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# Abstract Book

**DIVERSE**
**InTeRaCTiONS**
**The Elements of Success**

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## Plenary Lecture: Ecology, Economy, and the Sea

### 1. Ecology, Economy and the Sea

**Jean-Michel Cousteau**, Ocean Futures Society, Santa Barbara, CA

For decades, environmental groups and industries have been portrayed as near mortal enemies with little or no dialogue to resolve disagreements. In some cases, this conflict was justified. But, in the 21st Century more is being achieved for the environment by finding common ground and working together to solve challenges. In this abstract the author describes the new dynamic among corporations, governments and environmental organizations that puts their mutual interests in the forefront of progressive public and economic policy.

## Advanced Materials for Portable Energy Devices

**Organizer:** Susan J. Babinec II Dow Chemical Company, Midland, MI

### 2. Studies of Fast Ionic Conductors using 6Li/7Li Solid-State 2D Exchange NMR

**Gillian Goward**, McMaster University, Hamilton, ON, Canada

Many cathode materials have been explored as alternatives to the classic layered transition metal oxide materials used in rechargeable lithium ion batteries. In particular, recent attention has focused on transition metal phosphates which have open-framework structures, facilitating high ionic conductivity. Here we present multidimensional solid-state 6Li/7Li NMR studies of the monoclinic Li3V2(PO4)3 material and several members of the electrochemically cycled materials. We correlate our results with related studies of the parent material.

### 3. "Understanding Surface Instabilities In Solid State Lithium Metal Batteries: An experimental and theoretical investigation'"

**Madan Somasi**[1], Susan Babinec[1], Richard Varjian[1] and David West[2], (1)The Dow Chemical Company, Midland, MI, (2)The Dow Chemical Company, Freeport, TX

Lithium dendrite formation resulting from electrochemical cycling of liquid based batteries is one of the critical limitations keeping lithium metal batteries from becoming commercialized. Dendrite formation is normally associated with slow mass transport of lithium ions to the electrode surface. In this paper we present results of our modeling of the instabilities of Li metal in a solid state system, and have shown that a certain amount of interfacial (and solid state) reconstruction is an inevitable result of the energetics of the any interface. Thus, only kinetic stabilizations are feasible. Lithium will always reconstruct when cycled.

### 4. Composite Cathode Structure/Property Relationships

Susan Babinec, Gregg Meyers, Andrew Talik, Staphanie Hughes and **Sean Tang**, The Dow Chemical Company, Midland, MI

Traditional engineering composite designs employ well established mechanical theories to optimize physical properties, such as modulus, impact strength, and flexibility. In contrast, electroactive composites have been developed with the sole objective of optimizing electrochemical properties– energy density, cyclelife, electrochemical stability, etc. These two composite design approaches must merge in order for batteries to reach their full potential, especially as they enter into newer, more physically demanding applications such as EV and HEV. This study is a preliminary comparison of properties achieved when using both the mechanical and electrochemical paradigms for preparation of electroactive composites. Results will be presented for composites based on the traditional materials of construction for a Li-Ion cathode – cathode particles of LiCoO2, binders of either poly(vinylidene fluoride) (PVDF) or polyethylene oxide (PEO), carbon black, and standard cyclic carbonate liquid electrolytes. In our model system, the structure-processing-property relationships will include compositional ratio, electroactive particle size, crystallinity of the binder, and type of processing (melt vs. solution casting). The microstructure of the composites is evaluated with electron microscopy (scanning and transmission electron microscopy), X-Ray diffraction, DSC, and surface analysis (atomic force microscopy, X-Ray photoelectron spectroscopy); the mechanical properties are evaluated via dynamical mechanical test, tensile test and nano-indentation; and the electrochemical properties via standard button cell tests. The learnings from this study should serve as preliminary guidelines for design and processing of similar cathode composites.

### 5. Highly Efficient Compact Power Sources Based on Direct Fuel Alkaline Energy Cells With Low Resistivity Membrane Materials

**John Shewchun**, Charles H. Winter and Ming-Chia Lai, Wayne State University, Detroit, MI

The electrical loads for next-generation systems such as battlefield sensors or unmanned aerial vehicles cannot be met with conventional sources such as batteries. We are examining a solution to this problem which uses an energy cell (commonly referred to as a fuel cell) as the electrical generator and hydrogen as the fuel or fuel carrier. While such compact power sources, using direct methanol as the fuel and a polymer electrolyte membrane (PEM) fuel cell, already exist in an experimental stage, methanol cross-over through the membrane and severe poisoning of the anode catalyst by reaction intermediates such as CO cause serious and unacceptable performance degradation (ref.1). In addition, high resistivity membranes used in PEM fuel cells lead to heat generation and low operating efficiencies. To avoid these deleterious effects, our concept uses an anion exchange membrane (AEM) alkaline fuel cell (AFC) and direct ammonia as an example of one of the hydrogen sources we will consider. The AFC technology is proven, since it has enabled the Apollo spacecraft to reach the moon and the Shuttle Orbiter to provide vital access to low Earth orbit missions such as the Space Station (ref.2). The critical facet of our approach is the development of low resistivity anion exchange membranes, which should increase the efficiency of the overall energy cell up to 90%, while minimizing heat generation. Successful development of our proposed energy cell system would allow the fabrication of small, highly efficient power sources that run on lightweight, high energy density fuels. These sources would provide sufficient energy to enable new munitions and battlefield systems.

1. C. Lamy, J. M. Leger, First International Symposium on New Materials Fuel Cell Systems, p. 296 (1995). 2. H. A. Wagner, “Space-shuttle fuel cell,” NASA Johnson Space Center, Houston, Handbook of Fuel Cells, Vol. 4, 1224, Wiley (2003).

### 6. An Overview of Hydrogen Sorption Measurements and their Impacts on Hydrogen Storage Materials Research

**Ned T. Stetson**, Hy-Energy LLC, Lake Orion, MI

There has been a dramatic rise in groups involved with research on hydrogen storage materials. This has been driven in part by the belief that hydrogen fuel cell technology may provide an answer to the problem being experienced with energy storage for portable electronics. The energy and power demands for portable electronics has been far outpacing advancement in battery technologies, fuel cells offer a decoupling of power generation from energy storage which might solve some of this problem. To accurately characterize a materials' capabilities for practical hydrogen storage however, it is critical to understand proper sorption measurements and their relation to practical application. This paper therefore reviews various analytical methods currently used for characterizing hydrogen sorption properties and includes how the results relate to practical application and pitfalls associated with the methods.

## Biotechnology I

**Organizer:** James Hand Dow Corning Corporation, Midland, MI
**Organizer:** Andreas Bommarius Georgia Institute of Technology, Atlanta, GA

### 7. Enzyme-Catalyzed Polymer Synthesis and Modification Reactions

**Richard Gross**, Polytechnic University, Brooklyn, NY

New and versatile biocatalytic methods were developed that offer mild and efficient options for polymer synthesis. Lipase B from *Candida antartica* (CALB) physically immobilized on hydrophobic macroporous resins was found to be remarkable catalysts for both ring-opening and step-condensation reactions. A new family of aliphatic polyesters was discovered using sugar alcohol building blocks such as *glycerol* and *sorbitol.* The step-condensation polymerizations proceed without solvent under mild conditions (e.g. 50 to $90^oC$). Lipase regioselectivity allows the direct copolymerization of polyols with a range of diols and diacids to give non-crosslinked products with weight average molecular weights up to 200 000. The mild reaction conditions allow the incorporation of chemically and/or thermally sensitive co-monomers such as silicones. Studies of fundamental aspects of reactions have lead to a better understanding of the polymerization mechanism and remarkable improvements in polymerization efficiency.

Cutinases from different micro-organisms were evaluated for polymer synthesis and modification reactions. It was discovered that cutinases also possess impressive catalytic activity for lactone ring-opening and diacid/diol polycondensation reactions. In addition to polymer synthesis, cutinases have been discovered that have interesting activities for polymer modification and hydrolysis. As examples, the results of cutinase-catalyzed hydrolysis of PET and de-acetylation of poly(vinyl acetate) will be presented. To improve cutinase activity for selected polymer hydrolysis reactions we have made significant progress in engineering the cutinase from *Fusarium solanii*.

Finally, the development of a new family of polyethylene-like polyesters based on long-chain w-hydroxyfattyacids or their corresponding lactones will be discussed. Alternative synthetic routes to monomers by chemical and biotransformations were studied. Progress in engineering lipase B from Candida antartica for polyester synthesis, and the physical-mechanical properties of poly(w-hydroxyfattyacids), will be discussed.

### 8. Better proteins faster: Tools and tricks for speedier protein engineering

**Karen M Polizzi**, Javier Chaparro-Riggers, Bernard W Loo, Anshul Dubey, Matthew J Realff, Jay H Lee, and Andreas S Bommarius, Georgia Institute of Technology, Atlanta, GA

In recent years, great strides have been made in the engineering of proteins for improved properties, from increased stability to changing substrate specificities. Still, there is room for improvement in the process of protein engineering in terms of ease, efficiency, and speed of development. Our laboratory seeks to improve the process at every stage possible. Researchers are no longer limited to rational design and combinatorial methods of engineering; a third class of methods, data-driven protein design have been developed for improving proteins more quickly.

The strategy of protein engineering begins with the choice of diversity generation method. Is there enough knowledge for rational design? Is a combinatorial approach better? If so, what are the biases inherent in different methods of combinatorial engineering? To answer this question, we have systematically evaluated two different classes of recombination methods: fragmentation-based protocols (DNA shuffling) and PCR-based methods (StEP, RDA-PCR) to determine the extent and type of bias in the crossovers generated by each. In other cases, we combine the advantages of rational design and combinatorial engineering, using bioinformatics and/or computational methods to develop semi-rational methods of engineering, such as our modified version of the consensus method for increasing stability and the identification of critical residues in proteins based on sequencing of both successful and unsuccessful variants. Finally, following the diversity generation step, we have developed methods for more efficient screening of the resulting library. Strategies, such as pooling multiple variants into the same well for the first stage of screening, can increase assay throughput and lead to the identification of more and different winning variants in less screening time that traditional methods. Examples from various projects ongoing in our laboratory will be provided to highlight our strategies for increasing the efficiency of protein engineering.

### 9. Biocatalytic Transformation of Aryl Silanes using Aromatic Dioxygenases

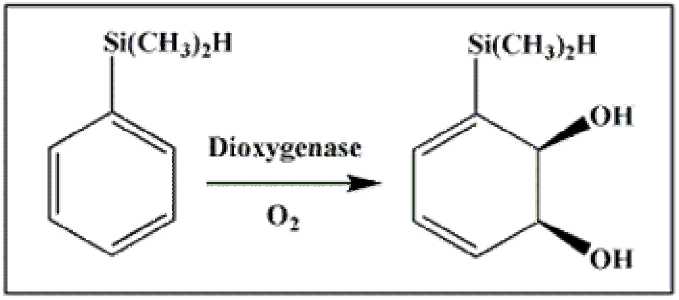
**Wyatt C. Smith**[1], Joseph C. McAuliffe[1], Gregg M. Whited[1], Tom H. Lane[2] and Karl Sanford[1], (1)Genencor International, Palo Alto, CA, (2)Dow Corning Corporation, Auburn, MI

Aromatic dioxygenases are a well-characterized class of enzymes that catalyze the *cis*-dihydroxylation of a diverse range of aromatic substrates.[1] Owing to their high efficiency and enantioselectivity (usually >95%ee), these enzymes are commonly exploited in a biocatalytic route to prepare useful *cis*-diols as chiral intermediates for organic synthesis. We describe here an extension of this methodology to create a group of silicon-containing *cis*-diols directly from aryl silanes.

Over 25 commercially available aryl silanes were screened as dioxygenase substrates by contact with whole cells expressing either toluene dioxygenase (TDO) or naphthalene dioxyenase (NDO), and by the DDT-degrading organism *Ralstonia eutrophus* A5. Under the conditions employed, six of these compounds were shown to be efficiently and stereospecifically converted to the corresponding diols by TDO in >98% ee.

Similarly, these compounds could be converted in a second biocatalytic step to silicon-functional catechols by treatment with cells expressing the enzyme *cis*-diol dehydrogenase. These silicon-containing chiral *cis*-diols and catechols represent a new class of compounds having potential application in the synthesis of fine chemicals and pharmaceuticals, enantioselective separations, and optical materials.

1. Hudlicky, T.; Gonzalez, D.; Gibson, D. T. *Aldrichimica Acta* **1999**, *2*, 32.



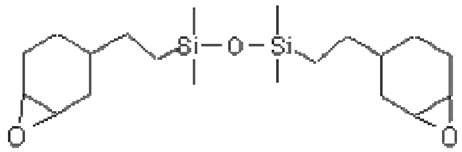
### 10. Chemoenzymatic Synthesis of Epoxy-Functional Silanes and Siloxanes

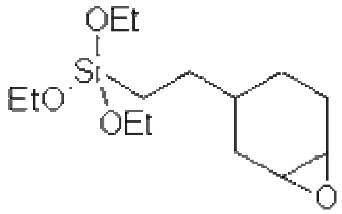
**Margo L. McIvor**[1], Kurt Brandstadt[1], Jim Hand[1], Hahn Vo[1], Thomas Lane[1], Don Takehara[2], Frans van Gastel[3] and Rafael Sala[3], (1)Dow Corning Corporation, Auburn, MI, (2)Taylor University, Upland, IN, (3)Genencor International, Inc., Palo Alto, CA

The synthesis of epoxy-functional silanes and silicones was studied as an example of biotransformation, where bioprocessing is used to make compounds that are difficult or expensive to make using conventional chemistry.  A single-pot, bio-assisted process was developed where an enzyme (lipase) was used to catalyze the formation of peracetic acid from ethyl acetate and hydrogen peroxide.  Subsequently, alkenyl-functional organosilicon molecules dissolved in the ethyl acetate were chemically epoxidized by the peracetic acid.  Finally, the chemoenzymatic by-products (acetic acid and ethanol) reacted to reform ethyl acetate and water.  The reaction for an internal alkene was completed in less than three hours at 50C.  This technology was used to produce epoxy-functional siloxane endblockers and polymers for radiation cure coatings, as well as epoxy-functional cyclic adhesion promoters and a trialkoxysilane coupling agent.

The ability to epoxidize an alkoxysilane without condensation in the presence of water was a surprise.  However, the biocatalytic rate and mild reaction conditions promoted the successful formation of the target functional group.  The reactions were scaled-up in a one-liter reactor to provide products to assess applications within the Paper Coatings and Electronics business functions.

Example molecules include





### 11. Biomimetic $S_x^{2-}$ Synthesis of Pentathiabenzocycloheptene-1,2-diols and Thianthrene Tetraols from Ortho-benzoquinone

**David Aebisher**, Edyta Brzostowska and Alexander Greer, CUNY Brooklyn College, Brooklyn, NY

We have undertaken a biomimetic synthesis of polysulfanes using catechol o-benzoquinone as a model for dopamine o-benzoquinone. Inorganic polysulfanes (H2Sx) add to o-benzoquinone at the 3 or 4 position to form hydropolysulfidocatechols that ultimately give rise to 3-mercaptobenzene-1,2-diol, 4-mercaptobenzene-1,2-diol, pentathiabenzocycloheptene-1,2-diol, and thianthrene tetrols. The regiochemistry of attack is found to be pH dependent. Mechanistic evidence will be presented for formation of these products.

## Catalysis I - Olefin Catalysis and Plastics Materials

**Organizer:** Shaoguang Feng Dow Chemical Company, Midland, MI
**Organizer:** Eric E. Stangland Dow Chemical Company, Midland, MI

### 12. Mechanistic aspects of metallocene-catalayzed alkene polymerization

**Clark R. Landis** and Matthew D. Christianson, University of Wisconsin-Madison, Madison, WI

Determination of the mechanism of metallocene-catalyzed alkene polymerization is complicated by general uncertainties concerning the number of active sites, the overall speciation of the catalyst, the strong influence of relatively rare events such as stereo- and regio-errors, and the extremely fast rates exhibited by extraordinarily sensitive catalysts. Recent progress in this area has been enabled by new methods for determining active site concentrations, novel instrumentation, and direct observation of catalyst intermediates and time-dependent concentrations using NMR spectroscopy. Special focus in placed on the changes that occur when the anion is made less-coordinating and the potential impact of metallocenium-allyl formation during the catalytic reactions.

## 13. Synthesis of a series of metal complexes from two novel multi-dentate ligands

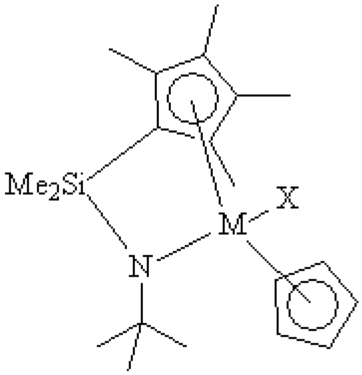
**Muhammad Naeem**, Meghann Mouyianis and Mark Benvenuto, University of Detroit Mercy, Detroit, MI

The following ligands: N-Pyridin-2-ylmethyl-N'-(3-tetradecyloxy-propyl)-propane-1,3-diamine (DA18-Py), and N-Pyridin-2-ylmethyl-N'-{2-[2-(2-{2-[(pyridin-2-ylmethyl)-amino]-ethylamino}-ethylamino)-ethylamino]-ethyl}-ethane-1,2-diamine (N8), have been synthesized via the Schiff's base condensation of 2-pyridine carboxaldehyde and the corresponding amine, followed by subsequent reduction. These ligands are isolated as hydrochloride salts. Further addition of metal salts such as Zn2+, Al3+, Hg2, Fe2+ and Ru3+ afford the mono-metal – ligand complexes. All complexes are characterized by multi-nuclear NMR, and by GC-MS or LC-MS when possible.

## 14. Preparation of monocyclopentadienyl metal complexes by nucleophilic substitution of bis(cyclopentadienyl) metal complexes

**David R. Wilson**, The Dow Chemical Company, Midland, MI

A new class of constrained geometry group 4 complexes (Zr and Ti) containing a second cyclopentadienyl group has been discovered. The non-chelated cyclopentadienyl group can be displaced by LiR nucleophiles to yield monocyclopentadienyl derivatives. Interconversion between Ti(III) and Ti(IV) oxidation states proceeds easily and in high yield. Olefin polymerization studies have been carried out using the new complexes as catalyst precursors.



M = Ti, Zr
X = Cl, Me, o-dimethylaminobenzyl

## 15. Improved Catalysts for Ethylene-Styrene Interpolymers

**Francis J. Timmers**, Ravi Shankar and Daniel J. Arriola, The Dow Chemical Company, Midland, MI

Ethylene-styrene interpolymers are new thermoplastic materials discovered and developed by The Dow Chemical Company. Improvements in catalyst polymerization performance were necessary for a commercially viable offering of these materials. This paper will present some key catalyst development milestones in the discovery process.

### 16. The Use of High Throughput Techniques for Catalysis and Materials R&D

**David R. Neithamer**, The Dow Chemical Company, Midland, MI

Combinatorial chemistry was introduced 10-15 years ago in the pharmaceutical and agricultural research arenas to speed the discovery of new drugs and bioactive molecules. Typically thousands of molecules were produced daily in small quantities and screened against an optical binding assay such as colorimetry or fluorescence for a digital response to detect a “hit”. Within the last 6-7 years, industrial, academic, and government labs have begun to apply novel, high throughput research (HTR) techniques to solve various catalyst, formulation, and materials related problems. Unlike the combinatorial approach, catalyst and materials discovery research requires the preparation of more material and screening for multiple responses. Furthermore, experimental design must be used to maximize understanding since the throughput is limited to several hundred reactions and screens per day. Within Dow, we have begun to tackle a variety of internal projects and provide rapid, meaningful, and often surprising results to the sponsoring business units. This seminar will describe some of our current HTR tools, methodology, and analytical screening capabilities and highlight several successful projects related to olefin polymerization.

## Coatings Technology I

**Organizer:** Theodore Provder Eastern Michigan University, Ypsilanti, MI

### 17. Chromate-free corrosion protection of Al alloys by metal-rich coatings based on Mg pigments

**Gordon P. BIERWAGEN**, Dante Battocchi and Dennis E. Tallman, North Dakota State University, Fargo, ND

A new class of protective coatings has recently been developed within a basic research program at NDSU sponsored by the Air Force Office of Scientific Research (AFOSR) that addresses one of the greatest material needs of the Air Force (AF) and all other users of high-strength aircraft alloys. These coatings have been described as Mg-rich primer coatings in a manner analogous to the Zn-rich primer coatings commonly used in the protection of steel. Mg is too reactive to interface directly to the environment, but when imbedded in a binder matrix, it provides Cr-free protection of alloys such as AA 2024 T-3 for which SrCrO4-pigmented primers and acid chromate-based metal pretreatment baths currently are required. These Mg-rich primers along with high performance aircraft polyurethane topcoats have given in excess of 6000 hours of protection to AA 2024 T-3 in ASTM B-117 salt fog exposure. The cathodic protection has been verified by Open Circuit Potential (OCP) measurements (the free corrosion potential, Ecorr) that the metal substrate takes when it is in contact with the Mg-rich primer) and potentiodynamic scans. Scanning Vibrating Electrode Technique (SVET) measurements at freshly scratched surfaces of AA 2024 T-3 immersed in electrolyte solution show the metal surface changing from anodic to cathodic within a short time after the free surface is exposed. Scanning Electrochemical Microscopy (SECM) indicates a depletion of oxygen near the Al alloy substrate in electrolyte solution when the alloy is connected to the Mg-rich primer, with a concomitant pH increase. This primer, when used without any chromate pretreatment and top-coated with a standard high performance AF aircraft topcoat, out-performs the current system, indicating one of the most severely polluting coatings systems in present use can be eliminated based on new, superior technology.

### 18. Characterization and Performance of new Zr-Polymer Conversion Coating for Aluminum and its Alloys

**Jianping Liu**, Bruce Goodreau and Bill Fristad, Henkel Technologies, Henkel Corporation, Madison Heights, MI

Chromate conversion coatings on aluminum surfaces offer good protection against corrosion and excellent adhesion to organic paints. However, hexavalent chromium is carcinogenic and hazardous to human health and the environment. A new non-chromate conversion coating has been developed for aluminum and aluminum alloys. This non-chromate conversion coating, consisting of zirconium oxide and polymers showed performance equal to chromate conversion coatings. The characterization of the new conversion coating on aluminum surfaces by SEM, EDX, and XPS, as well as its performance in various accelerated tests will be presented.

### 19. Nanoceramic Pretreatment: Simple, Effective Corrosion Resistant Pretreatment for all Metal Substrates

Jeng-Li Liang, **Bruce Goodreau**, Todd Bryden and William E. Fristad, Henkel Co., Madison Heights, MI

Phosphate conversion coatings have been widely used on metal substrates where corrosion protection is important. Environmental regulations are continuously reducing the levels of phosphate compounds permitted in the effluent from metal finishing processes. This paper presents a new nanostructured metal oxide (nanoceramic) coating that provides advantages over phosphate-based conversion coatings in terms of cost, simplicity, corrosion protection, and environmental concerns. The formation of the nanoceramic coating, coating morphology, and its corrosion performance will be discussed.

### 20. Novel Autodepositing Epoxy/Acrylic Coating Process

**Omar L. Abu-Shanab**, Henkel Corporation, Madison Heights, MI

Autodeposition is an immersion, direct-to-metal process that coats substrates by a chemical reaction between an aqueous paint dispersion and the base metal. This paper describes the development of a new generation epoxy/acrylic waterborne coating system, which combines the positive anti-corrosive properties of an epoxy with the good film formation characteristics of an acrylic latex. The new autodeposition technology has been cross-utilized in the automotive industry as a stand-alone coating layer and as a primer for general industrial applications. A technology description, chemistry, and performance attributes including corrosion and physical characteristics will be presented.

## Environmental Challenges - Issues & Solutions I

**Organizer:** Sudarsanan Varaprath Dow Corning Corporation, Midland, MI
**Organizer:** Shihe Xu Dow Corning Corporation, Midland, MI

### 21. Eco-Nano: The Impact of Engineered Nanomaterials on the Environment

**Vicki Colvin**, Rice University, Houston, TX

Traditionally, nanotechnology has been motivated by the growing importance of very small (d < 50nm) computational and optical elements in diverse technologies. However, this length scale is also an important and powerful one for living systems. We believe that the interface between the ‘dry' side of inorganic nanostructures and the ‘wet' side of biology offers enormous opportunities for medicine, environmental technologies, as well as entirely new types of nanomaterials. As part of our work on the potential biological applications, we also consider the unintended environmental implications of water soluble nanomaterials. Given the breadth of nanomaterial systems, we use a carefully selected group of model nanoparticles in our studies and focus on natural processes that occur in aqueous systems. We characterize the size and surface-dependent transport, fate and facilitated contaminant transport of these engineered nanomaterials. Models from larger colloidal particles can be extended into the nanometer size regime in some cases, while in others entirely new phenomena present themselves.

As an example of biological interfaces with nanoparticles, we examine the interactions of a classic nanomaterial, C60, with cellular systems. While the water-suspendable nano-C60 nanocrystal is apparently cytotoxic to various cell lines, the closely related fully hydroxylated, C60(OH)24, is non-toxic, thus producing no cellular response. Time permitting, we will examine another example system demonstrating that functionalized single-walled carbon nanotubes are non-toxic to cells in culture. More specifically, as the functionalization density of the SWNT increases, the nanotube becomes more inert to cultures.

### 22. Ionic Liquid High Temperature Gas Sensors

**Lei Yu** and Xiangqun Zeng, Oakland University, Rochester, MI

Identifying and correcting emissions from high-polluting vehicles require small sensors working at high temperatures to monitor pollutants in exhaust gas or leaking fuels. An ionic liquid piezoelectric gas sensor was demonstrated for detection of polar and nonpolar organic vapors at high temperature with fast linear and reversible response. We demonstrate that the IL high temperature piezoelectric gas sensor using phosphonium dodecylbenzene-sulfonate as sensing material works from room temperature to as high as 200 oC. Linear relationship of the totally reversible sensor response to the concentrations of vapor was obtained over the 0% to 100% saturation vapor pressure range. The detection limit could reach as low as 7 mg/L of ethanol at 120 oC.

## 23. Organosilicon Compounds in Ambient Air of the Great Lakes Basin

**Sean M. Backus**, John Kraft, Derek C.G. Muir and Mehran Alaee, Environment Canada, Burlington, ON, Canada

Silicone fluids possess many desirable properties, such as low surface tension, water repellency, thermal and chemical stability, resistance to ultraviolet radiation and presumed biological inertness. These desirable properties have led to their extensive use in industrial and domestic applications, including use as anti-foaming and release agents, polishes for automobiles and as cosmetic additives. Silicon is present in the Earth's atmosphere as a consequence of several processes including the release of Si compounds from anthropogenic sources, but little information is available on airborne Si compounds of anthropogenic origins. In this study ambient air samples from the Great Lakes Basin were collected by sorbent tubes for the determination of concentrations of volatile organosilicon compounds. Samples were analysed by thermal desorption followed by a GC–MSD technique for compound identification and quantitative analysis. The cyclic siloxanes hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) were determined in the samples along with the linear siloxanes hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD2M), and dodecamethylpentasiloxane (MD3M). Spatial distributions and analyte concentrations will be discussed.

## 24. Octanol-Air Partition Coefficients of Volatile Methylsiloxanes and Their Implication for Long Range Transport

**Shihe Xu** and Bruce Kropscott, Dow Corning Corporation, Midland, MI

Octanol-air partition coefficient (KOA) is a key parameter used to predict the potential for long range transport (LRT) for volatile and semi-volatile organic compounds. Any compound with log KOA between 6.5 and 10 has a tendency to be widely distributed in a remote environment far from the source through global distillation. Despite the enormous importance of this parameter, KOA values or methods suitable for their determination are not available for volatile methylsiloxanes (VMS), especially at the environmental relevant concentrations. In this study, an analytical method was developed for simultaneous determination of log KOA of multiple VMS at low concentrations in a

mixture. Using this method, log KOA values were determined for common VMS including hexamethyldisiloxane, octamethyltrisiloxane, docamethyltetrasiloxane, octamethylcyclotetrasiloxane and docamethylcyclopentasiloxane. It was found that KOA values of VMS range from 2.8 to 4.8 at room temperature, well below the cutoff value of 6.5. In addition, they are much less dependent on temperature than most organic compounds of similar molecular weights. Statistical analysis reveals that more than 99% variation in measured log KOA values for VMS could be attributed to the boiling point and equilibrium temperatures. Judged by these data, all the tested VMS have little potential for LRT due to lack of back-deposition to the surface media of a remote environment.

### 25. The Electrochemical Remediation of Atrazine Using Boron-Doped Diamond Electrode on Ti Substrate

**Yang Song** and Greg M. Swain, Michigan State University, East Lansing, MI

Electrically conducting diamond thin films provide scientists and engineers with an entirely new type of electrode material that meets the requirements for a wide range of applications. Boron-doped diamond thin film coated on Ti (diamond/Ti) was found to be a dimensionally stable anode material that supported the anodic degradation of the herbicide, atrazine to $CO_2$. The film morphology and microstructure were investigated by scanning electron microscopy (SEM), Raman spectroscopy, and X-ray diffraction (XRD). The general electrode activity was probed by cyclic voltammetry using $Ru(NH_3)_6^{3-/2-}$ and $Fe(CN)_6^{3-/4-}$, both in 1 M KCl. The stability of the diamond/Ti electrode was evaluated during anodic polarization in 0.1 M $H_2SO_4$. The diamond/Ti electrode exhibited a stable response over time, good activity for these two redox systems and excellent morphological and microstructural stability during the anodic polarization. The electrooxidative degradation of atrazine was investigated by bulk electrolysis at constant current density. The degradation was reproducible from film-to-film and quite stable long-term for a given electrode. For example, the diamond/Ti anodes could be used for months without loss of performance. It was found in radio labeling studies that 81% of the $^{14}$C-labeled atrazine could be oxidized to $^{14}CO_2$ within an electrolysis period of 2 hours. The results further portend that dimensionally stable diamond anodes are useful materials for the electrochemical treatment of contaminated water.

## Optoelectronics & Photonics - Polymers, Devices, and Applications I

**Organizer:** Jon V. Degroot Dow Corning Corporation, Midland, MI
**Organizer:** Ann W. Norris Dow Corning Corporation, Midland, MI

### 26. Doping semiconductor nanocrystals

**David J. Norris**, University of Minnesota, Minneapolis, MN

Doping - the intentional introduction of impurities into a material - is fundamental to controlling the properties of bulk semiconductors. The prospect of new technologies has motivated efforts to dope semiconductor nanocrystals since their discovery two decades ago. Despite some successes, many of these efforts have failed, for reasons that remain mysterious. For example, Mn can be incorporated into nanocrystals of CdS and ZnSe, but not into CdSe - despite comparable bulk solubilities near 50 percent. These difficulties, which have hindered development of new nanocrystalline materials, are often attributed to "self-purification," an allegedly intrinsic mechanism whereby impurities are expelled to the nearby surface. We propose instead that doping is controlled by the initial adsorption of impurities on the nanocrystal surface during growth. We find that adsorption - and therefore doping efficiency - is determined by three main factors: surface morphology, nanocrystal shape, and surfactants in the growth solution. Calculated Mn adsorption energies and equilibrium shapes for several nanocrystals lead to specific doping predictions. These are confirmed by measuring how the Mn concentration in ZnSe varies with nanocrystal size and shape. Finally, we use our predictions to incorporate Mn into previously undopable CdSe nanocrystals. This success establishes that earlier difficulties with doping are not intrinsic, and suggests that a variety of doped nanocrystals - for applications from solar cells to bioimaging - can be anticipated.

### 27. Photosensitive organogermanosilicon polymers

**Nina Popova**, SSC GNIIChTEOS, Moscow, Russia

We worked out the method for production of phenyl-substituted polygermanosilanes and polygermanocarbosilanes through Wurtz-Kipping reaction by the condensation of dichlorophenylsilanes and dichlorodiphenylgermane mixtures with ultra fine sodium suspension. The using of high effective sodium suspension permits to prepare perphenylated polysilanes, polygermanes and mixed polygermanosilanes with a good yield (not less than 83%). The influence of the side organic substitutions nature on the yield, structure and chemical composition of produced polymer derivatives have been investigated in detail by methods of 1H, 13C, 29Si NMR, IR, UV spectroscopy, chemical and fluorescent analysis. The carrying out of the reaction in a presence of hydride-derivative GeH groups.≡Si-H and ≡silanes permitted to yield the polymers with an active Using of vinylsilanes in an initial mixture we produced three-dimension high-branched polygermanocarbosilanes. The UV-vis absorption maximum peaks of the resulting polymers in THF solution appeared in the wavelength range of 300-375 nm. Upon photoexitation with light of wavelength 320-380 nm their photoluminescence spectra exhibited an emission maximum peak around 380-470 nm, corresponding to blue light emission. H, Me, Vin Ph-substituted polymers and were studied by methods of exclusion chromatography and thermogravimetric researches. It was investigated the possibility of polygermanocarbosilane preparing by means of polygermanes and mixed polygermanocarbosilanes conversion under action of high temperature and UV-irradiation. We found out the particularities of both Si-Ge and Ge-Ge bonds dissociation reactions as well the formation of new Si-C and Ge-C links.

### 28. Optoelectronic properties of Alq3 based OLEDs as a function of temperature from 10 to 300 K

**Ajith DeSilva**, Hans-Peter Wagner, Robert A. Jones, Weixin Li and Andrew J. Steckl, University of Cincinnati, Cincinnati, OH

The photoluminescence (PL) of Alq3 films as well as the electroluminescence (EL) and current-voltage (I-V) characteristics of Alq3 based OLED structures are investigated as a function of temperature between 10 and 300 K. With increasing temperature the PL spectrum of Alq3 films is shifted to lower energy and the PL reveals a maximum intensity at 180 K. The observed behavior is tentatively explained by a thermally activated formation of self-trapped excitons in the nanocrystalline Alq3 film. The temperature dependent I-V measurements in Alq3 OLEDs reveal a trap charge limited current behavior with characteristic trap energy of 53 meV. The OLED luminescence saturates at 10,000 cd/m^2 (V = 15 V) at room temperature. The temperature dependent EL is compared with the PL of the Alq3 film. The EL spectrum reveals a similar temperature dependent shift as the PL of Alq3 films. In contrast to the PL intensity the EL intensity peaks at 260 K. However, the EL efficiency (at constant forward bias of 8 V) shows a maximum of 2.2 cd/A at 180 K. The similar temperature dependent behavior of the PL and the EL efficiency is again attributed to the formation of self-trapped excitons within the Alq3 layer.

### 29. Si-based materials for organic light emitting diodes

**Toshio Suzuki** and David Witker, Dow Corning Corp., Midland, MI

Organic Light Emitting Diode (OLED) is regarded as one of the most promising technologies for flat panel displays, flexible displays and solid state lighting. OLED is already adopted for small display applications such as mobile phones and digital camera finders and the sales are growing very rapidly. OLED is characterized by its simple structure, very small thickness (less than a micron for active layers), no need for back lights, natural color, wide viewing angle, low energy consumption, etc.

Many organosilicon materials have been proposed for OLED in various functions. Examples include: siloles for light emitting and electron transport layers, self-assembled silanes for hole injection layers, polysilanes and polysiloxanes for hole transport layers, organosilanes for precursors of CVD barrier coatings, aromatic silanes for host materials for phosphorescent light emitting layers. Si-based materials show unique characteristics and enhance device performance in these applications. The talk will review these technologies and discuss the potential of Si-based materials in this new and exciting area.

### 30. Molecular modeling of water diffusion in amorphous SiC

**Haiying He**[1], Mrinalini Deshpande[1], Richard Brown[1], Ravindra Pandey[1] and Udo C. Pernisz[2], (1)Michigan Tech University, Houghton, MI, (2)Dow Corning Corporation, Midland, MI

The diffusion of water in amorphous SiC was investigated by molecular modeling methods. It was assumed that the structure of a-SiC at the molecular level can be described by a model that takes into account a distribution of cage structures which consist of SiC units forming n-member rings from a suitable precursor in a chemical vapor depostion process. Electronic strucure calculations are then performed to determine the energy barrier that the water molecule encounters when it penetrates through SiC rings of various sizes. It has been found that along its diffusion path through the SiC network the water molecule neither breaks up nor attaches itself to the SiC network and the energy barrier for diffusion depends mainly on the local SiC ring topology.

## Polymer Characterization I - Characterization of Polymer Branching

**Organizer:** Patrick B. Smith Dow Chemical Company, Midland, MI

### 31. Molecular Topology-Based Polymer Separations

**David M. Meunier**, Patrick B. Smith and Ted M. Stokich, The Dow Chemical Company, Midland, MI

Control of molecular architecture in polymeric systems and in particular, long chain branching (LCB) architecture, is an area of considerable interest in materials science because molecular architecture can have a dominating effect on polymer rheology. Currently no analytical technique provides a quantitative description of the LCB topologies in these materials beyond a basic estimation of the number of branch points per molecule. Neither the molecular weight of the branch, nor the shape of the branched molecule (e. g. star, comb, “H” or other) can be determined using current state of the art methodology such as size exclusion chromatography with molecular weight sensitive detectors or nuclear magnetic resonance spectroscopy. In our laboratory, we have developed a new fractionation method that sorts polymer solutes based on LCB topology. The approach, which we term Molecular Topology Fractionation (MTF), utilizes a separating medium consisting of a tortuous path having dimensions of similar order to the dimensions of the macromolecules being analyzed. Dissolved solute molecules are forced, via an applied flow field, to navigate through the array of obstacles presented to them within the tortuous path column. Retention in MTF is consistent with a pinning (i. e. entanglement) mechanism. As such, solutes containing long chain branches are expected to be retained longer than linear chains of the same molecular weight. In this presentation, an overview of the MTF experiment will be provided. Evidence to support the proposed mechanism will also be presented. The use of MTF to separate LCB chains from linear chains and LCB chains based on topology will be discussed. Finally, because MTF is able to produce relatively pure fractions of LCB molecules, estimates of the radii of gyration of the MTF-sorted fractions provide a clear test of the Zimm-Stockmayer model for predicting the dimensions of LCB molecules.

### 32. Visualizing polymer dynamics in separation media

**David A. Hoagland**, Chad DeLong, Chad DeLong, Dmytro Nykypanchuk and Dmytro Nykypanchuk, University of Massachusetts Amherst, Amherst, MA

Single molecule visualization by fluorescence microscopy can provide molecular level mechanistic insights into polymer separations achieved by methods such as GPC, electrophoresis, hydrodynamic chromatography, and molecular topology fractionation (MTF). The added insights are especially important when the molecular attribute (chain topology, copolymer composition, hydrodynamic size, etc.) that induces separation is difficult to pinpoint through conventional means, i.e., the correlation of separation trends to a molecular property that has been measured independently. Here, we will present visualizations of single chains moving within or through two types of pore structures important to polymer separation. The first is a pair of unequally sized closed spherical cavities connected by a small hole. Because of the unequal cavity size, a flexible polymer preferentially partitions to the larger cavity where the polymer gains configurational freedom. This type of partitioning is the basis of GPC; we quantitatively compare the partitioning we observed microscopically for single molecules with the partitioning predicted by GPC theory, finding good accord. The second structure is a packed bed of small spheres through which large polymers are driven by pressure-driven flow of solvent. The migration of a linear polymer reflects the flow rate (Deborah number) and the ratio of polymer-to-particle size. At higher flow rate, such polymers become highly extended. The dynamics of branched polymers in the same environment are sensitive to chain topology, a sensitivity we are attempting to better understand so as to improve/explain MTF.

## 33. How polymers worm through pores

**M. Muthukumar**, University of Massachusetts, Amherst, MA

When polymer molecules are forced to navigate through narrow pores and channels, their dynamics and transport are controlled by entropic barriers and entanglements. Using entropic barrier theory for polymer dynamics, we have developed a model for polymer translocation through synthetic pores and protein channels. The predictions of our theory and accompanying simulations will be compared with the recent electrophysiology experiments on single DNA molecules. An extension of this theory, in conjunction with a consideration of entanglements, to the transport of polymers through columns of packed spheres will be presented. Insights obtained from molecular modeling of this phenomenon will be discussed.

## 34. Analysis of long-chain branching in polymers using rheology

Ronald G. Larson, Seung Joon Park, Qiang Zhou and **Sachin Shanbhag**, University of Michigan, Ann Arbor, MI

Rheological data show higher sensitivity to both numbers and types of long-chain branching than do other analytical methods and can provide, in principle, the most accurate characterization. However, inferring branching information quantitatively from rheology has not proved possible so far, due to lack of sufficiently accurate theories for complex branched polymers and to the ill-posed problem of fitting rheological data with models of long-chain branching in which there are too many parameters, including the density of branch points, branch lengths, the locations of the branches along the polymer backbone, and the polydispersity of molecular weight. Using concepts developed over the years by de Gennes, Doi and coworkers, Marrucci, McLeish, Milner, and others, we have produced a general "hierarchical algorithm" to predict the relaxation of general mixtures of the branched polymers. We show that the general algorithm can predict accurately the linear rheology of both simple linear and star-branched polymers, and their mixtures, and also lightly branched commercial metallocene polymers. New work with high-powered computers and more microscopic models, including "slip link" and pearl-necklace molecular dynamics simulations is giving deeper insight into the nature of entanglements and their rate of relaxation in linear and branched polymers. The implications of this work for the development of improved general models of rheological properties of polymers will be discussed.

### 35. Characterization of hyperbranched polymers

**Dale J. Meier**, Michigan Molecular Institute, Midland, MI

Dendritic polymers and their hyperbranched cousins are receiving considerable attention these days because of their unique properties and potential applications. The molecular characterization of dendrimer systems is relatively straightforward because of their uniform structure (at least ideally). In contrast, the molecular characterization of hyperbranched systems presents extreme difficulties because they typically have a broad distribution of degrees of branching and molecular weights. In this presentation, I shall focus on the characterization of hyperbranched polymers by GPC or SEC techniques, in which I shall point out the problems and what results can be obtained using these techniques GPC or SEC techniques separate polymers on the basis of their size (hydrodynamic volumes). Molecules detected at each elution volume will have the same hydrodynamic volume, but since branching affects molecular sizes, the molecules at a given elution volume can have a wide distribution of both molecular architectures and molecular weights. Typically, the "molecular weight" of the polymers at a given eluation volume is based on the calibration with "standards", i.e. linear polymers of known molecular weights, or by light scattering techniques that (ideally) gives the weight-average molecular weight. Finally, "molecular weight distributions" are calculated from the distribution of these values. It is obvious that results based on the use of linear polymer standards will be grossly in error (results will be too low). However, results based on light-scattering can provide a true weight-average molecular weight for the distribution as a whole, but the calculated number-average or other average molecular weights will be in error. A discussion of the magnitude of the errors will be made using the results from a few model branched systems.

## Poster Session, Lunch, Exposition

**Organizer:** Michael K. Lee Dow Corning Corporation, Midland, MI

### 36. Kinetics of the Ligand Exchange Reactions of NiTetren with 2,2'-Bipyridine and 2,2':6',2"-Terpyridine

**Larry Kolopajlo**, Eastern Michigan University, Ypsilanti, MI

The kinetics of the ligand exchange reactions of tetraethylenepentamine nickelate(II) (NiTetren) with both 2,2'-bipyridine (bipy) and terpyridine (terpyr) was examined spectrophotometrically over the pH ranges 6.2 to 5.0 and 6.5 to 4.8 respectively at 25 degrees C. The rate of product formation, either $Ni(bipy)_3$ or $Ni(terpyr)_2$ , was followed at 307 nm and 335 nm respectively. The reactions were run under pseudo-first-order conditions with bipy or terpyr in excess over NiTetren by a factor of about 20. The reactions were found to be first-order in [Nitetren], [bipy], [terpyr] and $[H^+]$. The rate constant $k_{H,L}^{NiTetren}$ for the hydrogen ion dependent addition of either ligand L to NiTetren was about $4.5 \times 10^5$ $M^{-1}$ $s^{-1}$. The rate constant $k_L^{NiTetren}$ for the hydrogen ion independent addition of bipy or terpyr to NiTetren was below 1.0 $s^{-1}$. Based on these results, a mechanism is proposed in which either ligand attacks NiTetren by a predominantly hydrogen ion catalyzed pathway.

### 37. Syntheses and structures of new layered transition metal naphthalenesulfonate salts

**Dane J. Genther** and Philip J. Squattrito, Central Michigan University, Mount Pleasant, MI

In recent decades, compounds composed of alternating organic and inorganic layers have been synthesized and studied. These compounds are desirable for their potential ability to act as hosts for chemical processes in a similar manner to zeolites and functionalized clays. Our studies involve transition metal cations and naphthalenesulfonate anions as the inorganic and organic parts. The synthesis reactions occur in aqueous solution, and the compounds are crystallized via evaporation. Within these compounds, the metal ions hydrated with water molecules constitute the inorganic layer and the deprotonated organic acids constitute the organic layer. The layers are held together by electrostatic interactions and hydrogen bonding. The new compounds were characterized by X-ray diffraction and thermogravimetric analysis. The focus of this specific study is the elucidation of the structures and evaluation of structural trends based on the metal used and the positions of functional groups on the organic moieties.

### 38. Recent studies on asymmetric induction in photocycloaddition reactions

**Wendell L. Dilling**, Central Michigan University, Mount Pleasant, MI

Several recent studies on asymmetric induction in photocycloaddition reactions will be reviewed. Three types of cycloadditions will be considered: 2 + 2 + 2, 4 + 4, and 2 + 2. The 2 + 2 + 2 additions involved acetylenes and nitriles to give pyridines. The asymmetries were induced by asymmetric $Co^I$ complexes and involved hindered biaryl rotations. The 4 + 4 additions involved anthracene derivatives, either cross additions with a naphthyl amide, where the asymmetries were derived from an asymmetric crystallization and involved a hindered rotation around a carbon-carbon single bond, or dimerizations, where the asymmetries were derived from substituted $\gamma$-cyclodextrins. The

2 + 2 additions involved the dimerizations of coumarins in the presence of chiral diols and the cross additions of substituted cyclohexenones with ethylene. In the latter case the asymmetries were derived from classical chiral auxiliaries.

### 39. Fullerene-Coated Materials as Reusable Catalysts for Selective Oxidations

**Anton W. Jensen**, George Kirby, George Draughn and Nicole Baxter, Central Michigan University, Mount Pleasant, MI

Amine functionalized polymer resin beads and amine terminated dendrimers are coated with buckminsterfullerene (C60) by the reaction of the amine groups with the fullerene surface. The fullerene-coated materials generate singlet oxygen when suspended in a solution that is bubbled with oxygen gas and irradiated with UV light. These heterogeneous catalysts facilitate a variety of singlet oxygenation reactions including the Ene and Diels-Alder cycloadditions. Our ongoing work on improving catalysis by these materials will be presented.

### 40. Multi-potent polymer coatings based on chemical vapor deposition co-polymerization

**Yaseen Elkasabi**, Hsien-Yeh Chen and Joerg Lahann, University of Michigan, Ann Arbor, MI

The controlled and stable immobilization of multiple types of biomolecules to a surface is a critical challenge in several emerging research fields, such as the regulation of cell shapes, the development of advanced biological assays, or scaffolds for regenerative medicine. While a range of methods has been developed for the immobilization of a single type of biomolecule to artificial substrates, very few concepts are available for the precious immobilization of multiple biomolecules in a controllable fashion. Using chemical vapor deposition (CVD) co-polymerization, we have developed a simple strategy towards multi-functional surfaces presenting two different biological ligands in controllable ratios.

Towards this goal, CVD technology was used to co-polymerize two reactive monomers, 4-aminomethyl-[2.2]paracyclophane and 4-trifluoroacetyl-[2.2]paracyclophane in different ratios, without cross-reaction, to produce the corresponding co-polymers as thin film coatings. FTIR spectroscopy verifies the presence of both aminomethyl and ketone functional groups in their corresponding proportions. High-resolution $C_{1s}$ XPS on the surface also confirms the theoretical bulk composition. X-ray diffraction of the co-polymer films shows no crystallinity after annealing at 120 $^{o}$C, indicating homogenous mixing of monomers. As a proof of concept, an amine-reactive ligand (Atto 655 NHS ester) and a keto-reactive ligand (biotin hydrazide + rhodamine-linked streptavidin) were reacted on the copolymer surface in proportion to the monomer ratios, as verified by fluorescence scanning. These results have broader applications in biomaterials engineering, microfluidics, and diagnostic testing. For example, one could fine-tune two different surface properties independently, a powerful tool for optimizing many biological interfaces. Also, this technology could be used as part of a multivariable sensor or bioassay. An added advantage is that surface geometry is not a limiting factor for CVD.

Y. Elkasabi, H.Y. Chen, J. Lahann. *Adv. Mater.* **2006** In press.

### 41. Reaction of tea catechins with cytochrome c

**Lihua Wang** and Angela Maciejewski, Kettering University, Flint, MI

The reaction kinetics of cytochrome c with various tea catechins (EC: (-)Epicatechin; ECG: (-) Epicatechin-3-gallate; and EGCG: (-) Epigallocatechin-3-gallate) were studied at pH 7.0. The reaction was 1st order in both the catechin and cytochrome c. The rate of the reaction increased in the order of EC < ECG < EGCG.

### 42. Multi-element analysis of human blood with inductively coupled plasma-mass spectrometry

**Ali Bazzi**[1], Jerome O. Nriagu[2], Marcia C. Inhorn[2] and Aaron M. Linder[2], (1)University of Michigan-Dearborn, Dearborn, MI, (2)University of Michigan, School of Public Health, Ann Arbor, MI

An analytical method for multi-element analysis of whole blood using inductively coupled plasma-mass spectrometry (ICP-MS) will be presented. The sample preparation consisted of a nitric acid/hydrogen peroxide open digestion procedure and subsequent dilution with MilliQ water. The accuracy and precision of the method were assessed from quintuplet analyses of Seronorm™ trace elements whole blood reference materials and human blood samples. The precision for the determination of copper, lead, manganese, selenium, zinc, and cadmium was equal to or less than 5% RSD. The relative standard deviations for barium and arsenic determinations were 5.9% and 8.1%, respectively. The recovery was evaluated using Seronorm™ and was greater than 93% for all elements. Results obtained for 58 blood samples from adults and children will be reported.

### 43. Ab initio analysis of $H_2O/ZnO$

Zach Kohley and **C. M. Woodbridge**, Hillsdale College, Hillsdale, MI

Adsorption of water onto various-sized ZnO clusters was examined using ab initio calculations. Density Functional Theory (DFT) was used to optimize two atom clusters; these calculations showed the most favorable adsorption mechanism was dissociative adsorption of $H^+$ and $OH^-$ onto the oxygen and zinc atoms, respectively. Although not preferred, molecular adsorption of $H_2O$ was possible. Adsorption energies for the dissociative and molecular adsorption were -766.5 kJ/mol and -66.73 kJ/mol, respectively. Larger (>20 atoms) ZnO $(10\underline{1}0)$ clusters were analyzed at the RHF level of theory in order to gain additional insight into the effects of the surface potential. These calculations showed the opposite trend: in the large cluster, molecular adsorption was favored by 23.4 kJ/mol while dissociative adsorption onto bridging sites was possible. This study indicates that ZnO exhibits multiple adsorption mechanisms. The results obtained from the ab initio calculations provide insight into the reaction of $H_2O$ with the complex surfaces of metal oxides. In addition to the study of ZnO, comparative ab initio calculations were performed on two atom clusters of FeO and CuO.

### 44. Application of amphiphilic PAMAM dendrimers in biomimetic interfaces

**Tracy Zhang**, Steven N. Kaganove and Petar R. Dvornic, Michigan Molecular Institute, Midland, MI

Amphiphilic polyamidoamine (PAMAM) dendrimers of six different generations and with three different types of hydrophobes were synthesized for studying their properties as supported thin films. Attachment of long chain hydrophobes to the periphery of hydrophilic PAMAMs leads to star-shaped macromolecules that have flexible, medium-dependent shapes. Room-temperature film balance measurements were used to study monolayers at the air-water interface. Monolayer films were also deposited on mica, silicon and ITO substrates, and probed by AFM, elllipsometry, and electrochemical methods. Amphiphilic PAMAM monolayers have great potential as biomimetic interfaces due to their well-defined, monodisperse architecture, and controllable thickness of fabrication.

### 45. Heats of Formation of Chiral Enantiomers and Racemates: Tartaric Acid

**S. Alex Studniarz**, Penn State University, Sharon, PA

The difference in the heats of formation between the pure enantiomer and corresponding pure racemate can be sufficiently large to produce a large difference in their solubility. For example the tartaric acid enantiomer is 5 times more soluble in water than the racemate at room temperate. Using Hess's law and the measured activity coefficients for aqueous solution of enantiomers and racemate the difference in the heat of formation of tartaric acid enantiomers and racemate is given using the method that is described. It is shown that for tartaric acid the interactions of the d-molecule with the l-molecule (enantiomers) in an aqueous solution of racemate is within the experimental error equal to that of the d-molecule with another d-molecule (or an l with an l). This method permits a check on the reliability of heats of formation data since it depends on relatively small differences in enthalpy. The difference in enthalpy for tartaric acid agrees with the literature values for their heat formation and will be given.

### 46. Synthesis of an Isotopically–Labelled Analog of the Antimicrobial Peptide LL-37

Deborah Heyl-Clegg, Eastern michigan University, Ypsilanti, MI, **mahendar Budarapu**, Eastern Michigan University, Ypsilanti, MI and shyam prasad Samisetti, Eastern Michigan University, ypsilanti, MI

LL-37 is a cationic cathelin–associated broad spectrum antibiotic peptide of human neutrophils. It's mechanism of action is disruption of the bacterial cell membrane structure. LL-21 is a simplified form of the peptide that contains only the core portion of LL-37, which retains antimicrobial activity and is easier to synthesize. We synthesized an 15N –Val labeled LL-21 peptide which allows us to perform solid state NMR studies to measure helix tilt in the membrane. This will provide information on its precise mode of action, either detergent-like activity or pore formation.

### 47. Temperature Dependence of Ruthenium Complex Luminescence in Various Solvents

**Timothy R. Brewer** and Aaron Vogt, Eastern Michigan University, Ypsilanti, MI

Luminescence lifetimes and quantum yields of ruthenium complexes in various polar solvents such as water, acetonitrile, and methanol are reported. The radiative lifetimes were found to be correlated with the polarity of the solvent with a model that assumes a nearby set of energy levels from the excited luminescent level which undergo radiationless deactivation. The photophysical data seem to indicate a dependence of these levels with the solvent which are modified by the polarity of the solvent. Experiments on a few different ligands show the importance of structure on the temperature dependent lifetime.

### 48. Crystal growth of Zinc Oxide: Morphological control through solution chemistry

**Simon P. Garcia** and Steve Semancik, National Institute of Standards and Technology, Gaithersburg, MD

*Text Not Available*

### 49. Investigation of Adhesion Promoters at Polymer Interfaces using Sum Frequency Generation Vibrational Spectroscopy

**Sarah A. Spanninga**[1], Cheryl L. Loch[1], Dongchan (Shaun) Ahn[2] and Zhan Chen[1], (1)University of Michigan, Ann Arbor, MI, (2)Dow Corning Corporation, Midland, MI

Effective adhesion promoters are often an important aspect of adhesion to a polymer surface. Sum frequency generation (SFG) vibrational spectroscopy is a nonlinear optical laser technique that was used to investigate the interfaces formed between organosilane and titanate adhesion promoters and different polymers. SFG is a surface and interface sensitive technique that is able to detect interfacial functionalized groups and their orientation. This sensitivity combined with the ability to carry out experiments in situ in a non-vacuum environment make it a powerful tool to detect surface interactions between the adhesion promoters and the polymer surfaces. The interfaces probed included poly (ethylene terephthalate) (PET)/organosilane, poly (methyl methacrylate) (PMMA)/titanate, and polystyrene (PS)/titanate interfaces. The segregation of

organosilane adhesion promoters at the polymer/silicone elastomer interface was observed. The titanate was found to diffuse into the PMMA and PS. Understanding the molecular structures and interactions at the polymer/adhesion promoter interfaces will aid in the further improvement of the adhesion properties.

## 50. Mechanism of lipid peroxidation of arachidonic acid: a theoretical investigation

**Claire E. Tornow** and M. C. Milletti, Eastern Michigan University, Ypsilanti, MI

Lipid peroxidation is the oxidative modification of polyunsaturated fatty acids (PUFA) which leads to a hydroperoxide. Hydroperoxides that are derived from the lipid arachidonic acid serve as regulators of the enzymes involved in prostaglandin synthesis. Further oxidation of these hydroperoxides produces short chain aldehydes, such as 4-hydroxynonenal. The mechanism of lipid peroxidation is well established, yet it is difficult to predict the ratio of aldehydes produced. Since these aldehydes are markers of biological activity, quantitative prediction of product ratios is desirable. Molecular calculations using density functional theory are used to study the thermodynamic aspects of the mechanism of lipid peroxidation of arachidonic acid. The relative stability of resulting radical species is analyzed with respect to position in the chain and stereochemistry of double bonds.

## 51. Kinetics and mechanism of the abiotic hydrolysis reactions of permethylated cyclosiloxanes in dilute aqueous solution

**Gary E. Kozerski** and Jeremy A. Durham, Dow Corning Corporation, Midland, MI

In addition to being key intermediates in the manufacturing of poly(dimethylsiloxane), low molecular weight permethylated cyclosiloxanes, known as cyclic volatile methylsiloxanes (cVMS), are used widely in consumer products. From these applications, cVMS may enter aqueous compartments in the environment. In this situation, hydrolysis represents a potentially significant pathway for chemical transformation of cVMS in the environment. In part due to the significant vapor pressure and sparing aqueous solubility of cVMS compounds, few studies of the abiotic hydrolysis of the siloxane bond have been made under environmentally relevant conditions. A methodology based on $^{14}$C-labeling, sealed tube reaction vessels, and radiochemical analytical techniques was developed to study the hydrolysis reactions of cVMS compounds, including octamethylcyclotetrasiloxane ($D_4$) and decamethylcyclopentasiloxane ($D_5$). Using this design, the pH and temperature dependent hydrolysis of these compounds was investigated in aqueous solution at concentrations below their solubility limits. Despite a general reputation for stability, $D_4$ and $D_5$ were observed to hydrolyze readily in the pH 4 to 9 range. The hydrolysis of these compounds appeared to be both acid and base catalyzed, with the hydroxide catalyzed hydrolysis generally more efficient, especially at higher temperatures. From these data, catalytic constants for the hydronium and hydroxide catalyzed reactions were estimated, as well as the Arrhenius parameters describing the temperature dependence of the two mechanisms. Modeling of selected $D_4$ hydrolysis data was consistent with a mechanism involving ring opening followed by a series of consecutive irreversible pseudo-first order reactions involving the dimethylsiloxane-α,ω-diol oligomers, $HO(Me_2SiO)_nH$ (n = 2-5), leading ultimately to formation of the final product dimethylsilanediol, $Me_2Si(OH)_2$.

## 52. Analysis of American Chemical Society election procedures - improvements in majority representation and efficiency needed

**Wendell L. Dilling**, Central Michigan University, Mount Pleasant, MI

The mechanics of ACS elections have been of interest for many years. Several years ago we determined that the second-choice (instant runoff) voting procedure instituted in 1973 had prevented plurality winners with less than majority votes from being elected to several ACS offices. However there are still at least two problems with ACS elections. One is the election of directors-at-large by less than majority votes and the other is the unnecessary added effort and expense of runoff elections that are required in four (or greater)-way elections in which no candidate receives a majority of the votes. In the 2004 director-at-large election, the winning candidate received 170 votes (44%) while the other three candidates together received 215 votes (56%). Clearly the majority of voters (councilors) did not favor the winner for this position. The simple solution to this problem is to use the same instant runoff procedure for these elections as is used for president-elect and district director elections. The recent four-way District IV director election required a separate runoff. A multi-choice instant runoff procedure would eliminate the requirement for a separate election.

## 53. Structural and Spectroscopic Evidence for Formation of Trinuclear and Tetranuclear V(III)/Carboxylate Complexes of Acetate and Related Derivatives in Aqueous Solution

**Riya Mukherjee**[1], Brenda A. Dougan[1], Christopher J. Ziegler[2], Scott D. Bunge[1] and Nicola E. Brasch[1], (1)Kent State University, Kent, OH, (2)University of Akron, Akron, OH

The aqueous chemistry of vanadium(III)/carboxylate systems is of interest for a number of reasons. The presence of vanadium(III) complexes in azotobacteria (V(II)/(III)) and some species of ascidians is now well established. In addition, the formation of multinuclear, oxo/hydroxo-bridged V(III)/carboxylate complexes in organic solvents and/or neat carboxylic acid solutions with interesting spectroscopic and magnetic properties has been reported. It has also recently been speculated that oxo/hydroxo-bridged multinuclear V(III) complexes may be important in vanadium-accumulating ascidians. However, there is extremely limited structural evidence for the existence of V(III) complexes of nuclearity greater than 2 in aqueous solution. We will present structural and spectroscopic data for the formation of trinuclear and tetranuclear V(III) complexes for a range of simple carboxylic acids in aqueous solution.

## 54. Chemically related subjects on philatelic covers

**Wendell L. Dilling**, Central Michigan University, Mount Pleasant, MI

Philatelic covers have been issued covering a multitude of subjects including some relating to chemistry. This poster will display several such covers issued by the American Chemical Society, its subunits, and related organizations. Included in these covers are those commemorating the 75th, 100th, and 125th anniversaries of the ACS and anniversaries of the New York and California Local Sections and the Division of Analytical Chemistry. Also included is a series from 22 ACS National Meetings from 1984 to 1995 commemorating the first 21 presidents of the ACS, from John W. Draper (1876) to Ira Remsen (1902). Other covers include those for Pittcon '97, the Priestley House, and the Linus Pauling Award to George C. Pimentel in 1983. From the Midland Section came four covers in 1997 commemorating the Dow Brine Well as a Historical Chemical Landmark, 100 Years of The Dow Chemical Company, the 10th Anniversary of National Chemistry Week, and the Chemis-Tree. From the Cleveland Section came four covers in 1998 commemorating National Historic Chemical Landmarks, Production of Aluminum Metal by Electrochemistry – Developed by Charles HAll, Research on the Atomic Weight of Oxygen by Edward $MO_2$rley, Kem-Tone® Wall Finish, and The Sohio Acrylonitrile Process. Covers from countries outside the US include two from Great Britain commemorating the centenary of the Royal Institute of Chemistry and the annual Congress in 1977, one from East Germany for the 100th anniversary of the discovery of germanium in 1986, and one from Canada for the 3rd Chemical Congress of North America in 1988.

### 55. Reductions by titanium(II) as catalyzed by titanium(IV)

**Ritam Mukherjee**, Zhiyong Yang and Edwin S. Gould, Kent State University, Kent, OH

The cobalt(III) complexes, [Co(NH3)5Br]2+ and [Co(NH3)5I]2+ are reduced by Ti(II) solutions containing Ti(IV), generating nearly linear (zero-order) profiles that become curved only during the last few percent of reaction. Other Co(III) - Ti(II) systems exhibit the usual exponential traces with rates proportional to [Co(III)]. Observed kinetics of the biphasic catalyzed Ti(II) - Co(III)Br and Ti(II) - Co(III)I reactions support the reaction sequence:

[Ti(II)(H2O)n]2+ + [Ti(IV)F5]- [Ti(II)(HTi(II)(H2O)n-1]2+ + [(H2O)Ti(IV)F5]-

[Ti(II)(H2O)n-1]2+ + Co(III) Ti(III) + Co(II)

with rates determined mainly by the slow Ti(IV) - Ti(II) ligand exchange (k1 = 9 „e 10-3 M-1 s-1 at 22 „aC). Computer simulations of the catalyzed Ti(II) - Co(III) reaction in perchlorate - triflate media yield relative rates for reduction by the proposed active [Ti(II)(H2O)n - 1]2+ intermediate; kBr / kI = 8.

### 56. Continuous monitoring device for the collection of a group of herbicides

**Heather L. Distel** and James K. Hardy, University of Akron, Akron, OH

A continuous monitoring method for analyzing a group of herbicides has been developed. The continuous monitoring device, a permeation cell, is a stainless steel casing containing a membrane, which has an aqueous herbicide solution flowing past on one side and an inert gas stream on the other. The volatile herbicides can permeate through the membrane into the inert gas stream. The inert gas stream leads the permeated compounds to a gas chromatogram. The gas chromatogram allows for the determination of the permeation breakthrough times and lag times for each herbicide. The concentration and temperatures of the samples were varied to see the effects they had on the response of the flame ionization detector. An evaluation of different types of membranes, such as the SSP-M213 silicone polycarbonate blend and the SSP-M823 straight silicone membranes, was also performed.

## 57. Metal complexation and photocatalysis studies of EDTA

**Katherine C. Lanigan**, Katie L. Pidsosny, Sue J. Fronrath and Christina A. Pitters, University of Detroit Mercy, Detroit, MI

Investigations of the complexation between nickel and copper ions and EDTA (ethylenediaminetetraacteic acid) and EDDS (ethylenediamene-N, N'disuccinic acid) were carried out using Ultraviolet/Visible spectrophotometry and ATR-FTIR (attenuated total reflectance infrared spectroscopy). Experiments have been carried out in order to determine if photodegradation of metal-bound EDTA and EDDS adsorbed to TiO2 particles is possible by ultraviolet photocatalytic oxidation (PCO). UV/visible spectrophotometry was used to identify complexation between metals and ligands, as well as products of irradiation. After irradiation of Ni-EDTA/TiO2 and Cu-EDT/TiO2 suspensions with ultraviolet light, the data showed that a new chemical species was produced. Control experiments proved that the reaction is photocatalytic in nature and that the irradiation product is not adsorbed to TiO2 particles. Further analysis of the adsorption and irradiation products of Ni-EDTA/TiO2 by ATR-FTIR (attenuated total reflectance-infrared spectroscopy) has been carried out.

## 58. Multivariate data analysis of petroleum-based accelerants and consumer fuels

**Eric S. Bodle** and James K. Hardy, The University of Akron, Akron, OH

Arson investigators have used a wide variety of methods to detect accelerants in fire debris. The complex nature of petroleum-based accelerants can lead to misinterpretation of the sample. A novel method has been developed for the extraction and analysis of petroleum-based accelerants using solid phase microextraction with analysis by GC-FID. Multivariate data analysis is also employed to simplify these data allowing for more accurate classification. SPME in conjunction with multivariate data analysis is a new approach in accelerant sampling and classification.

Chromatograms of 20 household petroleum-based products have been evaluated using multivariate techniques to establish classifications based on their chemical properties. Principal component analysis (PCA) has been shown to group the accelerants into correct classifications. These groupings have been compared to the ASTM International numerical classification set. The method will also be evaluated for effectiveness in proper classification relating to the most recent more complex ASTM descriptive class system.

Consumer fuels have also been evaluated for chemical patterns. Gasolines of various grades have been examined using SPME GC-FID with analysis by PCA and soft independent modeling of classification analogy (SIMCA). Gasolines have shown patterns correlating with the research and motor octane number as well as the anti-knock index. Near-infrared spectroscopy has been used to determine these values for method validation. SIMCA is currently being employed to evaluate these samples for refinery, oil company, and summer/winter blends. Diesel and kerosene have also been examined for patterns relating to flash point and refinery.

### 59. Photocycloaddition reactions of and in dendrimers and dendrons - poster

**Wendell L. Dilling**, Central Michigan University, Mount Pleasant, MI

The title reactions will be reviewed. Photocycloaddition reactions have been reported where the moieties undergoing the cycloadditions are incorporated in dendrimers and dendrons, either near the ends of the branches, within the branches, or at the cores. Both intramolecular and intermolecular photocycloadditions have been reported. Synthetic and mechanistic aspects of these reactions will be presented. The cycloaddition reactions were of the types 2 + 2, 4 + 4, and 4 + 2. The 2 + 2 reactions included derivatives of cinnamide, stilbene, uracil, and norbornadiene. The 4 + 4 reactions included derivatives of anthracene and benzene, while a single example of a 4 + 2 process involved an anthracene derivative with fullerene-C60. Examples of using dendrimers as reaction media for photocycloaddition reactions (of acenaphthylene) will be presented.

### 60. Design, Synthesis, and Evaluation of MC1R Agonists For the Prevention of Skin Cancer

*Text Not Available*

### 61. Student adventures in Johnstone's triangle

**Thomas S. Kuntzleman**, Spring Arbor University, Spring ARbor, MI

Johnstone (1) has argued that scientists describe phenomena in three realms: macroscopic (reactivity, color), mathematico-symbolic (words, equations, notations) and submicroscopic (molecular structure and behavior). Practicing chemists demonstrate fluency in these domains, often using all three approaches simultaneously. Because professional scientists effortlessly visualize the intersection between these modes of processing information, Johnstone has argued that chemical instruction should enable students to do the same. Students are traditionally immersed in problem solving in General Chemsitry, which strengthens their ability to communicate mathematico-symbolically. However, studies have demonstrated that students who have mastered problem solving techniques do not display similar success in explaining the submicroscopic behavior of matter (2, 3). Therefore, lessons and studies have been published that focus on student's understanding of the molecular behavior of matter (4 – 8). Nevertheless, it has been questioned whether two opposing goals exist in chemical instruction: mastery in problem solving versus understanding of microscopic reality (7). Others have noted that “there must be some way that teachers can simultaneously give attention to the quantitative and qualitative nature of chemistry (8)”. Therefore, I am interested in the development of lessons that require students to simultaneously describe data using the microscopic properties of molecules and mathematical relationships. Lessons I have developed to this end will be presented, hopefully generating ideas for further activities that allow students to explore the intersection of the mathematical and conceptual domains of chemical thought.

References:

1. J. Chem. Ed. 1993 70, 701 – 705. 2. J. Chem. Ed. 1990 67, 254 – 255. 3. J. Chem. Ed. 1990 67, 253 – 254. 4. J. Chem. Ed. 2006 83, 48 A – 48 B. 5. Chem. Educator 2004, 9, 184 – 189. 6. J. Chem. Educ. 2003, 80, 304A-304B. 7. J. Chem. Educ. 2002, 79, 989-991 8. J. Chem. Educ. 2002 1991 68, 930 – 931.

## 62. Inhibition of histone deacetylase by retinoic acid and its derivatives

**Jessica Tischler**[1], **Basel Abuaita**[1] and Ali Zand[2], (1)University of Michigan-Flint, Flint, MI, (2)Kettering University, Flint, MI

In eukaryotic organisms, histone deacetylases (HDACs) play fundamental roles in the regulation of transcription. Recent findings show the ability of histone deacetylase inhibitors such as trichostatin (TSA) and phenyl butyric acid to inhibit cancer cell proliferation and induce apoptosis. Most of the compounds that show significant inhibition of histone deacetylase bear a hydroxamate group which suggests chelation with the active-site zinc ion. In a different manner, retinoic acid (RA) also shows the ability to induce growth arrest of many tumor cells. However, it does so by an unknown mechanism. Because of its structural similarity to TSA, retinoic acid ability to inhibit HDAC activity was examined in this study. Derivatives of retinoic acid were also synthesized to probe the effect of changes to the Zn-binding region.

## 63. Intrinsic tryptophan fluorescence as a structural probe of the streptavidin-biotin interaction

**Mark J. Waner**, Anthony T. Mustovich, Seema Patel and David P. Mascotti, John Carroll University, University Heights, OH

The streptavidin-biotin interaction is a ubiquitous tool in biotechnology due to the strength and specificity of the binding. Though used extensively, a number of important physical questions remain unanswered. One of those questions has to do with whether the binding of biotin to tetrameric streptavidin is cooperative. A survey of the literature of the past decade has found evidence indicative of both the presence and absence of cooperativity. Traditionally, cooperativity has been used to describe differential binding affinity, but there is some evidence that the streptavidin exhibits differential structural changes upon biotin binding. To probe the structural changes in streptavidin we have examined the intrinsic tryptophan fluorescence as a function of biotin saturation. The binding of biotin causes a quenching and a blue shift of the tryptophan emission, which saturates at stoichiometric binding. To better understand these structural changes, and their possibly cooperative nature, we have examined the effect of pH, competitive binding with biotin analogs, and acrylamide quenching. Using this data, as well as that found in the literature we will explain why we believe that structural cooperativity accompanies the binding of biotin to streptavidin.

### 64. Application of Advanced Data Analysis Techniques in ToF-SIMS: Toward Faster Relevant Observations for Industrial Problem-Solving

**Brandon J. Kern**[1], Gary Mitchell[1], Gregg Potter[1], Mary Beth Seasholtz[1], Chris Weikart[1] and Jeff McCoy[2], (1)The Dow Chemical Company, Midland, MI, (2)Superior, CO

One of the challenges in the application of time-of-flight secondary ion mass spectrometry (ToF-SIMS) to industrial materials is determining reliable differences in often complex series of spectra. To assist in this daunting task, many researchers are applying computationally intensive methods of data analysis, such as principal components analysis, to not only reduce the time required to make reliable conclusions from sample data but also allow new observations from the sample data. This report outlines a comparison of several popular data reduction techniques, including variations of data pretreatment, with ‘manual' interpretation of the same sample data applied to help determine the locus of failure in amorphous carbon / polypropylene systems. It was found that automated methods of data analysis could, with the proper data pretreatment, be as effective as the manual data reduction method. The advantages of this approach include considerable time savings and use of the entire high-resolution data set. Additionally, classical least squares analysis proved useful in moving toward quantifying the locus of failure in these interface systems once a manual or PCA analysis was performed. Additional observations and recommendations regarding the effectiveness of these methods to rapid industrial problem solving are presented.

### 65. A solvent-less method to quantify triazine based herbicides in water using a permeation sampler

**Jeff Tenney** and James Hardy, The University of Akron, Akron, OH

The method uses a passive sampler to determine seven triazine based herbicides, (Atrazine, Ametryne, Prometon, Prometryne, Propazine, Simazine, and Terbutryne), in water. The sampler is capable of being used in the field as well as in a laboratory. The method, when used in a field study will supply Time-Weighted Average, TWA, data for the seven herbicides without the need for a mechanical means to pull a representative sample.

The passive sampler design is relatively simple and cost effective. The sampler uses a glass tube that has one end covered by a silicone polycarbonate membrane, mem-213. A milliliter of water and an adsorbent are placed inside the sampler and covered. The total cost for the material to manufacturer the sampler is less than ten dollars and all materials can be reused.

The sampler mode of operation is best described by the solution-diffusion model. The herbicides diffuse through the silicone polycarbonate membrane based on Fick's law. They are then transported via the water to the adsorbent. The water is needed due to the extremely low vapor pressures of trazine herbicides. The adsorbent then collects the herbicides; this maintains concentration gradient across the membrane. The trazines are thermally desorbed off the absorbent and sent through a gas chromatograph where they are separated and then to a mass spectrometer where they are identified and quantified.

The method exceeds the detection limit for Atrazine set by EPA method 525.2. It has the ability to monitor water quality over an extended period of time. The method uses no regulated solvents. The method cuts analysis time by not requiring sample preparation, such as liquid/liquid extraction. The method is novel way to test for these trazine based herbicides.

## 66. Phosphorus-Containing Amide Compounds as Flame Retardants

**Chung-keun Ahn**, Central Michigan University, Mt. Pleasant, MI and **Bob A. Howell**, Central Michigan University, Mount Pleasant, MI

Nitrogen compounds, particularly amines, are often used as promoters for phosphorus flame retardants. This effect might be most pronounced for compounds containing both elements. A series of such compounds can be generated by treating 4-hydroxybenzoic acid, as the bis-trimethylsilyl derivative, first with 3-aminopyridine or related amine and then with dichloro(phenyl)phosphine.

## 67. Chemical compositions of Herodian copper coins – the biblical “widow's mites” – through energy dispersive X-ray fluorescence

**Meghann Mouyianis** and Mark Benvenuto, University of Detroit Mercy, Detroit, MI

Thirty six small, copper coins issued under the authority of Herod Aggripa I were analyzed via energy dispersive X-ray fluorescence spectrometry for copper, zinc, tin, lead, antimony, iron, gold, silver, and several other elements. This series appears to show significant adulteration of the coinage with lead. The metallurgical composition of the samples will be presented, and deductions based on the findings will be compared with those of other series of the period.

## 68. Preparation of precious metal nanoparticles using phage display techniques

Alan R. Bassindale, Peter Taylor, **Nunzianda Frascione** and Antonio Codina-Barrios, The Open University, Milton Keynes, United Kingdom

We have been applying biological techniques such as phage display libraries to control the synthesis and/or recognition of inorganic materials, together with the production of metal nanoparticles. We shall report the use of phage display to select peptides that bind to different precious metals. The metal powders were exposed to a 12mer library of peptides expressed in the surface of a M13 bacteriophage. In early studies, phages with some affinity were eluted by lowering the pH and subsequently amplified, re-exposed to the solids and characterised after three rounds of panning. In subsequent approaches, we used other techniques to identify phages that were still bound to the materials after acid washing. The sequence of the peptides bound to the materials was determined and key similarities highlighted. The peptides were then used as templates for the synthesis of novel materials.

## 69. Chemical and Microbiological Studies of the Effectiveness of Bioaugmentation to Prevent Algal Growth in Two Urban Lakes in the Doan Brook Watershed (OH)

**Michael A. Nichols**[1], Adrienne Clark[1] and Keith Jones[2], (1)John Carroll University, University Heights, OH, (2)Doan Brook Watershed Partnership, Cleveland, OH

The Doan Brook Watershed is located in the City of Cleveland and its surrounding suburbs and ultimately empties into Lake Erie. In summer 2002, a lake in its headwaters suffered an algal bloom, which was harvested from the lake at considerable expense. To curb the excessive algal growth in summers 2003-2005, the City of Shaker Heights, OH decided to apply bioaugmentation treatments (Live Liquid Micro Organisms, LLMO). A private firm sprayed the lakes with a proprietary mixture of three bacteria that removes ammonia from the system, preventing algal growth, and also oxidize organic material in the lake sediments. A bi-weekly treatment routine was enacted between June and October, 2004 and 2005. Extensive chemical monitoring of the two treated lakes was performed to determine the treatment's efficacy; the results of these chemical studies and preliminary evidence for the effectiveness of the LLMO treatments will be presented. A secondary benefit of using LLMO treatments is their purported ability to oxidize organic sediments, which would effectively dredge the lakes over several years. However, it was found that the lake sediments only contained 10-15% volatile (mostly organic) solids and therefore, the treatments would not increase the depths of the lakes significantly. Microbiological studies undertaken during the first summer indicated that one of the treated lakes had very high E. coli concentrations, most likely from urban or combined/sanitary sewer run-off infiltration. During the first summer's monitoring, it became clear that the sources of nutrients into the most affected lake needed to be identified and during the second summer, approximately 6 weeks worth of daily monitoring was performed at its two major inflows and one outflow. After a storm drain was found to be supplying moderate quantities of nutrients to the lake, the infiltration of a mis-connected sanitary sewer was corrected.

## 70. Synthesis of a new series of tetra-dentate ligands utilizing methylene dianiline

**Charlotte Hsu**, Ashley Gibbs and Mark Benvenuto, University of Detroit Mercy, Detroit, MI

A new series of ligands, all with methylene dianiline as a common starting material, have been synthesized. All are tetra-dentate moieties containing nitrogen or sulfur donor atoms. The stability of these ligands as free molecules and as hydrochloride salts will be presented, as will their aqueous and organic solubility. Characterization has been primarily by NMR. This, as well as their metal binding abilities, will be discussed.

### 71. Structure and symmetry comparison between two- and three-dimensional crystals - poster

**Katherine E. Plass**, Adam L. Grzesiak and Adam J. Matzger, University of Michigan, Ann Arbor, MI

Patterning surfaces on the low-end of the nanoscale can be accomplished using two-dimensional crystals, but the utility of these structures is limited by the current lack of understanding of self-assembly at interfaces and an inability to predict the packing motifs that will be adopted by a given molecule. Understanding of the self-assembly process in crystals has benefited from the availability of large databases, including the Cambridge Structural Database (CSD) and the Protein Data Bank (PDB), that allow characterization of this entire class of materials. The effects of interfaces on self-assembly, however, have only been explored on a case-by-case basis. To begin to address this deficiency, we have developed the first two-dimensional structural database (2DSD) to examine in general terms the features resulting from self-assembly at surfaces. It was found that molecular-scale patterns are dictated by the same factors that determine bulk crystal structure, but that these factors give rise to different preferred packing symmetries. Unlike in three-dimensional systems, achiral molecules are likely to adopt chiral structures in two-dimensional crystals, and racemic mixtures are expected to spontaneously resolve on the surface. The determination of plane group frequencies enable experimental verification of the theory of close-packing as applied to two-dimensional tiling. This comparison between bulk crystals and physisorbed monolayers provides new tools and directions for future exploration in the engineering of surfaces with prescribed two-dimensional patterns.

## Biotechnology II

**Organizer:** James Hand Dow Corning Corporation, Midland, MI
**Organizer:** Andreas Bommarius Georgia Institute of Technology, Atlanta, GA

### 72. Tools for describing and overcoming stability limitations in proteins

**Andreas Bommarius**, James M Broering, Javier F Chaparro-Riggers, Karen M Polizzi and Eduardo C Vazquez-Figueroa, Georgia Institute of Technology, Atlanta, GA

In contrast to their often superior selectivity, the relative lack of stability of protein biocatalysts in many, if not most, environments and reaction media is one of their main drawbacks. We will report on our latest results to develop quantitative, predictive models of both observable kinetic stability (irreversible chemical degradation or aggregation) and operating stability (lifetime stability while active in a process). Better prediction of deactivation effects on proteins will allow for more robust biocatalyst design and could facilitate better lifetime evaluation of biocatalysts and protein-based pharmaceuticals by observing deactivation at harsh conditions and extrapolating to milder process or shelf-life conditions. We are able to predict temperature stability of protein biocatalysts. The deactivation of protein biocatalysts even at relatively low temperatures is one of the principal drawbacks to their use. We have derived an equation for both time- and temperature-dependent activity of the biocatalyst based on known concepts such as transition state theory and the Lumry-Eyring model (Lumry & Eyring, 1954). We then derived an analytical solution for the total turnover number (ttn), under isothermal operation, as a function of the catalytic constant kcat, the unfolding equilibrium constant K, and the intrinsic first-order deactivation rate constant(s) kd,i . We are also able to link observable protein biocatalyst kinetic stability to salt (buffer) type. We also have investigated the stability, in homogeneous aqueous solution and at gas-liquid interfaces, of formate dehydrogenase (FDH), important for cofactor regeneration, from Candida boidinii and overexpressed in E. coli. Lastly, we apply the consensus concept, a purely computational tool, to raise temperature stability. We predict mutations that have been proven to increase thermostability of glucose dehydrogenase from various Bacilli sp.

## 73. Biomolecule Applications in Silicone Emulsions

**Eric J. Joffre**, Dow Corning Corp., Auburn, MI

Emulsions exist in biological systems to facilitate the transport of hydrophobic molecules in an aqueous environment. Silicone fluids are commercially important hydrophobic synthetic polymers that are emulsified for ease of use and compatibility with other water based products. This work explores the intersection of biomolecules and silicone emulsions in the areas of delivery, catalyzation and demulsification. Silicone emulsions were prepared using selected biomolecules, across a range of silicone fluids of varying molecular weights and endgroup functionality. Silanol functional emulsions were used to screen a selection of enzymes and taurocholic acid for silanol condensation activity. A phospholipid/ phospholipase C system was evaluated for demulsification. Phosphatidylcholine (PC) rich lecithin, sodium taurocholate, and bovine serum albumin stabilized silicone emulsions resulting in particle sizes of 0.2 – 3.1 microns. Plasma lipoprotein transport of cholesterol esters and triacylglycerols for metabolism provides a particle stabilization model for silicone emulsions. Chylomicron and VLDL analogs prepared using siloxane as the internal phase had particle sizes ranging from 150-300 nm and 80-120 nm, respectively. The bile salt derived taurocholic acid was established as a unique silanol suspension polymerization catalyst. The second order rate constant, kf, of 2.1 L/mol/h, was lower than the industrial surfactants dodecyl sulfonic acid (4.4 L/mol/h), while suppressing the final octamethylcyclosiloxane concentration by 40-50%. The enzymes evaluated were ineffective at increasing the molecular weight of the emulsion internal phase. Phospholipase C enzyme was found to be effective in destabilizing phospholipid stabilized polydimethysiloxane emulsions. This work has shown that biomolecules have utility in silicone emulsions as surfactants, catalysts and demulsifiers.

### 74. Structure-antimicrobial activity relationship for silanols, a new class of antimicrobials, in comparison to alcohols and phenols

**Yunmi Kim** and Ronald, H. Baney, University of Florida, Gainesville, FL

Alkyldimethylsilanols, $R(CH_3)_2SiOH$, were found to exhibit unexpectedly strong antimicrobial effects. The antimicrobial activity of alkyldimethylsilanols was significantly higher than their analogous alcohols. A study of the structural dependence of their antimicrobial activity was conducted with four bacteria, *Escherichia coli*, *Staphylococcus aureus*, *Psudomanos aeruginosa*, and *Enterococcus faecalis.* Silanols, alcohols with structures analogous to the silanols, $R(CH_3)_2COH$, and substituted phenols as shown in figure 1 were evaluated as a single class of materials. The minimum lethal concentrations (MLC) defined as the concentration required for a 7-log reduction in viable bacteria after 1hour exposure period were used to measure the antimicrobial activity. Octanol/water partition coefficients (log P) and H-bond acidities ($\Delta\nu$) measured as the shift in frequency of OH stretching band between free OH and hydrogen bonded OH to diethyl ether oxygen by infrared spectroscopy were utilized as dispersive and polar structural parameters. The correlation established by multiple regression analysis between antimicrobial activities and structural properties of silanols and carbinols against the four bacteria was $\log(1/MLC)=0.679\log P+0.0035\ \Delta\nu-1.897$, n=94, r=0.97, s=0.19. This equation and a significantly high correlation coefficient r suggest that the lipophilic properties and the H-bond acidities are primary factors for antimicrobial action of silanols and carbinols. Fungicial activity of silanols against *Aspergillus niger* was also found. Cell membrane damage of the bacteria after triethylsilanol treatment was detected by TEM and fluorescent dye techniques. These studies strongly support the hypothesis of a common kill mechanism involving cell membrane disruption of bacteria through lipophilic and hydrogen bonding interactions for silanols, alcohols, and phenols.

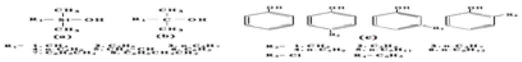


Figure1. Compounds in antimicrobial study

### 75. Studies on the Factors Affecting Viral Panning/Phage Display Results

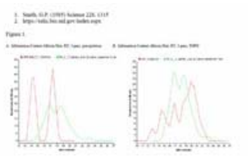
**R.M. Malczewski**, Dow Corning Corporation, Midland, MI

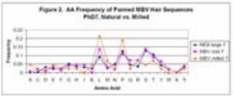
Since first described by Smith (1), viral panning/phage display has seen increasing use as a high throughput screening mechanism for identifying peptide sequences with enhanced binding affinity for targeted substrates. The number of annual patents and publications relating to uses of phage display, for example, rose from <10 in the early 1990s to >250 per year in 2004.

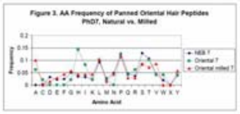
We have implemented panning to identify binders for hair, skin, and other substrates, in order to understand delivery or “blocking” requirements. Experimental output is examined several ways, including analysis with software available from government websites (2). We tested the reproducibility of panning as well as of specific product amplification mechanisms, and also the effects of amplification types on final results. Three such schemes (TOPO isomerase, TempliPhi DNA polymerase, and plaque growth/column purification) were evaluated, and these appear in some cases to provide peptide sets with different “information content”(2) (Figure 1).

Additional studies examined the effects of hair pretreatment, temperature, and lot-to-lot sample variability. Cryogenic milling of hair (a damage model) seems to produce only a few significant changes in panned sequences; milled Oriental and Medium Brown Virgin (MBV) hair appear to bind to more nonpolar residues (L and P are increased for MBV, V and A for Oriental). Fewer S bind milled MBV, and binding of H residues decreases to background levels for Oriental after milling (See Figures 2 and 3).

The results of the above studies will be presented, and their importance for understanding the relevancy and applicability of panning outcomes will be discussed.







## 76. Quantitation of proteins in bacterial fermentation process samples using capillary electrophoresis-sodium dodecyl sulfate

**Grant A. Von Wald** and June Zhu, The Dow Chemical Company, Midland, MI

In order to monitor and optimize the expression of target proteins in bacterial hosts, quantitation of the target protein in process samples that contain many host cell proteins is necessary. Capilliary Electrophoresis-sodium dodecyl sulfate (CE-SDS) is an automated analogue to the well established SDS-polyacrylamide gel electrophoresis (PAGE) technique. Data are presented to demonstrate the capabilities of CE-SDS to measure the concentration of a protein in a mixture of many other proteins. The Beckman Instruments PACE/MDQ instrument and Beckman's CE-SDS separation kit were used to measure linearity, recovery, repeatability, resolution, and limit of detection of proteins in complex bacterial fermentation process samples. CE-SDS can be a more quantitative, efficient alternative to SDS-PAGE.

### 77. The functional role of cysteine residues on c-Abl kinase activity

**Yuh-Cherng Chai** and Amanda Leonberg, John Carroll University, University Heights, OH

The function of c-Abl nonreceptor tyrosine kinase is activated under oxidative stress. Cysteine residues in particular are susceptible to oxidative post-translational modification by reactive oxygen species. S-glutathionylation, i.e. formation of mixed disulfides of glutathione (GSH) with cysteine residues of proteins (protein-SSG), is a modification broadly observed physiologically. In this study, we show that cysteine residues of c-Abl are modified by S-glutathionylation, and by thiol alkylating agents such as 4-acetamido-4'-maleimidylstilbene-2, 2'-disulfonic acid and N-ethylmaleimide. Modification of cysteine residues of c-Abl tyrosine kinase using glutathione disulfide and thiol alkylating agents subsequently inhibits kinase activity. Our results strongly suggest that cysteine residues are required for c-Abl kinase activity. We also show that S-glutathionylation of c-Abl can be reversed using a physiological system involving glutaredoxin. Reversal of S-glutathionylation, i.e. removing GSH from protein-SSG, restores c-Abl kinase activity. Our data suggest that the reversible modification of cysteine residues of c-Abl may prevent this protein from irreversible modification under oxidant stress.

## Catalysis II - Catalysts and Advanced Materials for Clean Energy

**Organizer:** Shaoguang Feng Dow Chemical Company, Midland, MI
**Organizer:** Eric E. Stangland Dow Chemical Company, Midland, MI

### 78. Nanostructured Materials for Hydrogen Production

**Levi T. Thompson**, University of Michigan, Ann Arbor, MI

Hydrogen is seen by many as the energy carrier for the future, and development of the science and technology needed to produce, store and utilize hydrogen has emerged as a national research priority. Hydrogen has the highest energy density of any non-nuclear fuel and can be easily converted to electrical and thermal energy via highly efficient, non-polluting processes. Hydrogen is also the most abundant element on the planet but it does not exist naturally in pure form. Our research focuses on the design and discovery of better performing catalysts and reactors for hydrogen production, and less expensive fuel cells. The presentation will highlight our work in the development of new, nanostructured materials for hydrogen production including nanocrystalline gold, and early transition metal nitride and carbide catalysts. These materials have been demonstrated to outperform currently available commercial catalysts. Activity and selectivity patterns, reaction mechanisms and key surface characteristics of these new catalysts will be described in the presentation.

### 79. Degradation of Pt and C under automotive PEM fuel cell operations

**Chi-Hum Paik** and George W. Graham, Ford Motor Company, Dearborn, MI

Electrocatalyst, Pt/C, can degrade under acidic, cyclic, and high-voltage (e.g., > 0.9 V vs. RHE) conditions found in an automotive polymer electrolyte membrane fuel cell (PEMFC). This work focuses on characterizing the decay mechanisms to predict and mitigate the catalyst losses. In particular, influences of cyclic amplitude and Pt loading are considered in this paper. First, in the case of amplitude (cell voltage), catalyst activities responding to upper voltage exposures at +0.8 to +1.6 V vs. reversible hydrogen electrode (RHE) were examined. Electrochemical area (ECA) of Pt typically decreased when an electrode potential was cycled. In particular, the upper voltage of a cycle played an important role on the Pt catalyst dissolution rate. At the same time, the double layer capacitance current was found to increase to reflect the surface oxidation. An oxidized Pt/C electrode typically revealed a higher oxygen-bonded carbon content by X-ray photoelectron spectroscopy (XPS), and a lower contact angle, reflecting a decrease in hydrophobicity, necessary for water removal. Second, potential cycling (0.6-1.2 V vs. RHE) was conducted on electrodes with 0.25 and 0.5 mg/cm2 Pt loading. The normalized ECA values decreased with time of cycling with a small difference (< 5% ECA) between the electrodes with two Pt loadings. The growth of double layer current, however, was found to decrease with higher Pt loading. It is speculated that the growth of the carbon surface species may be regulated electrocatalytically by higher population of Pt catalyst on C surface. Effects on Pt and C, as well as an intimate interaction between Pt and C, can influence both activity (platinum) and mass transport (carbon) regions of the PEMFC performance.

### 80. Understanding NO oxidation catalysis on Pt(111) through the use of density functional theory

**Rachel Getman** and William F. Schneider, University of Notre Dame, Notre Dame, IN

NOx compounds (x =1 or 2), which form mainly through fuel combustion, are harmful to health and to the environment, and therefore there is interest in their effective removal from emissions. One of the most elementary and generally important catalytic reactions of NOx is the catalytic oxidation of NO to NO2. Pt-based catalysts are widely used for this catalysis, but to date agreement has not been achieved as to the kinetics or mechanism of the reactions. In this work, we use density functional theory calculations to study the reactions of NOx on the {111} face of platinum. We characterize the composition, energies, and vibrational spectroscopy of possible surface species derived from NOx and O2. Further, we explore the variations in these properties as a function of the coverage of NOx and O on Pt. We find that the thermodynamics of the oxidation process on Pt{111} are strong functions of the oxygen coverage and thus of the available chemical potential of oxygen. The results suggest that there exists a window in chemical potential where oxidation is possible on the metal due to the similarities in the Pt-O bond energy and the NO -> NO2 oxidation energy. These results form the basis for thermodynamic and kinetic models of Pt-catalyzed NO oxidation under development, models that ultimately can be exploited to more effectively and efficiently reduce NOx emissions.

### 81. Development of NOx traps and NH3-SCR technologies for the catalytic treatment of diesel NOx emissions

**Karen M. Adams**, Ford Motor Company, Dearborn, MI

Interest in diesel engines for passenger cars and light trucks has come about because of the benefits of improved fuel economy and reduced CO2 emissions over gasoline vehicles, however a major challenge has been the catalytic treatment of NOx in diesel emissions. Gasoline vehicles use three-way catalysts, which operate in stoichiometric exhaust but cannot reduce NOx in the typically lean (O2-rich) exhaust of diesel. NOx traps and urea-SCR are the prime technologies currently being developed for diesel vehicles. NOx traps store NOx in lean exhaust, and then a rich diesel exhaust must be generated to reduce the stored NOx to N2. SCR is selective catalytic reduction of NOx, a process that selectively partitions oxidation of a reductant, such as NH3, using low (ppm) levels of NOx in the presence of high (%) levels of O2. The reductant for urea-SCR is NH3 from hydrolysis of urea. To meet increasingly more stringent NOx regulations, two critical issues for these diesel technologies are low temperature (< 200C) performance and durability. To address these issues for NOx traps, lean vs. rich aging was studied for a Pt-Ba/Al2O3 model trap. Also, including ceria in a NOx trap were examined for its effect of NOx, HC and CO activities. For NH3-SCR, the impact of feed gas NO:NO2 ratio on light-off activity was investigated for different zeolite SCR catalysts. Practical implications of this work are discussed.

### 82. Defect- and stress-free boron-doped diamond thin film on titanium deposited using a dual coating strategy

**Michael A. Lowe**, Anne E. Fischer and Greg M. Swain, Michigan State University, East Lansing, MI

Titanium is a technologically-important metal that is widely available and has superior mechanical properties. However the use of titanium in electrochemical applications is limited because the metal dissolves in the minimal presence of fluoride ions and is susceptible to structural degradation in extreme oxidizing or reducing conditions. Such conditions are found in certain industrial processes and at bipolar plates in polymer electrolyte membrane fuel cells (PEMFCs). A method is presented for forming a stress-

and defect-free coating of boron-doped diamond thin film on titanium. Boron-doped diamond coatings are electrically conductive and chemically inert, even in severely corrosive conditions and in the presence of fluoride ions, and may extend the use of titanium for electrochemical applications.

Coatings of diamond on titanium often crack or fail because of the large internal stresses that develop during the diamond deposition process. This problem has been overcome by a new strategy for diamond growth. Using microwave plasma-assisted chemical vapor deposition, a layer of boron-doped nanocrystalline diamond was first deposited on titanium, followed by deposition of a layer of boron-doped microcrystalline diamond. The electrochemical properties of the diamond/Ti film were studied before and after accelerated corrosion testing that involved both (i) extensive potential cycling over a wide potential range and (ii) potentiostatic polarization at 1.4 V vs. Pt quasi-reference in the presence of F- at 50 ºC. There were no indications of film degradation or corrosion of the Ti substrate. Moreover, no morphological or microstructural changes were noted with SEM and Raman spectroscopy. In contrast, severe pitting was observed for bare titanium during the same accelerated corrosion testing due to the formation of Ti 4+.

### 83. Surface Chemistry Effects on the Nucleation and Growth of Metal Particles on Diamond Thin-Film Electrodes

**Jason A. Bennett** and Greg M. Swain, Michigan State University, East Lansing, MI

Conducting diamond thin-film electrodes have emerged as an attractive candidate for many electrochemical applications. It has been shown, at least in a preliminary manner, that diamond functions well as a support material for electrocatalyst metal particles. Diamond possesses several properties that make it an attractive support material including superb morphological and microstructural stability. For the development of a new support material, it is important to understand how metal particles nucleate, grow and adhere to the surface. For example, nanometer-sized Pt particles can be electrodeposited on the surface of hydrogen-terminated diamond thin films using pulsed galvanometry with typical particle diameters of less than 50 nm and particle densities of greater than $10^9$ particles $cm^{-2}$.

Metal electrodeposition on polycrystalline diamond is a complex, surface-sensitive reaction. Unlike most electrode materials used for metal deposition studies, polycrystalline diamond is quite heterogeneous morphologically with diamond crystallites or grains, grain boundaries, and a multitude of other defects. The film morphology and microstructure, as well as the surface chemistry and electrical properties will exert a strong influence on metal nucleation and growth, as well as the spatial distribution of the metal phases. This presentation will cover the effect the surface chemistry has on metal phase formation. Details will be presented about the electrodeposition of Pt on diamond surfaces terminated with hydrogen, oxygen and nitrophenyl or 4-methoxebenzene adlayers. The oxygenated surface was formed chemically by exposing the film to warm aqua regia. The nitrophenyl and 4-methoxybenzene modified surfaces were formed by well established diazonium salt chemistry. Results from scanning electron microscopy, x-ray photoelectron spectroscopy and electrochemical studies of the electrode reactivity using the oxygen reduction reaction as a probe will be reported

## Coatings Technology II

**Organizer:** Theodore Provder Eastern Michigan University, Ypsilanti, MI

### 84. Study of tribological properties of coatings with Nano-Indenter and Scanning Probe Microscope (SPM)

**Weidian C. Shen**, Eastern Michigan University, Ypsilanti, MI

Mar/scratch resistance is an important tribological characteristic of coatings in many applications. In the 80s, quite a few empirical methods were used to evaluate it. However, they might not subject the tested coatings to the stresses and damages encountered in the real application field. With the development of the nano-instruments, the single-probe tests have become a popular technique to study the mar/scratch resistance of coatings. In the tests the damages are made under well-controlled conditions, thus making it possible to study different marring/scratching mechanisms under different test conditions. The tests can be carried out with atomic force microscopes, home-made devices, or commercial nano indenters/scratchers. As an illustration, a Nano-Indenter XP of MTS, combined with a NanoScope IIIa of Veeco, is used in this presentation. Morphologies of the mar/scratch damages are much diversified, and can be classified into different categories, for example, mar, rough trough, cracking, delamination, and chipping. The mar refers to light damage, while the latter four refer to medium to severe damages. The Indenter and SPM can be used to measure the micro mar resistance, different responses of the coatings to the marring stress, i.e., elastic response, plastic deformation and abrasive wear, quantitatively, and to evaluate the critical force for rough trough, at which mar transits to rough trough, as well as the critical force for cracking, delamination and chipping, if any. To comprehensively characterize the mar/scratch resistance of a coating in a specific environment, a quantitative index is useful. The concept of the index and the procedure for obtaining it will be introduced. Due to the variety of coatings' properties and various application requirements, some complementary test methods will be described. The measurement of hardness and elastic modulus of hard and soft coatings will be described, too.

### 85. Film Formation Process Monitoring

**Sarjak H. Amin**[1], Theodore Provder[1], Antonio Saranillo[1], Allayna Lee[1], Nawshova Tasmeen[1], Alice Brun[2] and Laurent Brunel[2], (1)Coatings Research Institute, Eastern Michigan University, Ypsilanti, MI, (2)Formulaction, L'Union, France

During the film formation process an applied liquid film transforms into an adherent solid film through physical and/or chemical processes. The film formation process involves changes in rheology, evolution of mechanical properties and the determination of the ultimate film structure and morphology. In this study, the film formation process of coatings was monitored using a novel and innovative technology denoted as Adaptive Speckle Imaging Interferometry (A.S.I.I.), which is based on diffusing wave spectroscopy theory. Film formation data obtained from A.S.I.I. is compared with information obtained from more traditional methods such as set to touch time, tack-free time and dry hard time (from BK mechanical recorder), rate of volatiles evaporation ( from TGA), and degree of chemical cure ( from DSC). Combining information from several techniques provides a more complete picture of the film formation process for a wide variety of waterborne and solvent based coatings: architectural interior and exterior coatings, industrial maintenance, marine, gel coat, autorefinish and inks. Repeatability and reproducibility of A.S.I.I. drying curves, drying over various substrates, and drying as a function of film thickness, PVC and VOC were investigated.

## 86. Reactive Phenol-functional Polyesters Containing UV-absorbing Moiety And Their Coating Applications

**Vijay M. Mannari**, Paul Ziemer, Akash Saraf and Frank Jones, Eastern Michigan University, Ypsilanti, MI

Reactive Polyester resins are widely used as principle film-formers for industrial thermosetting coating applications due to their versatility and good cost –performance balance. These resins typically have –OH functionality and when thermally cross-linked with melamine-formaldehyde type cross-linkers, form cross-linked structure with imino-ether linkages between polyester chains and cross-linker. While mechanical properties of such coatings can be excellent for many applications, they are not very resistant to photo-gradation when exposed to exterior environment.

Our research group has designed and developed a reactive polyester system containing a UV-absorbing moiety onto the polymer backbone. These novel polyesters, when cured with melamine-formaldehyde cross-linkers, are capable of forming rigid heterocyclic cross-links while retaining UV-absorbing characteristics and hence resisting photo-degradation of their films when exposed to sun-light. Reactive Phenol-functional polyester (PPE) resins have been synthesized using p-hydroxy cinnamic acid (p-HCA) as one of the components, by direct polyesterification reaction. The spectroscopic characterization of PPE resins confirms the presence of free phenolic –OH groups and retention of ethylenic unsaturation present in p-HCA. Various thermosetting coating compositions have been prepared using PPE and melamine-formaldehyde type cross-linking agent. The heat -cured coatings have been found to have excellent physical and mechanical properties, believed to be due to the formation of rigid heterocyclic cross-links of benzoxazine structure. The UV-absorption spectroscopic study shows that PPE-based coatings strongly absorb in ultraviolet region below 330 nm wavelength. The coatings, when subjected to the accelerated weathering test showed substantial yellowing tendency but exhibited superior resistance to photo-degradation, as indicated by their excellent gloss retention characteristic.

## 87. Fouling release coatings based on thermoreversible block copolymers

Rainer Schwarz, Steffen Schellenberger, Markus Mahn and **John Texter**, College of Technology, Eastern Michigan University, Ypsilanti, MI

It has become very well recognized in the drug delivery community that particles coated with PEO (polyethylene oxide) have a low affinity for protein adsorption, and this aspect provides greatly enhanced circulation lifetimes. Various experiments with PEO grafted planar surfaces have shown greatly reduced protein adsorption, and experiments with alkyl-PEO surfactants in sea water tests. While most fouling release approaches are focusing on ultra-low surface energy formulations, comprising mainly siloxanes and fluorinated moieties, exploiting PEO formulations is a high surface energy approach. In considering how to make an erodible PEO coating, that may or may not also contain a biocide, we have begun exploring PEO thermoreversible gels based on the BAB block copolymer family known as Pluronics®, where the B blocks are PEO blocks and the A blocks are oligomers of PPO (polypropylene oxide). These triblock copolymers form micelles that self-assemble into thermoreversible cubic gels. We have begun exploring the polymerization of hydrogels in the interstices of these gels in order to try to capture this three dimensional structure, and results for acrylamide, PEO methacrylate, and PEO-acrylate-based monomers will be presented. Durability will require substantial hardening, and we have begun studying direct incorporation of nano silica and in situ sol-gel synthesis of silica as means for increasing the modulus. Phase behaviors, polymerization results, and preliminary coatings will be discussed. This work was supported by the Office of Naval Research through Grant Award No. N00014-04-1-0763.

## 88. Long-term Antimicrobial Performance of Cotton Textile Treated by 3-(trimethoxysilyl) propyldimethyloctadecyl Ammonium Chloride

**Le Song** and Ronald, H. Baney, University of Florida, Gainesville, FL

The long-term antimicrobial performance of cotton textile treated by 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride (Si-QAC) was evaluated in this research. Si-QAC was hydrolyzed at three different concentrations, i.e., 0.1%, 0.5% and 1% respectively in deionized water. The cotton textile stripes were immersed in each of Si-QAC solutions for half hour. The treated samples were then dried to immobilize Si-QAC on the cotton textiles. The ASTM E2149-01 dynamic shaking method was employed for antimicrobial experiments. Antimicrobial activities of surface-treated samples in *E.Coli* suspensions ($10^5$ to $10^6$ CFU/ml (Colony Forming Unit/milliliter)) as well as the leachates from treated samples in deionized water were investigated in thirty-cycle experiments. Each cycle consisted of twenty-four hours continuous shaking. After one hour shaking, the survival number of bacteria was counted for samples in *E.Coli* suspensions; the leachates of treated samples in deionized water were removed to evaluate the antimicrobial activities. Two-stage antimicrobial activities were observed for surface-treated samples for all three-treatment concentrations. The initial high activity (ca. six log reduction) was caused by the combined antimicrobial activites from surface-bound antimicrobial agent and active leachate, six log reductions were also observed for the leachates from 0.5% and 1% treated samples. The antimicrobial activites of surface – treated samples continued to decrease until a constant log reduction was achieved (ca.

two log reduction), no antimicrobial activities were detected for leachates in second stage. These residue antimicrobial activities may come from the surface-bound antimicrobial agents. Further studies showed the initial antimicrobial activities of Si-QAC treated samples were much reduced in the artificial seawater (ca. one log reduction) in comparison to deionized water (ca. six log reduction).

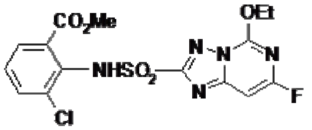
## Environmental Challenges - Issues & Solutions II

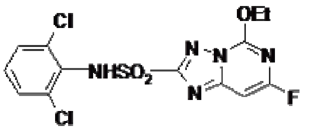
**Organizer:** Sudarsanan Varaprath Dow Corning Corporation, Midland, MI
**Organizer:** Shihe Xu Dow Corning Corporation, Midland, MI

### 89. The Discovery of Florasulam and Penoxsulam Herbicides

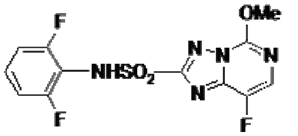
**Timothy C. Johnson**, Dow AgroSciences, LLC, Indianapolis, IN

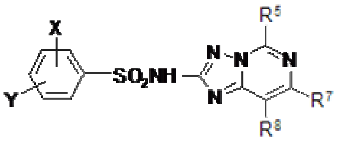
The discovery of the sulfonamide herbicides, which inhibit the enzyme acetolactate synthase (ALS), has resulted in many investigations to exploit their herbicidal activity.[1] One area which proved particularly productive was the *N*-aryltriazolo[1,5-*c*]pyrimidine sulfonamides, providing three commercial herbicides, chloransulam-methyl (**1**), diclosulam (**2**) and florasulam (**3**). Cloransulam-methyl and diclosulam control broadleaf weeds in soybeans. Florasulam controls broadleaf weeds in cereals with very low use rates. Additional investigations in this area led to the discovery of compounds with the general structure of **4**. A number of compounds related to **4** were shown to have nearly equivalent activity on both grass and broadleaf weeds species. This was interesting since commercial levels of grass weed control had not previously been observed with the sulfonamide class of herbicides. Research efforts to exploit these high levels of grass activity ultimately led to the discovery of penoxsulam (**5**), a new herbicide developed for grass, sedge and broadleaf weed control in rice. Synthetic efforts and structure-activity relationships leading from the discovery of florasulam to the discovery penoxsulam will be discussed.



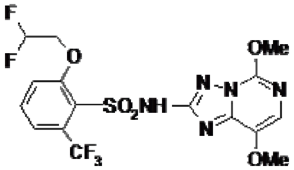


Cloransulam-methyl (**1**) Diclosulam (**2**)





Florasulam (**3**) **4**



Penoxsulam (**5**)

### 90. A Linear Free Energy Approach to Prediciting Distribution Properties of Environmental Interest

**Colin F. Poole**, Hamad Ahmed and Jing Qian, Wayne State University, Detroit, MI

A number of free energy relationships are available for modeling the distribution of compounds in two phase systems that can be described by an equilibrium constant. These were initially applied to well-defined chemical systems like liquid-liquid partitioning and retention in chromatography but are now increasingly used to model more complex systems of biological and environmental interest. They provide an alternative approach to quantitative structure-property relationships that offer little insight into the physical processes controlling the system and often lack predictive ability for new compounds. The most general of the linear free energy models is Abraham's solvation parameter model, set out below for distribution between condensed phases

$$\log SP = c + eE + sS + aA + bB + vV$$

where SP is some free energy related property. The capital letters (E, S, A, B, V) are solute descriptors characteristic of defined intermolecular interactions and the lower case letters (e, s ,a ,b ,v) are system constants representing the complementary properties of the system. Solute descriptors are available for about 6000 compounds and further values can be calculated for new compounds based on solubility, partitioning and retention in chromatographic systems, etc, as will be explained. For compounds with known descriptors the calculation of physicochemical properties ( e.g. aqueous solubility, log P, non-specific toxicity to fish, soil-water adsorption, adsorption to air particulates, interfacial adsorption to liquid and frozen water, skin permeability, etc.) will be demonstrated. The quality of predictions will be described by statistical and chemometric tools demonstrating the applicability of the information for regulatory purposes and the insights that the models provide into the driving forces that control these system.

### 91. Monitoring trace levels of heavy metal ions in environmental and clinical applications using anodic stripping voltammetry and boron-doped diamond electrodes

**Elizabeth A. McGaw** and Greg M. Swain, Michigan State University, East Lansing, MI

Monitoring heavy metal ions is important in environmental and clinical applications. High levels of these ions in the human body are associated with numerous health problems. Because these toxins can accumulate in tissues it is important to have an analytical technique that can quantify the level in both water supplies (allowable levels, set by the Environmental Protection Agency (EPA), in the low ppb range) and in biological fluids (e.g. blood, urine).

Anodic stripping voltammetry (ASV) is a useful method for monitoring heavy metal ions because of its wide linear dynamic range, low detection limit (ppb), and multimetal analysis capability. The working electrode is the most important factor in ASV. The choice of electrode material affects the analytical detection figures of merit (e.g., sensitivity, reproducibility, selectivity and stability) and the metals that can be analyzed. Historically, Hg electrodes have been used because of the large cathodic working potential window, good sensitivity and reproducibility. However, Hg is toxic and volatile so there is a need for an alternate electrode material possessing the same ideal properties.

Boron-doped diamond (BDD) is proposed as a suitable alternative to Hg-coated glassy carbon electrodes. BDD provides detection limits comparable to those obtained with Hg and it has been previously shown that its use in analysis of real environmental samples (e.g. water, soil, sludge) is a viable option. A direct comparison of the analytical figures of merit for these two electrodes for Ag(I), Cu(II), Pb(II), Cd(II) and Zn(II) in water will be presented along with analysis in complex biological matrices (e.g. blood).

### 92. Trace metal mercury levels in residential homes in Kuwait

**Abdul Rehman Khan**, Layla Al-Awadhi and Rabia Al-Kandari, Environment and Urban Development Division, Kuwait, Kuwait

Kuwait is an oil rich state on the northeastern corner of Arabian Peninsula and has faced the unprecedented man made environmental disaster in early 1991 of igniting over 600 oil wells those continually burnt for a period of over six months. The use of crude and heavy fuel oil in the power generating facilities has aggravated the pollution due to particulate matters that carry trace metals. The climatic conditions in this part of the world result into very frequent dust storm transporting particulate matters short and long distance. Mercury in atmosphere is mainly due to burning of fossil fuel, incinerators, crematoriums, extraction of precious metals and salt-chlorine industries. This study has been initiated for mercury measurements from an old salt-chlorine industrial site that has been closed since 1984.To compare the mercury levels elsewhere, a comprehensive measurement program was devised and conducted to obtain mercury levels in most of the urban areas in Kuwait. Domestic dust samples from selected residences were collected for a period of a week. These samples were analyzed using KISR/T0-345 method especially developed for precise measurements of trace metals in particulate matter. It is required to identify the sources of mercury that resulted into such mercury levels in indoor air in the urban areas. For those areas where mercury levels are substantially high mitigation methods have been proposed to reduce the impact on to the residents.

## 93. Improved gas chromatography – mass spectrometry determination of estrogenic hormone steroids in aquatic environments

**Yuegang Zuo** and Kai Zhang, University of Massachusetts Dartmouth, North Dartmouth, MA

Estrogenic chemicals, particularly the synthetic contraceptive steroid 17a-ethynylestrodiol and natural steroid estrone and 17b-estradiol, have attracted a great deal of scientific and public attention during recent years due to their occurrence in surface waters and sewage treatment plant effluents and their potential adverse effects on the development and reproduction of fish, wildlife and even humans. Concentrations of estrogenic steroids have usually been detected at the low-ng/L levels using GC-MS after silylation. Trimethylsilyl derivatives are probably the most widely employed. The combination of N,O-bis(trimethylsilyl)trifluoroacetamide + trimethylchlorosilane is amongst the most popular silylating reagents used for the determination of estrogenic steroids in water. However, several studies reported on the formation of different derivatization products of EE2 with this silylating reagent and thus suggested that derivatization with BSTFA + TMCS might not be suitable for the determination of EE2 by GC-MS under the previously reported conditions. In this study, a procedure for the simultaneous determination of both natural and synthetic estrogenic steroids in water is described. Analytes were derivatized with BSTFA + 1%TMCS in pyridine solution and determined by GC-MS. The effects of solvent, temperature, and reaction time on the derivatization of EE2 were investigated in order to prevent the formation of undesired multiple products and conversion of trimethylsilyl derivatives of EE2 formed to their respective E1 derivatives reported in previous studies. The identity and mechanism of formation of multiple derivatives have been discussed. A new silylation mixture was employed to overcome these pitfalls and generate a single product of di-TMS derivative of EE2. In the presence of pyridine, variations in reaction temperature and time did not significantly affect the derivatization efficiency and stability of the di-TMS derivative of EE2 formed. A good linearity of response in the concentration range from 1.0 to 800 μg/mL estrogens for quantitative analysis was also achieved.

## 94. Water quality assessment of the Saltcreek watershed in eastern Muskingum County, Ohio

**Lois Zook-Gerdau**[1], Jared Molden[1] and Kylene Wilson[2], (1)Muskingum College, New Concord, OH, (2)Muskingum Soil and Water Conservation District, Zanesville, OH

The Salt Creek Watershed in southeastern Ohio encompasses approximately 96 miles of water bounded on the west by the Muskingum River. Because non-point pollution has

overtaken point-source pollution as a major cause of impairment within watersheds, watershed management must take into account water quality and the effects of land use. Land usage in the watershed includes agricultural, commercial, and residential. Types of impairments in the Salt Creek Watershed include the following: failed septic systems, sedimentation, improperly managed manure storage, inadequate usage of fertilizers, and lack of riparian buffer. Assessment of the watershed has been on-going for three summers (2003, 2004, & 2005) via a number of methods including chemical data collection, physical data collection utilizing the Ohio EPA's Qualitative Habitat Evaluation Index (QHEI), and biological data collection (e.g. macro invertebrate counts). Chemical data was used to generate an overall water quality index (WQI) for each sample. ANOVA testing was used to determine if there were spatial or temporal differences within the watershed, and whether temperature and precipitation correlated with WQI values. There were no spatial differences found within the watershed, and there was no correlation between WQI values and weather conditions. Small negative temporal impacts were observed for the three years studied, with increases in total phosphorous and fecal coliform having the largest contribution on the degradation of water quality. Small increases in total dissolved solids and decreases in dissolved oxygen were also found to negatively impact water quality over the three year study, while pH levels and nitrates showed small improvements. Large fecal coliform levels are of greatest concern, and the Muskingum Soil and Water Conservation District is now implementing an agricultural fencing program based on results from this study.

## Optoelectronics & Photonics - Polymers, Devices, and Applications II

**Organizer:** Jon V. DeGroot Dow Corning Corporation, Midland, MI
**Organizer:** Ann W. Norris Dow Corning Corporation, Midland, MI

### 95. Siloxanes in supramolecular condensed systems

**Terry Clapp**, Dow Corning, Cambridge, United Kingdom

A number of advanced supramolecular macromolecular materials including silicon modified liquid crystalline systems have been developed (at the lower molar mass end of the scale). These materials seem to provide a radical property set afforded by the unique properties of the siloxane modification. In collaborative studies in Cambridge University (the Centre for Advanced Photonics and Electronics), conducted within Professor Coles group and Professor Crossland's group, we are engaged in unravelling and understanding the role of the silicon moiety in these sytems. The emergent understandings are very much synonymous with those that are the signal features of many studies in contemporary molecular sciences. In this paper I will survey the broader reach of supramolecular studies as it pertains to the study of advanced functional electro-optic materials and the desires of many to marry biomimetic studies with molecular design to enable radical new synthetic materials. In so doing I will lightly touch upon the energetics of such systems and the mechanistic insights that these afford into the condensed state and macroscopic physical parameters of such systems.

## 96. Dynamic electro- and photo-optic liquid crystal/polymer systems

**T. J. Bunning**, E. R. Beckel, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, J. Wofford and P. Lloyd, Air Force Research Laboratory, WPAFB, OH

Photonic materials and devices will be pervasive in the future. Soft matter, including low molar mass organic, liquid crystalline, bio-macromolecular, colloidal and polymeric materials, afford specific opportunities due to the ease of processing and control of molecular structure and function. Lithographically patterned devices with sub-wavelength spatial resolutions are of great interest in the photonics community for a variety of applications. In this area, patterns parallel to a surface are needed, as opposed to perpendicular patterns generated by conventional lithographic techniques. Holographic photopolymerization is a versatile tool enabling the fabrication of two-phase (component) films with a wide range of applications. We briefly describe work in several areas including electrically switchable 1- and 3-dimensionally ordered polymer/LC systems and static organic/inorganic periodic structures. Holography allows for large area film formation, fine control over periodicity on optical wavelength scales, any geometry fringe planes including curved, and fast (sec), scalable photoprocessing to occur. Discussion on novel photo-switchable structures will center around azo-doped holographically patterned systems. Cholesteric liquid crystal materials, of interest due to their natural band-gap structure and thus selective reflection, are also being examined. Examples of polymer-stabilized CLC's, holographically patterned CLC's, and azo-doped, photoswitchable CLC's will be discussed.

## 97. Siloxane materials for opto-electronic applications

**Kai Su**, Bonnie Ludwig, Jon DeGroot and Jonathan Hannington, Dow Corning Corporation, Midland, MI

Siloxanes, which can be viewed as a hybrid of glass and organic materials, have been used to in various photonic applications including fabrication of waveguides, as well as devices that exploit the large thermo-optical effect of this material. Materials with large electro-optical coefficient have been the subject of intense research, because such materials will allow the hybrid integration of tunable functionality on planar silica-on-silicon and planar polymer light circuits. In this presentation, the formation of siloxanes dispersed liquid crystals, phase transitions, particle size, properties and potential applications will be discussed. The liquid dispersion in siloxanes was prepared by a polymerization induced phase separation (PIPS) process from a vinyl functional siloxane, a crosslinker and nematic liquid crystals.

## 98. Four-channel Variable Optical Attenuator

**Elizabeth Drotleff**, David Nippa, Steven Risser, Melissa Dixon, Richard Higgins, Dirk Schoellner and Louis Vassey, Optimer Photonics, Inc., Columbus, OH

This paper describes a variable optical attenuator (VOA) that uses an electrooptic polymer-dispersed liquid crystal (EO-PDLC) to remove light from a silica-clad silica waveguide. The novel waveguide design provides good extinction (>15 dB), low PDL (<1 dB), low drive power (< 10 mW) and low insertion loss (2 dB) in a very small size. The PDLC is formed on the silica and the VOA can be integrated with an arrayed waveguide grating (AWG) to form high value telecommunications components, including reconfigurable optical add-drop multiplexers (ROADM) or VOA-multiplexers (V-Mux.)

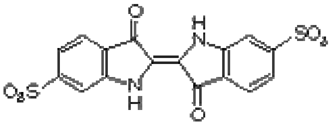
## Physical Chemistry

**Organizer:** Randal M. Hill Dow Corning Corporation and The Massachusetts Institute of Technology, Cambridge, MA

### 99. Theoretical study of the reaction path of singlet oxygen with indigo dyes

**Aaron T. Frank** and Alexander Greer, CUNY Brooklyn College, Brooklyn, NY

The reaction of singlet oxygen ($^1O_2$) with indigo carmine (**1**), indigo (**2**), 1H,1'H-[2,2']-bipyrrolylidene-3,3'-dione (**3**), and vinyl amine (**4**) was conducted computationally to compare to the previous indigo photooxidation studies of Kuramoto et al. Computations were used to investigate the mechanism of oxidative cleavage of the carbon-carbon double bond of **1-4** by singlet oxygen in terms of relative transition state barriers. Density functional theory calculations aided in explaining the contributions of the [2+2] vs heteroatom-ene pathways in this reaction, which will be discussed.



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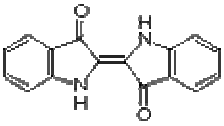

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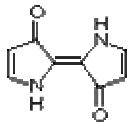

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### 100. Speciation and fragmentation of complexes containing poly-propylene imine (PPI) dendrimers and divalent metals

**William D. Price**, Jason D. Batchelor and Gwendolyn A. Harbour, Marshall University, Huntington, WV

A relatively new class of biomimetic nanoparticle containing amine-based dendrimers and divalent metals offers a wide range of exciting possibilities in catalysis, non-linear optical properties and rationally designed physiological delivery systems. Dendrimers are hyperbranched molecules with a well-defined 3-D replicating chemical structure. A convenient aspect of these dendrimers is the ability to precisely control their size, composition, character, and chemical reactivity. Although, this class of nanoparticle has great potential for host-guest chemistry and site-specific delivery via molecular recognition, characterization of the structure and stability of these macromolecular structures is lacking. Here, we present the Electrospray Ionization speciation and gas-phase dissociation pathways of the first generation of polypropyl imine (PPI) dendrimers complexed with various ionic ligands. Complexes are formed in solution by mixing 2 mM aqueous en, diaminobutane, spermidine, spermine, or PPI dendrimer solution with 10 mM aqueous solutions of divalent metal (Ca, Mn, Co, Ni, Cu, Zn, & Hg) acetate or monovalent metal (H and Ag) acetate. Mixed solutions are diluted 1:1 with acetonitrile and electrosprayed into the quadrupole ion-trap mass spectrometer at a flow rate of 3 μL/min and a source potential of 4.1 kV. Gas-phase complexes are isolated and activated by collisions with He. Fragments are identified and tabulated based on charge state, collision energy, and complex partner.

## 101. Structure and symmetry comparison between two- and three-dimensional crystals

**Katherine E. Plass**, Adam L. Grzesiak and Adam J. Matzger, University of Michigan, Ann Arbor, MI

Patterning surfaces on the low-end of the nanoscale can be accomplished using two-dimensional crystals, but the utility of these structures is limited by the current lack of understanding of self-assembly at interfaces and an inability to predict the packing motifs that will be adopted by a given molecule. Understanding of the self-assembly process in crystals has benefited from the availability of large databases, including the Cambridge Structural Database (CSD) and the Protein Data Bank (PDB), that allow characterization of this entire class of materials. The effects of interfaces on self-assembly, however, have only been explored on a case-by-case basis. To begin to address this deficiency, we have developed the first two-dimensional structural database (2DSD) to examine in general terms the features resulting from self-assembly at surfaces. It was found that molecular-scale patterns are dictated by the same factors that determine bulk crystal structure, but that these factors give rise to different preferred packing symmetries. Unlike in three-dimensional systems, achiral molecules are likely to adopt chiral structures in two-dimensional crystals, and racemic mixtures are expected to spontaneously resolve on the surface. The determination of plane group frequencies enable experimental verification of the theory of close-packing as applied to two-dimensional tiling. This comparison between bulk crystals and physisorbed monolayers provides new tools and directions for future exploration in the engineering of surfaces with prescribed two-dimensional patterns.

## 102. Kinetic and Mechanistic Studies of the Deprotonation of Isobutyrophenone Using a Sterically-hindered Lithium Amide Base (LiHMDS)

**Michael A. Nichols** and Christina Leposa, John Carroll University, University Heights, OH

Kinetic and mechanistic studies of the deprotonation reaction of a sterically-hindered ketone (isobutyrophenone) with a sterically-hindered lithium amide base (lithium bis(trimethylsilyl)amide, LiHMDS) at room temperature in benzene or toluene will be presented. Unlike a majority of deprotonation reactions using lithium amide bases, this

reaction occurs a rate slow enough to be monitored at room temperature using NMR. Proton NMR kinetic studies indicate that the reaction is first-order in ketone and, surprisingly, increasing the concentration of LiHMDS base inhibits the reaction. The thermodynamics of the complexation of the ketone to the lithium amide dimer and the overall deprotonation reaction have also been determined using isothermal titration calorimetry. These values have been compared to theoretical values obtained using semi-empirical PM3 calculations. The aggregation state of the initial lithium amide base has been previously determined using 6Li and 15N NMR using isotopically-enriched LiHMDS and this technique was used to determine and observe the intermediates of the reaction. The aggregation state of the lithium enolate product was found to be a hexamer in the solid-state by x-ray crystallography and is being determined in solution using vapor pressure osmometry. The rate of this deprotonation reaction also varies in the presence of ligands, such as THF or TMEDA. The effects of these ligands on the rates and their potential mechanisms will also be presented and discussed.

### 103. A theoretical investigation of structural differences between eicosapentaenoic and arachidonic acids in the cyclooxygenase site of prostaglandin

**Mark A. Lukowski** and M. C. Milletti, Eastern Michigan University, Ypsilanti, MI

Eicosapentaenoic (EPA) and arachidonic acids (AA) exhibit very different rates of oxygenation in the active site of prostaglandin. This difference is supposedly due to the presence of an additional double bond in eicosapentaenoic acid. The crystal structures of eicosapentaenoic and arachidonic acids in the cyclooxgenase active site were used as the starting point for the theoretical investigation of the interaction between substrate and enzyme. The structures of EPA and AA were optimized in the gas phase and in the presence of a solvent cage at the B3LYP/6-31G(d,p) level of theory. QM/MM ONIOM calculations were carried out on the entire protein plus substrates. Seemingly small differences between the structures of EPA and AA are responsible for the significant differences in the interactions between substrate and amino acid residues within in the active site.

## Polymer Characterization II - Functional Polymers

**Organizer:** Patrick B. Smith Dow Chemical Company, Midland, MI

### 104. Optimizing Conditioning Performance and Silicone Deposition on Hair

**Bethany K. Johnson**[1], Lylenette E. Canfield[1], Stephane Van Oycke[2], Christophe Dubois[2], Anne Dupont[2], Claude Letouche[2] and Tina Scavuzzo[2], (1)Dow Corning Corporation, Auburn, MI, (2)Dow Corning S.A., Seneffe, Belgium

Silicones have been used as a key ingredient in shampoo formulations for many years. Maximizing the conditioning benefits of silicone continues to be an area of investigation in the industry. It has been demonstrated that the deposition of insoluble silicones onto hair from a shampoo can be increased significantly by the use of specific cationic

polymers through the mechanism of coacervation. For fine particle size polydimethylsiloxane emulsions (<2 microns), this mechanism ensures the most efficient deposition onto the hair from a shampoo.

The objective of this study was two-fold. First, it was important to determine how broadly this deposition mechanism can be applied to several different types of polyquaternium materials and silicones. Secondly, a new analytical method was developed to quantify the amount of silicone deposited on hair. The deposition results were then compared to the combing results to determine the correlation between the two methods.

The new deposition method is based on acidic digestion and derivatization of the silicone polymer followed by analysis by capillary gas chromatography with a flame ionization detector. The method is selective for the determination of the dimethylsiloxy- units and was demonstrated to be applicable to all common silicone derivatives (dimethyl, amino, quats) used in hair conditioning.

The deposition results correlated well with the conditioning results. Polyquaternium-10 in combination with Dimethiconol and TEA-dodecylbenzenesulfonate or Divinyldimethicone/dimethicone Copolymer and C12-C13 Pareth-23 and C13-C15 Pareth-3 resulted in the highest level of deposition onto the hair, followed by cationic guar and Polquaternium-7. By maximizing the synergy of silicone emulsions with polyquaternium materials, formulators are able to provide consumers with the specific conditioning benefits they desire.

### 105. Interactions in aqueous mixtures of hydrophobically modified polyelectrolye and oppositely charged surfactant: fluorescent probe methodology

**Deidre A. Strand**, Patrick B. Smith and Angela Shrestha, Dow Chemical, Midland, MI

The design and characterization of functional polymer systems is one of the most challenging frontiers in polymer science today due to their complexity. Interfacial chemistry dominates the performance of these systems and controlling the interface is a daunting task. These systems are often composed of complex distributions of polymer sequence (which is normally different at the interface than in bulk), size and aggregation, each of which greatly affects interfacial performance. Each of these attributes is difficult to characterize and control in isolation, but when complicated with their location at the surface of a system and often in an aqueous environment, the task rises to enormous complexity.

Fluorescent probe molecules may be used to probe the interactions between cationically charged polymers and anionically charged surfactants. Fluorescence spectroscopy with hydrophobic dyes that associate with the micellar phase provide a simple but effective way to characterize the critical micelle concentration (CMC) as well as the critical aggregation concentration (CAC), a similar transition in the presence of a polymeric hydrophobe. Changes in polymer structure can be evaluated in terms of the effect on the interaction with the surfactant, as measured with these fluorescent techniques.

### 106. Surface analysis of polymeric materials – an industrial perspective

**Gregg Potter**, Brandon J Kern and Gary E Mitchell, The Dow Chemical Company, Midland, MI

The characteristics of a polymer's surface dictate many important properties of that material: adhesion to other materials, gloss, weatherability, compatibility, appearance, molding properties, etc. These properties enable certain applications and can drastically alter the value of the polymer system. Surface analysis as a means to determine the relationships of the surface chemistry to the performance (or lack thereof) of the polymer in question can then be a key to optimizing performance and solving problems involving these material properties. The use of surface analysis to understand surface chemistry is not without its challenges, however. For instance, surface analysis techniques often involve indirect means of observation, often require an ultrahigh vacuum environment, and rarely involve pure materials. Indeed, unless highly controlled model systems are used, all surfaces are mixtures. To provide perspective into some of these challenges, the practical industrial application of popular surface analysis and microchemical characterization techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron spectroscopy (XPS), x-ray microscopy (XRM), as well as others, will be discussed. In addition, practical advances in data treatments pertinent to polymer surface analysis will be discussed.

### 107. Probing Supramolecular nanostructures Using Diffusion NMR

**Minghui Chai**[1], Keith A. Freel[1], Nicolas Bedford[1], Luvena Ong[1] and Shanmin Zhang[2], (1)Central Michigan University, Mt. Pleasant, MI, (2)The University of Texas Medical Branch, Galveston, TX

In this presentation, a novel accurate diffusion NMR method has been employed to study supramolecular nanostructures such as host-guest complexes and self-assemblies. The hosts used in the study are dendrimers and cyclodextrins; and the guests are pharmaceutical drugs, amino acids and fatty acids. Using the self-assembled systems of PPI [poly(propylene imine)] dendrimers and fatty acids as model systems, a sequential binding method is established to quantitatively analyze the host-guest binding or encapsulation. Based on the diffusion coefficients measured via NMR, the sequential binding method can calculate the binding constant as well as the percentage of the binding or interaction of the supramolecular nano-systems including host-guest encapsulation and self-assembly.

### 108. Nonlinear Optical Technique for Examining Molecules at Interfaces: Introduction to Sum Frequency Generation Spectroscopy

**David J. DeShazer**, Dow Corning Corp., Midland, MI

Thin films, barrier coatings, adhesives and release coatings are all Dow Corning technologies that succeed or fail depending upon interactions at interfaces. However, many of these systems are hidden from analytical techniques by the fact that they are buried under a bulk of silicones or other materials.

Vibrationally resonant Sum Frequency Generation (SFG) spectroscopy provides a route to study thin films and interfaces without interference from bulk material signatures. As the name implies, the second order nonlinear optical phenomenon of sum frequency generation occurs as the frequencies of two incident beams (nominally a resonant IR beam and a nonresonant visible beam) are summed as the beams mix. The symmetry of the second order nonlinear interaction requires a noncentrosymmetric medium, i.e. an interface between two materials. This symmetry requirement also results in the lack of a signal from the bulk of the material that would normally obscure the interface being probed.

An introduction to the theory of SFG spectroscopy, a comparison to conventional characterization techniques and a survey of results utilizing SFG will be presented.

### 109. Control of the Block Copolymer Morphology in Templated Thermosets

**Theresa J. Hermel-Davidock**[1], H. Sean Tang[2], Dan J. Murray[2] and Steve F. Hahn[1], (1)The Dow Chemical Company, Freeport, TX, (2)The Dow Chemical Company, Midland, MI

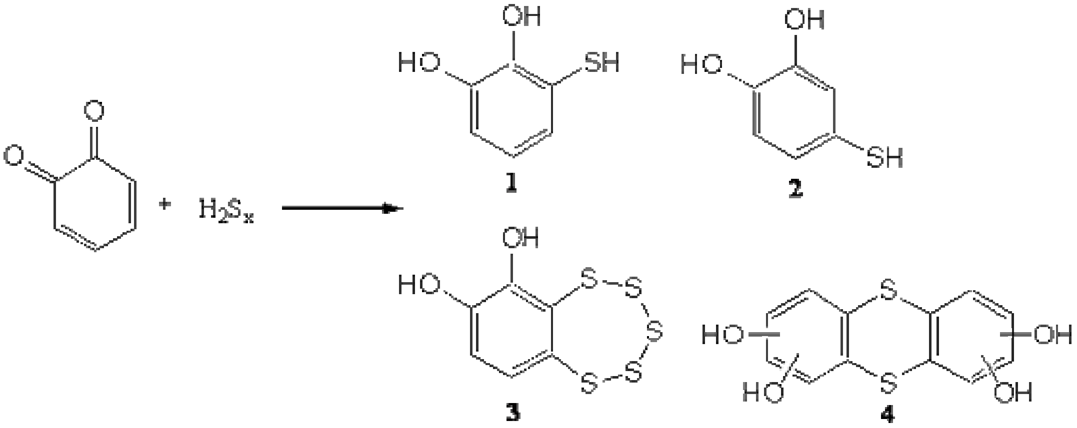
It has been found that by the addition of low concentrations of an amphiphilic block copolymer to an epoxy resin, novel disordered morphologies can be formed and preserved through cure. It has also been found that the addition of small amounts of block copolymer can improve the fracture resistance significantly without sacrificing the high modulus and glass transition temperature of these thermoset materials. This report will focus on characterizing the influence of the block copolymer and casting solvent on the morphology achieved in the thermoset sample and the resulting physical properties. The ultimate goal of this work is to be able to determine the parameters that would produce the microphase morphology offering the greatest enhancement of the fracture toughness for these thermoset samples. Epoxy resins blended with a series of amphiphilic block copolymers based on hydrogenated polyisoprene (polyethylene-alt-propylene or PEP) and polyethylene oxide (PEO), specifically, were investigated. In this report the cure-induced order-order phase transition from the spherical to wormlike micelle morphology will also be discussed. It is proposed that the formation of the wormlike micelle structure from the spherical micelle structure occurred similar to the phase transition behavior that occurs in dilute block copolymer solutions as a function of the solvent.

## Synthetic Chemistry

### 110. Biomimetic Synthesis of Pentathiabenzocycloheptene-1,2-diols and Thianthrene tetrols from $H_2S_x$ and Ortho-benzoquinone

**David Aebisher**, Edyta Brzostowska and Alexander Greer, CUNY Brooklyn College, Brooklyn, NY

We have undertaken a biomimetic synthesis of polysulfanes using catechol o-benzoquinone as a model for dopamine o-benzoquinone. Inorganic polysulfanes ($H_2S_x$) add to o-benzoquinone at the 3 or 4 position to form hydropolysulfidocatechols that ultimately give rise to 3-mercaptobenzene-1,2-diol (**1**), 4-mercaptobenzene-1,2-diol (**2**), pentathiabenzocycloheptene-1,2-diol (**3**), and thianthrene tetrols (**4**). The regiochemistry of attack is found to be pH dependent. Mechanistic evidence will be presented for formation of these products.



## 111. A simple preparation of 2-thiohydantoins

**Zerong Wang**, University of Houston-Clear Lake, Houston, TX

2-thiohydantoins are known to exhibit a variety of biological activities and have been applied as inhibitor of angiogenesis, hypolipidemic, anticarcinogenic, antimutagenic, antithyroid, antiviral (e.g., against herpes simplex virus (HSV), human immunodeficiency virus (HIV), and tuberculosis), antimicrobial (antifungal and antibacterial), anti-ulcer, anti-inflammatory agents, and pesticides. Therefore, more than ten different synthetic methods have been developed to prepare 2-thiohydantoin derivatives. However, more or less these methods have at least one of the limitations for large-scale preparation, such as the application of expensive starting materials (e.g., fluorous-phase supporting material, ester isothiocyanate), moisture sensitive materials (isothiocyanate, ?-halo acid, etc.), and toxic materials (?-halo acid, ?-halo amide). During our practice of preparing nitrogenous heterocycles, we find and will present a novel and simple method to prepare 2-thiohydantoins from ?-amino acids and thiourea that can easily be scaled up to an industrial production. This new reaction is a fast, simple, low cost reaction that can especially prepare some 2-thiohydantoins that other common methods fail.

## 112. Methyl Ester Formation in Polyunsaturated Fatty Acids using the Reagent Trimethylsilyldiazomethane

**Wan Hsin Lim**, Basu Hemendra and Steven J. Pernecky, Eastern Michigan University, Ypsilanti, MI

In this study, trimethylsilyldiazomethane (TMSD) is used as an alternative to diazomethane in the preparation of methyl ester derivatives of polyunsaturated fatty acids (PUFA). The TMSD reagent is a stable and safe substitute for diazomethane because it is less hazardous and is easier to handle than diazomethane in the methylation reaction. The PUFA methyl esters are prepared by treatment of lipids with TMSD in the presence of methanol and then subjected to resolution by gas chromatography and mass spectral analysis. Three different solvent systems, 10% methanol in ether, 20% methanol in acetone, and 20% methanol in benzene were investigated for the methylation of PUFAs. Reaction conditions were evaluated for linoleic acid, linolenic acid, arachidonic acid, eicosapentanoic acid, and docosahexaenoic acid. The results indicated that the formation of methyl ester fatty acids is greatest in the ether solution containing 10% methanol. Fewer side products are formed with arachidonic acid than for the other PUFAs regardless of the solvent system used. However, the amount of side product relative to the formation of methyl ester is minimal and does not appear to affect the validity of the method. In addition, TMSD was used in the methylation of prostaglandin $F_{2\alpha}$ ($PGF_{2\alpha}$) and prostaglandin $E_2$ ($PGE_2$). A reaction to form an oxime is carried out for $PGE_2$ prior to the methylation reaction, which is then followed by a silylation reaction. A silylation reaction is carried out for $PGF_{2\alpha}$ after the methylation reaction with TMSD. The methylation of PUFAs with TMSD was simple and less deleterious than diazomethane and can be used to identify and quantify a number of physiologically relevant PUFAs.

### 113. 1,2-Oxazines as Novel Alkoxyamine Initiators for Mediated Radical Polymerization

**Jin Zhang** and Bob A. Howell, Central Michigan University, Mount Pleasant, MI

N-Phenyl-1,2-Oxazines may be generated from cycloaddition reactions involving nitrosobenzene as the dienophile and a variety of dienes followed by catalytic reduction of the double bond in the adduct. The resulting oxazines contain an N-O bond which undergoes thermally-induced homolysis to generate a carbon radical capable of initiating polymerization and a nitroxyl radical suitable for capping the propagating polymer chain to prevent unwanted side reactions(radical coupling, transfer. etc.)

### 114. Photocycloaddition reactions of and in dendrimers and dendrons

**Wendell L. Dilling**, Central Michigan University, Mount Pleasant, MI

The title reactions will be reviewed. Photocycloaddition reactions have been reported where the moieties undergoing the cycloadditions are incorporated in dendrimers and dendrons, either near the ends of the branches, within the branches, or at the cores. Both intramolecular and intermolecular photocycloadditions have been reported. Synthetic and mechanistic aspects of these reactions will be presented. The cycloaddition reactions were of the types 2 + 2, 4 + 4, and 4 + 2. The 2 + 2 reactions included derivatives of cinnamide, stilbene, uracil, and norbornadiene. The 4 + 4 reactions included derivatives of anthracene and benzene, while a single example of a 4 + 2 process involved an anthracene derivative with fullerene-C60. Examples of using dendrimers as reaction media for photocycloaddition reactions (of acenaphthylene) will be presented.

## Plenary Lecture: This is not your grandmother's beauty company!: Using biotechnology to drive consumer-noticeable benefits in skin care

### 115. This is not your grandmother's beauty company!: Using biotechnology to drive consumer-noticeable benefits in skin care

**Jim Thompson**, Procter & Gamble, Cincinnati, OH

The consumer desire for effective anti-aging skin care products continues to grow. Included in this growth is a desire for skin improvement against a wider array of imperfections and a greater magnitude of benefit. To meet consumers' needs, P&G Beauty is utilizing state-of-the-art biotechnology tools for technology screening and identification. Genomics, proteomics, and bioinformatics are utilized to identify relevant biochemical pathways and cosmetically-actionable targets. High-throughput screening and assay development are then used to identify potential technologies via mechanism-based assays. State-of-the-art in vitro human skin equivalents provide tier II non-mechanism-specific confirmation, and human clinical screening and testing is used to demonstrate benefits. Both internal and external sources of potential technologies are used. This talk will highlight the overall technology development process used to identify new skin care technologies and a successful example of a technology derived from the utilization of this process.

## Alternative Feedstocks I - Petroleum Alternatives

**Organizer:** Bob R. Maughon Dow Chemical Company, Midland, MI
**Organizer:** Mark E. Jones Dow Chemical Company, Midland, MI

### 116. From carbon feedstocks to alcohols and ethers – pathways and catalysts

**Kamil Klier**, Lehigh University, Bethlehem, PA

Natural gas and coal are gasified by known technologies to syngas, CO/H2/CO2 of varying composition and impurity content. Subsequent conversion to hydrocarbons, alcohols, esters, ethers and derived chemicals is carried out by heterogeneously catalyzed processes the economics and efficiency of which is controlled by the catalyst activity, selectivity and process conditions. The knowledge of chemical mechanism assists in designing new or improving existing catalysts. In this presentation I will briefly review the two fundamentally different pathways to alcohols over oxide-based (high H2/CO syngas, large promotion by CO2) and sulfide-based catalysts invented at Dow (low H2/CO syngas, moderate retardation by CO2), the effect of promoters, and some knowledge derived from single crystal studies. Downstream, the dual acid-site catalyzed

SN2 pathway to unsymmetrical ethers from two different alcohols is shown to be far more effective than the carbenium mechanism and is proven by product composition (e.g. high-cetane MIBE vs high-octane MTBE), 18O and 13C label flow, and chirality inversion. The classes of solid-acid catalysts entail polymers, derivatized inorganic oxides, zeolites, and mesoporous silicas derivatized with high-density flexible alkyl-sulfonic acid groups. Further, direct methylated amine synthesis from lower amines and syngas will be shown to occur via aldehyde intermediates. The experimental mechanistic results are supported by a high-level theory which not only allows selection of acceptable pathways but also quantitatively accounts for the barriers via locating and calculating properties of the Transition State (TS). An animation of the imaginary frequency of the TS for ether formation will be shown for the SN2 ether-forming dehydrocondensation and E2 olefin-forming dehydration.

### 117. Selective partial oxidation of methane

**Ayusman Sen**, Pennsylvania State University, University Park, PA

The selective oxidative functionalization of methane is one of the most challenging chemical problems, in addition to being of great practical importance. In this context, we will describe two different methane conversion systems. The first involves radical initiated reaction of methane with sulfur trioxide to form methanesulfonic acid, a methanol precursor. Selectivity for methanesulfonic acid is > 98%. When used as the limiting reagent, the conversion of sulfur trioxide is nearly quantitative with methane conversion > 40%. The second system uses NOx as the catalyst and converts methane to formaldehyde in the gas phase in relatively high yield. The scope and the mechanism of the two systems will be described.

### 118. Insights into the Use of Molecular Oxygen in Aerobic Oxidation Catalysis

**Shannon S. Stahl**, University of Wisconsin-Madison, Madison, WI

Molecular oxygen is among the most desirable oxidants for chemical synthesis; however, its use also presents numerous challenges. We have been investigating "palladium oxidase" reactions that promote the selective and efficient oxidation of organic chemicals with molecular oxygen as the oxidant. This talk will describe recent advances in our mechanistic understanding of reactions between molecular oxygen and reduced palladium complexes relevant to catalytic turnover. Insights gained from theses studies are contributing to the development of improved palladium-catalyzed aerobic oxidation reactions.

### 119. The E2V story: Novel catalysts enable the Dow ethane-to-vinyl process

**Mark E. Jones**, Daniel A. Hickman and Michael M. Olken, Dow Chemical Company, Midland, MI

Lanthanum-based catalysts have been found to be useful in the oxidative chlorination of ethane to vinyl chloride. Lanthanum oxychloride provides a means to produce a catalyst capable of converting ethane to a mixture of ethylene and vinyl chloride. Under the same conditions, the catalyst also converts ethylene to vinyl chloride with high selectivity. Bulk lanthanum oxychloride suitable for use in a fluidized bed reactor was developed and tested. Under reaction conditions, this material is transformed into lanthanum trichloride, the active catalytic species. Use of bulk metal chlorides as catalysts and there use in oxidative chemistry are both novel.

## 120. Innovation in Chemical Reaction Engineering.The CREC Riser Simulator

**Hugo I. De Lasa**, University of Western Ontario, London, ON, Canada

The implementation of FCC is by now a well-established industrial scale technology. Recent years have seen however, new FCC reactors (e.g. down flow instead of risers) and novel catalysts to meet more stringent gasoline specifications. Even more new catalytic processes are currently implemented or considered for other key fluidized chemical processes. Excellent examples of those are the oxy-de-hydrogenation of ethane, the steam and dry reforming of methane and other feedstocks using membrane reactors, the desulfurization of gasoline via de-hydro-sulfidation, the catalytic gasification of biomass and the manufacturing of solar grade silicone. CREC researchers have invented a new experimental tool called the “CREC Riser Simualtor. This bench scale mini-fluidized bed unit (50 cm3capacity, 1 gr. of catalyst)(de Lasa, 1991) mimics the operating conditions of a riser/downer reactor in terms of reaction time, temperature, hydrocarbon partial pressures and catalyst/oil ratios. An impeller located in the upper section and a basket containing the catalyst placed in the central section, are the main components. Upon rotation of the impeller, gas is forced downwards in the outer reactor annulus. The CREC riser simulator provides key data for: a) intrinsic kinetic parameters of complex reactions, b) adsorption constants and effective diffusivities, allowing the development of phenomenologically based heterogeneous kinetic models, c) reaction enthalpies for overall energy process balances . A typical application of the CREC Riser Simulator to FCC is illustrated via the 1,3,5- tri-isopropyl-benzene reaction with two typical FCC catalysts with close acidity and structural properties and different crystallite sizes, CAT-SC (0.4μm) and CAT-LC (0.9μm). Using experimental data of the CREC Riser Simualtor the intrinsic kinetic and effective diffusivity parameters are evaluated showing the value of this methodology for establishing heterogeneous models for FCC and other catalytic processes.

de Lasa, H.I., (1991). Riser Simulator for Catalytic Cracking Studies. U.S. Patent #5,102,628.

## 121. Autothermal Reforming of Renewable Feedstocks

**Paul Dauenhauer** and Lanny D. Schmidt, University of Minnesota - Twin Cities, Minneapolis, MN

Hydrogen production from ethanol-water mixtures allows low-cost transportable energy storage that works with the current liquid fuels infrastructure as well as the coming "hydrogen economy." On-board reforming of ethanol and ethanol-water mixtures can produce hydrogen rich streams by converting more than 95 % of the fuel autothermally. The ability to utilize ethanol without completely removing water provides a significant improvement in the energy demand and cost of ethanol production for transportation. The reaction process occurs by contacting ethanol and water in air on noble metal catalysts fast enough (less than 10 milliseconds) that a reforming system for a car could be the size of a shoebox. The heat generated in the reaction can be used to vaporize the liquid fuel allowing the entire system to produce a cooled hydrogen stream directly from liquid ethanol and water without any external heat. This process has been extended to additional biomass-derived fuels including methanol, glycerol and biodiesel producing either hydrogen or value-added chemicals depending on the reactor conditions.

## Emulsion Polymerization and Latex Technology: Preparation, Properties, and Applications I

**Organizer:** Raymond E. Drumright Dow Chemical Company, Midland, MI
**Organizer:** Thomas H. Kalantar Dow Chemical Company, Midland, MI

### 122. Core-shell latex particles - how do they actually achieve that configuration?

**Donald C. Sundberg**, University of New Hampshire, Durham, NH

It is very often a goal of the chemist or engineer to make core-shell latex particles for a variety of interesting applications. In order to make such particles people most often begin with a first stage, or seed, latex particle and then add the second stage monomers to the reactor. Often it is simply assumed that the second stage monomers will polymerize in such a way to result in a shell of the second polymer around a core of the seed polymer. We have spent quite a bit of time investigating the chemical reactions and molecular diffusion responsible for the ultimate placement of the two polymers within the latex particle and have come to learn that there are many alternatives other than the core-shell structure. The purpose of this discussion is to focus on the reactions that take place in the aqueous phase, the events leading to oligomeric radicals entering and penetrating the particle, as well as polymerization and phase separation within the particles. This discussion will include a number of examples in which core-shell particles should be achievable but in reality are not, and will describe a set of complementary investigatory tools (e.g. electron microscopy and thermal analysis) to examine the particle structure in detail, including quantitative modeling.

### 123. Morphology Characterization of Core/Shell and Hollow Latex Particles by TEM, Near Edge X-Ray Absorption Fine Structure Spectroscopy, and Focused Ion-Beam SEM

**Melinda Keefe**[1], Gary Mitchell[1], Joseph Harris[1] and Elvin Beach III[2], (1)Dow Chemical, Midland, MI, (2)The Ohio State University, Columbus, OH

The characterization of the morphology of core/shell latex particles by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is compared to standard transmission electron microscopy. NEXAFS can identify and quantify the chemical structure of a material from the fine scale details of the absorption spectrum. This technique is a combination of spectroscopy and microscopy which provides compositional information at a spatial resolution of approximately 30-50 nm. The preparation and characterization of cross-sections of hollow latex and core/shell particles using a focused ion-beam (FIB) SEM in a dual beam FIB-SEM instrument will also reviewed. These techniques will be demonstrated on core/shell latex particles comprised of a styrenic polymer shell encapsulating an acrylate polymer core and on hollow styrenic-based latex particles.

### 124. Polymer interdiffusion in latex films of randomly branched vinyl acetate copolymers

**Jung Kwon Oh**, Carnegie Mellon University, Pittsburgh, PA and Mitchell Winnik, University of Toronto, Toronto, ON, Canada

Film formation and polymer diffusion at a molecular level were investigated in poly(vinyl acetate-butyl acrylate) (P(VAc-BA)) latex films. From a practical perspective, this copolymer was chosen as a model for architectural coatings. From a theoretical perspective, this polymer allowed us to investigate polymer diffusion in films of randomly branched polymers. Polymer diffusion was studied by fluorescence resonance energy transfer (ET) measurements. This methodology requires latex particles labeled with donor and acceptor dyes. Different dye-labeled latex particles were synthesized. Donor-labeled P(VAc-BA) latex particles were prepared with phenanthrene (Phe) as the donor group. Attempts to synthesize latex particles labeled with anthracene (An) as the corresponding acceptor group failed because An derivatives inhibited VAc polymerization. New polymerizable dimethylaminobenzophenone (NBen) derivatives were developed. These NBen derivatives proved to be useful energy transfer acceptors for Phe and they were compatible with VAc polymerization. A broad series of P(VAc-BA) latex particles labeled with Phe and with NBen were prepared. These latex particles contain significant amounts of gel. This gel has a strong influence on polymer diffusion in latex films. The amount of gel in the polymer could be reduced or eliminated by adding a chain transfer agent to the polymerization reaction. Fluorescence decay measurements of ET efficiency were used to study polymer diffusion in films of these latex samples. The most important variables that affect the polymer diffusion rate are temperature, molar mass, the nature of phase separation in the latex polymers, and the presence of gel. It was found that temperature enhances the rate of polymer diffusion, while high molar mass and a phase-separated morphology largely slow the rate of polymer diffusion. The presence of gel limits full mixing of polymers in these latex films.

## Functionalized Polymer Interfaces and Adhesion I

**Organizer:** Dongchan Ahn Dow Corning Corporation, Midland, MI
**Organizer:** Zhan Chen University of Michigan, Ann Arbor, MI

### 125. Adhesion and Failure Mechanisms of Pretreated Aluminum Bonded with Epoxy Adhesives

**Susan M. Ward**, Ford Motor Company, Dearborn, MI

Since the use of chromate pretreatments is being discontinued in many countries of the world due to environmental concerns, the development of alternative pretreatments for aluminum to provide good corrosion resistance and a basis for adhesive bonding is paramount to many industries. In the automotive industry, pretreatments are applied to both aluminum coils and to individual aluminum parts, which often leads to utilization of different pretreatment chemistries. Several pretreatment chemistries will be discussed along with proposed mechanisms of bonding between epoxies and the pretreatments. Results of adhesive bonding and aging studies will also be presented. In addition, failure mechanisms of several adhesively-bonded aluminum systems after long-term aging will be presented.

### 126. Reconfigurable Polymeric Bio-Interfaces

**Shuichi Takayama**, University of Michigan, Ann Arbor, MI

The interfaces between extracellular matrices and cells are dynamic, and crucial for regulating cellular processes including signal transduction, growth, differentiation, motility, and apoptosis.1 In vitro cellular studies and biomaterials development would benefit from matrices that allow reversible modulation of the cell adhesive signals at a size scale comparable to individual adhesion complexes. Here, we describe the fabrication of substrates containing arrays of cracks with cell-adhesive proteins selectively adsorbed inside them. The widths of the cracks (120-3200 nm) are similar to that of individual adhesion complexes (typically 500-3000 nm)2 and can be regulated by adjusting the mechanical strain applied to the substrate. Morphology of cells can be reversibly manipulated multiple times through in situ adjustment of crack widths and hence the amount of the cell accessible ECM proteins. These substrates provide a new tool for assessing cellular responses associated with exposure to matrix proteins. Other topics that will be discussed include reprogrammable microfluidic systems.

### 127. High throughput approach to correlating interface composition with adhesion in thermally activated adhesives

**Dongchan (Shaun) Ahn**[1], Patricia A. Olney[1], Christopher S. McMillan[1], Nick E. Shephard[1], Cheryl L. Loch[2], Sarah A. Spanninga[2] and Zhan Chen[2], (1)Dow Corning Corporation, Midland, MI, (2)University of Michigan, Ann Arbor, MI

Adhesion of heat-cured silicone elastomers relies upon interfacial segregation of adhesion promoting species for most substrates. The interface structure and composition that evolves during curing is controlled by a complex combination of competitive reaction and diffusion events. Studies of strongly bonded interfaces are hindered by the fact that a well-adhered interface, by definition, cannot be readily separated and exposed for analysis. Hence, the molecular mechanism of adhesion in these systems is not well understood. In this study, we present a new approach to this problem by combining a high throughput thermal gradient peel test methodology with x-ray photoelectron spectroscopy (XPS) and sum frequency generation (SFG) vibrational spectroscopy to study changes in the interface composition and structure as adhesion develops with increasing cure temperature. Comparison of the free surface, bulk and substrate interface of the elastomer provides direct evidence of strong interfacial segregation of a model titanate adhesion promoter. By analyzing adhesion test specimens prepared on a linear thermal gradient device, we directly seek compositional and structural changes at the elastomer-substrate interface associated with the thermal onset of adhesion. This methodology reveals distinct maxima in adhesion promoter concentration and spectroscopic signatures of adhesion promoter reactivity and diffusion at the interface.

### 128. Suppress polystyrene thin film dewetting by modifying substrate surface with aminopropyltriethoxysilane

**Sung-Hwan Choi** and Bi-min Zhang Newby, The University of Akron, Akron, OH

Many polymer thin films (< 100 nm) undergo morphological transition on nonwettable substrates when they are annealed over Tg of the polymer. Holes form in the unstable melt of the polymer film, grow, and coalesce with each other. The materials removed from the holes eventually break up into droplets on the substrate. For practical applications of the films, it is critical to maintain the homogeneity and continuity of the films against this “dewetting” process. 3-aminopropyltriethoxysilane (APTES), which has been widely utilized as adhesion promoters, was also found to have the ability to prevent dewetting of polymer thin films from substrates. When deposited at ambient conditions, the APTES molecules form a loose but complex network due to hydrogen bondings between its terminal amino group and the multiple hydroxylated head groups and/or hydroxyl groups on a substrate. Upon heating, the hydrogen bonding can be broken, and a tight network can be achieved by condensation among those unreacted silanol groups. When a polymer thin film is in contact with the APTES layer during the thermal process, the polymer chains can diffuse/penetrate into the APTES network while the network is being tightened by the additional crosslinking. The penetrated chains subsequently anchored into the APTES network, leading to the inhibition of the thin film from dewetting. This hypothesis was verified by dewetting studies of polystyrene (PS) thin films, having molecular weights above and below the entanglement molecular weight (Me), from APTES and control surfaces when the systems were subjected to various treatments. Dewetting suppression was observed for PS/APTES that was thermally treated prior to the annealing of the thin film at higher temperatures. Much stronger suppression was noticed for PS having a molecular weight higher than Me. When PS thin films were deposited onto a precured APTES network, no dewetting suppression was observed.

### 129. Adhesion modification of polyolefin surfaces with sodium hypochlorite in acidic media

**Lars, G. Beholz**, Beholztech, Inc., Flint, MI and Ali Zand, Kettering University, Flint, MI

Increased surface adhesiveness of HDPE is achieved by immersing it in an aqueous solution of sodium hypochlorite (bleach) mixed with an acid. This process results in the addition of functionality to the polymer surface vastly altering its adhesive, polarity and surface reactivity. Analysis of the modified polymer surfaces by ESCA has shown that chlorine atoms have been added to the surface. Studies regarding the chlorination of small molecules have also shown that the chlorination process is amenable to a variety of chlorination objectives and offers a route toward the functionalization of a variety of polymeric and non-polymeric substrates. In particular, this treatment renders unpaintable substrates such as HDPE more receptive to application of paints and adhesives.

## Knowledge Management and Data Mining I

**Organizer:** Terrence K. Hilty Dow Corning Corporation, Midland, MI
**Organizer:** Shruti Bahadur Dow Corning Corporation, Midland, MI

### 130. Mopping up the flood of data with web services

**Gary Wiggins**, Indiana University, Bloomington, IN

The core of informatics is the relationships between the meaning of information and its representation as data. Our burgeoning ability to both generate and collect scientific information has created a number of challenges. The principal challenges are how to extract meaningful, sometimes latent, novel information and how to manage the information. The new field of Knowledge Discovery in Databases (KDD) seeks to provide answers to both of these problems. Data mining involves a strong machine-learning component to semi-automatically detect information that is useful. Unfortunately for the scientist, there is no set of standard tools at their disposal to conduct data mining. Furthermore, the sophisticated creation of algorithms, heuristics and their implementation is generally outside the expertise of scientists. Another distinguishing characteristic of scientific information is the much greater role played by "metadata" (data about data). The metadata problem has long vexed scientific information. With a fixed table approach, programs must be rewritten frequently to keep pace with changes in data representations. The huge increase in data volumes that stream from modern laboratory instruments has magnified the problems. Informatics schools train students to deal with scientific data handling problems, utilizing not only locally generated data, but the full spectrum of databases and resources available on the Web. Indiana University's approach to a Chemical Informatics and Cyberinfrastructure Collaboratory will be presented as an example of one solution to the data deluge problem.

### 131. Collaboration and communities at Hewlett-Packard

**Stan Garfield**, Hewlett-Packard Company, Livonia, MI

Collaboration is one of the key processes used in the HP Services Consulting & Integration knowledge management program. Two of the ways HP collaborates are collaborative team spaces and communities of practice.

This presentation will provide details on how collaborative team spaces are created and used at HP. It will also explain how HP creates and manages communities of practice, how community members participate, and how tools are used to support communities.

### 132. Moving from knowledge to experience—A simulation approach to Best Practice-based behavior change

**Ken Spero**, Humentum Corporation, Philadelphia, PA

Abstract- How does an organization apply experience to improve capabilities? This session will present a methodology to use simulation to capture and deploy usable best practices. To illustrate this approach, the audience will participate in a Best Practices simulation on regulatory implications in product development.

The traditional approach to capturing best practices is via documents or slides created by practitioners and then saved to a knowledge management system. The problem with this approach is that it usually has no effect on actual behavior, and consequently, on the progress of the organization. Not only do employees fail to seek out best practices when they have a need, but even if they do, it is rare that the best practices directly apply to their real-life situation, much less result in a change in behavior.

To address this challenge, Humentum has developed an alternative approach that seeks to address the underlying behaviors and skills associated with best practices. The approach enables employees to experience the application of specific best practices, bringing them to life in a way that results in true performance change.

This presentation will present a methodology to: - capture best practices around a specific initiative or process - immerse employees in a real-life experience that demonstrates those best practices - develop and deliver those experiences effectively, quickly, and flexibly - use simulation as a vehicle for experiential learning, analysis, and knowledge capture and delivery

About Humentum - Humentum builds simulations that give organizations and employees firsthand experience with an initiative's best practices in a real-world but risk-free environment. Employees experience complex interpersonal and organizational issues through powerful storytelling that brings new behaviors to life. Simulation authoring and maintenance capability is easily transferable to client teams to build their own story-based simulations, quickly and at low cost in time, resources, and expense.

### 133. Text mining: capitalizing on the value hidden in textual data

**Jeff Wright**, SAS Institute, Inc., Independence, OH

With the ongoing proliferation of text data, businesses are looking for ways to integrate, access, and manage text and database information. Text mining software equips companies to find patterns across large document collections. Furthermore, by analyzing both structured and unstructured data together, companies can move beyond traditional ‘structured-data-only' analysis to gain additional information and competitive advantage from this data. This talk will introduce text mining and SAS Text Miner, survey some common applications, review some customer success stories, and briefly overview potential applications in the chemical industry.

### 134. Practicing text mining at Dow

**Mani Shabrang**, Bryan Warner, Gary McNamee and Bob Gulotty, The Dow Chemical Company, Midland, MI

Text mining is constantly evolving in its reach and scope as progress in computing technology opens new horizons for our quest to acquire further knowledge with maximum achievable efficiency.

Text mining, or text analytics in its more recent characterization, is often suggested as a methodology to discover knowledge and patterns that are non-retrievable or inefficient to retrieve by search tools only or by database management tools only. Text analytics allows you to explore complex relationships among hundreds and thousands of documents in a textual database by providing a visual interface to your documentation, among other pieces of knowledge.

A typical chemistry example dealing with heterogeneous catalysis is reviewed. New trends in text analytics and its unavoidable overlap with many related disciplines are presented from a practitioner's perspective. Finally, subsequent challenges to the developers and practitioners are discussed.

## Nanocomposites: Science, Technology, and Commercial Applications I - Science and Technology

**Organizer:** Juan M. Garces Consultant, Midland, MI
**Organizer:** Richard F. Fibiger Dow Chemical Company, Midland, MI

### 135. Polymeric Nanocomposites off the Beaten Path

**Patrick Mather**, Case Western Reserve University, Cleveland, OH

Research into nanostructured polymeric materials has exploded during the past 10-12 years, based primarily on the outstanding properties observed in the nylon-organoclay system pioneered by Toyota researchers. While some significant successes have been reported using similar approaches, more often failures have resulted. This lecture will examine new approaches to polymeric nanocomposites – off the beaten path – to reveal an array of new materials and processing techniques that enable property tailoring.

Drawing from research in our own lab as well as others, example materials will include nanostructured POSS polymers, in-situ biocatalyzed ceramic/polymer composites, and hyperbranched polymeric nanoparticles. Example nanometer-scale processing techniques will include rapid layer-by-layer polymeric coatings, electrospinning of nanofibers, and nanolayer extrusion methods. By the end of this presentation, it is intended that the audience will have available a menu of new approaches to polymeric nanocomposites.

### 136. Clay aerogel/polymer nanocomposites

**David A. Schiraldi**, Suneel A. Bandi and Matthew D. Gawryla, Case Western Reserve University, Cleveland OH, OH

Smectic clays have been incorporated into polymer matrixes for the past 15 years, depending upon exfoliation of the clay in order to enhance thermal/mechanical properties of the composites. A different approach to incorporating clay into polymers is to pre-form a low density aerogel structure from the clay, then combine this material with polymer to produce a foam-like composite. In this manner, co-continuous, interpenetrating organic/inorganic composites have been produced, providing both polymer property enhancements and the potential for producing high performance/low density structures.

### 137. Palygorskite as an epoxy polymer reinforcing agent

**Siqi Xue**[1], Marc Reinholdt[2] and Thomas J. Pinnavaia[1], (1)Michigan State University, East Lansing, MI, (2)University of Illinois at Urbana-Champaign, Urbana, IL

Layered clay minerals have been attractive reinforcement agents for polymer nanocomposites since the pioneering work of Toyota researchers. Remarkable material properties can be achieved when clay layers are dispersed in polymer matrices on nanometer scale. Unlike layer clay minerals, palygorskite, a silicate clay with a pleated 2:1 layered structure, has a unique lath-like particle morphology and low ion-exchange capacity, which make it an attractive candidate for the formation of polymer nanocomposites. Palygorskite-thermoplastic polymer nanocomposites have been reported with improvement in material properties. Here we report using palygorskite as a reinforcement agent for thermoset epoxy polymers. To enhance the affinity between palygorskite and epoxy matrices, three silylation reagents were used for surface modification of the mineral, namely, g-aminopropyltrimethoxysilane (APTMS), N-dodecyltriethoxysilane (DTES), and 1,1,1,3,3,3-hexamethyldisilazane (HMSZ). The dispersion of palygorskite particles are improved after the silylation modification, and consequently the composites made from the silylated palygorskites afford better improvements in mechanical properties at low loadings levels of 2 and 5 % (w/w). But at higher loadings where increases in the viscosity of the pre-polymer helps to stabilizes the mineral dispersion, little or no differences were observed for the reinforcement benefits provided by the pristine and silylated forms of palygorskite. Only marginal improvement in tensile properties is observed in glassy epoxy nanocomposites made from both pristine and silylated palygorskite regardless of the mineral loading level, indicating that the tensile strength of palygorskite laths may be approaching that of the polymer matrix.

## 138. Synthesis and characterization of hybrid polymer-TiO2 nanocomposites via in situ polymerization

**Leonardo C. Simon** and Feng Lin, University of Waterloo, Waterloo, ON, Canada

Polymer nanocomposites have important applications in automotive and aerospace, electronics and electrical engineering, household products and appliance components, packaging, and defense systems. Among many nanocomposite precursors, TiO2 nanopowder is being increasingly investigated due to its specific properties. This presentation will discuss the preparation of hybrid polymer-TiO2 nanocomposites. When dispersed at the nanoscale level, TiO2 nanopowders can act as visually transparent UV filters and high thermo-mechanical performance materials. Unfortunately, the dispersion of nanoscale TiO2 in hydrophobic polymers, like polyolefins, is difficulty to obtain because most of the TiO2 readily available from commercial sources has agglomeration of primary nanoscale particles forming secondary particles in the micrometer range. The objective of this research is to prepare hybrid nanocomposites using in situ polymerization. The synthesis strategy involved two steps. Firstly, TiO2 was modified with 3-(trimethoxysilyl)propylmethacrylate. The grafting density and efficiency were quantified and the particle size distribution in suspension was measured. Secondly, styrene was polymerized using free radical mechanism to attempt copolymerization with groups on the surface of the modified TiO2 resulting in the formation of nanocomposites with polymer chains chemically bonded to the surface of TiO2 nanopowders. The final polymer nanocomposites structure was characterized. The presentation will also discuss the preparation and the properties of polyethylene-alumina and polyethylene-clay nanocomposites obtained using in situ polymerization.

## 139. Thermoplastic vulcanizate nanocomposites

**Lloyd A. Goettler**, Keung Yong Lee and Hemant Thakkar, The University of Akron, Akron, OH

Thermoplastic vulcanizates (TPVs) are rubbery blends of a continuous molten thermoplastic phase with an immiscible elastomer phase that is crosslinked into dispersed micron-sized particles during the compounding process. Depending upon the mixing protocol, either phase may be selectively reinforced with a nanoscale inclusion, such as an organically modified smectic silicate. In addition to compatibility between the organoclay and either polymer that would affect clay swelling and interface strength, the mechanical properties of such a composite blend are shown to depend upon the phase partitioning of the reinforcement.

Specifically, olefinic TPVs comprising polypropylene combined with either a polar or a non-polar rubber phase are modified with nanoclays of variable surface treatment. The measured TPV modulus of elasticity is related to the resulting phase structure, including the phase location of the reinforcement as well as its degree of swelling, through a mechanics of materials analysis.

A higher stiffness in the TPV with reinforced plastic phase can be attributed to the higher modulus of that polymer, the continuity of that phase and its deformation with potential alignment of the reinforcement during thermoplastic compounding and fabrication. Conversely, the lower stress/strain levels experienced by nanoclay dispersed in the cured rubber domains of solid/molten TPVs would have distinctive effects on their ultimate and rheological properties.

### 140. Nanocomposite Technology in Tire Innerliners

**Brendan Rodgers**, Robert Webb and Weiqing Weng, ExxonMobil Chemical Company, Baytown, TX

Improvements in tire performance over the last 15 years have been dramatic. Significant enhancements in tire tread wear and traction, reductions in rolling resistance, and improvements in durability have enabled development of products of the highest quality. Though design changes have been made and new reinforcements materials have been introduced, many of the major improvements can be attributed to developments such as the introduction of the silica tread compound, functionalized and coupled solution SBR and improvements in compound aging and reversion resistance.

Since the introduction of bromobutyl rubber, however, there have been very few significant changes to the composition and form of the tire innerliner. With improvements in other tire components, the innerliner now offers many more opportunities to improve performance parameters such as air retention and tire casing durability that is of particular importance for commercial tires. Innerliners based on nanocomposites and other new materials may allow gauge adjustments and permeability reductions with potential improvements in tire casing durability and, for example, reductions in truck fleet tire casing attrition rates. Nanocomposites based on brominated isobutylene p-methylstyrene copolymers with organically modified layered silicates enable permeability reductions not possible with conventional halobutyl elastomers and filler systems. The use of nanocomposites may require reformulation of compounds and modification of processing specifications. This paper discusses potential innerliner permeability reduction as well as the impact of formulation and compounding parameters on the properties of model nanocomposite based innerliners.

## Personal Care

**Organizer:** Jim Thompson Procter & Gamble, Cincinnati, OH

### 141. Screening Botanicals for Anti-inflammation Activities in vitro and in vivo

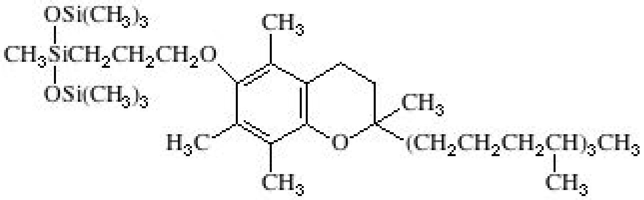
Tao Wang, Weihan Zhang, Jifeng Duan, Yu Cai, Weiguo Su and **Xiaoqiang Yan**, Hutchison Medipharma Ltd., Shanghai, China

The development of safe therapeutics for chronic diseases has been a tremendous challenge for the pharmaceutical industry. Botanical therapeutics has attracted much attention recently in industry, academia and regulatory agencies worldwide. Different from the conventional NCE drugs, the botanical drugs deliver a mixture of multi-functional molecules that may synergize or potentiate for treating diseases by acting on multiple cellular targets and pathways. The long history of using botanical drugs, such as in the traditional Chinese medicine (TCM) and Ayurvedic medicine, has demonstrated their safety and efficacy for many diseases. However, the puzzle of unknown, or occasionally contradicted, mechanisms of action (MOA) for the botanical therapeutics hinders the wide acceptance by the Western medical community in addition to the challenges of CMC (chemistry, manufacturing and control) processes. We intend to re-examine the popular botanicals widely used in China against inflammatory diseases. We have established a number of cell-based high through-put (HTS) assays to screen botanicals that are capable of inhibiting inflammatory cytokine expression, transcriptional activation and in vivo animal models to validate the biological activities identified in vitro. The botanicals and natural compounds identified in this effort could potentially be used to develop anti-inflammation skin care products.

### 142. Tocopherol-Substituted Silanes

**Youlin Pan**[1], Jane Hollenberg[2] and Barry Arkles[1], (1)Gelest, Inc., Morrisville, PA, (2)JCH Consulting, Red Hook, NY

There is a great interest in the personal care industry in biologically derived substances that are perceived to provide passive benefits in cosmetic performance. Silicone soluble derivatives of tocopherol were prepared and evaluated for suitability for formulation into personal care products. Trisiloxane and telelechelic siloxane derivatives of tocopherol were prepared by forming an ether linkage via a hydrocarbon bridge between the phenolic hydroxyl and the siloxane.



These compounds have a broad range of solubility/compatibility with materials used in the formulation of skin care and color cosmetics. They have the additional advantage of being more resistant to becoming rancid or colored during formulation.

Unlike many silicones and silicone derivatives these compounds are easily incorporated into cosmetic products such as skin-care and color cosmetics including lipsticks and foundations due to their solubility in a range of polar compounds such as castor oil and a variety of cosmetic esters. The synthetic chemistry of the compounds are presented along with examples of formulation into color cosmetics including lipsticks.

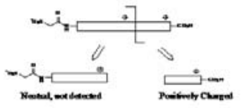
## Polymer Characterization III

**Organizer:** Ronald E. Tecklenburg Dow Corning Corporation, Midland, MI

### 143. Chemically Assisted Fragmentation: A breakthrough for peptide sequencing using MALDI mass spectrometry

**R. Scott Youngquist**, Procter & Gamble, Cincinnati, OH

We have addressed a key Company need by developing a new analytical method for fast and efficient protein sequencing using MALDI Mass Spectrometry. Singly charged tryptic peptides do not fragment well in the mass spectrometer. Ions with two charges fragment well although not predictably under ion-spray conditions; however, doubly charged ions are difficult to generate by MALDI. Our strategy was to derivatize the N-terminus of the peptide with a sulfonate so that a singly charged peptide will carry an extra proton to compensate for the sulfonate's negative charge. Chemically, these singly charged ions are very similar to doubly charged ions and in practice they fragment efficiently at the amide bonds. An additional benefit is that the negative charge from the sulfonate prevents detection of the N-terminal ions making the spectra simpler and easier to read. The peptide sulfonation step is conveniently carried out on solid-support enabling us to automate and multiplex the chemistry. We have used this technology to sequence enzymes for consumer products and for protein identification in proteomics studies.



### 144. Characterization of the polymeric by-products from the synthesis of chlorophosphazenes

**Claire A. Tessier**, Amy J. Heston, Debashish Banerjee, Alyison Leigh, Peter L. Rinaldi and Chrys Wesdemiotis, University of Akron, Akron, OH

The reaction of $PCl_5$ with $NH_4Cl$ at ~140° gives a mixture of oligomeric rings $[PCl_2]_n$ (largely n = 3-6) and linear, higher molecular-weight oligomers or polymers. The oligomers/polymers are usually formulated as $PCl_2(NPCl_2)_nCl$ or $PCl_2(NPCl_2)_nPCl_6$ but their structure is not well understood. We will present the characterization of the $^{15}N$ labeled oligomer/polymers by NMR and mass spectral data. The 2D $^{15}N/^{31}P$ NMR spectrum shows that the oligomers and polymers consist of at least five major fractions.

From DOSY NMR studies, the molecular weight of the fractions is estimated to be in the range ~1450-37500. Mass spectrometric studies of the fractions also will be reported.

### 145. Branch content in polyolefins using small angle scattering: A new approach using fractal geometry

**Amit S. Kulkarni**, Gregory Beaucage and Doug Kohls, University of Cincinnati, Cincinnati, OH

The presence of branching and its impact on structure-property relationships is ubiquitous in a wide array of materials. In commercial polyolefin polymers, branching is inevitable, though not always beneficial. Though recent advances in synthesis chemistry have made precise control of polymer topology possible; even a very low level of branching has been shown to have a profound effect on the dynamic properties due to formation of quiescent networks. Though quantification of branch content in polymers has been an active field of research for over five decades, no single technique has been able to describe branching in totality. Small angle scattering can be put to use to characterize branching in terms of the fraction of material contained in branches; an aspect critical to the dynamic properties but often neglected by other techniques. Application of scattering techniques to quantify branch content in polymers and ceramic aggregates will be discussed.

### 146. Study of Chain Dynamics of Polyaniline by Solid-State NMR

**Wendy Lewis** and Matthew P. Espe, University of Akron, Akron, OH

Polyaniline (PANI) is a conductive polymer that has many industrial applications such as, corrosion protection, radio frequency shielding, batteries etc. The conductivity of this polymer varies by eight orders of magnitude and is sensitive to dopant, solvent and processing conditions. The conductivity of the polymer is also related to its morphology, as more ordered material has a higher conductivity. The more ordered regions of the polymer have tighter chain packing and less chain mobility, and one motion that is restricted in the crystalline or nearly crystalline regions are $180^{o}$ (pi)-flips of the phenyl rings. The extent of the polymer that can undergo these ring flips, a measure of the disorder in chain packing, has been measured by using the solid-state NMR technique of even dipolar rotational spin-echo (EDRSE) NMR. The effect of polymer characteristics and processing conditions - molecular weight, heating, cross-linking, or the solvent used in casting a film - on the number of phenyl ring flips has been studied. Our studies have shown that chain packing is little changed for the molecular weight range of 50-300 kDa or when the polymer is heated to $75^{o}$C. However, the disorder in chain packing of films cast from N-methyl pyrrolidinone is actually higher than in the as-synthesized polymer. Cross-linking the polymer is observed to enhance disorder of the chains and increase the number of chain segments that can under ring flips. The NMR technique of wide-line separation (WISE) was used to determine if the ordered and disorder regions are separated into domains that have diameters greater than 10 nm. The WISE data showed that the regions are intimately mixed and there is no evidence of domains. T1rho ($^{13}$C) measurements show that the frequency of the rings flip is centered around a frequency of ~50 kHz.

### 147. Impact of exposure to mixed aqueous organic solvents on the stability of vinylidene chloride copolymers

Bob A. Howell and **Stephen M. June**, Central Michigan University, Mount Pleasant, MI

Vinylidene chloride copolymers display low permeability toward a variety of compounds. This property places them in a position of prominence in the barrier plastics packaging industry. The utilization of these materials has been hampered by their propensity to undergo degradative dehydrochlorination at process temperatures. It has often been noted that exposure to a high humidity environment during isolation and drying of the polymer tends to accelerate this process. The impact of moisture on the thermal stability of these polymers has been examined systematically. Solutions of the polymer in tetrahydrofuran or o-dichlorobenzene containing five to ten volume percent water were stirred at room temperature. Samples were removed as a function of time and examined by thermogravimetry. Polymer stability decreased strongly after contact with the solvent mixture. Infrared analysis of the samples indicated that a carbonyl absorption increased in intensity after stirring in the solution.

## Rubber and Elastomer Technology I

**Organizer:** Timothy Okel PPG Industries, Inc., Monroeville, PA

### 148. Carbon Black and its use in Filled Rubber Compounds

**Thomas F. Carlson**, Sid Richardson Carbon & Energy Co., Fort Worth, TX

Carbon black is a soot-like material produced by the thermal decomposition of organic precursors, typically heavy aromatic oils. Key among its many uses is its application as a reinforcing filler for cured rubber compounds, most notably tires and other industrial goods, to which it imparts mechanical strength and wearability due to polymer-filler and filler-filler interaction between carbon aggregates. These aggregates are among the earliest nanomaterials and display an aciniform morphology, being composed of spherical nodules or particles fused together like a cluster of grapes. As such, they are very robust and are designated by a combination of surface area and degree of branching, or structure. This structure/surface area relationship leads to different behaviors in mixing, curing, and elastomer reinforcement, as well as associated rubber properties such as wear, traction, and heat buildup. This paper will address the production and physicochemical characteristics of carbon black and the influence of various grades on filled rubber compounds.

### 149. Precipitated Silica: Fundamental Technology, Production, Compounding and Applications

**Timothy Okel**, PPG Industries, Inc., Monroeville, PA

Precipitated silica is a particulate, amorphous material, typically produced by the acid neutralization of a sodium silicate solution. Precipitated silica consumption is estimated to be in excess of 800 thousand metric tons with a value in excess of $640 million. Its largest market is as a filler for rubber, primarily in tires. Traditionally precipitated silicas have been used to provide a number of performance enhancements such as: cut, chip and chunk resistance, tear resistant, stiffness, and adhesion. In the last decade there has been a significant increase in the usage of precipitated silicas in passenger treads where, in combination with appropriate silanes and polymers, they provide an improvement in the rolling resistance, traction, and treadwear triangle. This presentation will review the fundamental technology, production, compounding and applications of precipitated silica.

### 150. New-generation precipitated silica for tire-tread compounds

**Doug J. Kohls**[1], Dale W. Schaefer[1], Andrey Vorobiev[2] and Ephraim Feinblum[1], (1)University of Cincinnati, Cincinnati, OH, (2)Dimona Silica Industries, Beer-Sheba, Israel

A new method for production of precipitated silica has been demonstrated by Dimona Silica Industries and evaluated in lab-scale tire compounds. The silica, Dimosil®, is made from porcellanite, a amorphous-silica containing mineral, through a low-temperature solution process without the use of caustic acids or high pressures. The developmental process is capable of producing silica having specific surface areas (BET) with a range of 100-200 m2/g and the ability of achieving surface areas as high as 400 m2/g. The process is being optimized with a planned annual silica production of 40,000 metric tons.

Several pilot-plant silicas were investigated. The silica was evaluated using light scattering and ultra-small angle x-ray scattering to determine the particle structures at different size scales. The scattering data was analyzed using a unified fit model and fractal scaling laws. Distinct differences were observed the size of the primary particles, aggregates, and agglomerates, depending on process protocol. Sonication studies were performed to observe the break up of the agglomerated structures. The results showed that the Dimona process produces silica with a highly ramified structure that can be modified through processing changes. The second part of this study incorporated the silica into model formulations for tire compounds and the resulting mechanical properties were measured. The Dimosil® compounds are compared to compounds reinforced with conventional precipitated silica. The Dimosil® shows excellent dispersion and reinforcement properties.

### 151. Comparison of Silica and Carbon Black Natural Rubber Compounds under Aging

**Edward R. Terrill**, Abraham Pannikottu, Uday P. Karmarkar and Blake Matthies, Akron Rubber Development Laboratory, Akron, OH

With the need to understand and improve compound performance during aging (e.g., service life of tires and rubber articles) a study was conducted which compared a silica-filled, carbon black-filled, and unfilled natural rubber compounds. The work included aerobic as well as anaerobic aging. In this work we evaluated a wide range of performance indicators. The testing included strain sweep (Payne effect), pulsed Nuclear Magnetic Resonance relaxation time, tear strength, Goodrich blowout, crosslink density, tensile, bound rubber, crosslink distribution, crack growth resistance. The work elucidates the effects of fillers on aged and un-aged compounds. The fillers affected aged properties, including crosslink density, tensile modulus, and the Payne effect. The carbon black filler did not appear to affect crosslink types, while the silica coupling agent may affect the cure and the crosslink types.

## Alternative Feedstocks II - Renewable Feedstocks

**Organizer:** Steven J. Martin Dow Chemical Company, Midland, MI
**Organizer:** Patrick B. Smith Dow Chemical Company, Midland, MI

### 152. Formation of Organic Acid Esters via Reactive Distillation

**Dennis J. Miller**, Navinchandra Asthana, Carl T. Lira, Aspi Kolah and Dung T. Vu, Michigan State University, East Lansing, MI

Reactive distillation involves simultaneous chemical reaction and product purification in a single unit of process equipment. We illustrate here the application of reactive distillation to the efficient production of biorenewables-based organic acid esters, a class of products that have low toxicity, excellent solvent properties, and a wide range of industrial applications. The prototypical system examined is ethyl lactate formation from ethanol and lactic acid: we have demonstrated ethyl lactate production in our five-meter tall pilot-scale reactive distillation column and have characterized the thermodynamics and chemical kinetics of the system in laboratory-scale studies. Based on those results, we have developed a detailed computer simulation of a commercial-scale facility using AspenPlus process simulation software. The design accommodates the formation of lactic acid oligomers and oligomer esters formed in concentrated lactic acid solution by including a transesterification step with ethanol to transform oligomers to ethyl lactate. Economic analysis of the commercial-scale design indicates that ethyl lactate can be produced in high yields at costs competitive with petroleum-based solvents. Additional esters systems, including triethyl citrate and diethyl succinate, are under examination in ongoing studies.

### 153. Biomass based polymers: science and applications

**Shaw L. Hsu** and Kaoru Aou, University of Massachusetts, Amherst, MA

Biomass-based polymers, e.g. poly (lactic acid) (PLLA), are interesting from fundamental and practical aspects. Applications are limited because some aspects of their structures are unknown. A combination of techniques has been employed to elucidate the structure of PLLA. It is now possible to understand and predict the changes in both amorphous and crystalline regions of PLLA upon deformation. In addition, the molecular parameters governing structural stability in the condensed state can be identified. Phase equilibria and separation kinetics that are crucial aspects to PLLA applications have been studied. Insights into new applications of PLLA in drug delivery and other multi-component systems will be discussed.

### 154. The Use of Renewable Feedstocks for the Production of Chemicals and Materials

**Joseph J. Bozell**, Until 4/7/06: National Renewable Energy Laboratory, Golden, CO

Since its establishment in 1976, the National Renewable Energy Laboratory (NREL) has pursued new technology to develop biomass as a viable and economical source of raw materials for the production of chemicals. As a result, NREL has developed a unique position within the DOE national lab system in for directly addressing these challenges. The promise of renewables as a feedstock for chemicals is great. The need for renewables as a feedstock for chemicals is clear. The sources are numerous, sustainable, and domestic. Ever-improving methods of agriculture and biotechnology will ensure a continuing, environmentally friendly supply of these materials. Yet, despite the availability of an almost inexhaustible domestic source of raw materials, the use of renewables lags far behind the use of nonrenewables, particularly in the production of chemicals. What stands between the concept and realization of a vibrant renewables to chemicals industry is technology development. This seminar will discuss some of the rationale behind the use of renewables as chemical feedstocks, and illustrate these principles with a discussion of research carried out at NREL, specifically looking at work in biomass separation, and chemical conversion of the components of these separations into new chemical building blocks and polymers.

### 155. Soy-based polyol for flexible slabstock foam

**David A. Babb**, The Dow Chemical Company, Freeport, TX

In 2003 Dow began the process of developing polyols from natural, renewable oils for the flexible foam market. In 2005 that development program reached a significant milestone when a commercial development quantity of polyol was produced on a semi-commercial scale, and full commercial scale production of flexible slabstock foam was achieved. Production of slabstock foam containing soy-based polyols at levels from 30% to 50% was demonstrated. All indications are that flexible foams produced via this technology will be commercially viable. This presentation will include a brief overview of the Dow NOP polyol technology and the results of the commercial-scale trial.

### 156. Corn to chemicals: research sponsored by the National Corn Growers Association

**Clark Gerstacker**, National Corn Growers Association, Midland, MI

The National Corn Growers Association (NCGA) has sponsored considerable research in the US to convert corn to higher valued products including reactive distillation to produce ethyl lactate and ethyl acetate, the hydrogenolysis of corn sugars to produce ethylene glycol and propylene glycol, and genetic modification of corn to enhance yields. Clark will speak about these and other projects as well as the motivation of the NCGA for investing in such research. He will also provide information regarding the strategy of the NCGA relative to corn production in order to meet the increased demand for ethanol.

### 157. Product Opportunities from Sugars in the Context of a Biorefinery

**Todd Werpy**, Pacific Northwest National Laboratory, Richland, WA

This presentation will discuss the efforts at DOE-EE-OBP in assessing the role of products within the context of a biorefinery. A major effort of this process is the identification of potentially viable products and the associated technology needs to make these products economically viable. To this end, OBP has published a “Top Ten” report that analyzes the potential of making products from sugars. This report has actually identified twelve building block chemicals that can be produced from sugars via biological or chemical conversions. The twelve building blocks can be subsequently converted to a number of high-value bio-based chemicals or materials. Building block chemicals, as considered for this analysis, are molecules with multiple functional groups that possess the potential to be transformed into new families of useful molecules. The twelve sugar-based building blocks are 1,4-diacids (succinic, fumaric and malic), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol.

The synthesis for each of the top building blocks and their derivatives was examined as a two-part pathway. The first part is the transformation of sugars to the building blocks. The second part is the conversion of the building blocks to secondary chemicals or families of derivatives. Biological transformations account for the majority of routes from plant feedstocks to building blocks, but chemical transformations predominate in the conversion of building blocks to molecular derivatives and intermediates. The challenges and complexity of these pathways, as they relate to the use of biomass derived sugars and chemicals, were briefly examined in order to highlight R&D needs that could help improve the economics of producing these building blocks and derivatives. Not surprisingly, many of the transformations and barriers revealed in this analysis are common to the existing biological and chemical processing of sugars.

## Computational and Theoretical Science

**Organizer:** Jozef Bicerano Bicerano & Associates, LLC, Midland, MI
**Organizer:** Joey W. Storer Dow Chemical Company, Midland, MI

### 158. Nanoscale Dielectric Theory and Intermolecular Forces

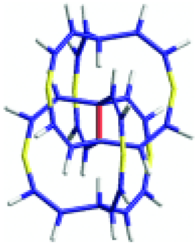
**Katharine C. Hunt**, Xiaoping Li, Ruth Lafuente Jacobson and Piotr Piecuch, Michigan State University, East Lansing, MI

On the nanoscale, molecules act as dielectric media, but the intramolecular dielectric function is not constant. Instead, the dielectric function is nonlocal, because it depends on the point where an electrical perturbation is applied to the molecule, and also on the point where the screening is probed. Quantum mechanically, the dielectric function depends on a charge density susceptibility, which characterizes the redistribution of electronic charge within a molecule, when a perturbing electrical potential is applied to it. The same susceptibility can be used to derive the exchange-correlation energy, and thus to obtain an exact, closed expression for the electronic energy of a molecule, within density functional theory. In addition, the van der Waals interaction energy between two molecules depends on the charge density susceptibility. This relation makes it possible to prove a conjecture by Feynman about the van der Waals forces between atoms in S states, and to prove its generalization to interacting molecules of arbitrary symmetry.

### 159. Squeezing C-C bonds: Designing molecules that come up short

**Deborah Huntley**[1], Georgios Markopoulos[2], Patrick Donovan[3], Lawrence Scott[3] and Roald Hoffmann[2], (1)Saginaw Valley State University, University Center, MI, (2)Cornell University, Ithaca, NY, (3)Boston College, Chestnut Hill, MA

**Squeezing C — C bonds: Designing molecules that come up short** Deborah R. Huntley, Georgios Markopoulos, Patrick M. Donovan, Lawrence T. Scott, Roald Hoffmann



**It's not how short you make it**, it's how you make it short! A diverse collection of compounds with short C — C single bonds whose lengths range from 1.32 Å to 1.46 Å have been theoretically designed (see structure of a “spiderane ”). The strategies for squeezing the C — C bonds (encapsulation, strapping back, and stiffening) allow shorter bonds than hybridization and conjugative effects alone.

Can one find hydrocarbons with short single C-C bonds between two four-coordinate carbons, in which the shortening is not primarily due to hybridization or conjugative effects? The anharmonicity of the C-C potential is not as big a barrier to this as one might imagine; the problem is more that strain dissipates effectively, in a number of ways. We have designed theoretically several hydrocarbon families, quite diverse, in which our various strategies -- encapsulation, strapping back, stiffening and strapping with a three-fold constraint -- are used to squeeze a C-C bond. Bonds as short as 1.32 Å may be possible.

### 160. Symbolic Regression via Genetic Programming for Nonlinear Data Modeling

**Mark Kotanchek**, Evolved Analytics, Midland, MI

Extracting insight and exploitable models from data is a problem spanning the scientific, engineering and business fields. Recent algorithmic advances have vastly increased the speed and effectiveness of using symbolic regression via genetic programming to evolve nonlinear models from data sets as well as identify driving variables for the response behavior of interest. Real-world chemical industry data will be used to illustrate the model development and exploitation for inferential sensors, process emulators, human insight, etc. Additionally, synergies with other nonlinear modeling techniques such as support vector regression, neural networks and stacked analytic networks will be discussed.

### 161. Simulation of polymeric liquids by Dissipative Particle Dynamics (DPD)

**Charles W. Manke**, Wayne State University, Detroit, MI

Dissipative Particle Dynamics (DPD) is a mesoscopic simulation technique suitable for representing polymer molecules with a wide variety of architectures in both solutions and melts. Here, we present DPD simulations of linear polymer chains in three regimes of concentration: dilute solution, semi-dilute solutions, and melts. In the dilute solution regime, the DPD simulations exhibit the correct scaling of both radius of gyration and relaxation time with chain length, indicating that excluded volume and hydrodynamic interaction effects are represented, and realistic rheological responses in steady shear flow. As the polymer concentration is increased to the semi-dilute regime, the DPD simulations are able to represent the polymer-polymer frictional interactions giving rise to non-linear dependence of viscosity on concentration, and realistic values of the Huggins coefficient are obtained. In the polymer melt regime, a segmental repulsion model is introduced to impede unphysical chain crossing events, and thereby impose topological constraints for chain motions. The DPD melt simulations show evidence of a plateau modulus in the relaxation modulus, and a transition in the scaling behavior of both viscosity and diffusion coefficient with chain length indicative of entanglement dynamics.

## Emulsion Polymerization and Latex Technology: Preparation, Properties, and Applications II

**Organizer:** Raymond E. Drumright Dow Chemical Company, Midland, MI
**Organizer:** Thomas H. Kalantar Dow Chemical Company, Midland, MI

### 162. Colloidal atoms and molecules: design and fabrication

**Darrell Velegol**, Penn State University, University Park, PA

Technologies in sensors, robotics, MEMS, drug delivery, computing, and other applications will increasingly require assemblies of colloidal and nanocolloidal particles. Such small particles must be built from the "bottom-up", meaning that the particles must be designed so that they can assemble themselves. Thus, just as atoms assemble into molecules with structures ranging in complexity from carbon monoxide to DNA, our goal is to design and synthesize particles that self-assemble into larger structures. We are currently working with polymer, oxide, and metal particles.

Several techniques exist to produce simple bottom-up assemblies, and all techniques have limitations. In this talk a new method from our lab called "particle lithography" will be shown. Currently we have used this technique to produce high-yield, accurate heterodoublets of micron size particles, with initial progress on more complex assemblies. This talk will focus on the basic technique, as well as a few methods for engineering complexity of assembly and scaleup of production.

### 163. Stability of Water-in-Crude Oil Emulsions in the Burgan Oilfield, Effects of Oil Aromaticity, Resins and Asphaltene Content, and Water pH

**Adel Elsharkawy**[1], Harvey Yarranton[2], Tahar Al-sahhaf3[1] and Mohamed .Fahim3[1],
(1)Kuwait University, Kuwait, Kuwait, (2) University of Calgary, Calgary, AB, Canada

Asphaltenes and resins separated from emulsion samples collected from Burgan oil field were used with heptane-toluene mixtures as model oil to study the effect of oil aromaticity, resin content, and pH of the aqueous phase on the stability of water in model emulsions. It was confirmed that, as long as the asphaltenes are completely solubilized, increasing aromaticity leads to less stable emulsions. A consistent correlation between emulsion stability and relative resin mass content (R/(R+A)) was observed for all three of the field samples. There was a sharp decrease in stability when the R/(R+A) value exceeded 0.75. Emulsion stability was enhanced at high pH and possibly at very low pH (< 2).

### 164. Synthesis and process of novel aqueous polyurethane dispersions

**Bedri Erdem**, The Dow Chemical Company, Midland, MI, Debkumar Bhattacharjee, The Dow Chemical Company, Freeport, TX and Friederike Stollmaier, Dow Deutschland GMBH &Co.OHG, Rheinmuenster, Germany

Polyurethanes offer unique physical and mechanical properties and are used for a variety of applications. As a result of increasing health and environmental concerns requiring elimination of solvents, isocyanate monomers and other difficult to handle chemicals used in polyurethane synthesis, aqueous polyurethane dispersions (PUDs) have recently emerged to replace their solvent-based counterparts in various applications. Majority of commercially available and academically studied PUDs are produced from isocyanate terminated prepolymers containing carboxylic acid group in the polymer backbone in a batch process. This approach requires the use of solvents and volatile neutralizing agents like triethylamine for the dispersibility and stability of PUDs. In addition, PUDs produced in this process, in general, have low solid content, e.g. 35-45 wt. %, and it is difficult to produce PUDs from prepolymer having excess aromatic isocyanates due to their high reactivity with water.

This paper will focus on the preparation of solvent-free and high solids content (>60 wt%) aqueous PUDs using prepolymers based on aromatic and aliphatic isocyanates in combination with polyether and polyester polyols using a high shear continuous mechanical dispersion process. A mechanistic study on isocyanate kinetics, colloidal and interfacial science showed that chemical composition of the prepolymer (nonionic or anionic), type and amount of surface active agents(s) play critical role in the formation and stabilization of submicron size colloidally stable particles in this process. This understanding allowed the preparation of polyurethane dispersions for a myriad of applications from a well-designed combination of a variety of commercially available raw materials.

## Functionalized Polymer Interfaces and Adhesion II

**Organizer:** Dongchan Ahn Dow Corning Corporation, Midland, MI
**Organizer:** Zhan Chen University of Michigan, Ann Arbor, MI

### 165. Interfacial segregation of highly branched polystyrenes

**Mark D. Foster**, The University of Akron, Akron, OH

One route to functionalizing interfaces or tailoring adhesion is through the design of branched architectures, which are preferred at interfaces over linear architectures. The contributions of junctions and the number of chain ends to the interfacial segregation of branched polystryrenes in blends with linear polystyrene has been studied using a series of novel, well-defined polystyrenes prepared by anionic polymerization. Interfacial excesses were measured using Neutron Reflectometry (NR) and surface compositions corroborated using Surface-Enhanced Raman Spectrometry (SERS). Comparison is made to a linear response theory.

### 166. Sum Frequency Generation Vibrational Spectroscopic Studies on Molecular Interactions between Polymer Surfaces and Adhesion Promoters

Cheryl L. Loch[1], Dongchan (Shaun) Ahn[2] and **Zhan Chen**[1], (1)University of Michigan, Ann Arbor, MI, (2)Dow Corning Corporation, Midland, MI

We examined molecular interactions between adhesion promoters and polymer surfaces using sum frequency generation (SFG) vibrational spectroscopy to understand the adhesion mechanisms at interfaces between plastics and elastomeric adhesives. We studied interfaces between polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) and various silanes including n-octadecyltrichlorosilane (OTCS), n-octadecyltrimethoxysilane (OTMS), and 3-aminopropyltrimethoxysilane (ATMS) using SFG. When OTCS or OTMS contacted a polymer surface, a stable and ordered interface immediately formed and the silane molecules adopted different conformations at the interface, depending on the surface structure of the polymer. Such interfacial structures revealed evidence of different interfacial molecular interactions. Conversely, ATMS molecules tended to diffuse into PS or PMMA. Using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATM) as an example, the details of the diffusion of an amino silane into PMMA was revealed by SFG. Amino silanes do not diffuse into all polymers. Stable SFG spectra were collected from the poly(ethylene terephthalate) (PET)/ATMS interface, indicating ATMS did not diffuse into PET. SFG studies show that hydrogen bonds between the PET surface and the ATMS molecules are formed. We have applied SFG to practical problems of adhesion to polymer surfaces. Specifically, a hydrosilylation-cured silicone elastomer that contains an adhesion promoting mixture of (3-glycidoxypropyl)trimethoxysilane (gamma-GPS) and a methylvinylsiloxanol (MVS) adheres well to polymers such as PET and Nylon 6,6, but poorly to polymers such as PS and polycarbonate. We have denoted such a mixture of these two components as a Silicone Adhesion Promoting System (SAPS). We examined the various interfaces between polymers and a cured silicone elastomer with SAPS using SFG to elucidate adhesion mechanisms. Such SFG studies have been correlated to high throughput adhesion testing results.

## 167. Engineering Biointerfaces with Controlled Properties

**Joerg Lahann**, University of Michigan, Ann Arbor, MI

Future biomaterials will use advanced surface engineering technologies to actively modulate cellular microenvironments. Three technological examples towards materials with controllable biointerfaces will be presented. To create stable surfaces, vapor-based polymer coatings have been interesting candidates for the coating of biomedical or microfluidic devices, because of their advanced processibility. A diverse class of polymer coatings (functionalized poly-p-xylylenes) has been prepared by chemical vapor deposition (CVD) polymerization that provides chemically reactive groups for the immobilization of biomolecules. In addition, bioinertness (Suppression of unspecific protein adsorption and cell adhesion) has been identified as a critical design criterion and efforts towards bioinert coatings will be outlined. The design and synthesis of polymer-based particles with two distinct phases will be reported. The biphasic geometry of these Janus particles is induced by the simultaneous electrohydrodynamic jetting of parallel polymer solutions under the influence of an electrical field. The high electrical potentials (typically several thousand volts) applied between the jetting liquids that are fed through a capillary and a collecting substrate will induce jetting of the charged liquid. The final morphologies of the resulting nano-objects are mainly determined by the properties of the jetting liquids and the process parameters.

K.H. Roh, D.C. Martin, J. Lahann. Biphasic Janus particles with nanoscale anisotropy. Nature Materials (2005) 4, 759-763. J. Lahann, I.S. Choi, J. Lee, K. Jensen, R. Langer, A New Method toward Micro-Engineered Surfaces based on Reactive Coating, Angew. Chem., Int. Ed. 2001, 40, 3166-3169. H.-Y. Chen, Y. Elkasabi, J. Lahann, Surface Modification of Confined Microgeometries via Vapor-Deposited Polymer Coatings. Journal of the American Chemical Society 2006, 128(1), 374-380.

### 168. Functional and Nanostructured Polyelectrolyte Multilayer Films

**Ilsoon Lee**, Michigan State University, East Lansing, MI

The ionic layer-by-layer assembly technique, introduced by Decher in 1991, has emerged as a versatile and inexpensive method of constructing polymeric thin films, with nanometer-scale control of ionized species. Films formed by electrostatic interactions between oppositely charged poly-ion species to create alternating layers of sequentially adsorbed poly-ions are called “Polyelectrolyte Multilayers (PEMs)”. PEMs have long been utilized in such applications as sensors, eletrochromics, and nanomechanical thin films but lately they have also been shown to be excellent candidates for biomaterial applications due to 1) their biocompatibility and bioinertness, 2) the ability to incorporate biological molecules, such as proteins, and 3) the high degree of molecular control of the film structure and thickness providing a much simpler approach to construct complex 3D surfaces as compared with photolithography. The development of new methods for fabricating thin films that can provide chemical functionality, controlled morphology, wetting property, and biomolecular adhesion will be presented. These films could lead to significant advances in the fields of tissue engineering, drug delivery and biosensors which have become increasingly germane applications in the field of chemical engineering and materials science.

### 169. Mechanism and catalyst considerations of trialkylborane promoted adhesion to low surface energy plastics

**Mark F. Sonnenschein**, Steven P. Webb, Benjamin L. Wendt, Patrick E. Kastl, O. David Redwine and Nelson G. Rondan, Dow Chemical Co, Midland, MI

Excellent adhesion to low surface energy subtrates such as polypropylene, polyethylene, and fluroinated polymers is obtained with acrylic polymerization initiated by trialkylboranes at room temperature and without need for surface pre-treatment. The mechanism of adhesion is a consequence of a series of radical processes resulting from the initial oxidation of the trialkylborane followed by the production of alkoxy and alkyl radicals. This presntation will elucidate the mechanism of adhesion and the catalyst characteristics that make useful adhesives.

### 170. Molecular Level Studies on Interactions between a Pet Surface and Model Ink Components to Understand Adhesion

**William C. Johnson**[1], Cheryl L. Loch[1], Zhan Chen[1], Priya Varadan[2], William Lim[2], Wladyslaw Koziol[2] and Graham Battersby[2], (1)University of Michigan, Ann Arbor, MI, (2)Flint Group, Ann Arbor, MI

To ensure inks produce graphics with superb quality on various substrates such as paper, polymer film, foil, board and metal, it is necessary to understand detailed molecular interactions at the interface between inks and these substrates. This is very challenging because such an interface is buried. It is difficult to selectively probe such an interface between two bulk media. It is possible to break the interface and expose two resulting surfaces to air and examine their structures. However, the structural information obtained from two such surfaces may not represent that of the buried interface. The separation of the two materials for analysis destroys the in situ interaction. Therefore, it is necessary to apply or develop techniques that can provide detailed structural information of buried interfaces between inks and substrates to understand their interactions. Sum frequency generation (SFG) vibrational spectroscopy is a submonolayer surface sensitive analytical technique that can provide in situ vibrational spectra of surfaces and interfaces. From such spectra, detailed structural information and chemical activity of surfaces and interfaces, such as interfacial segregation, order, and alignment of functional groups and molecules, interfacial hydrogen bonding, interfacial diffusion, and interfacial chemical reactions can be monitored. We applied SFG to study molecular structures of interfaces between a model polymer, poly (ethylene terephthalate) (PET), and individual as well as mixtures of model ink components to understand adhesion properties between ink and polymer substrates. Such ink components include urethanes, nitrocellulose, plasticizers, and adhesion promoters. Our results indicate that the PET-ink interactions are very complicated. Various factors, such as segregation and ordered alignment of ink components at the interface, interfacial hydrogen bonding, as well as interfacial Van der Waals interactions play roles in adhesion. The strong adhesion of the ink on polymer substrates is achieved by a cooperative effect of the individual ink components.

## History of Chemistry in the Midland ACS Section Area

**Organizer:** Wendell L. Dilling Central Michigan University, Mount Pleasant, MI

### 171. History of Chemistry in The Dow Chemical Company

**Etcyl H. Blair**, The Dow Chemical Company (retired), Midland, MI

The Dow Chemical Company from its beginning has been a research oriented company. Herbert Henry Dow began his experiments on the electrolysis of brine while still a university student. In 1897 he formed The Dow Chemical Company in Midland, Michigan where he developed his unique electrolytic process, which gave him pure chlorine, bromine, elemental magnesium and derivatives. In time these would become the building blocks for a vast chemical enterprise. To find more uses for chlorine and

bromine he turned to organic chemists. What followed was an explosion of knowledge and products. The company was soon producing phenol by a novel Dow process and Dow was learning how to crack hydrocarbons into monomers. By 1930 organic chemistry was on the front burner, followed closely by polymer chemistry, which still reigns supreme.

From Dow's laboratories, during the 1940's, came products such as STYRON polystyrene, Saran resins, Styrofoam brand plastic foam, latex, ion-exchange resins and others. In the 1950's Dow commenced building chemical plants in Europe and by the 1960's would be recognized as a global chemical company. During the 1970's Dow would introduce novel agricultural chemicals based on chlorinated pyridines.

By the 1980's Dow had entered the electronics arena and began using polymers in integrated circuits and in flat panels and for insulation in chips. In the 1990's Dow scientists had perfected their metallocene catalyst and launched a new technology called INSITE. With INSITE technology Dow is able to develop polymers that meet specific customers needs.

In one hundred years, Dow's R&D has progressed from one man with an idea about a bromine cell to an organization of over 3200 professionals, creating scientific platforms for products of the future.

### 172. The History of Chemistry in Dow Corning Corporation

**James R. Falender**, Central Michigan University (Dow Corning Retiree), Mount Pleasant, MI

This presentation will aim at supplying information to help the audience in thinking about two important philosophical questions: How did diverse interactions among people, institutions, and cultures lead to today's Dow Corning? What has driven Dow Corning innovation in the past and what will in the future?

### 173. Evolution of Programs in the Chemical Sciences at mid-Michigan Academic Institutions

**Bob A. Howell**, Central Michigan University, Mount Pleasant, MI

The geographic area served by the Midland Section of The American Chemical Society contains four academic institutions: Central Michigan University (CMU, a research intensive university); Saginaw Valley State University (SVSU, a four-year university); Alma College (Alma, a four-year college), and Delta College (Delta, a two-year college). All have strong programs in the chemical sciences and related areas. The formation and growth of these programs will be described.

## Knowledge Management and Data Mining II

**Organizer:** Terrence K. Hilty Dow Corning Corporation, Midland, MI
**Organizer:** Shruti Bahadur Dow Corning Corporation, Midland, MI

### 174. Academia Liaison of KM/Data Mining to Industry

**Timothy Pletcher**, CMU Research Corporation, Mt Pleasant, MI

This presentation describes some of many benefits and challenges academia and industry encounter when jointly working together on data mining or KM projects. Such issues include ensuring security and confidentially, intellectual property rights, publishing opportunities, and use of students or faculty on projects. A detail review of the CMU-RC business intelligence methodology for industry-academia collaboration will be shared and expanded upon to highlight ways to help ensure a successful joint project that achieves innovative results, protects corporate trade secrets, and produces results on-time and on-budget. A discussion of the pros and cons of having common or different analytical tools and infrastructure, and the difficulties typically encountered bringing academic teams up to speed on the intricacies of one or more corporate data sets will be addressed. Finally, the presenter will walk through a number of examples of predictive models and data mining projects that highlight the many innovative elements that including faculty on a corporate data mining or KM project can offer.

### 175. Electronic notebooks and the creation of corporate knowledge infrastructure

**Richard Stanton**, Waters Corporation, Milford, MA

Laboratory notebooks create the foundation of all scientific documentation. Experiments recorded in a notebook include the goal of the investigation, experimental or theoretical background, experimental description, parameters, and experimental results, as well as to note information through QA/QC applications. When properly kept, a laboratory notebook permanently records, what was done on a project, and particularly what inventions were made and when.

The documentation of experimental design, process and results represents the knowledge of an individual investigator collected over time. The ability now, to link all of this scientific and personal documents, represents an opportunity to create a corporate knowledge base. Responding to this opportunity and competitive pressures, organizations are interested in moving to digital laboratory recording. This transition process must be controlled, and all data collected must be archived following an intelligent data management strategy.

Besides providing functionality that mirrors the normal lab workflowused to document in paper-based laboratory notebooks, Waters® eLab Notebook™ Software is equipped with other powerful discovery and data-management tools. By capturing and storing information digitally with the Waters eLab Notebook software, science-based organizations will be able to take greater advantage of the knowledge generated by their researchers and to create an environment of collaboration not previously possible.

## 176. Developing a Data Mining Technology Platform

**Tim D. Rey**, The Dow Chemical Company, Midland, MI

Bringing a technology like Data Mining to a large Fortune 100 company isn't simply a technology play. Measuring, tracking, and proving value capture along with aligning the right people, processes, methodology and technology, all become essential ingredients to a successful company wide Data Mining implementation. Examples of projects as well as the business model and supporting technology for successful implementation will be discussed.

## 177. Cyber Security - Industry Trends and Tools

**Bill Knapp**, Jack Brahce and Mark Lachniet, Analysts International, Lansing, MI

Information security is a business concern for all organizations. With security threats increasing in number and sophistication, businesses need to gain protection, control, and visibility over their security systems, preventing incidents and threats that disrupt productivity, impact customer relationships, and erode profits. Government regulations concerning the protection of information also add to the growing emphasis on security.

The economic damage from malevolent network security threats was between $157 billion and $192 billion worldwide in 2004, according to mi2g, a U.K. research firm that specializes in security.

Historically, security-related costs have been roughly 2% to 4% of IT budgets; with the onset of new government information security regulations, that has increased to nearly 15%.

A systems approach to security enables tighter integration with the network, which delivers better overall security. Point-product strategies rely on connecting disparate products that address individual aspects of security whereas an integrated, collaborative, adaptive approach uses the network to provide consistent and thorough protection to all parts of the organizational infrastructure.

Organizations need to align security policy to their business requirements, while having the agility to adapt easily as needs change. Integrating security into the network infrastructure enables security professionals to control, deploy, and enforce policies according to business requirements, remaining secure yet flexible and agile. The systems approach also provides greater visibility and control for overall network security, allowing organizations to operate according to security best practices and comply with government regulations.

A systems approach to security results in improved value of your investment over time, because it's more flexible and enables security policy to more quickly change and keep up with changing business objectives.

In addition to reviewing the industry trends for network and information security, the tools and procedures for implementing and maintaining this systems approach will be presented and discussed.

### 178. Geographic Information Systems (GIS) and Business Intelligence

**Kevin Bolger**, ESRI, Inc, St. Pau, MN

Geographic Infomation Systems (GIS) offer unique ways to view and analyze any data with a geographic component. Most of the data used in Business Intelligence has a geographic component. In fact, nearly every data warehouse includes a geographic dimension together with a time, product, and customer dimension. But the tools to view and analyze the geographic dimension are not well understood and exploited. This session will describe what GIS is and how it is used to help understand and solve business problems where geography matters. We will address the main business functions or problems GIS is used for in business as well as how GIS is being integrated with other business systems (such as ERP or CRM) and BI tools from the major tier 1 BI vendors such as SAS, Business Objects, Hyperion, Microstrategy, and Information Builders. Analytic and data mining tools unique to GIS will be illustrated through real-life examples.

### 179. New tools for multivariate processing and comparative visualization of analytical data

**Leo W. Collins**, Bio-Rad Laboratories, Informatics Division, Philadelphia, PA and Gregory Banik, Bio-Rad Laboratories, Phila, PA

The use of methods such as Principal Component Analysis (PCA) to perform multivariate analyses on spectral and chromatographic data has been a mainstay of chemometrics for years. A new method is described that combines cheminformatics tools with chemometrics tools in an intuitive environment for performing such analyses. Also included is a new technology--Overlap Density (OD) Heatmaps--to allow the comparative visualization of heretofore unheard of numbers of spectra or chromatograms. The OD heatmaps provide information about the most (or least) commonly occurring spectral or chromatographic features in the data set. Case studies from the chemical and pharmaceutical industries comprising IR, NMR, and chromatographic techniques will be discussed.

## Nanocomposites: Science, Technology and Commercial Applications II - Commercial Applications

**Organizer:** Juan M. Garces Consultant, Midland, MI
**Organizer:** Richard F. Fibiger Dow Chemical Company, Midland, MI

### 180. Nanoclays and Nanocomposites: Evolving Products and Applications

**Karl W. Kamena**, Southern Clay Products, Austin, TX

Layered smectite nanoclays with very large surface areas (750 m²/gram) are being developed for incorporation into a variety of host polymer systems. Nanoscopic phase distribution can impart enhanced stiffness and strength at low levels of addition as well as improving barrier and flame retardant properties. Traditionally, the focus has been on the development of nanocomposites with nanoclays being the principal non-polymer ingredient. In the early stages of the nano "revolution", nanoclays appeared to be a quick route to breakthrough product performance, but as we learn time and again, there is no shortcut to success. Increasingly, product developers are combining nanoclays with other inorganic and organic modifiers to generate the desired formulation properties and cost/performance characteristics. Developments with existing nanoclay products using conventional amine chemistries are leading the way for future composite technologies involving thermoplastic, thermoset, and rubber formulations. Nanoclays are demonstrating unique, multi-dimensional capabilities to synergistically enhance overall polymer performance.

## 181. Role of Specific Interactions and Miscibility in Reinforcement of Polymers using Nanofillers

**Subramanian Iyer** and David A Schiraldi, Case Western Reserve University, Cleveland, OH

Polyhedral oligomeric silsesquioxanes (POSS®) are unique inorganic/organic hybrid nanoparticles which have been gaining increasing importance in nanocomposites. Due to their inorganic silicate core they are capable of reinforcing polymers. At the same time, these inorganic silicate particles are surrounded by organic groups which act to increase their compatibility with organic polymers. The mechanism of reinforcement using these particles has been well demonstrated in copolymers. However no clear reinforcement mechanism has been demonstrated in polymer/POSS blends. When phenyl trisilanol POSS is blended with two similar materials, phenoxy resin (PKFE®) and polycarbonate (both are polymers based on bisphenol A), the phenoxy resin is reinforced while polycarbonate is plasticized. The present talk will explain the theory behind these differences in the systems based on hydrogen bonding interactions and pi-pi stacking of the POSS with the benzene groups in the backbone of the polymers.

## 182. Acoustic mixing – a novel technology for processing and compounding

**Manfred Biermann**, Scott Coguill, Harold Howe and Cameron Reagor, Resodyn Corporation, Butte, MT

Mixing is an integral and vital part of most industrial processes. Its purpose is to overcome concentration, phase and temperature, inhomogeneities in order to insure safe and efficient processing.

Drivers for the development and implementation of new mixing technologies are: cost savings for existing processes and the evolution of new processing requirements. In particular, new challenges for mixing are continuously evolving and are spanned by a broad range of novel emerging material and processing technology needs, such as the mixing of advanced nanocomposites or culturing of sensitive tissue cells.

Resodyn Corporation has developed a novel mixer platform technology that uses low-frequency, high-intensity acoustic energy for mixing, meeting many of these new demands. The technology, termed ResonantAcoustics®, can be operated under high intensity conditions to mix difficult media including highly viscous materials and nanocomposite formulations, or alternatively can be configured to provide low-shear acoustic streaming that enables the enhanced growth of fragile tissue cultures.

ResonantAcoustics® mixing offers several advantages over conventional technologies in regard to material handling and processing. The technology has no moving parts inside the mixing vessel, can be sealed, pressurized or evacuated and has real time feed back of material response to the acoustic energy which can be used for control and/or measurement of mixing quality.

The technical principles of ResonantAcoustics® mixing will be presented and its capabilities illustrated.

### 183. Comparative ion-exchange, thermal analysis and structural studies of montmorillonite, fluoro-mica and magadiite: Model of the organoclay structure and design of nanofillers for polymer nanocomposites

**Juan M. Garces**[1], Steve R. Lakso[2], Mike Paquette[2] and Mark H. McAdon[2], (1)Consultant, Midland, MI, (2)The Dow Chemical Company, Midland, MI

Comparative ion-exchange, thermal analysis and XRD studies of montmorillonite, fluoro-mica and magadiite was performed and used to develop a theoretical model of the surface structure of alkyl cations in these clays. The results were applied to design organoclay nanofillers for a variety of polymer nancomposites. The cation exchange capacity and the clay composition play key roles in the loading and orientation of the alkyl chain molecules in the interlayer space of the clays. The mechanical properties of clay-PP nanocomposites depend on the organoclay structure and the clay type used to make the composites.

### 184. Scratch-resistant nanocomposite clearcoat technology

**Michael Zalich** and Daniel Rardon, PPG Industries, Allison Park, PA

New automotive clearcoat technology with improved mar and scratch resistance will be discussed. Through development of a novel nanoparticle composite coating technology, PPG has commercialized a clearcoat that provides enhanced robustness toward surface abrasions, typically encountered on vehicles through repeated washing and incidental contact. The loss of gloss that can result from extensive marring of the coating surface tends to get worse upon aging and weathering. A key benefit of this nano-composite clearcoat is “retained” mar resistance over the life of the coating. This is shown to be attributable to 1) the optimized balance of crosslink density and flexibility, 2) the type and effective dispersion of the nanoparticles, and 3) the mechanism of particle orientation at the surface of the cured film. Technology development was enhanced through the use of microscopic and physical analysis techniques, such as Nano Indentation. Field performance continues to confirm the efficacy of PPG's coating breakthrough to provide superior exterior appearance over a greater portion of the vehicle lifetime.

### 185. Dendrimer-based Organo-inorganic Nanocomposites

Petar R. Dvornic and **Steven N. Kaganove**, Michigan Molecular Institute, Midland, MI

The future of nanotechnology greatly depends on the ability to control the structural organization of matter at the lower end of the nanoscopic size scale. For this purpose, dendrimers are particularly well suited because they generationally increase in diameter in regular increments from about 1 nm to about 10 nm, and may be prepared with a high degree of structural uniformity and unprecedented functional group density. No other species of either classical organic or polymer chemistry offer this unique combination of properties. Poly(amidoamine-organosilicon) (PAMAMOS) dendrimers are radially layered copolymeric dendrimers that consist of hydrophilic polyamidoamine (PAMAM) interiors and oleophilic, organosilicon (OS) exteriors. They are unique globular nano-scaled organic-inorganic molecular hybrids which can be prepared with a variety of reactive silicon end-groups and used for preparation of more complex nano-structures, such as multi-layer block-copoly-dendrimers, multi-arm star-polymers, dendrimer-based networks and interpenetrating networks, organo-inorganic hybrid nano-complexes, nano-composites, etc. In this presentation, particular attention will be given to PAMAMOS networks, the first known dendrimer-based materials that can be processed into mechanically useful elastomeric or plastomeric films, sheets, membranes or coatings. The ability of PAMAMOS to incorporate metal cations, nanoscopic zero-valent metal particles or other electrophiles into hostile environments, such as solvents in which these are normally insoluble, and the ability of their networks to template such guests in predesigned, patterned nano-structures will also be discussed. Since recently PAMAMOS are commercially available, promising exciting applications in areas such as electronics, photonics, sensors, catalysis, biomedical processes, antifouling protection, semi-permeable membranes, specialty coatings, etc.

## Rubber and Elastomer Technology II

**Organizer:** Timothy Okel PPG Industries, Inc., Monroeville, PA

### 186. Vulcanization and Protection of General Purpose Elastomers

**Byron H. To**, Flexsys America L.P., Akron, OH

The process of vulcanization of elastomers is a chemical change by which individual rubber molecules are linked to each other at various points throughout the polymer. The points of linkage behave as crosslinks and give a mechanically stable and elastic network. Sulfur was the original vulcanizing agent used and is still the most widely used material to-day. It is well known that the durability of rubber products depends on the thermal and oxidative stability of these crosslinks.

Compounding of elastomers to resist degradation involves a number of factors including proper selection of polymer type, antidegradant system and vulcanization system. For example, saturated polymers such as butyl and EPDM are inherently more resistant to degradation than either SBR or natural rubber because the former have little to no unsaturation, or weak links, in the polymer chains. Antidegradants selection for polymer depends upon service conditions encountered, staining and discoloration constraints, and of course, cost. A wide range of antidegradants are available to the compounder, but they generally fall into one of two classes, namely, antioxidants capable of slowing the reaction of oxygen with rubber and antiozonants prevent deterioration due to ozone attack

This presentation focuses on compounding additives for vulcanization and protection of the general purpose elastomers such as natural and styrene butadiene rubbers. Vulcanization and protection systems which provide a balance in processing, curing and performance properties will be discussed.

### 187. Vulcanization Systems fro Butyl Rubber, Halobutyl Rubber, and BIMSM Elastomers

**Brendan Rodgers**, Scott Solis, Nitin Tambe, Bharat Sharma and Walter Waddell, ExxonMobil Chemical Company, Baytown, TX

The vulcanization of isobutylene-co-isoprene rubber (IIR), brominated isobutylene-co-isoprene rubber (BIIR), chlorinated isobutylene-co-isoprene rubber (CIIR), and brominated isobutylene-co-para-methylstyrene elastomer (BIMSM) differs from that of general-purpose rubbers (GPR). Butyl rubber has approximately 2% unsaturation in the backbone. Halobutyl rubber (BIIR and CIIR) incorporates the butyl backbone with either bromine or chlorine, which significantly increases the chemical reactivity of the isoprenyl units located in the butyl backbone. Similarly, in BIMSM the bromine atom is bonded to the para-methylstyrene (PMS) group, thus affording the completely saturated polymer backbone a site of chemical reactivity. Utilization of the unique attributes of butyl rubber and halobutyl rubbers with their minimal backbone unsaturation and of BIMSM elastomers with no backbone unsaturation is found in many areas of industry. These properties are excellent vapor impermeation, resistance to heat degradation, and improved chemical resistance as compared to general-purpose rubbers. However, this low amount of reactivity requires special consideration to vulcanize these isobutylene-based polymers. The type of vulcanization system selected is a function of the composite structure in which it is used, and the cured product performance requirements. Therefore, vulcanization systems vary and may include an accelerator package along with resins, zinc oxide, zinc oxide and sulfur, and quinoid systems. This review will discuss the types and selection of appropriate vulcanization systems for isobutylene-based elastomers.

### 188. Enhance Mixing Productivity of Natural Rubber Compounds Using Quinone Diimine

**Frederick Ignatz-Hoover**, Flexsys America L.P., Akron, OH

Conventional means of improving the processability of natural rubber compounds often lead to reductions in performance properties of the final vulcanizate. Additions of soaps, oils, or peptizers may lead to lower process viscosity but may bring deleterious changes in performance characteristics. Most importantly, changes in modulus, hysteretic properties and or abrasion and fatigue resistance may suffer by over use of these materials. The quinone diimine molecule reacts quickly to terminate mechanically cleaved polymer chains. Mixing natural rubber compounds in the presence of quinone diimines provides for lower process viscosities with no loss and in some cases improvements in final properties. This can lead directly to improved productivity (as much as 25%) and lower processing costs while maintaining product performance characteristics. Terminating the radicals leads to a faster drop in viscosity with less oxidative degradation of the polymer during the mix. Mixing with quinone diimines thus provides improvements in the balance between processing and performance properties. This paper will discuss the mechanism and benefits mixing natural rubber compounds with quinone diimines.

### 189. Moisture-Curable Silicone Hot-Melt Adhesive Technology

**Loren D. Lower** and Glenn V. Gordon, Dow Corning Corporation, Midland, MI

Silicone hot-melt adhesives (Si HMAs) are usually made from mixtures of silanol-terminated pol(dimethylsiloxane)s and resinous silanol-functional "MQ" silicates. The silicate, which is a glass at ambient conditions, functions as a tackifier by reducing the rubbery plateau modulus of the polymer. In the absence of a solvent, mixtures containing a greater proportion of the silicate will produce a viscoelastic composite that will exhibit a significant change in viscosity above room temperature. While not a true "melting" behavior, the net change in viscosity at elevated temperatures is substantial enough to provide a practical means of delivering or applying these Si HMAs at 100% solids compositions. The HMAs can be further modified to allow for moisture cure while maintaining its hot-melt character in the uncured state. This paper will review the development of moisture-curing Si HMA technology, discuss its viscoelastic properties, and talk about some potential applications.

## Plenary Lecture: Challenge of Preparing Disilynes, Triplet Ground State Silylenes, Heavy Group 14 Cations, Anions, and Dimetallenes

### 190. Challenge of Preparing Disilynes, Triplet Ground State Silylenes, Heavy Group 14 Cations, Anions, and Dimetallenes

**Akira Sekiguchi**, University of Tsukuba, Tsukuba, Japan

After the preparation of the silene >Si=C< and disilene >Si=Si<, many stable unsaturated silicon compounds have been synthesized to date. However, there were few known unsymmetrical $R_2Si=SiR'_2$ or heteronuclear $R_2Si=E'R_2$ (E' = heavier group 14 elements). We have developed a straightforward method for the synthesis of dimetallenes of the type >Si=E< by a coupling reaction of $(^tBu_2MeSi)_2SiLi_2$ (**1**) with 1,1-dihalosilanes, -germanes and -stannanes, which provides disilenes (**2a**), germasilenes (**2b**) and silastannenes (**2c**), respectively. The reaction of **1** with 1,1,2,2-tetrachloro-1,2-dimesityldisilane produced a tetrasila-1,3-butadiene derivative 1,1,6,6-tetra-*tert*-butyl-2,5-(di-*tert*-butylmethylsilyl)-3,4-dimesityl-1,6-dimethylhexasila-2,4-diene (**3**), which afforded $R_2Si=SiRLi$ (**4**) by the treatment with $^tBuLi$. A highly crowded cyclotrisilene $(^tBu_2MeSi)_2SiSi_2(Si^tBu_3)_2$, prepared by the reaction of **1** with $^tBu_3SiBr_2SiBr_2Si^tBu_3$, was converted to cyclotrisilenylium ion **5+**, all-silicon aromatic ring, upon the one electron oxidation by triphenylmethylium tetraarylborate. A stable compound with a silicon-silicon triple bond, 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyl-2-tetrasilyne (**6**), was also prepared by the debromination of corresponding precursor. Despite the steric protection, the Si-Si triple bond in **6** does undergo addition reactions with halogen, *cis*-butene, and *trans*-butene. The reactivity of the disilyne **6** to produce the stable 1,2-disilabenzene derivatives, disilenyllithiums, amino-substituted disilenes, and stable disilyne anion radicals will be presented. For the challenge of preparing such fundamentally important species as disilynes, triplet ground state silylenes, heavy group 14 cations, radicals, anions, and dimetallenes, the following topics will be given.

1. Synthesis of the stable 1,1-dilithiosilanes (-germanes) and their application to the synthesis of heavy alkenes of the type >E=E'< (E = Si or Ge, E' = heavier group 14 elements).

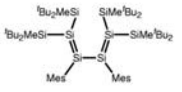
2. Synthesis of a stable disilyne with a silicon-silicon triple bond.

3. Synthesis of free silyl cations and their heavier homologs by aromatic stabilization.

4. Synthesis of stable silyl radicals and their heavier homologs.

5. Generation of ground-state triplet silylenes and EPR observation.

6. Synthesis of cyclobutadiene dianion, cyclobutadiene, tetrahedrane, tetrahedranyllithium, and tetrahedranyltetrahedrane.



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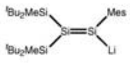

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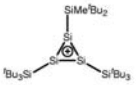

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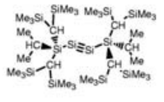
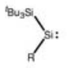


6



R = $Si^tBu_3$, Li, K

## Analyzing the World Around Us I

**Organizer:** Janet M. Smith Dow Corning Corporation, Midland, MI
**Organizer:** Susan V. Perz Dow Corning Corporation, Midland, MI

### 191. Dihydrogen mono-oxide... My water has WHAT in it?

**Wendy J. Klein** and John D. Blizzard, QuadSil inc., Midland, MI

This talk will skim the surface of water testing capabilities from bacteria, to inorganics, and look out to the horizon of testing for organics in drinking water, industrial process water, waste water and storm water. Drinking water is strictly regulated by the Environmental Protection Agency; and Industrial process, waste and storm waters are monitored by agencies such as the Department of Environmental Quality and others. Answer the When, What, Why and How's regarding water testing for your home, lake, river, or business as presented by Raven Analytical Laboratory-Midland, a subsidiary of QuadSil inc.

### 192. What in the Construction World do We do With "Goo?"

**Robert P. Mortensen**, Dow Corning, Auburn, MI

In the construction industry silicone materials are used in many places that are not obvious, this presentation will highlight some of those applications. The three areas that will be examined are building envelope weathersealing, structural glazing and commercial and residential window manufacturing.

### 193. Surfing the Surface of Microscopy

**Debbie Bailey**, Dow Corning, Auburn, MI

Microscopy plays a critical role for characterizing the surface and inner structures of materials. This helps researchers better understand and optimize properties of their materials. Microscopy makes visible what the eye can't see, letting the researcher collect information about roughness, uniformity, topography, feature size, elemental composition, and other surface properties. This presentation provides a basic overview of the type of surface and / or inner structure information that can be gained by optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, atomic force microscopy, and contact angle. With these powerful tools one could analyze features from a micron scale down to angstroms.

### 194. Analyzing Fully Hydrated Samples Using a Conventional Scanning Electron Microscope and Energy Dispersive Spectroscopy

**Janet Allen**, Dow Corning, Auburn, MI

Examination of fully hydrated samples using conventional SEM/EDS analysis usually requires timely sample preparation, expensive sample preparation equipment and skillful analysts. However, with the advent of newer technology it is now possible to quickly and easily examine fully hydrated samples in their native state using EM. A company called QuantomiXTM developed a unique capsule that has a thin, electron transparent membrane (made from polyimide) which protects the wet specimen from the high vacuum of an SEM. The capsules can be used to study a diverse range of hydrated samples which include; cosmetics, oils, foods, emulsions/dispersions, pharmaceuticals, inks, biological specimens and many more. This new technique is currently being assessed within the Analytical Sciences department at Dow Corning to determine the versatility and reliability of the capsules primarily for the analysis of DC materials.

### 195. NMR – Unraveling Molecular Mysteries:

**Cheryl Roggenbuck** and Don Eldred, Dow Corning, Auburn, MI

The molecular story, as revealed by the NMR spectrum, is one of intermolecular spies, electronegative rivalry, and diverse environmental conditions. This presentation unravels the mystery behind NMR through a general understanding of how NMR works, basic information relating to 1H, 13C and 29Si NMR experiments, real life polymeric applications, and limitations to the technique.

### 196. Plasma Enhanced Chemical Vapor Deposited Film Process Development for Improved a-SiC:H Films

**Jeff Seifferly**, Dow Corning Corporation, Auburn, MI

Dow Corning partnered with a major Department of Defense contractor under pressure to significantly reduce the cost to produce advanced radar systems having improved functionality. We determined we had the technology and expertise needed to help them meet their cost-reduction challenge. Our solution was to replace their more costly hermetic packaging technology with our own proven technology is this area. We provided a Plasma Enhanced Chemical Vapor Deposition (PECVD) process technology to deposit a-SiC:H films, using Dow Corning® Z3MS™ precursor gas. Subsequent improvements to the original PECVD process were made to integrate the a-SiC:H passivation into their manufacturing process and develop film properties compatible with their GaAs wafers. This presentation will detail the process development used to select a new, higher temperature film deposition process to meet the customers' requirements exactly.

## Behavior of Polymeric Materials in Severe Environments

**Organizer:** David Moll Dow Chemical, Midland, MI

### 197. Microscale Flammability Measurements on Nylon-6 Polymer Clay Nanocomposites and Polypropylene Carbon Nanofiber Nanocomposites

**Alexander B. Morgan**, University of Dayton Research Institute, Dayton, OH

Materials flammability continues to be an area of increasing interest and concern to regulators, producers, and consumers. There is also an increase in demand for what a material can do, including achieving multi-functionality so that the material can be used in more than one application. In this paper we present some nanocomposite materials designed for film and tape applications with either barrier properties or electrical conductivity as the primary application, and we will show that they have reduced flammability as well due to their nanocomposite structure. Effects of clay loading in Nylon-6 will be shown, along with new flammability data for carbon nanofibers, which have not typically been analyzed for flammability performance, but seem to show some improvements due to reduced fuel release/mass loss during fire. Finally we will discuss potential applications for these materials along with how these materials can and cannot be used for fire safe applications.

### 198. Thermal Stability of Vinylidene Chloride/Methyl Acrylate/4-Vinylpyridine Coploymers

**Adeyinka O. Odelana** and Bob A. Howell, Central Michigan University, Mt.Pleasant, MI

Vinylidene chloride copolymers are prominent in the barrier plastic packaging industry.These materials display excellent barrier to the transport of oxygen (and other small molecules)as well as flavor and aroma molecules.However,they suffer from a propensity to undergo degradative dehydrochlorination at process temperatures.To scavenge hydrogen chloride formed and prevent its interaction with the metallic components of process equipment a passive base is usually included as an additive prior to processing.The base is most often an inorganic oxide or salt.These may negatively impact the properties of the polymer,particularly as a film.An organic base that could be covalently incorporated into the copolymer might display better behavior.Accordingly,a series of copolymers containing low levels of 4-vinylpyridine (0.05-3 mole percent)have been prepared,characterized,and examined by thermogravimetry to assess thermal stability.In all cases,polymers containing 4-vinylpyridine units are less stable than the polymer containingnone of this comonomer.Clearly,the pyridine moiety is a sufficiently

strong base to promote E2 elimination of hydrogen chloride to generate dichloromethylene units in the mainchain from which thermal degradation may be initiated.

### 199. Dendritic polymer approaches for the decontamination of vapor phase cyanide

**Steven N. Kaganove**, Tracy Zhang and Petar R. Dvornic, Michigan Molecular Institute, Midland, MI

The varying ability of several metal-chelated PAMAM dendrimers to remove HCN from vapor streams will be discussed. Particular attention is focused on curable formulations of PAMAMOS, a family of radially layered copolymeric dendrimers that have polar, hydrophilic polyamidoamine (PAMAM) interiors and hydrophobic organosilicon (OS) exteriors. They are commercially available from Dendritech, Inc. Their nanoscopically-organized PAMAM interiors chelate with a variety of metal ions through interaction with numerous tertiary amine groups present within their structure. Glass fiber liquid filtration disks were coated with curable PAMAMOS chelated with either Cu(II), Zn(II) or Ni(II) cations. A 270 ppm HCN vapor challenge flowing at 500 mL/min was used. Cu-PAMAMOS and Zn-PAMAMOS were the most effective at scrubbing HCN vapor, while Ni-PAMAMOS was significantly less effective. Two types of filter disks were used in these experiments, and the difference in relative porosity between them dramatically impacted their ability to scrub HCN. Hence, intelligent filter substrate design was found to be equally important as the choice of chemically interactive coating material for scrubbing HCN.

### 200. Behaviour of boron-based lubricants in a polymer matrix

**Katherine Helmetag** and Gabriel Kirsch, Henkel Corporation, Madison Heights, MI

Boron-based additives are used to mitigate friction in a variety of industrial lubricants. Current technologies employ polymer matrices to disperse and deliver the additive to the frictional interface as a dry film lubricant on aluminium. Performance differences seen in practical use of these lubricants are not seen in testing of the neat additives. Differences in friction modification are more clearly observed when the boron-based additives are dispered in a polymer matrix.

Various phenomena associated with boron-based lubrication will be explored.

### 201. Carbon composite aircraft brake material resistance to alternative runway deicers

**Dale LeCaptain**[1], Megan McCallum[1] and Dilum Dunuwila[2], (1)Central Michigan University, Mt. Pleasant, MI, (2)Diversified Natural Products, Scotteville, MI

Airport and airbase runways are specialty applications for deicing materials that have expanded performance requirements from typical road deicing. Chloride based de-icers cause corrosion of concrete and aircraft metals while currently used glycol based deicers are being scrutinized because of their environmental impact. KCl is corrosive because the ionization of the salt solution results in oxidation of surfaces and is detrimental to the environment. Over-saturation of K+ in the soil damages the vegetation and oxidizes iron making it impractical for high cost applications. The use of glycol based deicers is not favored because of its high biological oxygen demand (BOD). As the glycol solution degrades, the dissolved oxygen concentration in the runoff water greatly depletes. This results in a very high depletion of oxygen, which can be toxic to the ecosystem. Acetate and formate alternatives are being marketed as replacement de-icer materials to address the concerns of metal and concrete corrosion while minimizing the environmental impact. However, recent literature demonstrates that these alternative deicers cause degradation of the carbon-carbon composite brake material and other aircraft components. According to Carabineiro, S.A et.al. (1), the cause of deterioration of the composite material is due to the oxidative properties of K+. Although this problem with the use of potassium is described, it is unclear the mechanism or reason for this problem. Environmentally, an ideal deicer would be non-toxic, biodegradable, effective, and benign to the application environment. To aide the development of green chemical alternative deicers such as succinate salts, this research seeks to determine the degradation mechanism of the carbon carbon composite braking material in the presence of succinate and acetate salts.

## Brewing Science Symposium I

**Organizer:** Gary E. Kozerski Dow Corning Corporation, Midland, MI
**Organizer:** Paul J. Popa Dow Chemical Company, Midland, MI

### 202. Malt, marzen, molecules and modification: beer and brewing as an artform in chemistry

**Charles Bamforth**, University of California (Davis), Davis, CA

The chemistry of brewing and beer is immensely complicated and challenging. The chemical and biochemical reactions occurring throughout the processes of barley modification into malt, malt extraction into wort, boiling of wort and attendant hop extraction, fermentation and conditioning are complex, yet astonishingly well-controlled. As for beer, it may comprise more than 2,000 different types of molecule, contributing to flavor, foam, clarity and color. And the unstable nature of beer means that the mix of molecules is in continual flux. This paper presents an overview of this demanding topic.

### 203. Brewers Yeast: A journey from chemistry to biochemistry

**Christopher White**, White Labs Inc., San Diego, CA

Beer is created from malted barley, hops, water, and yeast. Yeast converts malt sugars to CO2, flavor compounds, and ... ethanol. This seminar will discuss the evolution of our knowledge of brewers yeast, and what we now know about the contribution from brewers yeast. Methods that brewers use to harness the power from yeast will also be discussed.

### 204. A review of non-biological stability and methodology for its extension

**John P. Haggerty**, New Holland Brewing Co., Holland, MI

The goal of the presentation is to review various methodologies for extending the non-biological (i.e. colloidal) stability of beer. This will be accomplished by defining the compounds in beer that comprise non-biological stability, how these compounds function to create haze problems, with a review of how external influences can accelerate this haze and turbidity formation. Once the paramters of non-biological stability and its degradation are established the routes to extending the stability of beer will be reviewed. This review will encompass a brief discussion of the role of raw material parameters, past methods that have fallen from favor culminating in modern techniques available to today's brewer - i.e. pvpp and silica gels. A discussion of how these modern techniques work, are applied and an illustration of how non-biological stability is improved are to be included.

### 205. Practical advice for the beginning home brewer

**John M. Warakomski**, The Dow Chemical Company, Midland, MI

In this talk I will share my personal experiences of brewing 75 five-gallon batches of beer, including some award winners. I will describe the equipment (mostly simple, inexpensive, or homemade), ingredients, and techniques I use. I will provide a step-by-step description, with liberal use of photographs. The presentation will not be highly technical, but at each step I will also briefly describe the chemistry that is occurring. I will propose a list of “Top Ten Rules” for making good home-brewed beer. This is not a definitive talk on the way to make beer, but rather describes one way that I have successfully brewed beer over the past fifteen years.

### 206. The History of Brewing in Frankenmuth

**Greg Rummel**, Historian, Frankenmuth, MI

An informal presentation on the history of brewing in Frankenmuth as well as the town's prominent role in the Michigan Brewing Industry. From the founding of Frankenmuth's first commercial brewery in 1857 to its present day brewpubs, we will outline and discuss brewing methods, contributions from local agriculture, prohibition, the beer boom of the 1950s to the stagnation of the '90s, and the rebirth of beer in the new millenium.

## Chemical Education I

**Organizer:** David Baker Delta College, University Center, MI
**Organizer:** John D. Blizzard QuadSil inc., Midland, MI

### 207. Microwave Experiments for the Organic Chemistry Laboratory

**David Baker**, Delta College, University Center, MI

A series of microscale experiments using microwave technology have been developed for use in the organic chemistry laboratory courses Five very proficient and interesting experiments using microwaves have been developed. These experimental procedures will be described. These experiments are designed to expose the students to new developments and perspectives in microwave synthesis and combinatorial chemistry. They are intended to expand the student's knowledge of multiple syntheses.

### 208. Getting the Most Out of Animations in Chemical Education

**Bernadette Harkness**, Delta College, University Center, MI and Brian L. Aldrich, Heritage High School, Saginaw, MI

In recent years chemical animations have been a widely used tool because they can facilitate molecular-level understanding of chemical phenomena. Often the target audience for these animations is comprised of chemistry students who have limited background knowledge and so would seemingly benefit from these animations. But in what way does viewing animations enhance student comprehension? We investigate two approaches to determine what and/or when the gains in student comprehension of chemical phenomena are made. The first approach is made by following a traditional topic sequence of a chemistry course that uses animations to initiate the inquiry with subsequent exposure to the particulate nature of matter using Lewis structures, particulate diagrams and molecular models. The second approach is to give early introduction of these same tools and then subsequent exposure to the animations. Comprehension of chemical phenomena such as dissociation and precipitation is then measured through student-generated illustrations and/or written descriptions of the animated presentation. The work of students given early exposure to molecular-level topics is then compared to the work of others who followed the traditional topic sequence in their chemistry course.

### 209. Engaging Students with Discovery Oriented Methods (Small Scale & P2)

**Michael T. Garlick**, Delta College & Saginaw Valley State University, University Center, MI

Currently we are being asked to do more with less. How can you do this given, less funding, equipment, chemicals, and time to accomplish this task? We are also asked to do this, and if we could, also please make, less mess, and less waste at the same time. On the surface the only answer seems to be, to give up traditional chemical & biological lab activities, use more dry labs, videos, and lecture more instead. We all remember how exciting plain lectures, dry labs and old school movies were in our day, and this is no solution to our problems.

Small Scale Techniques allows us to use less chemicals, purchase less costly equipment, which isn't made of fragile glass, and you can do the same reactions on a smaller scale producing much smaller amounts of waste with less hazards. The State of Michigan is offering grants to help schools adopt this method, and empty storerooms of old hazardous chemicals provided you develop a plan to implement this change.

Learn what you can do to take advantage of this opportunity and learn about small-scale chemical techniques you can use in your classroom tomorrow.

### 210. Can quantum concepts be learned by students in general chemistry?

**Morton Z. Hoffman**, Dan Dill, Peter Garik and Alexander Golger, Boston University, Boston, MA

Because of the counterintuitive nature of the quantum world, which renders difficult the imagining of its reality, students, understandably, acquire myths and misconceptions, and miss critical connections in their study of atomic and electronic structure. Despite the efforts of their instructors and the authors of their textbooks, students in general chemistry have a great deal of difficulty understanding, for example, the distinction between electron orbital energy and the energy of the quanta of electromagnetic radiation absorbed and emitted during transitions. Because a picture is worth (at least) a thousand words, students remember the static images that they are shown as modified through their personal prisms, and not the written and oral explanations and disclaimers that are presented for clarification. In fact, the quantum world is not static, and time dependence is the basis of change. We have developed guided-inquiry computer activities that provide a visual means to understand the temporal properties of electron waves and how their mixtures account for the interaction with light. In this way, students can visualize the beats that correspond to dipole excitations of atoms, which form the basis of the selection rules for quantum absorption and emission.

### 211. Use of gas chromatography to illustrate the basics of design of experiments (DOE) methodology

**Chris Bowers** and Matt Tupps, Ohio Northern University, Ada, OH

Statistical design of experiments (DOE) is a methodology which is used to examine the relationship between the inputs and outputs of a process. It is widely applied in studies seeking to minimize defects, optimize processes, improve yield, or gain an understanding of which variables have a significant effect on the process output. This work focuses on the use of a series of gas chromatography experiments to illustrate the basics of a two level factorial DOE study. Data analysis basics will be covered and the power of replicates will be illustrated. A brief discussion of the use of DOE in the teaching of instrumental analysis will be included.

### 212. Enhancing chemistry instruction with mass spectrometry

**Rebecca W. Corbin**, Ashland University, Ashland, OH

Undergraduate students are exposed to the versatility and wide-spread utility of mass spectrometry (MS) throughout their experience with chemistry at Ashland University. For non-science majors, *The Chemistry of Crime Scene Investigation* is a forensics-themed, laboratory-focused exploration of chemistry. Students enrolled in this course use gas chromatography-mass spectrometry (GCMS) to investigate “real world” samples for the presence of drugs and accelerants. Furthermore, mass spectrometric measurements are presented to science majors throughout the entire chemistry curriculum. For example, GCMS as well as matrix-assisted laser desorption/ionization (MALDI) MS are used in the analytical chemistry courses for a wide range of laboratory projects, including natural products identification and synthetic polymer characterization. Upper-level science majors completing biochemistry coursework have the opportunity to engage in both manual and database-assisted sequencing of proteins. These classroom and laboratory projects readily enable students to take an active role in aspects of experimental design, sample preparation, instrument operation, data interpretation, and the communication of results. Moreover, several of the MS-centered exercises have been successfully adapted for use with middle school and high school students.

### 213. “Students' Performance and Appreciation of Internet-based Instructional Technology Applications in Pharmaceutical Analysis Laboratory Course”

**Konstantinos Ghirtis**[1], Marissa Helene Waldman[1], Mustapha A. Beleh[1], Kevin G. Rice[2] and Ronald W. Woodard[1], (1)University of Michigan, Ann Arbor, MI, (2)University of Iowa, Iowa City, IA

Due to a larger demand for pharmacists, class sizes are increasing nationwide burdening courses with a laboratory component. Maintaining high standard science training is important if pharmacy graduates are to practice knowledgeably, responsibly and confidently in any setting. Instrumentation and resource constraints are maximal in the case of the pharmaceutical analysis laboratory due to the nature of the experiments that need to be conducted and the need to provide an as individual as possible learning experience. Therefore our body of 1st year PharmD students is separated into two groups each consisting of 3 subgroups of a 12-13 student size. The 9 experiments are executed in three cycles with each of the subgroups doing one of the three experiments one week alternating with other subgroups in the next week. Although this optimizes the space, instrument and resource utility, it creates inevitable educational gaps in the association of each subgroup's experiment with the lectures' content and how to conduct a prelaboratory instructional session to better prepare the students before the actual laboratory. Having 2x3 = 6 such sessions would be too burdensome. Therefore we prepared online

instructional videos of theoretical background and technique demos as well as accompanying online quizzes that each student had to view and pass before coming to the laboratory. Also we would like to provide our students with problem solving skills beyond the essential technical ones. It is not always feasible to include a purposefully erroneous experiment not least because it could harm the expensive and sensitive instrumentation used. So we designed virtual laboratories that students had to perform as part of a particular experiment in addition to the wet one. As shown by online quizzes, this and past years' student surveys and individual interviews these changes were well received and improved student competence, comprehension and problem solving.

## Silicon Symposium - 25 Years of Multiple Bonds to Silicon

**Organizer:** Robert West University of Wisconsin, Madison, WI

### 214. Discovery of multiple bonds to silicon - the history

**Adrian G. Brook**, Universtiy of Toronto, Toronto, ON, Canada and **Robert West**, University of Wisconsin-Madison, Madison, WI

Before 1981 the general belief, as stated in the "double bond rule", was that elements outside the first row of the periodic table did not form multiple bonds. However in 1981 at the 15th Organosilicon Symposium in Durham, NC, stable compounds containing Si=C and Si=Si double bonds were reported in sequential sessions. The result was a paradigm shift, which led to a great flowering of multiple-bond chemistry involving essentially all of the nontransition elements. To mark the 25th anniversary of silicon multiple bonds, we will outline the history of the original discoveries, and describe some of the consequent advances in multiply-bonded silicon chemistry.

### 215. The Fascinating World of Multiply-Bonded Silicon Compounds. Experiment and Theory in Synergy

**Miriam Karni** and Yitzhak Apeloig, Technion - Israel Institute of Technology, Haifa, Israel

Silicon is the closest congener of carbon. Yet the fundamental properties of many silicon and carbon compounds are very different. This is especially evident for low-coordination compounds, such as multiply-bonded silicon compounds or silylenes, whose chemistry has begun to be unraveled only in the last three decades, following the synthesis of the first stable compounds of these types in 1981.

Because until recently many of these compounds did not exist, theory played a major role in predicting and understanding their structural, chemical and physical properties and in directing experiments in this field. Examples of this fruitful interplay and synergism between theory and experiment will be demonstrated in this talk. The discussion will focus mainly on the intriguing properties of doubly- and triply-bonded silicon compounds, in particular, disilenes ($R_2Si=SiR_2$), trisilaallenes ($R_2Si=Si=SiR_2$), disilynes ($RSi\equiv SiR$) and silynes ($RSi\equiv CR$).

## 216. Unique reactions of stable trisilaallene and related compounds

**Takeaki Iwamoto**, Takashi Abe, Shintaro Ishida, Hidenori Masuda, Chizuko Kabuto and Mitsuo Kira, Tohoku University, Sendai, Japan

Although several types of stable disilenes have been reported since the synthesis of tetramesityldisilene as the first stable disilene by West and coworkers, stable silicon-based dienes are still quite rare. Recently we have synthesized stable trisilaallene (**1**, $R_2Si=Si=SiR_2$, $R_2$ = 1,1,4,4-tetrakis(trimethylsilyl)-1,4-butanediyl) as the first stable compound with the cumulative Si=Si double bonds and formally *sp*-hybridized silicon atom. Trisilaallene **1** shows remarkably bent allenic structure and unique fluxional behavior both in the solid state and in solution. In the presentation, the unique reactions of trisilaallene **1** and related compounds are discussed. The addition of **1** to water and alcohols occurred in a regiospecific manner to afford 1,3-dihydroxy- and 1,3-dialkoxytrisilanes in high yields. The additions are explained by a stepwise mechanism involving the initial nucleophilic attack of a hydroxy (or alkoxy) oxygen to a terminal allenic silicon atom to give an intermediate unsymmetric disilene. The regiospecificity can be rationalized by the polar nature of the Si=Si double bond in **1** and the intermediate disilene that are evidenced by the shape of the frontier orbitals and the NPA charge distribution of model compounds for **1** and the intermediate disilene. The reaction of **1** with *t*-butylisonitrile and 2,6-diisopropylphenylisonitrile gave different types of cyclic silaketenimines in good yields. Although the mechanism for the formation of the silaketenimines remains open, the corresponding 1,2-disila-4-azabutatrienes are suggested to be involved in the mechanism as key intermediates. Detailed molecular structures of the silaketenimines and the reactions of **1** with other reagents will be also discussed.

## 217. Cycloaddition Reactions of Doubly-Bonded Silicon Compounds: Past to Present

**Kim M. Baines**, University of Western Ontario, London, ON, Canada

As was only natural, immediately following the synthesis of stable doubly-bonded derivatives of silenes and disilenes, researchers in this field turned their attention towards exploring the reactivity of these exciting compounds. Cycloaddition reactions were extensively investigated, in part, because they provided a direct and simple means of synthesizing a variety of new and interesting ring systems. However, despite twenty-five years of research in this field, it is surprising that relatively little is known about the mechanistic details of many of these reactions. An understanding of the reactivity of these compounds will be critical for the development of applications of this chemistry. Our efforts to understand the mechanism of the addition of both aldehydes and alkynes to silenes and disilenes using hypersensitive mechanistic probes will be described.

### 218. Recent progress in the chemistry of kinetically stabilized disilenes

**Norihiro Tokitoh**, Yusuke Sugiyama and Takahiro Sasamori, Kyoto University, Kyoto, Japan

In the course of our studies on sterically congested molecules, we have developed very efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt), and successfully applied them to the kinetic stabilization of a variety of low-coordinated organosilicon compounds leading to the synthesis of extremely hindered tetraaryldisilenes [*(E)*- and *(Z)*-Tbt(Mes)Si=Si(Mes)Tbt], the first silylene-isocyanide complexes, Tbt(Mes)SiCNR [R = 2,4,6-triisopropylphenyl, 2,4,6-tri-t-butylphenyl, or Tbt], silicon-containing heavy ketones [Tbt(R)Si=Ch; Ch = S, Se, Te; R = 2,4,6-triisopropylphenyl or 2,6-diisopropylphenyl], and stable silaaromatic compounds (Tbt-substituted silabenzene, 1- and 2-silanaphthalenes, 9-silaanthracene, and 9-silaphenanthrene).

In this paper, we wish to present our recent studies on the synthesis and properties of much less hindered, functionalized disilenes, such as 1,2-dihalodisilenes and 1,2-dihydrodisilenes having Tbt or Bbt group as a steric protection group. Although the reductive coupling of $TbtSiBr_3$ using lithium naphthalenide resulted in the formation of a yellow solid almost insoluble in common organic solvents, similar treatment of $BbtSiBr_3$ afforded the corresponding dibromodisilene, *(E)*-Bbt(Br)Si=Si(Br)Bbt (**1**), as stable yellow crystals. Hydrogenation reactions of **1** were examined under several reaction conditions to give $BbtSiH_2SiH_2Bbt$, while the reductive coupling reactions of $ArSiHBr_2$ (Ar = Tbt or Bbt) using lithium naphthalenide gave the corresponding 1,2-dihydrodisilenes, ArSiH=SiHAr (**2a**; Ar = Tbt, **2b**; Ar = Bbt), as stable compounds. The $^{29}$Si-NMR measurement on INEPTNON mode revealed that $^{1}J$(Si-H) and $^{2}J$(SiSi-H) of **2a** are 212 and 19 Hz, respectively. Thermal stability and spectroscopic properties of the newly obtained disilenes, **1** and **2a,b** will also be described.

## Small Chemical Businesses I

**Organizer:** Diana A. Phillips Kettering University, Flint, MI

### 219. ACS perspectives on Small Chemical Businesses - Bill Carroll (ACS Past-President)

**William F. Carroll Jr.**, Occidental Chemical Corporation, Dallas, TX

Abstract will be added

### 220. Don't Quit your Day Job: Lessions from My Small Membrane Reactor Company

**Robert E. Buxbaum**, REB Research & Consulting, co., Ferndale, MI

I started my small membrane reactor, hydrogen generator business, REB Research & Consulting while still a professor of chemical engineering at Michigan State. Starting a small business while still in my old job is a low-risk approach especially suited to the chemical industry, where development times are long. It allowed me avoid taking on debt or investors, two things that I'd avoid if possible, while building a business that today has $500,000/year in revenues revenues (OK, it's not Exxon/Mobile). I think there were benefits to my college students as well, and to my old department. Still, every employer is different. Most jobs will not give you as much flextime as a professor at a research university allows, nor does every job encourage freelance consulting to the private sector. Still, this approach is worthwhile, even for the non-professor, once you find ways to deal with money, time, employees, and intellectual property. I'll talk about these issues and my experiences dealing with them as they affected my company. I'll also tell you my thoughts about hiring students, and abut when to make the break to working for yourself full time. The approach I offer may not be applicable to everyone, but perhaps you'll find something helpful or funny.

### 221. An over night success really can take 10 years: how a revolutionary technology came to be and what I have learned

**Lars, G. Beholz**, Beholztech, Inc., Flint, MI

In 1997 I developed a water-borne method to render inert polymers such as polyethylene adhesive. This year we are going into production. In this presentation, I will tell the tale of what this technology is, how it came to be and address some of the many hurdles I have overcome to bring this technology to industry. It has certainly been a journey.

## Surface Characterization - Improved Efficiency and Quality of Analysis

**Organizer:** Gregory F. Meyers Dow Chemical Company, Midland, MI

### 222. Probing the Heterogeneity in the Electrical and Electrochemical Properties of Hydrogen-Terminated Diamond Electrodes with Conducting Probe Atomic Force Microscopy and Scanning Electrochemical Microscopy

**Shihua Wang** and Greg M. Swain, Michigan State University, East Lansing, MI

We report herein on heterogeneity of the electrical and electrochemical properties of hydrogen-terminated, boron-doped microcrystalline and nanocrystalline diamond thin films by conducting-probe atomic force microscopy (CP-AFM) and scanning electrochemical microscopy (SECM). CP-AFM was used to simultaneously map the topography and electrical conductivity of both types of hydrogen-terminated diamond as a function of the boron-doping level. Specifically, the dependence of electrical conductivity on the boron-doping level, topography and bias voltage polarity were investigated. Heterogeneity in the electrical conductivity was observed for all films, with the fraction of highly conductive area increasing proportionally with the doping level. The results clearly show that both types of polycrystalline thin film do not possess

uniform electrical properties over the surface. Rather, they are composed of regions of high electrical conductivity isolated by regions of low conductivity. The spatially heterogeneous conductivity likely results from a non-uniform distribution of boron dopant and hydrogen within the film which leads to a non-uniform charge carrier concentration. Scanning electrochemical microscopy (SECM) was also used to probe the spatial heterogeneity of the electrochemical activity consistent with the CP-AFM measurements, isolated regions of high electrochemical activity were found for $Ru(NH3)_6^{+3/+2}$, $Fe(CN)_6^{3-/4-}$ and $IrCl_6^{2-/3-}$. The electrochemically active regions behaved as a “metallic” rather than a “semiconductive” material. The results have important implications for understanding how these materials function as electron emitters and electrochemical electrodes.

## 223. High contrast nano-Raman spectroscopy with optimized polarization

**Nam-Heui Lee**[1], Ryan D. Hartschuh[1], Disha Mehtani[1], Alexander Kisliuk[1], Mark D. Foster[1], Alexei P. Sokolov[1] and John F. Maguire[2], (1)The University of Akron, Akron, OH, (2)Air Force Research Laboratory, Dayton, OH

For nanoscale characterization of chemical composition, structure, stresses and conformational states, tip-enhanced Raman spectroscopy (TERS) is an attractive tool. A TERS spectrometer based on side illumination geometry that shows reproducible enhancement of the order of $10^3 \sim 10^4$, for a variety of molecular, polymeric and semi-conducting materials using silver- and gold-coated silicon nitride tips, will be presented. The radius of the spot from which the Raman signal comes is estimated to be 20nm for CdS thin films. For thick samples, such as a silicon wafer, polarization was optimized to achieve high contrast between the near- and far-field Raman signals. Additionally, systematic studies to estimate the localization volume of the detected near-field Raman signal with the optimized polarization are being performed. Raman imaging with sub-wavelength lateral resolution will be demonstrated on several nano-structures.

## 224. Characterizing 3-D Shape Function and Microstructure of a Nano-AFM Tip with Transmission Electron Microscopy and Electron Tomography

**H. Sean Tang**, Greg F. Meyers, Steve J. Rozeveld and Elvin Beach, The Dow Chemical Company, Midland, MI

Atomic Force Microscopy (AFM) has been frequently used to characterize the surface mechanical properties of various materials. The accuracy of these measurements is directly related to the accuracy of the tip shape function used to describe the indenter. This report describes a proof of concept study of using transmission electron microscopy (TEM) tomography to characterize the 3-D shape of an AFM indenter tip at a spatial resolution down to nanometer scale. A TEM sample of an AFM indenter was prepared with Focused Ion Beam (FIB) technology using a novel procedure. The sample was studied with high resolution transmission electron microscopy (HR-TEM) and electron tomography. Major results from this study are summarized below: 1. There was a thin layer of amorphous SiOx at the surface of the Si tip, which was about ~10 nm in thickness near the end of the indenter and thinner (~3 nm) away from the end; 2. Electron tomography could reconstruct the 3-D shape of AFM indenters at very high spatial resolution—the tip of the indenter had a radius of curvature about 20 nm. In the tomogram, this tip was clearly resolved; 3. An effective image processing method was developed to reconstruct the 3-D surface profile of the indenter, even though the detailed structure of the bulk of the indenter was difficult to reconstruct due to diffraction effect from high crystalline structure 4. A 3-D tetrahedral mesh was built directly from the tomogram, which could be used as FEM modeling input file directly. Based on this work, it is possible to obtain a 3-D shape function of an AFM indenter after using the same indenter to measure surface mechanical properties. With a high spatial resolution 3-D shape function, the accuracy of mechanical property measurements with AFM can be significantly improved.

### 225. Identification and measurement of layer structures and barrier properties in multiple layer films for the packaging industry

**Matthew K. Stephenson**, Rebecca S. Ortiz and Katherine A. Robertson, Impact Analytical/MMI, Midland, MI

Data from barrier properties testing, polarized light microscopy, and Fourier-transform infrared spectroscopy are incorporated into one comprehensive analysis of multiple layer packaging films. Microscopy data delineates layer structure, enabling image analysis to measure layer thicknesses. Resulting layer structures inform deconvolution and interpretation of multiple FT-IR scans across the film cross section, allowing in some cases interpretation beyond the resolution limit of the infrared microscope. Identification of layer composition through FT-IR spectroscopy is used to interpret barrier properties data to improve quality control, support research and development, and provide competitive analysis for customers in the packaging industry.

### 226. Automated Scanning Force Microscopy as a New Tool for High Throughput Polyolefin Research

**Jing Li**, The Dow Chemical Company, Freeport, TX, Gregory F. Meyers, Dow Chemical Company, Midland, MI, Stephen Werner, The Dow Chemical Compnay, Freeport, TX and Carl Reinhardt, The Dow Chemical Company, Midland, MI

The application of combinatorial principles to materials science characterization promises to influence the future direction of research and development. In fact, the combinatorial process is already occurring in the discovery of new catalysts in polymer research. The characterization of the morphology of polymeric materials is one area where combinatorial methods are just beginning to find applications. This presentation will describe the development of automated AFM and application to polymeric films and impact polypropylene materials. Automated AFM capability not only allows multi samples programmed with multiple scan parameters at any indexed position within a run, but also incorporates custom scripts for a post-processing, roughness and bearing analysis for selected routines. The success of this automatic AFM program has immediate impact on research effort by reducing sample turn around time significantly; lowering customer cost; and, greatly increasing the quality of analysis by enabling improved statistical sampling. Automatic AFM is only the first step toward combinatorial research. High throughput workflows that include automatic imaging acquisition, automatic imaging analysis and automatic screening and reporting will be reported in the future. The success of this development will have significant impact on polymer research and expedite product development.

## Poster Session, Lunch, Exposition

**Organizer:** Michael K. Lee Dow Corning Corporation, Midland, MI

### 227. Changes in conjugation result in changes of color

**Robert A. Rome** and Bruce W. Baldwin, Spring Arbor University, Spring Arbor, MI

A look at color change as the length of conjugation increases in a ferrocene molecule. Acetylferrocene and acetylruthenocene were reacted with cuminaldehyde in separate reactions to lengthen the conjugation of the molecule. The changes in conjugation resulted in marked color change on both chalcone products. This gives the undergraduate student a great vehicle to see the effects of polarity and conjugation, as well as sharpening laboratory skills.

### 228. The Effect of Guided Inquiry on Student Misconceptions in Chemistry

**Leslie McSparrin**, Sharpsville Area High School, Sharon, PA

The research in this study was designed to answer the research question: Does teaching chemistry by the method of guided inquiry correct student misconceptions? Two chemistry concepts were the focus of the study. One concept studied was the production of light by atomic emissions (including characteristic properties of both waves and light). The other concept studied was acid/base theory. A two-tiered multiple-choice pretest was administered to participants before the start of each unit. Following each unit, the same two-tiered multiple-choice test was administered as a posttest. Sixty-four students from a semi-rural high school in Northwestern Pennsylvania participated in the study across three levels of chemistry: Advanced Placement Chemistry, Chemistry I, and Conceptual Chemistry. The mean score increased in the positive direction for participants in all three levels of chemistry by the time of the posttests. In addition, many students provided answers with written responses that indicated that certain previously documented misconceptions had been corrected. Also, most of the participants were able to successfully apply the scientific method to complete culminating authentic assessments during the study. These conclusions are substantiated by both quantitative statistical data and qualitative written response and interview data. Students in Chemistry I experienced the most substantial gains among the participants. The students in this study reported that they had gained more understanding from guided inquiry activities and preferred this form of science instruction in chemistry.

## 229. Analytical Issues in the Determination of Silicones at Trace Levels – Challenges and Artifacts

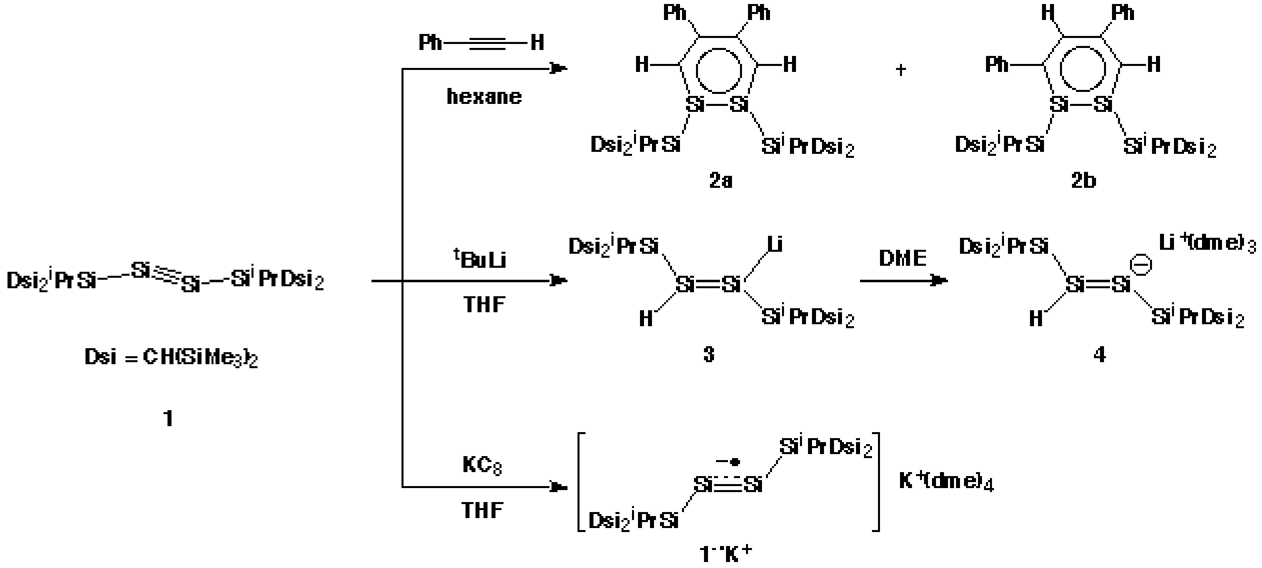
**Sudarsanan Varaprath**, **Debra H. Stutts** and Gary E. Kozerski, Dow Corning Corporation, Midland, MI

Being endowed with outstanding properties, silicones (polydimethylsiloxanes) find use in a wide variety of industrial and consumer product applications. The estimated global production volume of silicone materials in 1995 was 1.39 billion pounds with net sales reaching $5.7 billion. Potential human exposure to silicones occurs at the work place during manufacturing and product formulation, as well as through the normal use of consumer products that contain them. The entry of silicones in various environmental compartments raised concerns on health and safety aspects from potential exposure and mandated undertaking numerous environmental and toxicological studies. Such studies require qualitative and quantitative determination of silicone species at trace levels. However, the ubiquitous presence of silicones coupled with the uniqueness of its chemistry (ease of condensation, isomerization, rearrangement reactions due to high affinity to oxygen atom) in contrast to that of organics renders their analysis at trace levels challenging. The presentation provides a consolidated account of various aspects silicones that must be borne in mind to obtain reliable data. The following are some of topics discussed: differences in the chemistry of silicones vs carbon; precautions in sample handling to avoid losses and inadvertent chemical transformation; potential sources for artifacts and interferences that could lead to systematic errors and data misinterpretation; sources for background and the need for matrix matched blank experiments; distinguishing silicones from silicates to avoid overestimation; potential for incorrect structural assignments; preventing inadvertent contamination; questionable claims on the presence of silicones in biological matrices including that of silicone implants.

## 230. Reactivity of Disilyne: Synthesis and Structure of 1,2-Disilabenzene, Disilenyllithium, and Disilyne Anion Radical

**Rei Kinjo**, Masaaki Ichinohe and Akira Sekiguchi, University of Tsukuba, Tsukuba City, Japan

The chemistry of silicon-silicon triple bond species, disilyne, is one of the most fascinating topics in the organosilicon chemistry. Recently, we succeeded to isolate disilyne **1** and its structure was confirmed by X-ray crystallography and spectroscopic properties. However, the reactivity of disilyne still remains open. Herein, we present the novel reactivity of disilyne **1** with various reagents to reveal unprecedent results. The reaction of **1** with an excess of phenylacetylene resulted in the formation of 1,2-disilabenzene as a mixture of regio-isomers (**2a** and **2b**; **2a** : **2b** = 4 : 6). The structure of **2a** was determined by X-ray crystallography. 1,2-disilabenzene ring of **2a** is almost planar, and the length of skeletal Si–Si bond is 2.2018(18) Å. The bond lengths of Si–C and C–C in 6-membered ring are intermediate between those of each double and single bonds, respectively. Thus, 1,2-disilabenzene has a considerable delocalization of 6π electrons over the six-membered ring. The treatment of **1** with $^{t}$BuLi gave a new disilenyllithium **3** via a hydrogen abstraction from $^{t}$Bu radical by the disilyne anion radical intermediate $\mathbf{1}^{\bullet-}\mathbf{Li}^{+}$. Upon additions DME, **3** was converted to free disilenylanion species **4**, whose structure was determined by the X-ray crystallography. Indeed, the radical anion $\mathbf{1}^{\bullet-}$ was obtained when the reaction was carried out in the absence of the hydrogen source. Thus, the reaction of **1** with equivalent amount of KC$_8$ produced the $\mathbf{1}^{\bullet-}\mathbf{K}^{+}$, which was isolated as brownish crystals in 63% isolated yield. X-ray crystallography disclosed the structure of $\mathbf{1}^{\bullet-}\mathbf{K}^{+}$. The central Si–Si bond length of $\mathbf{1}^{\bullet-}\mathbf{K}^{+}$ is 2.1728(14) Å, which is 5% longer than that of disilyne **1**, but 1.3% shorter than that of disilenylanion **4**. The bond angles (112.84° and 113.97°) of tetrasilane unit are found to be essentially equal to each other, indicating the delocalization of the radical anion between two unsaturated silicon atoms.



## 231. Biocidal effects of biodiesel on Fusarium oxysporum

**Jenna L. Manby**, Bruce W. Baldwin and Michael Buratovich, Spring Arbor University, Spring Arbor, MI

With the knowledge that ethyl chaulmoograte (chaulmoogra biodiesel) has inhibitory effects on the growth of Mycobacterium smegmatis, a non-pathogenic relative of the leprosy bacterium, we were eager to find whether ethyl chaulmoograte, as well as a variety of other biodiesels, were capable of inhibiting the growth of the fungus Fusarium oxysporum, which commonly grows in the gas lines of diesel vehicles. We proceeded to test the anti-fungal properties of seven different biodiesels (made from the oils of macadamia nut, soybean, chaulmoogra, ghee, coconut, codliver, and olive) on the growth of the fungus against controls. Based upon our results, we conclude that five out of the seven biodiesels do inhibit the growth of F. oxysporum, macadamia and soy being the most effective, showing inhibition at all concentrations. This project shows undergraduate students the cross-disciplinary nature of real-world problems in fuel chemistry.

## 232. The selective reduction of a citronal chalcone

**Timothy J. Ewert** and Bruce W. Baldwin, Spring Arbor University, Spring Arbor, MI

We selectively reduced the carbon-carbon double bonds of a citronal chalcone made from acetyl ferrocene and lemon grass extract. Through the use of a hydrogen-filled balloon and stir plate we were able to complete the hydrogenation reaction to produce a long chain alkyl ketone. The selective reduction is accompanied by dramatic color changes and major polarity changes. These changes make the experiment very attractive for undergraduates studying the correlation of chemical structure with characteristics.

## 233. Polyhydrosiloxane Induced Shape Controlled Synthesis of Gold Nanoparticles

Bhanu P. S. Chauhan*, **Manik Mandal** and Rajesh Sardar, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, City University of New York at CSI, Staten Island, NY

The properties of nanoparticle depend mainly upon their shape, size, composition etc. So by gaining control over this parameter one can manipulate nanoparticle properties. Here a novel approach for producing shape-controlled synthesis of gold nanohexagon has been reported. The reaction between gold precursor in acetonitrile under reduction with polymethylhydrosiloxane and trioctylamine gives nanohexagon. The same reaction under different condition gives different morphology. By varying different parameters like precursor concentration, aging time we have been able to synthesize different shaped nanoparticle like nanorod, nanowire etc. The Transmission Electron Microscope (TEM) study indicates the formation of nanohexagon with edge length ~ 11nm. Trace amount of nanowire and nanoprism are formed in this reaction. UV-vis spectra indicates the characteristic peak for Au nanoparticle. The topography and morphology of this nanoparticle was also carried out by AFM and SEM analysis.

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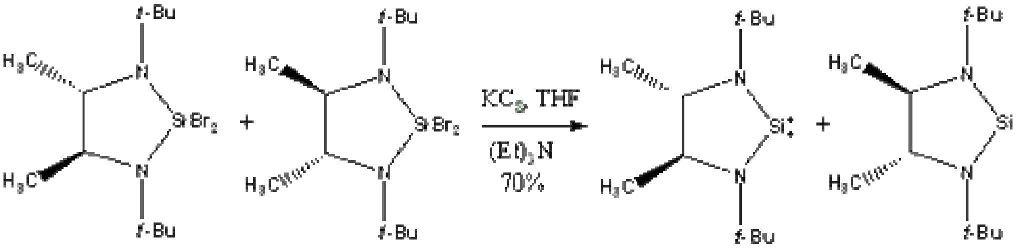
### 234. A New Monomeric Saturated Silylene as a Racemic Mixture

**Wenjian Li**, Nicholas J. Hill, Adam C. Tomasik, Galina Bikzhanova and Robert West*, The University of Wisconsin, Madison, WI

A new stable silylene, rac-N,N'-di-(tert-butyl)ethylene-4,5-dimethyl-1,3-diaza-2-silacyclopentane-2-ylide, has been made by reaction of the corresponding dibromide with KC8. The silylene is formed as a racemic mixture of two enantiomers. Unlike the analogous silylene lacking the two methyl groups, which tetramerizes in concentrated solution or as a solid, the new silylene shows no tendency to oligomerize. Instead, it persists as a stable colorless liquid. The reactivity of this silylene will also be discussed.



### 235. Synthesis and characterization of a bridged anthacene as a molecular clamp

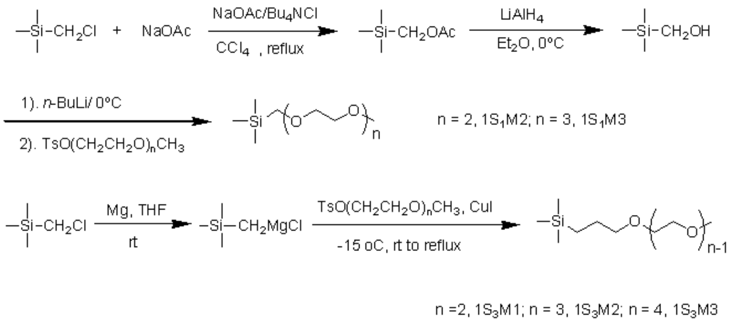
**Bruce W. Baldwin**, Spring Arbor University, Spring Arbor, MI

With student interest increasing about nanomolecular machinery, a simple synthesis of a host molecule with associated research on appropriate guests was attempted. A molecule with planned rigidity and flexibility was designed and synthesized based on a Diels-Alder reaction on anthracene followed by an imidation reaction with benzyl amine. The product was analyzed most informatively by proton NMR and molecular modelling. If a properly modified host molecule was synthesized, the resulting undergraduate level experiment would be an interesting addition to the organic and advanced chemistry laboratory curriculum. Preliminary results will be presented.

### 236. Synthesis and Conductivity of Organosilicon-Based Electrolytes for Energy Storage Applications

**Lingzhi Zhang**[1], Viacheslav Dementiev[1], Robert West[1], Zonghai Chen[2], Khalil Amine[2] and Leslie Lyons[3], (1)University of Wisconsin-Madison, Madison, WI, (2)Argonne National Laboratory, Argonne, IL, (3)Grinnell College, Grinnell, IA

Organosilicon-based electrolytes containing trimethylsilyl and oligo(ethylene oxide) units were synthesized and characterized. After doping with lithium bis(trifluorosulfonyl) imide (LiTFSI), the ionic conductivity of the electrolytes was measured by AC impedance experiments. These electrolytes exhibit high conductivity at room temperature; 1S3M2 has a very large conductivity of 1.5„e10-3 S/cm. Their viscosity, dielectric constants and cyclic voltammetry were also measured and compared.



## 237. Synthesis of Alkylated Ferrocenes

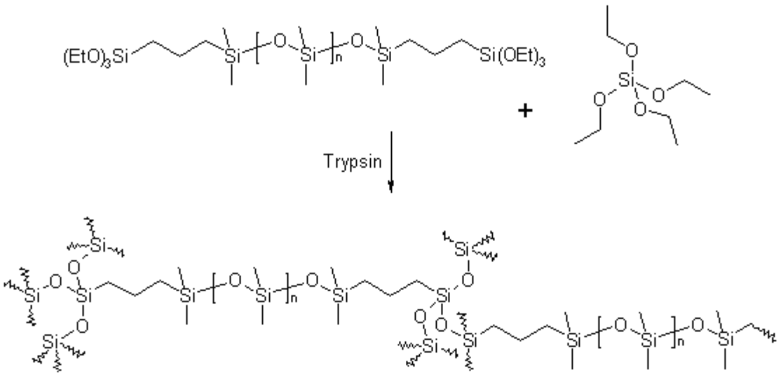
**Paula C. Knoblauch** and Bruce W. Baldwin, Spring Arbor University, Spring Arbor, MI

In recent years, there has been an increased interest in the synthesis of alkyl ferrocene compounds due to their potential use as fuel additives and antimicrobial agents. Given that ferrocene has chemical properties that are similar to aromatic benzene, Friedel Crafts alkylation might seem like a feasible way to produce such compounds. Unfortunately, these reactions are very inefficient and often result in multiple alkylations. This present project shows how alkyl ferrocenes can be synthesized from unsaturated acetyl ferrocene chalcones. Such ferrocene derivatives can be easily produced via aldol condensations between acetyl ferrocene and a variety of aldeyhydes. The transformation from the chalcone to the alkyl derivative is accompanied by changes both in color and in polarity, enabling undergraduate students to see how changes in chemical behavior are related to alterations in chemical structure.

## 238. Trypsin-catalyzed cross-linking of α,ω-triethoxysilyl-terminated polydimethylsiloxane: A green approach to cross-linking silicones

**Paul M. Zelisko**, Karen R. Arnelien and Glenda Hooper, Brock University, St. Catharines, ON, Canada

Dibutyltin dilaurate is typically employed as a catalyst to bring about the hydrolysis, and subsequent condensation, of silicones to form cross-linked networks in the room temperature vulcanization (RTV) process. However, given the interest in silicones as biomaterials, the use of potentially toxic tin compounds as catalysts can limit the use of polydimethylsiloxane compounds in such applications. This study describes the use of trypsin as a catalyst for the cross-linking of alkoxysilyl-functionalized polydimethylsiloxane in comparison with the more traditional, and somewhat more toxic, tin-based catalyst system. Preliminary results have demonstrated that trypsin effectively catalyzes the cross-linking of α,ω-(triethoxysilyl)ethyl-polydimethylsiloxane (TES-PDMS), like dibutyltin dilaurate, with both systems yielding macroscopically homogeneous, brittle, solids under the given experimental conditions. $^{29}$Si-NMR experiments revealed little difference between the products of the dibutyltin dilaurate catalysis and the trypsin catalyzed system. The development of enzyme-based methodologies for performing “green” silicone reactions will be discussed.



## 239. Functionalization of dodecaphenylsilsesquioxane, Chemistry and properties

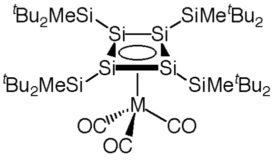
**Kunio Takahashi**, Santy Sulaiman, Mark Roll and Richard M. Laine, University of Michigan, Ann Arbor, MI

Nanomaterials science and engineering has a continuing need for well-defined, functionalized nano building blocks that allow construction of numerous materials nm x nm with precise control of nanoarchitecture, imbued with diverse functionality. Polyhedral oligomeric silsesquioxanes offer such access. Synthesis and applications of octahedral or cubic silsesquioxanes (cubes) and their derivatives have been discussed by many groups, but the effects of cage structures on properties have not been explored in detail. We report here first comparisons of silsequioxanes with different cage sizes to identify properties derived from individual cage structures. Syntheses of dodecahedral phenyl silsesquioxane (DPS) derivatives and cage size effects on the chemical and physical properties of DPS derivatives compared to octahedral phenylsilsesquioxane (OPS) are discussed. Cage size/structure does not affect substitution patterns; however, it does affect in photoluminescent behavior and the coefficient of thermal expansions (CTE) of their derivatives.

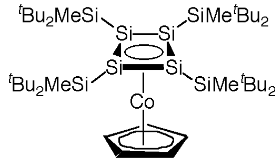
## 240. Synthesis and Structure of Tetrasilacyclobutadiene Transition Metal Complexes

**Kazunori Takanashi**, Vladimir Ya. Lee and Akira Sekiguchi, University of Tsukuba, Tsukuba, Japan

The chemistry of cyclobutadiene transition metal complexes has been widely developed, and now (cyclobutadiene)tricarbonyliron ($\eta^4$-$H_4C_4$)Fe(CO)$_3$ and (cyclobutadiene)cyclopentadienylcobalt ($\eta^4$-$H_4C_4$)CoCp are the most important cyclobutadiene complexes. On the other hand, only two examples of heavy cyclobutadiene transition metal complex are currently known. Herein we present the synthesis and structure of the heavy analogues of the above-mentioned complexes, (tetrasilacyclobutadiene)-tricarbonyliron and -cyclopentadienylcobalt. The reaction of 3,4-dibromocyclotetrasilene $R_4Si_4Br_2$ (R = SiMe$^t$Bu$_2$) with an excess of $Na_2Fe(CO)_4$ results in the formation of (tetrasilacyclobutadiene)tricarbonyliron ($\eta^4$-$R_4Si_4$)Fe(CO)$_3$ **1**, isolated as air- and moisture-sensitive pale-yellow crystals in 42% yield. X-ray crystallography of **1** revealed the square-planar tetrasilacyclobutadiene ligand; the bond lengths between endocyclic Si atoms range from 2.2610(7)-2.2802(7) Å and folding angle of $Si_4$-ring is 1.8 °. In IR spectrum of **1**, the signals assigned to the stretching vibration of CO are observed at lower energy (1922, 1973 cm$^{-1}$) in comparison to the parent cyclobutadiene complex ($\eta^4$-$H_4C_4$)Fe(CO)$_3$. This indicates that the tetrasilacyclobutadiene is stronger $\pi$-donating ligand comparing to cyclobutadiene. The corresponding ruthenium complex ($\eta^4$-$R_4Si_4$)Ru(CO)$_3$ **2** was also synthesized by the reaction of tetrasilacyclobutadiene dianion dipotassium salt $[R_4Si_4]^{2-}\cdot 2K^+$ **3** with $[RuCl_2(CO)_3]_2$. The treatment of **3** with $CpCoI_2(PPh_3)$ gave a new sandwich complex, ($\eta^4$-$R_4Si_4$)CoCp **4** through the elimination of $PPh_3$. The structure of **4** was determined by the X-ray crystallography, tetrasilacyclobutadiene ligand in **4** is more square-planar comparing to that in **1**. Such structural features would be explained by the shape and spatial-orientation of ligands, tricarbonyl vs. cyclopentadienyl.



**1** M = Fe
**2** M = Ru



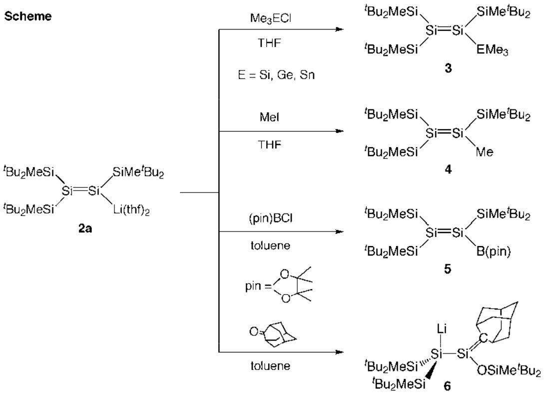
**4**

## 241. $sp^2$-Type silylanion: synthesis and it's reactivity

**Shigeyoshi Inoue**, Masaaki Ichinohe and Akira Sekiguchi, University of Tsukuba, Tsukuba, Japan

Silylanions are very useful reagents for synthesizing various silicon-containing derivatives. However, the chemistry of compounds having $sp^2$-type silylanions was severely limited due to their synthetic diffculty until recently. We report here the synthesis and reactivity of novel $sp^2$-type silylanion with various reagents. Recently we reported synthesis of tetrakis[di-tert-butyl(methyl)silyl]disilene (**1**) with a highly twisted Si=Si double bond. Upon the two-electron reduction of disilene **1**, we succeeded in synthesizing a stable disilenyl anion, which provides a method for the novel synthesis of an $sp^2$-type silylanion **2**, including not only $sp^2$-type silyllithium **2a** but also $sp^2$-type silylsodium **2b** and silylpotassium **2c**. The reactions of **2a**, with $Me_3ECl$ (E = Si, Ge, Sn), MeI, (pin)BCl produced X-substituted disilene (X = $Me_3Si$, $Me_3Ge$, $Me_3Sn$, Me, (pin)B) (Scheme). **2a** also reacts with 2-adamantanone to give silyl anion-substituted silene **6** , which would be formed by the addition of the resulting siloxy anion to 1,2-disilaallene intermediate produced via sila-peterson type reaction. The molecular structure of **6** was determined by X-ray crystallograpy. Lithium atom was solvated by two THF molecules, and Si-Li bond lengths was 2.684(3) Å. The Si=C doubly bond lengths was 1.7432(17) Å, which is a typical Si=C bond length.

**Scheme**



## 242. Steric and electronic influence of silyl versus alkyl substitution in bis(indenyl) zirconium and iron complexes

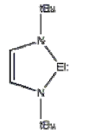
**Christopher A. Bradley**, University of California, Berkeley, Berkeley, CA and Paul J. Chirik, Cornell Univeristy, Ithaca, NY

The unique steric and electronic environment imparted by silyl substituted indenyl ligands results in divergent reactivity when compared to the analogous alkyl substituted indenyls. For example, isobutyl hydride reductive elimination to form the $\eta^9$, $\eta^5$ bis(indenyl)zirconium sandwich complexes is facile from silyl substituted bis(indenyl)zirconium isobutyl hydride compounds but relatively slow from complexes containing alkyl groups, presumably due to the electron withdrawing nature of the silyl substituent. Support for inductive withdrawing by the silyl group relative to an alkyl substituent is provided by infrared stretching data on the bis(indenyl)zirconium dicarbonyl derivatives and from oxidation potentials of the corresponding dibenzoferrocene complexes. In the $\eta^9$, $\eta^5$ bis(indenyl)zirconium sandwich complexes, alkyl versus silyl substitution affects both the rate of ring exchange as well as the thermodynamic preference for $\eta^9$ bonding. Based on computational and experimental data, these effects can be rationalized on the basis of different steric and electronic environments imparted by the two ligand substituents. The kinetic destabilization of the silyl $\eta^9$, $\eta^5$ bis(indenyl)zirconium sandwich compounds with respect to C-O bond cleavage and oxidative addition of dihydrogen, among other reactions, in comparison to alkyl substituted complexes will also be discussed. Steric effects of silyl versus alkyl ligands will also be presented in the context of rotamers in dibenzoferrocene complexes and bis(indenyl)zirconium dihydride ligand adducts. Taken together, these results demonstrate subtle manipulations of indenyl substituents can drastically alter the observed reactivity.

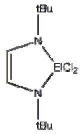
## 243. Comparative Study of Aromaticity of Stable Heterocyclic Carbene, Silylene and Germylene by Raman, UV-Vis and IR Spectroscopy

Larissa A. Leites[1], Sergey S. Bukalov[1], Gaidar I. Magdanurov[1], Alexander V. Zabula[1] and **Robert West**[2], (1)A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia, (2)University of Wisconsin-Madison, Madison, WI

The Raman, UV-vis and IR spectra of solid samples of a stable heterocyclic carbene (**1**) and its Si (**2**) and Ge (**3**) analogues as well as of corresponding compounds of tetravalent El atoms (**4**,**5**) were studied in detail. Quantum-chemistry calculations of the normal mode frequencies and eigenvectors were carried out for **1-3** at the DFT PBE level of theory using 6-31G(d) basis set.



El = C(1), Si (2), Ge (3)



El = Si (4), Ge (5)

The molecules **1-3** contain six p-electrons in the ring, and so may be considered to be aromatic compounds. As a test of aromatic delocalization, in this study we use the frequency and intensity of the stretching vibration of the C=C bond ($\nu_{C=C}$), in accord with Shorygin's works. Normal coordinate analysis shows that this approach is warrantable because the vibration studied is rather well-localized (PED ~60%) and does not include any displacement of the El atom.

| Compound | $\nu_{C=C}$, cm$^{-1}$ | | PED C=C, % | **$r_{C=C}$, Å** | | **nearest UV band position, nm** |
|---|---|---|---|---|---|---|
| | exp. | calc. | | exp. | calc. | |
| **1** | 1556 | 1554 | 61 | 1.34 | 1.37 | 228 |
| **2** | 1570 | 1582 | 63 | 1.32 | 1.37 | 302 |
| **3** | 1552 | 1573 | 60 | 1.36 | 1.37 | 347 |
| **4** | 1623 | - | - | | - | |
| **5** | 1628 | - | - | | - | |

The $\nu_{C=C}$ frequencies for **1-3** (see Table**)** are significantly lowered compared to those of tetravalent compounds **4,5.** This evidently reflects the lowering of the $K_{C=C}$ force constants. The intensity of the $\nu_{C=C}$ Raman line for **1-3** is enhanced dramatically compared to that for **4,5**. These facts provide strong evidence for cyclic p-conjugation in **1-3** with participation of the vacant $p_z$ orbital of the $El^{II}$ atom. As for the degree of aromaticity, the results are somewhat contradictory: the experimental frequency data and C=C bond lengths point to a series Si<C≈Ge, whereas the Raman intensities suggest a sequence C<Si<Ge.

## 244. Synthesis, Structure, and Isomerization of Novel Alkyl-Subtituted Cyclotetrasilenes

**Kei Uchiyama**[1], Takeaki Iwamoto[2], Chizuko Kabuto[2] and Mitsuo Kira[2], (1)Graduate School of Science, Tohoku University, Sendai, Japan, (2)Tohoku University, Sendai, Japan

Electrocyclic interconversion among C4H6 isomers such as cyclobutene, bicyclobutane, and 1,3-butadiene has been well-studied both experimentally and theoretically. Although stable Si4R6 compounds (cyclotetrasilene, bicyclo[1.1.0]tetrasilane, tetrasila-1,3-butadiene, an so on) have been synthesized recently, their interconversion has been elucidated still quite rarely. Previously, we have reported that hexakis(t-butyldimethylsilyl)cyclotetrasilene 1a isomerizes to the corresponding bicyclo[1.1.0]tetrasilane 2a upon irradiation, which thermally reverts to 1a. We report herein the synthesis, structure and isomerization of 1,2-di(t-butyl)-3,3,4,4-tetrakis(t-butyldimethylsilyl)cylotetrasilene (1b) as the first alkyl-substituted cyclotetrasilene . Cyclotetrasilene 1b was synthesized as yellow-orange crystals by the reduction of a 1,1-di(t-butyldimethylsilyl)-2-(t-butyl)trihalodisilane with sodium in toluene. X-ray structural analysis shows that the Si=Si double bond distance of 1b is 2.1553(9) Å, which is shorter than that of 1a (2.174(4) Å). The geometry around the unsaturated silicon atom is planar with the sum of the bond angles of 360.0 ° and the Si=Si double bond is twisted with the angle of 19.9 °. Irradiation of cyclotetrasilene 1b at –77 ºC afforded 1,2-di(t-butyl)-2,3,4,4-tetrasilylbicyclo[1.1.0]butane (2b) almost quantitatively similarly to the photochemical isomerization of persilylcyclotetrasilene 1a to 2a. The formation of 2b is rationalized by the 1,2-silyl migration as evidenced for the isomerization of 1a to 1b. Whereas 1a does not show the thermal isomerization into 2a, the thermolysis of cyclotetrasilane 1b upon heating at 55 ºC for 5 h gave a mixture of 2b and the corresponding 1,3-di(t-butyl)tetrasilylbicyclotetrasilane 2b'. The formation of 2b' is interesting because it is not incompatible with the 1,2-silyl migration but suggestive of the intermediary formation of the corresponding tetrasilabuta-1,3-diene. Theoretical investigations on the mechanisms for the thermal isomerization of 1b to 2b and 2b' will be also discussed.

## 245. Water chemistry of Brewster Lake in Barry County, Michigan

**Melissa Conklin**, Meghann Broderick and Elizabeth Jensen, Aquinas College, Grand Rapids, MI

Brewster Lake is located on the property of Pierce Cedar Creek Institute for Ecological Education in Barry County, Michigan. The lake and surrounding lands have been protected from most human activities, including agriculture, for at least the past fifty years. During the summer of 2005, we analyzed the water of the lake to determine pH, water temperature, total alkalinity, and conductivity, as well as concentrations of nitrates, phosphates, and dissolved oxygen in order to discover whether these properties change throughout the summer months and also whether they vary geographically. In addition, we compared the results from Brewster Lake, which is relatively pristine due to its

protected status, to other bodies of water in West Michigan which have not been specifically protected from agricultural, residential, and/or industrial pollution. Our results show that the water temperature increased while dissolved oxygen, alkalinity, and conductivity decreased during the study period (May to July). Also, nitrate concentrations and pH remained constant. We were unable to determine the concentration of phosphate in the lake, due to very low levels of that species.

### 246. Bis(dialkylsilylene)palladium

**Chieko Watanabe**, Takeaki Iwamoto, Chizuko Kabuto and Mitsuo Kira, Tohoku University, Sendai, Japan

Low coordinate group-10 metal complexes with NHC-type carbenes have received much attention as useful catalysts and key intermediates in various catalytic transformations. Although several group-10 metal complexes of silylenes are known, dicoordinated bis(silylene)-complexes of group-10 metals have never been reported so far. Using 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopentane-1,1-diyl (**1**, $R_2Si$) synthesized by our hands as the first isolable dialkylsilylene, the synthesis of the first 14-electron dicoordinate bis(silylene) palladium complex [$(R_2Si)_2Pd$ (**2**)] has been achieved. In this presentation, the molecular structure and reactions of **2** and related complexes are reported. The reaction of silylene **1** with 0.5 equiv of bis(tricyclohexylphosphine)palladium gave bis(silylene)palladium **2** as dark red crystals in 40% yield. Structure of **2** was determined by X-ray analysis and NMR spectroscopy. In the solid state, the two silylene units of **2** coordinate linearly to the central Pd atom and two terminal five-membered rings are almost perpendicular to each other. The $^{29}Si$ resonance of the unsaturated silicon nuclei of **2** appears at the remarkably low field (448 ppm), indicating the base-free nature of the complex. DFT calculations of a model compound, bis(silacyclopentane-1,1-diyl)palladium **3**, show that the optimized structure (**3**[opt]) is bent with the Si-Pd-Si angle of 135.2°, while the linear structure (**3**[lin]) is located as a saddle point with two imaginary frequencies. The steric repulsion between two bulky $R_2Si$ groups in **2** would be responsible for its linear geometry. Natural atomic population analysis shows that the $\pi$ back donation of **3**[lin] is stronger than that of the palladium complexes of NHC-type carbenes and silylenes. Reactions of **2** with excess carbon monooxide gave a tricoordinated palladium complex $(R_2Si)_2Pd(CO)$ (**4**) in 90% yield. The X-ray analysis shows that the palladium center adopts a trigonal planar geometry with the Si-Pd-Si angle of 140.4 °. Detailed molecular structure of **4** and other reactions of **2** will also be discussed.

### 247. Applications of a new variant of MRPT to small molecules

**Jie Song**, University of Michigan-Flint, Flint, MI

A new variant of multi-reference perturbation theory (MRPT), 2nd-order Generalized Van Vleck Perturbation Theory (GVVPT2), was developed a few years ago. Implemented with the Macroconfiguration technology to truncate the model space, GVVPT2 is able to handle with a relative big active space. In this study, GVVPT2 combined with Macroconfiguration has been applied to certain diatomic and triatomic molecules where a large active space is necessary.

### 248. Synthesis, Structures, and Reactions of Stable Dialkylsilaketenimines

**Takashi Abe**, Takeaki Iwamoto, Chizuko Kabuto and Mitsuo Kira, Tohoku University, Sendai, Japan

Ketenimines have been extensively studied as useful synthetic intermediates for N-heterocyclic compounds. Although their bonding characteristics are often described as an intermediate between allenic ($R_2C=C=NR'$) and zwitterionic ($R_2C(\delta-)\text{-}C\equiv N(\delta+)R'$) structure, all known stable heavy group-14 element analogues of ketenimines are not characterized to be allenic or zwitterionic but an isocyanide complex of the corresponding divalent species ($R_2E\leftarrow C=NR'$, E = Si, Sn, and Pb). Here we report the synthesis, structures and reactions of dialkylsilaketenimines, which are the first silaketenimines with strong allenic character.[1] Stable (N-aryl)- and (N-alkyl)dialkylsilaketenimines [$R_2Si=C=NR'$; R = 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl, R' = 2,6-diisopropylphenyl (**1a**) and 1-adamantyl (**1b**) ] were synthesized as blue and red crystals by the reaction of isolable dialkylsilylene $R_2Si$: [2] with the corresponding isocyanides R'NC. Molecular structures of **1a** and **1b** were determined by X-ray crystal analysis. The Si-C bond lengths of **1a** (1.794(3) Å) and **1b** (1.782(2) Å) are shorter than the typical Si-C single bond length (1.860 Å), while being comparable to the typical Si=C double bond length for common silenes (1.693-1.764 Å). The C-N distances of 1a (1.203(3) Å) and 1b (1.210(3) Å) are much longer than the N-C distance of aryl isocyanides (ca. 1.160 Å). These structural features indicate the allenic character of **1a** and **1b**. The reactions of **1a** and **1b** with methanol at –40 ˚C gave the corresponding adducts $R_2SiH\text{-}C(OMe)=NR'$ in high yields. Isoprene added to **1a** and **1b** at –40 ˚C to afford the corresponding [2+2] cycloadducts, 4-(2-propenyl)-2-silacyclobutanimines in 60 % and 57 % yields, respectively. Reactions of **1a** and **1b** with various other reagents will be also discussed.

[1] A part of the results has been published: Abe, T.; Iwamoto, T.; Kabuto, C.; Kira, M. J. Am. Chem. Soc., in press. [2] Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. J. Am. Chem. Soc. 1999, 121, 9722.

### 249. Post-Synthetic Modified Poly(dimethylsiloxane)s Studied by Mass Spectrometry

**Alyison M. Leigh**, Chyrs Wesdemiotis and Claire A. Tessier, The University of Akron, Akron, OH

Introduction

When synthesized, most polymers may contain components with different end groups. Since differences in the end groups change the mass, MALDI and ESI mass spectrometry (MS) are ideally suitable to obtain both qualitative and quantitative information about the mixture composition. This study reports the mixtures generated in the synthesis may undergo post-synthetic modifications such as ring-opening polymerizations, crosslinking, addition, and condensation reactions, which often complicate the analysis. Often the biproducts are a result of MS sample preparation. Hence, finding the proper sample preparation protocol is an important step in the MS characterization of polymers.

Method

Preliminary results have been obtained using Poly(dimethylsiloxane), PDMS, polymers with ethoxy-, 3-aminopropyl-, and trimethylsiloxy- groups at both chain ends. Stock solutions in THF of the polymers, LiTFA, and DCTB matrix were used to prepare samples for MALDI MS analysis. Sample preparation involved mixing two polymer solutions in varying concentration ratios with LiTFA and matrix solutions. ESI-QIT mass spectra were also acquired from stock solutions in MeOH of the polymers and NaTFA combined in the same varying concentration ratios as above.

Preliminary Results

Poly(dimethylsiloxane)s with different end groups were mixed in a variety of concentration ratios to form a library of PDMS products. These products with different end groups and there corresponding intensities of their quasimolecular ions were monitored and compared. Several trends emerged on careful analysis of the mass spectra of two-component mixtures. Depending on the chemical composition of the mixed oligomers, interactions (addition, condensation) were observed. Furthermore, there was a clear relationship between the concentration of the mixed polymers and the observed polymer distributions. This study elucidates the origin and relative ion yields of the post-synthetically modified oligomers in the simulated mixtures.

## 250. Synthesis, Characterization and Functionalization of Octa(*p*-Iodophenyl) Silsesquioxane

**Mark Roll**[1], Chad Brick[2], Kunio Takahashi[1], Santy Sulaiman[1], Michael Asuncion[1] and Richard M. Laine[1], (1)University of Michigan, Ann Arbor, MI, (2)Kyoto University, Kyoto, Japan

There is widespread interest in the development of star polymers, dendrimers and supramolecular materials as building blocks for constructing materials with architectures tailored at nanometer length scales. Tailoring at such length scales should provide high reproducibility, and the opportunity to precisely predict and fine-tune final global properties. Thus there is keen interest in identifying nanometer-sized molecules that offer very high symmetry, high functionality and a means to modify that functionality at will and finally to use the introduced functionality to build 1-, 2- or 3-D structures nanometer by nanometer.

Here we report the synthesis, characterization and functionalization of a new building block, octa(*p*-iodophenyl)silsesquioxane. Iodination of octaphenylsilsesquioxane was accomplished through aromatic electrophilic substitution at and below room temperature. After workup, the product is readily recrystallized. Functionalization through Pd and Cu catalysis allows for Heck olefination, Suzuki couplings and aminations.

## 251. Cycloaddition of Carbonyl Compounds to Silenes: Mechanism of Siloxetane Formation

**Kaarina K. Milnes** and Kim M. Baines, University of Western Ontario, London, ON, Canada

The addition of aldehydes and ketones to silenes, compounds containing a silicon-carbon double bond, results in the formation of siloxetanes or formal ene-addition products. Many synthetic examples of this reaction are known, as well a number of studies aimed at understanding the mechanism of such cycloaddition reactions, both experimental and theoretical, have been performed. The results of the mechanistic and theoretical studies indicate that the mechanism of the cycloaddition reaction may vary depending on the substituents on both the carbonyl and the silene. The focus of this project is to provide evidence for the mechanism by which these reactions occur. This study will be done using a phenyl-substituted cyclopropyl aldehyde, which has been developed in our lab as a mechanistic probe. The results of the addition reactions and the mechanistic interpretation will be discussed.

## 252. On the Synthesis of Tetramesityldigermene

**Krysten L. Hurni** and Kim M. Baines, University of Western Ontario, London, ON, Canada

There are two well-known methods for the synthesis of tetramesityldigermene, the prototypical digermene. The first involves the photolysis of hexamesitylcyclotrigermane in the presence of triethylsilane in toluene. In the absence of triethylsilane, the cyclotrigermane is recovered in good yield. The silane is necessary to trap the equivalent of dimesitylgermylene which is also formed during the photolysis and to drive the reaction forward. As a result, this synthetic method requires an unavoidable separation step. We have developed an improved method for the synthesis of tetramesityldigermene. Photolysis of the cyclotrigermane in tetrahydrofuran proceeds cleanly to the digermene and obviates the need for the triethylsilane. Hence, the separation step is avoided. To illustrate the effectiveness of this new procedure, alkyl and aryl carboxylic acids have been added to tetramesityldigermene to produce novel digermyl esters.

The second method involves the photolysis of dimesitylbis(trimethylsilyl)germane to give tetramesityldigermene. However, when we repeated the synthesis on a preparative scale, the anticipated digermene is, in fact, not formed. Instead, a complex product mixture of mesitylene, trimethylsilylmesitylene, and a germacyclobutane ring is obtained. The results of these experiments will be discussed.

## 253. Novel I/O hybrid materials as host of nanosized metals and their catalytic applications

Bhanu P.S. Chauhan*, **Umar Latif** and Gilchris Burton, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

Among numerous unusual features of I/O hybrids are their utility and potential as catalysts, sensors, optical and electronic applications. In this presentation, we expand our previously reported strategy1 to a further step.1 We use cyclic and cubic siloxanes as the "I" part to synthesize I/O hybrid materials by covalently attaching a plethora of diols and alcohols as the "O" part. These hybrids are further applied as stabilizers for metal nanoparticles for their use as catalysts, possible precursors to drug delivery, and another possible route to novel POSS technology. Pt and Pd nanoparticles were synthesized using these hybrid materials as reducing and stabilizing agents and were further used as catalysts for hydrosilylation and hydrogenation of different alkenes.

1. Chauhan, B. P. S.; and Latif, U. Macromolecules 2005, 38, 6231.

## 254. Silyl Functionalization: An Efficient Route for Polyolefin Modification

Bhanu P.S. Chauhan*, **Bharthi Balagam** and **Michael Raghunath**, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

A highly selective and clean synthetic route to silyl-functionalization of 1,2-polybutadienes (PBD) has been achieved using Pt-nano clusters as catalysts.1 High conversions of pendent double bonds of PBD with exclusive formation of â-product (anti-Markovnikov product) have been observed (95-98%) with variety of functional silanes such as alkyl, alkoxy, and chlorosilanes. All hydrosilylated polymers were characterized using GPC and multi nuclear NMR techniques. The GPC chromatograms of the products have clearly been shifted towards the high molecular weight region, while retaining a narrow molecular weight distribution (Mw/Mn~ 1.4-1.5). The structure and regioselectivity of these functionalized polymers were determined by 1H, 13C, DEPT and 29Si NMR studies. Distortionless Enhancement by Polarization Transfer (DEPT) technique was used to differentiate between á and â product of hydrosilylated polymer. The regioselectivity of the products was further established by comparing the spectroscopic results with the hydrosilylation reaction of 1-heptene, which were in good agreement with those of hydrosilylated polymer products.

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1. Bhanu P. S. Chauhan and Bharathi Balagam Macromolecules, 2006 (ASAP Article)

## 255. Hybrid materials based on Alkoxysilanes in materials consolidation

**Ma. del Carmen Salazar Hernández**, Guanajuato University, Guanajuato, Gto., Mexico, Jorge A. Cervantes J., Guanajuato University, Guanajuato, Gto. and Sergio Alonso Romero, CIATEC, Leon Guanajuato, Mexico

The materials consolidation concept has been applied to architectural conservation; this process consists in the introduction of a chemical substance (consolidant) in degraded stone. The ideal consolidant performance will restore the mechanical, physical and chemical properties of the decay stone. Silicon compounds such as tetraethoxysilane (TEOS) are frequently used as a base of consolidante formulations [1] due to their ability to be hydrolyzed and form siloxane polymer as SiO2 [2]. However one problem commonly observed during consolidation process is the gel cracking during the drying stage.

In order to improve the properties of consolidants, new formulations have been investigated [3,4,5]. An interesting approach to solve such problems is the use of hybrid materials based on alkoxysilanes and fillers such as silica nanoparticles (200nm in diameter) and polydimethylsiloxane hydroxy terminated (PDMS-OH), both additives improve the gel properties.

On the other hand, the gel properties are close related to the sol characteristics. In this direction, rheological studies of the sol precursors are needed and will be discussed. The idea is that sols with properties of Newtonian fluids will form ordered gels, because the particles suspended in the solvent are more homogeneously distributed in the fluid before the gelification point.

Acknowledgment. We would like to thank a CONACyT (México) and CONCyTEG (Guanajuato-México) for financial support.

References 1) http:www.b72.com/objects/stone/axhome.html 2) C.J. Brinker and G. E. Scherer, Sol –Gel Science, (1990) 1a Ed., Academic Presss. 3) P. Cardino, R.C. Ponterio, S. Sergi, S.Lo Schiavo and P. Piraino, Polymer (2005), 46, 1857-1864 4) M.J. Mosquera, M. Brjarano, N. de la Rosa-Fox and L. Esquivias, Langmuir (2003),19, 951-957 5) M.R. Escalante, J. Valenza and G.W. Scherer; 9th International Congress on Deterioratio and Conservation of Stone; June 2000.

## 256. Highly Regio- and Stereo- Selective Hydrosilylation of Functional Alkynes Achieved via Nanocluster Catalysis

Bhanu P.S. Chauhan*, **Alok Sarkar** and **Katrina Caroccia**, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

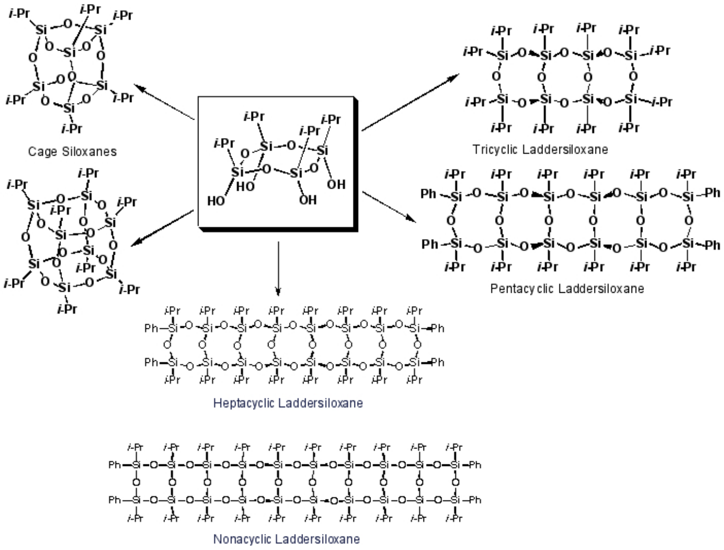
Hydrosilylation of various disubstituted and functional monosubstituted alkyne have been achieved using Pt-nanocluster catalyst. Excellent yield and selectivity were obtained for almost all varieties of silane substrates. The methodology is tolerant of a range of functionalities such as carboxylic acid, ester, amine and fluorine present in the alkyne.

The advantageous features of Pt-nanocluster catalysis are (a) The heterogeneous mixture of Pt-nanocluster homogenizes after the addition of silane. (b) After the completion of the reaction, the catalyst precipitates out from reaction mixture and product purification is not required as in homogeneous catalysis. (c) The precipitated nanoparticles (brown solid) retain their original catalytic activity after repeated cycles of catalysis. The nature of the catalyst during the catalytic process has been investigated via Transmission Electron Microscopy and UV-Vis studies in combination with quantitative poisoning studies during the catalysis.

## 257. Syntheses of Highly-regulated silanols and silsesquioxanes

**Masafumi Unno** and Hideyuki Matsumoto, Gunma University, Kiryu, Japan

Synthesis of various new silanols and silsesquioxanes are summarized. All four isomers of tetraisopropylcyclotetrasiloxanetetraol were prepared, and subsequent reaction afforded cage silsesquioxanes, ladder silsesquioxanes (laddersiloxanes) up to nonacyclic, and supramolecular aggregates. The structures of all compounds and their unique properties are described.



## 258. Star Acetylenes from Octaiodophenylsilsesquioxane as a Route to Star-Polyacetylenes (Nano-Sea Urchins)

**Michael Asuncion** and Richard M. Laine, University of Michigan, Ann Arbor, MI

Octaiodophenylsilsesquioxane [IPhSiO$_{1.5}$]$_8$ is > 95% para substituted, offering perfect cubic symmetry with a functional group in each octant in Cartesian space. Because of its octahedral structure and nanometer size, it represents a potentially very useful nanoconstruction site. We report here that I$_8$OPS reacts readily with acetylenes under mild Sonogashira conditions to produce the corresponding octa-acetylenes. The resulting materials, because of their 3-D octahedral structure, are highly soluble in a variety of common organic solvents. They are also stable to temperatures exceeding 400 °C in air, making them quite robust and easily processable. The resulting compounds themselves offer potential for further functionalization and thus offer high utility, as in the processing of high temperature polymers, for example. Additionally, initial thermal studies indicate that octa-acetylenes may self-polymerize at elevated temperatures, creating 3-D star networks of polyacetylenes.

### 259. A study on the effects of some topographical feature, surface grafted modifications and added leachants upon the settling of the marine biofouler, Ulva, (Green Algae), onto Silastic® T2*

**Ronald H. Baney**[1], Anthony B. Brennan[1], Leslie H. Wilson[1], Thomas G. Estes[1], Michelle L. Carman[1], James F. Schumacher[1], Yunmi Kim[1], Maureen E. Callow[2] and James A. Callow[2], (1)University of Florida, Gainesville, FL, (2)The University of Birmingham, Birmingham, United Kingdom

Tin based marine antifouling agents are being phased out globally due to their negative environmental impact. Silicone elastomers have long been considered as replacement candidate. It has been recognized for some time now that cells respond to surfaces through cues arising from topographical features or chemical signals often referred to as contact guidance.

One of the major marine biofoulers is Ulva (Green Algae) which starts fouling by initial settling of its spores onto a surface. It has also been recognized for some time that some natural surfaces do not foul, presumable due to topographical features on their surface, for example, a water lily leaf or shark skin. We have observed an 86% decrease in Ulva spore settlement onto a shark like 5µm patterned surface of Silastic® T2 produced by lithographic techniques. Settling onto a similar paralleled channel feature was increased by 155%. The surface of Silastic® T2 was modified by ”grafting” Polyethyleneglycol, polysulfones or perfluoropolyethers to Silastic® T2 surfaces by first functionalizing the OH ended polymer precursors by reaction with isocyanatopropyltriethoxysilanes, followed by coupling to generated OH rich surfaces on the Silastic® T2. Adhesive strength (ease of removal) of the spore from the surface modified Silastic T2 generally decreased with decreasing wettability. Trimethylsilanol, bistrimethylsiloxymethylsilanol and tristrimethylsiloxysilanol were added at 2% loading to Silastic® T2 before curing. Setteling of Ulva spores against these surfaces was examined. Spore death was indicated by bleaching of the spore color and significant amounts cell debris. Spore motility was compromised as observed by their retarded ability to move from light. Misshapen spores and extended flagila further indicate the toxic nature of the added silanols in the environments close to the Silastic® surface.

* Silastic® T2 ---A hydrosilyation curing silicone elastomer from Dow Corning

## 260. In vitro absorption of decamethylcyclopentasiloxane (D5) in human skin: a comparison to octamethylcyclotetrasiloxane (D4)

J.M. McMahon[1], K.P. Plotzke[1], **M.L. Jovanovic**[1], D.A. McNett[1], R.H. Gallavan[2] and R.G. Meeks[1], (1)Dow Corning Corporation, Midland, MI, (2)formerly of Dow Corning Corporation, currently employed by Pfizer

The absorption of $^{14}$C-decamethylcyclopentasiloxane ($^{14}$C-D5) was evaluated when applied to human skin using flow-through diffusion cells. Human skin membranes from six donors were prepared by dermatoming previously frozen intact abdominal skin. Barrier integrity of the skin was initially screened with $^{3}$H-$H_2O$. Percutaneous absorption was evaluated on two separate days. On day one, skin samples from each of the three donors were dosed with neat D5 and three were dosed with a generic anti-perspirant formulation containing D5. On day two, new skin samples from the same six donors were dosed with the opposite formulations. Immediately after dosing, charcoal baskets were placed above the skin into a custom designed cap to capture volatilized material. A physiological receptor fluid was pumped underneath the skin samples for 24hr and collected in a fraction collector. At the end of 24hr, the charcoal baskets were removed and extracted, skin was washed and solubilized, and the receptor fluid was collected. The radioactivity content in each sample was measured by liquid scintillation counting. The percent dose absorbed was determined as the amount of radioactivity in the receptor fluid combined with the amount remained in the skin after washing. Results were compared with another siloxane, $^{14}$C-octamethylcyclotetrasiloxane ($^{14}$C-D4) which was evaluated under a similar protocol. Data analysis indicated that 0.04 ± 0.01% and 0.50 ± 0.07% of the applied dose of neat D5 and D4, respectively was absorbed at the end of the assay and that this was not significantly different from that seen with formulated D5 or D4 (0.02 ± 0.01% and 0.49 ± 0.18%, respectively). The percent of applied dose recovered from all analyzed samples for neat D5 and D4 was >91%, and for D5 and D4 formulated in an antiperspirant was >98%. Funded in part by the Silicones Environmental, Health and Safety Council.

## 261. Synthesis and use of a radiolabeled polymer for understanding fate and distribution in the body

**M.L. Jovanovic**, S. Varaprath, D.A. McNett, K.P. Plotzke and R.M. Malczewski, Dow Corning Corporation, Midland, MI

Silicones are endowed with outstanding properties such as hydrophobicity, film forming abilities, release and lubrication properties, antifoam etc., rendering them invaluable in a wide variety of industrial, consumer and health care products. The main routes of direct human exposure to the linear polymeric species, polydimethylsiloxanes (PDMS), are skin contact and oral intake. In order to understand the fate and effects of these polymers during typical applications, a radiolabeled analog was synthesized for use in dermal and oral absorption studies. Results of these studies demonstrated that very little of the $^{14}$C-PDMS, 350 cSt was absorbed through the human skin or vaginal tissue, and little if any was absorbed following oral administration. Both mass balance and whole body autoradiography data in oral absorption studies suggest that $^{14}$C-PDMS, 350 cSt was rapidly excreted in the feces unchanged.

## 262. Kinetic and Mechanistic Studies of the Silyl Substitution Reaction in a Tantalum Disilyl Complex

He Qiu and **Zi-Ling Xue**, The University of Tennessee, Knoxville, TN

Silyl ligands in tantalum disilyl complex $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$ (**1**) were found to undergo an exchange reaction with $Li(THF)_3SiBu^tPh_2$. Kinetic and mechanistic studies of the first silyl substitution reaction reveal that it follows a dissociative pathway. In the presence of excess $Li(THF)_3SiBu^tPh_2$, the rate of the disappearance of **1** is pseudo first-order with respect to **1**. Tetrahydrofuran (THF), a polar solvent, was found to promote the substitution with 1.7(0.3) order on THF.

## 263. Rifle river water testing by Ogmew Heights high school students

**Douglas B. Grezeszak**, Ogemaw Heights High School, West Branch, MI

Our primary goal is to present the data from our weekly testing program in an all-inclusive and logical fashion. Our data includes the weekly test results from five different sites along the Rifle River in Ogemaw County. Graphs comparing test results from different sites as well as to other tests will be displayed. The testing covers air and water temperature, flow rate, pH, hardness, nitrates, phosphates, dissolved oxygen, dissolved carbon dioxide, and chloride levels over the last two years. Our display will also include photographs of team members testing the water on location, newspaper articles referencing to the project, and a map of the testing area.

## 264. Self-assembled Hybrid Polymer Nanotubes From Siloxy-Functional Polybutadienes

Bhanu P.S. Chauhan*, **Alok Sarkar** and **Bharthi Balagam**, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

Recently, we have disclosed a new route to silyl functionalization of polyolifines.1 In this presentation, we will disclose formation of I/O hybrid polymer nanotubes, which have been achieved from silyl-functional polybutadienes and hydrosilylation reactions of 1,3,5,7 tetramethylcyclotetrasiloxane (D4) and polydimethylsiloxane (PDMS). This route provides a one step template free access to hybrid nanotubes in good yields. The morphology studies by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and AFM will also be presented. It was found that the size and morphology of nanotubes were affected by the size and structure of hydrosilane. The diameter of nanotubes obtained from the polymer hydrosilylated with D4 system and PDMS was in the range of 200-500nm and 100-200nm respectively while the length of the tubes was several microns.

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1. Bhanu P. S. Chauhan and Bharathi Balagam Macromolecules, 2006, 39, 2010

## 265. Lewis Acid Catalyzed Hydrosilylation of 1,4 &1,2 -Polybutadienes

**Moni Chauhan***[1], Bharthi Balagam[2], **Kristina Foulias**[1] and Bhanu P.S. Chauhan*[2], (1)Queensborough Community College, Bayside, NY, (2)Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

A highly efficient method for the Lewis acid catalyzed hydrosilylation of 1,4 & 1,2-polybutadienes has been developed using B(C6F5)3 as catalysts. 1,4-Polybutadienes having internal double bonds were found to be much reactive with this system, which are otherwise found to be very less reactive towards the transition metal catalysts. Hydrosilylation of 1,4 & 1,2-Polybutadienes have been achieved selectively (Anti-Markovnikov's product) with a wide variety of hydrosilanes, substituted with aryl and alkyl groups. The silanes with bulky groups such as diphenyl- and triphenyl-silanes have efficiently been hydrosilylated at room temperature using this methodology. All silyl-substituted polymer products were characterized by 1H, 13C, 29Si NMR and GPC techniques.

## 266. Preparation and Reactivity of Silicon-Functionalized Siloles

**Janet Braddock-Wilking**, Yan Zhang, Joyce Y. Corey, Nigam P. Rath, R. Brett Cothran and Kevin A. Trankler, University of Missouri-St. Louis, St. Louis, MO

Several substituted silacyclopentadienes (siloles) containing substituents on the ring carbons and functional groups at the silicon center have been synthesized and characterized. The substituted siloles, 1,1-bis(diethylamino)-2,5-dimethyl-3,4-diphenyl silacyclopentadiene (1) and the related 1,1-bis(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenyl silacyclopentadiene (2) ring systems were prepared. Compounds (1) and (2) were found to react with HCl followed by $LiAlH_4$ to afford the corresponding 1,1-dihydrido-2,5-dimethyl-3,4-diphenylsilacyclopentadiene (3) and 1,1-dihydrido-2,5-bis(trimethylsilyl)-3,4-diphenylsilacyclopentadiene (4). In addition, compound (2) can be converted to the dimethoxy-substituted silole, 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenylsilacyclopentadiene (5) by reaction with MeOH in the presence of a substoichiometric amount of $AlCl_3$. Complex (2) reacts with $Br_2$ to give a stable dibromosilole, 1,1-(dibromo)-2,5-bis(trimethylsilyl)-3,4-diphenylsilacyclopentadiene (6) whose structure was confirmed by X-ray crystallography (Fig. 1). In contrast, a ring-opened product, (7) $(MeO)_2BrSiC(SiMe_3)=C(Ph)C(Ph)=C(SiMe_3)Br$ (X-ray, Fig. 2) was obtained when (5) was treated with $Br_2$. Compound (3) was found to react with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ to give a symmetrical dinuclear complex (8) containing two bridging silole rings at platinum, $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiR_2)]_2$ (where $SiR_2$ denotes the silole ring). The structure of complex (8) (Fig. 3) was confirmed by X-ray crystallography.

Characterization of complexes (3-7) will be described as well as other reactions of siloles with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.

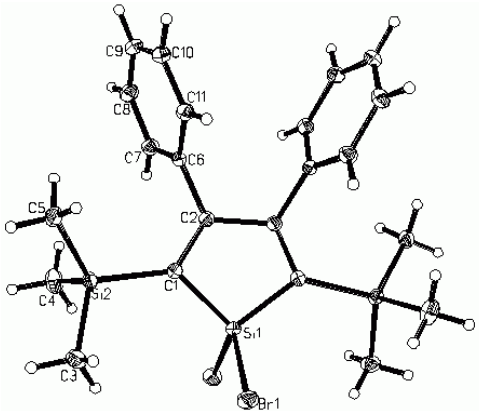


Figure 1. Molecular structure of (6)

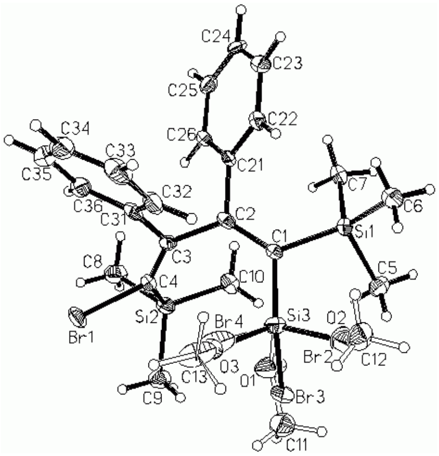


Figure 2. Molecular structure of (7)

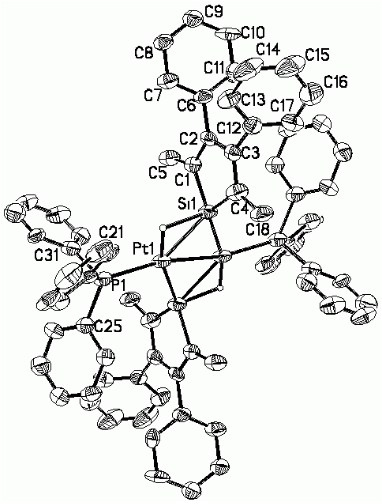


Figure 3. Molecular structure of (8)

## 267. Synthesis and cyclic voltammetric studies on 1-sila-3-ferracyclobutanes, [ƒØ5-C5H4Fe(LL')CH2SiMe2] and [ƒØ5-C5H5Fe(LL')SiMe2Fc] (Fc = ferrocenyl; L = CO, L' = PPh3; LL' = diphosphine)

**Mukesh Kumar**[1], Francisco Cervantes-Lee[2], Keith H. Pannell[2] and Hemant K. Sharma[2], (1)U. T. El Paso, El Paso, TX, (2)U. T. El Paso, El Paso, TX

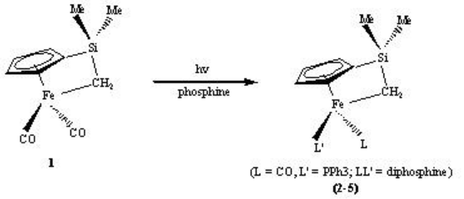
We report the synthesis of phosphine derivatives of 1-sila-3-ferracyclobutane, $h^5\text{-}C_5H_4Fe(CO)_2CH_2SiMe_2$ (**1**) by the substitution of labile carbonyl groups from **1** with phosphine ligands under photochemical conditions (Scheme 1). **1** cannot be isolated since it rapidly ring-opens to form a polymer, however, conversion of **1** into phosphine derivatives provides a facile synthetic route to isolate the corresponding metallacyclic in stable solid-state form. The cyclic voltammetric studies of **2-5** have been conducted to understand the structural/electrochemical properties and their utility as redox-active materials. It has been found that these undergo one electron reversible redox process, which is not observed in **1**.

We have also been able to synthesize bimetallic compounds, $[h^5\text{-}C_5H_5Fe(LL')SiMe_2Fc]$ (, Fc – ferrocenyl; LL' = diphosphine) (**7-10**) (Scheme 2) which exhibit interesting redox properties.

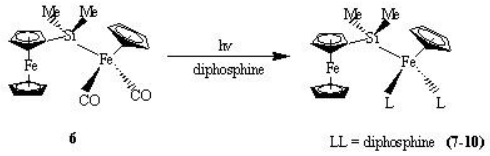
## 268. Synthesis and cyclic voltammetric studies on 1-sila-3-ferracyclobutanes, [η5-$C_5H_4Fe(LL')CH_2SiMe_2$] and [η5-$C_5H_5Fe(LL')SiMe_2F$

**Mukesh Kumar**, Francisco Cervantes-Lee, Hemant K. Sharma and Keith H Pannell, U. T. El Paso, El Paso, TX

We report the synthesis of phosphine derivatives of 1-sila-3-ferracyclobutane, h5-C5H4Fe(CO)2CH2SiMe2 (1) by the substitution of labile carbonyl groups from 1 with phosphine ligands under photochemical conditions (Scheme 1). 1 cannot be isolated since it rapidly ring-opens to form a polymer, however, conversion of 1 into phosphine derivatives provides a facile synthetic route to isolate the corresponding metallacyclic in stable solid-state form. The cyclic voltammetric studies of 2-5 have been conducted to understand the structural/electrochemical properties and their utility as redox-active materials. It has been found that these undergo one electron reversible redox process, which is not observed in 1. We have also been able to synthesize bimetallic compounds, [h5-C5H5Fe(LL')SiMe2Fc] (Fc – ferrocenyl; LL' = diphosphine) (7-10) (Scheme 2) which exhibit interesting redox properties



Scheme 1

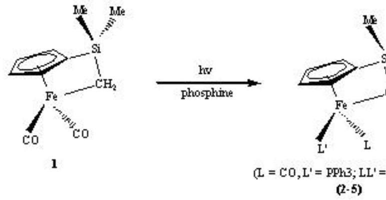


Scheme 2

## 269. Synthesis, structural and cyclic voltammetric studies on 1-sila-3-ferracyclobutanes and related bimetallic derivatives

**Mukesh Kumar**, Francisco Cervantes-Lee, Hemant K. Sharma and Keith H. Pannell, U. T. El Paso, El Paso, TX

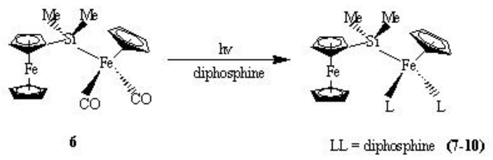
We report the synthesis of phosphine derivatives of 1-sila-3-ferracyclobutane, $\eta^5$-$C_5H_4Fe(CO)_2CH_2SiMe_2$ (1) by the substitution of labile carbonyl groups from 1 with phosphine ligands under photochemical conditions (Scheme 1). 1 cannot be isolated since it rapidly ring-opens to form a polymer, however, conversion of 1 into phosphine derivatives provides a facile synthetic route to isolate the corresponding metallacyclic in stable solid-state form. The cyclic voltammetric studies of 2-5 have been conducted to understand the structural/electrochemical properties and their utility as redox-active materials. It has been found that these undergo one electron reversible redox process, which is not observed in 1. We have also been able to synthesize bimetallic compounds, [$\eta^5$-$C_5H_5Fe(LL')SiMe_2Fc$] (Fc – ferrocenyl; LL' = diphosphine) (7-10) (Scheme 2) which exhibit interesting redox properties



1

(L = CO, L' = PPh3; LL' = diphosphine)
(2-5)

Scheme 1



6

LL = diphosphine (7-10)

Scheme 2

### 270. Synthesis, structural and cyclic voltammetric studies on 1-sila-3-ferracyclobutanes

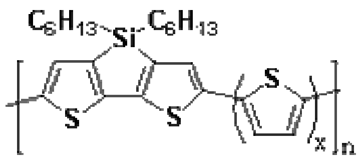
**Mukesh Kumar**, U. T. El Paso, El Paso, TX

*Text Not Available*

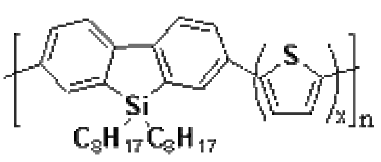
### 271. Synthesis and Characterization of AreneSilole-Thiophene Copolymers as New Semiconductors for Organic Thin-Film Transistors

**Hakan Usta**, Gang Lu, Antonio Facchetti and Tobin J. Marks, Northwestern University, Evanston, IL

Solution-processable conjugated polymers which have high charge carrier mobilities and show stable device performances have been investigated as the active semiconducting material in organic thin-film field-effect transistors (OTFT) for low cost, printed electronics. We present here the synthesis and characterization of a new class of silole-containing conjugated polymers, **S6T1**, **S6T2**, **BS8T1** and **BS8T2** and their performances as active semiconductor layer in Organic Field Effect Transistors as an effect of introducing an aromatic arenesilole core into the conjugated polymer backbone. Thin Film Transistors with mobilities as high as 0.07 $cm^2/V$ s in air, low turn-on voltage, and current on/off ratio > $10^6$ are fabricated using solution process techniques under ambient conditions with the above polymers as active channel layer. This new class of silole-containing polymers containing electron-withdrawing arenesilole moiety show great device operation stability in air. Our results demonstrate that silole-based copolymers can achieve much higher FET performance than those achieved so far and could be competitive materials to widely investigated regioregular polythiophenes and **F8T2**.



x=0 **S6**



x=0 **BS8**

| | |
|---|---|
| 1 **S6T1** | 1 **BS8T1** |
| 2 **S6T2** | 2 **BS8T2** |

### 272. Synthesis and Characterization of GaS nanoparticles via Photoluminescence and TEM*

**Lisa A. Linhardt**, Iliana Medina and Mark Fink, Tulane University, New Orleans, LA

A study was done on the different routes for the synthesis of GaS nanoparticles and the affects these routes had on the optical spectra obtained. The GaS nanoparticles were also characterized by TEM and a comparison between the photoluminescence maximum and the average diameter of the nanoparticles was performed. Nanoparticles of GaS capped with TOPO (tri-n-octylphosphine oxide) or hexanethiol were prepared by a single source route using $(EtGaSSiPh_3)_2$, $(MeGaSSiPh_3)_2$, and $(MeGaSSi^{i}Pr_3)_2$ as the precursor.[i][ii] The nanoparticles obtained show quantum size effects in their optical spectra. The photoluminescence show an emission maximum that is characteristically red shifted in relation to the band edge. Because the band gap energy for GaS is 2.59 eV at 300 K, GaS is considered to be a promising material for near-blue light emitting devices.[iii] It exhibits both electroluminescence and PL in the green–blue region. By correlating the emission maximum and half bandwidth with the TEM average diameter and size distribution a more simplified and less expensive quality control procedure can be developed for the larger scale production of photoluminescence nanoparticles.

*Supported by Lousiana Undergraduate Research Assistantship(LURA)

[i] Castro, Stephanie L et al.; “Nanocrystalline Chalcopyrite Materials (CuIn S2 and CuInSe2) via Low-Temperature Pyrolysis of Molecular Single-Source Precursor,” Chem. Mater. 2003, 15, 3142-3147

[ii] Trindade T. et al.; “Synthesis of PbSe nanocrystallites using a single-source method. The X-ray crystal structure of lead (II) diethyldiselenocarbamate,” Polyhedron 1999, 18, 1171-1175

[iii] Aydinli, Gasanly, and Gök°en; “Donor–acceptor pair recombination in gallium sulfide,” J. Appl. Phys., Vol. 88, No. 12, 15 December 2000

## Analyzing the World Around Us II

**Organizer:** Janet M. Smith Dow Corning Corporation, Midland, MI
**Organizer:** Susan V. Perz Dow Corning Corporation, Midland, MI

### 273. Regeneration of Strong Base Anion Exchange Resins Used in Gold Slurry Mining

**Chris Eicher**, Dow Chemical, Delta College, Midland, MI

The efficient recovery of metallic gold from gold containing ore is an important process in industry today because of the depletion of naturally occurring reserves of metallic gold. Extraction techniques using ion exchange resins have been found to be economically viable, however there is currently no environmentally safe and effective technique for regenerating the capacity for gold so that the resin can be reused. This experiment showed that many common chemical regenerants currently in use for other applications are not effective for use in gold recovery, however two regenerants, thiourea and iron (III) chloride, show promise for resin capacity recovery.

### 274. Optically transparent boron-doped diamond electrodes for chemical analysis

**Yingrui Dai** and Greg M. Swain, Michigan State University, East Lansing, MI

The use of electrically conductive diamond film as an electrode material is a relatively new field of research. Boron-doped diamond (BDD) possesses attractive qualities, such as a wide optical window from near UV into far IR (0.25-100 mm) regions of the electromagnetic spectrum, a wide working potential window, low background current, microstructural stability during cathodic and anodic polarization and fouling resistance, making it an obvious choice for utilization as an OTE in spectroelectrochemical measurement.

The boron-doped diamond film was deposited on undoped Si by microwave assisted chemical vapor deposition using a 0.5%$CH_4/H_2$ source gas mixture at 45 torr and 1000 W for 4h. The thin-film electrode was characterized by cyclic voltammetry, atomic force microscopy, and IR spectrophotometry. The film's electrochemical response was evaluated using methyl viologen, $Ru(NH_3)_6^{+3/+2}$ and $IrCl_6^{-2/-3}$, all in 1M KCl. The film exhibited a low background current, and a stable and active voltammetric response for all these redox systems. The spectroelectrochemical performance of the diamond OTE was evaluated in a specially designed, transmission thin-layer cell. The spectroelectrochemical response for $K_4Fe(CN)_6$ in 1M KCl was used to evaluate the electrode performance. The difference FTIR spectrum (Oxidized minus Reduced) clearly showed the absorption peak for $Fe(CN)_6^{-4}$ disappeared (negative peak at 2039 $cm^{-1}$) and $Fe(CN)_6^{-3}$ was produced (positive peak at 2115 $cm^{-1}$) during the potential step measurement. The results demonstrate that diamond OTE offers the possibility of sensitive, reproducible and stable spectroelectrochemical measurements.

### 275. High throughput research: a continuously evolving capability within the Dow Chemical Company

**Robert D. Krystosek**, The Dow Chemical Company, Midland, MI

The competitive and global nature of the chemical industry has resulted in the shortened lifetimes of many products. In addition to this, new products need to be brought to the marketplace more rapidly. This puts a great deal of pressure on research and development, demanding more innovative ideas, higher success ratios, shorter lead and development times, and lower research costs per product. The implementation of High Throughput Research (HTR) techniques in such companies as Bayer, BASF, DuPont, Shell, General Electric, Eastman Kodak and Dow have allowed these companies to respond to this new pressure on R&D. Within Dow, HTR techniques have played a key role in the areas of catalysis, materials and process improvement. This presentation will review why Dow is one of the leaders in the chemical industry in terms of the implementation of high throughput research.

### 276. Fish,CT,PBDEs,Powders & Analytical Chemistry

**Paul R. Loconto**, Michigan Department of Community Health, Lansing, MI

The Analytical Chemistry Section within the Division of Chemistry and Toxicology, Bureau of Laboratories, Michigan Department of Community Health is currently engaged in three established areas of applied analytical chemistry: trace organochlorine pesticide/PCB residue analysis in Great Lakes fish, trace chemical warfare agent and agent metabolite analysis in urine and blood, and trace persistent organic pollutant analysis in human serum, breast milk and tissue. A fourth area is about to emerge: chemical terrorism triage testing. All four areas will be introduced including some recent analytical method development on PBDEs.

### 277. Sci-Fest and National Chemistry week give children the opportunity to analyze the world around them with a new understanding of Science and Chemistry

**Dave Stickles**, Dow Corning Retiree, Midland, MI

Most schools have a limited science curriculum at the elementary and middle school level. The purpose of Sci-Fest is to give some additional exposure of science to school children with the hope that it may draw their attention to science courses and possibly one day a career in a science field. This is done by exposing children to a variety of scientific areas allowing them to analyze the world around them from different perspectives than what they are typically exposed to.

### 278. Employment Trends-The Technician of the Future

**Jim Birney**, Kelly Services, Midland, MI

Employment trends will be discussed

## Brewing Science Symposium II

**Organizer:** Gary E. Kozerski Dow Corning Corporation, Midland, MI
**Organizer:** Paul J. Popa Dow Chemical Company, Midland, MI

### 279. My Beer and Biotechnology

**Inge Russell**, Dept. of Biochemical Engineering, University of Western Ontario, London, ON, Canada

A look at what is happening in the world of biotechnology: cloning, genetics and gene chips. What do these technologies have to do with the making and tasting beer? Can you really hear a yeast cell scream if you stress it? Who has the most taste buds? Humans, pigs, dogs or catfish? A thought provoking and fun journey through some of the latest scientific advances in biotechnology, and how these advances relate, both now and in the future, to the production and tasting of beer.

### 280. Chemical Engineering in the Tavern

**Jaime Jurado**, Director of Brewing Operations, The Gambrinus Company, and President, Master Brewers Association of the Americas, San Antonio, TX

Much of the world's social history has been framed around the inn, pub, or as the Romans called them, the tabernae. We often take for granted that the beer in the glass came from a keg, and that the requirements for gentle transport of the sensitive liquid are similar to what one would expect from many costlier materials: the product is shear-sensitive, highly sensitive to bacterial infection, and carbonation levels and target dispense temperature in the beer must be maintained. The customer demands the beer to be served in a tight temperature range, with a nice head of foam. After a quick overview, we will explore design aspects of beer draft dispense systems, and look at cleaning and dispense parameters in an engineering framework. The presentation includes a simple kinetics-based model and closes with a brief look at analytical calculations related to carbonation and bubbles from a Stefan-Maxwell perspective.

### 281. Beer Tasting for the Professional Chemist

**James J. Hackbarth**, The Gambrinus Company, San Antonio, TX

A brief overview of the origins and significance of key beer favors must incorporate contributions from malted barley or other grains, hops, yeast and water. These variables can be manipulated in almost infinite ways by the Master Brewer. An often unappreciated aspect of beer flavor is 'mouthfeel' and that is driven by factors including ingredients and brewhouse and fermentation protocols. A review in broad strokes of the flavors found in beers provides a basis for formal taste evaluation.

Beer Flavor Standards will be used to deliver six key beer flavors in a taste training session. These standards create and maintain flavor awareness and a common flavor language within product development, process improvement, and quality compliance. Importance, origins, typical concentrations, and thresholds will be discussed.

## Chemical Education II

**Organizer:** David Baker Delta College, University Center, MI
**Organizer:** John D. Blizzard QuadSil inc., Midland, MI

### 282. Rough Science from the BBC - turning people on to Science

**Mike Bullivant**, The Open University, Milton Keynes, United Kingdom

As the UK's largest distance-learning organisation, The Open University co-produces a number of prime-time radio and TV series with the BBC. The programmes cover a wide range of subjects and are all aimed at the general public. One such is Rough Science, a hugely successful BBC TV series that aims to popularise Science and Technology. Running to 34 half-hour episodes, Rough Science has been shown in over 70 countries worldwide, and is aired on PBS in the States.

This presentation by one of the on-screen Rough Scientists, Open University Chemist Mike Bullivant, will explain what Rough Science is all about and will look at some of the multimedia educational materials that have been produced to accompany the TV programmes.

### 283. Molecular Architecture: a non-majors course focusing on molecular structure, spectroscopy, and synthesis

**Perry S. Corbin**, Ashland University, Ashland, OH

As part of the undergraduate core-curriculum of Ashland University, each student is required to take two natural science courses. As such, the Department of Chemistry is strongly committed to offering non-major's courses which are focused in regards to content and that are “seminar-based”. These courses rely minimally on lecture and promote active learning both in the classroom and laboratory. A description of a recently developed non-major's chemistry course, *Molecular Architecture*, will be presented. In *Molecular Architecture*, students undertake an intensive look at how chemists model the unseen—in this case molecular structure—and support their models with experimental data. Most importantly, *Molecular Architecture* focuses on the development of scientific-thinking skills. Three major themes of the course are: isomerism in organic molecules, including an extended investigation of chirality; the characterization of organic molecules using infrared spectroscopy, nuclear magnetic resonance spectroscopy, and mass spectrometry; and the structure and properties of synthetic polymers and proteins. The aforementioned themes are somewhat unique for a course offered to students with non-science-related majors. In regards to instructional approach, topics are often introduced by pre-class assigned readings from *The Same and Not the Same* by Roald Hoffmann, along with reflective writing assignments. Classroom sessions include discussion and/or a brief lecture by the instructor, followed by cooperative work involving problem-solving, laboratory activities, and computer modeling. Student progress is assessed through in-class work, extensive writing assignments, and oral presentations. The instructional approach and content of *Molecular Architecture* is highly adaptable, and the course has been offered in a variety of formats—for example, as a traditional three-hour course, as a once per week evening course, as a five-week summer course, as a course within Ashland University's Honor's Program, and as a week-long summer intensive course for gifted high-school students.

### 284. Rifle river water testing by Ogemaw Heights high school students

**Douglas B. Grezeszak**, Ogemaw Heights High School, West Branch, MI

We will be presenting the direct results of, and issues pertaining to, our weekly testing program. Our data includes the weekly test results from five separate sites along the Rifle River in Ogemaw County. The presentation will include graphs of the test results that compare different sites as well as the results of different tests to each other (i.e. dissolved oxygen vs. water temperature). Our testing process covers basic observations, air and water temperature, flow rate, pH, hardness, nitrates, phosphates, dissolved oxygen, dissolved carbon dioxide, and chloride levels over the last two years.

Our initial goal was to establish a baseline. Discussion on how we accomplished this and what remains to be done will be held. Attempts to include other schools in the program, problems we have encountered and how we overcame them, and our efforts to engender water quality awareness among our community will be covered as well.

Our exhibit will include multiple speakers and a PowerPoint presentation. The PowerPoint presentation will not only include raw data but photographs of team members testing the water on location, newspaper articles referencing to the project, and a map of the testing area as well.

### 285. The Great Lakes Process Technology Alliance: where industry, education, and community leaders partner to develop a respected, qualified, and successful Process Technology workforce

**Mary E. Haslam**, The Dow Chemical Company, Midland, MI and **Ronald J. Good**, Delta College, University Center, MI

What happens when education, business and industry, and community members unite not only locally but regionally to collaborate in preparing a qualified workforce? Who are the winners? The Great Lakes Process Technology Alliance (GLPTA) is a not-for-profit member organization comprised of education providers, regional businesses, process industries, and community advisors who work toward shared goals, including developing a qualified workforce and improving global competitiveness for the process industry. The purpose of the Alliance is to increase the ability of its members to deliver quality education services to all stakeholders including, but not limited to Industry, Education and Community. The establishing of standards, learning outcomes and objectives, and assessment for Delta College's Process Technology Program will be discussed, with application to other programs in the region.

### 286. Peer led team learning workshops at a small liberal arts college

**Lois Zook-Gerdau**, Deepa Perera and Paul Szalay, Muskingum College, New Concord, OH

Peer-Led Team-Learning (PLTL) was implemented into both semesters of the General Chemistry curriculum during the 2004-2005 academic year through a grant received from Workshop Project Associates (WPA), at Muskingum College, in New Concord, OH, a Liberal Arts institution of about 1,600 students. The model consisted of one general chemistry section taught with PLTL and another section taught by the same instructor without PLTL in both semesters of General Chemistry I & II. Preliminary data reveals that there were more A grades in the sections that required PLTL compared to the other sections, and overall grades were slightly higher in the PLTL sections, although this difference was not statistically significant. However, once student profiles, including high school GPA's, class rank, and ACT scores were used to correct for differences between the students in the two different formats, it was found that PLTL students performed better despite the fact that they had weaker background preparation. Evaluations of the PLTL experience completed by the general chemistry students revealed a great deal of satisfaction with the experience. PLTL has been continued in the general chemistry curriculum for the 2005-2006 academic year, and the additional data from this year will be available for presentation in May.

### 287. Integration of conducting polymers across the undergraduate chemistry curriculum

**Ted M. Pappenfus**, University of Minnesota, Morris, Morris, MN

This presentation will outline proposed curricular innovations from a recently funded NSF award. The project will focus on conducting polymers which are an important class of polymers currently under intense investigation in both industry and academia for electronic materials applications. These polymers have stimulated interest across many fields including chemistry, materials science, chemical engineering, and physics. This project introduces this important area of science to undergraduate students through inquiry-guided exercises selected from established literature methods and procedures. A major emphasis of this project is the integration of conducting polymers across the undergraduate chemistry curriculum. This integration will assist in creating a curriculum which is more interdisciplinary with respect to both teaching and research that introduces a topic with a practical focus and real-life applications.

### 288. NATURAL Bond Orbital Insight in Teaching Chemical Reactivity: Radical Addition Reactions of Alkenes with Hydrogen Halides

**Mohamed Ayoub**, University of Wisconsin-Washington, West Bend, WI

A vast majority of chemical reactions can be explained using the donor-acceptor interaction approach, i.e. interaction between an occupied Lewis-type NBO ($\phi_o$) and vacant non-Lewis-type NBO ($\phi_{v*}$), leading to lowering energy. This approach in teaching about chemical reactions provides a platform on which students can examine all aspects of any chemical reaction and construct their interaction diagrams from which gross features of reactivity and structure flow naturally.

We show how mechanistic issues and reactivity differences between halogens when added to alkenes can be addressed in the framework of modern electronic structure methods, specifically the B3LYP hybrid density functional method with 6-311++G** basis set. We demonstrate that subtle differences in electron delocalization associated with the pi electrons of carbon-carbon double bond ($\pi_{CC}$) and vacant nonbonding orbital of the halogen radical ($n_{X*}$) account for the reactivity of chlorine compared to heavier halogens. The calculated values for the stabilization energy ($\Delta E^{(2)}$) and resonance weight shifts for $\pi_{CC} \rightarrow n_{X*}$ interactions are given along with orbital interaction diagrams showing the bonding and antibonding pattern for such interaction.

## Nanotechnology: It's a Small Small World - An Undergraduate Symposium

**Organizer:** Sharyl Majorski Central Michigan University, Mt. Pleasant, MI

### 289. Nanotechnology: From Hype to Applications

**Bradley D. Fahlman**, Central Michigan University, Mount Pleasant, MI

The term "nanotechnology" has evolved from science fiction to the real world in a short timeframe. This important size regime is now broadly recognized as being essential for circumventing the looming energy crisis, as well as continuing our prowess in next-generation electronics, medicine, and "smart materials". This talk will focus on the current and future application trends for nanotechnology, as well as important issues that may affect these advancements. Appropriate for an undergraduate symposium, a discussion of keys for success in graduate school will also be presented.

### 290. Research Trends in Nanotechnology

**Minghui Chai**, Central Michigan University, Mt. Pleasant, MI

Current research trends in nanotechnology include but not limit to the following areas: Nanomaterials; Nano-engineering; Nanoelectronics; Nanoscale Devices; Nanoparticle; and Nanobiotechnology. The impact of nanotechnology on the world can be significant because nanotechnology would exceed $1,000 billion by end 2010 in the world economy based on "The World Nanotechnology Market 2005" published by RNCOS. The increase in demand for nanoscale materials, tools and devices would reach $28.7 billion in as soon as 2008. These will help medical scientists, engineers and other researchers to invent and innovate in the fields of health, IT, communications and consumer goods. Such scientific revolution also creates a challenge for the academic community to educate students with the necessary knowledge, understanding, and skills to interact and provide leadership in the emerging world of nanotechnology.

### 291. Undergraduate Presentations

**Sharyl Majorski**, Central Michigan University, Mt. Pleasant, MI

To be determined

## Silicon Symposium - Silicon Chemistry I

**Organizer:** J. Patrick Cannady Dow Corning Corporation, Midland, MI

### 292. Time-resolved gas-phase kinetic and quantum chemical studies of the reaction of silylene with methyl chloride

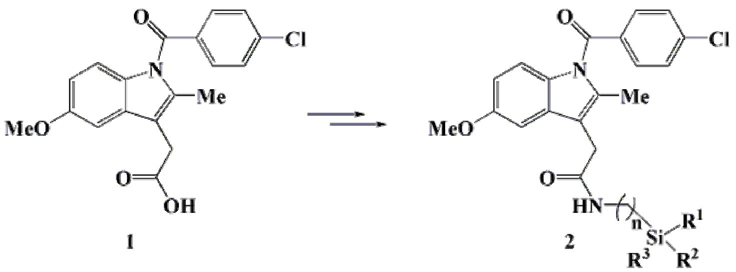
**Rosa Becerra**, Consejo Superior de Investigaciones Cientificas (CSIC), Madrid, Spain, J. Patrick Cannady, Dow Corning Corporation, Midland, MI and Robin Walsh, University of Reading, Reading, United Kingdom

Direct kinetic studies of the reaction of $SiH_2$ + $CH_3Cl$ have been carried out using laser flash photolysis of phenylsilane and silacyclopente-3-ene to generate $SiH_2$. The reaction was studied in the gas phase at five temperatures in the range 294-606 K. The second order rate constants gave a curved Arrhenius plot with a minimum value at $T \cong 370$ K. The rate constants showed no pressure dependence in the presence of up to 100 Torr ($SF_6$ bath gas). However, rate constants showed a weak dependence on laser pulse energy. Ab initio calculations (G3 level) support a mechanism in which the formation of a zwitterionic complex (ylid) is the initial step, but a high energy barrier rules out the subsequent insertion step. The significance of these findings and their relationship to other reactions of $SiH_2$ will be described at the meeting.

### 293. Synthesis, characterization, and anticancer activity studies of new sila-indomethacin amides

**Galina A. Bikzhanova**, Daniel Lecoanet, Hannah Bishop and Robert West, University of Wisconsin, Madison, WI

Indomethacin (**1**) is a non-steroidal anti-inflammatory medicine (nonselective COX inhibitor) commonly used to reduce fever, pain, and swelling. It was first discovered in 1963 and approved for use in the USA in 1965. Since then, **1** has been found to be effective for a variety of other purposes such as a premature labor delay, cancer treatment and its prevention. However, indomethacin is a potent drug with many serious side effects which limit its use due to significant gastrointestinal toxicity and bleeding associated with COX-1 inhibition. The purpose of our study was to modify **1** to synthesize less toxic and more active analogs. Therefore, a number of sila-amide indomethacin derivatives were designed, prepared, and spectroscopically characterized:



1 2

**2a:** $R^1 = R^2 = R^3 = Me$; $n = 3$
**2b:** $R^1 = R^2 = Me$; $R^3 = Ph$; $n = 1$
**2c:** $R^1 = R^2 = R^3 = Me$; $n = 1$
**2d:** $R^1 = R^2 = R^3 = OEt$; $n = 3$

Preliminary biological activity studies showed that several of our compounds are selective COX-2 inhibitors superior to indomethacin. In addition, some of our compounds are highly effective against various human cancer cells.

## 294. Silicone Based Controlled Release Dressing for Accelerated Proteolytic Debridement

**Csilla Kollar**[1], Kurt F. Brandstadt[1], James W. Crissman[1], Paal C. Klykken[1], Thomas H. Lane[1], Xavier Thomas[1], Gregory S. Whitaker[1], Richard Bott[2], Grant Ganshaw[2], Mark S. Gebert[2], Isabelle Mazeaud[2], Mae Saldajeno[2], Lillian B. Nanney[3] and Jeffrey M. Davidson[3], (1)Dow Corning Corporation, Midland, MI, (2)Genencor International, Inc, Palo Alto, CA, (3)Vanderbilt School of Medicine, Nashville, TN

Unique solutions for rapid enzymatic debridement were developed by the combination of silicone materials that have demonstrated utility in wound care applications with the performance of a genetically engineered, broad spectrum protease. Silicone emulsion technology enables hydrophilic enzymes to be stabilized with hydrophobic silicone materials. The enzyme is a serine protease of the subtilisin family, which has not been tested previously as a debriding agent. The dried emulsion incorporates a protease in a dehydrated state that shows excellent performance in accelerated stability tests, with retention of ~90% of the initial activity for an equivalent of 18 months' storage at room temperature. The combination was tested in a porcine burn model. The silicone delivery device acted synergistically with the enzyme to promote rapid debridement in the moist wound environment. Tissue fluids from the wound triggered reproducible and complete release of enzyme from the emulsion within eight hours. There was essentially complete removal of hardened eschar from full thickness burns after a single 24-hour treatment. Rapid debridement by the test material resulted in considerable exudate, which was easily managed with an absorbent dressing layer. There was a clear dose-response with various enzyme concentrations. Compared to controls and the benchmark material, debridement and progression to the healing phase were faster, and tissues unaffected by thermal injury appeared to remain normal. This technology, with the core silicone attributes of oxygen permeability, moisture retention, and friendly skin adherence properties, can serve as the basis for a number of drug delivery and wound care applications.

## 295. Rhodium plus allyl scetate induced curing of hydridosilane via transient acetoxy silanes

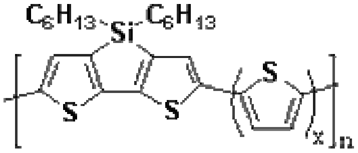
**Anthony Revis**, Jeffrey A. Kosal and Diane M. Kosal, Dow Corning Corporation, Midland, MI

The chemistry of acetoxy silanes has been well exploited, especially in the area of sealants, where moisture curing takes place with the elimination of acetic acid. The acetoxy silanes are prepared by well known routes, including reaction of chlorosilanes with acetic anhydride or carboxylate salts, and reaction of silazanes with carboxylic acids, to name a few. This paper will discuss a novel route to acetoxy silanes using rhodium catalyzed reaction of hydridosilanes with allyl acetate. For example, the rhodium trichloride catalyzed reaction of trimethylsilane with allyl acetate yielded 60% trimethylsilyl acetate, with presumed elimination of propene. The platinum catalyzed reaction yielded timethylsilyl acetate as only a minor product. When the reaction was extended to hydridosilioxanes, films were formed when processed in the open air. The mechanism appears to involve internal hydridosilane addition to the double bond, followed by beta-elimination of the silyl ester and propene. A more detailed discussion will be presented along with examples of film forming reactions.

## 296. SYNTHESIS, Characterization, and Field-Effect Transistor Behavior of New Arenesilole-Thiophene Copolymers with Excellent Hole Mobility and Air Stability

**Gang Lu**, Hakan Usta, Antonio Facchetti and Tobin J. Marks, Northwestern University, Evanston, IL

The development of p-type semiconducting polymers exhibiting high field-effect carrier mobility and good stability when functioning in ambient is of importance for the development of low cost, printed electronics. We present here the synthesis and characterization of four new soluble arenesilole-thiohene copolymers, S6T1, S6T2, BS8T1 and BS8T2 and examine the effect of introducing an aromatic arenesilole core into the p-conjugated polymer backbone. We have demonstrated that air stable thin-film field-effect transistors (FETs) with mobility up to 0.07 cm$^2$/V s, low turn-on voltage, and current on/off ratio > $10^5$ could be fabricated using solution process techniques under ambient conditions with the above polymers as active channel layer. This new class of polymers, which contains the electron-withdrawing arenesilole moiety, greatly stabilize device operation in air. In ambient, TFTs based on three of the abovementioned polymers exhibit comparable/much greater hole mobility to that of widely investigated regioregular polythiophenes and F8T2.



| | | | |
|---|---|---|---|
| x=0 | **S6** | x=0 | **BS8** |
| 1 | **S6T1** | 1 | **BS8T1** |
| 2 | **S6T2** | 2 | **BS8T2** |

### 297. Surface Functionalization of Silica Nanoparticles for Direct Synthesis of DNA Capture Oligomers

**Weian Zhao**[1], Elodie Pacard[2], Carole Chaix[2], Christian Pichot[2] and Michael A. Brook[1], (1)McMaster University, Hamilton, ON, Canada, (2)CNRS/BioMerieux, Lyon, France

DNA assays generally require the synthesis of oligomers on supports, cleavage, and reassembly on the detection matrix. In this study, silica nanoparticle aggregates were prepared for ultra-high sensitivity DNA microarray applications. Stöber silica nanoparticles (~ 280 nm) were functionalized with 3-aminopropyltrimethoxysilane (APTES) to yield a silica colloid bearing amino groups, which was then capped with excess 1,6-diisocyanatohexane (HDI) to create an isocyanato-functionalized surface. The isocyanato-modified silica nanoparticles were bridged by poly(ethylene oxide) (PEO) to form large aggregates (> 5 μm). This covalent bond-induced aggregation process was systematically studied at various experimental parameters, such as PEO molecular weight and concentration as will be discussed: deaggregation could be induced under reductive conditions to regenerate individual colloidal particles.

The silica nanoparticle aggregate was used as solid support for oligonucleotide synthesis in a standard DNA synthesizer. The major advantage of the aggregate is its high surface area, which ensures the high density DNA immobilization. The resulting DNA-immobilized nanoparticle aggregate was demonstrated to bind fluorescently labeled DNA: one aggregate can be readily detected fluorescently. Since the use of this silica nanoparticle aggregate increases the specific surface area being offered for DNA capture, and thus the number and accessibility of oligonucleotide probes immobilized on the surface, this approach should be useful for ultra-high sensitive DNA detection.

## Silicon Symposium - Silicon Chemistry II

**Organizer:** Gary M. Wieber Dow Corning Corporation, Midland, MI

### 298. In situ detection of methoxysilane hydrolysis intermediates in a biomatrix by Raman spectroscopy

**Mary M.J. Tecklenburg**[1], Paul Wrzesinski[1], Martin Bennett[1], Lindsey Suhr[1] and Kurt F. Brandstadt[2], (1)Central Michigan University, Mt. Pleasant, MI, (2)Dow Corning Corporation, Midland, MI

Raman spectroscopy was assessed as an analytical method to support the development of bioprocessing of silicon-based materials because it's rapid and requires little or no sample preparation. Recent studies have demonstrated enzyme catalysis of silicon reactions, specifically hydrolysis and condensation to produce siloxanes. The search for appropriate conditions for biosilification reactions relies upon appropriate detection methods for intermediates and products. A series of methylmethoxysilanes (tetramethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, and trimethylmethoxysilane) underwent hydrolysis and condensation in solutions that varied in ionic strength at circum-neutral pH while the reaction was monitored by Raman spectroscopy. The Si-O and Si-C stretches of silanes were vibrationally coupled so that a single intense peak was observed in the 600 – 800 $cm^{-1}$ region of the Raman spectra. The Si-O/Si-C stretch could be assigned for all of the solvated reactants and silanol intermediates of each hydrolysis step in solutions of low ionic strength and neutral pH. Assignments compared favorably with frequencies calculated by a DFT method. Kinetic plots for each intermediate were modeled by several mechanisms (first order, second order). The general result is that the hydrolysis rate increases as the number of OH groups on the silicon increases.

## 299. Bio-Conjunction of Streptavidin on $SiO_2$ and $TiO_2$ Particles

**Lu Ye**, Robert Pelton and Michael Brook, McMaster University, Hamilton, ON, Canada

The immobilization of streptavidin on $SiO_2$ and $TiO_2$ particles was performed using biotin-streptavidin conjugation. Biotinylated $SiO_2$ and $TiO_2$ particles were prepared by treating preformed particles with 3-aminopropyltriethoxysilane (APTS) in an anhydrous DMSO followed by reaction with N-hydroxysuccinimido-biotin. The biotinylated particles were characterized with $^{29}Si$ CP-MAS NMR and FT-IR. The amount of biotinyltriethoxysilane on the particles was established using TGA. The amount of biotin attached is related to the initial quantity of APTS-derived amino-groups that modified the particle surface. It was found that prolonging the silanization reaction time leads to thicker coating layers, which subsequently increases the biotin density on the particle surfaces. The binding of the biotinylated particles to (fluorescently labeled) streptavidin was studied using transmission electron microscopy (TEM), dynamic light scattering (DLS) and confocal microscopy. The results demonstrated that the biotin was covalently bonded to the particle surfaces. However, in the thicker layers not all biotin molecules are accessible to streptavidin. While streptavidin was readily able to bind to biotinylated $SiO_2$ and $TiO_2$ particles by biological affinity, streptavidin did not act as a strong flocculating agent for the particles.

## 300. Synthesis of Isolable Nanocluster Catalysts and Their Applications in Macromolecular Hydrosilylation Catalysis

Bhanu P.S. Chauhan* and **Jitendra Rathore**, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

Synthesis of isolable and catalytically active nanoclusters in multigram scale is a challenging area of research. Besides providing ease of handling and storage, such nanoclusters can easily be characterized, thus, their compositional identity can be confirmed. Additional advantages to such isolable nanoclusters can be redispersibility and recyclability. Recently, our laboratory has been developing new strategies for the generation of catalytically active metal.1, 2, 3 In this presentation, we will report the synthesis and characterization of isolable "Pt"-nanocluster and their use as regioselective hydrosilylation catalyst. A fair number of electronically and sterically varied olefins were quantitatively and regioselectively grafted to Si-H terminated silicones. Furthermore, hybrid nanoarchitectures were generated by selective incorporation of organic molecules on predefined nanostructures, such as Octakis(dimethylsiloxy)-T8-silsesquioxane (Q8M8H) and 1,3,5,7 Tetramethylcyclo-tetrasiloxane (D4H).

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(1) Chauhan, B. P. S.; Rathore, J. S. J. Am. Chem. Soc. 2005, 127, 5790-5791. (2) Chauhan, B. P. S.; Rathore, J. S. and Bandoo, T. J. Am. Chem. Soc. 2004, 126, 8493 (3) Chauhan, B. P. S.; Rathore, J. S., Chauhan, M. and Krawicz, A. J. Am. Chem. Soc. 2003, 125, 2876.

### 301. Acetoacetate Functional Silicones

**Donald T. Liles**, Dow Corning Corporation, Midland, MI

The acetoacetate moitey is a very interesting functional group as it contains both an active methylene and a ketone carbonyl, both of which can participate in reactions that form covalent bonds with numerous polymeric systems. For example, an acetoacetate active methylene group reacts with melamines, isocyanates and aldehydes. It can also participate in Michael reactions. The ketone carbonyl of acetoacetate reacts with amines to form enamines. Acetoacetate can also form chelates with polyvalent ions. Thus siloxanes and silanes possessing acetoacetate functionality are capable of reacting with a variety or polymers or compounds having the above mentioned functional groups. Acetoacetate functional silicones are best prepared by reaction of diketene or its equivalent (synthon) with carbinol functional silanes or siloxanes. Silicone polyethers and a silane have been functionalized with the acetoacetate moiety. This poster describes the chemistry of the acetoacetate functional group and preparation of some acetoacetate functional silicones. Some possible uses of acetoacetate functional silicones are also described, such as reactive silicone surfactants and coupling agents.

## Silicon Symposium - Silicon in Catalysis

**Organizer:** T. Don Tilley University of California, Berkley, Berkley, CA

### 302. Catalysis on the Surface of Silica: Well-defined Catalytic Centers and Surface Modification

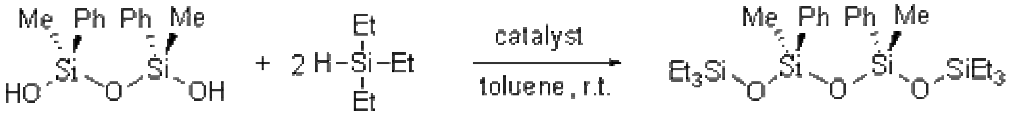
**T. Don Tilley**, Richard Brutchey and Daniel Ruddy, University of California, Berkeley, Berkeley, CA

For many heterogeneous catalysts, it is apparent that desirable properties are associated with well-defined active sites containing one or only a few metal centers on the surface of a support. Given the increasing interest in the structure and catalytic chemistry of supported metal centers, we have attempted to develop reliable routes to stable, well-defined catalytic centers bound to a silica support. We have described a process for the introduction of isolated metal centers onto a silica surface, involving grafting reactions with molecular precursors. This method produces sites that can be remarkably stable with respect to thermal degradation to oxide clusters. The resulting catalysts display good activities and selectivities for the oxidation of various hydrocarbons, using a nvariety of oxidants. Considerable effort has ben devoted to the study of isolated titanium centers for the catalytic epoxidation of olefins. More recently, the thermolytic molecular precursor method was used to introduce site-isolated Ta(V) centers onto the surface of mesoporous SBA15 silica. The resulting surface Si-OH and Ta-OH sites of the Ta/SBA15 catalysts were modified with a series of (N,N-dimethylamino)trialkylsilanes. Compared to the unmodified catalysts, the surface-modified catalysts exhibit excellent selectivity for epoxide formation (75-95%) in the oxidation of cyclohexene using aqueous H2O2 as the oxidant. The local structure of the Ta(V) site was also investigated.

## 303. Siloxane formation reactions-New catalysts and applications

**Yusuke Kawakami**, Japan Advanced Institute of Science and Technology, Nomi, Japan

Some new efficient catalysts were found for the formation of siloxane bonds from silanols and silanes. Stereochemistry of the silane and silanols in the reactions was also studied. Meanwhile, optically active disiloxane derivatives with phenyl and naphthyl substituents were separated on chiral stationary phase. The siloxane formation reactions were used to synthesize siloxane-containing polymeric systems with three dimentional structure, and optically active polymeric systems with chirality on silicon atoms. The chemical structures of the polymers were elucidated by $^{1}$H, $^{13}$C, and $^{29}$Si NMR.



R,R-**1**

Possible applications of these systems will be discussed.

## 304. Nanocluster Catalyzed Selective Routes to Functional Vinyl Germanes and Silanes: Investigations of Real Catalysts in Metal Catalyzed Hydrosilyl(germyl)ation Reactions

**Bhanu P.S. Chauhan*** and Alok Sarkar, Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY

Our laboratory has been investigating noble metal nanocluster catalyzed transformations, which can provide functional silicon compounds and polymeric materials.1 In the light of previous investigation,2,3 metal catalyzed hydrosilylation reaction has been topic of considerable debates regarding the nature of the true catalyst.

In our investigation since we employ pre-synthesized well-defined nanocluster1 as catalyst, there is an opportunity to delineate the real catalyst in hydrosilylation/hydrogermylation reactions. In an attempt to shed the light on nature of true catalyst in hydrosilylation process we have derived various strategies, which may permit to answer vital question raised about the real nature of the hydrosilylation catalyst.

We will present our results of investigations of the hydrosilylation/hydrogermylation reactions of acetylenes which formally supports the participation of nanocluster as active catalytic species.

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1.Chauhan, B. P. S.; Rathore, J. S. J. Am. Chem. Soc. 2005, 127, 5790.

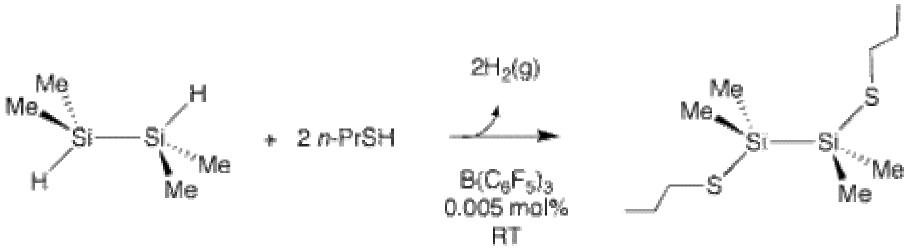
2. Lewis, L. N.; Lewis, N. J. Am. Chem. Soc. 1986, 108, 7228.

3.Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A.; J. Am. Chem. Soc. 1999, 121, 3693.

## 305. Borane-catalyzed Si-H activation: highly selective derivatization of oligohydridosilanes

Daniel J. Harrison, Danielle N. Kobus and **Lisa Rosenberg**, University of Victoria, Victoria, BC, Canada

Our interest in probing the relationship of chain conformation to electronic and optical properties of polysilanes has led us to explore new routes to functionalized oligosilanes and methods for their structural modification. We have focused on exploiting the reactivity of residual Si-H bonds in oligosilanes prepared by metal-catalyzed dehydrocoupling of primary or secondary silanes, but have found that the Si-Si bonds in these compounds are susceptible to cleavage during traditional Si-H transformations such as halogenation, or transition metal-catalyzed hydrosilylation or dehydrocoupling. However, the Lewis acidic borane $B(C_6F_5)_3$ mediates highly chemoselective hydrosilylation of aldehydes and ketones by 1,2-dihydridodisilanes, and heterodehydrocoupling of catechol with these disilanes, without compromising the Si-Si bonds. Interestingly, and relevant to the mechanism of catalysis by this Lewis acidic, electrophilic reagent, $B(C_6F_5)_3$ shows exceptionally high activity for analogous transformations of sulfur-containing substrates, providing new routes to Si-S bonds. We report here the borane-catalyzed hydrosilylation of a thioketone, and dehydrocoupling of mono- and disilanes with both aromatic and straight chain aliphatic thiols.



### 306. Polystyrene Chain Growth from Silica Nanoparticles

**Young J. Cho** and Bob A. Howell, Central Michigan University, Mount Pleasant, MI

The surface of silica nanoparticles may be modified by covalent attachment of compounds which may be utilized as initiation sites for atom transfer radical polymerization (ATRP). Polymers of fixed size may then be grown from the nano sized silica surface. The resulting polymeric structures may have a variety of applications including the preparation of novel chromatographic systems.

## Small Chemical Businesses II

**Organizer:** Diana A. Phillips Kettering University, Flint, MI

### 307. SiGNa Chemistry: A new technology for clean chemistry and hydrogen fuel generation

**Michael Lefenfeld** and James L. Dye, SiGNa Chemistry, LLC, New York, NY

SiGNa Chemistry creates proprietary technologies based on the stabilization of reactive metals that make chemical manufacturing more efficient, safer and cost effective in a variety of industries including the pharmaceutical, petrochemical/desulphurization, organometallic and general synthesis industries. Additionally, the product has applications in the hydrogen fuel cell and environmental remediation markets. Our alkali metal-silica powders allow the chemical industry, such as pharmaceutical development, to combine chemical reactivity and product-stream purification in one easy step. The chemist will be able to take the danger from performing reactions that are violently explosive by transforming the reaction into a smooth solution process. Also, our SiGNa powdered fuels produce hydrogen instantly when the powder is introduced to any water. The entire powder reacts with water, releasing hydrogen gas and forming a safe soluble sodium silicate. The SiGNa material produces large yields of H2 gas (>DoE 2015 target) instantaneously when introduced to any water. These materials have all been submitted for patent approval, manufactured at large scale, and sold to customers. SiGNa leverages these proprietary technologies by collaborating with industry leaders in each of its target markets to develop innovative solutions. We work closely with these partners to combine our specialized expertise and technology with their core competencies to address multiple industry opportunities.

### 308. The Importance of "Intangibles" in Operating a Small Business

**Ronald J. Versic**, Ronald T. Dodge Co., Dayton, OH

The formation and operation of a new small business are often planned and described in terms of a business plan and quantitative income statements and balance sheets. This presentation deals with the "soft" side of a small business in terms of the personal benefits that accrue to the owner/managemant and their employees. The presenter speaks from twenty years of experience in such a business. Thus, the long term effects of such benefits have been observed and are presented here.

### 309. Small chemical businesses: managing the quagmire of data and documentation

Susan Hulett, **Ann Birch**, Judi Zima and Audrey Diadiun, ERS Corporation, Midland, MI

Both small and large chemical businesses face the challenge of collecting, managing, documenting, and communicating data. Although “data” often signifies process or other technical information, it also encompasses human resources and business data, vendor and customer information, and data reportable to government or other institutions. There are literally thousands if not millions of records and electronic files to manage, not to mention the paper in what was intended to be the “paperless environment.” With millions of dollars at their fingertips, large businesses have the money and the personnel to either purchase expensive solutions or develop them in-house. Small businesses are left to deal with a time-consuming problem that grows worse as their business expands. There are affordable tools on the horizon to help small chemical businesses manage their business information and their technical data as well as improve documentation and communication. We will introduce a new web-based service that enables small businesses to collect data in a consistent manner and maintain it 24/7 from any Internet-accessible location. Management and operations personnel can monitor and optimize individual production or laboratory processes and projects. Electronic files can be attached to specific records, making them easy to find and access. Material data can be tracked from raw-material inventory through final product shipment, including related waste streams and OSHA- and SARA-related requirements. Because the service is aligned with ISO specifications, businesses wishing to become ISO-certified get a head-start. We will also show how “mapping” business structure will provide the direction a small business needs while facilitating management tools such as the service described above. Finally, we will show how the use of customized, automated templates streamlines documentation and communication, making customer and internal technical reporting easier and more professional.

## Plenary Lecture: A Stretchable Form of Single Crystal Silicon and High Performance Electronics on Elastomeric Substrates

### 310. A Stretchable Form of Single Crystal Silicon and High Performance Electronics on Elastomeric Substrates

**John A. Rogers**, University of Illinois, Midland, MI

High performance circuits on unconventional substrates with unusual form factors could enable a range of interesting applications: flexible paperlike displays and optical scanners, curved focal plane arrays and conformable sensor skins. Many electronic materials can provide good bendability when prepared in thin film form. Full stretchability is a different and much more challenging circuit characteristic. This feature is required for devices that can flex, stretch or reach extreme levels of bending or for those that can be conformally wrapped around supports with complex, curvilinear shapes. Examples of target applications range from sensors and drive electronics for integration into artificial muscles or biological tissues, to structural health monitors wrapped around aircraft wings. In these systems, strains at the circuit level can exceed the fracture limits of nearly all known electronic materials. This talk describes a stretchable form of silicon that consists of thin (sub-micron) single crystal elements structured, by controlled mechanical manipulation, into shapes with microscale periodic, wave-like geometries. This ‘wavy' silicon, when supported by an elastomeric substrate, can be reversibly stretched and compressed to large levels of strain without damaging the silicon: the amplitudes and periods of the waves change to accommodate these deformations, thereby avoiding significant strains in the silicon itself. Dielectrics, patterns of dopants, electrodes and other elements directly integrated with the silicon yields fully formed, high performance ‘wavy' transistors, pn diodes and other devices for circuits that can be stretched or compressed to similarly large levels of strain. This approach could be useful route to stretchable electronic systems.

## Silicon Symposium - Silicon Chemistry III

**Organizer:** J. Patrick Cannady Dow Corning Corporation, Midland, MI

### 311. Characterization of Trichlorosilane Direct Process Residue

**Arthur J. Tselepis** and Patrick J. Harder, Dow Corning Corporation, Midland, MI

The direct process reaction of Silicon metal with Hydrogen Chloride to form SiHnCl(4 – n ) monomers produces a high-boiling residue (DPR). This material contains a mixture of chlorodisilanes and chlorosiloxanes. Historically, Dow Corning has experienced several safety incidents when handling this stream. This prompted an effort to better understand the hazards associated with direct process residue ( DPR ) and through better understanding we hope to improve the safe handling practices for this class of materials. Trichlor DPR from the Dow Corning Midland Plant was analyzed for composition, flash point, pyrophoricity, etc. New test methods were developed to quantify the shock sensitive nature of the hydrolyzed gels which commonly form when handling this stream. This testing was performed on individual fractionated DPR species and the hazards of each component were quantified. It was determined that SiH containing chlorosiloxanes played a key role in several past safety incidents. Further work led to the discovery that these dangerous SiH containing chlorosiloxanes can be made to rearrange to form HSiCl3 and larger polysiloxanes. This was demonstrated both in the lab and in the manufacturing process. The effect of varying process conditions and the presence of catalytic species on this reaction are discussed. The role of this rearrangement chemistry and the conditions and properties that favor shock sensitive gel formation are also presented. This work has resulted in an increased understanding of the hazards associated with handling this stream and the steps which can be taken to mitigate these hazards.

### 312. Highly-regulated Ladder Polysilsesquioxane

**Masafumi Unno**, Shengho Chang and Hideyuki Matsumoto, Gunma University, Kiryu, Japan

The preparation of cis-trans-cis-Tetrabromotetramethylcyclotetrasiloxane was performed by facile two-step reaction from methylphenyldichlorosilane. This tetrabromide spontaneously decomposed in air to afford a white powder insoluble in organic solvents. Measurements of the TG, IR, and solid-state NMR spectra of the product revealed that a ladder polysilsesquioxane with high thermal stability and stereoregularity was obtained.

### 313. Formation of an Oxo Siloxy Complex from the Reaction of Tungsten Alkylidyne $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ with Water

Laurel A. Morton, Albert A. Tuinman and **Zi-Ling Xue**, The University of Tennessee, Knoxville, TN

Tungsten alkylidyne complex $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ (**1**) was found to react with $H_2O$, yielding oxo siloxy complex $O{=}W(OSiMe_3)(CH_2SiMe_3)_3$ (**2**) and methane. **2** was isolated as $(Me_3SiCH_2)_3(Me_3SiC{\equiv})W{\leftarrow}O{=}W(OSiMe_3)(CH_2SiMe_3)_3$ (**3**), an adduct with **1**. In this reaction, the silyl group in the $\equiv CSiMe_3$ ligand migrates to an oxo ligand, and the $\equiv$C-atom is converted to $CH_4$. Reaction of $(Me_3SiCH_2)_3(Me_3SiC{\equiv}C)W{\leftarrow}O{=}PMe_3$ (**4**) with $H_2O$ was also studied, and found to yield the oxo complex **2** as well.

### 314. Pt-nanocluster Catalyzed Highly Selective Transformation of Triorganosilane to Corresponding Silanols

Alok Sarkar[1], **Moni Chauhan***[2], Abhishek Roka[2] and Bhanu P.S. Chauhan*[1], (1)Nanomaterials Laboratory of Center for Engineered Polymeric Materials, Department of Chemistry, City University of New York, Staten Island, NY, (2)Queensborough Community College, Bayside, NY

Pt-nanoclusters catalyzed, mild, high yielding, selective transformation of silane to silanols (no disiloxane) using water. It is evident that this novel transformation (figure) takes place via the oxidation of Si-H bond, where water acts as oxidant. The methodology is tolerant of the functional groups such as alkene and alkyne, where it is noteworthy that in the presence of platinum metal complexes alkenes and alkynes are known to undergo hydrosilylation reaction. The catalytic activity of various platinum metal complexes was also compared with the present catalytic system. The nature of the true catalytic species was investigated via TEM, UV-vis and Poisoning Studies during the catalysis.

### 315. Superhydrophobic Silicone Nanofibers

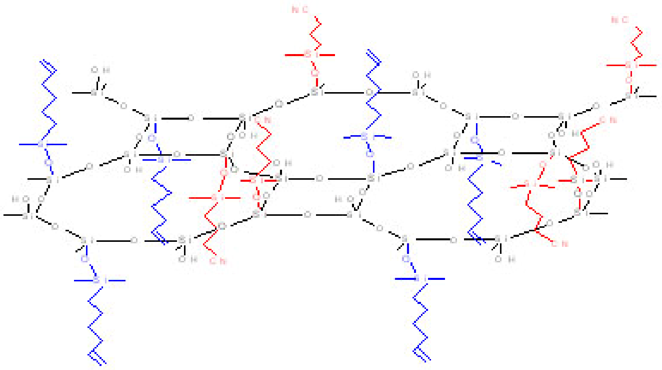
**Randal M. Hill**[1], Gregory C. Rutledge[2] and Minglin Ma[2], (1)Dow Corning Corporation and The Massachusetts Institute of Technology, Cambridge, MA, (2)Massachusetts Institute of Technology, Cambridge, MA

Superhydrophobic mats composed of randomly oriented polystyrene-polydimethylsiloxane AB block copolymer fibers with submicron diameters have been created by electrospinning. Contact angle measurements indicate that the nonwoven fibrous mats possess water contact angles up to 165° and contact angle hysteresis of 15°. The superhydrophobicity is attributed to the combined effects of surface enrichment in silicone as revealed by X-ray photoelectron spectroscopy and the surface roughness of the electrospun mat itself. The relationship between the morphology of the fiber mat and hydrophobicity will be discussed. Fibers range in morphology from beaded nano-fibers to ribbons and span multiple size scales depending on processing conditions. The combination of nanoscale and micron-scale roughness required to achieve superhydrophobicity can be engineered in several different ways. The strong incompatibility between the silicone and the polystyrene blocks cause this copolymer to microphase phase separate even in dilute solution and the fibers also show a disordered microphase separated structure by transmission electron microscopy. Calorimetric studies confirm the strong segregation between the polystyrene and polydimethylsiloxane blocks.

### 316. Apophyllite-derived organosilicon polymer nanocomposite preparation

**M.A. Boucher**[1], D.E. Katsoulis[2], E.A. McQuiston[2], B. Zhu[2] and Malcolm E. Kenney[3], (1)Utica College, Utica, NY, (2)Dow Corning Corporation, Midland, MI, (3)Case Western Reserve University, Cleveland, OH

A mineral-derived organosilicon sheet polymer was studied as a filler in a silicone polymer.  The silicon polymer was a vinyldimethyl silicon polymer.  The organosilicon polymer was A--HEM$_2$-CM$_2$, $[((C_6H_{13})(CH_3)_2SiO)_{\sim 0.25}((NCC_3H_6)(CH_3)_2SiO)_{\sim 0.25}(OH)_{\sim 0.50}SiO_{1.5}]_n$. It was synthesized from apophyllite ($KCa_4Si_8O_{20}(F,OH)$°¤$8H_2O$) and a mixture of two chlorosilanes, 5-hexenyldimethylchlorosilane and 3-cyanopropyldimethylchlorosilane.  The multiple functional groups on the silicate backbone create a system in which the silicate layers can be easily exfoliated in non-polar fluids and also allow for further reactivity including hydrosilylation.  A--HEM$_2$-CM$_2$ was processed by gelling it with an organic solvent, lyophylization of the gel, and the processed A--HEM$_2$-CM$_2$ was mixed with the silicone polymer and sonicated. The mixture was polymerized using hydrosilylation. This method avoided mechanical mixing and gave nanocomposite monoliths in which the silicate filler was very well dispersed.



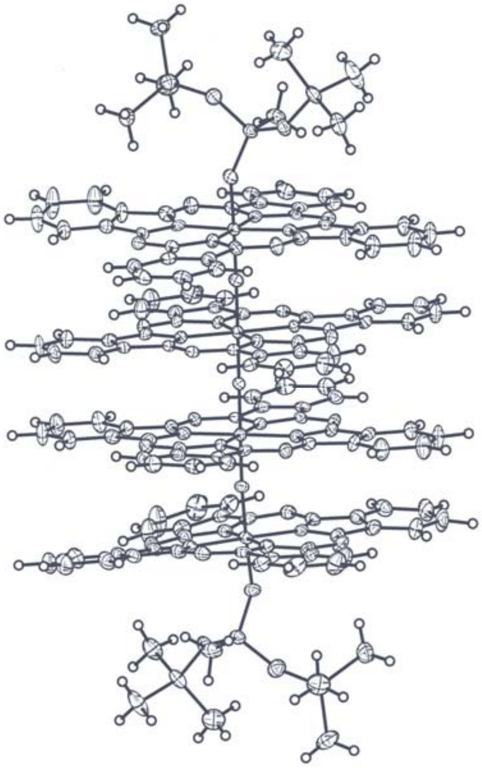
## Silicon Symposium - Silicone and Organosilicone Materials I

**Organizer:** William J. Schulz Jr. Dow Corning Corporation, Midland, MI

### 317. Octahedral Organosilicon Oligomers

**Malcolm E. Kenney**[1], Vance O. Kennedy[1], Dainius Macikenas[1], Andrew A. Pinkerton[2] and John Protasiewicz[1], (1)Case Western Reserve University, Cleveland, OH, (2)University of Toledo, Toledo, OH

A set of monomeric, dimeric, trimeric and tetrameric silicon phthalocyanines terminated with OSiOSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$ groups has been prepared and crystallized, and the structure of each has been determined. In examining the results, particular attention has been paid to the ring–ring distances, the degree and kind of ring warping and the amount of rotation of the rings with respect to each other. This has allowed comparisons to be made of the effects of terminal group structure and crystal packing on ring–ring distance, degree of ring non-planarity, and relative ring rotation in oligomeric silicon phthalocyanines.



### 318. Ring opening polymerization of cyclsoiloxane in surfactant templates

**François Ganachaud**, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, France, Matthieu Barrère, DuPont Performance Coatings, Wuppertal, Germany, Mariusz Kepczynski, Jagiellonian University, Krakow, Poland and Patrick Hémery, Université Pierre et Marie Curie, Paris, France

The ring opening polymerization of cyclosiloxanes, most specifically $D_4$, in aqueous dispersion has long been applied by silicone manufacturers to prepare tailored polydimethylsiloxane emulsions of use in various applications, including cosmetics and textile industries. Polymerization in miniemulsion or suspension were largely studied by our team and others, whereas emulsion processes are difficult to carry out, because of big monomer droplet nucleation, and remains confidential. This presentation aims at describing a different approach, where surfactant supramolecular assembly in water are used as templates for further cyclosiloxane polymerization. In a first part, water-filled nanocapsules of highly crosslinked silicone are prepared by hydrolysis/condensation of $D_4^H$ inside the bilayer of catanionic vesicles. In a second part, microemulsions of $D_4$ are used as main reactors for polymerization of starved feed monomer to generate silicone nanodroplets as low as 12 nm in size. A genuine process of “dynamic ostwald ripening”, which transforms an emulsion of 50 nm or less in diameter into larger isodisperse nanodroplets (150 nm), will also be shown in this latter case.

## 319. Liquid/liquid separation of polysiloxane-supported catalysts

**Melissa A. Grunlan**, Katherine R. Regan and David E. Bergbreiter, Texas A&M University, College Station, TX

Polysiloxane-supported catalysts may be isolated from reaction products and recycled following a monophasic reaction by using a simple liquid/liquid separation strategy. The phase-selective solubility behavior of polysiloxanes was studied in a thermomorphic and a latent biphasic solvent system. Polysiloxanes (RR'Si-O) (where R = Me and R' = Me or octyl) were tagged with a visible dye probe and their solubility behavior in a thermomorphic (heptane/DMF) and a latent biphasic (heptane/EtOH-H2O) system studied with UV-vis spectroscopy. An organocatalyst, quinine, was immobilized onto a polydimethylsiloxane (PDMS) and used to catalyze Michael addition reactions of several substrate pairs. A latent biphasic liquid/liquid separation was used to recover and reuse the polymeric catalyst though 5 cycles. Product yields were similar to those catalyzed by the “unbound” catalyst.

## 320. Minimally adhesive siloxane and fluorosiloxane surfaces

**Melissa A. Grunlan**, Texas A&M University, College Station, TX and William P. Weber, University of Southern California, Los Angeles, CA

Noninteractive minimally adhesive polymer surfaces (MAPs) which resist adhesion are of interest for next-generation marine coatings as well coatings for implantable medical devices. Siloxanes, fluoropolymers, and fluorosiloxanes have been shown to be effective non-toxic foul-release surfaces. Multiple synthetic strategies have been utilized to prepare several series of well-defined siloxane and fluorosiloxane films. Their properties (e.g. storage modulus, glass transition temperature, and surface wetting behavior) have been correlated with their ability to resist adhesion of marine biofoulers. Linear as well as star polymer architectures have been explored. In addition, the degree of fluorination and molecular weight has been systematically varied. Photochemical and thermal crosslinking methodologies have been used to prepare siloxane and fluorosiloxane films.

## 321. Surface characterisation of siloxane coatings prepared using atmospheric pressure plasma liquid deposition

**Lesley-Ann O'Hare**[1], Alan M Hynes[1] and Morgan R. Alexander[2], (1)Dow Corning Plasma Solutions, Midleton, Ireland, (2)University of Nottingham, Nottingham, United Kingdom

Atmospheric pressure plasma liquid deposition - APPLD, combines atmospheric pressure plasma with injection of atomised liquid from the delivery nozzle directly into the plasma. As such, the liquid within each droplet is protected from the plasma, and is carried intact to the surface, where it spreads and polymerises to form a conformal, high-value functional coating, which retains the properties of the original precursor molecule.

The relationship between the chemistry of coatings deposited using this technique and the plasma deposition parameters has been investigated using a complementary suite of surface analytical techniques: contact angle analysis, X-ray photoelectron spectroscopy and atomic force microscopy.

A new methodology for curve-fitting of the XPS Si 2p and C 1s core levels of siloxane materials has been developed using siloxane standards. This method has been expanded to be used on siloxane coatings thinner than the depth of analysis of XPS. This enabled the chemistry of the coatings to be determined from XPS analysis without interference from the substrate.

The chemistry of siloxane coatings deposited on poly(ethylene terephthalate) film have been related to the plasma parameters utilised during deposition. Up to 95% polymeric siloxane [(CH3)3SiO1/2 and (CH3)2SiO2/2] have been retained for deposition of poly(dimethylsiloxane) precursor. The use of a poly(hydrogenmethylsiloxane) precursor led to a more oxidised coating, with up to 25% siloxane in (CH3)SiO3/2 environment. The trends in deposition rate for PDMS and PHMS were also found to be different.

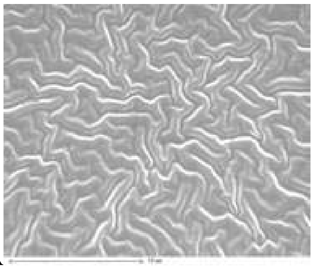
Siloxane coatings durable to immersion in boiling water for 30 minutes have been achieved by plasma treatment of the substrate prior to deposition, and by plasma treatment of the coating following deposition.

## 322. Structuring silicone interfaces with hydrophilic biocompatible polymers

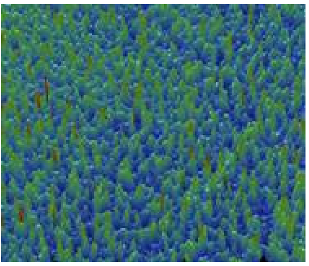
**Michael A. Brook**[1], Heather D. Sheardown[1], Daniel (Yang) Chen[1], Amro Ragheb[1] and Hong Chen[2], (1)McMaster University, Hamilton, ON, Canada, (2)Wuhan University of Technology, Wuhan, China

While silicones have many advantageous properties for use as biomaterials, their very high hydrophobicity can compromise their use in certain application. We shall outline a series of generic steps that permit control of the surface morphology of silicones and tethering of a variety of biological molecules that render the surfaces hydrophilic. Hydrophilic polymers such as poly(ethylene oxide) can be encouraged to bloom to RTV-based silicone elastomer surfaces where either bimodal or spinodal decomposition leads to surface of controlled roughness (1 μ, **A**). Alternatively, acid catalyzed equilibration of silicone elastomers leads to controlled erosion of the silicone surface and introduces functional groups such as Si-H that serve as handles for grafting of hydrophilic polymers (120 nm, **B**). In this case, the patterning is affected by the acidic conditions used. Once modified by a biocompatible PEO spacer, these surfaces serve as generic platforms for the attachment of biological molecules that can include saccharides and proteins. A discussion on the correlation of silicone surface properties to biocompatibility, including ability to support cell growth (corneal epithelial cells, **C**), will be presented.

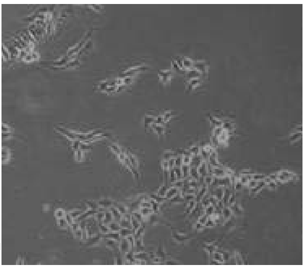
**A**



**B**



**C**



## Silicon Symposium - Synthesis of Organosilicon Compounds and Intermediates I

**Organizer:** Binh T. Nguyen Dow Corning Corporation, Midland, MI
**Organizer:** Charles E. Neal Jr. Dow Corning Corporation, Midland, MI

### 323. Nonclassical silyl hydrides of iron studied by DFT calculations

**Georgii I. Nikonov**, Brock University, St. Catharines, ON, Canada and Sergei F. Vyboishchikov, Universitat de Girona, Girona, Spain

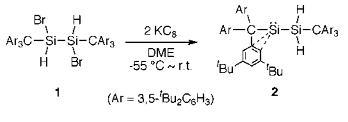
The DFT calculated structures of $Cp(L)Fe(SiMe_nCl_{3-n})_2H$ (L = CO, $PMe_3$; n = 0-3) exhibit an unusual distortion from the ideal piano-stool geometry in that the silyl ligands are strongly shifted toward the hydride and there is a strong trend towards flattening of the $FeSi_2H$ fragment. Such a distortion leads to short Si—H distances (range 2.030–2.075 Å) and large Mayer bond orders for two equivalent H···Si interligand interactions. A novel feature of these extended H···Si interaction is that they are rather insensitive towards the substitution at the silicon atom and the orientation of the silyl ligand relatively the Fe—H bond. We rationalize these structures in terms of double Si-H σ-complexation of tentative hypervalent monoanions $(R_3Si—H—SiR_3)^—$ to the cationic fragment $[Cp(CO)Fe]^+$. In contrast, the calculated structural and NMR features of the related complexes $Cp(L)Fe(SiMe_nCl_{3-n})(H)(Me)$ (n = 0-3) allow for their rationalization as usual $\eta^2$-Si—H silane σ-complexes. The series of "dihydride" complexes $Cp(OC)Fe(SiMe_nCl_{3-n})H_2$ (n = 0-3) is different from the previous two families in that the type of interligand interactions strongly depends on the substitution on silicon. They can be classified either as usual dihydrogen complexes, e.g. $Cp(OC)Fe(SiMe_2Cl)(\eta^2-H_2)$, or as compounds with nonclassical H···Si interactions.

## 324. Synthesis, structure, and reactions of intramolecularly stabilized silylene by arene coordination

**Masaaki Ichinohe**, Tomoyasu Honda and Akira Sekiguchi, University of Tsukuba, Tsukuba, Japan

Divalent silicon compound, silylene is one of the fundamental species in organosilicon chemistry, which was postulated as a reactive intermediate until mid-1970s. But now some isolable silylenes are known. In this paper, we want to report the synthesis, structure, and reactivity of intramolecularly stabilized silylene by the arene coordination by using tris(3,5-di-*tert*-butylphenyl)methyl group as a new steric protecting group. Reductive debromination of dibromodisilane derivative **1** with potassium graphite (KC8) in 1,2-dimethoxyethane gave silylsilylene **2** instead of the expected disilene (Scheme 1). The structure of **2** was unequivocally determined by X-ray crystallography. Characteristic structural parameters of **2** are follows: 1) silylene silicon atom (Si1) is very close to ipso (C2) and ortho (C3) carbons of one 3,5-di-*tert*-butylphenyl ring [atomic distances of Si1-C2 and Si1-C3 are 2.214(3) and 2.259(3) Å, respectively], 2) silylene interacting benzene ring is distorted; C2-C3 bond is apparently elongated [1.433(4) Å], and bond alternation is observed in another C-C bonds of coordinated benzene ring. These structural features indicate that **2** is not a free silylene, but intramolecular arene-coordinated silylene. Reactivity of **2** showed typical silylene reaction. The reactions of **2** with methanol, triethylsilane, and acetylenes were not so rapid, but the corresponding adducts were clearly formed. The mechanism to form **2** upon the reduction of **1** will be also discussed.

***Scheme 1***



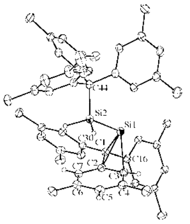


***Figure 1.*** ORTEP drawing of **2**. Methyl carbon atoms on *tert*-butyl groups and hydrogen atoms except for hydrogen atoms on C3, C5, and C7 are omitted for clarity.

## 325. Hydrosilylation of 1,3-Cycloalkadiene with Hydrochlorosilane

**Bok Ryul Yoo**, Weon Cheol Lim, Yoo Kyong Jeon and Joon Soo Han, Korea Institute of Science and Technology, Seoul 130-650, South Korea

1,3-Cycloalkadienes such as cyclopentadiene and cyclohexadiene undergo the hydrosilylation reaction with hydrochlorosilanes to give (chlorosilyl)cycloalkenes and bis(chlorosilyl)cycloalkanes. Generally 1,3-cycloalkadienes reacted with a variety of hydrochlorosilanes $RHSiCl_2$ (R= Cl,[1] H, Me,[2] i-Pr, Ph, c-pentyl) at temperatures ranging from room temperature to 80 °C in the presence of group 10 metal (Ni, Pd, Pt) complex to afford 3-(chlorosilyl)cycloalkenes in good yields. Interestingly, the thermal reaction of dicyclopentadiene with the hydrochlorosilanes in hydrocarbon solvent at 250 °C give 3-(chlorosilyl)cyclopentenes in 21-76% yields. The thermal hydrosilylation of 3-

(chlorosilyl)cycloalkenes with the hydrochlorosilanes occurred effectively at the high temperature of 300-320 °C to give bis(chlorosilyl)cycloalkanes as major products. The reactivity of $RHSiCl_2$ decreases as the bulkiness of R-substituent on the silicon increases. In this presentation we will discuss the results in details. 1. Marinetti, A. *Tetrahedron Lett.* **1994**, *35*(32), 5861-4. 2. Okada, T.; Morimoto, T.; Achiwa, K. *Chem. Lett.* **1990**, 999-1002.

### 326. Isomerization between (Disilanylidene)iron and (Disilene)iron

**Katsunori Suzuki**, Wataru Setaka, Chizuko Kabuto and Mitsuo Kira, Tohoku University, Sendai, Japan

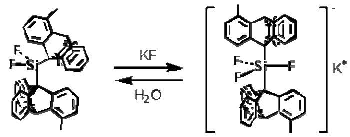
We have recently reported the synthesis and unique isomerization of iron complexes of (*E*)- and (*Z*)-1,2-dichlorodisilenes, {**1E**; $Fe(CO)_4[\eta^2$-(*E*)-($^t$$Bu_2MeSi$)(Cl)Si=Si(Cl)(Si$^t$$Bu_2Me$)], **1Z**;$Fe(CO)_4[\eta^2$-(*Z*)-($^t$$Bu_2MeSi$)(Cl)Si=Si(Cl)(Si$^t$$Bu_2Me$)]}, which constitute not only the first disilene complexes with *E*, *Z*-isomerism but also the first complexes with halogen-substituted disilene ligands1. A mechanism involving a (disilanylidene)iron as a key intermediate has been proposed for the preferable formation of **1Z** during the synthesis and the thermal isomerization of **1Z** to **1E**. We report herein that in the presence of a strong donor such as DMAP, the (disilanylidene)iron that is proposed as a key intermidiate in the synthesys of **1E** and **1Z**, is isolated and that the mode of isomerization between (disilene)iron and (disilanylidene)iron is remarkably modified in the presence of a donor. The reaction of tetrachlorodisilane **2** [($^t$$Bu_2MeSi$)$SiCl_2SiCl_2$(Si$^t$$Bu_2Me$)] with $K_2Fe(CO)_4$ in the presence of 4-dimethylaminopyridine(DMAP) as a strong donor gave (disilanylidene)iron complex **3-DMAP** [{$(OC)_4Fe$=Si(Si$^t$$Bu_2Me$)$SiCl_2$Si$^t$$Bu_2Me$}-DMAP] instead of **1E** or **1Z**. Complex **3-DMAP** was isolated as yellow crystals in 48% yield and characterized by NMR and ESI-MS. Interestingly, (disilene)iron complex **1E** was found to isomerize in the presence of DMAP at room temperature to give **3-DMAP**. The reaction of less bulky tetrachlorodisilane **4** [($^t$$BuMe_2Si$)$SiCl_2SiCl_2$(Si$^t$$BuMe_2$)] with $K_2Fe(CO)_4$ in dimethoxyethane(DME) gave the corresponding solvent coordinated (disilanylidene)iron complex **5-DME** {[$(OC)_4Fe$=Si(Si$^t$$BuMe_2$)$SiCl_2$Si$^t$$BuMe_2$]-DME}, which isomerized to the corresponding (disilene)iron in $C_6D_6$ solution. The present results indicate that the relative stability and isomerization rates among (disilanylidene)iron and (*E*)- and (*Z*)-(disilene)iron complexes are very sensitive to solvents, an additional donor, and bulkiness of the substituents at the unsaturated silicon atoms.

1) Hashimoto, H.; Suzuki, K.; Setaka, W.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2004**, *126*, 13628.

### 327. Di(triptycyl)difulorosilane and Anti-Apicophilic Di(triptycyl)trifluorosilicate. Introduction of a Clutch Function in a Molecular Gear System

**Wataru Setaka**, Takayoshi Nirengi, Chizuko Kabuto and Mitsuo Kira, Tohoku University, Sendai, Japan

Correlated rotation of two triptycyl groups in ditriptycyl methanes and related compounds has been investigated as typical molecular gear systems by Mislow's and Iwamura's groups [1]. We report herein the synthesis of di(methyltriptycyl)difluorosilane (**1**) as a novel molecular gear and the successful introduction of a clutch function in this system using structural changes between **1** and the corresponding silicate. Di(methyltriptycyl)difluorosilane **1** was synthesized as a diastereomeric mixture of two phase isomers (*dl* and *meso*) by the reaction of methyltriptycyl lithium with tetrafluorosilane. Gear rotation of the two triptycyl groups was confirmed by $^1$H NMR spectroscopy. The reaction of silane **1** with potassium fluoride gave the corresponding silicate **2** quantitatively. Although electronegative atoms prefer to occupy apical positions in a trigonal bipyramidal (TBP) structure of a usual silicate (apicophilicity), the two triptycyl groups of silicate **2** was found by X-ray crystallography to be located at the apical positions of the TBP structure in crystals probably due to the steric bulkiness of the two triptycyl groups. No phase isomers of **2** were observed by $^1$H NMR spectra in the range of 300 – 193 K, indicating that the two triptycyl groups in **2** rotate independently. Because silane **1** is reproduced quantitatively from **2** by the reaction with an excess amount of water, the interconversion between **1** and **2** constitutes the first successful introduction of a clutch function in a molecular gear. [1] Mislow, K. et al. *J. Am. Chem. Soc.* **1981**, *103*, 957; Iwamura, H. et al. *J. Am. Chem. Soc.* **1981**, *103*, 958.



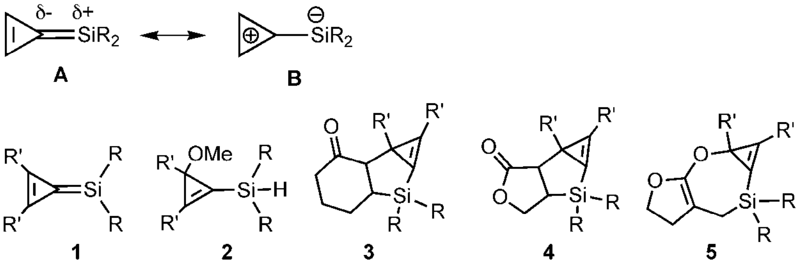
1
Gear Rotation

2
Free Rotation

### 328. Reactivity of the inversely polarized 4-silatriafulvene

**Kenkichi Sakamoto**, Yoshihiro Kon, Kazuhiro Tsuchida, Chizuko Kabuto and Mitsuo Kira, Tohoku University, Sendai, Japan

Among various silicon-carbon doubly bonded compounds, 4-silatriafulvenes have attracted much attention because of their unique electronic properties. The intrinsic polarity of the Si=C double bond in 4-silatriafulvene (**A**) is expected to be reduced by the significant contribution of resonance structure **B**. We have recently synthesized the first isolable 4-silatriafulvene (**1**, R = t-BuMe$_2$Si, R' = t-Bu). Compound **1** reacts with methanol to give **2** quantitatively. The regioselectivity is completely opposite to that for the alcohol addition to common silenes; the OH hydrogen and methoxy groups of methanol are bonded to the unsaturated silicon atom and a ring carbon atom in **1**, respectively. The result indicates the significant contribution of the resonance form **B** and the unsaturated silicon atom reacts as a nucleophile. The unusual nucleophilic reactivity of **1** is also observed for reactions of conjugated ketones and esters, such as cyclohexenone, 2(5H)-furanone and α-methylene-γ-butylolactone. These compounds react with **1** to give 1:1 adducts, **3**, **4**, and **5**. The first step of the reactions would be a Michael-type nucleophilic attack of the unsaturated silicon atom of **1** to the conjugated carbonyl compounds. Structures and formation mechanism of the adducts will be discussed.



## Silicon Symposium - Silicon Chemistry IV

### 329. Heavy analogues of cyclopropene: new class of reactive organometallics of group 14

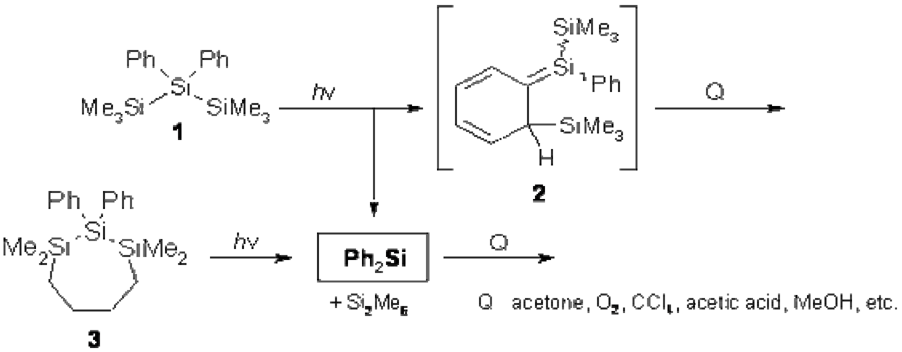
**Vladimir Ya. Lee**, Hiroyuki Yasuda, Masaaki Ichinohe and Akira Sekiguchi, University of Tsukuba, Tsukuba, Japan

The heavy analogues of cyclopropenes, that is unsaturated three-membered ring compounds of Si, Ge and Sn atoms, represent one of the most attractive synthetic challenges in the chemistry of group 14 elements of the past decade. This research field of the highly reactive organometallics is currently very intensively developing, and here we present our recent contributions to the field, particularly the synthesis of the hybrid heavy cyclopropenes. 3*H*-disilagermirene $R_4GeSi_2$ **1** with a skeletal Si=Si bond was prepared by the coupling reaction of $R_2GeCl_2$ and $RSiBr_3$ with Na in toluene. Either thermal or photochemical isomerization of **1** resulted in a quantitative formation of 1*H*-disilagermirene **2** featuring a skeletal Si=Ge bond. 1*H*-siladigermirene $R_4SiGe_2$ **3**, as well as 1*H*-trigermirene $R_4Ge_3$ **4**, both featuring the skeletal Ge=Ge bonds, were synthesized by the reaction of $RGeCl_2GeCl_2R$ with either $R_2SiLi_2$ or $R_2GeLi_2$ in toluene. The particular structures and reactivity of compounds **1-4** will be also presented.

### 330. Direct detection and characterization of diphenylsilylene by laser flash photolysis of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane

**Andrey G. Moiseev**, Erica Held and William J. Leigh, McMaster University, Hamilton, ON, Canada

Diphenylsilylene has been generated and detected in solution for the first time by laser flash photolysis of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane (**1**), as a short-lived species exhibiting $\lambda_{max}$=520 nm and $\tau$~2-3 μs in anhydrous hexane at 25°C. The absorptions due to the silylene are superimposed on much stronger transient absorptions that have been assigned to the silene derivative **2** ($\lambda_{max}$=460 nm; $\tau$~200-300 μs), on the basis of comparisons of its spectrum and reactivity with corresponding data for other, related silene derivatives. The silylene is formed in even higher yields relative to other transient products upon laser photolysis of the cyclic trisilane **3**. Absolute rate constants have been determined for reaction of silene **2** and diphenylsilylene with a wide variety of trapping agents, including alcohols, carboxylic acids, ketones, silanes, alkenes, alkynes, dienes, and oxygen.

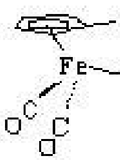


## 331. Oligosilaferracycles: variety of chemistry dependent upon the silicon atom content

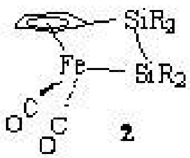
**Keith H. Pannell**, Hemant K. Sharma, Paula Apodaca and Francisco Cervantes-Lee, U. T. El Paso, El Paso, TX

We recently reported that base-treatment of cyclopentadienylirondicarbonyl complexes of chloromethylsilanes, ($\eta^5$-$C_5H_5$)Fe(CO)$_2$SiMe$_2$CH$_2$Cl, or their isomers ($\eta^5$-$C_5H_5$)Fe(CO)$_2$-CH$_2$SiMe$_2$Cl, led to the formation of a new class of silametallacycle, **1**[1a]. Furthermore, base-treatment of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$SiR$_2$SiR$_2$Cl could lead to disilaferracycles, **2**[1b].

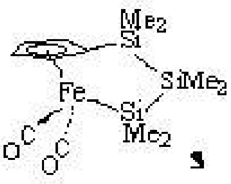
We have extended this chemistry to trisilferracyles, **3**, and tetrasilaferracycles, **4.** Whereas the chemistry of **1** can be dominated by a ring-opening reaction to form organometallic polymers, complexes **3** are generally stable while complexes **4** exhibit a ring contraction both with and without isomerization, upon photolysis but, to date, no polymerization chemistry.



1



2



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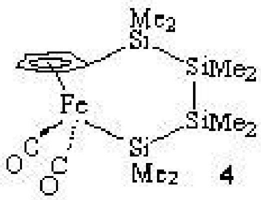


4

The most readily ring-opened silaferracycle, **1**, R = Me, may be used as a catalyst to facilitate ring-opening in those systems that have previously resisted such chemistry, e.g. **1,** = $^{n}$Bu providing a new route to polymer formation.

References: 1(a) Sharma, H. K.; Cervantes-Lee, F.; Pannell, K. H. *J. Am. Chem. Soc.* **2004**, *126*, 1326. 1(b) Sharma, H. K.; Pannell, K. H. *Chem. Commun.* **2004**, 2556.

### 332. Acid Catalysed Interconversion of Cyclosiloxanes

**Khristopher E. Alvarez**[1], Peter G. Taylor[2], Thomas H. Lane[1] and Alan R. Bassindale[2], (1)Dow Corning Corporation, Midland, MI, (2)The Open University, Milton Keynes, United Kingdom

The polymerisation of cyclosiloxanes is an active area of research. Base catalysed ring opening polymerisation of cyclosiloxanes is well understood, but the mechanism of acid catalysed polymerisation of cyclic siloxanes is more controversial. An interesting example of an acid catalysed reaction of a cyclosiloxane was published in 1978 by Spielvogel and Frye who reported the interconversion of 2,6-trans-diphenylhexamethylcyclotetrasiloxane to an equimolar mixture of the cis and trans isomers of the cyclosiloxane.1 The interconversion was reported to occur rapidly in the presence of a Lewis acid and a polar aprotic solvent. No production of the 2,4- isomers or linear oligomers were reported.

We have further defined this system and offer mechanistic insights for the acid catalysed interconversion of cyclosiloxanes without polymerisation. The use of a proton sponge prevented both the interconversion and the polymerization reactions. The reaction is influenced by water, but is not controlled by acid strength. Instead, this interconversion reaction is dominated by the nucleophilic counteranion, with attack at silicon to form an extra-coordinated intermediate, which undergoes facial Berry pseudo-rotations to yield the observed mixture of isomers (i.e. without breaking a siloxane bond). Triflic acid in polar aprotic solvents promotes the interconversion without the formation of any products from redistribution. This behaviour is unique given that other protic acids (H2SO4, HNO3, HCl,,$^{a}$H2O) yield only products from redistribution. This observation underscores the importance of the nucleophilic behaviour of the acid counteranion in the reaction scheme.

Spielvogel, D. E.; Frye, C. L. J. Organomet. Chem. 1978, 161(2), 165.

### 333. The impact of silane T-groups on the yield and morphology of treated silicas

**Anthony Revis**, Csilla Kollar, Anil K. Tomar and Lisa M. Boswell, Dow Corning Corporation, Midland, MI

Treatment of silicas with organosilanes has found a wide variety of uses, especially in the area of compounded rubbers. Deposition of silanes containing hydrolyzable D-groups under aqueous conditions is a popular route for treating the silicas, making them hydrophobic. For applications where permanent attachment or stronger interactions are needed, hydrolyzable silanes having a reactive side chain are added. This is typically done at less the 10% of the total formulation weight. One of the shortfalls of the aqueous process is a deposition yield that can be less than 70%. This paper will discuss how to improve the deposition yield by adding a small amount of silanes having three hydrolyzable sites, T-group silanes. It will also discuss the mechanistic implications on the hydrolysis steps leading to deposition. In addition, the paper will discuss the potential impact of T-group silanes of various chain lengths on the rheological properties of tire rubber. Specially, the paper will discuss reason why the chain length of the T-group silane does not seem to dramatically distort the particle to polymer interface or particle coverage based on the modulus results. The reasons for this will be discussed.

## Silicon Symposium - Silicone and Organosilicone Materials II

**Organizer:** Alan R. Bassindale The Open University, Milton Keynes, United Kingdom

### 334. Glucose oxidase immobilibzation into organosiloxane membranes

**Olga I. Shchegolikhina**[1], Yulia A. Molodtsova[1], Lilia V. Lukachova[2], Elena E. Karyakina[2] and Arkady A. Karyakin[2], (1)A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia, (2)M.V. Lomonosov Moscow State University, Moscow, Russia

Biosensors are devices where an effect of analyte on the sensitive biological element – enzyme – is transdused into signal suitable for the registration and following treatment. Design of biosensors requires a search for suitable matrices for enzyme immobilization. Selectivity, sensitivity, reprodusibility and lifetime of a biosensor depend on individual features of enzyme-containing membrane. Earlier it was found that these features could be improved by use of water insoluble membranes obtained from water-organic mixtures with high content of organic solvent [1]. In this work siloxane membranes were used as inert matrices for glucose oxidase (GOD) immobilization. For this purpose phenylsilantriol PhSi(OH)3 and cyclic stereoregular polysilanols [PhSi(O)OH]n (n = 4, 6, 12) [2] were used as precursors. GOD immobilization was carried out from water-acetonitrile mixtures containing the enzyme and the silanols. It was found that on the one hand the high content of acetonitrile (80-90 %) in water-organic mixture does not effect the enzyme activity. On the other hand it provides a good solubility of the silanols. Activity and stability of GOD-containing membranes obtained were investigated. A calibration plot was obtained for the glucose detector designed from a membrane on the base of [PhSi(O)OH]6 which was stable and had better properties than other ones. On the base of these data optimal concentrations of the water-organic mixture components (GOD, silanols, water) for a perspective GOD immobilization were established.

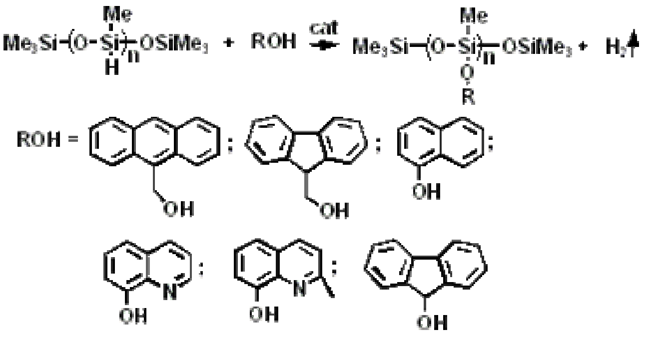
[1] A.A. Karyakin, E.E. Karyakina, L. Gorton, O.A. Bobrova, L.V. Lukachova, A.K. Gladilin, A.V. Levashov, Anal. Chem., 1996, 68, 4335-4341. [2] O.I. Shchegolikhina, Yu.A. Pozdniakova, Yu.A. Molodtsova, S.D. Korkin, S.S. Bukalov, L.A. Leites, K.A.

Lyssenko, A.S. Peregudov, N. Auner, D.E. Katsoulis, Inorg. Chem., 2002, 41, 6892-6904.

## 335. Highly Fluorescent Polysiloxanes: Possible Photonic Materials

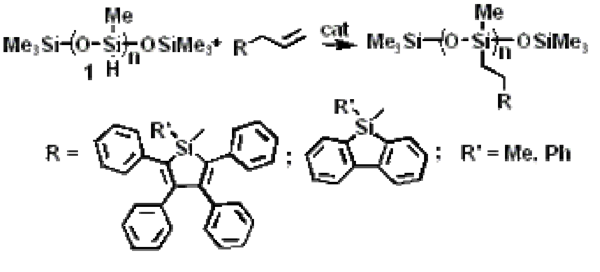
**Irina Toulokhonova**, Ben Bjerke-Kroll, Steve Kehoe, Joyce Ai Vee Er, Julie L. Harris and Robert West, University of Wisconsin, Madison, WI

Fluorescent polysiloxanes were synthesized by: a) dehydrocoupling of alcohols or phenols with poly(methylhydrosiloxane) (PMHS) (Scheme1):



Scheme **1**. Dehydrocoupling of alcohols and phenols with PMHS.

and b) hydrosilylation of novel allylsiloles with PMHS (Scheme 2):



Scheme **2**. Hydrosilylation of allylsiloles with PMHS.

The synthesis, electronic absorption and emission of these polymers will be described. Several of these polysiloxanes exhibited very strong fluorescence, making them candidates for polymer light emitting diodes or other photonic materials.

## 336. Silicone Micro and Nanofibers

**Steven A. Snow**[1], Randal M. Hill[2], Gregory C. Rutledge[3], Minglin Ma[3], Aneta I. Clark[1], Brad R. Fogg[1], Omar Farooq[1], Randall Schmidt[1] and Peter Y. Lo[1], (1)Dow Corning Corporation, Auburn, MI, (2)Dow Corning Corporation and The Massachusetts Institute of Technology, Cambridge, MA, (3)Massachusetts Institute of Technology, Cambridge, MA

We have fabricated superhydrophobic micro- and nanofibers (diameters of 10 to 10,000 nm) from organosilicone polymers via an electrospinning process. Nonwoven mats of the fibers were characterized by SEM and their contact angles versus water. The mats were superhydrophobic membranes with contact angles between 150-171 degrees. Silicone-organic copolymer fibers possessed a low surface energy because the silicone block of the copolymers preferentially segregated to the surface of the fibers during the electrospinning process. Along with the low surface energy, the superhydrophobicity of the fibers was also due to a combination of nanoscale (fiber diameter) and micron-scale (fiber-fiber spacing) roughness. The mats were porous with water repellency greater than standard test methods were able to measure. The combination of the useful high surface area properties of nanofibers with the attractive features of silicones (low surface energy, fire retardancy, thermal stability) should lead to many diverse applications of these fine fiber mats including filtration,protective garmenting and biomedicine.

## 337. Syntheses of Linear Ethoxysiloxanes from Triethoxysilane

**Takahiro Gunji**, Koji Arimitsu and Yoshimoto Abe, Tokyo University of Science, Noda, Japan

Linear ethoxysiloxanes are promising compounds which are formed by the acidic-hydrolysis of tetraethoxysilane in sol-gel process. The formation of these linear oligomers are indirectly confirmed by NMR and theoretical calculations, but they have never been isolated because of the difficulty in the isolation due to the low selectivity. Recently, an oxidative coupling of hydrosilyl groups was reported by means of the reaction in the presence of Wilkinson's catalyst. Although the reaction process is unknown, this reaction is applicable for the stepwise synthesis of ethoxyoligosiloxanes. In this work, a selective synthesis of ethoxyoligosiloxanes was studied by the oxidation of triethoxysilane (TES) and following substitution reaction. TES was charged in a flask equipped with oxygen gas inlet-tube and reflux condenser followed by addition of toluene and Wilkinson's catalyst. After introducing oxygen gas into the solution, it was heated for several hours. The progress of the formation of pentaethoxydisiloxane (PEDS) was monitored by gas chromatography. After evaporation and fractional distillation, PEDS was isolated in good yield. This reaction includes some reactions: oxidation of TES to form silanol, substitution of silanol to TES and coupling reaction of silanol and ethanol. The production of triethoxysilanol and hexaethoxydisiloxane supports the reaction pathway. The yield of PEDS was dependent on the temperature, molar ratio and the rate of the oxygen introduced. A further reaction was carried out by using PEDS in the same procedure. In this reaction, nonaethoxytetrasiloxane was synthesized less selectively. The production of decaethoxytetrasiloxane and octaethoxycyclotetrasiloxane was confirmed

by gas chromatography, which were formed by the coupling reaction with ethanol and an intramolecular cyclization.

### 338. Making new siloxanes: Routes to alternating cyclics and polymers

Kim-Anh Thi Nguyen[1], Stephen Clarke[1], **Janis Matisons**[1] and Brian W. Skelton[2],
(1)Nanomaterials Research Group, Flinders University, Adelaide, Australia,
(2)University of Western Australia, Australia

Polydimethylsiloxanes (PDMS) are well known siloxane polymers with high thermal and oxidative stability, high gas permeability, low glass transition temperature, low surface energies, low solubility, and low dielectric constants, etc. However, introduction of phenyl groups attached directly to the silicon atoms of a polymer improves its low temperature properties, thermal oxidative stability and the radiation resistance of the polymer. The association between the methyl and phenyl groups on the siloxane backbone in a controlled manner may be useful in commercial applications. Alternating cyclotetrasiloxanes and high molecular weight alternating siloxane copolymers have been synthesised by heterofunctional condensation and fully characterised by NMR, FTIR, elemental analysis, GPC, TGA, DSC and XRD spectroscopy where applicable.

### 339. Last development in hybrid fluorosilicones

**François Ganachaud**, Claire Longuet, Amédée Ratsihimety, Francine Guida-Pietrasanta and Bernard Boutevin, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, France

The synthesis of multiblock silicone copolymers, made of alternated perfluorinated alkyl chains and dimethylsiloxane oligomers, has been studied in our laboratory for the last 20 years, on the impulsion of Dow Corning and Daikin, respectively. The materials resulting from blending and crosslinking these polymers are high tech elastomers, which specifications are sufficient elastivicity and solvent resistance in a wide range of temperature, typically between -80 to 350°C. Recent developments in our laboratory focused on the chemistry and physicochemistry of these polymers, in order to improve the average molar masses which are generally too low to prepare materials with good mechanical properties. We observed that some tailored fluoroalkyl chains end-capped by silicone knees, gave an apparent cross-link material upon polyhydrosilylation and silanol polyondensation. In the first case, side reactions between methyl groups attached to the silicium atom and vinyl fluorinated molecules explained the formation of a chemical network. In the latter case, physical gelling arose from the generation of physical “knots” in the material. The self-assembly of the hybrid silicone blocks into lamellar phases was observed by AFM, TEM and DSC analyses. Such observations may explain the almost perfect non-solvency of these gels that disrupt only in the presence of a chaotropic salt.

## Silicon Symposium - Synthesis of Organosilicon Compounds and Intermediates II

**Organizer:** Charles E. Neal Jr. Dow Corning Corporation, Midland, MI
**Organizer:** Binh T. Nguyen Dow Corning Corporation, Midland, MI

### 340. Functionalization of Octavinylsilsesquioxane via Cross-Metathesis

**Santy Sulaiman**[1], Chad Brick[2], Mark Roll[1] and Richard M. Laine[1], (1)University of Michigan, Ann Arbor, MI, (2)Kyoto University, Kyoto, Japan

There is widespread interest in the development of star polymers, dendrimers and supramolecular materials as building blocks for constructing materials with architectures tailored at nanometer length scales. Tailoring at such length scales should provide high reproducibility, and the opportunity to precisely predict and fine-tune final global properties. Thus there is keen interest in identifying nanometer-sized molecules that offer very high symmetry, high functionality and a means to modify that functionality at will and finally to use the introduced functionality to build 1-, 2- or 3-D structures nanometer by nanometer.

Here we report the functionalization of octavinylsilsesquioxanes ($Vi_8T_8$) with R-styrenes via cross-metathesis reactions to obtain octa(R-styryl)silsesquioxanes (R-$styryl_8T_8$). A variety of R groups were used in this study to demonstrate the versatility of this reaction. Octa(bromostyryl)silsesquioxane (Br-$styryl_8T_8$) was further functionalized with R-styrenes to give octa(vinyl-R-stilbene)silsesquioxane (vinyl-R-$stilbene_8T_8$), which luminesce with quantum efficiency of 20%.

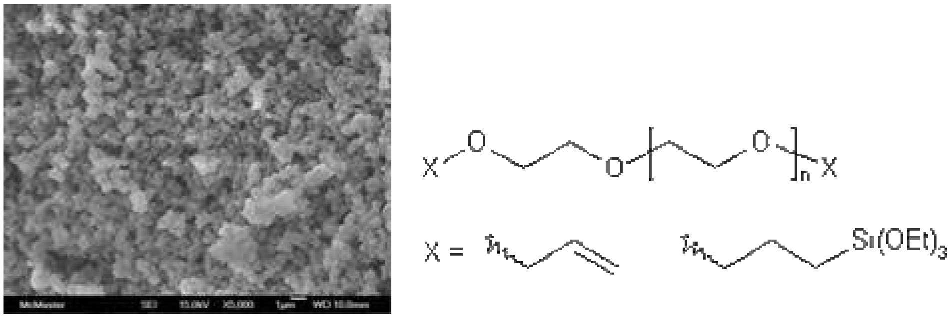
### 341. A biocompatible process for the preparation of macro-porous silica materials

**Rebecca Voss**, Yang Chen, John D. Brennan and Michael A. Brook, McMaster University, Hamilton, ON, Canada

Macroporous, monolithic silicas offer excellent matrices for proteins; the resulting composites can be used as immobilized enzymes or for drug screening. These materials can be prepared using a sol gel process in which high molecular weight hydrophilic polymers (>10000 MW), particularly poly(ethylene oxide)(PEO), facilitate phase separation of the sol prior to gelation. We report in this work the surprising result that macroporous structures can also be induced with low molecular weight PEO provided that functionalized polymers are used.

Silicas were formed using the polyol-based silane, diglyceroxysilane (DGS), at neutral pH. PEO of different molecular weights and end-group functionalities including allyl or propyl-triethoxysilane were employed to facilitate phase separation to give macropores even at MW < 2000 (Figure). The PEO was subsequently removed through repeated washing steps to give macro-mesoporous structures in which the total pore volume and surface area could be further increased with calcination. The mechanistic origins of the macropores, which are dependent on MW, and the specific chemical nature of the end groups, will be discussed.

**Figure**: SEM image of a macroporous silica prepared from DGS and allyl modified PEO with a molecular weight of 2000 g/mol.



### 342. Synthesis and Structure of Tricyclic Ladder Oligomethylsilsesquioxane

**Ken-ichi Suyama**, Koji Arimitsu, Takahiro Gunji and Yoshimoto Abe, Tokyo University of Science, Noda, Japan

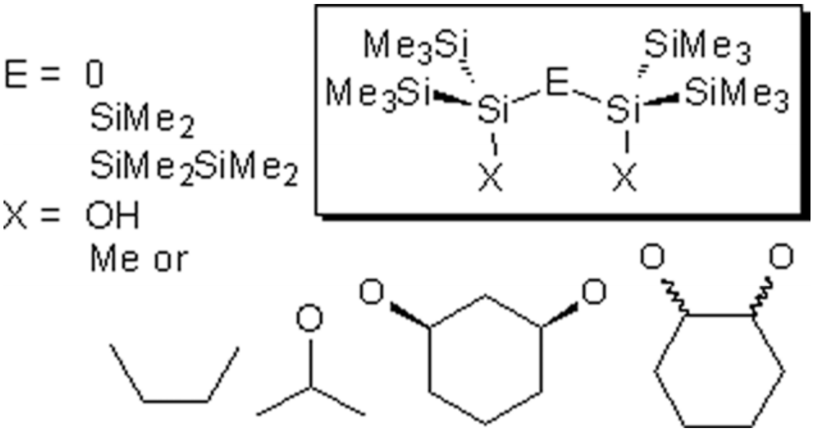
Synthesis and characterization of polycyclic oligosiloxanes provide the solution to controversy on the structure of ladder polysilsesquioxanes. Ladder oligosiloxanes have been synthesized by the oxidation of ladder oligosilanes and also by condensation of oligosiloxanes. In the latter method, cyclic ladder oligosiloxanes of 1 - 5 ring systems were afforded by the heterofunctional condensation between sila-functional siloxanes such as cyclotetrasiloxanes and disiloxanes or the self-condensation of disiloxanes with phenyl, isopropyl, or 1,1,2-trimethylpropyl groups. Recently, we have reported the facile method for the selective synthesis of oligoisocyanatodi- and tetrasiloxanes1). These siloxanes are suitable candidates as building blocks for ladder polysilsesquioxanes. For the preparation of ladder oligosiloxanes, we have examined the condensation of 1,3,5,7-tetraisocyanato-1,3,5,7-tetramethylcyclotetrasiloxane (1) and 1,3-di-t-butoxy-1,3-dimethyldisiloxane-1,3-diol (2). A mixture of 1 and 2 in the molar ratio of 1:2 was stirred in the presence of triethylamine at room temperature in THF for 1 h. The reaction was monitored by gas chromatography to observe the disappearance of peaks due to 1 and 2. After removal of cyanuric acid formed as a precipitate, THF was distilled. The mixture was purified by recycle-type HPLC to show five stereoisomers. Two of the five isomers, provided a single crystal, which X-ray analysis revealed the structure of syn and anti configuration tricyclic ladder oligosilsesquioxane structures (3).

1) Abe, Y.; Suyama, K.; Gunji, T. Chem. Lett., 2006, 35, 114-115.

### 343. Oxo functionalized branched Oligosilanes - Synthesis, Structure, and unusual electronic Properties

**Clemens Krempner**, University of Rostock, Rostock, Germany

Recent studies on a series of linear oligosilanes with discrete conformations have unveiled the conformational dependence of sigma-conjugation; anti conformers (SiSiSiSi dihedral angle of 180°) extend the conjugation, while conformers with small dihedral angles such as syn, cis or gauche (0-60°) do not. We report herein on the synthesis, structure and unusual UV absorption behavior of various branched oligosilanes (figure). The attachment of oxo groups to the silicon backbone strongly perturbs sigma-conjugation resulting in a red shift of the absorption maximum compared to that of permethylated analogues. This is attributable to an optical band gap reduction arising from interactions between silicon (sigma) and oxygen lone pair (*n*) orbitals. We show that recent findings regarding the conformational dependence of linear oligosilanes are not strictly evident for branched structures.



## 344. New class of stereoregular cyclosiloxanes

**Olga I. Shchegolikhina**[1], Yulia A. Pozdniakova[1], Yulia A. Molodtsova[1], Konstantin A. Lyssenko[1], Victor G. Vasil'ev[1], Mikhail I. Buzin[1], Elena V. Matukhina[2] and Dimitris E. Katsoulis[3], (1)A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia, (2)Moscow State Pedagogical University, Moscow, Russia, (3)Dow Corning Corporation, Midland, MI

Metal ions directed hydrolytic condensation of organotrialkoxysilanes, RSi(OR')3, leads to the formation of metallasiloxane molecules those contain only one type of cyclosiloxanolate fragments coordinated to a metal ions matrix. Mainly, the size of cyclic fragments depends on the type of metal ions used. The subsequent elimination of the metal centers by the reaction of the metallasiloxanes with triorganylchlorosilanes or dilute solutions of acides allows the formation of stereoregular cyclosiloxanes of different size in high yields. Thus a series of new cyclic compounds, [RSi(O)OSiMe2R']n (n = 3, 4, 6 , 8, 10, 12; R = Ph, Vi, Me, Et, Pr; R' = Me, Vi, CH2Cl, H) and [RSi(O)OH]n (R =Ph, n = 4, 6, 12; R = Me, n = 4) was produced. Many of these cyclics can not be synthesized by traditional reaction routes. A distinctive feature of their molecular structure is the presence of two different types of "covering groups" on both sides of the plane of the cycle creating a strong anisotropy of intermolecular interactions. This feature gives a whole series of unique properties to these cyclic materials. Many of them are mesomorphic compounds in spite of the fact that they do not contain classic mesogenic groups. The XRD, DSC, TGA investigations and the rheological properties of the cyclics obtained will be presented.

### 345. Current perspectives on the mechanisms of Diels-Alder reactions involving tetramethyldisilane

**Peter P. Gaspar**, Mrinmoy Nag and Dong Zhou, Washington University in St. Louis, St. Louis, MO

Tetramethyldisilene was first generated by a formal retro-Diels Alder reaction, and it has been suggested that 1,1,2,2-tetramethyl-1,2-disilacyclohex-4-ene undergoes clean extrusion of tetramethyldisilene upon pyrolysis in the gas-phase. We have found that rearrangement to 1,1,3,3-tetramethyl-1,3-disilacyclohex-4-ene competes with extrusion of tetramethyldisilene and dimethylsilylene. A stepwise, diradical mechanism is supported by computational studies. Results from the addition of independently generated tetramethyldisilene to butadiene will be reported, together with new computational results that clarify the relationship between rearrangement and addition/extrusion processes in the disila-olefin Diels Alder reaction. This work receives financial support from the National Science Foundation (CHE-0316124).

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