POLY Workshops

For Technical Workshop Information and Registration, contact Leslie Linkous

Submit a proposal for a workshop

POLY Sponsored and Co-Sponsored Meetings

For Technical Program Information and Registration, contact: the organizers of the specific meeting

May 20, 2014 - Materials Science and Engineering Division Centennial Celebration

- Gaithersburg, MD.
- Contact: http://www.nist.gov/mmi/msed/msed-centennial.cfm

2014 11th National Graduate Research Polymer Conference

- Louisiana State University, Baton Rouge, LA,
- June 1-4, 2014
- Organizers: John A. Pojman, Donghui Zhang, Kerry Dooley

Polycondensation 2014

- September 8 - 11, 2014
- Tokyo, Japan

Macromex 14

- December 3-6, 2014
- Paradise Village Resort Nuevo Vallarta, Nayarit, Mexico
- US Chairs: Advincula, Matyjaszewski, Wynne,
- Mexico Chairs: Rodriguez-Fernandez, Gaytan, Saldivar-Guerra, Martinez-Richa

Pacific Polymer Conference 14-“PPC-14”

- December 9-13, 2015, Grand Hyatt Kauai Resort and Spa, Kauai, HI
- Chair: Krzysztof Matyjaszewski, Carnegie Mellon University
- Organizing Committee:
  Roberto Advincula (Case Western Reserve University)
  H. N. Cheng (USDA)
  William H. Daly (Louisiana State University)
  Robert B. Moore (Virginia Tech)
  Kenneth Wynne (VCU)
  Peter Zarras (US Navy)
  Greg Tew (UMASS)
  Tim Lodge (UMINN)

Recently past meetings

The Southwest Regional Meeting of the American Chemical Society 2012
IUPAC World Polymer Congress 2012