IX International Symposium on Stimuli-Responsive Materials

October 20-22, 2013
Santa Rosa, California
USA
Welcome to Sonama!

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 year 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 the 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
9TH INTERNATIONAL SYMPOSIUM ON STIMULI-RESPONSIVE MATERIALS
Symposium Organizers: Marek W. Urban and Brent S. Sumerlin

Hilton Sonoma Wine Country
3555 Round Barn Blvd., Santa Rosa
California 95403, USA

SUNDAY, OCTOBER 20, 2013

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

4:00 – 4:05 Introductory Remarks; M.W. Urban, B.S. Sumerlin

OPENING SESSION

4:05 – 4:40 TOUGHENING MECHANISMS IN MUSSEL BYSSUS AND BIOLOGICALLY INSPIRED STIMULI RESPONSIVE HYDROGELS; PHILLIP B. MESSERSMITH; Departments Of Biomedical Engineering, Materials Science And Engineering And Chemical And Biological Engineering; Chemistry Of Life Processes Institute; Institute For Bionanotechnology In Medicine; Northwestern University, Evanston, IL, USA.

4:40 – 5:15 SUPRAMOLECULAR COLLOIDAL POLYMERIZATION OF MAGNETO-RESPONSIVE HETEROSTRUCTURED NANORODS; JEFFREY PYUN; †Department of Chemistry, University of Arizona, 1306 E. University Blvd, Tucson, AZ 85721, ‡School of Chemical and Biological Engineering, World Class University Program for Chemical Convergence for Energy & Environment, Seoul National University, Seoul, 151-744 Korea.

5:15 – 5:50 LARGE NEGATIVE THERMAL EXPANSION OF A POLYMER DRIVEN BY SUB-MOLECULAR CONFORMATION CHANGE; JENNIFER LU; UC Merced, USA.

5:50-6:25 STIMULI-RESPONSIVE METALLOSUPRAMOLECULAR POLYMERS; CHRISTOPH WEDER; Adolphe Merkle Institute and Fribourg Center for Nanomaterials, University of Fribourg, Rte de l'Ancienne Papeterie, CH-1723 Marly, Switzerland.

6:25-8:30 WINE SOCIAL
MONDAY, OCTOBER 21, 2013

AM SESSION: STIMULI-RESPONSIVE NANOPARTICLES
Session Chair: B. Lokitz

8:15 – 8:50 STIMULI-RESPONSIVE MICROPARTICLES ENABLED BY COMPARTMENTALIZATION; JOERG LAHANN, University of Michigan, USA.

8:50 – 9:25 LOCKING NANOPARTICLES; IGOR LUZINOV, Sergiy Malynych, Bogdan Zdyrko, Alexander Tokarev, Konstantin Kornev; Clemson University, USA; Mikhail Motornov, Yuri Roiter, Ihor Tokarev, Sergiy Minko, Clarkson University, USA.

9:25 – 10:00 STIMULI-RESPONSIVE POWDER CAPSULES; SHIN-ICHI YUSA, University of Hyogo, Japan.

10:00 – 10:15 COFFEE BREAK

AM SESSION: RESPONSIVE BIOMATERIALS
Chair: Srinivasa Raghavan

10:15 – 10:50 NEW DEVELOPMENTS IN POST-POLYMERIZATION MODIFICATION: EFFICIENT SYNTHESIS OF STIMULI-RESPONSIVE POLYMERS; PATRICK THEATO; University of Hamburg, Germany.

10:50 – 11:25 SYNTHESIS AND STIMULI-RESPONSE OF HELICALLY FOLDED POLY(PHENYLENEETHYNYLENE)S; FUMIO SANDA, Kansai University, Japan.

11:25 – 12:00 INDUCING SIZE EVOLUTION IN HIGHLY AMPHIPHILIC MACROMOLECULAR SOLUTION ASSEMBLIES; THOMAS EPPS; University of Delaware, USA.


12:55 - 2:00 LUNCH BUFFET; OPEN AFTERNOON
TUESDAY, OCTOBER 22, 2013

AM SESSION
Session Chair: Craig Duvall

8:30 – 9:05 SYNTHESIS AND EVALUATION OF THERMALLY-RESPONSIVE COATINGS BASED UPON DIELS-ALDER CHEMISTRY AND RENEWABLE MATERIALS; Dahlia N. Amato, Gregory A. Strange, Anton D. Chavez, Kim L. Varney and PHILIP J. COSTANZO; California Polytechnic State University, USA.

9:05 – 9:40 Dale Huber

9:40 – 10:15 Brad Lokitz

10:15 – 10:30 COFFEE BREAK

AM SESSION
Session Chair: P. Costanzo

10:30 – 11:05 HYBRID POLYMER HYDROGELS COMPRISING ZONES OF DISTINCT STIMULI-RESPONSIVE PROPERTIES; SRINIVASA R. RAGHAVAN; University of Maryland, USA.

11:05 – 11:40 LIGHT-INDUCED RECONFIGURATION AND DIRECTED MOTION OF CHEMO-RESPONSIVE GELS; OLGA KUKSENOK, a Debabrata Deb, a Pratyush Dayal, a,b Anna C. Balazs, a b University of Pittsburgh, USA; b present address; IIT - Gandhinagar, INDIA.

11:40 – 12:15 EVOLUTION OF THE SELF-OSCILLATING POLYMER GEL AS NOVEL SMART MATERIALS; RYO YOSHIDA, The University of Tokyo, Japan.

12:15 – 2:00 LUNCH BUFFET

PM SESSION
BIORESPONSIVE SYSTEMS
Session Chairs: B. S. Sumerlin, M. W. Urban

2:00 – 2:35 "SMART" BIOMACROMOLECULES BY ENZYME CATALYZED POLYMERIZATION OF DNA, STEFAN ZAUCHER; Duke University, USA.

2:35 – 3:10 ENZYME-RESPONSIVE PARTICLES AND THEIR UTILITY IN TISSUE TARGETING, NATHAN GIANNESCHI, University of California, San Diego, USA.

3:10 – 3:45 Matthew Backer

3:45 – 4:00 COFFEE BREAK
4:00 – 4:35 pH-RESPONSIVE MRI CONTRAST AGENTS BASED UPON POLYMER MODIFIED NANO PARTICLES, STEPHEN G. BOYES, Colorado School of Mines, USA.


5:10 – 5:45 STIMULUS RESPONSIVE NANOTECHNOLOGIES FOR CARDIOVASCULAR REGENERATION, CRAIG L. DUVALL, Vanderbilt University, USA.

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

BEST RESEARCH POSTER AWARD PRESENTATION

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ABSTRACTS

9TH INTERNATIONAL SYMPOSIUM ON STIMULI-RESPONSIVE MATERIALS
Symposium Organizers: Marek W. Urban and Brent S. Sumerlin

SUNDAY, OCTOBER 20, 2013

4:50 – 4:40 TOUGHENING MECHANISMS IN MUSSEL BYSSUS AND BIOLOGICALLY INSPIRED STIMULI RESPONSIVE HYDROGELS; PHILLIP B. MESSERSMITH; Departments Of Biomedical Engineering, Materials Science And Engineering And Chemical And Biological Engineering; Chemistry Of Life Processes Institute; Institute For Bionanotechnology In Medicine; Northwestern University, Evanston, IL, USA.

The mussel byssus is a remarkable mechanical system composed of protein threads anchored onto surfaces via adhesive pads. The structure is synthesized from liquid protein precursors in a process akin to polymer injection molding, is enriched in transition metals, and confers tremendous mechanical stability through high strength and toughness. Understanding the underlying molecular basis for this behavior can help motivate the design of high performance synthetic materials. In this talk I will describe our efforts to understand and exploit the mechanical toughening mechanisms arising from noncovalent interactions between iron and catechol residues of byssal proteins. The nature of chemical interactions between Fe$^{3+}$ and the catechol side chains of DOPA residues is strongly pH dependent, with a weakly cross-linked covalent network being formed during byssus formation, which is later fortified by noncovalent coordination interactions upon equilibration to alkaline seawater pH. The noncovalent coordination bonds serve as sacrificial bonds, rupturing under applied load to increase energy dissipation. Synthetic polymer mimics were used to illustrate this toughening mechanism and examples of these systems will be described. The approach can be easily adapted for other toughening mechanisms and cross-linking strategies, representing a general approach that can be employed to enhance mechanical properties of polymer hydrogels.

4:40 - 5:15 SUPRAMOLECULAR COLLOIDAL POLYMERIZATION OF MAGNETO-RESPONSIVE HETEROSTRUCTURED NANORODS; JEFFREY PYUN; †Department of Chemistry, University of Arizona, 1306 E. University Blvd, Tucson, AZ 85721, ‡School of Chemical and Biological Engineering, World Class University Program for Chemical Convergence for Energy & Environment, Seoul National University, Seoul, 151-744 Korea.

We will discuss our recent efforts the synthesis and dipolar assembly of a polymer stabilized Janus nanoparticle composed of a single dipolar cobalt nanoparticle conjugated to a heterostructured semiconductor nanorod. These types of magnetically responsive nanoparticles serve as intriguing nanoscopic monomers to form mesoscopic colloidal polymer like structures. Blending experiments with various types of dipolar nanoparticles and
nanorods will be discussed to form “colloidal copolymers” of varying composition and sequence.

5:15 – 5:50  LARGE NEGATIVE THERMAL EXPANSION OF A POLYMER DRIVEN BY SUB-MOLECULAR CONFORMATION CHANGE; JENNIFER LU, UC Merced, USA.

A polyarylamide type of film that contains s-dibenzocyclooctadiene (DBCOD) can generate unconventional and completely reversible thermal contraction under low-energy stimulation, e.g. near infrared (NIR) irradiation or heating a few degrees above room temperatures. These films possess a giant negative thermal expansion (NTE) coefficient of greater than 1200 ppm/K under ambient conditions, much higher than any known NTE materials at similar operating conditions. Mechanical characterization, calorimetry, spectroscopic analysis and density-functional theory calculations all point to the conformational change of the DBCOD moiety, from the thermodynamic global minimum (twist-boat) to a local minimum (chair) as the origin of this abnormal thermal shrinkage. Furthermore, exploiting the ability of few-walled carbon nanotubes (FWCNTs) to effectively convert photon energy into heat and to provide conductive pathways, the NIR-induced unexpected contraction stress can be further increased dramatically. At 3 wt% FWCNTs, the enhancement factor for contraction stress is almost 24: 166 kPa with 3 wt% FWCNTs vs. 7 kPa without FWCNTs. The colossal thermal contraction of the DBCOD-containing polymer system upon low-energy stimulation will enable new NIR transducers, actuators and sensors, e.g. for biological applications and for ambient thermal energy harvesting.

5:50 - 6:25  STIMULI-RESPONSIVE METALLOSUPRAMOLECULAR POLYMERS; CHRISTOPH WEDER; Adolphe Merkle Institute and Fribourg Center for Nanomaterials, University of Fribourg, Rte de l'Ancienne Papeterie, CH-1723 Marly, Switzerland.

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. Metal-containing polymer systems are of particular interest, because they combine the functionality of metal complexes with the attractive features of polymers. We have shown that metallosupramolecular polymers, formed by the supramolecular assembly of telechelic ditopic ligands with metal salts, are an attractive class of materials, as they are easy to process and exhibit interesting mechanical properties. We have recently demonstrated that metallosupramolecular polymers can readily be healed after being damaged. It was shown that light can be used to locally deliver heat, which facilitates the temporary disengagement of the metallosupramolecular motifs, concomitant with a reversible decrease of the polymer’s molecular weight and viscosity. This allows small cracks to be filled with the constituting components and upon re-polymerization the damaged material is eventually healed. We also discovered that both reversible and irreversible disassembly of such materials is also possible by way of mechanochemical transduction. We demonstrate this with a new metallo-polymer assembled from a europium salt and a telechelic poly(ethylene-co-butylene) with 2,6-bis(1'-methylbenzimidazolyl)pyridine ligands at the termini. The Eu$^{3+}$ complexes serve as mechanically responsive motifs and their characteristic fluorescence allows one to monitor the extent of assembly. Dose-dependent, reversible metal-ligand dissociation occurs upon
exposure to ultrasound. We show that this is possible in the solid state and permits mending of damaged objects with ultrasound.

6:30 - 8:30 WINE SOCIAL

MONDAY, OCTOBER 21, 2013

AM SESSION: STIMULI-RESPONSIVE NANOPARTICLES
Session Chair: B. Lokitz

8:15 – 8:50 STIMULI-RESPONSIVE MICROPARTICLES ENABLED BY COMPARTMENTALIZATION; JOERG LAHANN, Departments of Chemical Engineering, Materials Science and Engineering and Biomedical Engineering, University of Michigan, Ann Arbor, MI, USA.

Compartmentalized particles enable co-presentation of dissimilar sets of properties. The ability to place dissimilar materials into the close proximity of a micro- or nanoparticle can open a broad design space for multifunctional particles. Electrohydrodynamic co-jetting is a simple, yet versatile fabrication technique that can be used to prepare such multicompartmental particles and fibers. Compartmentalization, in conjunction with size, shape and surface topology are important design parameters of particles. In fact, nature’s particles, e.g., cells, bacteria or viruses, utilize these design criteria highly effectively to create unique biological functions. In a biomimetic approach, we have designed multicompartmental particles that are able to respond to changes in their environment through active movement. These microactuators rely on a selective transition in a specific compartment to create local surface stresses that induce actuation. Specifically, we will outline a particle design that can “grasp”, transport and release an object.

References:

8:50 – 9:25 LOCKING NANOPARTICLES; IGOR LUZINOVA, Sergiy Malynych, Bogdan Zdyrko, Alexander Tokarev, Konstantin Kornev; Department of Materials Science and Engineering, Clemson University, SC, USA; Mikhail Motornov, Yuri Roiter, Ihor Tokarev, Sergiy Minko, Department of Chemistry, Clarkson University, NY, USA.

We report an approach to surface modification of nanoparticles with responsive mixed polymer brushes. It was demonstrated that the nanoparticles are capable of reorganization in an external magnetic field, which can turn on interactions between the particles. The interaction remains unchanged even after removal of the external magnetic field. The “locking particles” can be unlocked by applying external stimuli. In essence, we have shown that the balancing Brownian motion, the short-range attractive and long-range repulsive forces due to the specially tailored mixed polymer brush shell of the particles, and the forces experienced by the particles in the external field constitute a method to fabricate and reversibly lock 1D
wires/chains in liquid matrixes (solvent or polymer melt). We also demonstrated that a mixture of two populations of nanoparticles with different surface functionalization that provide control over intermolecular forces can be used to regulate the length of self-assembled 1D wires.

Recently, there has been an increasing interest in solid particles adsorbed to liquid-liquid, gas-liquid and gas-solid interfaces. Liquid marbles are liquid-in-gas dispersed systems prepared using hydrophobic particles adsorbed to a gas-liquid interface. They have attracted increasing attention with respect to their potential applications in cosmetics, pharmaceuticals in the home, and personal care products. It has been reported that inorganic particles such as silica, graphite, synthetic polymer particles, and surface-modified lycopodium powder can be used as effective liquid marble stabilizers. The liquid marbles which are coated with hydrophobic particles can float on a water surface (Figure 1).

It is important to develop pH-responsive liquid marbles stabilized with anionic polymer-modified particles, which can be disrupted on the addition of alkaline solution. However, there has been no study on alkaline-induced breakable liquid marbles. Herein, we have studied the stability control of liquid marbles prepared using poly(6-(acrylamido)hexanoic acid) (PAaH) grafted micrometer-sized silica particles (PAaH-SiO$_2$). These particles were used as liquid marble stabilizers, by the tuning of their surface hydrophobicity/hydrophilicity with external pH-stimuli. Under acidic and neutral pH conditions, the surface of PAaH-SiO$_2$ is hydrophobic because the pendant carboxyl groups in PAaH are protonated. However, under alkaline conditions PAaH can dissolve in water and the wettability of the surface of PAaH-SiO$_2$ increases. This is because the pendant carboxyl groups are deprotonated to form carboxylate ions. It is expected that PAaH-SiO$_2$ can stabilize liquid marbles on the surface of an acidic or neutral pool of water however, the liquid marbles would disintegrate upon the addition of an alkali solution.

PAaH was grafted onto the surface of the silica particles to prepare a high density polymer layer. Many researchers have studied the controlled radical polymerization at the surface of a solid particle. In this work, PAaH-SiO$_2$ was prepared via the “grafting from” approach with reversible addition-fragmentation chain transfer (RAFT) controlled/living radical polymerization. The stability of pH-responsive liquid marbles formed on a water surface using PAaH-SiO$_2$ was studied at various levels of pH. These PAaH-SiO$_2$ particles are shown to be an interesting novel pH-responsive particulate liquid marble stabilizer.

References:
Designing a polymer usually involves the incorporation of multiple functional units into a polymer chain. By combining various functional units, a myriad of polymer properties can be fine-tuned. As an example, stimuli-responsive polymers are investigated, which are synthesized from well-defined reactive pre-polymers. This route enables us to incorporate multiple functionalities, which render the obtained polymer responsive to multiple stimuli. Stimuli of interest are: temperature, light and redox. Particular focus will be laid on recent developments in post-polymerization modifications utilizing modern multicomponent reactions, which allow the synthesis of complex functionalities in facile synthetic steps. Various examples will be presented to provide an overview of the possibilities of modern polymer synthesis when it comes to precision synthesis. These examples document the valuable contributions synthetic polymer chemistry can make to the future of highly specialized functional polymers.

Biomacromolecules, such as proteins and DNA, exhibit sophisticated and intricate functions largely depending on their well-defined higher order structures. For the past decade, artificial helical polymers, including polymethacrylates, polyisocyanides, polysilanes, poly(phenyleneethynylene)s and polyacetylenes have been extensively synthesized by imitating naturally derived helical polymers. Artificial helical conjugated polymers are important not only from the viewpoint of fundamental study but also for their potential use in practical applications (molecular recognition, chiral catalysis, chemical sensing, etc. based on their electronic and optical properties. Recently, we reported the synthesis and chiroptical properties of various novel D-hydroxyphenylglycine-/L-tyrosine-derived poly(m-phenyleneethynylene-p-phenyl -eneethynylene)s, as well as the photo-response and stabilization of the conformation by intramolecular crosslinking at the side chains. The key importance for helix formation for these polymers is amphiphilicity caused by the hydrophobic exterior (alkyl groups and phenyleneethynylene main chain) and hydrophilic interior (hydroxy groups). It should be noteworthy that the amphiphilic balance of the helices formed by these polymers is opposite to that of typical poly(m-phenyleneethynylene) derivatives. p-Stacking between the phenylene moieties on the main chain and intramolecular hydrogen bonding
Poly(phenyleneethynylene)s bearing azobenzene moieties in the main chains formed predominantly one-handed helically folded structures in CHCl_3/THF mixtures. The polymers underwent a reversible conformational change between folded and unfolded structures upon UV and visible irradiation, as a result of trans–cis isomerization of the azobenzene moieties.

References:

11:25 – 12:00 INDUCTING SIZE EVOLUTION IN HIGHLY AMPHIPHILIC MACROMOLECULAR SOLUTION ASSEMBLIES; THOMAS EPPS; University of Delaware, USA.

The solution self-assembly of macromolecular amphiphiles offers an efficient, bottom-up strategy for producing well-defined nanocarriers, with applications ranging from drug delivery to imaging and diagnostics. Typically, the generation of uniform nanocarrier architectures is controlled by processing methods that rely upon cosolvent mixtures. These preparation strategies hinge on the assumption that macromolecular solution nanostructures are kinetically stable following transfer from an organic/aqueous cosolvent into aqueous solution. However, we demonstrate that unexpected yet unequivocal step-change shifts in micelle populations occur over several weeks following transfer into a highly selective solvent. Furthermore, we provide the first experimental evidence for a micelle fusion process that evolves through a distinct bimodal size distribution. We note that current theoretical energy treatments of micelle fusion cannot explain this growth process. Importantly, this non-equilibrium size increase can have a major impact on the shelf-life and overall stability of solution assemblies, for which performance is dictated by nanocarrier size/structure.


Hybrid self-assemblies based on the adsorption process of poly(N,N-dimethylacrylamide) [PDMA], poly(N-isopropylacrylamide) [PNIPA] or poly(ethylene oxide) [PEO] with silica
nanoparticles are reported. From adsorption isotherms and calorimetric experiments, it is shown that $N$-alkylacrylamide derivatives strongly interact with silica surfaces while PEO chains exhibit lower affinity. When such oligomers are grafted onto a non-adsorbing poly(acrylamide-co-sodium acrylate) backbone [PAMH], the binding process of these adsorbing side-chains with silica nanoparticles proceeds very similarly and gives rise to the formation of hybrid hydrogels as sketched in Figure 1 below.

![Figure 1: Schematic representation of hybrid self-assembly between adsorbing grafts and silica particles.](image)

The viscoelastic properties of these networks are controlled by the concentration of inorganic cross-links and the fraction of adsorbing grafts involved in the formation of bridges between particles. For all hybrid formulations investigated, an optimum weight ratio between silica and grafts was found for the viscoelastic properties, in agreement with the saturation of silica beads by the graft precursors. Due to the temperature dependence of the solubility of PNIPA side-chains in aqueous solutions (LCST behavior), the PAMH-g-PNIPA copolymer is also able to self-assemble with temperature, giving rise to a hybrid co-network in the presence of added silica\textsuperscript{1,2}.

While the formulation of these hierarchical hybrid assemblies remains limited to mixtures involving low polymer concentrations (≤ 2 wt%), we show that homogeneous hybrid networks can be readily prepared by direct polymerization of DMA monomer within the suspension of silica nanoparticles. In this case, the specific interactions taking place between the silica filler and the polymer matrix, as well as the covalent cross-links between PDMA chains, give rise to highly deformable tough hydrogels with a strong time-dependence of their mechanical properties\textsuperscript{3,4}.

References:
\textsuperscript{1} Petit L., Bouteiller L., Brûlet A., Lafuma F., Hourdet D. \textit{Langmuir} 2007, 23, 147-158.
\textsuperscript{2} Hourdet D., Petit L. \textit{Macromolecular Symposia} 2010, 291–292, 144–158.
\textsuperscript{3} Carlsson L., Rose S., Hourdet D., Marcellan A. \textit{Soft Matter} 2010, 6, 3619-3631.
\textsuperscript{4} Rose S., Dizeux A., Narita T., Hourdet D., Marcellan A. \textit{Macromolecules} 2013, 46, 4095-4104.

12:55 - 2:00  
**LUNCH BUFFET; OPEN AFTERNOON**

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TUESDAY, OCTOBER 22, 2013

AM SESSION STIMULI-RESPONSIVE COATINGS
Session Chair: Craig Duvall

8:30 – 9:05 SYNTHESIS AND EVALUATION OF THERMALLY-RESPONSIVE COATINGS BASED UPON DIELS-ALDER CHEMISTRY AND RENEWABLE MATERIALS; Dahlia N. Amato, Gregory A. Strange, Anton D. Chavez, Kim L. Varney and PHILIP J. COSTANZO; Chemistry and Biochemistry, California Polytechnic State University, 1 Grand Ave, San Luis Obispo, CA 93407, USA.

A soybean based coating with thermally responsive Diels-Alder linkages has been prepared following an automotive 2-component formulation. The resulting coatings displayed the capability to be healed following physical deformation by a thermal stimulus, and such a material has significant potential for end users. Various curing agents were employed, and resulted in variation of scratch resistance and re-healablility. Different thermally responsive soybean resins were synthesized to have varying amounts reversible and nonreversible linkages when incorporated into the coating. Additionally, different isocyanates were added at differing ratios of NCO:OH in search of the optimum coating. It was found through the analysis of rehealabilty, hardness, gloss, and adhesion that the optimal combination was an acetylated resin (no irreversible crosslinks) with 54% reversible Diels Alder linkages at an NCO:OH ratio of 5:1 using isophorone diiscocyanate. Materials were evaluated via differential scanning calorimetry (DSC), scratch resistance, Koenig hardness, gloss measurements, and topographical analysis.

9:05 – 9:40 DALE HUBER

9:40 – 10:15 BRAD LOKITZ

10:15 – 10:30 COFFEE BREAK

AM SESSION HYBRID STIMULI-RESPONSIVE SYSTEMS
Session Chair: P. Costanzo

10:30 – 11:05 HYBRID POLYMER HYDROGELS COMPRISING ZONES OF DISTINCT STIMULI-RESPONSIVE PROPERTIES; SRINIVASA R. RAGHAVAN; Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA.

Soft materials found in nature often have complex architectures. An example is the spinal discs that lie between adjacent vertebrae in the spine: these discs have a hard core surrounded by a soft shell. We are interested in creating new hybrid materials based on polymer hydrogels that can mimic such architectures. Towards this end, we have developed a new approach to creating hybrid hydrogels that comprise two different gel types (gel 1 and gel 2) juxtaposed in predetermined zones or patterns and with the unique properties of each gel being retained. The key to our approach is to ensure that the viscosities of the pregel mixtures are high when they are brought into contact and subsequently polymerized; this
limits the diffusion at gel/gel interfaces. The final gel appears as a single, homogeneous, transparent material with smooth, robust interfaces between the dissimilar zones. However, its hybrid nature is revealed by specific tests. In one example, we use different monomers for gels 1 and 2. The polymer of gel 1 changes volume in response to pH or temperature changes while the polymer of gel 2 does not. As a result, when the hybrid gel is exposed to a temperature or pH value that induces volume change of gel 1, gel 2 remains unaffected. The overall approach described here can be extended in myriad ways for the generation of gels possessing new and unique properties.

11:05 – 11:40 LIGHT-INDUCED RECONFIGURATION AND DIRECTED MOTION OF CHEMO-RESPONSIVE GELS; OLGA KUKSENOK, Debabrata Deb, Pratyush Dayal, Anna C. Balazs; Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA, USA; present address: Department of Chemical Engineering, IIT, Gandhinagar, INDIA.

Remarkable features of certain biological species involve their ability to alter their shape and functionality in response to environmental cues. Polymer gels undergoing the Belousov-Zhabotinsky (BZ) reaction are unique self-oscillating materials that can be used to design a variety of soft materials with biomimetic functionality. Herein, we focus on chemically-mediated communication between multiple pieces of BZ gels. We show that these pieces can both emit and sense a chemical signal and thus, drive neighboring pieces to spontaneously self-aggregate, so that the system exhibits autochemotaxis. We also find that the aggregated gel pieces undergo spontaneous, autonomous rotation. Moreover, the gels' coordinated motion can be controlled by light, allowing us to achieve selective self-aggregation and control over the shape and motion of the aggregates. Finally, we also focus on photo-responsive polymer gels that contain spirobenzopyran (SP) chromophores and demonstrate that they can be patterned remotely and reversibly by illuminating the samples through photomasks and thus, "molded" into a variety of shapes. Furthermore, we show that by repeatedly rastering the light source over the sample, the system can be driven to exhibit sustained, directed motion. The results point to a robust method for controllably reconfiguring the morphology of polymer gels and driving the self-organization of multiple reconfigurable pieces into complex architectures.

11:40 – 12:15 EVOLUTION OF THE SELF-OSCILLATING POLYMER GEL AS NOVEL SMART MATERIALS; RYO YOSHIDA, Department of Materials Engineering, School of Engineering, The University of Tokyo, Japan.

We have been studying polymer gels with an autonomous self-oscillating function, since firstly reported in 1996. We succeeded in developing novel self-oscillating polymers and gels by utilizing the oscillating reaction, called the Belousov-Zhabotinsky (BZ) reaction. The polymer gel undergoes spontaneous cyclic swelling–deswelling changes or soluble–insoluble changes (in the case of uncrosslinked polymer) without any on–off switching of external stimuli. Potential applications of the self-oscillating polymers and gels include several kinds of functional material systems, such as biomimetic actuators, mass transport systems, and functional fluids. For example, it was demonstrated that an object was autonomously transported in the tubular self-oscillating gel by the peristaltic pumping motion similar to an intestine. Further, it is possible to create a new dynamic interface by immobilizing the self-oscillating polymer. We prepared a self-oscillating polymer brush surface on the inside surface of a glass capillary and evaluated its dynamic behavior. Besides, autonomous...
viscosity oscillation was realized via metallo-supramolecular terpyridine chemistry\textsuperscript{10}, by preparing microgels\textsuperscript{9}, etc. Self-oscillation between unimer and micellar structures was also realized for a synthetic block copolymer\textsuperscript{12}. And recently, novel comb-type self-oscillating gels were designed\textsuperscript{13}. In this presentation, such recent progress on the gel will be introduced.

References:

12:15 – 2:00 LUNCH BUFFET
The synthesis of biologically-inspired macromolecules with well-defined sequence, dispersity, and assembly function has large potential for applications ranging from delivery vehicles of medical therapeutics, sensing applications, to scaffolds for tissue regeneration. Here I report the progress of our work where we exploit the ability of a template-independent DNA polymerase, terminal deoxynucleotidyl transferase (TdT), to polymerize long chains of single strand DNA (ssDNA) and to incorporate unnatural nucleotides with useful functional groups into the growing polynucleotide chains. Specifically, I report on a method that allows the facile synthesis of ssDNA amphiphiles (0.6 to 2.7 kilobases) with useful self-assembly properties. Our approach entails a two-step enzymatic polymerization reaction in which the MW and composition of the polynucleotide chains are controlled by the ratio of monomer to initiator concentration and the type of nucleotides, respectively. The hydrophobicity, resulting from incorporation of unnatural nucleotides, can be tuned to drive the assembly of these polynucleotides into star-like, hairy micelles. We used high resolution AFM to directly visualize the condensed core and hairy corona of the star-like micelles. In addition, we investigated the hydrodynamic radius ($R_h$) of our polynucleotides and the resulting micellar structures by dynamic light scattering (DLS). Coarse-grained, dynamic particle dissipations (DPD) simulations confirm our experimental observations and provide predictive capability for engineering with this new class of materials. Finally, by harnessing the molecular recognition ability of DNA we demonstrate that our polynucleotides form ordered networks on surfaces, and can be used to template metallic nanowire meshes over large areas.

The goal of targeted therapeutics and molecular diagnostics is to accumulate drugs or probes at the site of disease in higher quantities relative to other locations in the body. To achieve this, there is tremendous interest in the development of nanomaterials capable of acting as carriers or reservoirs of therapeutics and diagnostics in vivo. Generally, nanoscale particles are favored for this task as they can be large enough to function as carriers of multiple copies of a given small molecule, can display multiple targeting functionalities, and can be small enough to be safely injected into the blood stream. The general goal is that particles will either target passively via the enhanced permeability and retention (EPR) effect, actively by incorporation of targeting groups, or by a combination of both. Nanoparticle targeting strategies have largely relied on the use of surface conjugated ligands designed to bind overexpressed cell-membrane receptors associated with a given cell-type. We envisioned a targeting strategy that would lead to an active accumulation of nanoparticles by virtue of a supramolecular assembly event specific to tumor tissue, occurring in response to a specific signal. The most desirable approach to stimuli-induced targeting would be to utilize an endogenous signal, specific to the diseased tissue itself, capable of actively targeting materials introduced via intravenous (IV) injection. We present the development of
nanoparticles capable of assembling in vivo in response to selective, endogenous, biomolecular signals. For this purpose, we utilize enzymes as stimuli, rather than other recognition events, because they are uniquely capable of propagating a signal via catalytic amplification. We will describe the development and implementation of these stimuli-responsive materials.

3:10 – 3:45 Matthew Backer

3:45 – 4:00 COFFEE BREAK

4:00 – 4:35 pH-RESPONSIVE MRI CONTRAST AGENTS BASED UPON POLYMER MODIFIED NANOPARTICLES, STEPHEN G. BOYES, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden CO, 80401, USA.

Despite recent advances in the understanding of fundamental cancer biology, cancer remains the second most common cause of death in the United States. One of the primary factors indicative of high cancer morbidity and mortality and aggressive cancer phenotypes is tumors with a low extracellular pH (pHe). Thus, the ability to measure tumor pHe in vivo using non-invasive and accurate techniques that also provide high spatiotemporal resolution has become increasingly important and is of great interest to researchers and clinicians. Despite this interest, there is currently no clinical method available for the in vivo determination of pHe and, notwithstanding the existing research in this area, in vivo applications have been limited due to problems with low changes in relaxivity limiting sensitivity, poor specificity due to lack of molecular targeting, solubility issues due to changes in ligand structure, and difficulty in tuning the pH response to match tumors. 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 in vivo pHe 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 and the surface attachment of these polymers to the nanoparticles.

4:35 – 5:10 ENGINEERING RESPONSIVE POLYMERIC NANOPARTICLES FOR ADVANCED APPLICATIONS, Jinna Liu, Johan Basuki, Hien T.T. Duong, Thomas P. Davis, CYRILLE BOYER, Centre for Advanced Macromolecular Design (CAMD), Australian Centre for NanoMedicine (ACN), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia.

Soft core-shell polymeric nanoparticles are an area of great research interest, due to their potential advantages in the sustained and targeted delivery of therapeutic payloads. These systems can offer significant improvements in the temporal and spatial control of drug delivery. In this talk different polymeric nanoparticles that have been specifically designed to deliver anti-cancer drugs and to image specific tissue, will be discussed. The first system presented will be based on pH- and redox- responsive nanoparticles which are able to deliver different payloads in different cellular compartments. The synthesis and the characterization of these nano-objects will be outlined in detailed. As an example, the delivery of nitric oxide will be presented using these nanoparticles for the treatment of liver fibrosis and neuroblastoma. We have also demonstrated synergistic effect when we combine nitric oxide
(NO) with chemotherapy drugs for the treatment in multi-drugs resistance in cancer. In a second part of this talk, the synthesis of new hybrid organic/inorganic nanomaterials, based on iron oxide, gold and gadolinium, will be reported for use as MRI contrast agents. The effect of the architecture and the nature of polymers will be correlated with the magnetic properties of these nano-objects. In addition, the polymeric shell of these nanomaterials can be designed to conjugate with anti-cancer drugs, and to control their release under specific conditions, such as pH, temperature, etc.

5:10 – 5:45

STIMULUS RESPONSIVE NANOTECHNOLOGIES FOR CARDIOVASCULAR REGENERATION, CRAIG L. DUVALL, Vanderbilt University, Department of Biomedical Engineering, USA.

This talk will provide updates on two projects in the Duvall lab focused on development of polymer-based technologies for intracellular delivery of biological drugs to improve cardiovascular function and regeneration.

The first project that will be discussed focuses on a polymer-based “nanoplex” for efficient delivery of an anti-inflammatory and anti-fibrotic peptide drug. Recent testing of this nanomedicine in the Duvall lab has shown that it decreases vasoconstriction and intimal hyperplasia in human saphenous vein and improves performance of vascular bypass grafts in a preclinical rabbit model.

The second part of the talk will highlight the development of an injectable, tissue engineering scaffold-based approach for local delivery of siRNA nanoparticles. This system has been applied to effectively stimulate angiogenesis and tissue regeneration in vivo in subcutaneous implants.

6:00 – 8:00

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A SYNTHETIC GEL BASED APPROACH TOWARD SELF-REGULATED INSULIN DELIVERY SYSTEM; AKIRA MATSUMOTO, Takehiko Ishii, Kazunori Kataoka, Yuji Miyahara. Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan; Department of Bioengineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan; Department of Materials Science and Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan; Division of Clinical Biotechnology, Center for Disease Biology and Integrative Medicine, Graduate School of Medicine, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

Diabetes is not an infectious disease but its increasingly rapid and worldwide prevalence has been recognized as "pandemic". Despite the necessity for continuous and accurate glycemic control in the management of insulin dependent diabetes mellitus (IDDM), the current palliative treatment relies almost solely on the patient-self injection of insulin, which not only impinges on quality of life of the patients but also fails to precisely control dose of insulin where the overdose must be strictly avoided otherwise causing serious hypoglycemia. Development of self-regulated insulin delivery systems is a long-standing challenge of materials science, for which exploitations of glucose oxidase and sugar-binding lectin are two prevalent rationales to install the function of glucose-sensitivity. These protein-based components, however, intolerant of long-term use and storage with their denaturing and cytotoxic natures, are hardly suitable for any implantable applications thus have not yet been in clinical usage to date. Here we describe a thoroughly synthetic and remarkably simple alternative. A polymer gel bearing phenylboronic acid (PBA) derivative was chemically optimized as to elicit abrupt and glucose-dependent transition in the state of hydration under physiological aqueous condition. During this transition, development of a thinly surface-dehydrated layer or "skin layer" was identified as a mode that is able to discretely switch the release of gel-loaded insulin, providing an ability to synchronize the dosage with the surrounding glucose-fluctuation in the range between normo- and hyperglycemia. This synthetic alternative may offer a new material basis for the self-regulated insulin delivery systems to treat diabetes with long-term stability and safety.

References:
Surfaces that switch their properties in response to stimuli are highly interesting for a wide range of applications such as sensors, smart coatings, and tissue engineering. Various polymers that respond to stimuli such as temperature, light, pH etc. have been utilized to form stimuli-responsive hydrogel films on surfaces. Upon applying stimulus, such gels show large changes in degree of swelling that lead to changes in their properties such as elastic modulus, refractive index, etc. In this study, we prepared fluorophore conjugated thermoresponsive hydrogel patterns that show fluorescence switch in response to temperature changes.

Figure 1. Fluorescence micrographs of checkerboard patterns of hydrogels having different volume phase transition temperatures (VPTT = 33 °C and 41 °C for gels stained red and green, respectively). Upon increasing the temperature above VPTT, the fluorescence is quenched for the respective gel. Upon cooling, the fluorescence is recovered for both gels. Scale bar= 10 µm.

Oligo(ethylene glycol) methacrylate based thermoresponsive polymers having amine end-groups were patterned on silicon surfaces by electron beam lithography. Then, self-quenching fluorophores were conjugated to the patterned hydrogels utilizing the amine end-groups. At room temperature, the fluorophore conjugated hydrogels were brightly fluorescent in water (Figure 1). Upon increasing the temperature to values above the volume phase transition temperature of the respective gel, a dramatic decrease in the fluorescence intensity was observed due to self-quenching of fluorophores in the collapsed state of the gel. Importantly, the fluorescence could be recovered when the temperature was decreased back to room temperature indicating that the temperature induced fluorescence switch is thermoreversible. In a similar manner, three polymers were patterned to generate morphing structures that display different messages at different temperatures. We have investigated the fluorescence switching behavior of the hydrogels for up to ten cycles and the swelling-collapse behavior by AFM analyses. The presented platform could be highly useful in applications such as sensors and encryption.
102. CONTROLLING CATECHOL BASED ADHESION OF MUSSEL FOOT PROTEIN 5 AT OXIDIZING PH WITH BORATE; ERIC W. DANNER, a Yajing Kan, b Jacob Israelachvilli, c J. Herbert Waite; d aMolecular, Cellular and Developmental Biology, UCSB, USA; b Jiangsu Key Laboratory for Design and Manufacture of Micro-Nano Biomedical Instruments, Southeast University, China; c Dept. Chemical Engineering, UCSB, USA, dMaterial Research Laboratory, UCSB, USA.

Mussels produce a biomaterial that adheres well on surfaces as diverse as titanium and Teflon. The proteins that make up this proteinaceous material have been isolated and an interfacial protein, Mefp-5, that is particularly high in the catechol moiety has been subjected to extensive physical characterization on the surfaces forces apparatus. This device is able to construct force distance profiles on thin films of these proteins on a diversity of substrates with angstrom resolution and Pico newton sensitivity. This characterization has led to both a quantification of the extreme adhesive prowess of the protein Mefp-5 as well as better characterizing the susceptibility of these proteins to oxidation.

A protection system that allows for avoiding the chemical oxidation has been developed that both allows for oxidation protection but is removed upon being brought into proximity with a suitable substrate and an irreversible bond is produced. This has broad potential as chemistry based off the mussel biomaterial is now finding its way into novel hydrogels, wet adhesives, coatings, molecular scaffolds, sensors, therapeutic agents, fuel cells, molecular electronics and solar cells.

103. LIGHT-MEDIATED POLYMERIZATIONS AND REACTIONS FOR MODIFYING SURFACES; JUSTIN E. POELMA1,2, Brett P. Fors1, Matt S. Menyo4, Gregory F. Meyers5, John W. Kramer5 and Craig J. Hawker;1,2,3 1Materials Research Laboratory, 2Materials Department, 3Department of Chemistry and Biochemistry and 4Biomedical Science and Engineering, University of California, Santa Barbara, CA 93106, 4The Dow Chemical Company, Midland, MI 48667, USA.

This work will introduce surface patterning applications of a visible light-mediated controlled radical polymerization and atom transfer radical addition (ATRA) reaction. The temporal and spatial control enabled by light as an external stimulus for polymerizations and addition reactions is ideal for surface patterning applications. Surfaces with spatially defined regions
containing polymer brushes or small molecules can be formed from a uniform initiating layer using a simple photomask. The living nature of the photocontrolled polymerization allows for precise control over chain end functionality and the fabrication of block copolymer architectures. Furthermore, chemical gradients of small molecules and complex three-dimensional brush structures can be obtained by modulating light intensity with a grayscale photomask. Together, light-mediated polymerizations and addition reactions offer many advantages over existing techniques for patterning surfaces and generating gradient structures. The unique capabilities of these processes offer significant promise for applications ranging from photolithography to one-step, high throughput patterned substrates.

104. EFFECT OF THE POLYMER ARCHITECTURE TO THE BIO-IMAGING; Mariana Beijia, Sophie Larurent, Tomas P. Davis, Cyrille Boyer, YANG LI; Australian Centre for Nanomedicine (ACN), School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia; NMR and Molecular Imaging Laboratory, Department of General, Organic and Biomedical Chemistry, University of Mons, 7000 Mons, Belgium.

Macromolecular ligands for Gadolinium contrast agents (CAs) with various architectures were prepared via a “grafting to” strategy. Copolymers of oligoethyleneglycol methyl ether acrylate (OEGA) and an activated ester monomer, pentafluorophenyl acrylate (PFPA), were synthesized and modified with a 1-(5-amino-3-aza-2-oxypentyl)-4,7,10-tris(t-butoxycarbonyl-methyl)-1,4,7,10-tetraaza-cyclododecane (DO3A-tBu-NH2) chelate for the complexation of Gd(III). The relaxivity properties of the ligated Gd(III) agents were then studied to evaluate the effect of macromolecular architecture on their behavior as magnetic resonance imaging (MRI) CAs. Ligands made from linear and hyperbranched macromolecules showed a substantially increased relaxivity in comparison to existing commercial Gd(III) MRI contrast agents. In contrast, star polymers exhibited a slightly lower relaxivity per Gd(III) ion (but still substantially higher relaxivity than existing low molecular weight commercial CAs). This work shows that macromolecular ligands have the potential to serve as components of Gd MRI agents as there are enhanced effects on relaxivity, allowing for lower Gd concentrations to achieve contrast, whilst potentially imparting control over pharmacokinetics.
105. PH-RESPONSIVE AND BIODEGRADABLE NANOPARTICLES CAPABLE OF LOADING AND RELEASING SMALL-MOLECULE CARGO; MEGAN R. HILL, a Elliot M. Mackrell, a Brent S. Sumerlin; a Center for Macromolecular Science and Engineering, The George & Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, FL 32611, USA.

While pH-responsive materials have been extensively studied in the realms of biology and medicine, less attention has been given to the use of pH-responsive materials within agricultural science. Responsive nanoparticles have significant potential as vehicles for the site-specific delivery of pesticides and nutrients due to variations in pH, ionic strength, and other small molecule triggers within plants. We demonstrate the synthesis of biodegradable and, pH-responsive nanoparticles designed to capitalize on the higher pH of the phloem, the tissue that aids with transport of organic nutrients made during photosynthesis, compared to its surrounding environment.

Polysuccinimide (PSI), a precursor to biodegradable poly(aspartic acid) (PASP), was synthesized from the condensation of L-aspartic acid and functionalized with primary amines to form random structure amphiphilic copolymers. The copolymers formed stable nanoparticles in aqueous medium via nanoprecipitation and allowed for the fine-tuning of size and pH response based on the concentration prior to precipitation and degree of functionalization, respectively. Lastly, the nanoparticles were loaded with a model hydrophobic molecule, Nile Red, to demonstrate their potential for delivery of a guest compound.

106. TUNABLE SUPRAMOLECULAR HYDROGELS CROSSLINKED THROUGH BIO-INSPIRED METAL/LIGAND COORDINATION; MATTHEW S. MENYO, a Craig J. Hawker, b J. Herbert Waite, a Department of Biomolecular Science and Engineering, University of California, Santa Barbara, CA, USA; b Materials Research Laboratory, University of California, Santa Barbara, CA, USA.

The mussel byssal cuticle employs DOPA-Fe³⁺ complexation to provide strong, yet reversible crosslinking. Synthetic constructs employing this design motif based on catechol units are plagued by oxidation-driven degradation of the catechol units and the requirement for highly alkaline pH conditions leading to decreased performance and loss of supramolecular properties. We present a platform based on a 4-arm poly(ethylene glycol) hydrogel system which has been used to explore the utility of DOPA analogues such as the parent catechol and derivatives, 4-nitrocatechol (nCat) and 3-hydroxy-4-pyridinonone (HOPO), as structural crosslinking agents upon complexation with metal ions. HOPO moieties are found to hold particular promise, as robust gelation with Fe³⁺ occurs at physiological pH and is found to be
largely resistant to oxidative degradation. Gelation is also shown to be triggered by other biorelevant metal ions such as $\text{Al}^{3+}$, $\text{Ga}^{3+}$ and $\text{Cu}^{2+}$ which allows for tuning of the release and dissolution profiles with potential application as injectable delivery systems.

Figure 1: Cartoon highlighting translation of the strong, healable DOPA-$\text{Fe}^{3+}$ crosslinks of the cuticle of Mytilus californianus, and the structure of the 4-arm poly(ethylene glycol) (PEG) backbone with pendant catechol (Cat), nitrocatechol (nCat) and 3-hydroxy-4-pyridinone (HOPO) chelating moieties.

107. MESOSCOPIC STUDY OF SALT-RESPONSIVE POLYMERIC MICELLES: STRUCTURAL INVERSION MECHANISM VIA SEQUENTIAL ADDITION OF INORGANIC SALTS; César Soto-Figueroa, a Maria del Rosario Rodríguez-Hidalgo, b LUIS VICENTE; c aFacultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, México; bDepartmento de Ciencias Químicas, UNAM-Cuatitlán; cDepartamento de Física y Química Teórica, Facultad de Química, UNAM, Mexico.

The structural inversion mechanisms of salts-responsive polymeric micelles formed by poly(N-(morpholino)ethyl methacrylate)-b-poly(4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PMEMA-b-PSVBP) diblock copolymer in different saline environments were explored from a mesoscopic point of view using dissipative particle dynamics (DPD) simulations and coarse-grained models. The results of mesoscopic simulation reveal that the PMEMA-b-PSVBP copolymer can generate stable spherical micelles with a specific structural conformation of PSVBP-core and PMEMA-corona in a purely aqueous environment at room temperature. The structural inversion of these polymeric micelles takes place via the sequential addition of inorganic salts ($\text{NaBr} \rightarrow \text{Na}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4 \rightarrow \text{NaBr}$ and salts mixture of $\text{NaBr}/\text{Na}_2\text{SO}_4$) in the aqueous environment. Three structural inversion mechanisms were explored by means of mesoscopic simulations: (i) structural inversion mechanism via a micellar dissociation ($\text{NaBr} \rightarrow \text{Na}_2\text{SO}_4$), (ii) structural inversion mechanism via simultaneous ascent and immersion of polymeric segments ($\text{Na}_2\text{SO}_4 \rightarrow \text{NaBr}$) and (iii) structural inversion mechanism by means of a purely intermicellar fusion (salts mixture of $\text{NaBr}/\text{Na}_2\text{SO}_4$), the transitory stages of each structural inversion mechanism are described and analyzed in this document. The structural inversion mechanisms explored in this work are dependent on concentration and specific order in which the inorganic salts are added into the aqueous environment. The results obtained from these mesoscopic simulations can contribute to elucidate the structural inversion mechanisms of salts-responsive polymeric micelles and are consistent with available experimental outcomes.
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