X International Symposium on Stimuli-Responsive Materials

October 26-28, 2014
Santa Rosa, California
USA

2015 SYMPOSIUM DATE
OCTOBER 25-27, 2015
Welcome to Sonoma!

On behalf of all scientists, researchers, and scholars whose research and scholarly efforts focus on the development of a new generation of materials with stimuli-responsive attributes, we welcome you to the 2014 International Symposium on Stimuli-Responsive Materials. This week marks the 10th anniversary of this event that has become a benchmark in the field and continues to offer many diverse scientific contributions from around the world. The success of this event is possible only through the outstanding research contributions from leaders in this field, graduate students, post-doctoral research associates, and other researchers. In the enjoyable settings of Sonoma Wine Country, the symposium has developed into one of the best annual opportunities for academic, industrial, and government researchers to discuss the most recent advances in the areas of responsive and adaptive materials. Presentation themes range from smart materials, polymer synthesis, responsive biological materials, biomimicry, engineering of shape-adaptive objects, nanomaterials design, and theoretical predictions/simulations. We hope that this event will be as professionally fruitful and personally rewarding as the past symposia. We sincerely thank the Royal Society of Chemistry for partial support of this event.

Marek W. Urban and Brent S. Sumerlin
Symposium Co-Chairs

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SUNDAY, OCTOBER 26, 2014

3:00 – 7:30  REGISTRATION; Hilton Sonoma Lobby

4:00 – 4:10  Introductory Remarks; M.W. Urban, B.S. Sumerlin

OPENING SESSION

4:10 - 4:40  SELF-ASSEMBLY OF NANOCONJUGATES AT CELL SURFACE INDUCES APOPTOSIS; JINDŘICH KOPEČEK, UNIVERSITY OF UTAH, USA.

4:40 - 5:10  CHEMICAL POTENTIAL GRADIENTS FOR ACCELERATED MOLECULAR TRANSPORT; HENRY HESS, COLUMBIA UNIVERSITY, USA.

5:10 - 5:40  BLOCK POLYMER NANOSTRUCTURES IN IONIC LIQUIDS: STIMULI RESPONSIVE AND FUNCTIONAL MATERIALS; TIMOTHY P. LODGE, UNIVERSITY OF MINNESOTA, USA.

5:40 - 6:10  DESIGN AND APPLICATIONS OF STIMULI RESPONSIVE BIOLOGICALLY INSPIRED POLYPHENOL COATINGS; PHILLIP MESSERSMITH, UNIVERSITY OF CALIFORNIA, BERKLEY, USA.

6:10-8:30  WINE SOCIAL
MONDAY, OCTOBER 27, 2014

AM SESSION: BIOMATERIALS AND CELLULAR RESPONSES
Session Chair: Jon Pokorski, Case Western Reserve University

8:30 – 9:00 UTILIZING THE UNEXPECTED - POLYMERS WHICH EXPLOIT CELLULAR RESPONSES; CAMERON ALEXANDER, UNIVERSITY OF NOTTINGHAM, UK.

9:00 – 9:30 MANIPULATING SOLUTION-ASSEMBLED COPOLYMER NANO-STRUCTURES THROUGH CHEMISTRY AND PROCESSING: NUCLEIC ACID DELIVERY AND MICELLE STABILITY; THOMAS EPPS, UNIVERSITY OF DELAWARE, USA.

9:30 – 10:00 SMART NANOSTRUCTURED SURFACES AS POWERFUL TOOLS FOR BIOMEDICAL APPLICATIONS; PAULA MENDES, UNIVERSITY OF BIRMINGHAM, UK.

10:00 – 10:30 DISEASE-ASSOCIATED BIOMOLECULES AS STIMULI FOR RESPONSIVE NANOMATERIALS; NATHAN GIANNESCHI, UNIVERSITY OF CALIFORNIA, SAN DIEGO, USA.

10:30 – 10:45 COFFEE BREAK

AM SESSION: RESPONSIVE NANOMATERIALS
Chair: Cyrille Boyer, University of New South Wales, Australia

10:45 – 11:15 RESPONSIVENESS OF POLYPEPTIDE-BASED STAR AND TRIBLOCK COPOLYMERS: FROM BOTTOM-UP DESIGN TO FUNCTION; DANIEL SAVIN, UNIVERSITY OF SOUTHERN MISSISSIPPI, USA.

11:15 – 11:45 ANISOTROPIC ADAPTIVE MATERIALS: DIGITALLY PROGRAMMING COMPLEX SHAPE CHANGE IN LIQUID CRYSTALLINE ELASTOMERS; TAYLOR H. WARE, WRIGHT-PATTERSON AFB, USA.

11:45 – 12:15 BIORESPONSIVE, ULTRASOFT MICROGELS DISPLAYING HIGH DEGREES OF DEFORMABILITY; ASHLEY C. BROWN, GEORGIA TECH., USA.

12:15 - 1:30 LUNCH BUFFET; OPEN AFTERNOON
### TUESDAY, OCTOBER 28, 2013

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3:00 – 3:30  pH-RESPONSIVE POLYMERS FOR DIAGNOSTIC EMERGING APPLICATIONS; STEPHEN G. BOYES, COLORADO SCHOOL OF MINES, USA.

3:30 – 3:50  COFFEE BREAK

3:50 – 4:20  PREPARATION OF SMART STAR BLOCK COPOLYMERS; DIRK KUKLING, UNIVERSITY OF PADERBORN, GERMANY.

4:20 – 4:50  RESPONSIVE NANOCONSTITUENTS - INTERFACIAL BEHAVIOR AND ROBUST MATERIALS SYNTHESIS; TODD EMRICK, UNIVERSITY OF MASSACHUSETTS, AMHERST, USA.

4:50 – 5:20  pH- AND REDOX-RESPONSIVE POLYMERIC NANOPARTICLES FOR SEQUENTIAL DRUG RELEASE, CYRILLE BOYER, THE UNIVERSITY OF NEW SOUTH WALES, AUSTRALIA.

6:00 – 8:00  POSTER SESSION AND WINE SOCIAL

BEST RESEARCH POSTER AWARD PRESENTATION

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ABSTRACTS

10TH INTERNATIONAL SYMPOSIUM ON STIMULI-RESPONSIVE MATERIALS
Symposium Organizers: Marek W. Urban and Brent S. Sumerlin

SUNDAY, OCTOBER 26, 2014

4:10 – 4:40  SELF-ASSEMBLY OF NANOCONJUGATES AT CELL SURFACE INDUCES APOPTOSIS; JINDRICH KOPEČEK, TE-WEI CHU, JIYUAN YANG, RUI ZHANG, AND PAUL SHAMI; DEPARTMENTS OF BIOENGINEERING, PHARMACEUTICS AND PHARMACEUTICAL CHEMISTRY, AND HEMATOLOGY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112, USA.

We designed a new paradigm in macromolecular therapeutics for the treatment of B-cell malignancies, e.g. non-Hodgkin lymphoma (NHL). It is based on the biorecognition of two complementary morpholino oligonucleotides (MORF1, MORF2) at cell surface. CD20 is a non-internalizing surface antigen highly expressed at B-cell surface; its crosslinking can trigger apoptosis. The therapeutic system is composed from two nanoconjugates: (a) anti-CD20 Fab'-MORF1 conjugate; (b) N-(2-hydroxypropyl)-methacrylamide (HPMA) copolymer grafted with multiple copies of MORF2 (P-(MORF2)x). The exposure of CD20+ Raji B cells to Fab'-MORF1 results in the decoration of cell surface with MORF1. Further exposure of decorated cells to P-(MORF2)x instigated MORF1-MORF2 hybridization at cell surface. This biorecognition process induced crosslinking of CD20 antigens and triggered apoptosis of B-cells. When evaluated in a mouse model of human NHL, the drug-free system eradicated cancer cells and produced long-term survivors. MRI, histology, and flow cytometry analysis indicated that no residual tumors were found in the surviving mice. This approach might be also efficient in the treatment of other blood-related malignancies (AML, CLL) as results on patient cells indicate.

The research was supported in part by NIH grant GM95606 (to JK) from the National Institute of General Medical Sciences and the University of Utah Research Foundation.

4:40 - 5:10  CHEMICAL POTENTIAL GRADIENTS FOR ACCELERATED MOLECULAR TRANSPORT; AMIT SITT AND HENRY HESS; DEPARTMENT OF BIOMEDICAL ENGINEERING, COLUMBIA UNIVERSITY, USA.

Advances in nanotechnology enable the construction of nanoscale sensors with high sensitivity as a result of low intrinsic noise. However, due to their small size, diffusion mediated collection in such sensors is extremely slow and requires concentrated samples or long collection times.

Here, we theoretically examine the ability to improve collection efficiency of nanoscale cargo in a sensor by using a chemical potential gradient, which imposes a directional transport by conversion of chemical into mechanical energy. We present a general theoretical framework for describing the transport of chemical species along the gradient, and analyze the effect of the gradient on the diffusion coefficient and drift velocity. The model is applied to
transport on chemically modified surfaces and in hydrogels with built-in chemical potential gradients, and its predictions show good agreement with experimental results obtained by the groups of Prof. Paul Braun (UIUC) and Prof. Joerg Lahann (U Michigan). The model sheds light on the phenomenon of chemical gradient-induced transport and allows the identification of key factors affecting the transport and the collection efficiency. Such understanding is important to many fields beyond sensing, including self-assembly, molecular sorting and surface catalysis, and enables the design of chemical potential gradients for optimal collection efficiency.

5:10 – 5:40

BLOCK POLYMER NANOSTRUCTURES IN IONIC LIQUIDS: STIMULI RESPONSIVE AND FUNCTIONAL MATERIALS; TIMOTHY P. LODGE; DEPARTMENT OF CHEMISTRY AND DEPARTMENT OF CHEMICAL ENGINEERING & MATERIALS SCIENCE, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MN 55455, USA.

Block polymers provide a remarkably versatile platform for achieving desired nanostructures by self-assembly, with lengthscales varying from a few nanometers up to several hundred nanometers. Ionic liquids are an emerging class of solvents with an appealing set of physical attributes. These include negligible vapor pressure, high chemical and thermal stability, tunable solvation properties, high ionic conductivity, and wide electrochemical windows. For various applications it will be necessary to solidify the ionic liquid into particular spatial arrangements, such as membranes or gels, or to partition the ionic liquid in coexisting phases, such as microemulsions and micelles. We have initiated a systematic exploration of ways to achieve this by block copolymer self-assembly. In so doing, a number of fascinating physical phenomena have emerged, which will be highlighted. Examples include the “micelle shuttle”, whereby intact micelles transfer reversibly between an aqueous phase and an ionic liquid as a function of temperature, and doubly responsive micelles, which undergo demicellization and inverse micellization upon heating. Thermoreversible gelation of triblock copolymers provides a simple route to “ion gels” with tunable modulus and ionic conductivity, and photosensitive systems allow for photopatterning and in situ crosslinking. Applications of these gels in plastic electronics and membranes will also be described.

5:40- 6:10

DESIGN AND APPLICATIONS OF STIMULI RESPONSIVE BIOLOGICALLY INSPIRED POLYPHENOL COATINGS; PHILLIP MESSERSMITH, DEPARTMENTS OF BIOENGINEERING AND MATERIALS SCIENCE AND ENGINEERING, UNIVERSITY OF CALIFORNIA AT BERKELEY, BERKELEY, CA, USA.

Polyphenols are found in both plant and animal tissues, where they serve a variety of functions including mechanical adhesion, structural support, pigmentation, radiation protection, and chemical defense. In animals, polyphenols are found in the adhesive proteins secreted by sessile marine organisms. In mussels, the adhesive proteins are known to contain high levels of 3,4-dihydroxy-L-alanine (DOPA), an amino acid that is believed to be important in adhesion to substrates. In plants, polyphenolic compounds containing benzenediol (catechol) and/or benzenetriol (gallol) functional groups are widely distributed secondary metabolites with a variety of biochemical and physical functions. Included among these are anti-inflammatory and anti-oxidant properties. Consumption of foods and beverages rich in polyphenols, such as chocolate, tea and wine, are claimed to be beneficial to one’s health.
Exploiting their natural interfacial adhesion properties, we have engineered a method to form thin adherent polymerized films on substrates immersed in solutions of biological polyphenols. Deposition is facile from an aqueous polyphenol solution onto a variety of solid, porous and nanoparticulate metals, ceramics and polymers. In addition to possessing inherent antibacterial and antioxidant properties, the deposited polyphenol films serve as versatile ‘primers’ facilitating secondary modifications of the primer coating such as metallization and covalent grafting of biomolecules and synthetic polymers. These coated nanoparticles are being exploited for biological targeting and photothermal ablation of bacteria and cancer cells.

6:10-8:30 WINE SOCIAL
Polymers which can change their conformation in response to external stimuli are now widely studied for potential applications in biology, engineering and medicine. However, there is also a growing interest in developing materials which can respond to biological stimuli, or which can exploit biological mechanisms to acquire new properties or change existing behaviour. This talk will include some recent work on polymers which respond to stimuli for applications in drug delivery, sensing and microbiology, and will also consider how prokaryotic and eukaryotic cells can respond in turn. The consequences of the interplay between synthetic and biological responses are not always as they are expected to be.

Figure 1: In MCF 7 cell lines (plates i and ii), thermoresponsive polymers with a transition temperature of 39°C enter cells only above this temperature (red fluorescence visible only in plate ii). However, cell entry is lower for similar polymers in HCT-116 cell lines (iii, iv).

Figure 2: Polymers grown in the presence of two *E coli* strains show different cell binding characteristics, reflecting a templating mechanism by which monomer sequence changes during formation of the polymers at the bacterial cell surface.

References:
Amphiphilic block polymers consist of covalently-bonded hydrophobic and hydrophilic polymer segments. Akin to small molecule amphiphiles, these macromolecules self-assemble into a variety of well-defined structures in aqueous solution such as micelles and vesicles. However, the macromolecular nature of the hydrophobic block can lead to very slow and seemingly nonexistent micelle dynamics. This kinetic entrapment is an attractive advantage of amphiphilic block polymers for therapeutic agent delivery applications; however, it also leads to path-dependent solution assembly and unknown longer-term stability. Consequently, careful optimization of preparation conditions is necessary to produce well-defined, uniform, and reproducible macromolecular solution assemblies. We are interested in two specific areas: (1) exploring the ability to externally control the delivery of nucleic acids to various cellular targets using copolymer nanocontainers, and (2) understanding the effects of common processing conditions and interfacial interactions on the structure, dynamics, and long-term stability of block polymer micelles. In the first area, we are designing cationic diblock copolymers containing PEG and o-nitrobenzyl moieties that facilitate tailorable nucleic acid complexation and light-activated release. Our design unlocks a new approach to advance non-viral gene packaging by overcoming the dual constraints of tight extracellular packaging and facile intracellular decomplexation. In the second area, we are investigating the influence of air-water interfaces (and interfacial regeneration rates) on micelle stability and rearrangement. Our studies reveal that the micelle stability is critically dependent on solution “stirring,” and demonstrate the influence of kinetically-controlled processes (and commonly overlooked mixing protocols) on block polymer micelle dynamics.

Just as biology is offering inspiration and components to nanotechnology, nanotechnology is providing new tools and technology platforms to measure, understand and control biological systems. Whereas important progress on static biological surfaces has been made in the past, much research is now focusing on the development of switchable biological surfaces as it can be tremendously useful in diverse biological and medical applications, including biofouling, chromatography, drug delivery, cell culture and tissue engineering. Albeit there is progress and scientific advances in the field, exciting future developments are ahead of us. One of the major challenges in the field of switchable biological surfaces today is the design of new and more versatile surfaces with tunable non-specific and specific biomolecular interactions. The lecture will highlight recent progress in the preparation of these switchable surfaces and their applications in biological environments. The lecture will also outline the first demonstration of a direct interface of vertically aligned single walled carbon nanotubes (VASWCNTs) with eukaryotic cells. The technology developed provides an alluring platform to enable electrochemical study of an intracellular environment.

We describe a strategy for rendering peptide-based polymeric materials and nanostructures responsive, or resistant to proteolysis by formulating them as high-density brush polymers and particles. The utility of this approach is demonstrated by polymerizing well-established cell-penetrating peptides (CPPs) or substrates for disease-associated proteases, and showing that the resulting materials exhibit unusual properties both in tissues in vivo, and within cellular assays in vitro. We contend that resistant materials offers a plausible method of preparing peptides for in vivo use, where rapid digestion by proteases has traditionally restricted their utility. Similarly, enzyme-responsive materials open doors for the directed assembly of structures within tissues. This second application will be described in terms of their potential in drug delivery, and in guided surgery.
AM SESSION: RESPONSIVE NANOMATERIALS
Chair: Cyrille Boyer, University of New South Wales, Australia

10:45 – 11:15 RESPONSIVENESS OF POLYPEPTIDE-BASED STAR AND TRIBLOCK COPOLYMERS: FROM BOTTOM-UP DESIGN TO FUNCTION; DANIEL SAVIN, UNIVERSITY OF SOUTHERN MISSISSIPPI, USA.

This study involves the bottom-up design and tunability of responsive, peptide-based block copolymers. The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic triblock and star copolymers containing poly(lysine) (PK), poly(leucine) (PL) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. These materials exhibit hydrodynamic size that is responsive to pH, due in part to the helix-coil transition in the peptide chain, but also due to changes in curvature of the assembly at the interface. This talk will present some recent studies in solution morphology transitions that occur in these materials, and how we exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH.

11:15 – 11:45 ANISOTROPIC ADAPTIVE MATERIALS: DIGITALLY PROGRAMMING COMPLEX SHAPE CHANGE IN LIQUID CRYSTALLINE ELASTOMERS; TAYLOR H. WARE, MICHAEL E. MCCONNEY, JEONG JAE WIE, AND VINCENT P. TONDIGLIA, TIMOTHY J. WHITE; WRIGHT-PATTERSON AFB, USA.

Liquid crystalline materials are ubiquitous stimuli-responsive materials that are the basis of the $2B display industry. Here, we report on our recent efforts to explore stimuli-induced mechanical adaptivity in liquid crystalline polymer networks. Previous examinations of these materials have reported dramatic planar shape change exceeding 400% strain. Here, we describe our recent efforts to digitally program the self-assembly of both glassy and elastomeric liquid crystalline polymer networks to yield monolithic, shape-changing structures triggered with both heat and light. Through control of the molecular alignment of the liquid crystalline polymer network, complex three-dimensional shapes can be generated where the direction and type of actuation can be locally controlled.

11:45 – 12:15 BIORESPONSIVE, ULTRASOFT MICROGELS DISPLAYING HIGH DEGREES OF DEFORMABILITY; ASHLEY C. BROWN1 and ANDREW LYON2; 1GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GA, 2CHAPMAN UNIVERSITY, ORANGE, CA, USA.

Microgels are colloidal stable, hydrogel microparticles that have previously been used in a range of biomaterial applications due to their tunable mechanical and chemical properties. Thermo and pH-responsive poly(N-isopropylacrylamide) (pNIPAm) microgels can be fabricated by precipitation polymerization in the presence of the co-monomer acrylic acid (AAc). Traditionally pNIPAm microgels are synthesized in the presence of a crosslinking
agent, such as N,N'-methylene bisacrylamide (BIS), however, microgels can be synthesized under 'cross-linker free' conditions. The resulting particles have extremely low (<0.5%), core-localized, crosslinking resulting from rare chain transfer associated chain branching events. AFM force mapping of these ultralow cross-linked (ULC) particles indicate that they are soft, with a Young’s modulus of ~10kPa. Furthermore, ULC microgels are highly deformable as indicated by a high degree of spreading on glass surfaces and the ability to translocate through nanopores significantly smaller than the hydrodynamic diameter of the particles. The size and charge of ULCs can be easily modulated by altering reaction conditions, such as temperature and monomer/sodium dodecyl sulfate (SDS) concentration, and through the addition of co-monomers. ULC microgels based on the widely utilized, biocompatible polymer polyethylene glycol (PEG) can also be synthesized under cross-linker conditions. Due to their softness and deformability, ULC microgels are a unique base material for development of biomaterials. We have utilized ULCs for thin film fabrication, hemostatic material development, and creation of bioresponsive particles through the coupling of extracellular matrix (ECM) binding motifs.

12:15 - 1:30  LUNCH BUFFET; OPEN AFTERNOON

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http://www.californiawineryadvisor.com/regions/view/Sonoma_County
TUESDAY, OCTOBER 28, 2013

AM SESSION  STIMULI-RESPONSIVE DEVICES
Session Chair:

8:30 – 9:00  NANO-MATERIALS FOR PHOTO-MECHANICAL ACTUATORS;
HONGRUI JIANG, UNIVERSITY OF WISCONSIN, MADISON, USA.

Actuators are critical components for microelectromechanical systems (MEMS). Recent development of materials that can be driven by light and provide photo-mechanical response have caught much attention since they have great potential to form actuators that can be remotely controlled by light. Of these materials, nanocomposites incorporating nanomaterials in polymer matrices are especially promising. In this talk, I will present our work on light-responsive hydrogels and liquid crystal elastomers, utilizing gold nanoparticles, carbon nanotubes and graphene oxide. I will also describe some applications of thus formed actuators in tunable liquid microlenses, endoscopy, and autonomous light tracking.

9:00 – 9:30  NEAR INFRARED DRIVEN POLYMER ACTUATORS; Alex Shen, Jasper Zeng, JENNIFER LU, UNIVERSITY OF CALIFORNIA, MERCED, USA.

Mechanoresponsive polymers hold great technological potential in tissue engineering, drug delivery, ‘smart’ optical systems and microelectromechanical systems, just to name a few. It is highly desirable to have a system that can generate mechanical deformation using the energy sources in the “NIR window” (690–900 nm). The “NIR window” offers many unique advantages that include:
- **Large response**: The deep penetration of low-energy NIR photons can actuate the entire depth of a thicker sample and deliver large mechanical strain;
- Remote actuation with both spatial and temporal control;
- Straightforward miniaturization;
- **Biocompatible**: It offers deeper tissue penetration and less photo-damage.

We are investigating two systems that can generate mechanoresponse based on thermally induced conformational changes. One is the use of dibenzocyclooctadiene (DBCOD), a flexible cyclooctane group connecting two rigid phenyl rings, as a near infrared switch. We have demonstrated that an anomalous giant mechanical contraction, up to -2300 ppm/K can be generated by properly tuning the local physical environment. This finding further validates that the NIR stimulus can induce DBCOD moieties to undergo a thermodynamic transition from the global energy minimum (twist-boat) to a local minimum (chair).

To conformational changes of poly(N-isopropylacrylamide) (PNIPAM) by NIR, few-walled carbon nanotubes (FWCNTs), nanoheaters, have been judiciously incorporated. Only 0.1 wt% FWCNTs will result in roughly 2.5 fold enhanced surface modulus, and more impressively result in fast and reversible mechanoresponse, swelling (NIR off) and de-swelling (NIR on). To impose strain induced force from the conformational change of PNIPAM chains, a bilayer system that comprises a thin top layer for improving cell adhesion that penetrates into the bottom FWCNT doped PNIPAM gel has been designed and fabricated. We have demonstrated that this new system can produce spatially and temporally
controlled mechanical deformation by NIR. Furthermore, mechanical strain imposed by NIR stimulation can be transmitted onto cells and induce cell shape change.

The creation of these NIR mechanoresponsive polymers is expected to enable fundamental investigation, e.g. understanding of mechanical cues in cell growth and differentiation and pave a path for technological innovations, NIR enabled switches and pumps for biological applications.

**9:30 – 10:00**  **FACIALLY SELECTIVE FUNCTIONALIZATION OF GRAPHENE OXIDE; EMILY PENTZER, CASE WESTERN RESERVE UNIVERSITY, USA.**

Two-dimensional platelets have received much recent attention for the preparation of new materials and composites, specifically when assembled at interfaces and dispersed in polymer matrices. For example, smectite-type clay, graphene, graphene oxide, and metal chalcogenides such as molybdenum disulfide (MoS₂) can yield conductive and/or mechanically robust composites with commodity polymers. Tailoring and controlling how platelets interact with each other, as well as the polymer matrix and surfaces can overcome the propensity of these particles to aggregate. Moreover, selective functionalization of the platelets dictates how they interact with each other and interfaces, such as at fluid-fluid and air-fluid. We will report recent work from our group on the covalent modification of two-dimensional platelets, specifically reduced graphene oxide, as well as their selective functionalization for interfacial assembly. The chemistries used for these modifications are robust and scalable, allowing for functionalization with a variety of small molecules and polymers, giving materials of tunable solubility and assembly. This synthetic routes can be used to control the dispersion of platelets, as well as their assembly.

**10:00 – 10:20**  **COFFEE BREAK**

**AM SESSION**  **TAILORING RESPONSIVE BEHAVIOR**

Session Chair:

**10:20 – 10:50**  **RESPONSIVE MAIN CHAIN CONJUGATED POLYMERS; HEIKKI TENHU, UNIVERSITY OF HELSINKI, FINLAND.**

Interesting amphiphilic polymers have been prepared by connecting water-soluble units to conjugated polymers. The polymers may be dispersed or dissolved in water or organic solvents, and in certain cases they show thermo-responsive behavior. Poly(benzimidazobenzophenantroline), BBL, is a fully conjugated ladder-type polymer which can be used a p- and n-type semiconductor. The potential applications of BBL are limited because of its insolubility in most solvents. By binding poly(ethyleneoxide) chains to the carboxylic chain ends of BBL, water-dispersible material is obtained. The product, PEO-BBL, forms stable colloids owing to both electrostatic and steric stabilization.¹ Electrochemical properties of PEO-BBL are similar to those of unmodified BBL.² With high enough solids content, the dispersions form gels upon standing at room temperature. When the colloidal stabilization is realized by using poly(N-isopropylacrylamide), PNIPAAM, dispersions are obtained which lose their stability upon increasing temperature.
Polymers which respond to light and temperature have been synthesized by polymerization of nitrated calix[4]arenes via reductive coupling. The calixarene units have been locked into cone conformation by substituting them either with alkyl, or tetraethyleneglycol monomethyl ether chains. Thus, the polymer main chain is composed of calixarenes joined together via azo linkages. The azo units undergo trans-to-cis photoisomerization upon irradiation with 365 nm. Isomerization back to the trans state occurs either by irradiation (450 nm) or by thermal relaxation. The chain conformation has been shown to affect the host-guest complexation properties. Tegylated poly(azocalix[4]arenes) also exhibit thermo-responsive properties. An LCST type transition occurs in water, being strongly dependent on the degree of polymerization and concentration. The same dependence is observed for the UCST type transitions of the polymers in alcohols.


A new type of extrusion based nano-fibrous polymeric scaffold is described, in which chemical modifications can be easily implemented to introduce new chemical moieties for bioconjugation. We have introduced peptides and proteins onto the surface of the fibers, for use as cell seeding scaffolds. Our process begins by using a multi-layered co-extrusion and multiplication method. Poly(e-caprolactone) (PCL) and polyethylene oxide (PEO) are co-extruded through a series of dye multipliers within the extruder to yield a multi-component polymeric tape. The resulting tape is comprised of a matrix of PCL nanofibers embedded within a PEO film. The PEO layer is easily removed to yield PCL nanofibers of controlled cross-sectional dimensions. Once the fibrous mat is processed, the fibers can be photochemically modified with functionalized benzophenones to yield new functional groups on the fiber surface. We have incorporated reactive handles for performing the copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction and/or oxime ligation, for example. On the surface of the PCL fibers, we have attached numerous substrates, such as small molecules, peptides, and proteins. Subsequent cell-based studies have shown that, following immobilization, peptides are available to provide biochemical cues to promote cellular adhesion and elongation down the fiber axis. Several peptides and peptide gradients have been attached to the fibers and were able to increase cellular adhesion and spreading versus PCL control surfaces. The ease by which we can incorporate biological molecules takes a simple fiber scaffold processed from commodity polymers and transforms it into a biologically responsive material. The co-extruded fibers are of clear use due to their modularity and scalability, opening a potentially new avenue for biomaterials fabrication.
Due to their dynamic, stimuli-responsive nature, non-covalent interactions represent a versatile design element for the creation of stimuli-responsive polymers with unusual functions. Supramolecular polymers assembled through the interactions of hydrogen-bonding motifs are one class of materials that is based on this design principle and which display a range of useful stimuli-responsive properties. This presentation will provide an overview of our recent activities in this area. Polymers in which defects can be repaired are attractive, because this feature can extend the lifetime and improve the functionality of these materials.\(^1\) We recently introduced light-healable nanocomposites based on a telechelic poly(ethylene-co-butylene) that was functionalized with hydrogen-bonding ureidopyrimidone (UPy) groups (UPy-PEB-UPy) and cellulose nanocrystals (CNCs) decorated with the same binding motif.\(^2\) On account of high strength and stiffness of the CNCs, these nanocomposites display much better mechanical properties than the neat supramolecular polymer alone. Upon exposure to ultraviolet radiation, the UPy motifs convert the absorbed energy into heat, which causes the disengagement of the hydrogen-bonding motifs and a (reversible) decrease of the material’s molecular weight and viscosity. As a result, defects can be filled quickly and efficiently, even at a filler content of 20% w/w. When the light is switched off, the supramolecular nanocomposite re-assembles and their original properties are restored. We show that UPy-PEB-UPy is also useful as reversible adhesive, which permits bonding and debonding on demand.\(^3\) Lap joints bonded with the material (which contains an auxiliary light-heat converter) display appreciable shear strength, but can be rapidly debonded upon exposure to heat or UV light.

Figure 1. Chemical structure of the components of a new hydrogen-bonded supramolecular polymer based on the isophthalic acid-pyridine pair, schematic representation of the supramolecular networks formed, and a picture of the material, together with a polarized optical micrograph.

With the objective to identify a simpler and modifiable hydrogen-bonding motif that supports the formation of supramolecular polymers, we investigated the isophthalic acid-pyridine (IPA-Py) pair, which appears to have been forgotten in the context of supramolecular materials.\(^4\) Gratifyingly, materials assembled from IPA-terminated telechelic poly(ethylene-co-butylene)
(IPA-PEB-IPA) and bis-pyridines display a storage modulus of 12-21 MPa, which is comparable to that of the corresponding UPy-PEB-UPy. We show that the properties of the resulting supramolecular polymers are significantly influenced by the nature of the bispyridine, and by the fact that the IPA-Py motifs assemble into particularly well-defined hard phases. Finally, we introduce a supramolecular glass that is based on a low-molecular weight building block featuring three UPy moieties.\textsuperscript{5} The material displays an intriguing combination of optical and thermomechanical properties.

Acknowledgements

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12:00 – 1:30 LUNCH BUFFET

PM SESSION PROGRAMMING AND MEASURING ADOPTABILITY
Session Chairs: B. S. Sumerlin, M. W. Urban

2:00 – 2:30 STIMULI RESPONSIVE OSMOTIC BRUSHES BY ADSORPTION FROM SOLUTION; JOHN TEXTER, EASTERN MICHIGAN UNIVERSITY, USA.

Stimuli responsiveness in polymer design is burgeoning and is providing basis for diversely new and advanced materials.\textsuperscript{1,2} These advanced materials include switchable porosity in membranes and coatings,\textsuperscript{3} switchable particle formation and thermodynamically stable nanoparticle dispersions,\textsuperscript{4} mechanochemically-coupling polymers that provide directed mechanical stress in response to intensive fields,\textsuperscript{5,6} and switchable stabilization and compatibility of nanomaterials in changing environments, among others.\textsuperscript{7} The growth of ionic liquid applications and the concomitant incorporation of ionic liquids into polymeric materials have resulted in a plethora of new polymers based on the imidazolium group. Such polymers exhibit all of the above-articulated properties and can be distinguished as a class of cationic polyelectrolytes.\textsuperscript{1,2}

In water and other solvents the interaction strength of various anions with the imidazolium group follows a Hofmeister series that imparts highly solvophilic character to highly solvophobic character depending on the particular anion-imidazolium ion-pair. We show that the dynamic range of these interactions spans $10^4$ in concentration, and is the basis for tuning various stimuli responsive interactions. The most fundamental effect is how these interactions affect polymer solubility. Switching solubility from high to low forms a basis for advanced dispersion phase transfer. It also provides approaches to switching between transparent gels and open cell porous materials. These effects are shown to be applicable to the formation of thin films by nanolatexes, and that subsequently can be transformed into porous membranes. Another exciting application area is the incorporation of such imidazolium groups into block copolymers. Block copolymers\textsuperscript{8} and nanolatexes\textsuperscript{3} have been demonstrated to be excellent stabilizers for nanocarbons and other materials in water. When
used by adsorption from solution, these nanolatexes behave as osmotic spheres and the triblocks as osmotic brushes; both classes of polymer are shown to immunize against Debye-Hückel charge screening induced coagulation. Particularly interesting are demonstrations that di-stimuli responsive diblocks can reversibly form thermodynamically stable dispersions.

The highly stable and concentrated nanocarbon dispersions in water are also shown to provide high performance new materials, including templated coatings with very high thermal conductivities (0.8 to 3 kW/m/K). Waterborne graphene dispersions are shown to form optical-rheological fluids that become light reflecting in shear fields. These graphene dispersions are also used to demonstrate a new type of deposition/coating process based upon the stimuli responsiveness of the stabilizing copolymer.

Figure 1. Stimuli responsive pore gating.


2:30 – 3:00

NEW CHEMICAL IMAGING TOOLS FOR IMAGING POLYMER STRUCTURE AND DYNAMICS; ROHIT BHARGAVA, UNIVERSITY OF ILLINOIS, URBANA-CHAMPAIGN, USA.

Chemical imaging is an emerging modality that can provide molecular information without dyes, probes or human interpretation. In one implementation of chemical imaging, spectroscopy is used to measure both intrinsic molecular composition and structure of materials. Computer algorithms then convert the rich data into biomedical information. Here, we describe the development of mid-infrared spectroscopic imaging instrumentation, associated analytical methods and applications of this new technology. We describe the past developments and future potential applications of these methods to study polymeric systems and provide recent examples.
For many years researchers have understood the importance of the extracellular pH in solid tumors in relation to cancer morbidity and mortality. However current diagnostic imaging techniques do not allow for the non-invasive determination of pH \textit{in vivo}. Recent research in the use of pH-responsive polymers for the preparation of imaging agents capable of imaging pH \textit{in vivo} has demonstrated the tremendous potential of these materials in overcoming many of the problems associated with low molecular weight pH-responsive imaging agents. We have developed pH responsive nanoscale multimodal contrast agents for magnetic resonance imaging and computed x-ray tomography that demonstrate large changes in relaxivity to improve both the selectivity and sensitivity of \textit{in vivo} pH measurement. This presentation will focus on the design and development of the pH responsive polymers that enable the nanoparticles to demonstrate changes in relaxivity at biologically relevant pH, the surface attachment of these polymers to the nanoparticles, and the correlation between the imaging response and the environmental pH.

3:30 – 3:50 COFFEE BREAK

3:50 – 4:20 PREPARATION OF SMART STAR BLOCK COPOLYMERS; ARTJOM DOERING, MARTIN SCHNEIDER, AGNES WYCISK, DIRK KUKLING, UNIVERSITY OF PADERBORN, GERMANY.

Our research is dedicated to the synthesis and characterization of “smart” polymers with different architectures. Star polymers with N-isopropyl acrylamide (NIPAAm) as monomer are one example for three dimensional macromolecules containing several arms with similar molecular weight connected to a central core. Due to their compact structure and their enhanced segment density in comparison to linear polymers of the same molecular weight they attracted significant attention during the last years.

Here, we report the synthesis of star-shaped polymers with different cores via atom transfer radical polymerization (ATRP). Using pentaerythritol and β-cyclodextrine as core molecules possessing a well-defined number of hydroxyl groups (up to 21) multifunctional initiators could be prepared by esterification reaction of the hydroxyl groups with 2-chloropropionyl chloride. In the next step, these multifunctional initiators were utilized to synthesize star polymers under ATRP conditions with a Cu(II)/Me6TREN catalyst complex.

Poly(NIPAAm)-based star polymers with 4, 7, 14 and 21 arms as well as commercially available poly(styrene) star polymers with 3 and 8 arms were characterized intensively using size exclusion chromatography (SEC) with a refractive index and a viscosity detector. Molecular weight distributions of the polymers were calculated by universal calibration based on narrowly distributed PMMA standards. Including the inherent viscosity determined by the viscosity detector Kuhn-Mark-Houwink-plots could be obtained for both linear and star polymers. The more compact structure of the star polymers could be expressed by calculating the contraction factor g’. Due to the fact that the structural density of a polymer depends on the number of branches the contraction factor g’ was used to determine the number of arms.
RESPONSIVE NANOCOMPOSITES - INTERFACIAL BEHAVIOR and ROBUST MATERIALS SYNTHESIS; TODD EMRICK, UNIVERSITY OF MASSACHUSETTS, AMHERST, USA.

This presentation will describe polymers, nanoparticles, and their combination for the preparation and study of responsive systems. In general, functionalized nanoparticles exhibit behavior in fluids that can be manipulated (reversibly or irreversibly) through the implementation of functional polymer ligands. This lecture will specifically highlight three areas of responsive systems involving nanoparticles and polymers: 1) harnessing the behavior of nanoparticle-stabilized emulsions through the use of functional ligands; 2) uncovering the capabilities of polymer-stabilized droplets to locate nanoparticles on surfaces and transport them across and/or off the surface; and 3) advancing the solution deposition of nanoparticles to prepare ribbons and helices with outstanding mechanical properties and responsiveness to the surrounding fluidic medium.

pH- and REDOX-RESPONSIVE POLYMERIC NANOPARTICLES FOR SEQUENTIAL DRUG RELEASE, CYRILLE BOYER, THE UNIVERSITY OF NEW SOUTH WALES, AUSTRALIA.

Soft core-shell polymeric nanoparticles have been widely investigated as potential vectors for the sustained delivery of therapeutic payloads. In the first part of the talk, the synthesis of responsive nanoparticles will be shown to deliver consecutively nitric oxide (NO) and a therapeutic agent (doxorubicin) via two different stimuli: pH and redox. These nanoparticles are used for the treatment of multidrug resistant in cancers (MDR). We have demonstrated that the treatment of MDR cells using NO allows the reduction of the production of proteins responsible to the resistance. We have designed biocompatible nanoparticles able to store NO and doxorubicin, and to release specially. In-vitro data show promising synergetic effects when NO is combined with an anti-cancer drug. In a second part of the talk, the synthesis of dual responsive polymeric nanoparticles for the co-delivery of two different therapeutic agents will be presented.

POSTER SESSION AND WINE SOCIAL

BEST RESEARCH POSTER AWARD PRESENTATION

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100. SURFACE PROPERTY PATTERNING OF THERMOSTABLE PHOTO-RESPONSIBLE POLYMERS; TAKASHI YAMASHITA, SCHOOL OF COMPUTER SCIENCE, SCHOOL OF BIOSCIENCE AND BIOTECHNOLOGY, TOKYO UNIVERSITY OF TECHNOLOGY, JAPAN.

We have reported several materials whose properties such as conductivity, refractive index [1], color, nano-sized orientation [2], expansion or collapse state of a liquid crystalline droplet [3] can be directly converted and patterned by external stimuli such as photo-irradiation, and those materials whose emission can be controlled by external stimuli such as thermal treatment [4] or vortex stirring [5].

Figure 1 shows nano-sized phase separated structure of a photo-responsive polymer, which can be aligned uni-axially by polarized light irradiation. The direction of the aligned structure can be controlled by the direction of polarized light, and the phase-separated structure can be written or erased by photo irradiation.

Figure 2 shows surface relief pattern generated on a transparent polyimide only by photo-irradiation without development process. Positive or negative tone can be controlled by the choice of the additives [6]. Surface wettability of a polyimide containing t-BOC group and photo-acid-generating group in the same main chain can be modified by photo irradiation, whose contact angles to water droplets are shown in Figure 3.


101. pH-RESPONSIVE SUPRAMOLECULAR G-QUADRUPLEXES; YAZMARY MELENDEZ-CONTÉS, LUIS M. NEGRÓN, & JOSÉ M. RIVERA,* DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PUERTO RICO – RIO PIEDRAS, PUERTO RICO.

Recently, we reported the preparation and drug encapsulation studies of non-polymeric thermo-responsive supramolecular G-quadruplexes (SGQs) made from aryl-2'-deoxyguanosine (8ArG) derivatives. Although these supramolecular systems are potentially attractive for biomedical applications (e.g., drug-delivery) the narrow window of physiological temperatures complicates their implementation. This motivated us to redesign the constituent 8ArG subunits to incorporate an imidazole moiety that would lead to the formation of pH-responsive SGQs. We will present synthesis, characterization and self-assembly studies of the resulting 8ArG derivatives. Characterization studies (1D/2D-NMR, DLS, DSC) indicate the
formation of hexadecameric SGQs that are isostructural to previously reported thermosensitive SGQs. Turbidity measurements showed that the LCST above and below pH 6 were, ~4 °C and 28 °C, respectively. Isothermal measurements at 26°C demonstrated a transition pH of 5.6. Ongoing studies are aimed at testing these pH-sensitive systems for the encapsulation and controlled release of biologically active molecules.

102. PROSPECTIVE APPLICATIONS OF pH RESPONSIVE GENIPIN CROSSLINKED CHITOSAN-POLYVINYL PYRROLIDONE HYDROGELS: GLENN ADAM HURST, KWONG YUEW CHUNG, SPYRIDON DIAKAKIS, MARYAM MADZI, CHINYELUMNDE JENNIFER NWOSU, MARK BIRCH and KATARINA NOVAKOVIC; SCHOOL OF CHEMICAL ENGINEERING AND ADVANCED MATERIALS, MERZ COURT, NEWCASTLE UNIVERSITY, UK.

Chemically crosslinked chitosan-polyvinylpyrrolidone (G-Ch-PVP) hydrogels are both pH responsive and known for their biocompatibility. Traditional crosslinkers such as glutaraldehyde are inherently toxic hence more benign alternatives such as genipin are of particular interest. Genipin crosslinked hydrogels have prospective applications as tissue engineering scaffolds as well as in drug delivery. However synthesis of gels that are stable, responsive and can be tailored to the desired application are essential.

In this work variables that can influence gel characteristics have been extensively studied using optical techniques. Hydrogels were prepared containing varying quantities of chitosan, polyvinylpyrrolidone and genipin and their response to changes in pH evaluated. The influence of post-synthesis freezing and freezing-thawing treatments on the stability and smart characteristics were also assessed. Following post-synthesis treatment, well defined porous structures and enhanced stability was observed for all samples. Samples which were continuously frozen showed higher response to pH change than those that were subject to freeze-thaw treatment. Detailed SEM analysis of the pore formation during freezing was conducted to further understand the phenomena observed. Amoxicillin release studies were performed to assess G-Ch-PVP suitability for prospective drug delivery applications. Following, the antibacterial properties of the gels are examined and reported against gram-negative E.coli bacteria and gram-positive Bacillus Subtilis. In addition gels have been shown viable as scaffolds for osteoblasts cells proliferation.

103. LIGHT-RESPONSIVE IRON(III)-POLYSACCHARIDE HYDROGELS: PHOTOCHEMICAL STUDY AND DESIGN OF CONTROLLED DELIVERY SYSTEMS; ALEXIS D. OSTROWSKI, A,B GIUSEPPE E. GIAMMANCO, B,A* DEPARTMENT OF CHEMISTRY; B CENTER FOR PHOTOCHEMICAL SCIENCES, BOWLING GREEN STATE UNIVERSITY, OH, USA.

We report the formulation and quantitative photochemical study of coordination materials prepared from iron(III) and two plant-origin polysaccharides: alginate and pectate. These materials are responsive to visible light, undergoing noticeable changes in color and physical state upon illumination. The photochemical reaction is the same for both polysaccharides, involving a photo-induced ligand-to-metal electron transfer that causes the reduction of the metal, decarboxylation of the polymer, and a change in the physical state of the sample (sol-gel transition). The efficiency of the reaction, however, is very different for alginate and
pectate-based materials, suggesting that the photo-reactivity is affected differences in stereochemistry in the polysaccharide. This finding provides knowledge about important structure-property relationships that are key for controlling and tuning the photo-responsive behavior in these materials. Also, coordination hydrogel beads were formulated and loaded with different drug-models, which could be released from the beads only upon activation with light. Current research in our group is focused on using the iron-sugar dynamic bonding interactions for creating functional materials with improved stimuli-responsive properties for biological applications.

104. SELF-REPAIRABLE POLYURETHANE NETWORKS BY ATMOSPHERIC CARBON DIOXIDE AND WATER; YING YANG AND MAREK W. URBAN,* DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING and CENTER FOR OPTICAL MATERIALS SCIENCE AND ENGINEERING TECHNOLOGIES (COMSET), CLEMSON UNIVERSITY, CLEMSON, SC. USA.

These studies explore uncharted areas of self-healing by incorporating sugar moieties into polymer networks. When methyl-α-D-glucopyranoside (MGP) molecules are reacted with hexamethylene diisocyanate trimer (HDI) and polyethylene glycol (PEG) to form crosslinked MGP-polyurethane (PUR) networks, these materials are capable of self-repairing upon exposure to carbon dioxide and water. This process does not occur in the presence of any other gases, but requires atmospheric amounts of CO₂ and H₂O, thus resembling plant’s behavior during photosynthesis. Molecular processes responsible for this unique self-repair process involve physical diffusion of cleaved network segments as well as the formation of carbonate and urethane linkages. The role of each network component as well as mechanisms of self-repair were elucidated using chemical imaging and mechanical analysis. Mechanical properties are recovered during self-repair process. Unlike plants, MGP-PUR networks require no photo-initiated reactions, thus are capable of repairs in darkness under atmospheric conditions. By incorporating sugar moieties into polyurethanes, upon mechanical damage, these materials are able to reform covalent linkages capable of bridging destroyed network segments.

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