ABSTRACTS FOR TECHNICAL SESSIONS

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CONTE CENTER FOR POLYMER RESEARCH
UNIVERSITY OF MASSACHUSETTS AMHERST

Structural Characterization of Biodegradable Poly(lactic acid)

Shuhui Kang and Shaw Ling Hsu, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

Biodegradable poly(lactic acid) is the only polymer approved by FDA for food packaging. Its' utility as fibers, films, or other three-dimensional objects is limited by the difficulty in relating molecular structure to the extremely rapid aggregation behavior. Using a combination of spectroscopic, thermal and diffraction techniques, we were able to characterize the nature of the molecular chain. Effects of configurational defects have also been examined. Our analysis showed that the rotational isomeric state reported in earlier work leads to a chain that is much more flexible than the experimental data suggest. We conclude that the tgt conformation in a 3_1 helix is the dominant one, which is consistent with a characteristic ratio of 12. It is also possible to show that the molecular structural parameters dictate the formation of the anisotropic structures found in drawn poly(lactic acid) films and the overall dimensional stability. Our analysis has also contributed to the development of on-line monitoring of orientation and crystallinity in commercial processes. A molecular understanding of heat setting to reduce film shrinkage is also proposed. Our data from films that were heat set while physically constrained suggest that amorphous phase relaxation does not occur during heat setting. Rather, the level of crystallinity increases substantially indicating that the cause of low shrinkage in the films was due to crystalline network formation rather than amorphous phase relaxation.

Novel Processing-Blending Techniques with Biodegradable Polymers

Stephen McCarthy, Department of Plastics Engineering
University of Massachusetts Lowell
Lowell, MA 01854-5046

Fibers and films with nanophase morphologies were investigated. Reactive processing methods were employed to form co-continuous, immiscible, compatible blends between poly(lactic acid) and other biodegradable polyesters. These blends included poly(butylenes succinate-co-adipate), poly(caprolactone), and poly(ethylene terphthalate) copolyesters. These co-continuous blends exhibited a dramatic increase in ductility and biodegradation rate as compared to poly(lactic acid). The formation of nano-layered films as well as sheath core nano-fibers and hollow fibers were investigated. The effect of morphology, crystallinity, and physical aging on mechanical properties and biodegradation were studied. In addition, the use of these fibers as braided scaffolding for tissue growth was carried out in collaboration with the University of Massachusetts Medical School.

Use of Unmodified Carbohydrates for the Cyclotetramerizaton and Polymerization of Dicyanoalkenes and Arenes

Daniel J. Sandman, Center for Advanced Materials, Department of Chemistry
University of Massachusetts Lowell
Lowell, MA 01854-5046

The issues related to the use of simple unprotected sugars and related compounds readily derived from them for chemical synthesis are discussed in the context of green chemistry. Many sugars are very cheap and their agricultural and natural origins ensure that they are renewable rather than depletable resources. Sugars are also nontoxic and their degradation products are innocuous. Our reactions are carried out in aqueous alcoholic solutions under mild conditions. General considerations that are relevant to the use of sugars and closely related compounds as selective synthetic reagents are discussed. The properties of sugars that make them potentially useful reagents for synthesis include their enhanced acidity relative to simple alcohols and their reducing properties. We are the first to observe that unprotected sugars can initiate polymerizations, and specific examples are drawn from dicyanoalkene and –arene monomers[1]. The polymerizations can result from either cyclopolymerization or polymerization at one of the two cyano groups in a monomer. In these experiments, phthalonitrile and its 4-methoxy derivative[2] lead to mixtures of the cyclotetramer phthalocyanine derivative and an oligomeric material. Qualitative mechanistic issues relating to the reducing properties of the hemiacetal linkage and the role of sugar alkoxides are discussed as well as the physical properties of the polymers obtained. A number of very similar reactions can be carried with no solvent. In green chemistry, the best solvent is no solvent. These reactions are presented and discussed with reference to the crystal structure[3] of the reactant where possible. *References:*

1. D.J. Sandman, M.A. Rixman, Z-H. Tsai, D. Wu, and I-B. Kim, *Polymer Preprints*, **41** (2), 1215-1216 (2000); *Macromolecules*, submitted (2001); Z-H. Tsai, Ph.D. Thesis, University of Massachusetts Lowell, 2000.
2. Z-H. Tsai and D.J. Sandman, *J. Porphrins and Phthalocyanines*, **5**, 564-568 (2001).
3. I-B. Kim, B.M. Foxman, J Njus, and D.J. Sandman, *Polymer Preprints*, **42** (2), 459-460 (2001) and to be published.

High-Performance Polymers and Blends from Cyclic Oligomers of Recycled Polyesters

William J. MacKnight, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

The growth in the commercial use of polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) for beverage containers, automotive parts, and other products has brought with it increasing pollution problems. We have been working for several years to develop economical and environmentally benign conversion methods to produce high value-added end products from waste polyesters. (Some of this research was carried out under NETI sponsorship). Recently we have succeeded in converting a variety of waste polyesters to cyclic oligomers and subsequently polymerizing them quickly and completely to high molecular weight products. The cyclic polyester oligomers have many good properties, such as low melt viscosity and a low melt temperature. These cyclic oligomers are readily polymerized to high molecular weight polyesters in the presence of initiators within a few minutes with no emissions. The material produced from these cyclic oligomers can exhibit properties even better than those of virgin polymer.

An application of polymers from cyclic oligomers with enormous potential for novel structures and materials is in blends with other thermoplastics. These blends may be either miscible or immiscible. One of the direct applications of cyclic oligomers that have been carried out to date is the preparation of miscible PBT/poly(vinyl butyral) (PVB) blends by in situ polymerization of cyclic PBT oligomer in the presence of polyvinyl butyral. PVB is an industrially important polymer widely used in laminated safety glass for automotive windshields. The in situ prepared blend of PBT/PVB has enhanced properties and the cause of miscibility is being studied. There are unique possibilities for in situ processing by combining polymerization of cyclic polyester oligomers with blending and these possibilities are being explored.

Synthesis of Biodegradable Polyesters

Steve Goodwin, Department of Microbiology
Morrill Science Center, University of Massachusetts Amherst
Amherst, MA 01002-5720

Polyhydroalkanoates (PHAs) are produced by a variety of bacteria as storage materials. PHA synthases catalyze the polymerization of hydroxyalkanoates using CoA derivatives of hydroxyalkanoic acids, HA-CoA, as substrates. PHA synthases have been classified as short chain length (scl) PHA synthases, which polymerize C3-C5 HA-CoA monomers, and medium chain length (mcl) PHA synthases, which polymerize HA-CoA with C6-C14 carbon atoms. The enzymes from the two types have very different structures even though they both are specific for short chain length substrates. The potential applications of functionalized PHAs range from flexible films and elastomers to biodegradable adhesives. Further chemical modification of the functional groups can lead to the production of water-soluble polymers and super absorbent hydrogels. Functionalized PHAs can be produced from agricultural substrates during bacterial fermentation. For example poly(β-hydroxyoctanoate-co-undecylenic acid) (PHOU) with defined olefinic pendant groups was synthesized by bacterial fermentation. These olefinic units were epoxidized to produce poly(β-hydroxyoctanoate-co-epoxyundecylenic acid) (PHOE). These functionalized PHAs were demonstrated to have biodegradability comparable to unsubstituted poly(β-hydroxyoctanoate). PHAs can also be synthesized *in vitro* using an enzymatic approach. The poly(3-hydroxyalkanoate) synthase from *Ralstonia eutropha* was purified and used for the *in vitro* synthesis of poly(3-

hydroxyalkanoates) from the coenzyme-A esters of [R]-3-hydroxy fatty acids such as 4-hydroxy-butyric acid and 3-hydroxy-propionic acid.

The microbial degradation of designed biodegradable plastics follows the same principles as the microbial degradation of natural biopolymers. More than half of the municipal solid waste stream in the United States consists of natural organic materials, such as food, yard waste, and paper that are generally considered to be biodegradable. These materials are susceptible to microbial degradation, especially in systems designed to enhance aerobic microbial activity such as compost. While there is great variability in the rate and extent of degradation of natural organic materials, their status as biodegradable materials is rarely questioned. On the other hand, the synthesis of plastics designed to be biodegradable, has led to important questions concerning the fate of these materials in the environment. Of immediate concern is the development of approaches to measure the rate of degradation of specific plastics in different compost environments. Laboratory-scale tests have the advantages of being easier to control and reproduce but are always only simulations of conditions in different natural environments. Full-scale compost tests may be more realistic but are often difficult to reproduce. Biodegradation needs to be viewed as a series of interactions between the microorganisms, the polymers, and the environments in which the biodegradation is occurring.

'Green Dyes' for the Textile Industry

Sukalyan Sengupta, Department of Civil and Environmental Engineering
Yu Zhou and Bal Ram Singh, Department of Chemistry and Biochemistry
University of Massachusetts Dartmouth
North Dartmouth, MA 02747

The textile industry produces and uses approximately 1.3 million tons of dyes, pigments, and dye precursors, valued at around $23 billion. At present, almost all dyes are produced synthetically, primarily because synthetic production can deliver dyes with a wide range of color shades and a high degree of color-fastness for a reasonable cost. However, the drawbacks of synthetic production of dyes include: (i) it requires many toxic compounds under very aggressive conditions, thus worker safety is a primary concern, (ii) the price of dyes is very sensitive to the price of petroleum since petroleum is the starting point for all dyes, (iii) it generates toxic and hazardous waste, the disposal of which is very expensive and cumbersome, and (iv) it can produce allergic reactions. If synthetic dye production can be replaced with bioengineered natural 'green' dyes at a comparable price, these drawbacks could be eliminated. Moreover, additional benefits would include: (i) after extraction of the dye, the residual biomass could be utilized for energy generation, and (ii) the natural dye might provide higher UV absorption by the fabric resulting in reduced incidence of melanoma.

We have been conducting research on extracting dyes from two natural sources: the American Cranberry (*Vaccinium macrocarpon)* and the fungal species *Curvularia lunata and Curvularia pallescens*. The American Cranberry (*Vaccinium macrocarpon)* fruits produce red anthocyanin pigments under appropriate light, temperature, water, and nutrient conditions. However, it is not economically viable to extract pigment dyes for commercial textile dyeing because the cranberry crop is an annual crop requiring substantial maintenance. We have therefore cultured tissues of cranberry under laboratory conditions, and have devised environmental conditions (light and nutrients) under which tissues produce the pigment. A large-scale production of the dye in this way could reduce the use of synthetic dyes. The fungal species *Curvularia lunata and Curvularia pallescens* can also be harnessed to produce dyes or dye intermediates. There are some indications that they produce a compound cynodontin, which can be used as a precursor for a variety of anthraquinone dyes. Pure cultures of *C. lunata* and *C. pallescens* were obtained from American Type Culture Collection (ATCC) and cultured under controlled conditions to produce cynodontin. We will present details of the culture media, environmental conditions, separation procedures, and our research findings to date.

Models for Green Design: PCA Formation and Polymer Flammability

Phillip R. Westmoreland, Department of Chemical Engineering
University of Massachusetts Amherst
157A Goessmann, Amherst MA 01003-9303

Good chemical models are necessary to design green processes and materials. These models may be qualitative or semi-quantitative used estimate trends of how some change in operating condition or material composition can affect performance. Two examples from our work show how design can be improved by a more specific modeling approach. Polycyclic aromatics (PCA, PCAH, PAH, PNA, etc.) are formed in fuel-rich combustion. They make up a class of pollutants that includes several carcinogens ranging in hazard from "mild" skin-cancer agents to dioxin. Molecular-beam mass spectrometry reveals how combustible gases are attacked by H, O, and OH free radicals and converted to H_2 and CO, which in turn are attacked and exothermically converted to H_2O and CO_2. Unburnt and newly formed hydrocarbons can form benzene and other aromatics by reactions increasingly understood to involve C_3H_3 and acetylene, growing to PCA's and soot. Our PCA measurements and modeling will lead to engineering models that can be used in combustor design.

A different target is clean production of new, fire-safe polymers. Nonflammable polymers, polymers that decompose without toxic products, and polymers that can be synthesized with mild solvents are all valid targets for green chemistry. Using qualitative and quantitative models of flammability, we have identified existing and new polymers that are ultra-fire-resistant. Among these is polyhydroxyamide, a polymer that when exposed to fire decomposes at about 200°C to form 10% water and 90% polybenzoxazole, a strong, inert thermoset. Also, compared to direct synthesis of PBO, PHA synthesis does not require strong mineral acids. From a longer perspective, the interplay of data and computational chemistry in both these tasks shows how chemical modeling can aid chemical engineers and materials scientists.

Green Approaches to Polymer and Surface Modification

Thomas J. McCarthy, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

Two approaches to polymer modification are discussed. One involves the bulk modification of semi crystalline polymers using supercritical carbon dioxide as a solvent. A second monomer is infused into the amorphous regions of the solid polymer substrate where it polymerizes to form a continuous blend with nanoscopic phase segregation. The other approach that is described involves solventless surface modification using plasma chemistry to prepare water repellant surfaces

Synthesis of Biodegradable Polymers Activated by Microwave Radiation

B. Koroskenyi, Department of Plastics Engineering
University of Massachusetts Lowell
Lowell, MA 01854-5046

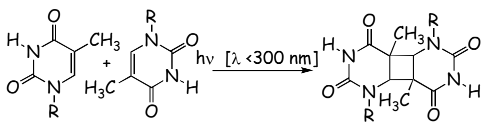
The application of a much more efficient energy source, microwave radiation, for the synthesis of biodegradable polymers has been demonstrated. The substitution of conventional heating with microwave energy offers a more economical and environmentally friendlier way to activate chemistry. The more efficacious energy utilization of reaction systems when using microwave radiation greatly reduces the reaction time, the energy input, and sometimes the amount of solvent. The latter can be completely eliminated in some cases. Such derivatization of polysaccharides by microwave radiation has been successfully carried out as carboxymethylation, cross-linking, acylation, and amination. The reactions were carried out in a conventional microwave oven. The reaction time in all cases was in the order of a few minutes to the order of hours in conventional methods. The yields were comparable to those obtained by conventional heating.

Hydrogen Bond Mediated Photo-Dimerization in Synthetic Analogs of DNA: Environmentally Benign Photoresists

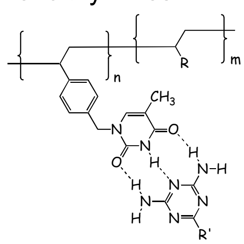
Lisa Lloyd-Kindstrand, Department of Chemistry
University of Massachusetts Boston
100 Morrissey Blvd, Boston, Massachusetts 02125-3393

Thymine, one of the four nucleotide base constituents of DNA, photodimerizes at wavelengths < 300nm. As pendant substituents of polymeric nucleic acid chains, this photocyclization reaction has been identified as a significant physiological event in both the cause and treatment of several afflictions. Synthetic polymers incorporating thymine have been investigated in order to exploit this process. This presentation will discuss the effect of hydrogen bonding on the photochemistry of polymeric thymines and environmentally benign applications of these systems will be illustrated.

Environmentally benign, water-soluble photoresists have been prepared. Highly efficient photosensitivity is observed.



Thymine and derivatives also participate in triple hydrogen bonding. It is possible to non-covalently link functional molecules to these polymeric thymines.



Catalytic Properties of Metal Oxides under Ambient Conditions

Michelle Foster, Department of Chemistry
University of Massachusetts Boston
100 Morrissey Boulevard, Boston, MA 02125-3393

The surface chemistry of metal oxides is important because of their wide use in catalysis as either supports or active components. Surface studies of oxides are challenging due to the intrinsic complexity of the substrate and the experimental difficulty of performing surface analysis on insulating crystals. Most published studies have been conducted under UHV conditions, even though this environment is not consistent with typical catalytic reactions. The ultimate goal of this study is to design synthetic transformations that occur under ambient conditions, while avoiding the use of organic solvents. Thin films of volatile reagents are adsorbed onto single crystal MgO in equilibrium with the vapor at carefully defined pressures and temperatures near ambient conditions. Using transmission infrared spectroscopy, film thickness can be monitored by recording the vibrational absorption of active transitions. Frequency shifts, bandwidths, and absorbance values are used to monitor surface reactions and interpret the structure of the interfacial region.

Peptide Structure In Thin Films Grown at Interfaces

Samuel P. Gido, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

Irregular amino acid sequence and three-dimensional assembly significantly complicate the selection of native protein conformation. Our work with silk fibroin and model genetically engineered polypeptides containing repetitive sequences focuses on conformation selection at two-dimensional fluid interfaces. In these simplified systems, the usual partitioning of hydrophobic and hydrophilic groups governs the structural assembly. The crystalline portion of the silk fibroin is built on the repetition of a simple hexapeptide sequence of $(\text{Gly-Ala-Gly-Ala-Gly-Ser})_n$. The air-water interface and various aqueous-organic, liquid-liquid interfaces are found to alter the beta-sheet structure of bulk silk, leading to the assembly of thin films containing a three-fold helical chain conformation. This occurs because the three-fold helical structure allows partitioning of hydrophilic and hydrophobic side chains in the crystallizable sequence to opposite sides of the interface while the beta-sheet does not. This interfacially directed structure, related hydrates and mesophases have been studied by TEM and electron diffraction under different interfacial conditions and in foamed solutions. Additional work correlating structure at interfaces to amino acid sequence has been conducted with model synthetic peptides with sequences derived from silkworm silk, spider silk, and collagen.

Engelhard TitanoSilicate-4 Membranes: Synthesis, Microstructure, and Their Use in Pervaporation and Gas Separations

Sankar Nair and Michael Tsapatsis, Department of Chemical Engineering
University of Massachusetts Amherst
159 Goessmann Laboratory, Amherst, MA 01003-9303

ETS-4 (Engelhard TitanoSilicate-4) is the first reported synthetic mixed tetrahedral/octahedral molecular sieve. Its discovery by Kuznicki at Engelhard Corporation was followed by the synthesis of other related materials with unique properties. In collaboration with Engelhard Corporation we have developed synthetic procedures for the fabrication of ETS-4 membranes and an overview of the current status of development and potential applications of these membranes is presented. First, some unique characteristics of the crystal structure of ETS-4 that allow tuning of the effective pore size and adsorption properties by ion exchange and dehydration at elevated temperatures is discussed. Secondly, the seeded growth technique that can lead to various microstructures (crystal orientation, degree of intergrowth) of ETS-4 films on porous alumina and titania supports is described. Finally, the performance of some of these membranes in water/alcohol separation by pervaporation is reported along with potential uses in gas separations.

Designing 'Green' Monomers for Radiation Curing: Challenges, Recent Accomplishments, and Possible Futures

Jacques Penelle, Xie Tao, Javid Rzayev, Shaw Ling Hsu, Andrei Stolov, and Kanad Das, Department of Polymer Science and Engineering, and Vincent M. Rotello, Department of Chemistry
University of Massachusetts Amherst
Amherst, MA 01003-4530

Polymer coatings are pervasive in our everyday life: they can be found as protective layers for furniture and automobiles, as well as durable films in advanced electronic devices, photolithography, and high-speed fiber optics. An increasing demand for polymer coatings has recently raised environmental issues that range from the toxicity and volatility of some monomers currently under use to the more difficult recycling of coated objects and long-term health problems associated with the progressive release of toxic residues into the environment. With this background in mind, our research group has been active during the last three years in the design of possible alternatives to acrylic- and methacrylic-based monomers. The long-term objective of this research is to identify suitable 'green' candidates that would maintain both acceptable polymerizabilities and suitable coating properties - such as hardness, clear finish, and good weathering properties - while minimizing the short- and long-term hazardous and toxicological features of currently used formulations. A systematic investigation of the influence of the alpha-substituents on acrylic monomers has identified several interesting candidates, including a family of coatings that display extremely good long-term adhesion to 'difficult' substrates such as noble metals and glass. The extensive character of our investigation has provided some clues on how the alpha-substituent affects the overall polymerizability of the monomer. This fundamental understanding of the structure-reactivity relationship can be of tremendous help in the rigorous design of the next generation of green(er) monomers.

Deposition of Metal Films from Compressed Carbon Dioxide: An Environmentally Benign Alternative to Metal Plating

D. L. Long, J. M. Blackburn, J. Lazorcik, and J. J. Watkins, Department of Chemical Engineering
University of Massachusetts Amherst
Amherst, MA 01003-9303

Electroless metal plating is used extensively in the electronics and metal finishing industries despite growing concerns over its environmental consequences and tightening regulatory controls. Typical aqueous plating solutions contain metal salts such as nickel or copper sulfate, toxic reducing agents such as hydrazine, formaldehyde and sodium hypophosphite and stabilizing agents. These plating and subsequent rinsing baths generate huge volumes of wastewater. Moreover, fugitive emissions from these systems pose health and environmental risks and can result in heavy metal contamination of ground water. In the absence of viable alternative deposition methods, the industry is presently focused on prophylactic measures including containment and remediation of spent baths. We have developed an alternative, environmentally benign method that obviates aqueous plating baths and toxic reducing agents. Here we report the deposition of adherent, high purity nickel, gold, copper and metal alloy films from supercritical carbon dioxide by the hydrogen reduction of organometallic compounds containing hydrocarbon ligands. The reaction products consist solely of the deposited metal and low molecular weight hydrocarbon decomposition products that can be easily stripped from the product stream or recovered for re-use. Since all by-products are soluble in CO_2, rinsing water is not required. Contaminated aqueous streams are thus eliminated and replaced by a benign effluent. Moreover, the nature of our deposition process renders distinct performance advantages relative to current practice. These include the ability to uniformly coat tortuous substrates, direct control of the composition of alloyed films and excellent adhesion to polymer substrates including polyimide without conventional surface preparations such as chromic acid etching.

Processing of Fibers, Films, and Laminated Composites Using Supercritical CO_2

Alan Lesser, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

Recently in our labs, a considerable effort has been applied to investigating the potential of using supercritical carbon dioxide as a processing aid in a variety of applications. New processes are discussed including drawing fibers in the presence of supercritical CO_2 (both the solid and melt state), welding laminated films, and fabricating new composites that demonstrate ultra-long-range order (nano to macro-scale) in terms of reinforcement. Key aspects emphasized in the presentation include the concomitant effects of stress state and plasticizing effect that supercritical CO_2 has on the amorphous and crystalline phases of material during deformation, as well as characterization of unique mechanical and physical processes of materials made with this environmentally benign process.

A Ring Fluorination Toolbox Using Fluoro-organometallic Building Blocks

G.B. Hammond, Q. Shen, Z. Wang, and Y. Lan, Department of Chemistry and Biochemistry
University of Massachusetts Dartmouth
North Dartmouth, MA 02747

Despite progress achieved in the syntheses of acyclic gem-difluorinated compounds, the construction of rings containing a CF^2 unit remains a challenge. A convenient synthesis of CF^2-containing cyclic, bicyclic or heterocyclic systems would facilitate the building of libraries aimed at designing enzyme-activated irreversible inhibitors and other biologically active species. If a vinyl CF^2 group were to become an intrinsic component of a substituted allene, diene or dienyne, the resulting compounds would be ideally suited for the construction of carbocycles because of the existing wealth of annulation and cycloaddition strategies. Our group's recent discovery of an environmentally benign synthesis of a r.t. stable fluoroallenylsilane indium has allowed access, for the first time, to densely functionalized gem-difluoroallenes (Wang, Z.; Hammond, G. B. J. Org. Chem. 2000, 65, 6547-6552.). We report an efficient synthesis of enynes, dienes, heterobicyclic and heterocyclic mono and difluoro functionalized derivatives using metal catalyzed, cross-coupling reactions.

Technical Session 4: Designing Less Toxic Materials

QCM-Based Detection of Harmful Ions in Aqueous Process Streams

Douglas W. Howie, Jr. and David Hoagland, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

Heavy metals and other ionic species must frequently be removed from aqueous process streams before release of these streams into the environment. Although various technologies such as ion exchange and reverse osmosis can successful remove such contaminants, a fundamental difficulty persists - how can contaminant removal be efficiently monitored on-line when regulatory thresholds are in the ppb and ppm range? The traditional monitoring method, conductivity, cannot discriminate between ambient salt species and harmful ions. In this project, we are investigating whether Quartz Crystal Microbalance (QCM) methods can allow rapid, inexpensive, selective, and sensitive detection of ions in aqueous media. The concept is to adhere an ion-sensitive layer to the gold surface of the QCM and use the exquisite mass sensitivity of this device to reveal how much contaminant is trapped within the layer. Various ion-sensitive layers have been considered. In each case, technical problems involving layer adhesion, ion transport, mechanical coupling to the QCM, and chemical stability must be solved. Because its release thresholds are relatively high, nitrate is the prototype ion of our study. We have been able to detect as little as 5 ppm of nitrate by embedding ion exchange functionality into the QCM-adhered layer. A poor theoretical understanding of QCM response when an attached mass is not a molecularly thin elastic film makes optimization of detection layers a difficult task.

Non-Covalent Derivatization: Pollution Prevention Using Molecular Recognition and Self-Assembly

Amy Cannon, Department of Chemistry
University of Massachusetts Boston
100 Morrissey Blvd., Boston, MA 02125-3393

In many sectors of the chemical industry a lead compound is often identified as having some behavior worthy of further exploration. To arrive at the physical and chemical properties specified by a particular application the synthetic organic chemist will traditionally modify the lead compound by altering functional groups within the molecule’s covalent framework. Structure-activity relationships are elucidated in order to determine the most effective molecular derivative for a particular application. The physical properties of the molecule (e.g., melting point, solubility, vapor pressure, and diffusivity) are thus manipulated. After a number of candidate molecules have been synthesized, they are then evaluated for performance within the specific application. A typical research and development program can involve the synthesis and evaluation of hundreds of derivative candidates. The environmental toll (e.g., organic solvent use, and generation of hazardous materials) and economic price (e.g., disposal costs and labor costs) of such a process is quite high. We describe a different approach to the manipulation of physical and chemical properties. Non-covalent derivatization is the specific application of the principles of molecular recognition and self-assembly to control the physical and chemical properties of a molecular species in which auxiliary molecules are added to modulate the interaction of the target molecules with each other and the surrounding chemical environment. This process is environmentally beneficial because of the reduction or elimination of conventional synthetic steps and the replacement of organic solvents with aqueous or solid state conditions. Along with applications currently being used in large scale manufacturing processes, some of the underlying molecular interactions are discussed.

Designing Less Toxic Materials: Reinforcement Properties of Biodegradable Polyesters in High Performance Polyurethanes

Amy M. Heintz, Daniel J. Duffy, and Shaw Ling Hsu, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

Incorporation of crystallizable polyesters into polyurethane formulations can simultaneously enhance mechanical properties and reduce the effective amount of isocyanate necessary. The polyesters were incorporated as a method of reinforcing the soft matrix, with attention to improving polyurethane stiffness while maintaining elasticity. Unlike other more traditional polymers, the crystallization behavior is highly dependent on the magnitude and specificity of intermolecular interactions. The barrier properties of these high performance polyurethanes can also be managed by adjusting the composition of polyester copolymers in the reacting system, reducing the amount of residual isocyanates in the final material. It has also been known that the phase equilibria of the various components determine the ultimate morphology formed. These polyesters added thus dictate the dispersion of water to enhance and control the formation of urea hard segment.

Enzymatic Polymerization of Amphyphilic Decyl Esters of D-Tyrosine for Use as Environmentally Benign Coatings in the Electronics Industry

Anastasios P. Angelopoulos, Department of Chemistry and Kenneth A. Marx, Department of Chemistry
University of Massachusetts Lowell
Lowell, MA 01854-5046

The surface coating properties of enzymatically polymerized decyl esters of d-tyrosine from aqueous solutions onto gold surfaces are investigated utilizing the complementary techniques of Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, and Quartz Crystal Microbalance. The aqueous-based coatings are of interest as environmentally friendly and cost-effective replacements for epoxy-based coatings currently employed in the microelectronics industry for both chemical protection and electrical insulation of gold-covered metallic conductors. Results with respect to polymerization pH, immersion pH, and immersion time are presented and compared to the ionization behavior of the monomers in solution obtained via potentiometric titration.

Understanding and Controlling the High-Temperature Exchange Chemistry of Cross-linked Rubbers - A Simple Method of Direct Recycling

Richard Farris, Jeremy Morin, Drew Williams, Amiya Tripathy, Dept. of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

In 1844, Charles Goodyear obtained a patent for the sulfur vulcanization of rubber. This invention created one of the most difficult materials to recycle, as these materials will not dissolve or melt. Interestingly enough, Goodyear recognized this problem and in 1853 he patented a process of grinding scrap-vulcanized rubber into a powder, adding small amounts of this powder into virgin uncross-linked rubber, and then vulcanizing the blend. Today, studies estimate there are roughly 2 billion scrap tires in U. S. landfills with more being added at a rate of over 270 million tires per year. History shows that these tires represent a serious fire and health hazard and that only a small percentage is recycled into rubber goods. Recently, a technique for recycling vulcanized rubber was re-discovered in our laboratory. In short, commercially available rubber powder made from scrap

tires can be “sintered” through the adhesion of rubber particles with only the addition of high temperature and high pressure. High pressure is required to force into contact all of the interfaces of these highly deformable powders. High temperature then triggers sulfur exchange chemistry that fuses the interfaces making a solid rubber mass. This method works for many types of rubbers including natural rubber and styrene-butadiene (SBR) rubber, the major rubbers used in tires. This technique could help solve one of mankind’s most difficult recycling problems, as it can yield a product with good physical and mechanical properties similar to that of many commercial elastomers (1.0 MPa modulus, 6.0 MPa Tensile Strength, 400% Strain to Break). Also, the powders can be blended with materials such as asphalt to create asphalt-modified rubbers with unique properties that could be used as adhesives and for roofing, waterproofing membranes, and road materials. The goal of our research is to understand, and thereby control, the fundamental mechanisms and chemistry of rubber particle sintering. We have discovered that small amounts of certain additives can greatly benefit this method of recycling, while others poison the process. Such information is vital if we are to optimize the processing conditions and properties of elastomers made by this method. It is also the key to formulating rubbers of the future to enable simple recycling by the high-pressure high-temperature sintering method.

Diblock Polyelectrolytes: Rheology and Applications in Waterborne Coatings

Surita Bhatia, Department of Chemical Engineering
University of Massachusetts Amherst
Amherst, MA 01003-9303

We present results on the rheology of amphiphilic diblock polymers in which the water-soluble block is a polyelectrolyte. These polymers self-assemble to form spherical micelles in aqueous solutions, and the micelles associate to create elastic, transparent gels at moderate polymer concentrations. We have used light scattering and small-angle neutron scattering to further elucidate the solution microstructure and quantify the intermicellar interactions. Finally, we discuss applications of these systems as water-based paints and coatings. The ability of block copolymers to self-assemble into ordered microdomains can be exploited to address current performance problems in coatings. We focus on two industrially relevant problems: the development of a waterborne coating to block tannin extraction from cedar siding, and the use of a block copolymer additive to reduce the need for spot-priming white pine boards.

Technical Session 5: Emerging Issues in Green Chemistry

Micro to Nanoscale Patterning Using Electric Fields

Zhiqun Lin, Tobias Kerle and Thomas P. Russell, Department of Polymer Science and Engineering
University of Massachusetts Amherst
Amherst, MA 01003-4530

The application of an electric field across an interface separating two polymers with different dielectric constants produces an electrostatic pressure, a force acting on the interface to enhance fluctuations and to align the interface parallel to the applied field lines. With homogeneous fluids, the surface and interfacial tensions oppose each other such that a fluctuation with a characteristic wavelength is amplified. Control over the wavelength can be obtained by varying the interfacial tension with block copolymers. Reducing the interfacial causes a reduction in the characteristic wavelength. This phenomenon has been used to replicate surface topographies with exceptionally high fidelity and represents a means of performing high-resolution lithography in a simple, direct manner without the use of any solvents.

Extraction, Preparation and Formulation of Eco-friendly Natural Dyes from Cranberry Fruits

B. R. Singh, Q. Fan, and Saurabh Bhalerao, Department of Chemistry and Biochemistry
University of Massachusetts Dartmouth
North Dartmouth, MA 02747

Fabric dyes used presently in industry are mostly synthetic compounds, which cause environmental pollution, both during synthesis and application, as is evident from the German ban on many commercial azo dyes, which is not desirable for the American chemical industry. Hence, there is a growing demand for 'green' chemicals, and plant and animal pigments are the best sources. The red dyes of cranberries are investigated for formulating dyestuffs, which can be useful for the industry. These dyes have recently been found to have therapeutic values against arterial diseases and cancer because of their anti-oxidant properties. Flavonols and anthocyanins are the pigments found in cranberry extract. They impart red color to the solution due to inter-molecular co-pigmentation. This increases the color intensity and causes the wavelength of maximum absorbance to shift towards a higher wavelength, generally known as a 'bathochromic shift'. Flavonols also have good UV-absorbance. We prepared the dye extract using the standard solvents of HCl, alcohol, and water. The red dye obtained belongs to the group of commercial acid-dyes and was applied to standard polyamide fibers like nylons and wool after proper pre-treatments of the fabric. The affinity and exhaustion relations have been determined using standard apectrophotometry techniques and our preliminary results suggest that this approach of using cranberry pigments for fabric dyeing is feasible.

Green Chemistry Efforts to Reduce the Use and Emissions of Lead and Dioxins

Paul Richard, Office of Technical Assistance, MA Executive Office of Environmental Affairs
251 Causeway Street, Suite 900
Boston, MA 02114-2136

Environmental regulations governing the use and distribution of raw materials present new challenges to the industrial materials scientist. The most recent regulations promulgated by U.S. EPA under EPCRA, and adopted by the Massachusetts Toxics Use Reduction program, will require a significant number of Massachusetts manufacturers to report the use and handling of compounds that have been designated as Persistent, Bioaccumulative, and Toxic (PBT) to federal and state regulators. The current list of PBTs includes lead, mercury, polycyclic aromatic compounds, and dioxins. These compounds are found in the manufacture of some widely used raw materials or occur as byproducts of various manufacturing processes. The PBT reporting thresholds are much lower than for non-PBTs and will therefore increase the number of small manufacturers required to comply with the regulations, thus adding to their environmental compliance costs. In an effort to help industries reduce or eliminate the use or discharge of these materials, while remaining competitive, the Massachusetts Office of Technical Assistance (OTA) is currently involved in several research efforts focused on two PBTs of significant concern – lead and dioxins.

Products such as plastics and rubber often contain lead compounds that act as stabilizers during the manufacturing process or as colorants. Lead has been used widely in many molecular varieties of plastics and rubber over the years, mainly for stabilizing chlorine-containing polymers. However, it may have been used in applications that did not require the performance of lead stabilizers or used for reasons other than its originally intended application. OTA has proposed several research projects to find alternatives to lead compounds or develop different manufacturing processes. The agency has worked with researchers at UMass Boston to characterize the surface of lead stabilized polymers using atomic force microscopy, and plans to continue the work with researchers at UMass Lowell. OTA is also working with UMass Amherst faculty and CUMIRP to start a new research cluster entitled Lead-Free Polymers. The goal of this group will be to develop new polymer systems that will ultimately eliminate lead from plastics and rubber products. Lastly, OTA and the Toxics Use Reduction Institute are working with suppliers of plastics and rubber additives to convince industry to switch from lead stabilizers to commercially available non-lead stabilizers where the properties of lead are not needed.

Dioxins have been identified as potent carcinogens and over the years have become widespread throughout the environment. Dioxins are formed by a variety of processes, such as the incineration of plastic products and the bleaching of wood pulp. Essentially, dioxins form when free chlorine comes into contact with partially reacted or fragmented organic molecules and as such, would be found in an incinerator, industrial processes using chlorine, or a municipal wastewater treatment facility. OTA is working with investigators at the Carnegie Mellon Institute on the development of catalysts, called TAML® activators, for the activation of hydrogen peroxide to accelerate the oxidation of organic compounds. With activation, hydrogen peroxide can achieve the

rates of reaction and sometimes the selectivity of chlorine-based oxidants. However, unlike chlorine-based oxidants, hydrogen peroxide does not produce dioxins. The initial objective is to use this technology to clarify textile and paper mill effluents by oxidizing the organic contaminants, including colorants, contained in the wastewater.

Green Chemistry: Towards Sustainable Materials and Processes

Ken Geiser, Department of Work Environment
University of Massachusetts Lowell
Lowell, MA 01854-5046

The concept of green chemistry is rich in opportunity, but it may easily be diluted in practice. If green chemistry is to succeed as a significant environmental benefit, it must meet and address four challenges. First, green chemistry must have a clear conceptual core of chemistry that is environmentally superior to conventional chemistries. This should involve at least: environmentally preferable feedstock or starting materials, environmentally sounder chemical processes, or more environmentally compatible products. Secondly, green chemistry must be attentive to the life cycle of materials and processes. Thus, environmentally sounder products that require environmentally hazardous starting materials or increase workplace hazards should not constitute green chemistry. Likewise, more environmentally benign chemical processes that require increased energy or resource consumption may not constitute green chemistry. Third, green chemistry should focus on sounder chemistry, not merely changes in processing technology. Thus, converting from one form of pollution control equipment to one that is more efficient at waste management should not be considered green chemistry. Finally, green chemistry needs to be tested in terms of biological and ecological outcomes. This means that chemists need to be able to explain the environmental benefits of green chemistry innovations in terms of human health and environmental systems.

Sustainability: Linking Education and Research Through Green Chemistry

John C. Warner, Department of Chemistry
University of Massachusetts Boston
100 Morrissey Boulevard, Boston, MA 02125-3393

Green chemistry is a revolutionary philosophy that seeks to unite government, academic, and industrial communities by placing more emphasis on tending to environmental impacts at the earliest stage of innovation and invention. This approach requires an open and interdisciplinary view of materials design, applying the principle that it is better to not generate waste in the first place, rather than disposing or treating it afterwards. Environmentally benign alternatives to current materials and technologies must be systematically introduced across all manufacturing applications. In some cases these environmentally benign, alternative technologies already exist and have been demonstrated to not only function as well as their less benign, traditional counterparts, but have also proved to be economically superior as well. If processes are designed that do not deal with hazardous materials, then the costs associated with the handling, transportation and disposal, as well as significant regulatory and environmental compliance costs can be reduced or eliminated. Unfortunately there are many applications where environmentally benign alternatives do not yet exist. In order to address this technological gap, scientists and non-scientists must learn the interconnectivity between the construction of materials and environmental protection. This awareness must begin as early as possible in education - as early as elementary school. Examples of how science education and an accelerated research agenda focusing on green chemistry can be accomplished through creative use of industrial, government and industrial resources is presented.