PSE Alumni Magazine

Winter 2006

Life in PSE just keeps getting better. Our 2006 graduates have been rewarded with excellent postdoctoral positions and jobs, our new faculty are off to great starts in their research programs, and support for PSE research from federal and industrial sources is at an all-time high.

Early in 2006, PSE faculty were under pressure at the halfway evaluation point of the 2002-2008 National Science Foundation-Materials Research Science & Engineering Center (NSF-MRSEC), led by Professor Tom Russell as PI. This mid-stream funding review, which included a visit to Amherst by NSF program officers and academic panelists, confirmed the excellent research and education/outreach taking place in the Center, and NSF-funding for the Center was maintained at the full level.

Later in 2006 marked the formal initiation of the NSF-Nanoscale Science & Engineering Center (NSEC), led by PSE faculty James Watkins as PI. NSEC is an especially exciting new development for PSE faculty, as its focus on building test-beds in materials science and biology will bridge the gap between the fundamental endeavors in PSE research labs and the practical needs of industrial research and development. A brief article describing the NSEC appears later in this Magazine.

A few examples from many accomplishments in PSE faculty in the past year should be noted: Tom Russell was named Distinguished Professor of the University of Massachusetts, Muthukumar received the prestigous Alexander von Humboldt Prize that includes six months of research and lecturing in Mainz and throughout Germany, Tom McCarthy gave the Langmuir lecture at the Fall 2006 American Chemical Society Meeting, Greg Tew won an IUPAC award, Maria Santore was named an Associate Editor of *Langmuir*, and Todd Emrick was promoted to Associate Professor with tenure.

In terms of new faculty, Ryan Hayward began as an Assistant Professor in January 2006, and is now ramping up his research group on the 3rd floor of Conte, on the preparation and properties of polymer micro- and nanostructures and assemblies. Harry Bermudez is *en route* to Amherst from the EPFL in Switzerland, to begin his appointment as an Assistant Professor in January 2007. Harry's work on polymeric biomaterials and drug delivery is described later in this Magazine.

Connections with *PSE Alumni* evolved throughout 2006, includng a terrific social reception at the Fall 2006 American Chemical Society meeting in San Francisco. Successful PSE alumni span the U.S. and world, and I enjoyed seeing PSE Alums during recent seminar trips, including Ilke Anac (McCarthy group, now postdoc at the MPI in Mainz) and Engin Burgaz (Gido group, now postdoc at Cornell). We continue to appreciate the generous support from PSE Alumni for first year graduate students, including a collective gift from a number of PSE Alums now working at Eastman Kodak, given in appreciation for their former mentor Dick Farris.

New PSE Alumni

Ilke Anac *Surface Modification by Adsorption of Macromolecules.* Advisor: Thomas McCarthy

Yoko Aoyama *Catalytic Hydrogenation of Heteroaromatic Polymers* Advisor: Bruce Novak

Kevin Calzia *Molecular Aspects of Yield and Fracture in Glassy Thermosets and Their Nano-Composites* Advisor: Alan Lesser

Gregoire Cardoen *Model Organic-Inorganic Hybrid Copolymers Based on Polyhedral Oligomeric Silsesquioxane* Advisor: Bryan Coughlin

Shujun Chen *Morphological Control in Nanostructured Polymers* Advisor: Samuel Gido

Ticora Jones *Synthesis and Characterization of Phenylene Ethynylene Oligomers* Advisor: Gregory Tew

Zhixiang Lu *Transport Polymerization for Materials Synthesis* Advisor: Thomas McCarthy

Bryan Parrish *Aliphatic Polyesters with Pendent Unsaturation and Poly(ethylene glycol) Groups: Synthesis and Use in Encapsulation* Advisor: Todd Emrick

James Sievert *Selective Metallization of Well-aligned Block Copolymers in Thin Films and Confined Geometries* Advisors: Thomas Russell and James Watkins

Kevin Sill *Nanoparticle-Polymer Hybrid Materials Based on Cadmium Selenide Quantum Dots* Advisor: Todd Emrick

Kevin Wier *Composite Polymer Coatings Prepared in Supercritical Carbon Dioxide* Advisor: Thomas McCarthy

Professor Shaw Hsu continues as Department Head

Following three productive years as Head of PSE, Professor Hsu starts his second three-year term. Given the many exhausting responsibilities of Department Headship, we all owe Professor Hsu a big thanks for his efforts!

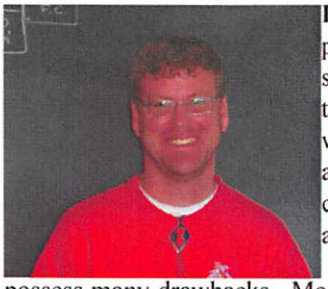
Upcoming events in 2007

- Polymers West Gordon Research Conference: Jan. 7-12
http://www.grc.org/programs/2007/polywest.htm
- CUMIRP-MRSEC-PSE meeting: May 15-17, 2007
http://www.pse.umass.edu/cumirp

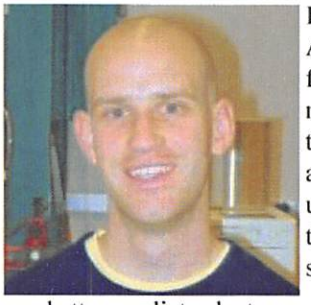
PSE Student Research

The research efforts of graduate students and postdoctoral associates have driven PSE to its high status in the global polymer community. Ph.D. candidates Qingling Zhang, Kevin Calzia, and Ryan Murphy discuss their Ph.D. research below, covering topics that span polymer and nanomaterials synthesis, mechanical and physical properties of polymers, and computuational approaches in polymer diffusion.

Qingling Zhang As a graduate student jointly advised by Professors Todd Emrick and Tom Russell, I started my Ph.D. research in 2003 on the self-assembly of nanoparticles, especially quantum dots, in block copolymer templates. While these assemblies are interesting and possibly useful in optoelectronic devices, I am frequently challenged by my advisors to tackle research problems with global implications, and am doing so by focusing nanoscale assemblies towards problems in energy. Surface modification of electron carrier nanorods, such as CdSe rods in the case of my research, coupled with assembly principles in polymer physics, are keys to my approach on hybrid solar cells. With my graduate student colleague Suresh Gupta, I have been working on the functionalization of CdSe semicondutor nanorods, and also their orientation by new "self-corralling" concepts that provide nanorods standing normal to underlying stubstrates, an ideal geometry for bridging electrodes in bulk heterjunction photovoltaics. If we can successfully prepare deivces from these new assemblies, we have a good chance to significantly improve on the state-of-the-art in the field of processible, spin-coatable bulk heterojunction solar cells.



Ryan Murphy For synthetic polyelectrolytes, there is still no robust and accurate technology for molecular weight determination. Current aqueous gel permeation chromatographpy experiments, although often used, still possess many drawbacks. Modification of the experimental protocol has been documented, yet it is easy to see that obtaining a more efficient characterization technique for molecular weight determination is needed. In an effort to find a solution to this problem, my research in Muthu's group has focused on the translocation behavior of synthetic polyelectrolytes through both biological and synthetic nanopores possessing diameters between 1.5 and 15 nm. This technique is extremely powerful as it allows a direct measure of single molecule dynamics, as a molecule threads an opening of well-defined dimensions. After graduation, I look forward to pursuing a career in polymer science, and hope to contribute to expanding the boundaries of science through cutting-edge research. I feel blessed to be a part of the unique and special research environment that is PSE.



Kevin Calzia My research in Alan Lesser's research group focused on how changes in the molecular architecture of glassy thermosets affect their mechanical and physical properties. By understanding how changes at the molecular level change larger scale mechanical behavior, we can better predict select properties, and also tailor properties through molecular scale reinforcement. We have synthesized a series of epoxy networks with controlled molecular weight between crosslinks and backbone stiffness. The yield response is governed by two physical parameters of the glass; one reflecting network stiffness and the other reflecting network strength. We have also correlated the yield response of different networks with a broad range of architectures tested at various temperatures, strain rates, and stress states through a proposed yield model. We have also studied the post-yield, strain-hardening response of these model epoxy networks. Similar to what has been reported in post-yield studies of thermoplastics, we have found the strain-hardening modulus of the model thermosets is inversely related to the molecular weight between crosslinks. We have also noted that several post-yield phenomena are independent of backbone stiffness, much like properties measured above the glass transition temperature of the networks.

Once a relationship between molecular architecture and the mechanics of the model network had been established, a unique class of molecules known as molecular fortifiers or antiplasticizers were introduced. Molecular fortifiers are small molecules that, unlike plasticizers, enhance properties by filling free volume and by specific physical interactions. We have introduced two types of phosphorus-based fortifiers, one as a simple additive and the other covalently bound to the network. The covalently bound fortifier created an additional point of crosslinking within the network giving unique mechanical and thermal properties. Nano-scale reinforcement of the networks was then considered with a focus on both the physical and chemical nature of the interface. Using compositional characteristics identified from our fortifier studies, we have introduced compatiblizers that promote both chemical and physical affinity between the polymer and nano-reinforcer. We have shown that these compatiblizers allow for intercalation of the polymer into the clay galleries during cure resulting in improved reinforcement of the nano-composite. Upon completion of my graduate research and dissertation, I will begin work at the Rohm and Haas Company in Springhouse, PA.

ACS-PMSE DOOLITTLE AWARD

During the Atlanta Spring 2006 ACS Meeting, PSE graduate student Kurt Breitenkamp and Assistant Professor Todd Emrick were chosen as the 2006 recipients of the Arthur K. Doolittle Award by the American Chemical Society Polymer Materials Science & Engineering Division (**http://membership.acs.org/P/PMSE/awards/doolittle.html**) for their paper titled: *Polymer Capsules Prepared by Photo-Induced Crosslinking of Aryl Azide Functionalized Amphiphilic Graft Copolymers at the Oil-Water Interface.* The presentation, given by Kurt, focused on his recent research on cross-linking PEGylated unsaturated polyolefins following their self-assembly at an oil-water interface. This assembly/cross-linking strategy was shown to give fluid-filled polymer capsules which may be used for the controlled release of drugs or other encapsulated compounds. ACS will present the official award during the Spring 2007 ACS Meeting in Chicago. Note that this continues a tradition of PSE Doolittle award winners, including Tom Russell (1985), and Tom McCarthy and Jim Watkins (1996).

PSE Students and Faculty at Polymers West GRC

January 5-12, 2007

Ph.D. candidates Qingling Zhang and Ms. Naomi DeLong will represent PSE students at the upcoming Polymers West Gordon Research Conference in Ventura, California (January 7-11, 2007). Qingling and Naomi will present their research during a specially organized student/postdoc GRC, held from Friday, January 5th to Sunday, January 7th. Professors Jimmy Mays (U. Tennessee) and Darrin Pochan (PSE Alumnus now at U. Delaware), and Dr. John Pochan (Darrin's dad, and recently retired from Eastman Kodak) have organized this event that gives students and postdocs at the cutting edge of research the opportunity to hold their own "mini-GRC" before the main event begins. Naomi will present her research on PEG-PLA-PEG triblock copolymers, and Qingling will discuss results on nanoparticle-polymer composites, including self-corralling nanorods of interest in photovoltaics, and self-healing nanocomposites (see cover article of the Nov. 17, 2006 issue of *Science*). During the regular GRC meeting, PSE faculty Greg Tew, Ken Carter, and Todd Emrick will make presentations.

PSE Alumni List

In our continuing effort to improve the PSE Alumni List, I ask that you update your own home and/or work mailing addresses, and encourage your classmates to do the same, online at http://www.pse.umass.edu/alum/index.html, or by contacting me directly at tsemrick@mail.pse.umass.edu.

OUTSTANDING TEACHER AWARD

presented to Professor Gustavo Carri

Congratulations to PSE Alumnus, Professor Gustavo Carri, honored by the University of Akron in the Spring of 2006 for his outstanding performance in teaching at the University. Carri, an Assistant Professor, graduated from PSE after completing his thesis under Muthu's supervision. Professor Carri's nominators noted that while he is one of the youngest professors in his college, he sets a very high standard among his colleagues. Professor Carri's excellent evaluations were found in the letters of both graduate students and undergraduates, making him a versatile and valuable asset at Akron, and in the broader polymer community. Carri follows in the tradition of his former mentor, who has won numerous teaching awards at UMass. Carri's research efforts at Akron, as he described in his recent invited seminar in PSE, center on statistical mechanics and simulations of synthetic and biopolymers, as well as nanocomposites.

Alumni recognition

Please do not hesitate to inform us when you receive recognition from your company, university, etc., as it is always gratifying to learn of alumni accomplishments, and advertise them in the Magazine.

Thanks to PSE Alumni Contributors!!!

We are extremely grateful for the financial gifts of PSE Alumni, as well as their committment to arranging for matching funds from their employers. The most recent contributors are listed below, and we encourage you to join your fellow Alums with contributions. Please keep in mind that these contributions enhance the life of first year PSE students during the period of study for classes and cumulative exams, prior to starting research under the supervision of a PSE faculty member. Also, if you receive contribution requests from the College of Natural Sciences & Mathematics, please indicate your preference for the use of your support towards PSE.

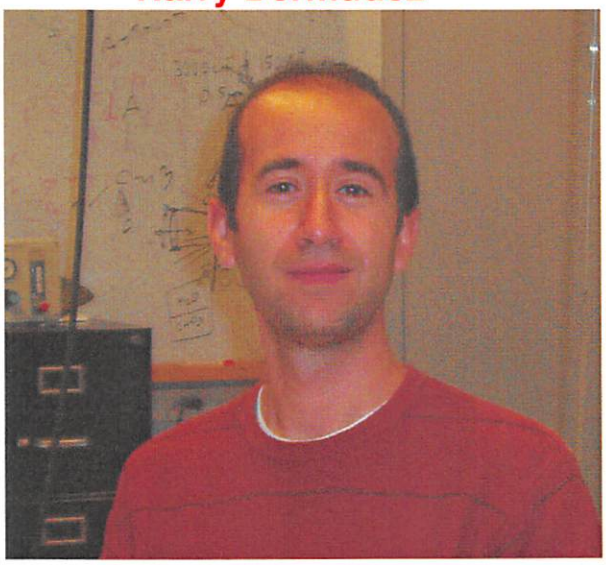
>$5,000
David Lipp Foundation ('71)

$1,000-$5,000
Richard J. Larson ('86)

$500-$999
Lothar W. Kleiner ('72)

$100-$499
Eric W. Kendall ('88)
Yuanqiao Rao ('95)
Margaret A. Rakas ('83)
Regina Valluzzi ('92)

New PSE Faculty
Harry Bermudez



PSE's newest hire, Assistant Professor Harry Bermudez, is set to begin his tenure-track position in January 2007. Harry earned his Ph.D. in Chemical and Biomolecular Engineering from the University of Pennsylvania in 2003, and is currently finishing his postdoc at the École Polytechnique Fédérale de Lausanne in Switzerland. He is excited to build his research program and start adding to the renowned history of PSE.

The main thrusts of Harry's research center around the application of polymers as biomaterials, and more specifically on the use of a variety of chemical and biological tools for engineering new delivery vehicles. As the local cellular microenvironment is increasingly appreciated as playing a major role in development, homeostasis, and wound repair, tailoring materials and interfaces to be compatible with, or facilitate, a desired physiological outcome remains a challenge. Several pathological (or otherwise undesirable) contexts such as the foreign body response still present major obstacles to current technologies such as implants, sensors, and controlled drug delivery systems. Addressing such problems forms a major thrust of Harry's planned research efforts.

Harry's specific research questions will focus on attenuating or promoting cellular recognition by using responsive materials, in the context of relevant physical, chemical, and biological cues. Pathogens such as viruses are the classical evaders of the immune system, and recapitulating essential elements of virus machinery in synthetic contexts presents new opportunities in biomaterials applications, for example by increasing the efficiency of drug and gene delivery. On the other hand, although viruses have certain "natural" attributes (e.g., nanometer size and ease of production) they also face limitations of their natural evolution. Incorporating synthetic character into viruses, through use of molecular biology and polymer chemistry, will lead to novel uses in biotechnology, such as robust yet biodegradable intracellular probes. Another approach to these types of questions can be posed entirely from a polymer perspective. For instance, by carefully tuning interfaces at the nanometer scale, cellular response may be guided to a particular phenotype. Polymeric systems provide a means to control important parameters such as elasticity, mobility, and interfacial chemistry. Again, modulating cellular recognition provides an important, and experimentally accessible, context for testing these ideas.

Harry was born and raised in the Queens section of New York City, and graduated from the prestigious Brooklyn Technical High School in 1994, where he discovered his interest in engineering disciplines. He then (wisely) attended UMass-Amherst, graduating in 1998 with a B.S. in chemical engineering, though by his own admission fair ignorance of polymers. This was remedied at the University of Pennsylvania, where Harry encountered the intersection of polymers and life sciences, which has interested him ever since. His Ph.D. research under Professors Dan Hammer and Dennis Discher focused on characterization of soft polymeric aggregates, specifically those capable of aqueous self-assembly. In many respects these materials are superior to natural amphiphiles, but their full range of capabilities is yet to be established. These systems offer numerous possibilities in drug delivery, artificial cells, and as nanoreactors.

During his postdoc at EPFL in the group of Professor Jeff Hubbell, Harry has worked towards engineering bacterial viruses for *in vivo* tissue targeting. The virus surface chemistry is altered initially by modifying the corresponding DNA; in a later independent step, polymers are attached covalently at precise locations of the virus. In this manner the surface is passivated while keeping a maximum of biological activity. The combination of synthetic chemistry tools with molecular biological techniques is a relatively new approach for tailoring these types of nanomaterials. Gene delivery and intracellular probes are other potential applications of these technologies.

Harry is a member of several professional societies including the American Chemical Society, the American Institute of Chemical Engineers, and the Materials Research Society. He hopes to make increasing contributions in terms of participation and organization over the forthcoming years, and also looks forward to participating in international meetings and fostering collaborative efforts. Certainly the current PSE faculty are very much looking forward to Harry's arrival, as he leads new and exciting endeavors in PSE.

Following his move across the Atlantic, Harry plans to rediscover the Amherst area, and to test his memory by revisiting favorite spots (if they still exist). In addition, he wonders about finding a place for his snowboard in New England that might be worthy of the Alps. It may take numerous excursions to test all the possibilities, but he's willing to try.

Please check the PSE website faculty page (http://www.pse.umass.edu/faculty/index.html) early in 2007 for further information about Harry Bermudez, and his complete contact information as he begins his position in PSE.

Fall 2006 Seminar Series

Date	Guest	Title	Faculty Host
September 8, 2006	Prof. Robert Grubbs Dartmouth College	*Controlled Radical Polymerization as a Tool for the Preparation of Nanomaterials*	Bryan Coughlin
September 15, 2006	Prof. Patrick Doyle MIT	*Dynamics of Complex Fluids in Microfluidic Devices*	Dave Hoagland
September 22, 2006	Prof. Dan Luo Cornell University	*Nucleic Acid Engineering: Using DNA as a Generic instead of a Genetic Material*	Shaw Ling Hsu
September 29, 2006	Prof. John Rogers UIUC	*Polymers for Nanofabrication: 3D Structures and Molecular Scale Resolution*	Ken Carter
October 13, 2006	Prof. Atsushi Takahara Kyushu University	*Ink-Jet Printing of Polymer and Metal Ultrathin Films on Surfaces with Wetting Anisotropy*	Tom McCarthy
October 20, 2006	Prof. Theresa Reineke University of Cincinnati	*PGAAs: Cationic Glycopolymers for Nucleic Acid Delivery*	Todd Emrick
October 26, 2006	Prof. Seong Kim Pennsylvania State University	*Surface Coatings from Non-Traditional Approaches – Easier and Better*	Tom McCarthy
November 3, 2006	Prof. Stephen Craig Duke University	*Controlling and Probing the Mechanical Properties of Single Molecules, Interfaces, and Bulk Materials*	Todd Emrick
November 10, 2006	Prof. L. Mahadaven Harvard University	*Soft Adhesion and Lubrication*	Ryan Hayward
November 17, 2006	Prof. Kari Dalnoki-Veress McMaster University	*Polymer Crystallisation, Dynamics and Morphology at the Nanoscale*	Al Crosby
December 1, 2006	Prof. Jeanne Hardy University of Massachusetts Amherst	*Regulating Biopolymer Function with Allosteric Small Molecules*	Alfred Crosby
December 8, 2006	Prof. Robert Cohen MIT	*Functional Thin Film Coatings Based on Polymer Multilayers and Block Copolymers*	Alan Lesser

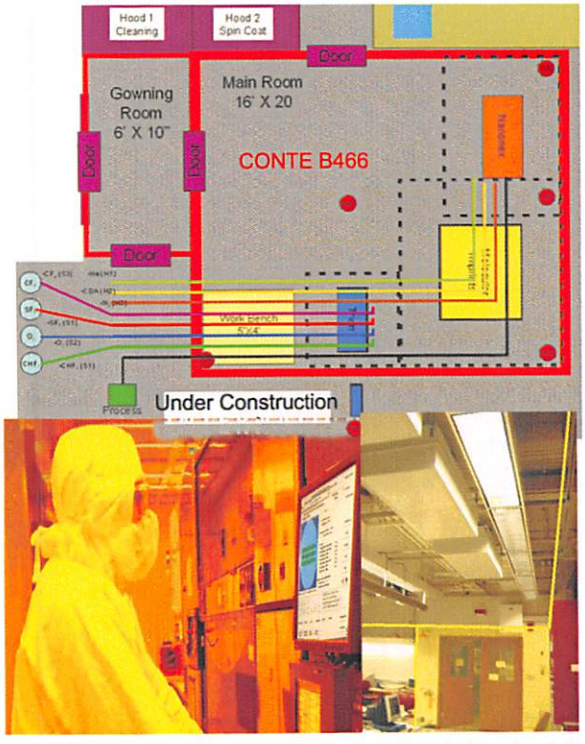
Polymers in Medicine in PSE

Thanks to co-organizers Shaw Ling Hsu, and Abbott Vascular scientist and PSE Alumnus Dr. Lothar Kleiner, state-of-the-art research and technology in the area of drug delivery was on display in PSE as part of the Fall 2006 CUMIRP-MRSEC-PSE presentations. The Symposium, titled *Polymers in Medicine and Biotechnology*, attracted over 100 academic and industrial scientists to the Conte Center on October 3rd. Four industrial scientists and four PSE faculty described their accomplishments and future directions in the area of controlled drug release, implantable drug eluting materials such as stents, injectable drug delivery vehicles, and anti-microbial polymers. Dr. Stuart Williams, from the University of Arizona, introduced new research efforts on characteristics of polymeric biomaterials that have the ability to direct tissue response, a key aspect of implantable device technologies. Dr. Robert Ward, from the Polymer Technology Group in Berkeley, CA, described *Surface Modifying End-groups* (SME) of long-chain polymers that can dictate surface properties and impart biological features to the polymers. Dr. Keith Cromack, from Abbott Laboratories, described the complexities associated with using medical grade polymers in medical applications, and the importance of control over polymer properties, sterilization, and stability. Dr. Fuh-Wei Tang of Abbott Vascular rounded out the industrial speaker session by presenting the phase behavior and morphological features that control drug elution from polymer matrices. The afternoon presentations by PSE faculty began with Shaw Hsu, who continued the discussion of drug delivery from both the experimental and modeling standpoint, especially focusing on the impact of polymer morphology and phase separation on release kinetics. Maria Santore presented her findings on protein adsorption on surfaces, the impact of ligand-receptor pairing on molecular mobility and surface arrangement, and the modeling of cell mobility and flow using silica nanoparticles. Todd Emrick discussed new approaches to polymer-drug conjugation and the controlled release of chemotherapeutic drugs, specifically camptothecin derivatives, as well as unusual approaches to encapsulation, for example using interfacial assembly and cross-linking of nanoparticles. Finally, Greg Tew concluded the afternoon session with a discussion of polymeric mimics of host defense peptides as anti-microbial materials.

CHM Nanocenter established

The Center for Hierarchical Manufacturing (CHM), a National Science Foundation-supported Nanoscale Science & Engineering Center (NSEC) is off to an exciting start in 2006. Three *Technical Research Groups* (TRGs) contained within the Center have initiated projects that aim to narrow the gap between fundamental research and manufacturing. PSE faculty James Watkins spearheads the effort as PI of CHM with Mark Tuominen of Physics. James is also co-leader with Tom Russell of TRG 1, titled *Nanoscale Materials and Processes*. TRG 2, titled *Nanoelectronics*, is co-led by Professors Seshu Desu (Computer Science) and Mark Tuominen . TRG 3, titled *Bionanotechnology*, is co-led by Professors Vince Rotello (Chemistry) and Suhrita Batia (Chemical Engineering), and includes research efforts at the bio/nano/materials interfaces, with targets in a number of areas including drug delivery using nanoscopic materials. CHM represents a bold move

CHM Cleanroom Design in PSE



forward on the part of the faculty involved, inspired by the desire to evaluate the manufacturing possibilities for many of the fundamental advances in polymer materials that have emanated from research in PSE and other Departments at UMass. CHM also offers strategic partnership with industry, and has garnered the support of a variety of companies, for example in the semiconductor industry which shares an interest in the test-bed concepts of CHM. CHM PI Watkins noted during a recent on-site review by NSF, that "over the past several years, many companies and UMass faculty have expressed the need to bridge the gap between fundamental research and the production line. The seamless-integration structure of the test-beds in CHM are thus timely and exciting for bringing new inventions closer to the production scene." Professor Ken Carter in PSE coordinates the test-bed activities, including the establishment of clean room facilities in the center that are suitable for preparing device components for the semiconductor industry.