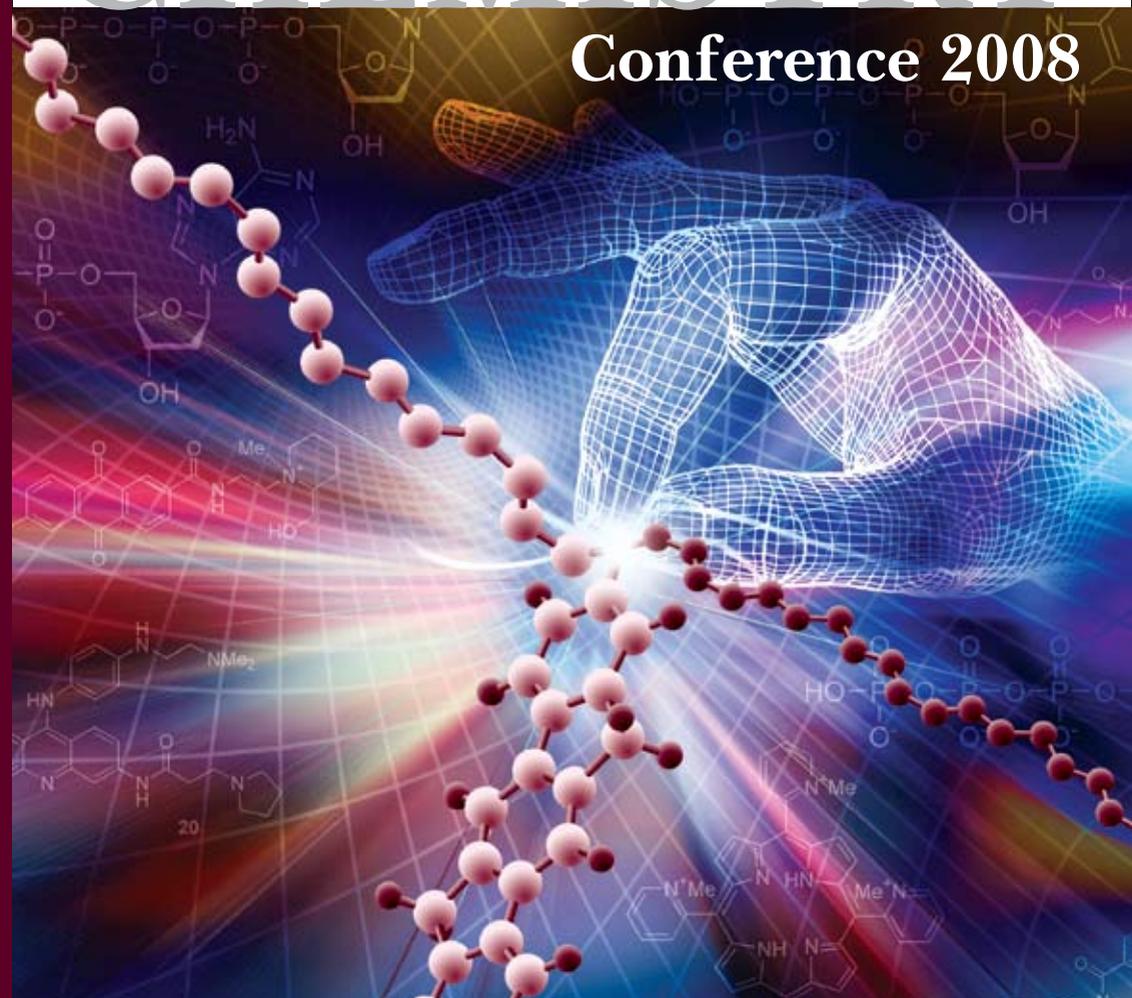




QAFCO - TAMUQ CHEMISTRY Conference 2008



TEXAS A&M
UNIVERSITY at QATAR

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Welcome to Aggieland



TEXAS A&M
UNIVERSITY at QATAR

January 9, 2008



TEXAS A&M
UNIVERSITY *at* QATAR

Welcome to Texas A&M University at Qatar and to the 2008 Qatar Fertiliser Company – Texas A&M at Qatar Chemistry Conference. The program for this year's conference is quite impressive, and, on behalf of the students, faculty and staff of Texas A&M at Qatar, I am delighted to welcome you to the new Texas A&M Engineering Building.

I am also pleased to recognize Qatar Fertiliser Company for its generous support of this meeting. QAFCO recognized the importance of gatherings like this when it sponsored the inaugural conference last year and that commitment to scholarship and research continues to help make this year's meeting possible.

Texas A&M at Qatar is a hub for leading academic research, and the QAFCO – TAMUQ Chemistry Conference is an important part of that effort. This meeting of chemists from around the world is a tribute to the timeless tradition of scholars gathering to share, discuss and develop their ideas. I hope that your participation in the conference proves to be productive and worthwhile.

Thank you for joining us for the QAFCO – TAMUQ Chemistry Conference. I hope that you will find the presentations stimulating and the discussions thought provoking. Again, welcome, and best wishes for an exciting conference.

Sincerely,

Dr. Mark Weichold

Dean and CEO

Texas A&M University at Qatar

QAFCO - TAMUQ Chemistry Conference 2008
Texas A&M University at Qatar, January 9, 2008
Doha Qatar

Schedule of Events

8:00	Registration Open and Light Breakfast
8:30	Welcome Session
9:00	Session I
10:30	Coffee break
10:50	Session II
12:20	Lunch
13:30	Session III
15:00	Coffee Break
15:20	Session IV
17:00	Student Poster Session

QAFCO - TAMUQ Chemistry Conference 2008
Texas A&M University at Qatar, January 9, 2008
Doha Qatar

Scientific Program

Welcome Session

08:30	Dr. Hassan S. Bazzi , Science Program Coordinator, TAMUQ
08:40	Dr. James C. Holste , Associate Dean for Research and Graduate Studies, TAMUQ
08:50	Mr. Khalifa Al-Sowaidi , Managing Director, QAFCO

Session I (Chair: **Dr. Hassan S. Bazzi**)

09:00 - 10:00	Keynote Speaker Dr. Krzysztof Matyjaszewski , <i>Carnegie Mellon University</i> "Nanostructured Polymeric Materials via ATRP Initiating Systems with ppm Cu Level"
10:00 - 10:30	Dr. Suresh Valiyaveetil , <i>National University of Singapore</i> "Role of Polymers in the Preparation of Nanoarchitectures: Nanospheres, Rings, Honey-Comb through Molecular Engineering"

Session II (Chair: **Dr. El-Metwally Noor**)

10:50-11:20	Dr. David E. Bergbreiter , <i>Texas A&M University</i> "Stimuli-Responsive Polymer Solvation"
11:20 - 11:50	Dr. Mariam A. Al-Ma'adeed , <i>Qatar University</i> "Modifications of Polymers by Gamma Irradiation"

11:50 - 12:20 **Dr. Dragomir Bukur**, *Texas A&M University at Qatar*
"Product Distributions and Reaction Pathways on Catalysts for CTL and GTL Conversion Processes"

Session III (Chair: **Dr. Mahmoud M. Khader**)

13:30 - 14:00 **Dr. Eric Simanek**, *Texas A&M University*
"Dendrimers Based on Melamine: Examining Applications from Medicine to Materials"

14:00 - 14:30 **Dr. Mahmood Mohsin**,
United Arab Emirates University
"Synthesis and Characterization of Medical Grade Polycaprolactone Based Polyurethane"

14:30 - 15:00 **Dr. Simon Waldram**, *Texas A&M University at Qatar*
"Polymerisations and Runaway Reactions: How Adiabatic Calorimeters Can Help us Predict Large Scale Behavior"

Session IV (Chair: **Dr. Dave Seapy**)

15:20 - 15:50 **Dr. Ben Zhong Tang**,
The Hong Kong University of Science & Technology
"Acetylenes with Multiple Triple Bonds: A Group of Versatile A_n -Type Building Blocks for the Construction of Functional Hyperbranched Polymers"

15:50 - 16:20 **Dr. Mahmoud M. Khader**, *Qatar University*
"A Comparison of the Redox Properties of Vanadia-Based Mixed Oxides"

16:20-16:50 **Chayanant Hongfa**, *Texas A&M University*
"Polyisobutylene Supported N-heterocyclic Carbene Ligand for Homogeneous Catalysts"

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Keynote Speaker

Professor Krzysztof Matyjaszewski is the J.C. Warner University Professor of Natural Sciences at the Mellon College of Science (MCS) at Carnegie Mellon University, a position held previously by late Professor John Pople, 1998 Nobel Laureate. He is recognized worldwide as one of the most distinguished professors of chemistry. He is a University Professor, director of the Center for Macromolecular Engineering at MCS (1998-present), and director of ATRP and CRP Consortia (1996 - present). He also holds adjunct professorial positions at the Polish Academy of sciences, Lodz (2000 - present) and University of Pittsburg (2000 - present). He has held many visiting positions at universities in France, Poland, and Japan.

He has received many internationally esteemed awards, these include:

2007 Hermann F. Mark Senior Scholar Award (ACS)

2007 Honorary Degree (Doctorate Honoris Causa) Lodz Polytechnic, Poland

2006 Member of US National Academy of Engineering

2006 Honorary Degree (Doctorate Honoris Causa) Russian Academy of Sciences

2005 UK Macro Medal for outstanding achievements in polymer science

2005 Foreign member of Polish Academy of Sciences

2004 Annual Prize of the Foundation of Polish Science (aka Polish Nobel Prize)

2004 Cooperative Research Award in Polymer Science & Engineering (ACS)

2002 Polymer Chemistry Award (ACS)

2002 Honorary Degree (Doctorate Honoris Causa) University of Ghent, Belgium

2001 Pittsburgh Award (ACS)
 2001 Polymeric Materials Science and Engineering Fellow (ACS)
 1999 Humboldt Award for Senior US Scientists
 1998 Elf Chair of French Academy of Sciences
 1995 Carl S. Marvel - Creative Polymer Chemistry Award (ACS)
 1989 Award of Presidential Young Investigator (NSF)
 1981 Award of Polish Academy of Sciences

Prof. Matyjaszewski is best known for the discovery of atom transfer radical polymerization (ATRP) which has been commercialized in the US, Europe and Japan. Over 40 companies are members of "ATRP and CRP" Consortia at CMU, a center where he serves as director since 1996. He has published over 500 peer-reviewed papers and 10 books. He holds 33 US and 81 international patents. His first groundbreaking paper on ATRP in 1995 has been cited over 1600 times and his citation record (more than 24,000) ranked him No. 6 scientist in all fields of chemistry worldwide in 2004, 2005 and 2006 and No. 4 in 2007.

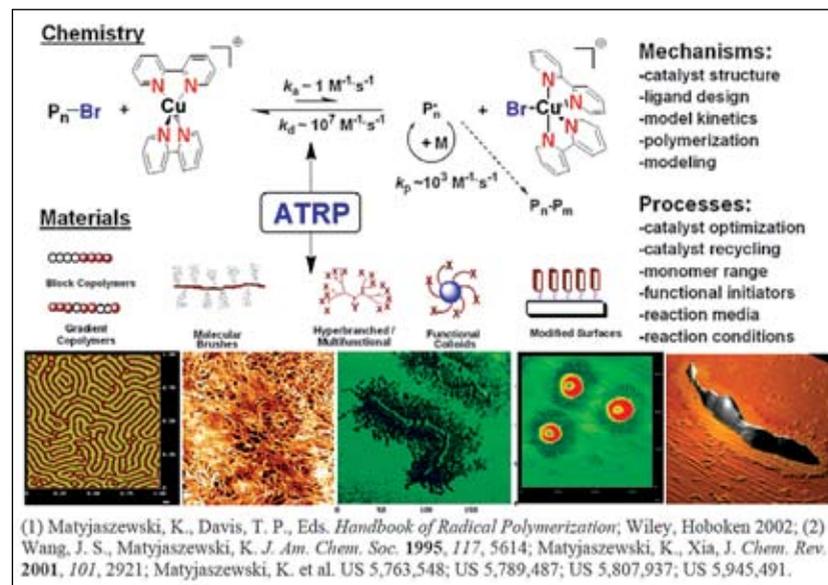
Prof. Matyjaszewski is the editor of *Progress in Polymer Science* and *Central European Journal of Chemistry* and serves on the editorial boards of fourteen other chemistry journals. He was elected as a foreign member of the Polish Academy of Sciences in 2005 and as a member of the US National Academy of Engineering in 2006.

Prof. Matyjaszewski earned his B.S. and M.S. at the Technical University of Moscow in 1972 and his Ph.D. at the Polish Academy of Sciences in 1976. He worked in Poland and France for few years, and then moved to the United States to join Carnegie Mellon University in 1985.

"Nanostructured Polymeric Materials via ATRP Initiating Systems with PPM Cu Level"

Krzysztof Matyjaszewski
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Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands such as bpy and aliphatic polyamines is among most efficient controlled/living radical polymerization systems.^{1,2} Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm.



ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and many other vinyl monomers provides polymers with molecular weights in a large range $200 > M_n > 20,000,000$ and with low

polydispersities. Polymers can be formed quantitatively in bulk, in solution and in dispersed media. Block, graft, star, hyperbranched, gradient and periodic copolymers as well as molecular brushes have been prepared.² The (co)polymers made by ATRP have many potential applications as components of advanced materials such as coatings, elastomers, adhesives, surfactants, dispersants, lubricants, additives, but also as specialty materials in biomedical and electronic areas and will affect the market of ~\$20 billion/year. Examples of design, synthesis, characterization and applications of nanostructured multicomponent polymeric materials prepared via ATRP will be presented.

“Role of Polymers in the Preparation of Nanoarchitectures: Nanospheres, Rings, Honey-Comb through Molecular Engineering”

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Fabrication of solid state structures at a nanometer scale on different surface attracts much attention because of its technological importance in nanoelectronics, nanofluidics and nanosensors. Recent developments in this field include, electrochemical nanolithography, in which patterns are on a substrate of interest using an AFM tip. However, exploring the patterning ability of various polymeric materials at different conditions is important to find the suitable materials for specific applications in polymer device fabrication. The focus of the current presentation would be on patterning substrates using

nanolithography and spin coating to develop nanosized lines, dots and complex structures such as honey-combs using electrostatic nanolithography. Also, properties of such patterned polymer films are investigated and the results will be discussed.

In another approach, controlled organization of nanocrystals of CaCO_3 in solution and on a substrate is explored in detail. The effect of other divalent cations such as Mg or soluble additives on the crystal growth and morphology was also analyzed. Reverse microemulsion method was used for the synthesis of these nanocrystals. Dependence of the crystal morphology and size with respect to temperature, cation/surfactant ratio and the role of inhibitor on the final structure were also studied. Different experimental techniques like SEM, TEM, EDX, FTIR and XRD were used to characterize the morphology and the lattice structure of these crystals. Hollow spheres of CaCO_3 were synthesized using a low temperature crystallization process in the presence of additives. The control achieved over the preparation of amorphous calcium carbonate makes it a promising candidate due to the isotropic properties of the precursor amorphous phase.

The talk will focus on providing sufficient details on synthesis, characterization and potential applications of interesting polymer/composite materials.

At Qatar University, gamma irradiation has been used to study changes in different polymers (i.e. PMMA, PE, PEO, and PVA). The talk will give a description of the effect of gamma irradiation on the morphology, microstructure and characterization of thermal, mechanical and optical properties of different types of polymers before and after irradiation.

“Product Distributions and Reaction Pathways on Catalysts for CTL and GTL Conversion Processes”

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Fischer-Tropsch synthesis (FTS) has been known for over 80 years as a process of converting synthesis gas into high molecular weight hydrocarbons. Recently, there has been a renewed interest in FTS. In particular the slurry phase process is expected to play a major role in production of transportation fuels from natural gas (gas - to - liquid conversion - GTL) and/or carbon rich sources (coal-to-liquids conversion - CTL). On FTS catalysts 1-olefins are the primary products, whereas n-paraffins are also formed directly but to a much lesser degree than 1-olefins. The 1-olefins may subsequently be hydrogenated to n-paraffins or isomerized to 2-olefins. The products yield decreases with increasing carbon number according to the so-called Anderson-Schulz-Flory (ASF) distribution. However, significant deviations from the ASF distribution has been observed in practice, in particular for methane, ethene and higher-molecular-weight products (so called “double-alpha” phenomenon). Another common experimental observation is that 1-olefin content decreases with increase in carbon number.

We will describe various approaches to explain experimentally observed product distributions, which include chemical factors as well as physical transport processes. The latter can have significant impact on residence time of reactants and primary products, and enhance secondary reactions. Results from recent studies at Texas A&M University will be presented which include quantitative modeling of observed product distributions through complex reaction networks coupled with the effect of increased solubility of high molecular weight 1-olefins in a slurry reaction medium.

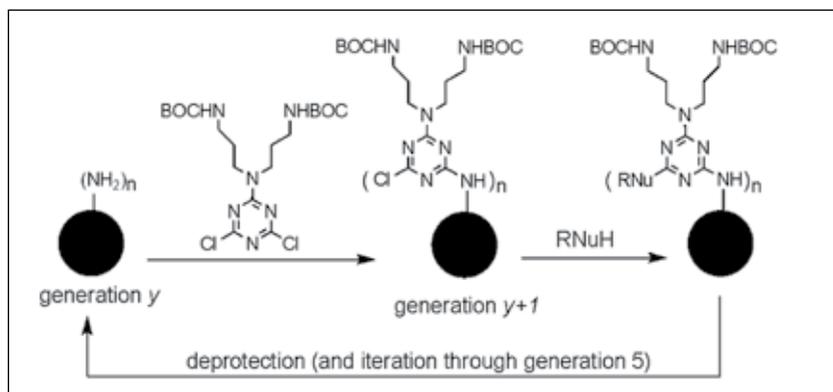
“Dendrimers Based on Melamine: Examining Applications from Medicine to Materials”

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Dendrimers are discrete polymers of snowflake-like perfection. Vögtle first reported these architectures in 1978 as the result of condensations of vinyl nitrile with primary amines. Subsequent reduction and iteration yielded the poly(propyleneimine) dendrimers which were later popularized by Meijer. Tomalia and Newkome offered the next reports in 1984 and 1985. Tomalia's seminal report on poly(amidoamine) dendrimers accurately laid out the synthetic challenges that the community continues to address; exercising control over size, shape, and the disposition of desired functionality. Fréchet's approach to poly(arylether) dendrimer architectures, converging from the outside toward the central core, was first described in 1991, marked the next conceptual advance in the field. The literature is replete with examples of dendrimers using other monomers and comonomers. Applications for these

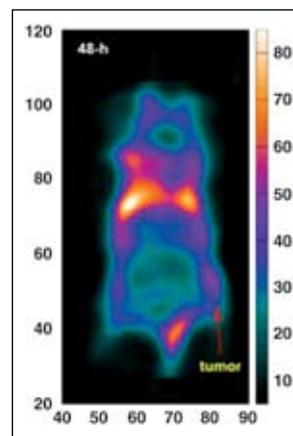
architectures continue to be sought. Indeed, this search has become inextricably linked to any basic inquiry into these architectures.

In 2000, our group introduced dendrimers based on melamine. These architectures are unique in a variety of ways and subsequent reports from our group have addressed synthetic aspects of these architectures. In our opinion, these dendrimers are the first and only class of molecules that reduce Tomalia's challenge to the synthetically trivial. The synthetic details to substantiate this belief



will be discussed including our ability to execute structure-activity relationships. Recently, we have developed inexpensive, facile and scalable chemistries that allow the preparation of a kilogram of these targets. Using either convergent or divergent approaches, nanometer-scale architectures that display different groups on the periphery can be prepared. Based on the choice of group, these materials might ultimately find application in drug delivery or materials science. While examples of both these applications will be described, most of our efforts focus on cancer therapy.

The primary challenge of chemotherapy is selectivity. The potent toxicity of cancer drugs leads to systemic toxicity that invariably kills the patient and tumor simultaneously. Whether the treatment was successful depends greatly on this balance. If the systemic toxicity of drugs could be reduced by selectively



delivering them to tumors, both the number of successes and the quality of patient life during chemotherapy could be increased. Dendrimers offer one avenue for this selectivity. The basis of this selectivity derives from the enhanced permeation and retention of macromolecules into tumors. If the macromolecule, a dendrimer, is laden with drugs, then selectivity is afforded. Over the last two years, we have established that our dendrimers are biocompatible, can be derivatized with anti-cancer drugs, and selectively accumulate in tumors. The long term goal is to push these drug delivery vehicles into the clinic to impact the outcomes of chemotherapy, to aid in early diagnosis of solid tumors, and to improve the quality of life during chemotherapy by reducing systemic side-effects. Large scale efficacy trials in prostate and breast tumor models have commenced. Preliminary data will be offered.

"Synthesis and Characterization of Medical Grade Polycaprolactone Based Polyurethane"

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Polyurethanes as biomaterials have been used in the augmentation and repair of human body with great success. The choice of materials for a particular application often hinges

on the body response, mechanical and physical properties, biodegradability and biocompatibility of the polymers. These polymers may be used for fabricating a medical implant devices, heart valves, controlled drug delivery, hard tissue repair and hip or knee prostheses. They may be naturally occurred or synthesized by various methods and can be designed to remain in the body for an indefinite period, or be safely degraded once their role is complete. When incorporated into hip or knee prostheses, polyurethane-elastomer layers are effective in reducing friction by improving the lubrication mechanisms. This results in reduced wear and increased service life.

In this investigation, a series of thermoplastic linear polyurethanes with a range of formulations based on soft-to-hard segment ratios were synthesized in bulk using Diphenylmethane-4,4'-diisocyanate (MDI), Butandiol (BD) as chain extender, and Polycaprolactone diol (PCL) with varying molecular weights. The polymers produced with chemical and structural variables that affect the overall properties were analyzed and characterized using Thermogravimetric Analysis (TGA), Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR) and Differential Scanning Calorimetry (DSC). Hardness tests were also performed in order to ascertain the suitability of the polymer to be considered as the acetabular bearing material for hip replacement.

Biocompatibility tests were carried out on selected polyurethane samples to assess the suitability of the polymer for fabrication a desired medical device such as hip prostheses.

The key finding was that some polyurethane samples with uniform distribution between hard and soft segments had the lowest adverse biological effect. Other samples caused severe irritation in the tissue and had noticeable surface erosion.

“Polymerisations and Runaway Reactions: How Adiabatic Calorimeters Can Help us Predict Large Scale Behavior”

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Statistics from the Health and Safety Executive indicate that approximately 50% of runaway chemical reaction incidents occurring in the UK are associated with polymerization or condensation reactions. Three examples of major accidents will be briefly discussed, two involving polymerizations and one the decomposition of a distillation residue.

The role of low phi factor adiabatic calorimetry when studying runaway reaction behavior will be reviewed and illustrated with experimental data for a variety of polymeric systems. This enables the chemical engineer to design the plant not only for the intended duty but also so that it is safe during “worst credible maloperations”. Good predictions can be made of the temperature and pressure trajectories that should be anticipated within large scale plant.

The concepts of inherent safety and the “criticality classes” of batch and semi-batch processes will also be discussed.

“Acetylenes with Multiple Triple Bonds: A Group of Versatile A_n -Type Building Blocks for the Construction of Functional Hyperbranched Polymers”

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AB_n -type monomers have been widely used for the synthesis of hyperbranched polymers. These monomers, however, suffer from the problems associated with the tendency of their mutually reactive A and B functional groups toward self-oligomerization. We have explored the possibility of synthesizing hyperbranched polymers using A_n -type monomers, which are stable and easy to prepare and handle, with some being even commercially available. In particular, we have tried to open new synthetic routes to hyperbranched polymers using diynes and triynes as monomers. We have developed metallic [TaBr₅, Cp*Ru(PPh₃)₂Cl, etc.] and nonmetallic catalysts (piperidine, DMF, etc.) for polycyclotrimerization, polycycloaddition and polycoupling of the acetylenic monomers. We have synthesized a variety of new hyperbranched polymers including polyarylenes, polytriazoles and polydiynes with high molecular weights and excellent solubility in high yields. The polymers exhibit an array of functional properties such as sensitive photonic response, high light refractivity, large optical nonlinearity, high thermal stability, strong optical limiting power and unusual aggregation-enhanced light emission. Utilizing these unique properties, we succeeded in generating fluorescent images, honeycomb patterns, polymer nanotubes, ferromagnetic ceramics, and nanoparticle catalysts.

“A Comparison of the Redox Properties of Vanadia-Based Mixed Oxides”

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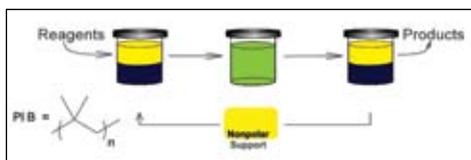
Oxidation isotherms for mixed oxides of vanadia, including LaVO₄, CeVO₄, AlVO₄, CrVO₄ and ZrV₂O₇, were measured using coulometric titration. The temperature dependence of the isotherms allowed values for ΔS and ΔH each redox reaction to be determined. For all the oxides studied only the vanadium cations were observed to undergo redox reactions at temperatures between 800 and 1000 K and oxygen partial pressures between 10⁻² and 10⁻²⁵ atm. Except for ZrV₂O₇, the only stable oxidation states for vanadium in the mixed oxides were +3 and +5. For ZrV₂O₇, which was the only compound in the series that contained V-O-V bonds V⁺³, V⁺⁴, and V⁺⁵ were stable.

"Polyisobutylene Supported N-heterocyclic Carbene Ligand for Homogeneous Catalysts"

Chayanant Hongfa¹, Hassan S. Bazzi², and David E. Bergbreiter¹

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Vinyl terminated polyisobutylene (PIB) oligomers can be easily transformed into a variety of end-functionalized PIB

oligomers. Previous work has shown that PIB oligomers possess nonpolar phase selective solubility that allows them to be used as polymer supports for ligands and catalysts. These nonpolar labeled materials can be utilized and recycled in various liquid/liquid biphasic systems. My research focuses on the use of PIB oligomers as a support for N-heterocyclic carbene, which is utilized as a ligand in the 2nd generation Hoveyda-Grubbs catalyst. The synthesis of PIB supported N-heterocyclic carbene involves a Friedel-Crafts alkylation with 2,6-dimethylaniline. The product PIB attached aniline is converted into diamide, then reduced into a diamine with borane dimethylsulfide. The diamine is then converted into an imidazolium salt via a reaction with ammonium tetrafluoroborate and triethylorthoformate. The PIB attached imidazolium salt can be converted into an N-heterocyclic carbene for the 2nd Generation Hoveyda-Grubbs catalyst that is phase selectively soluble in heptane. This PIB-supported Hoveyda-Grubbs ruthenium catalyst is used for both ring-opening metathesis polymerizations and ring closing metathesis reactions with high level of recyclability and minimal lost of ruthenium per cycle.