2010 Outstanding Graduate Research

Haifeng Gao
Carnegie Mellon (Krist Matyjaszewski)

The recipient of the 2010 Akzo Nobel Award for Outstanding Graduate Research in Polymer Chemistry is **Dr. Haifeng Gao**, who received his doctorate in 2008 from Carnegie Mellon University under the direction of Professor Krzysztof (Kris) Matyjaszewski, and is now a postdoctoral researcher in Professor Jean M. J. Fréchet's group in University of California, Berkeley.

Haifeng Gao's Ph.D. dissertation focused on the development of new synthetic methodologies for preparation of functional polymers with controlled architectures using atom transfer radical polymerization (ATRP) of divinyl crosslinker with monovinyl monomer. The structure of the polymers can be varied from soluble stars containing a crosslinked core and linear radiating arms to highly branched copolymers and/or insoluble gels by simply changing the polymerization sequence of the monomer and the crosslinker. The polymerization of monomer prior to addition of crosslinker (the "arm-first" method) or polymerization of monomer after crosslinker (the "core-first" method) results in the preparation of star-like polymers with a crosslinked core, but with different site-specific functionality. In contrast, a concurrent copolymerization of both monomer and crosslinker generates "randomly" branched polymers or gels depending on the polymerization conditions.

Traditionally, star polymers synthesized by using the crosslinker method have poorly controlled structure and broad size distribution. Haifeng Gao successfully solved this problem by developing a new "arm-first" method for synthesis of core-functional star polymers with low polydispersity using linear macromonomer (MM), instead of macroinitiator (MI), as the arm precursor. This breakthrough further inspired him to develop a simple and general method for synthesis of miktoarm star copolymers with controlled structures and freely varied arm compositions and arm ratios by one-pot crosslinking of a mixture of linear arm precursors, including both MMs and MIs. These synthetic strategies are not limited to ATRP, but are generally applicable in other controlled polymerization techniques. These research achievements provide an easy access to various polymer nanomaterials with controlled complexity and functionality, including star polymers and branched polymers. These materials have tremendous promise in numerous specialty applications including drug delivery, coatings, cosmetics, healthcare, and lithography.

Dr Rama Chandran; VP, Polymer Technology said that it is a great honor to present the AkzoNobel award in North America on behalf of our employees at the symposium held in honor of Dr. Haifeng Gao. Rama also indicated that Polymer Chemistry remains as one of the critical science platforms in AkzoNobel. AkzoNobel is a global leader in decorative paints, the largest manufacturer of performance coatings and a major supplier of specialty chemicals. The Polymer Division would like to thank AkzoNobel for their continued sponsorship. The award is a joint POLY/PMSE event. The symposium was held in the PMSE symposia this year and will be presented as a POLY award symposia in fall 2011.

POLY Awards
Outstanding Graduate Research- Past Awardees
2001-2010

2009 Outstanding Graduate Research

Christopher Bettinger
MIT (Robert Langer)

The recipient of the 2009 Akzo Nobel Award for Outstanding Graduate Research in polymer chemistry is **Dr. Christopher J. Bettinger** who received his doctorate in 2008 from MIT under the direction of Robert Langer

POLY Awards
Outstanding Graduate Research- Past Awardees
2001-2010

2008 Outstanding Graduate Research

Nicolay Tsarevsky
Carnegie Mellon (Krist Matyjaszewski)

The recipient of the 2008 National Starch and Chemical Award for Outstanding Graduate Research in Polymer Chemistry is **Dr. Nicolay (Nick) Tsarevsky** who received his doctorate in 2005 from Carnegie Mellon University under the direction of Professor Krzysztof (Kris) Matyjaszewski.

Tsarevsky studied the synthesis of functional polymers by atom transfer radical polymerization (ATRP). Various synthetic approaches were used to prepare polymers with polar functional groups, including post-polymerization modification of the repeating units or the end groups. Efficient chemical transformations employed included the nitrile-azide and alkyne-azide cycloaddition (click chemistry) and the reversible redox coupling of thiol to disulfide groups. Tsarevsky also studied mechanistic aspects of ATRP, emphasizing the development of rules for rational catalyst selection for "challenging" reaction media, including water-borne systems.

He established that several side reactions of the copper-based ATRP catalyst with protic/aqueous solvents led to poor polymerization control, namely loss of halide ligand from the higher oxidation state radical deactivator or disproportionation of the lower oxidation state activator. The ideal catalyst mediating well-controlled ATRP in protic media is characterized by i) a high ratio bII/ bI of the stability constants of the Cu(II) and Cu(I) states of the catalyst to guarantee high catalytic activity; ii) high halidophilicity of the Cu(II) complex, which is related to the degree of control; and iii) a low ratio bII/ bI)2 to avoid disproportionation. His mechanistic studies led to the development of two new initiation techniques, ICAR and ARGET ATRP, that allow the process to be carried out with very low amounts of catalyst. The scope of ATRP has now expanded significantly, particularly with regard to aqueous solvents and coordinating monomers. Importantly, ATRP has become a truly "green" method with markedly increased utilization in industry.

The award was presented at a symposium honoring Nick Tsarevsky in the PMSE Division of ACS during the American Chemical Society National Meeting in Philadelphia, August 17-21, 2008.

2007 Outstanding Graduate Research

Jason Rolland
UNC (Joe DeSimone)

The recipient of the 2007 National Starch & Chemical Award for Outstanding Graduate Research in Polymer Chemistry is **Dr. Jason Rolland**, who received his doctorate in 2005 from the University of North Carolina, Chapel Hill, under the direction of Professor Joseph M. DeSimone. Dr. Rolland's Ph.D. dissertation research focused on novel applications for perfluoropolyethers (PFPEs), primarily in the field of nanotechnology.

A versatile technique, Particle Replication in Non-wetting Templates, or "PRINT(TM)" was developed that uses low surface energy PFPEs, cast onto nano-featured master templates and cured to form transparent fluoroelastomers. These become molds containing billions of nano-scale cavities that can be filled with liquid precursors that are solidified and harvested to yield highly monodisperse populations of shape-specific, engineered nano-scale particles. PRINT(TM) has tremendous promise in several applications including delivery of therapeutics such as siRNA and drugs for cancer treatment.

In addition to the PRINT process, PFPE elastomers can be patterned with micron and nanometer sized features and used as molds for imprint lithography. In collaboration with IBM researchers, Dr. Rolland showed that features as small as 70 nm can be replicated in organic resins with 1 nm precision using PFPE molds. The PFPE molds are superior in terms of resolution, release, and compatibility when compared to either poly(dimethyl siloxane) (PDMS) or rigid materials.

Multifunctional PFPE formulations were also synthesized and used to fabricate transparent, elastomeric, microfluidic devices compatible with organic solvents and chemical reagents. These replace PDMS, which swells in most organic solvents and is not compatible with microchemistry platforms. Multilayer, complex microfluidic chips containing pneumatic valves were fabricated from PFPE materials. Due to their compatibility with chemistry platforms, PFPE-based microfluidic chips have recently been used in the synthesis of radiolabelled biomarkers, such as [F-18] 2-Fluoro-2-deoxy-D-glucose for PET imaging.

The award was be presented at a symposium in Dr. Rolland's honor in the Division of Polymer Chemistry at the American Chemical Society National Meeting in Boston August 19-23, 2007.

2006 Outstanding Graduate Research

Jiaxing Huang
UCLA (Richard Kaner)

The recipient of the 2006 National Starch & Chemical Award for Outstanding Graduate Research is **Dr. Jiaxing Huang**, who received his doctorate in 2004 from the University of California, Los Angeles, under the direction of Professor Richard B. Kaner. Dr. Huang's Ph.D. dissertation research led him to discoveries on the synthesis of high-quality polyaniline nanofibers with major impact in the fields of conducting polymers and nanoscience. These have led to advances in conducting polymer sensors, molecular memory devices and flash welding. He applied interfacial polymerization to produce uniform nanofibers without the need for difficult-to-remove templates, and demonstrated that these nanofibers could be used as sensors to detect parts-per-million or less of many acids and bases.

Following his elucidation of the fiber formation mechanism, he developed a method to create a stable colloidal dispersion of the nanofibers, suitable for processing to films or other forms, resolving a major roadblock to the widespread use of these materials. He discovered that the nanofibers could undergo wavelength and intensity dependent crosslink photo-thermal chemistry to form nanofiber connections, asymmetric films, photopatterns and polymer composites, and demonstrated that polyaniline nanofibers decorated with gold particles can serve as the active component in a device with a three order of magnitude change in conductivity between on and off states, and read, write, erase cycles at low voltages.

The Award, which will be presented at the San Francisco meeting of the American Chemical Society (Sept. 10-14), consists of a $2,000 prize, a plaque and travel expenses. This award, administered by the Polymer Education Committee of the Polymer Chemistry and Polymeric Materials Science and Engineering Divisions, was established in 1991 to recognize and encourage outstanding graduate research in polymer science and engineering. It is sponsored by National Starch & Chemical Co., a global manufacturer of adhesives, specialty polymers, electronic materials and specialty starches.

2003 Outstanding Graduate Research

Christopher W. Bielawski
CalTech (Bob Grubbs)

Warren Ford reports that the recipient of the 2003 Unilever Award for Outstanding Graduate Research is **Dr. Christopher W. Bielawski**, who received his doctorate in October 2002 from the California Institute of Technology, Pasadena, CA under the direction of Professor Robert H. Grubbs. Dr. Bielawski's research efforts were directed toward establishing new concepts and strategies in macromolecular synthesis through the development of designer Ru catalysts. For example, the efficient synthesis of copolymers with segments that require two or more different polymeriza-tion techniques remains challenging as multiple steps are usually necessary. To circumvent this drawback, Bielawski developed a series of catalysts that are capable of simultaneously mediating two mechanistically distinct polymerizations (i.e., ring-opening metathesis polymerization and atom-transfer radical polymerization). This has enabled the preparation of a variety of complex block copolymers in a single pot.

A second aspect of Bielawski's research was focused on the synthesis of cyclic polymers. Traditionally, such polymers are made through the intramolecular coupling of linear precursors. However, such cyclizations are rarely quantitative and extremely dilute conditions are required which places limits on the ability to prepare substantial amounts of pure cyclic polymer. By adding monomer to a "cyclic" catalyst, Bielawski demonstrated that both ends of the growing polymer chain remain attached to the catalyst so the topology of polymer remains cyclic throughout the entire reaction.

2002 Outstanding Graduate Research

Kristi L. Kiick
UMass Amherst (Dave Tirrell)

The recipient of the 2002 Unilever Award for Outstanding Graduate Research is **Dr. Kristi L. Kiick**, who received her doctorate in May 2001 from the University of Massachusetts, Amherst, under the tutelage of Professor David A. Tirrell, now of the California Institute of Technology, Chemistry and Chemical Engineering. Kiick directed her research to the preparation of proteins using non- natural amino acids, with functional groups different from those of the natural amino acids. She manipulated the activity of a single enzyme in the bacterial host to prepare engineered proteins with novel chemical and physical properties.

Her investigations focused on replacing the amino acid methionine with methionine analogues that carry chemical groups that are unusual in biology, such as alkenes, alkynes, and azides. Engineering E. coli to produce extra copies of methionyl-tRNA synthetase ? the enzyme that controls the fidelity of methionine incorporation into proteins ? allowed methionine to be replaced by six different methionine analogues normally rejected by the bacterial host. This simple modification to the bacterial host also increased the yields of protein obtained during protein expression. These investigations confirm the critical role of MetRS in controlling analogue incorporation and suggest new strategies for incorporating non-natural amino acids into proteins to create novel classes of protein-based materials.

The Unilever Award, which will be presented at the Boston, MA, meeting of the American Chemical Society (Aug. 18-22) consists of a $2,000 prize, a plaque and travel expenses. This award, administered by the Polymer Education Committee of the Polymer Chemistry and Polymeric Materials Science and Engineering Divisions, was established in 1991 and is sponsored by Unilever, a global manufacturer of consumer products, foods and specialty chemicals. The award recognizes and encourages outstanding graduate research in the design, synthesis and physical chemistry of polymers. The award symposium and presentation will take place at the ACS National Meeting in Boston August 18-22 2002.

2001 Graduate Research

Shu Yang
Cornell (Chris Ober)

The recipient of the 2001 Unilever Award for Outstanding Graduate Research is **Dr. Shu Yang**, who received her doctorate in August 1999 under the tutelage of Professor Christopher K. Ober of Cornell University, Materials Science & Engineering Department. Her research lead to the creation of "reworkable" thermosets that contain specially designed weak links that decompose at low temperatures to permit network breakdown. These thermosets, now licensed, are proving to be of great interest to the microelectronics industry where adhesives that are robust under normal use, but can be removed under specific conditions, are highly desirable.

In her thesis research, she also designed new photoresists with fluorine and silicon-containing units for use in next generation lithographies. Her superb synthetic skills enabled her to prepare these photoresists for development with supercritical CO2. This solvent, along with its environmental friendliness, offers many intriguing properties for photolithography and includes low viscosity and no surface tension - important properties for developing the smallest features in a patterned image. Dr. Yang, working with another student, was able to invent new fluoropolymers that could be patterned with a resolution of ~0.2 μm, in the size range of the best experimental resists yet produced.

The Unilever Award, which will be presented at the Chicago, IL, meeting of the American Chemical Society (Aug. 26-30) consists of a $2,000 prize, a plaque and travel expenses. This award, administered by the Polymer Education Committee of the Polymer Chemistry and Polymeric Materials Science and Engineering Divisions, was established in 1991 and is sponsored by Unilever, a global manufacturer of consumer products, foods and specialty chemicals. The award recognizes and encourages outstanding graduate research in the design, synthesis and physical chemistry of polymers.