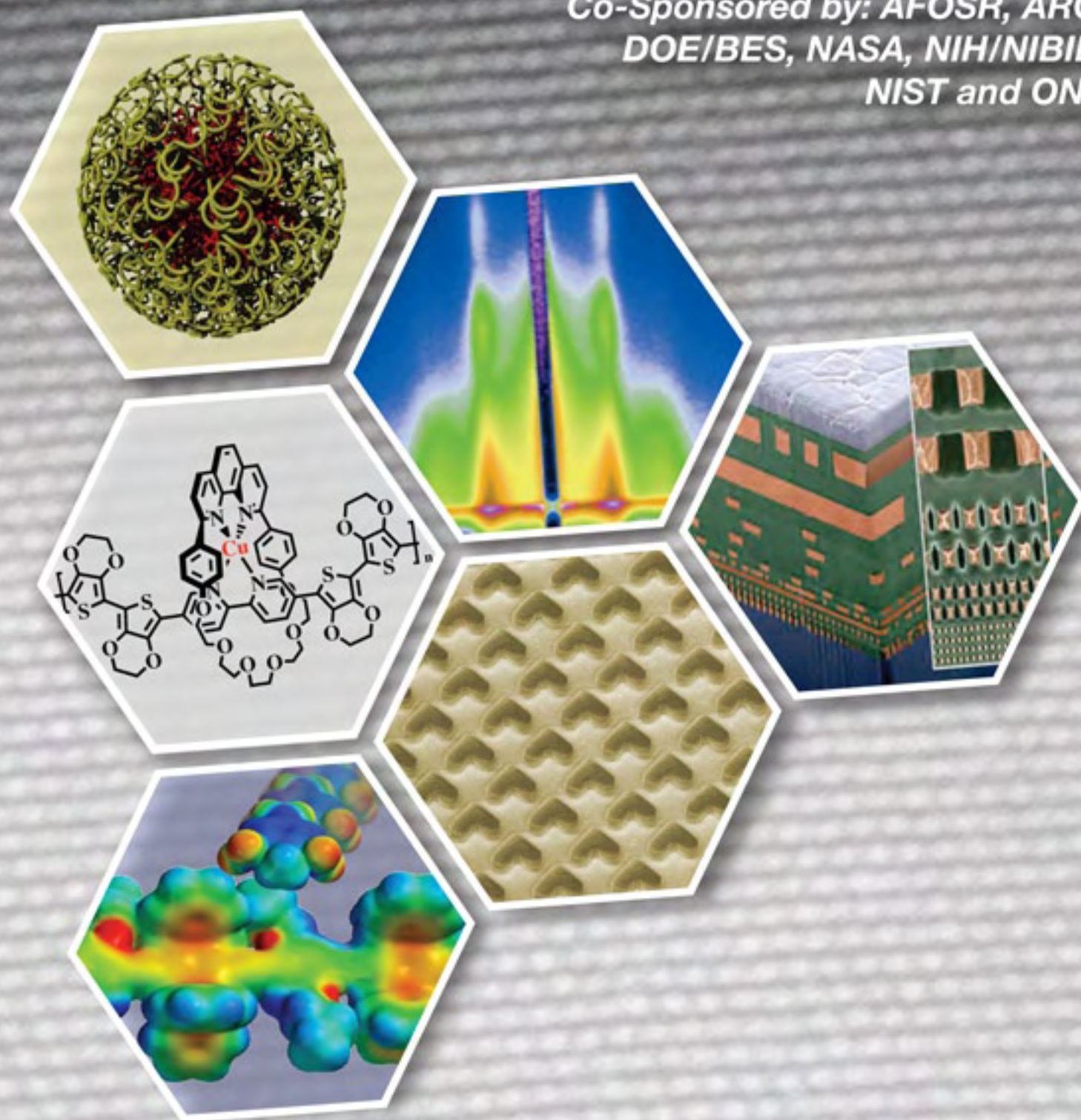


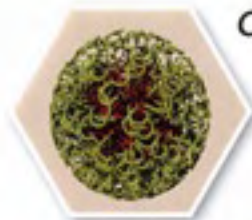
Interdisciplinary Globally-Leading Polymer Science & Engineering

2007 NSF Polymers Workshop

*Co-Sponsored by: AFOSR, ARO,
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On the Cover...



Complex Polymer Systems:

Shell Cross-Linked Block Copolymer Particles for controlled-release of therapeutics.

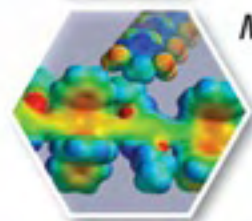
Image courtesy of Prof. Karen Wooley, Dept. of Chem., Wash. Univ. at St. Louis
K. B. Thurmond, T. Kowalewski, K. Wooley. *JACS* 118(30) **1996**, 7239



Polymer Synthesis & New Polymeric Materials:

A conducting metallorotaxane polymer exhibiting oxidation-sensitive conductivity with applications in polymer electronics and chemical sensing.

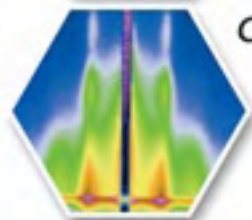
Image courtesy of Prof. Timothy Swager, Dept. of Chem., MIT
S. Zhu, T. Swager. *JACS* 119, **1997**, 12568



Modeling & Theory:

An electrostatic potential map of the most sensitive explosives detector ever made, showing the complementarity between the sensory polymer and TNT.

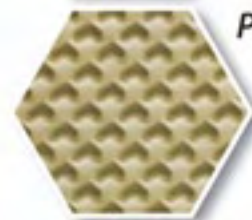
Image courtesy of Prof. Timothy Swager, Dept. of Chem., MIT
J. Yang, T. Swager. *JACS* 120, **1998**, 5321



Characterization & Properties:

Grazing Incidence Small-Angle X-Ray Scattering (GISAX) Pattern of Hexagonal Mesoporous Aluminosilicate Thin Films.

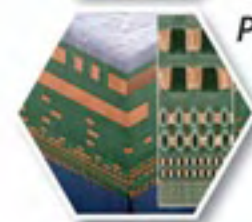
Image courtesy of Prof. Ulrich Wiesner, Dept. of Mats. Sci. & Eng., Cornell Univ.
P. Du, S. Gruner, U. Wiesner, C. Ober, *et al.* *Adv. Mater.* 16(12) **2004**, 953



Processing & Assembly:

SEM of "boomerang" PEG/magnetite particles for MR imaging made using the PRINT process (Particle Replication in Non-wetting Templates)

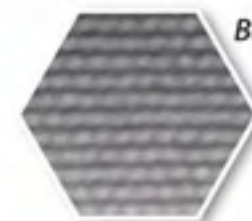
Image courtesy of Prof. J. DeSimone, Dept. of Chem. (UNC), C&BE (NC State)
J.P. Rolland, J. DeSimone, *et al.* *JACS*, 127, **2005**, 10096



Polymer Technology in the Service of Society:

Scanning Electron Microscopy image of an IBM microchip using block-copolymer templated air gaps to enhance processor speed and efficiency.

Image courtesy of IBM
J. Markoff. *The New York Times*, 05/03/07



Background image:

Transmission Electron Microscopy Image of Block-Copolymer Structure-Directed Inverse Hexagonal Mesopores in High-Temperature Ceramics.

Image courtesy of Prof. Ulrich Wiesner
M. Kamperman, U. Wiesner, *et al.* *JACS*, 126(45), **2004**, 14708

Interdisciplinary, Globally-Leading Polymer Science and Engineering

A National Science Foundation Sponsored Workshop
co-sponsored by AFOSR, ARO, DOE/BES, NASA, NIH/NIBIB, NIST and ONR

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NSF Headquarters
Arlington, Virginia
August 15 - 17, 2007

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Preface

The Workshop on Interdisciplinary, Globally-Leading Polymer Science and Engineering began with a phone call from Dr. Andrew Lovinger (Director of the Polymers Program at NSF) to discuss a follow-up to the 1997 Workshop on Macromolecular Science and Engineering (MMSE). The resulting 1997 report had a major international impact on new directions in polymer research. Given the importance of polymer science and engineering, it seemed timely to consider the many changes that have occurred since that last event. The purpose of the new workshop would be to explore emerging research opportunities and areas that are ripe for innovation in the field of polymer science and engineering over the next decade and to examine the critical issues of competitiveness, education, and diversity in the polymer community. As a result of this call, I was asked to chair the workshop and to assemble an organizing committee.

Consulting with the polymer community via e-mail postings, the committee identified six topics for the workshop: Polymer Synthesis and New Polymeric Materials; Complex Polymer Systems; Modeling and Theory of Polymers; Processing and Assembly; Characterization; and Technology and Societal Applications of Polymers. We felt that these themes broadly reflected the key areas of polymer science and engineering and that important future advances in research and education will require contributions from or consideration of each area. We also decided that the workshop should reflect important technological areas with enormous potential for societal benefit and for this reason the plenary talks would be aimed at these key areas. It was thought that such a focus would help to guide the discussion of scientific and technical questions in the breakout sessions and lead to a stronger report. Each working group was instructed to consider for the report not only a specific science and technology area, but also to address issues related to competitiveness, diversity, and education. As in the prior workshop report, the content of the recommendations made by each discussion group varies; some emphasize research directions and others educational issues or funding procedures.

What follows represents much thinking and hard work on the part of the workshop participants and co-organizers. Many thanks to everyone who took part in the workshop, including the sponsors from the funding agencies and in particular Dr. Lovinger (NSF), who catalyzed this effort. All the plenary speakers did a marvelous job of meeting our impossible demand to provide short but stimulating talks on a focused topic with plenty of time for discussion. I would also like to thank NSF Director Dr. Arden L. Bement for welcoming the workshop participants and Dr. Kathryn L. Beers (Assistant Director for Physical Sciences and Engineering, Office of Science and Technology Policy, Executive Office of the President) for her opening remarks.

Another important contribution was made by the panel, moderated by Dr. Elsa Reichmanis, with Dr. Kathryn Beers (OSTP), Prof. Stephen Cheng (University of Akron), Dr. Mary Galvin (Air Products), Prof. Peter Green (University of Michigan, and immediate past President of the Materials Research Society), Prof. Anne Hiltner (Case Western Reserve University and Director of an NSF Science & Technology Center), and Dr. Catherine Hunt (Rohm & Haas, President of the American Chemical Society) who discussed the issues of education and competitiveness with respect to the scientific enterprise. I thank them for their thoughtful and helpful contributions.

Of particular note, and I think representative of the importance of this workshop, was the presence of the current and past presidents of the American Chemical Society (Hunt and Reichmanis), the past president of the Materials Research Society (Green) and a representative of OSTP (Beers).

I especially want to thank my co-organizers Dean Stephen Z. D. Cheng, Prof. Paula T. Hammond, Prof. Murugappan Muthukumar, Dr. Elsa Reichmanis, and Prof. Karen L. Wooley, who began this effort many, many months before the workshop was held and who worked long hours on their sections of the report. I also want to acknowledge and thank the student participants in the workshop who brought a special freshness and excitement to the proceedings. I cannot thank all parties enough, since this report has taken considerable effort by many people. It is my personal hope that this document provides inspiration to those interested in research and education in polymers.

A handwritten signature in blue ink, appearing to read 'C. Ober'.

Christopher Ober

Ithaca, NY
Dec. 27, 2007

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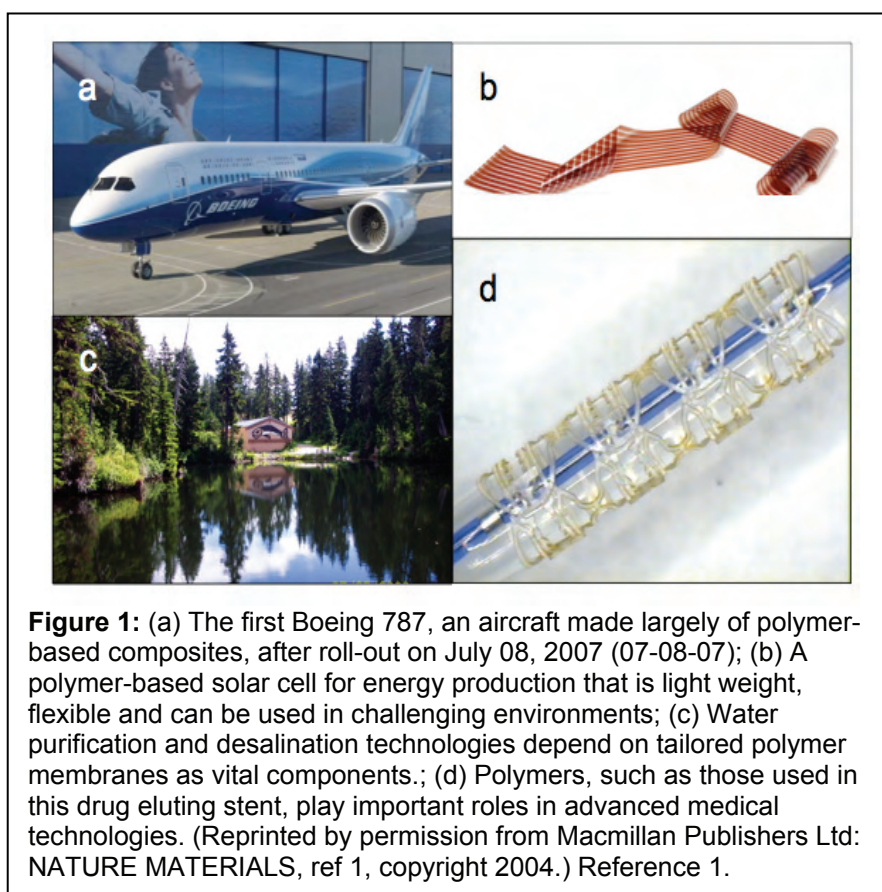
Executive Summary

The field of polymer science and engineering is a vibrant contributor to the US economy, not only in its own right, but also because of the wide array of industries and technologies made possible by the use of polymer materials. Polymers have unique, molecularly definable properties and process advantages unattainable in any other kind of material. Their attractiveness comes, in part, from the wide varieties of structure, molecular weight, and functionality available via rational synthesis of polymers and their characteristically broad range of possible processing modes. Thus polymers offer the potential for high performance at lower cost, sustainable use, and in many cases possible replacement of other materials in many fields. Polymers have as a result become indispensable items in everyday life in uses ranging from clothing, paints, secure food packaging to major parts of automobiles but also as essential components in virtually every emerging advanced technology.

Polymers are needed to address many of the most critical challenges we face today in areas such as energy; sustainability; clean water; health care; informatics; and defense and security. The enabling role of polymers is illustrated by their inclusion as a crucial material in building the Boeing 787. This new plane is 50% by weight and 80% by volume polymer-based composite. (Fig. 1a)

A major opportunity for the field of polymer science lies in the direct integration of functional polymers into an energy-generating device. Certainly, reducing our

dependence upon fossil fuels will have a positive impact on the environment, US competitiveness, and security. Polymers will play an important role in the shift to alternate fuels and energy sources. Polymers serve as the basis of advanced batteries, the membranes used in efficient, low temperature fuel cells and as the polymer photovoltaic diodes (solar cells) for energy production that are now being developed (Fig. 1b). The latter materials will also lead to advanced devices including more robust polymer-based light emitting diodes (LEDs) for flexible color displays, and high performance as well as long-lifetime polymer transistors. New polymers



will enable better-quality, more affordable technologies with more efficient energy use to aid more people around the globe than possible today.

Polymers are ideally positioned to impact most of the key aspects of economic, social, institutional and environmental sustainability. Polymers play a central part in the membranes used in water purification and desalination (Fig. 1c). Polymers are critical components in food production and in the storage of delicate, time sensitive materials such as food and medicine. Polymers are being developed that come from biological sources, do not compete with food for their feedstock as many biofuels do, and can be much more readily recycled than in the past. Polymers are used because they are light, robust, low cost, extremely effective materials.

Polymers possess another critically important and absolutely unique attribute, namely their similarity to biomacromolecules, the molecular basis of living organisms. Recent biomedical advances in areas such as artificial skin for wound healing and new methods of drug delivery such as that used in drug eluting stents (Fig. 1d) are vitally dependent on discoveries in the creation, processing and understanding of polymers. As a result of the features they share with biomolecular materials, the impact of polymers will continue to grow, as their use expands further into human tissue repair, disease detection, food supply monitoring and other aspects of homeland defense, and future medical technologies. In the near future, advances in polymers will enable superior healthcare to reach greater numbers of people in a more economical manner.

Thanks to the great conceptual advances made during the past six decades, researchers in polymer theory and simulations are well positioned to facilitate the discovery of newer concepts and phenomena for hierarchical polymeric materials. The key to these cyberscience and cyberdiscovery efforts lies in providing conceptual and mechanistic explanations of existing phenomena and to making predictions tested by experiments. Sustained efforts on the part of theorists and simulators will provide design rules for synthesizing polymers with tunable properties, methods for assembling polymeric structures at multiple length-scales, and processing protocols (strategies) to enable low-cost production of novel polymeric materials.

Until recently the United States and a few other developed countries dominated the fundamental research and manufacture of polymers. This is changing, however, and many developing countries are entering the polymer field. To retain its science and technology leadership, the United States will require a renewed and in some cases a dramatically enhanced focus on polymers with a significant investment of time and resources.

In order to assess the *current* state of polymer science and engineering and to identify essential *future* research and education opportunities a NSF workshop on “Interdisciplinary, Globally-Leading Polymer Science and Engineering” was held in August 2007 in Arlington, VA. The following section is intended to summarize the findings of this workshop. It consists of two parts: crosscutting recommendations and goals that appear in several locations of the report, and which were endorsed by all members of the organizing committee; and recommendations that are specific to the topical areas of the workshop, listed by report section. Whenever there was obvious duplication, a recommendation appears only once in the summary; however, all recommendations do appear at the end of each report section in their original form.

Crosscutting Recommendations and Goals

It is clear from the animated discussions held at the workshop that the field of polymer science and engineering holds the key to developing new and significant materials needed for many important technological breakthroughs. Common emerging themes came up repeatedly in the breakout sessions that will enable such developments to occur. These include the growing

importance of: i) complex, multicomponent polymeric systems (synthetic, biological and hybrid) used to achieve new materials properties; ii) *in situ*, real time, multidimensional characterization as important tools for understanding and refining complex polymer-based materials; iii) polymer synthesis and its role in the design and development of new polymers with exquisite control over molecular size, architecture, and chemical composition; iv) the need for processing with 2D and 3D structural control of polymers down to dimensions of a few nanometers; and v) computational modeling of new polymeric structures, predicting the influence of processing, and the resulting properties of polymer systems. The following bullets describe the major crosscutting recommendations and goals from the workshop.

- **Develop in concert the synthetic, analytical, theoretical/computational, and processing capabilities needed to master the structural control provided by new polymers and processes.** In order to achieve unparalleled science and engineering breakthroughs, we must bring separate research disciplines together. A common theme in all breakout groups was the tremendous need for theory and simulations performed in synergistic collaboration with researchers in synthesis, characterization, and processing to provide guidance for these efforts.
- **Be able to tailor-make polymers.** New synthetic methods with exquisite control over molecular structure and function possessing a precision rivaling biomolecules must be developed if we are to provide the materials needed for exciting future advances. In particular, new materials including complex, hybrid polymers with specific properties made in small quantities will be needed for the future applications envisaged by this workshop.
- **Develop real-time, high throughput, non-destructive, *in-situ*, multiscale polymer characterization techniques.** Multiple, simultaneous analyses will provide real time information of unrivalled precision to enable the implementation of precision processing and usher in the use of new self-assembling materials.
- **Be able to process polymers and complex hybrid materials with 2D and 3D structural control down to dimensions of a few nanometers using both directed and self-assembly.** Processing combined with new synthetic polymers that undergo self-assembly will permit materials with the molecular precision needed in emerging technologies. Using directed and self-assembly in combination provides unprecedented opportunities for tailored materials that must be explored.
- **Accelerate research in technology-focused, enabling polymer materials.** A common theme in the breakout sessions was the vital and growing role that polymers will play in the energy, life science, microelectronics, and information and communications technology fields. The use of polymers will increase dramatically in areas traditionally dominated by inorganic materials as a result of fundamental opportunities provided by the coupling of polymer synthesis, processing, characterization and theory.
- **Enhance cyberscience for the purpose of sharing modeling modules within the broad polymer community, and encourage the creation of digital libraries of extensive data on polymer systems.** Increasing amounts of information and new cyberscience tools are being produced, but there are few efficient means to access them in an organized fashion. Research and teaching would be boosted by improved accessibility to these new tools.

- **Reduce the environmental impact of polymer materials during their preparation, processing, and use.** The polymer community has the opportunity and responsibility to reduce the environmental impact of polymers in all aspects of their manufacture and use.
- **Maintain an emphasis on diversity.** Our nation is built on diversity—diversity in thought, interests, gender, religion, culture and ethnicity, etc. Underrepresented groups form a large and largely underutilized talent pool that we need to fully embrace.
- **Create and enhance outreach and education programs for K-12 students to prepare diverse future generations of globally leading polymer scientists.** Polymer science should be introduced to all students as a core part of their education because it reaches across all science and engineering disciplines.
- **Increase efforts to modernize the multidisciplinary curriculum in polymer science and engineering.** Polymers provide easily grasped concepts that should be taught across disciplines in the physical science and engineering curriculum. The polymer community should identify a new curriculum that reflects recent developments in polymer science and engineering and provides strong foundations in both the physical and biological sciences necessary to advance our discipline.
- **Provide sufficient staff and infrastructure to support central analytical facilities over the long term. Increasingly, we are not investing enough in facilities to provide polymer researchers access to the best equipment possible.** In an age of increasing international competition, US leadership in polymer science and engineering will erode without state-of-the-art facilities.

Working Group Recommendations

Polymer Synthesis and New Polymeric Materials

- We need research on new synthetic methods for producing macromolecules of precise size, composition, architecture, and shape, and with controlled homo- or heterogeneity to support emerging technologies and processing methods that demand increasing complexity in polymer systems.
- These new synthetic methods include high yielding/quantitative reactions to enable improved control over macromolecular composition and structure and orthogonal chemistries—chemistries that can be used in sequence without interference with each other must be developed further.
- We need to support transfer of knowledge and techniques between laboratories in a manner that enables a learning period with follow-up to successfully transfer methods and skills, perhaps in the form of small team grants, internships, etc.
- We need to develop accurate computational modeling to guide synthetic designs and to help identify useful structures that might be otherwise overlooked.

Complex Polymer Systems

- Natural materials make use of self-assembly to achieve functional behavior that is often impossible to replicate in today's synthetic materials. The self-assembly behavior of

biological molecules as well as the design and understanding of complex polymer systems to create tailored interfaces for controlled transport should be explored.

- The integration of unique polymer function with inorganic or organic nanostructures makes it possible to manufacture new materials with unmatched property profiles. Further understanding of charged polymers, polymer ionic complexes, and control of the supramolecular structures will enhance production of precision, complex materials.
- Control of kinetic and thermodynamic pathways in complex polymer and heterogeneous blend systems should be explored as a form of advanced processing to achieve specific structure. Adaptive systems that use assembly, disassembly, and controlled reversibility to achieve structural complexity provide another focus area.
- Through significant advances in the computational modeling of heterogeneous polymer systems, new polymer based materials with unique structure, phase behavior, and dynamics will be predicted and experimentally realized.
- There is an ongoing need for advances in the characterization of nanostructured complex materials. Only with a precise picture of complex materials can advances in the experimental and theoretical aspects of these materials be achieved.

Processing and Assembly

- New processing methods combined with self-assembly offer the potential to make materials with unmatched levels of molecular and structural precision. To accomplish this, we need to better understand, monitor, and control the processing methods and assembly strategies used to form polymer structure and functions in 2D and 3D.
- Research should be encouraged to combine the ability to make precise, arbitrarily shaped structures using top-down fabrication methods with the ease and precision of bottom-up self-assembly.
- As the sophistication of polymer structures increases and as biological motifs are incorporated into complex polymer systems, we need to develop efficient, ambient processing protocols. At the same time, environmentally benign processing methods should be developed for all polymers.
- As polymers are increasingly incorporated into advanced technologies, we see an increasing need to evaluate and develop new small volume/small quantity processing methods (e.g. micro/nanofluidics).
- As processing is applied to smaller-scale systems and as the quantity of material decreases, it will be increasingly important to develop instrumentation that can be used for routine diagnostics, enabling closed-loop feedback control.

Characterization and Properties

- With advances in polymer synthesis, the development of complex materials, and the use of sophisticated processing and assembly methods, there is a growing need to apply sophisticated tools to reveal the basic nature of a poorly-understood structure-formation processes.

- It is important to develop molecular-scale probes with which to determine chemistry and chemical distribution (functionality). With these methods it is possible to analyze the physical interactions of a single chain or particle directly and with precision to relate interactions to microscopic conformations and macroscopic properties.
- We should develop new characterization techniques that will allow the detection of inhomogeneities, whether intended (hybrids) or unintended (defects). Such methods should include the development of real-time, high-throughput, non-destructive, *in-situ*, multi-scale techniques as well as the streamlining of current techniques.
- To provide valuable input in the design of tailored materials, it will be important to establish standards (or at least expectations) for a broad range of properties including, but not limited to, electrical conductivity, thermal conductivity, biocompatibility, optical properties, and ion transport. This might lead to a readily accessed repository of data that makes use of developing cyber infrastructure.

Theory and Simulations

- It will be important to foster a research environment in which theory and simulations are performed in synergistic collaboration with researchers in synthesis, characterization, and processing. This combination will speed research, reduce time to discovery, and identify new materials that discovery and intuition alone cannot identify.
- Electrically charged systems provide an extremely rich area for computational research in complex polymers and therefore we encourage research to better understand this area. This might include developing an understanding of electronic-ionic transport in technologically important systems ranging from polymer-based batteries to devices to living cells.
- It will be important to cultivate force fields and algorithms to enable simultaneous modeling of multiple scales from monomers to polymer processing. The role of dielectric inhomogeneity, electrostatics, hydrophobicity, hydrogen bonding, and the structure of water in crowded environments will be important aspects of this work.
- Quantum mechanical computation for conformationally disordered systems as well as other polymer and complex polymer systems should be investigated in much greater depth.

Education

- Progress in polymer science and engineering benefits from research that draws on many disciplines. We therefore encourage new mechanisms to enable scientists and engineers to work together more effectively in research teams involving computational modeling, synthesis, characterization, and processing. Research in general and students in particular will benefit from working in multidisciplinary teams.
- We recommend increased efforts to create a sound multidisciplinary modern curriculum in polymer science and engineering. In particular, the incorporation of biology and biological materials into polymer science as well as computational modeling should be expressly encouraged.

- New degree programs should be designed that are more in line with future career paths, such as the implementation of an MD/Ph.D. - or an MBA-type science Ph.D. Students should be engaged in innovation and entrepreneurship at an early stage.
- To enhance outreach to prospective students, teachers, and the public, scientists should be encouraged to deliver polymer chemistry and materials science to Internet productions and other venues, for communication to a younger audience to improve diversity and societal awareness. Polymer science should be introduced to all students as it crosses all science and engineering disciplines and shows the impact of fundamental science on everyday lives.

Global Competitiveness

- Invest in science for the long term: fundamental studies related to the design and synthesis of new materials, the development of new characterization tools and methodologies, materials informatics, the design and development of new process methodologies and multiscale modeling.
- Invest in research aimed at the development of materials and process methodologies with which to transition polymer materials technologies from petroleum-based products to those derived from renewable resources.
- Create and maintain flexible immigration policies: US science and engineering disciplines in general and polymer science and engineering in particular have benefited from the ability to attract highly qualified talent from outside the US.
- Develop and support flexible intellectual property practices that will allow timely translation of technologies developed in the academic sector to the commercial sector. We should develop IP practices that will facilitate the translation of new discoveries into the industries of tomorrow.
- Continue to encourage interdisciplinary research activities: New discoveries are increasingly being made at the interfaces between disciplines. We need to continue to encourage and train students to work in an interdisciplinary environment and appreciate the value that different skill sets bring to the table.

Broadening Participation

- Identify, mentor, support, and proactively recruit a diverse set of participants into polymer science and engineering.
- Recruit and develop the American talent pool, employing a pre-college outreach component. As part of this effort, a determination of currently known best practices should be undertaken.
- Encourage undergraduate and graduate students to become involved in pre-college outreach
- Enhance programs aimed at educating and training pre-college teachers and counselors by giving them added information to help guide student career choices. Incorporate more pre-college teachers especially those from underrepresented groups into summer programs.
- To increase diversity, programs are needed for non-traditional career pathways, *e.g.*, to bring people back to science after family choices.

Workshop Program

National Science Foundation Headquarters, Arlington, VA

Day 1 – August 15, 2007, Morning (Room 375)

7:45 a.m. Check-in and refreshments

8:15 a.m. Introductions: Andrew J. Lovinger (Polymers Program Director, NSF)

8:20 a.m. Welcoming Remarks: Dr. Arden L. Bement (Director, NSF)

8:30 a.m. Opening Remarks: Dr. Kathryn L. Beers (Assistant Director for Physical Sciences and Engineering, Office of Science and Technology Policy, Executive Office of the President)

8:40 a.m. Workshop Goals: Prof. Christopher Ober (Cornell)

Plenary Talks

8:45 a.m. Prof. Frank Bates (U Minn) – Hierarchical functional materials

9:15 a.m. Prof. Sir Richard Friend (Cambridge) – Energy, electronics, photonics

9:45 a.m. Prof. Joseph Desimone (UNC Chapel Hill) – Environment and sustainability

10:15 a.m. Break

10:45 a.m. Prof. Kurt Binder (Mainz) – Computational Modeling of Polymers: Do We Need It?

11:15 a.m. Prof. Kristi Anseth (Colorado) – Polymers in biology, bioengineering and medicine

12:00 p.m. Working Lunch and Panel Discussion: Competitiveness and Education

Panelists: Dr. Elsa Reichmanis, moderator; Dr. Kathryn Beers (OSTP), Prof. Stephen Cheng (University of Akron), Dr. Mary Galvin (Air Products), Prof. Peter Green (University of Michigan), Prof. Anne Hiltner (Case Western), Dr. Katherine Hunt (Rohm & Haas)

Afternoon, Plenary Talks (Room 375)

1:30 p.m. Prof. Craig Hawker (UC Santa Barbara) – Nanomanufacturing

2:00 p.m. Prof. Tim Swager (MIT) – Polymers for Security and Protection

2:45 p.m. Breakout sessions

Polymer Synthesis and New Polymeric Materials (Topic Leader: Karen Wooley) Room 360

Complex Polymer Systems (Topic Leader: Paula Hammond) Room 365
Modeling and Theory (Topic Leader: M. Muthukumar) Room 370
Processing and Assembly (Topic Leader: Christopher Ober) Room 375
Characterization and Properties (Topic Leader: Stephen Cheng) Room 380
Technology and Societal Applications (Topic Leader: Elsa Reichmanis) Room 390

Evening

6:00 p.m. Dinner (on your own in Topic Groups)
8:00 p.m. Breakout sessions (Rooms 360, 365, 370, 375, 380 and 390)
9:30 p.m. Adjourn

Day 2 - August 16, 2007

Morning

8:00 a.m. Assembly and refreshments
8:30 a.m. Feedback session (Room 375)
10:00 a.m. Final breakout session for each group (Rooms 360, 365, 370, 375, 380, and 390)
12:30 p.m. Lunch on your own

Afternoon

1:30 p.m. Sub-committees write reports (Rooms 360, 365, 370, 375, 380 and 390)
4:00 p.m. Feedback to NSF
5:00 p.m. Concluding remarks and departure

Day 3 - August 17, 2007

All day; Organizing committee writes report (Room 360)

Section 1: Technology and Societal Applications of Polymers

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CHRISTINE ORTIZ, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

1.1 Introduction

As we survey our surroundings, polymer materials are ubiquitous. They play integral roles in the fabrication of our advanced technologies, they enable the advent of new and exciting technologies, and they will be critical to the development and implementation of new products. Historically, fundamental studies in polymer science and engineering have fueled the design of advanced lithographic materials that are critical to the fabrication of state-of-the-art semiconductor devices. They are essential to implantable drug delivery systems and are the basis for tissue engineering programs in which cells are combined with biomaterials to grow new tissues for advanced medical treatment. Research in polymer blends has allowed the development of engineering plastics, which has in turn led to their use in many manufactured products, for example in the automobile industry where they reduce weight and therefore energy use in cars. Equally critical is polymer processing that transforms these materials into usable products. Polymer technologies are and will continue to be needed to address many of the most critical challenges we face today in areas such as energy; sustainability; clean water; health care; informatics; and defense and security. This portion of the report assesses the societal and technological impact of polymer science and engineering.

1.2 Future Opportunities and Needs for Polymers

As a class, polymeric materials feature a wide range of properties that enable their use in many demanding applications. Their attractiveness comes, in part, from the wide varieties of structure, molecular weight, and functionality available via rational synthesis of polymers and their characteristically broad range of possible processing modes. Hence polymers offer the potential for high performance at lower cost, straightforward processibility, sustainable use, and in many cases possible replacement of other materials in many fields. For example, in the past several decades polymers have replaced metal structural materials in applications as demanding as modern aircraft or the automobile. Indeed, the coming generation of aircraft, including the Boeing 787 (50 wt% composite with nearly 100% of the skin, entire sections of fuselage made

from polymers and polymer-derived fibers), the Airbus 380 (25 wt% composite), newly emerging very light jets (Adam Aircraft, Honda, etc.) and a new generation of military fighters (F-22, JSF, etc.) is marked by extensive use of polymer composite materials.

In order for polymers to be exploited to maximum benefit, several breakthroughs will be required. These may be thought of as grand challenges and include:

- Designing, synthesizing, and integrating new polymeric materials into value-added products to be achieved by controlling structure, dynamics, and properties at scales ranging from the molecular through the macro
- Directing self-assembly and processing to realize the unique functionality of hierarchical polymer assemblies and control at the nano- and meso-scales
- Utilizing cyberinfrastructure to visualize the complexity of polymeric materials, including the development of a multiscale theoretical-predictive framework for polymer materials design

The following technology areas, critical to the competitiveness of the US, will be significantly impacted by developments in polymer science and engineering:

1.3 Energy

One of the greatest opportunity for the field of polymer science lies in the direct integration of functional polymers into an energy-generating device. Certainly, lessening dependence upon fossil fuels will have a positive impact on the environment, US competitiveness, and security. Polymers will play an important role in the US's shift to alternate fuels and energy sources. New polymeric materials will enable the development of batteries and fuel cells with significantly enhanced energy output and durability. Flexible, durable, lightweight polymer-based solar cells (Figure 1.1) will augment those made from heavier, costlier, and fragile silicon. Low permeability polymer hybrids will enable the development of lightweight tanks for the storage of hydrogen for fuel cell power systems for automobiles and aircraft. The use of nanoscale fillers and polymers with enhanced mechanical properties will enable the development of lightweight composites that will lead to lighter, more fuel-efficient aircraft, automobiles and transportation systems.



Figure 1.1: By blending ZnO nanoparticles and a conjugated polymer into a thin film, hybrid polymer solar cells can be made that give fourfold improved power conversion efficiency compared with that of existing hybrid solar cells based on metal oxides. Reference 2.

Significant technical advances will be required to fully realize the benefits of polymers in these applications. The development of new polymers with well-controlled architectures will be

needed to produce battery electrolytes and fuel cell membranes with enhanced ionic conductivity. Methods that make it possible to enhance interfacial bonding between polymer matrices and various fillers (fibers, clay, nanotubes) are required to produce new composites with better strength, stiffness, and toughness than conventional composites. Polymer-based solar cells will require the development of new materials with better charge-generation capability and enhanced carrier mobility. Cross-cutting technologies such as improved characterization methods and multiscale modeling are also necessary for the development of advanced polymeric materials to meet energy needs.

1.4 Sustainability

Polymers are, in general, ideally positioned to impact most of the key aspects of, economic, social, institutional, and environmental sustainability. One definition, which comes from the Brundtland Commission [3], defines sustainable development as development “that meets the needs of the present without compromising the ability of future generations to meet their own needs.” Polymers and complex polymer composites offer the potential to develop cheap, lightweight, and easy-to-process structural materials. However, we must continue to make progress in polymer and composite design to improve stability, lifetime, and mechanical strength.

The development of more “green” materials and composites is also critical. The drive to decrease our reliance on petroleum-based products has arisen because of the decreasing availability of petroleum reserves and the importance of minimizing the impact of manufactured goods on the environment. There is a need to identify alternative sources of raw materials and new methods of materials production that can continue technological progress, foster economic competitiveness, and have minimal impact on the environment. This includes cheaper and more environmentally benign processing conditions, and the development and utilization of more sustainable non-oil-based and less-toxic raw materials for monomers and polymers.

Flexibility in the design and processing of polymers makes it possible to form complex structures that can impact sustainability in a number of other ways. Polymeric membranes for water purification have attracted much attention from the academic and industrial communities in recent years. The concern regarding cost-effective water purification is a real issue in the U.S. and in national communities, as evidenced by a 2004 U.S. National Research Council Report that indicates that the total clean water production of the 15,000 desalination plants in the world generates only one-quarter of the capacity of U.S. consumption each year. Furthermore, across the globe, 1 billion people have no access to clean water [4], and 2.3 billion people live in water-stressed conditions—representing 41% of the world’s population. The need for water purification is rapidly growing as population increases, and rapidly developing countries increase consumption as industrialization expands. Thus, dramatic improvements in membrane technology are desirable to meet the growing need for cheap, clean water purification and management. For this we need complex polymer membranes with controlled morphologies and tailored chemical compositions designed to improve throughput, stability, anti-fouling characteristics, and production efficiencies. Advances in polymer science and technology are, potentially, capable of substantially reducing the impact of synthetic polymer materials on the environment, which is another indication of how vital polymer science can be in the future.

To summarize, anticipated exciting new developments include:

- Using plants as a renewable source of monomers that can be polymerized into new materials and eliminate the use of toxic solvents
- Designing polymers that are readily recycled or biodegradable to decrease the amount of waste
- Discovering new polymer synthetic routes, catalysts, and processes that use environmentally “friendly” solvents and require significantly less energy
- Using polymeric materials for water purification and waste treatment

1.5 Health Care

Polymer science and technology have contributed to transformative technological changes in healthcare through the development of artificial heart valves, contact lenses, and dental composites. Even with these advances, the full potential impact of polymers has not been realized. New advances in drug design and delivery, systems biology, nano-medicine, genomics, and control of cell differentiation and behavior ensure that the potential of polymer science and technology to improve health care is stronger than ever.

For instance, in the past decade, predictions issued via the previous NSF Workshop Report on Polymers have come to fruition, with polymeric materials becoming a core area for the development of new drug delivery, imaging, sensing, and responsive biomedical materials. A number of first- and second-generation developments in polymers for biomedical applications pertain to existing FDA-approved polymer backbones, which have led to many significant advances in medicine. Figure 1.2 presents just one example.

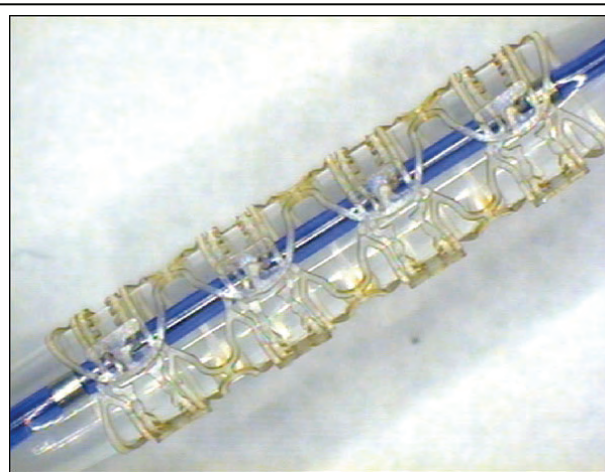


Figure 1.2: The new polymer used in this stent was developed within a nine-month period through a rational design approach that started from a combinatorially designed polymer library containing approximately 10,000 distinct polymer compositions. Using semi-empirical modeling techniques, only a small number of polymers needed to be synthesized and experimentally explored before a target polymer with optimum properties could be identified. In this process, the materials requirements were defined first, followed by a targeted search for polymers that satisfied the predetermined requirements. (Reprinted by permission from Macmillan Publishers Ltd: NATURE MATERIALS, ref 1, copyright 2004) Reference 5.

In the past several years, sophisticated polymer synthetic methods, combined with the ability to generate complex random, segmented, and block copolymers utilizing biodegradable or highly biocompatible blocks, have introduced novel polymers that merge new functionality with biologically relevant compatibility. Although progress has been made in polymeric biomaterials, several challenges exist in the implementation of such materials as medical tools or applications.

A key barrier is the difficulty of directly correlating structure-property relationships with cellular function; by incorporating signaling or labeling function onto polymeric systems, it should be possible to track the fate of the systems *in vitro* and *in vivo*, thus making it possible to understand the process by which the materials are internalized, absorbed, or incorporated within the body. An additional challenge in drug delivery includes the delivery of sensitive biological drugs such as proteins and antibodies, which are expensive and highly sensitive to process conditions due to their tendency to denature (thus greatly reducing the therapeutic activity of the drug). The design and utilization of water-soluble or water-processible polymers allows for the encapsulation of such drugs without destroying efficacy by avoiding harsh solvents or temperature conditions.

Over the next ten years, significant advances will be needed to move from current ‘passive’ polymer materials that serve as support structures for tissue or cells to ‘promoting’ polymer materials that can be designed to control the response of tissues, cells, or biological systems. Exciting new developments include:

- Designing well-controlled polymer systems that incorporate biological functionality to investigate and control cellular response
- Synthesizing unique polymer materials that increase the functionality of biomedical devices, e.g. incorporating drugs into stents
- Developing new strategies for delivering therapeutic agents (such as siRNA) to targeted areas to treat disease

1.6 Security and Informatics

Developments in the fabrication of polymeric materials will enable enhanced security strategies. The threat of terrorist attacks, as well as currency counterfeiting, piracy, and food tampering, have all been on the rise. The potential for the fabrication of low-cost, small, portable devices through high-volume production makes polymers uniquely suited for use in such applications as sensing devices as well as security identification and verification.

A key to this area will be the ability to incorporate functional polymers into hybrid or complex polymer systems so as to facilitate the active function required for a device application. A number of such polymers exist, but have not been readily manipulated into hybrid systems. Ultimately, the ability to generate devices using these systems implies the need to address multiple scales of self-assembly in these complex polymer systems. Here, it will be critical to link the development of self-ordering systems with guiding forces and lithographic or forced-assembly methods to generate devices.

Polymers also play a role in information storage. One of the challenges in achieving 2D storage systems is the generation of perfect order over large areas—a challenge that must be addressed in future work. It is likely that ordering will be achieved through the use of forced-assembly methods, unique processing schemes that impart order, or the formation of such structures within larger-scale structures that guide or induce order. Furthermore, storage media are likely to move from 2D to 3D systems, the latter being ideally suited for complex, multi-dimensional polymer systems. Figure 1.3 depicts a holographic image produced in a polymer-based matrix.

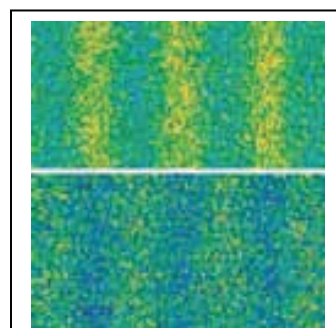


Figure 1.3: Manipulating nanoparticles dispersed in a photopolymer syrup proves a versatile method of fabricating high-performance holographic data storage media. Reference 6.

In summary, information gathering, verification, storage, and display are increasingly important as communication and data exchange becomes more widespread. Cybertechnologies depend on developments in polymer-based devices. In order to realize these potential applications of polymeric materials, gains in performance, stability and a detailed understanding of structure-property relationships are needed, especially as active structures approach the nanoscale. As with the switch from traditional construction materials to structural polymers over the last several decades, polymers will find increasing use as their performance and reliability are optimized.

1.7 Defense and Protection

Polymer science and engineering has and will continue to make significant contributions to the nation's defense. The use of lightweight composites in both airframe and engine components in military aircraft has already had a significant impact on their performance range and maneuverability. Further advances in the design of improved composite materials will lead to further enhancements in these aircraft. For example, mechanically actuated control surfaces (flaps and ailerons) on aircraft wings could be replaced with "morphing" wing components made from piezoelectric polymers that change shape under an applied electrical signal (Figure 1.4). Such a change would not only improve the maneuverability and performance of the aircraft but could also enhance its stealth capabilities. Polymeric materials with enhanced strength and toughness could be utilized in lightweight ballistic protection for the warfighter and vehicles. Low-permeability polymers can enable the development of inflatable structures (hangars, buildings, bridges) that can be easily and rapidly deployed and assembled on the battlefield. As

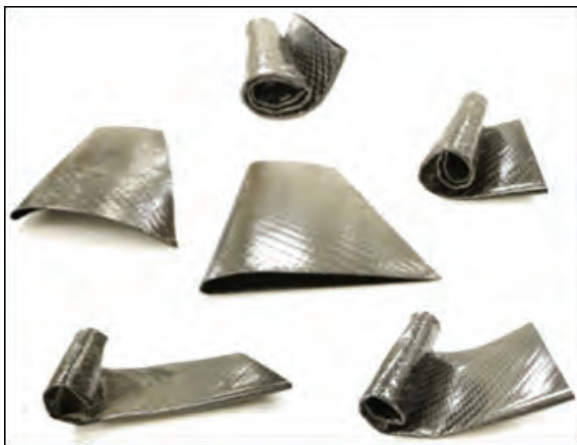


Figure 1.4: Cornerstone Research Group (CRG) specializes in smart materials, such as: conductive elastomers, shape-memory polymers and composites, and shape-memory foams. Their researchers are currently working with the Air Force Research Laboratories Munitions Directorate (AFRL) to develop and demonstrate morphing materials and technologies that are necessary to construct deployable morphing aircraft and other innovative adaptive structures critical to the Air Force in the future. Reference 7.

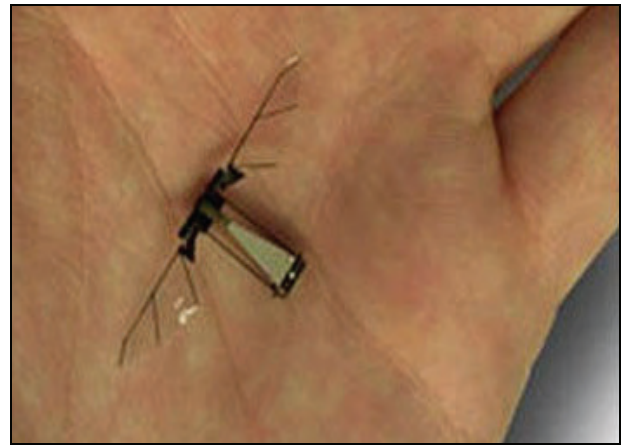


Figure 1.5: A 60 mg robotic insect has been developed in the hope that it will lead to stealth surveillance robots for the battlefield and urban environments. The Defense Advanced Research Projects Agency (DARPA), which is also interested in insect-cyborgs, is funding the project. To achieve moving parts for their robotic fly, the researchers used electroactive polymers, which change shape when exposed to voltage. Reference 8.

shown in Figure 1.5, polymers can also be used in robotics applications, some of which may be defense related.

Advances in polymer technology can also improve the safety and performance of soldiers on the battlefield. Protective clothing made from “smart” polymeric fibers and fabrics, such as those being developed at several universities, will be capable of detecting and responding to chemical or biological warfare agents and assess the overall health of the soldier. Improvements in elastomer technology will enable the development of selective or adaptive membranes that can protect the soldier from chemical or biological threats as well as allow for the administration of medicines to treat injury, sickness, or exposure to warfare agents. The development of flexible, lightweight lithium-polymer batteries will enable the incorporation of these power sources into combat uniforms for soldiers.

In summary, the above examples demonstrate that polymers will continue to enable essential developments in emerging technologies that are critical to our society and infrastructure. Beyond question, polymer science has a unique ability to design tunable materials enabling a high quality of life on a sustainable planet. Subsequent sections of this report provide recommendations for research, education, competitiveness, and diversity issues that are important in enhancing the positive impact that polymer science and engineering has on technology and society.

Section 2: Polymer Synthesis and New Polymeric Materials

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SPECIAL ACKNOWLEDGEMENTS:

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ILLUSTRATIONS TO THIS REPORT**

SUMMARY

Polymers are commonly considered to be “plastics,” primary materials that constitute everyday products such as trash bags, disposable diapers, etc. Even in such ordinary applications, however, polymer science and engineering represent extraordinary achievements. Polymers are all around us and are used as critical components in high technology devices. It may seem, therefore, that with sufficient capabilities and adequate materials polymer science is a mature field. This presumption is highly inaccurate. As societies and technologies continue to evolve, so do the materials required to support the fundamental infrastructure and emerging applications that drive progress. For instance, polymers are being utilized in, among other things, increasingly demanding structural engineering conditions as photo-active materials for solar cells, light-emitting diodes, and biomimicking nanostructures for medical applications. In each case, improvements in polymer structure and composition are expected to enhance performance. Moreover, as new polymer materials are designed and synthesized, the identification of unique properties will direct the development of new applications and technologies. This “Polymer Synthesis and New Polymeric Materials” discussion highlights the need to achieve higher degrees of control over the structures, compositions, and properties of synthetic polymers, including the ability to impart controlled heterogeneities, to expand the range of types of monomer units incorporated, and to develop coincident or sequential methodologies that employ efficient and orthogonal chemistries that increase the complexity and sophistication of polymer materials. We also describe here how important it is to design systems for programmed assembly/disassembly, healing, hybridization with other substances and, ultimately, degradation or destruction. We emphasize specific materials targets, but we also underscore the need for an educated workforce and greater societal awareness.

2.1 Introduction

Scientific research and development are critical for generating technological advances that will secure the current and future strengths of our nation. As recognized in the *American Competitiveness Initiative* report, [9] “as other countries build their economies and become more technologically advanced, America will face a new set of challenges. We must invest significant resources toward the advancement of our research infrastructure and the recruitment, training, and retention of human resources to ensure our future strength in global scientific innovation and technological advancement.”

Grand Challenge:

The driver for new technologies is the development of new or improved materials, and synthesis is what makes those materials available for practical applications. Polymers serve, arguably, as the most important materials in society today, as they are utilized in nearly every imaginable device: anti-reflective and protective coatings for glass; materials that allow for manufacturing of computer chips; the needles, tubing, and containers used for intravenous delivery of life-saving medications; components of those medications; construction materials in automobile manufacturing; clothing; packaging and containers; etc. In the “Polymer Synthesis and New Polymeric Materials” section of this report, we highlight the key ten-year goals, barriers to progress, and recommendations for overcoming those barriers that will enable polymer science and engineering to continue improving on such common applications and develop new materials for future applications. Ultimately, the recommendations are designed to meet the GRAND CHALLENGE for synthetic polymer materials over the coming decade:

TAILOR-MADE POLYMER MATERIALS

To realize this GRAND CHALLENGE will require the formulation of design strategies and the invention of synthetic methods to make and tailor polymer structures to fit new applications with programmed longevity and robustness. Such methods will include rational, functional design coupled with versatile covalent and supramolecular chemistries to achieve primary, secondary, and tertiary compositional and structural control. In turn, increasingly complex polymer systems will be constructed, relying upon tailored static and dynamic heterogeneities to afford multi-functional, partitioned polymer systems and gradient/hybrid materials, with unconventional properties at the molecular, nanoscale, microscale, and macroscale levels.

By developing techniques for growing and modifying polymer structures, controlling their sizes and shapes, placing distinctive chemical units in specific regions within the macromolecular frameworks, and by building polymers that contain units for their assembly with themselves and with other species, we can confidently anticipate the advent of new applications and enhanced performance for polymer materials. The needed advances will require molecular-

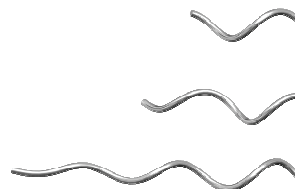
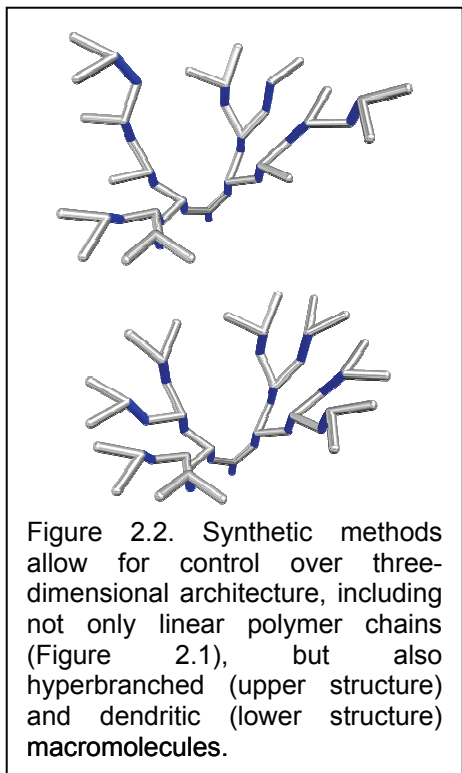


Figure 2.1. There are opportunities to gain greater control over the lengths and length distributions of polymer chains, a primary factor in controlling polymer materials properties.

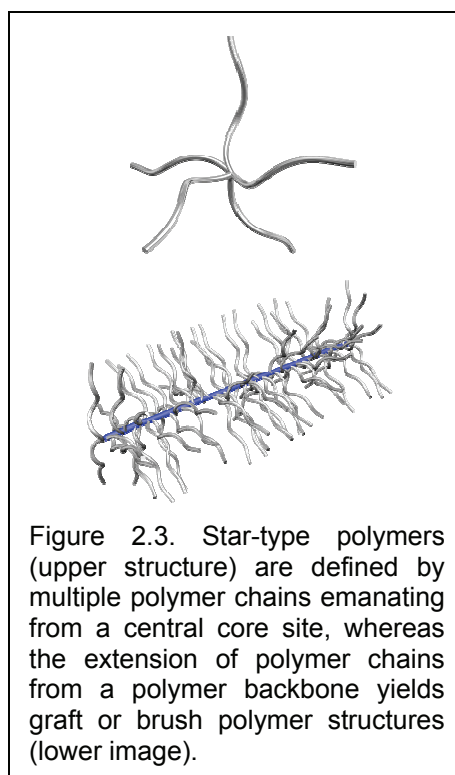


level control over the entire polymer framework, a level of control that is already ubiquitous in small molecule organic chemistry, but is increasingly fundamental to advances in polymer science. This growing convergence of organic and polymer chemistries has evolved during recent years to address new issues, such as accurate control over the spatial, stereochemical, and backbone location of atoms.

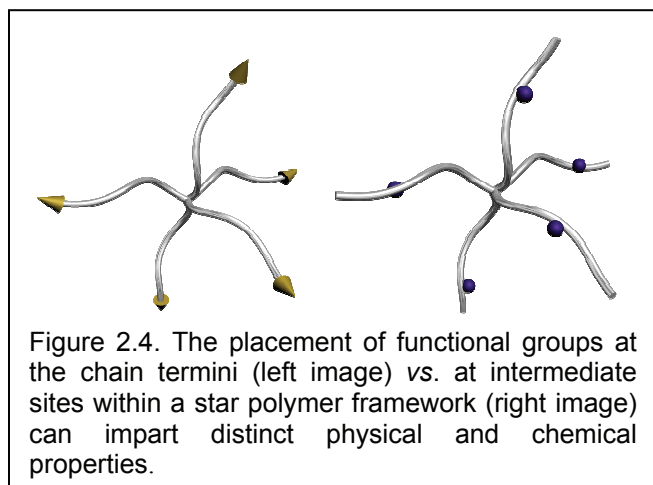
The relative complexity of dealing with polymeric structures as compared with small molecules has led to significant opportunities in the development of synthetic procedures for the preparation of these macromolecules. Two trends are clear: the realization that the synthesis of complex macromolecules poses significant challenges and opportunities, and the expectation that such materials will exhibit unique properties and functions. There are opportunities, for example, to tune the sizes of polymers through the catalysts and chemistries used for their construction or in purification procedures. We can, moreover, determine whether a set of polymers are all of the same length, or of a certain distribution of lengths/sizes (illustrated for linear polymer chains, Figure 2.1), and we can also configure the arrangement of units having

different compositions or structures, providing control over entire three-dimensional macromolecular objects (illustrated as hyperbranched or dendritic—perfectly-branched—structures, Figure 2.2). Polymer synthesis methods now being developed will yield complex synthetic macromolecules that are capable of mimicking many of the features of proteins (3-D folded structure, etc.) and other natural materials. These new generations of well-defined macromolecules have far-reaching potential for the study of molecular-level behavior at interfaces, thin films, and in solution while also enabling the development of novel encapsulation, drug delivery, and nanoscale patterning, among other technologies.

While we note that accurately controlling chemical structure and functionality at the macromolecular level shows considerable promise, we caution that this is not a simple case of directly transferring synthetic techniques from organic chemistry to polymer synthesis. The unique features of macromolecules, when compared with those of small molecules (large size, degrees of conformational freedom, number of functional groups, difficulty of purification techniques, etc.) turn the elucidation of polymer synthesis protocols that feature structural fidelity and high levels of functional group compatibility into a grand challenge.



Previously only a select few experts had access to well defined polymeric materials, but the discovery of simple and powerful approaches to polymerization reactions, not limited by the functional groups present, is a guiding principle that allows non-experts access to these same materials. Key developments in this regard include new chemistry and catalysts for controlled/living radical polymerizations (CLRP), ring-opening metathesis polymerizations (ROMP), and other controlled polymerization mechanisms. These new synthetic techniques afford a high degree of control over polymer topology (linear, branched, star, graft, etc., as illustrated in Figures 2.1-2.3), composition (statistical, gradient, block, or multisegmented copolymers) and placements of functional groups (as illustrated in Figure 2.4 for star polymers) through precise synthetic manipulation of the initiating moiety, the terminating unit, and the monomeric repeat units. Nevertheless, there is ample room for improvement. It is noteworthy



that controlled/living radical polymerization was just emerging when the last NSF workshop on polymers was held a decade ago. We expect that such controlled polymerization techniques will be used in greater concert with supramolecular assembly and other templating-based methods to afford macromolecular structures and nanoscale materials with increasing structural sophistication, properties, and functions over the coming decade. This combination of newly emerging techniques was a central focus of this current workshop. To remain

competitive, it is imperative that the US continue to lead the world in synthetic methodologies, as the pipeline to new materials fuels new technologies. We must develop new material syntheses and also train the next generation of scientists who will continue to advance polymer syntheses and the availability of new polymeric materials for extensive study and utilization, thereby contributing effectively to the *American Competitiveness Initiative*.

2.2 Significance, current state-of-the-art production processes, challenges and needs

2.21 Fundamental polymerization chemistries and polymers to investigate and achieve primary, secondary, tertiary structural control through rational covalent and supramolecular interactions

Methods for controlled heterogeneity

Synthetic polymer chemistry has succeeded in preparing polymers with well-controlled and uniform macromolecular architectures. These materials have figured prominently in the formulation of structure-property relationships for various (co)polymers. However, in order to optimize many materials properties, some diversity in molecular structure and uniformity is needed. Polymers with controlled heterogeneity should feature less-stringent reaction conditions and a wider processing window. For instance, it will be important to understand the effects of missing arms in star copolymers, partial loss of functionality in block copolymers, etc., on

macroscopic materials properties. These systems can be further refined to achieve cost-performance optimization.

Systematic variation in the heterogeneity of fundamental structural parameters could result in functional materials with novel and enhanced properties. Examples of such parameters include: (i) designed molecular weight distributions obtained in systems with dynamic exchange between active centers of different reactivities can be used as a tool for producing new polymer morphologies and also to relax constraints on polymer processes; (ii) precisely-tailored continuous variation of copolymer composition along a polymer chain will result in new molecular gradient materials with enhanced properties such as, for example, surfactants and noise- or vibration-damping materials; (iii) functionalities in the main and side chains that can link or disassemble polymer chains reversibly and on demand will generate polymer systems that can dynamically gel, rearrange, self-assemble and, potentially, self-repair; (iv) those advanced properties could be further enhanced by incorporation of functional moieties that respond reversibly to various stimuli such as light, magnetic or electric fields, temperature, pressure, pH, vapors, etc., in order to generate smart, interactive polymeric systems.

Copolymerization catalysts for industrial/high-volume production of commodity materials with improved performance

The final physical properties of linear macromolecules are determined largely by the relative degree of perfection of the incorporation of monomer units during the polymerization process. For commercially important, semi-crystalline materials, such as the ethylene-based polymers, for instance, the incorporation of short- or long-chain branches influences both primary and secondary characteristics; for stereoregular polymers, such as polypropylene, relative control of stereocenters during monomer introduction at the chain end is the dominant differentiating factor. The presence of chain “defects” allows for manipulation of final physical properties within limits, but in current state-of-the-art production processes, these are typically distributed randomly along the chain.

We know that creating linear blocky structures allows for a significant departure from the available physical property set using randomly constructed linear polymers, by the formation of discrete tertiary phases with unique morphological features. High-volume commercial polymerization technology generally does not readily allow for changes in composition along the chain *in situ*, however, without resorting to control of the growing chain end. We note that several strategies for making blocky linear polymers have been suggested, among them designing catalysts that alternately incorporate a stereoregular monomer repeat unit with atactic blocks of that same monomer. Recently, scientists have made progress in this arena by the use of chain-shuttling agents, in which two different catalysts exist in the same polymerization medium making two different polymers, which are able to switch the growing chain end back and forth between the different catalysts to create blocky structures.

We must continue to improve the quality and expand the compositional range of linear copolymers in which different monomers are preferentially sequestered to discrete block sequences while proceeding at rates of polymerization that allow for mass production. The extent to which these technologies allow for the commercial synthesis of new blocky materials using polymerization temperatures and pressures that are viable on an industrial scale will determine the economic impact of the venture. Breakthroughs have the potential to provide for new

polymeric materials that can be substantially differentiated from the simpler linear copolymers that have been produced commercially for the last 50 years.

Copolymerization of incompatible monomer mixtures to afford unique functional materials

The polymerization of olefins by coordination insertion polymerization is used to produce the largest-volume polymers prepared in the world, polyethylene and polypropylene. While variations of these polymers are made by the incorporation of other olefinic comonomers, the ability to introduce polar functionality to polyolefins at the polymerization step has been challenging, due to the incompatibility of most transition metal-based polymerization catalysts with polar monomers. Significant experimental and theoretical efforts have been expended on this challenge, with limited success. Alternatively, olefins can be copolymerized with polar monomers using radical mechanisms. By increasing the reactivity ratio of olefins in such a copolymerization, their enhanced incorporation can be achieved. The modification of polyolefins with polar species can be accomplished by post-polymerization methods, which are known to impart useful properties to these materials, but these methods are costly and inefficient. The incorporation of even low levels (*ca.* 1%) of polar species is sufficient to provide improved adhesion to surfaces and fillers, to modify the thermodynamics of polymer blends, for instance, and to provide chemical functionality that can be further differentiated. There remains a need to identify robust chemistries that take advantage of the versatility and throughput of coordination or alternative polymerization processes while allowing for the incorporation of polar comonomer species.

Simple and robust synthetic techniques to prepare tailored macromolecules

Chain (co)polymerization without chain-breaking reactions (termination and transfer) provides access to controlled/living polymerization (CLP). Recently, CLP has been extended from ionic polymerizations (requiring very stringent polymerization conditions) to radical polymerization and also to some polycondensation systems. Basic examples have demonstrated control of molecular weight and polydispersity as well as chain functionality, composition, and topology in these systems.

The remaining challenges include: (i) the design of new, inexpensive, robust, and simple polymerization procedures that can be conducted in aqueous or solventless media and tolerate air and protic impurities; (ii) identification of conditions allowing for enhanced control, for example, to diminish the proportion of terminated chains in radical polymerization by proper selection of reaction media, pressure, additives, compartmentalization, etc., without sacrificing reaction rates; (iii) expansion of the range of polymerizable monomers to broaden accessible polymer properties; (iv) rational design of novel polymeric architectures with controlled branching, model networks, and synthesis of segmented copolymers linking various incompatible units that will enhance materials properties (hard and soft, hydrophilic and hydrophobic, organic and inorganic, synthetic and natural, insulating and conducting, etc.) synergistically. Various types of hybrid materials can be prepared this way, by growing well-defined polymer chains from surfaces of inorganic wafers, colloidal particles, mesoporous structures, or membranes. Relying on progressively growing chains, the incompatibility can be avoided at the initial stages and polymeric brushes of unusually high densities can be prepared. This process makes materials with entirely new sets of properties possible, including lubrication, compressibility, anti-

biofouling behavior, and reduced corrosion. In a similar way, organic polymers can be grown from natural products, creating a new class of bioconjugates with carbohydrates, proteins, or nucleic acids.

Conjugated polymers and their applicability in electronic devices

Conjugated polymers have made extraordinary performance advances in electronic and photonic materials over the last decade and will be critical elements in many emerging technologies. The area of electronic materials pervades all aspects of human existence and, hence, this application area will only become more important in the future. The particular advantages of polymers relative to atomistic materials are realized directly when competitive technologies are very sensitive to materials cost, manufacturing, and the ability to control the energy levels of the electronic states. The ability of conjugated polymers to transport charge and emit light has led to the development of new generations of displays, for which the higher-efficiency materials can lead to energy-saving lighting technologies. Conjugated polymers have enabled new generations of chemical sensors with unprecedented sensitivities for the detection of explosives. Related sensory systems will not only find application in security technologies but will also impact healthcare diagnostics. Over the coming decades, we will need to create photovoltaic technologies capable of terawatt production, and polymers offer a scalable technology with which to meet this goal. Continuous improvement over the past few years in the semiconductor performance of conjugated organic polymers, and organic materials in general, indicates that these materials may replace conventional inorganic semiconductors in certain applications, especially those in which low processing costs are essential. Mobilities of holes in polythiophene derivatives already approach those of amorphous silicon, and mobilities of electrons in graphene and carbon nanotubes are orders of magnitude higher, indicating that organic materials with long-range electronic coherence can meet performance metrics for devices. Moreover, emerging processing and fabrication methods will enable the inexpensive fabrication of electronic circuits from conducting polymers that can allow for greater automation in many sectors of commerce. For example, inexpensive radio frequency identification (RFID) technologies will greatly simplify inventory management and consumer transactions.

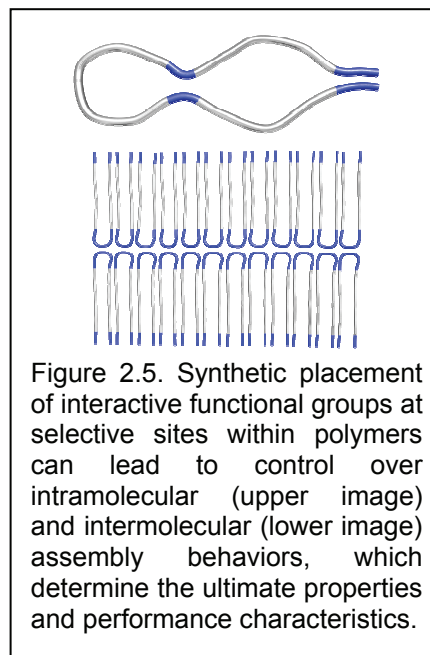
Continued investment in the synthesis of conjugated polymers with tailored electronic states is critical and will require innovative new designs. In general, the challenge is to combine high charge mobility, long-term stability, and facile processibility in an organic semiconductor. A specific unsolved problem in the area of polymer electronics is the design of polymers that are both stable in their n-doped states and have high electron mobilities. High performance n-type semiconducting polymers would enable complementary (“CMOS-like”) printable transistors.

Optoelectronic materials such as these are required to create commercially viable, polymer-based photovoltaic devices. Electronic structures that absorb a higher percentage of the solar spectrum will enable more efficient photovoltaic devices. There is an inherent efficiency gain in having both the electron- and hole-transporting materials function to absorb photons and transport excitons to interfaces. Precision design of these materials may enable large open-circuit voltages to be produced, a key attribute in achieving high photoelectric conversion efficiency.

Presently the synthesis of conjugated polymers is limited by the number of chain-growth methods that have been developed. Presently, most conjugated polymers are synthesized by step-growth methods and these methods seldom produce ultra-high molecular weights that will be critical to mechanical durability. Controlled (living) chain-growth methods will also enable the

synthesis of block polymers. The controlled microstructures that are possible from narrow polydispersity block polymers can enable self-assembly into structures for precision fabrication of devices. Photovoltaic devices could be readily fabricated using self-assembly, based upon polymers with both n- and p-type blocks. The nanostructure of conjugated polymer photovoltaic devices often dominates their performance. In addition, advances in the assembly of complex block copolymers should be extended to produce complex, stable, polymer architectures.

The stability of conjugated polymers in optoelectronic devices is a concern. For example, commercial photovoltaic panels must withstand decades of exposure to the elements and to direct sunlight with little degradation in performance. We recommend increasing efforts to create more inherently stable organic conjugated polymers. In addition, materials with exceptionally high oxygen- and water-barrier properties that can be applied by conventional coating methods are needed.



2.22 Macromolecules designed for tailored heterogeneity toward multi-functional, partitioned systems, with unconventional properties—*Supramolecular design in polymer synthesis*

Societal needs and emerging technologies demand advancement in the performance of polymer materials. Achievement of superior properties in macromolecules will depend on our ability to construct and control supramolecular interactions, that is, structure beyond that of the primary chain. We note significant progress during the past two decades in precision polymerization, setting the stage for innovation in the controlled construction of larger-scale structures. Control over intermolecular interactions will enable high-performance, adaptive, dynamic, and sustainable polymeric materials to support technological growth and to address human needs. Advances in this field will demand not only novel synthetic methodology to create designed superstructures, but also unique instrumentation to understand and characterize these structures.

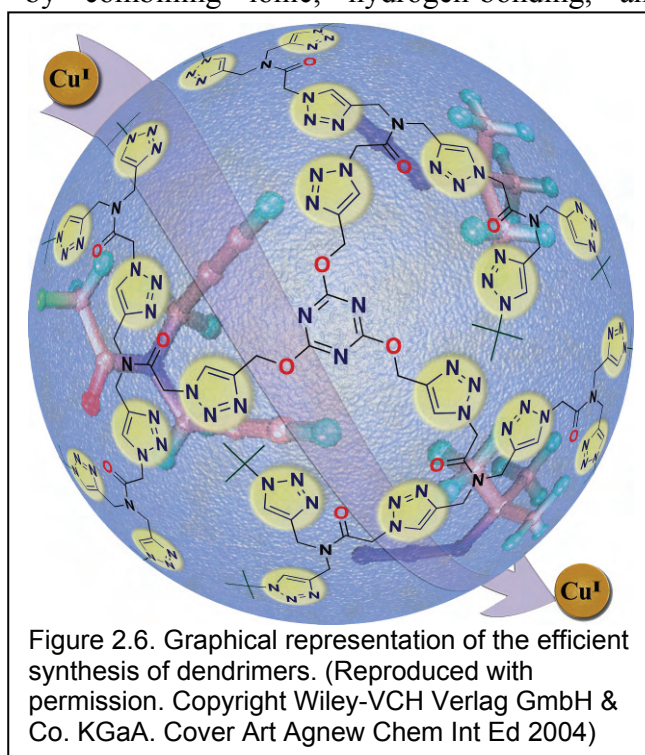
Supramolecular chemistry has evolved as an international focal point for the construction of novel, high-performance materials. The current state-of-the-art production process employs electrostatic interactions, hydrogen bonding, hydrophobic interactions, and metal-ligand interactions among polymer chains and between polymers and exogenous materials such as fillers and particles. Although these modalities have been widely implemented in both research-based and industrial materials, new opportunities exist to apply precision synthetic strategies to control the placement of interacting units in macromolecules on a larger scale, offering unprecedented ability to tune intermolecular interactions, and thereby access hitherto unattainable properties.

Control over supramolecular interactions may imbue materials with self-healing abilities, high physical performance while maintaining processibility, recyclability scenarios, and stimulus-responsive behavior. Self-healing improves the durability and material lifetime of

structural materials, reduces labor costs because of lowered frequency of replacement, and achieves positive environmental outcomes through reduced material and energy consumption. Stimulus-responsive properties enhance the development of novel sensor and electro-optical technologies, biomedical systems, etc. Further improvement of biomedical technologies will involve tuning the dynamic structure to achieve novel modes for the delivery of therapeutics and the response of biomaterials to stimulation in the human body.

The achievement of controlled supramolecular assemblies of polymers will of course require continued advancements in synthetic chemistry. Synthetic strategies are envisioned as evolving in a rational manner, leading to processes that consume less energy and labor, and offer improved safety. These positive attributes will address the problem of scalability that often plagues advanced materials, allowing for rapid adoption in industry to increase U.S. competitiveness.

The design of supramolecular polymer structures may seek synergy in multiple modes of intermolecular interactions, for example, by combining ionic, hydrogen-bonding, and hydrophilic or hydrophobic forces, to provide the unique properties of some biological materials. In addition, designed supramolecular structures might be extended to heterogeneous systems incorporating dissimilar materials with control over interfacial interactions and spatial distribution. The construction of complex polymer structures is grounded in proficiency in fundamental organic synthesis. This education and expertise must, however, be augmented by appreciation for the importance and potential applications of higher-order structures. Rational design strategies would therefore benefit greatly from appropriate predictive modeling (see Section 6: Theory and Modelling). In addition, the analytical tools required for future supramolecular scientists to succeed will go beyond those that are currently introduced in the classic laboratory setting.



2.23 Robust orthogonal quantitative chemistries for functionalization upon macromolecular and nanoscale substrates

One of the fundamental goals of any chemical synthesis is efficiency and, when coupled with the inherent appreciation of modularity in the fabrication of nanomaterials, the emerging importance of **Robust, Efficient, and Orthogonal (REO)** synthetic procedures in modern materials chemistry is explicit and undeniable. Preliminary experiments demonstrating the power of modularity and efficiency in the preparation of complex, multifunctional systems is helping to inaugurate an important new era of research in polymer science. When viewed as a whole, these

initial studies demonstrate that the difficulties associated traditionally with the synthesis of macromolecules—controlling multiple reaction sites, quantitative conversion, purification issues, etc.—are challenging and represent a significant opportunity for efficient and orthogonal strategies. If a range of chemistries that proceed with complete chemo- and regioselectivity and occur with quantitative yields and almost perfect fidelity in the presence of a wide variety of functional groups and reaction conditions could be developed, then the fabrication of well-defined, multifunctional materials would be greatly enabled. This robust/orthogonal “philosophy” embodies an attitude that is already second nature to polymer scientists: *Function matters most, and tools that achieve function are to be prized.*

What are the challenges for the future? New chemical transformations that satisfy all of the criteria of robustness, efficiency, and orthogonality are needed and an expanded palate of such tools would considerably benefit all materials-related communities alike. At present, the flagship reaction is the Cu(I)-catalyzed cycloaddition reaction between azides and alkynes (Figure 2.6), [10] which is helping to define the area but is open to further improvement. For example, the development of a catalyst with greater biocompatibility would help materials scientists operate in the biological realm, where the use of orthogonal chemistry removes the constraints of protection/deprotection strategies and cross-reactivity from the introduction of peptide sequences, sugar residues, etc., to macromolecular and nanoscale substrates. In a different area, the development of photochemically-activated REO procedures would enable a wide range of potential applications from thin films adhesives to cellular scaffolds to be addressed. The development of REO chemistry also opens up whole new avenues for materials in general to be prepared more efficiently and allows the range of possible nanostructures and macromolecular architectures to be greatly expanded. Just as importantly, the REO concept is expected to remove synthetic barriers to the implementation of new ideas and make materials synthesis more accessible. It is anticipated that REO chemistry will become a major theme and underlying consideration when the design and synthesis of organic materials is first contemplated.

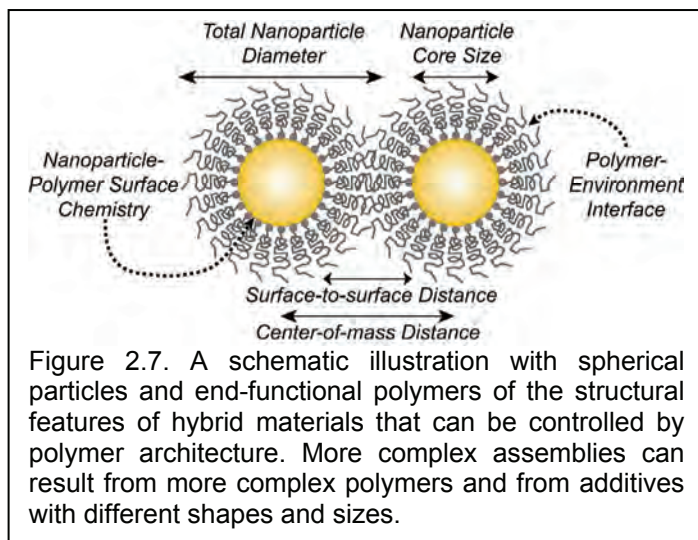
As always, Nature serves as both inspiration for and challenge to the ultimate goal: The cell is a soup of giant molecules, interacting with breathtaking specificity and orthogonality to achieve complex and interacting functions. If polymer scientists can realistically hope to engineer systems that even remotely approach the utility of Nature’s components, our synthetic methods must improve and do so, generally, without access to Nature’s evolved molecular machinery. Using synthetic building blocks, the grand challenge is to allow materials with similar complexity and control to be prepared under much simpler conditions. More and varied REO reactions would permit synthetic polymer designs not only to become ‘simpler,’ but also to become ‘better,’ allowing polymers to continue to underpin numerous technologies for the future. By doing so, polymer science will continue to significantly enhance the competitiveness of the American enterprise and enable the sustainable evolution of U.S. society.

2.24 Gradient/hybrid materials—at the molecular, nanoscale, microscale, and macroscale levels

It will be important over the next ten years to increase research efforts into the integration of polymers with other materials for the formation of hybrid materials. These hierarchical hybrid materials comprise systems in which organic and inorganic additives, including metal atoms, metal clusters, and nanoparticles, interact with polymers. Realization of these materials will

require polymer scientists to achieve control over the structure and dynamics of multiple high-molecular-weight species on multiple length-scales. A primary goal should be to develop advances in these hybrid materials to broaden the range of behaviors that they exhibit. The development of methods for precisely controlling the dispersion of these components within a polymer matrix will be of major importance. High levels of control over the structure and heterogeneity of hybrid materials should enable the development of new materials with controllable barrier, electronic, photonic, and magnetic properties. Incorporation of appropriate additives could lead to new reactive materials to be used, for example, for catalysis or water purification applications, and to new materials for medical applications, including diagnosis, imaging, and therapy.

We note a growing body of research on the preparation and characterization of specific polymer-containing hybrid systems, most of which rely upon precision synthesis for the preparation of specific polymer chemistries and architectures. Historically, many of these systems have involved functional homopolymers, but over the last ten years these systems have relied increasingly upon the use of polymer assemblies in solution or bulk to enable interaction with additives. The polymers involved in these systems include block copolymers, end-functional polymers, and organometallic polymers. Polymerization techniques that provide high levels of control over polymer architecture, including controlled radical and ring-opening polymerization methods, have aided greatly in the development of these systems. Copolymer self assembly provides the potential for the ordered arrangement and stabilization of nanoscale metallic objects, such as nanoparticles. The importance of the organic/inorganic interface in ligand-stabilized nanoparticles has recently been highlighted, as has the role of polymer ligands in these systems. There remains much room for the development of polymer-based hybrid systems.



The realization of dynamic composites with multiple functions will be of utmost importance in driving scientific and technological advances and in maintaining competitiveness. The major research goal in this area over the next ten years is the development of specific and general polymer chemistries for interaction with additives that enable control over the spatial distribution and heterogeneity of additives. In systems featuring the use of the polymer component as a template for formation of additives (e.g., nanoparticles), the use of polymer structural parameters to control the

structure and size of additives is also of great importance (Figure 2.7).

In all of these developing hybrid systems, the extent to which polymer chemistry can be used to control all aspects of polymer architecture will be crucial to tailoring the structure and properties. Polymer-defined nanoenvironments (e.g., block copolymer micelles, Figure 2.8, and multiphase bulk polymer systems) will provide continued utility in defining key structural parameters of additives. New synthetic chemistries should be exploited in the preparation of

these hybrid systems. Additives can be incorporated through direct covalent attachment or through modification with ligating functional groups. For example, alkyne-azide ‘click’ cyclization has recently been used to couple polymers to inorganic nanoparticles. The use of supramolecular interactions is also likely to be of growing importance in the development of these polymers. In the development of all of these systems, the overall environmental impact of the entire lifecycle of these materials should be minimized. Synthesis of these materials should be done in as simple a manner as possible without compromising the level of control needed to prepare these materials.

The development of hybrid polymer materials faces several important scientific challenges. A relatively limited set of functional chemistries exists for interaction of polymers with other materials and surfaces and there is little generality in the breadth of these interactions. The interactions between polymers and specific additives are not currently understood at the level at which they can be used to guide the design and specific syntheses of new hybrid materials. Although

the example here focused upon the coating of nanoparticles by polymer chains, there are many other types of hybrid materials that are becoming increasingly important. Each shares the common challenge of accomplishing selective coupling to control the numbers and placements of polymers relative to the substrate, which may be an inorganic nanoparticle, a protein, or a small molecule ligand for a cellular receptor, among many other possibilities. For example, in a recent article, Finke and co-workers sum up the current state of understanding in polymers as ligands for nanoparticles with the statement that “little is truly known about *how* polymers stabilize nanoclusters.” [11]

Full development of hybrid systems, from design to synthesis to characterization to implementation, will rely upon wide-ranging collaborations between researchers across disciplines. Definition and realization of new hybrid materials will require small teams of multidisciplinary investigators (sized between single-investigator and large-center grants), but funding sources for such groups are currently limited. Multidisciplinary interactions will also require researchers in this area to confront the scientific language barriers that exist between chemists (polymer, inorganic, physical, surface), physicists, engineers, materials scientists, and, increasingly, medical researchers and doctors. As techniques are transferred across disciplines and laboratories with varying levels of expertise, it will be important to address issues of quality control and reproducibility in the preparation and characterization of these hybrid materials. The lack of broadly accessible synthetic facilities that allow for scale-up in the preparation of hybrid materials, especially with specialty polymer ligands and high-value additives, is also an obstacle to growth in the realization of these materials.

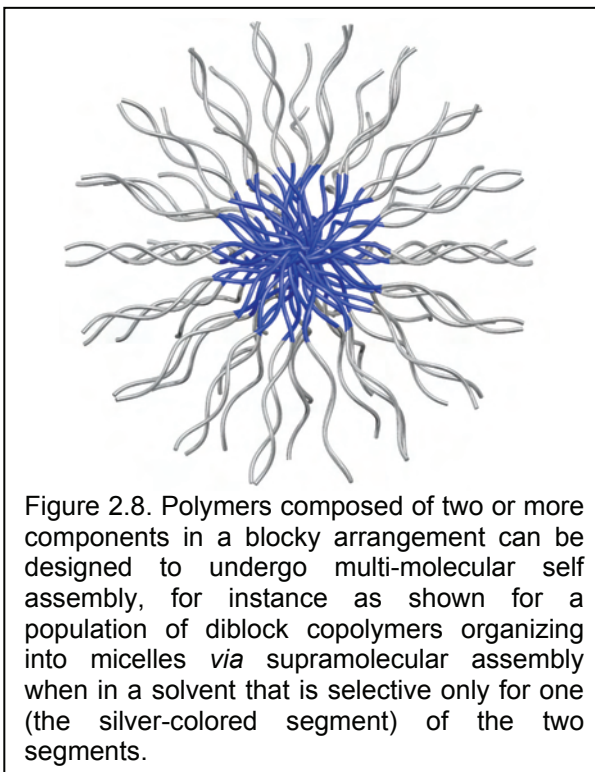


Figure 2.8. Polymers composed of two or more components in a blocky arrangement can be designed to undergo multi-molecular self assembly, for instance as shown for a population of diblock copolymers organizing into micelles *via* supramolecular assembly when in a solvent that is selective only for one (the silver-colored segment) of the two segments.

2.25 Synthetic methodologies and materials that reduce environmental impact

Traditionally, polymer synthesis has involved the use of petroleum-based feedstocks and often high processing temperatures. The use of petroleum-based syntheses by the polymer industry has reflected the low cost and wide availability of oil. In general, polymer synthesis presently involves use of volatile organic compounds (VOCs) on a huge scale, and uses energy-intensive polymerization and processing strategies. In addition, most traditional synthetic polymers are persistent when discarded into the environment and are difficult or cost-ineffective to recycle. In order to reduce the negative impact of polymers on the environment, we must adopt a new paradigm for polymer synthesis.

In “Cradle to Cradle,” McDonough and Braungart point out that the design of products that emerged from the Industrial Revolution reflected the opportunistic spirit of the time with unintended negative impact on the environment. [12] Instead, they propose a paradigm in which materials are created in harmony with Nature, using natural feedstocks, solvent-free or minimal solvent processing, with capacity for recycling or reutilization built in.

Presently, companies like DuPont and Cargill are focusing considerable attention on the use of biological feedstocks for making polymers, natural feedstocks to produce traditional monomers that are traditionally derived from oil, and biological methods for synthesis. For example, Cargill is manufacturing NatureWorks® polylactide, a polymer resin derived from plant sugars. In other works, bioengineering methods are developed and utilized to create artificial proteins by expression of artificial genes in microbial cells.

As noted above, organic solvent emissions during polymer production and use is an environmental concern. The paints and coatings industry is an example of a polymer-based industry in which, driven by regulatory agencies and environmental issues, negative environmental impact has been reduced significantly through the use of high solids or solvent-free coatings formulations. Synthetic polymer chemists must develop novel polymerization strategies that minimize solvent and energy usage, while producing tunable functional polymer structures with recycling capacity built in. Recent work has demonstrated the use of ionic liquids as a non-volatile and recyclable medium for conducting polymerization. Polymerization in CO₂ and CO₂-assisted polymer processing are now exploited commercially.

Waste from automobile tires is another significant environmental problem, since tires cannot be recycled or reprocessed due to irreversible crosslinking. Strategies for creating reversibly crosslinked polymer networks with tailored and tunable structures are needed.

We also need to develop new low-temperature polymerization processes, including those that allow synthesis of tailored architectures (e.g., there are relatively few large-scale thermoplastic elastomers—TPEs—and they are commonly made by solvent-intensive processes). Reducing the environmental impact of the polymer industry poses an enormous challenge to advances in catalysis, monomer design, polymerization mechanisms, etc.

2.3 Education, broadening participation (diversity), and competitiveness

Looking to the future, we believe it will be critical to have a scientifically savvy social and educational system in order to be globally competitive. With the diversity of the current work force, the ability to understand and communicate in an integrative manner will be a benchmark by which to judge the competitiveness required by our society on the global marketplace. It will require a high level of educational understanding of the material world to support societal wealth

creation in the next decade. This educational experience will, of necessity, be instilled at the K-12 level and must be followed by the development of a new generation of polymer researchers who are well versed in molecular biology, chemical synthesis, polymer physics, materials science, and engineering. This new generation of successful polymer researchers must also be able to communicate with the layperson.

Mentioning synthetic polymer chemistry in particular, it will be important to incorporate polymer chemistry experiments into the undergraduate chemistry laboratory experience. Opportunities abound for including experiments that involve the preparation and characterization of polymers into the organic, inorganic, and physical chemistry laboratory curricula. Presently, most students are exposed to the rigorous aspects of polymer science and engineering only at the graduate level, but polymers offer many unique features for investigating and explaining fundamental concepts while also tying them to real-world systems with direct societal relevance. To improve our education of the general population and also to attract the best and brightest students to advance polymer science toward many of the goals discussed above, it is important to provide early exposure in the form of meaningful lecture and laboratory course content.

2.4 Cyberscience and cyberinfrastructure

Although many synthetic methods have been developed for the preparation of a wide range of novel and functional polymeric materials, their designs and subsequent syntheses often stem from identified areas of need within polymer science. To ensure that the current synthetic efforts in polymer science have the greatest impact and expand the knowledge base, more accurate modeling and computational calculations are needed, coupled with a greater utilization of large equipment through cyberinfrastructure networks.

Importantly, the continued development of interdisciplinary coursework and workshops, and the exchange of students between synthetic, physical, and theoretical/computational laboratories will help build greater understanding of the expanding capabilities and current limitations of computational polymer science within the next generation of scientists.

Improved means for communication between the synthetic, physical, and computational polymer scientists, including managed and maintained forums for the exchange of ideas and a centralized database of current synthetically-available materials, could provide for additional levels of interaction between distant laboratories and the formation of new collaborations. However, these forums and databases will require significant cyberinfrastructure, resources, and dedicated staff members to implement, compile, and manage the information to be transferred.

To achieve the goals of reaching students early in their education, an increased cyber and internet presence of polymer science is needed to responsibly communicate with the public and young curious students. Websites such as Macrogalleria (<http://pslc.ws/macrog.htm>) developed and maintained by the University of Southern Mississippi, allow for independent exploration of polymer science and provide a resource for K-12 educators in search of demonstrations of polymer concepts. Additionally, the production of demonstrations, lectures, etc. as YouTube broadcasts will bring polymer science to a different, younger audience and continue to broaden the type of venues currently utilized in outreach activities.

2.5 Goals and Recommendations

As an outcome of this workshop, the key **TEN-YEAR GOALS** for polymer chemistry were identified as the following:

1. Achieve synthetic precision to allow for the preparation of macromolecules with ever-narrowing molecular weight distributions and increasing structural complexities
2. Introduce precise control of heterogeneity into polymer systems to achieve new properties, facilitate processing and cost-performance optimization
3. Develop simple and robust synthetic techniques for the preparation of complex, well-defined macromolecular architectures; transfer those techniques broadly into synthetic and non-synthetic laboratories in chemistry, physics, biology, and engineering
4. Develop self-replicating or template synthesis-based systems with corrections in place to ensure accuracy, approaching the reproducibility and control found in Nature
5. Advance molecular recognition systems to take full advantage of multiple, variable materials properties
6. Advance hybrid materials to broaden the range of materials behavior types
7. Improve the performance of conjugated polymers and their applicability in devices
8. Reduce the environmental impact of polymer materials, during preparation and during and after their utilization
9. Increase societal awareness of the importance of polymer materials
10. Promote a new generation of polymer researchers with simultaneous knowledge in molecular biology, medicine, chemical synthesis, and polymer physics

To realize these ten ten-year goals, the following **RECOMMENDATIONS** are made:

1. More high yielding/quantitative reactions and orthogonal chemistries need to be developed to improve control over macromolecular composition and structure and increased complexity in polymer systems
2. Simple and robust synthetic techniques that can be applied broadly should be developed for the preparation of complex, well-defined macromolecular architectures
3. Synthetic precision, guided by accurate modeling, must be improved to allow for the preparation of macromolecules with designed microstructure, topology, and functionality as well as pre-determined molecular weight distributions of any desired breadth
4. The environmental impact of polymer materials should be reduced, during preparation and during and after their utilization
5. Support is needed for transfer of knowledge, materials, and techniques between laboratories, including a transition period and follow-up to ensure quality control, perhaps as small team grants, internships, etc., to optimize transformational research, investigating fully the composition, structure, properties, processing, and utilization of new synthetic polymer materials
6. Support staff and infrastructure are needed to maintain and improve central analytical facilities over the long term with potential efficiencies and cost-savings through the development of facilities networks

7. Industrial internship opportunities and international travel grants for students should be expanded to provide help with their training for, attraction to, and retention in polymer science, and to improve global competitiveness
8. To increase diversity and competitiveness, new degree programs must be designed in line with future career paths, more graduate student support is needed to give students the freedom to study broadly and be exposed to international and industrial experiences, and programs are needed for non-traditional career pathways, e.g., to bring people back to science after choosing family obligations
9. Polymer chemistry and materials science should be broadcast through YouTube productions and other youth-oriented venues for communication to improve diversity and societal awareness
10. To improve diversity and societal awareness, polymer synthesis should be used as a foundation of activities for educating and attracting intellectual talent broadly, through more extensive introduction into the undergraduate curriculum and K-Grade education, including laboratory exercises, taking advantage of retired polymer scientists as an important resource and talent

Section 3: Complex Polymer Systems

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3.1 Introduction

The past decade has led to a number of new synthetic capabilities, as well as a greater understanding of the manipulation of secondary interactions and their potential role in the assembly of macromolecules. As these interactions have become better understood, the generation of more complex polymer systems with highly controlled shape, function, and molecular arrangement has made it possible in turn to generate unique organic-inorganic assemblies with controlled structure, materials systems that are responsive to the environment or external stimuli, and polymer networks with defined function and control. These include block- and hetero-copolymers, heterogeneous polymer blends, polymers that self-assemble into larger supramolecular forms with hierarchical order, and polymeric materials that combine or interact with other materials—from inorganic to biological—to generate hybrid functional materials. Complex polymeric systems have already underpinned advances in science, medicine, and industry; studies of such systems have led to important contributions to technology that can be observed today. Some recent successes have been achieved using complex polymers.

3.11 New Dielectric Materials for Semiconductors—Paving the Way to Smaller, Faster Microchips

In order to make faster, smaller, more efficient semiconductor chips, we must separate key components with a low dielectric material that divides individual circuits and blocks transfer of electrons across undesired channels. As semiconductor components become increasingly smaller, the patterning technology has surpassed the capabilities of traditional low dielectric materials, which have already reached their limitations for sub-100 nm-scale metal features. This problem was solved using the directed self-assembly of block copolymers in which nanoporous films are produced on the surface of an existing oxide dielectric. By ion beam bombardment,

IBM researchers transferred the template pattern into the oxide and, with subsequent oxide evaporation, air pockets were trapped within the oxide, reducing the dielectric constant of the oxide insulator to ~ 2.0 , much lower than the constant of 2.4 derived from the best performers in previous commercial processes. This simple process will allow the industry to sidestep “Moore’s Law,” a qualitative metric that has dictated the sizes and densities of components on microelectronic circuits. Implementation of this new “air gap” technology will occur in 2009, representing a wonderful example of the transfer of nanotechnology to the production line.

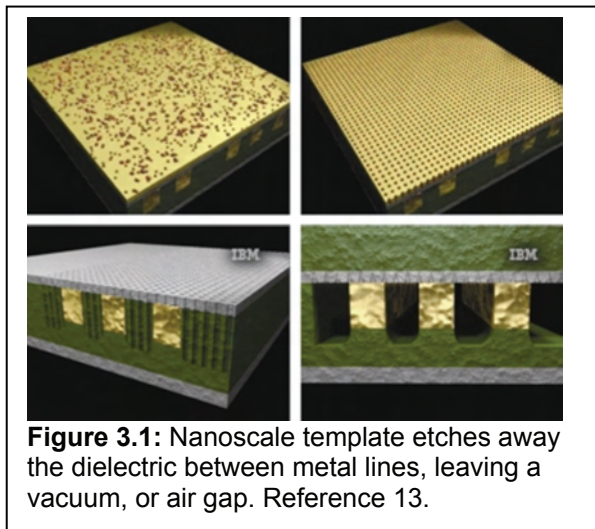


Figure 3.1: Nanoscale template etches away the dielectric between metal lines, leaving a vacuum, or air gap. Reference 13.

Polymer Drug Delivery and Therapeutics

Polymers offer important potential medical benefits due to their intrinsic ability to be designed for multiple functions; the availability of previously existing, naturally occurring polymer backbones, such as polysaccharides or polypeptides; the tunability of synthetic polymers by virtue of which it is possible to achieve biocompatibility and a degree fine control over biodegradation that can be readily altered for desired applications; and the availability of functional sites at which to attach ligands for targeting drugs. Polymer-based therapeutics can take the form of the design of polymers with some therapeutic or biologically active property—often such systems are drug-conjugated polymers or polymers designed to break down into a therapeutic molecule—or of polymers that are designed to combine with the drug during delivery. Because the broad range of polymer backbones includes some that can respond to changes in the environment such as pH, temperature, or light, responsive drug-delivery systems can be designed that contain a drug and protect it under certain circumstances, target the drug to the desired location, and enable delivery of the drug under appropriate circumstances, such as cellular uptake.

A decade ago, very few polymer-based therapeutics had been approved for clinical use—in general, polymers were more likely to be found in homogeneous polymer-drug blends designed for degradation or diffusion-based release from microparticles or solid materials. Over the past several

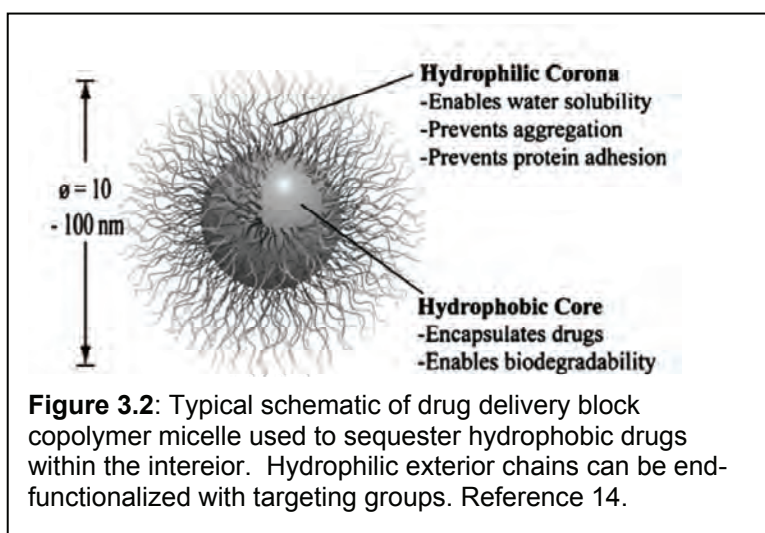


Figure 3.2: Typical schematic of drug delivery block copolymer micelle used to sequester hydrophobic drugs within the interior. Hydrophilic exterior chains can be end-functionalized with targeting groups. Reference 14.

years, complex polymer systems, including some used in biocompatible block copolymer

micelles, have been developed to transport drugs through the bloodstream, and have made it to clinical trials, with significant success observed in the development of cancer-targeting drug-delivery agents. Three recent clinical trials of drug-containing block copolymer micelle formulations for cancer drugs have led to promising results in human subjects. Enhancements of such systems have included increased drug half-life in the blood-stream and decreased drug clearance from the body. Similar trials with paclitaxel as the treatment agent of choice indicate that this drug, which is water insoluble, can be made much more efficacious in block copolymer carriers than when administered alone or using traditional surfactants. The ability to further tune these types of systems with targeting ligands to more efficiently direct chemotoxins to cancer cells can lead to chemotherapies with a much higher level of drug tolerance on the part of the patient, and a greater drug efficiency, thus offering great improvements over traditional methods available today.

3.12 Polymers in Flexible Photovoltaics

Photovoltaics (PV) have been dominated by silicon and other semiconductor-based technologies due to their superior photoconversion and electron-hole transport properties, which are critical for the fabrication of efficient solar cell devices. Fluid electrolyte-based solar cells, while less expensive, are limited due to their bulkiness and the associated difficulty with producing robust structures. Organic-based PV devices, on the other hand, while inexpensive to produce, have been plagued by low conversion efficiencies.

Recently, advances in processing conjugated polymers has led to the development of a commercially-viable, flexible thin-film PV device that integrates conducting polymers with nano-engineered metal oxides using coating or printing technologies. These plastic solar cells can access a broader range of the solar spectrum and claim a reported efficiency of 7%. This, along with their flexibility and light weight, make them potentially valuable as portable energy-converting devices. Yet, even though significant advances have been made, it still remains a challenge to produce an organic-based PV device with efficiencies, stabilities, and life-times that are competitive with those of inorganic devices, while maintaining low cost and ease of processing.

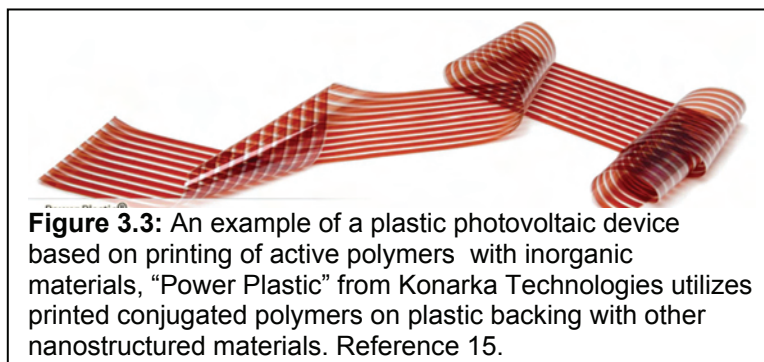


Figure 3.3: An example of a plastic photovoltaic device based on printing of active polymers with inorganic materials, “Power Plastic” from Konarka Technologies utilizes printed conjugated polymers on plastic backing with other nanostructured materials. Reference 15.

3.2 Grand Challenges of Complex Polymer Systems

Complex polymer systems are unique in their ability to assemble or combine with themselves or with other materials elements to generate new structure and function. Because the resulting function gained is particularly relevant to a number of technological advances, we have chosen to state in the following sections **1) the key technological challenges that can be addressed with complex polymer systems; 2) the key strategic challenges and fundamental knowledge needed to achieve the technological goal; and 3) the specific complementary needs that will greatly facilitate addressing the first two sets of challenges.**

Of these challenges, two grand challenges have been selected that represent, respectively, a grand technological challenge that should impact several other areas of technology, and a grand challenge in fundamental understanding and approach that will likely impact the development of complex systems for the next decade or more. We address the grand challenges for complex polymer systems below.

3.21 Grand Technological Challenge—Energy Applications of Polymer Systems

Identifying suitable sources of energy (generation and storage with zero carbon emission) is the single most important challenge facing the world today. The processibility of polymers, tremendous advances in the controlled self-assembly of multi-component polymer systems, and remarkable advances achieved in the last decade to synthesize polymers with well-defined architectures and molecular weights together place polymer science in a unique position to address this grand challenge. Yet however apparent it is that polymers can address this challenge, there are numerous fundamental scientific questions that must be addressed before the solution to the challenge is achieved.

Tailoring the chemical composition and architecture of polymer chains to optimize photo-efficiency poses a significant synthetic challenge, since the exciton (electron-hole pair) diffusion length is ~ 10 nm. This, however, must be balanced by the requirement that the resultant chain be highly ordered to optimize the transport of excitons to an interface where the exciton can be split and the electron subsequently removed and stored. Typical diffusion lengths over which the exciton must diffuse before recombination, and the morphology and ordering of the components in the device, are of equal importance. While exciton diffusion can be controlled, to some extent, by the structure and morphology of the light-absorbing polymer, dissociation of the exciton at the interface with the electron withdrawing domain is poorly understood. PV devices are macroscopic in size and, given the size scale of the elements, this mandates controlling hierarchical ordering of multicomponent or hybrid systems over multiple length scales. Yet the optimal geometry of such devices remains unknown, given the confinement effects on the polymer chains and processes, such as crystallization in confined geometries. Questions regarding the orientation of the crystallographic axes of the polymer or even the optimal morphology for the device remain to be answered. For composite systems, similar questions exist, with the added complexity of overcoming mismatches in the band gap structure of the polymeric and inorganic components. In addition to all of these issues, the final device that is produced must be cost effective. In particular, the polymers must be cheap, readily available, easily processed, and stable over long periods of time.

PV devices represent only one way to address the critical problem of energy generation and storage. Yet, even in seeking to solve this one problem, an integrated, multi-disciplinary effort will be required, with significant fundamental scientific and processing challenges. Every such challenge requires significant advances be made to address this global need.

Complex polymer systems can also be created via the combination of organic and inorganic materials systems in the form of polymer-inorganic nanocomposites. New and unique means of generating nanostructured materials using polymers in conjunction with inorganic species can lead to unique catalytic and photocatalytic electrodes, fuel-cell membranes, thin-film batteries, and heterojunction photovoltaic systems that can be readily implemented in multiple forms and on a diverse range of substrates, including flexible plastic and textiles.

3.22 Grand Fundamental Challenge—Biological and Biomimetic Synthesis and Assembly Approaches

Perhaps one of the greatest challenges in working with complex polymer systems is to gain a greater understanding of biological self-assembly, and eventually to extend that knowledge to develop and assemble polymer systems that are adaptable, evolvable, and sustainable. Nature has had millions of years to experiment with self-assembly and complex polymeric systems and as a consequence it has a plethora of examples that utilize such processes in a myriad of different ways. Over the years, biological systems that employ complex self-assembly, e.g., DNA, Tobacco Mosaic Virus, etc., or utilize complex polymeric materials systems, e.g., the extra-cellular matrix, have inspired polymer scientists to access a range of elegant architectures. In the next ten years further developments in the understanding of biological systems and the ways in which they use self-assembly and complex polymer materials will continue to inspire polymer scientists in creating the next generation of materials.

Biological systems represent a diverse collection of macromolecules that interact in a highly regulated manner to evolve, adapt, and sustain life. From a parallel perspective, complex polymer assemblies represent the organization of synthetic macromolecules using their chemical and physical interactions to create highly organized structures with desired organization and properties. Recent advances have demonstrated not only how the assembly occurs, but also how to synthesize, manipulate, and process macromolecules in ways that are regulated on multiple time and size scales. In many instances, the field has been catalyzed by bio-inspired approaches, but regardless of approach, these advances are facilitating the creation of systems that are no longer static in their Nature, but respond to changes in their environment, evolving and adapting, to impart desired properties and functions. Collectively, these results suggest new challenges and opportunities with which to address the complexity required for the application of self-assembled biosystems. These include i) expanding efforts in biologically based syntheses to create macromolecules of defined architectures; ii) integrating synthetic and biological components to create hybrid structures with new-found properties; iii) assembling particle systems with multiple functionalities that allow for targeting, imaging, sensing, and delivery; iv) developing advanced materials through multiple, cooperative, and synergistic assembly processes; and v) utilizing self-assembled materials to integrate functionalities that direct cell

signaling. By learning from the mechanisms used in Nature needed to achieve responsive, dynamic, active materials, it will be possible to utilize synthetic or biological polymer systems to design active membranes and sensors, adaptive mechanical structures, adaptive optics, unique cell-responsive biomaterials, and new systems for medical applications such as drug delivery and medical implants. Furthermore, it is also possible to harness the synthetic power of biology directly toward the formation of non-natural polypeptides that can exhibit significant differences

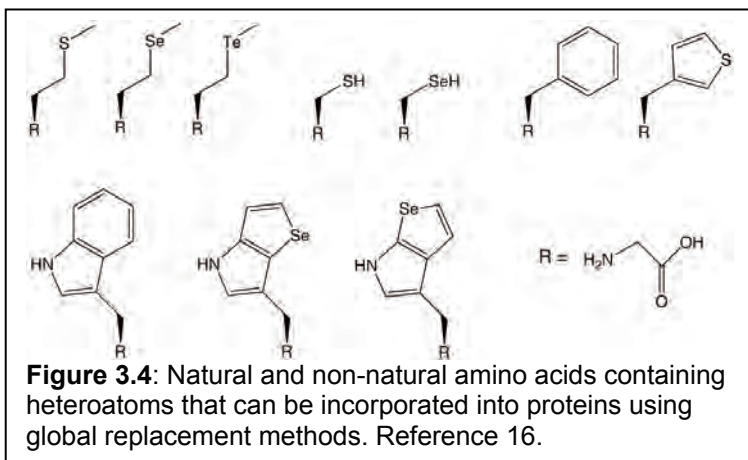


Figure 3.4: Natural and non-natural amino acids containing heteroatoms that can be incorporated into proteins using global replacement methods. Reference 16.

in function and assembly behavior, leading to new approaches to the development of hierarchical polymers, in which secondary and tertiary structure are inherent. We anticipate that this grand challenge will impact several areas of polymer science, and some aspects of the concept of biological inspiration are also reflected in many of the remaining challenges discussed below.

3.3 Key Technological Challenges for Complex Polymer Systems

As described in the previous section, complex polymer systems often combine unique assembly behavior and final materials function to achieve specific properties needed for a given application. Here we present primary areas for technological development of these systems. The areas were selected because of the clear and, in some cases, urgent need for new materials to address the challenges and the unique advantages that complex polymer systems offer in these areas. **In each case, complex and hybrid polymeric materials stand to offer significant contributions toward societal needs and advancement.**

3.31 Biomaterials for Biomedical and Biological Systems

New polymeric materials have demonstrated unique responsive properties, ranging from fluorescence or color-changing properties to changes in solubility, chain conformation, assembly behavior, and covalent linkages. The ability to design complex polymer assemblies that can respond to specific conditions leads to drug encapsulants that can release drugs only within the endosome, or in response to changes in the bloodstream. External triggers such as heat and light might be used to localize treatment, taking advantage of the unique ability to change or modify polymer backbones to achieve a broad range of functionality. Synthetic polymers offer the opportunity to intentionally design-in specific function, while tuning properties such as hydrophobicity, drug affinity, complex size, etc.; on the other hand, we remain far from being able to replicate the efficacy of Nature-designed systems such as viruses to achieve targeted delivery of drugs or genes. Similar challenges exist with respect to the ability to replicate biological tissues. There is a great need to generate highly controlled 2D and 3D structured materials that provide the mechanical, biochemical, and structural cues that lead to cellular differentiation and proliferation. Such systems can address important questions in the biological sciences about cell signaling, growth, and development. These developments can also play a key role in designing scaffolds for tissue engineering and regeneration. The introduction of responsive systems in such materials systems is still relatively unexplored, and could yield much promise in the controlled manipulation of cells in culture—for example, the use of an electrochemical stimulus to turn adhesion on or off or the use of temperature variation to induce reversible wettability of surfaces or changes in the mechanical modulus of materials which might induce new cellular behavior upon activation. By learning from Nature, it may be possible to make important gains in these areas. Potential new capabilities may develop from the ability to combine natural synthetic themes such as peptide sequences with synthetic systems such as highly charged dendrimers or cross-linkable methacrylates to generate hybrid synthetic-biologic structures. In this manner, multiple, cooperative, and synergistic (responsive) assembly structures might be achieved.

3.32 Sustainability

Polymers in general and complex polymer systems in particular are ideally positioned to impact most of the key aspects of sustainability, with economic, social, institutional, and environmental implications. Polymers and complex polymer composites offer the potential to develop cheap, lightweight, and easy-to-process structural materials. Water purification and air and soil clean-up represent key environmental issues. Complex polymer membranes with controlled morphologies and tailored chemical compositions designed to improve throughput, stability, anti-fouling characteristics, and efficiencies are required. Additional areas in which polymers can impact sustainability include the development of easy-to-recycle materials and re-healable materials. Such materials could mitigate the need to replace parts and dramatically affect the life-time use of a given system. Recent developments in re-healable materials include the use of polymer composites that mimic the 3D micro-vascular nature of the dermis layer of skin, and thus allow the delivery of a healing agent to cracks in a polymer coating. However, if we hope to expand the scope and type of plastics that have this capability, and thus the application areas in which such materials can be utilized, we must further develop autonomous, self-healing, or stimuli-responsive re-healable plastics.

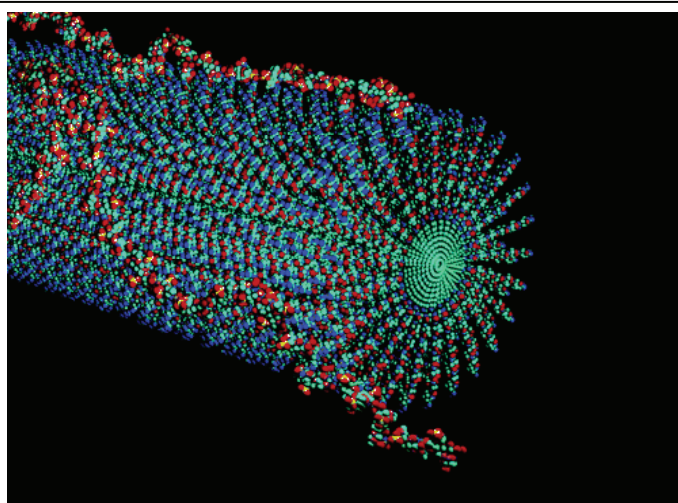


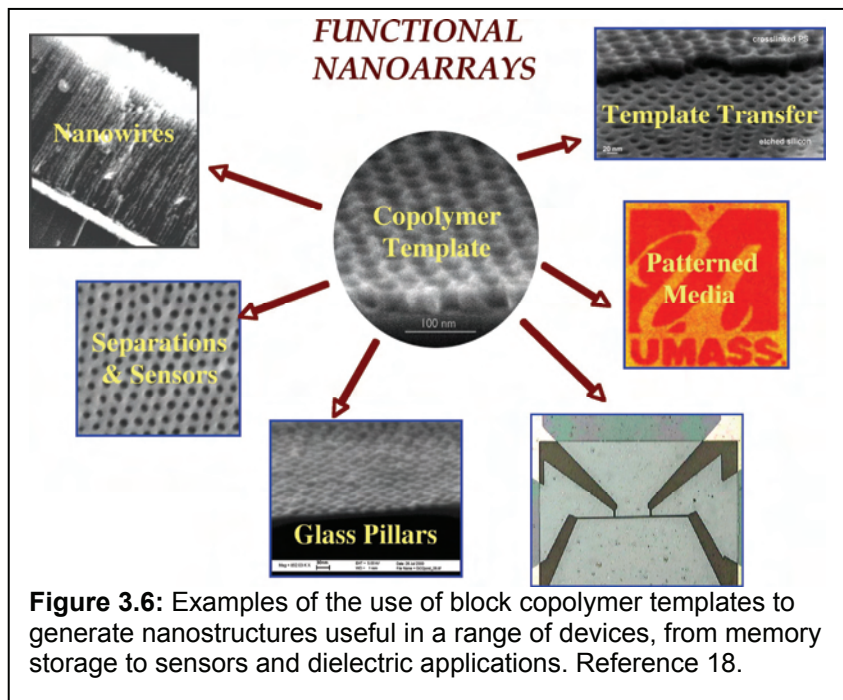
Figure 3.5: Schematic representation of a heparin-nucleated nanofiber. [17] The cylindrical nanostructure is formed by the aggregation of positively charged peptide amphiphile molecules. These peptide amphiphile molecules have the capacity to bind to the negatively charged heparin chains, and thereby the polyion nucleates the fiber. Reference 17.

3.33 Information Technology and Polymer Based Devices

The ability to control complex polymer systems, including hybrid polymers and supramacromolecular complexes, at the nanometer-length scale makes them natural candidates for information storage and electronic device technologies. An excellent example of the previous use of block copolymers in information technology was given in the introduction of this section, with regard to the creation of unique dielectric materials. The inherent nanometer-scale phase segregation of block copolymers can be controlled using modified surfaces or confined geometries to achieve near-perfect arrays of block copolymer domains with specific compositions. Controlled thin films containing such structures are highly applicable to magnetic storage, memory devices, and other means of storage that rely on the generation of arrays of carefully placed active elements on a matrix. The use of hybrid polymers containing active elements such as organometallic sequences, redox active systems, or conjugated polymers can be used to directly generate such active arrays. The newer frontiers of information science have moved to storage in three dimensions—here it is important to achieve perfection of order for

nanoscale assembly that is addressable in the block copolymer matrix. The ability to generate individual complex polymer “elements” that comprise singular or multiple polymer chains in specific complexes with quantum dots, inorganic nanoparticles, or nanoscale objects can lead to systems that are guided to appropriate points on a 2D or 3D matrix with efficiency.

Additional areas where complex polymers will offer new contributions include the generation of sensing and other electro-active, electrochemical, or mechano- or even chemo-responsive polymers that can act as elements in polymer-based devices. New capabilities to selectively imbed organic or inorganic nanoparticles or other nano-objects directly into block copolymer domains will lead to systems in which the separation and isolation of charge, generation and control of carrier transport, and the ability to implement active or responsive elements within adjacent polymeric regions will enable the development of new polymer-composite dielectrics, optics, sensors, and conduits in a variety of devices.



3.4 Key Fundamental Scientific Challenges and Strategies for Complex Polymer systems

To be able to address the above-mentioned technological challenges utilizing complex polymer systems, there are critical areas in which fundamental understanding must be achieved so as to generate materials with the desired structure and function. Many critical questions remain regarding the self-assembly of complex materials systems, the development of new hybrid materials systems that introduce biological, inorganic, and other less traditional components to synthetic polymer systems, and the means of creating and controlling order, morphology, and phase behavior in such systems. Several key scientific challenges must be addressed to develop the capabilities needed to achieve the next generation of complex polymeric systems.

3.4.1 Directing Structure via Controlled Kinetic Pathways and Thermodynamics

The molecular structure of polymers has evolved through advances in synthesis from chemically defective linear chains formed by a single monomer toward covalent chains with better defined backbone architectures, sequences, and molecular weight distributions. Over the

past decade the field of supramolecular polymers from ionic, hydrogen bonding, hydrophobic, and other non-covalent interactions using structurally complex and interactive monomers has flourished, yielding polymers that resemble nanostructures with well defined shapes. With a much more diverse set of molecularly defined polymeric structures, the possible configurations of supramolecular structure and their potential functions will diverge into a remarkable parameter space. From a thermodynamic and kinetic perspective, this implies that polymeric systems will be described by energy landscapes that are possibly more complex than those of proteins and organic crystals.

Often the more complex systems described above will be trapped in nonequilibrium states, but will have a rich set of kinetic pathways over which to organize them into local minima. The notion of molecular systems in metastable states, liquid or solid, that can gravitate to equilibrium through energy barriers using external forces, thermal energy, or contact with surfaces is a familiar one in dealing with polymeric systems. What is less familiar is the notion that systems may access thermodynamic minima in a specific sequence that uniquely generates a useful state of organization. If the target is a photovoltaic cell with acceptor and donor domains, the increase in the scale of long-range order connects two macroscopic electrodes and creates the efficient device. In a biomaterial, the long-range order may be critical to differentiating or organizing cells macroscopically in three dimensions for a specific biological outcome. Finally, a number of interesting and useful structural arrangements within block copolymers, supramolecular polymer assemblies, or heterogeneous polymer blends are the result of nonequilibrium formations. If we can predict the existence of such desired structures, and map out the kinetic pathways that must be followed to achieve them, the structures can be readily obtained and locked in place using covalent chemistry such as crosslinking, vitrification, or other means of quenching the desired non-equilibrium structures. Clearly, to deal with such complexity with the appropriate level of control, advances in modeling, the ability to experiment with and characterize a large parameter space, and insights from existing systems in Nature can serve as core facilitators.

3.42 Complex structure via chain architecture

Structure in polymeric materials and in complex polymer systems depends ultimately on molecular architecture. Well known examples include the dependence of crystallinity and crystal structure on regularity and symmetry, and the dependence of phase-separated structures in block copolymers on inter-segment interactions and relative block lengths. The design of more complex polymer systems will require further control of molecular architecture, including control of monomer sequence, topology, local conformational preference, and chain stiffness. Striking examples of the importance of chain sequence abound in biological polymers. Molecular recognition in biology is exquisitely sensitive to chain sequence; single “point mutations” can cause loss of macromolecular function and death of the host organism. Recent studies of synthetic DNAs have shown that engineering chain sequences can lead to remarkable control of symmetry and structure at nanometer-length scales, and the display of specific peptide sequences has enabled programmed control of interactions between cells and polymeric materials.

These examples raise important questions and provide hopeful opportunities for the future. Key challenges in this area address how the control of chain sequences can enable the design of new modes of organization in complex polymer systems, ascertaining the relevant length scales for compositional control from the level of individual monomer units to the refinement of

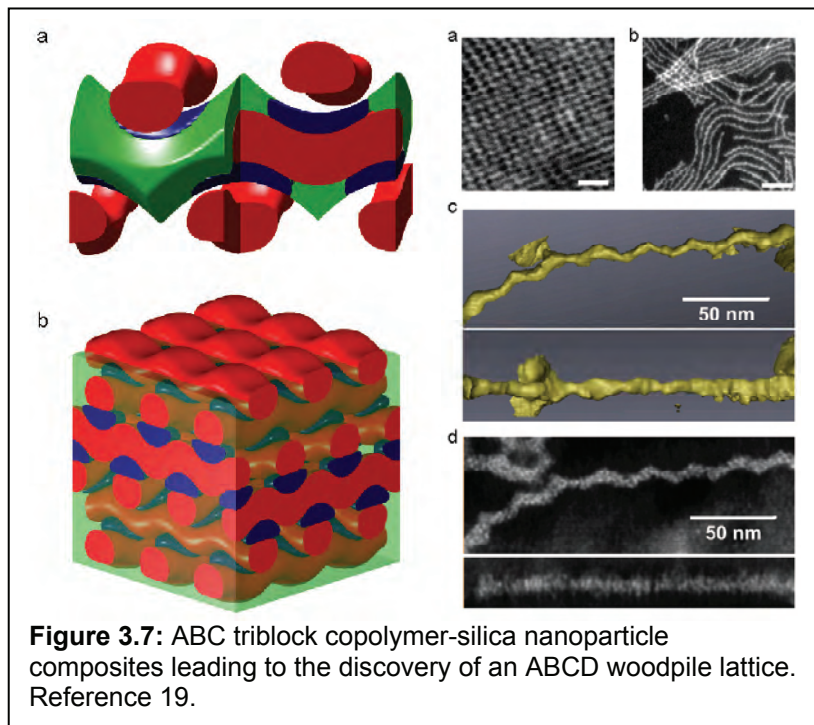
polymer block length in multi-block copolymers. Exploration of the assembly of complex structures by the design of hierarchical sequences (sequences within sequences), and the resulting control should be addressed at multiple length scales. Similar questions—and potential opportunities—arise with respect to control of topology, conformation, and chain stiffness. Exploration and exploitation of these opportunities will require significant advances in synthetic methodology.

3.43 Entropy driven assembly in multi-component hybrid systems

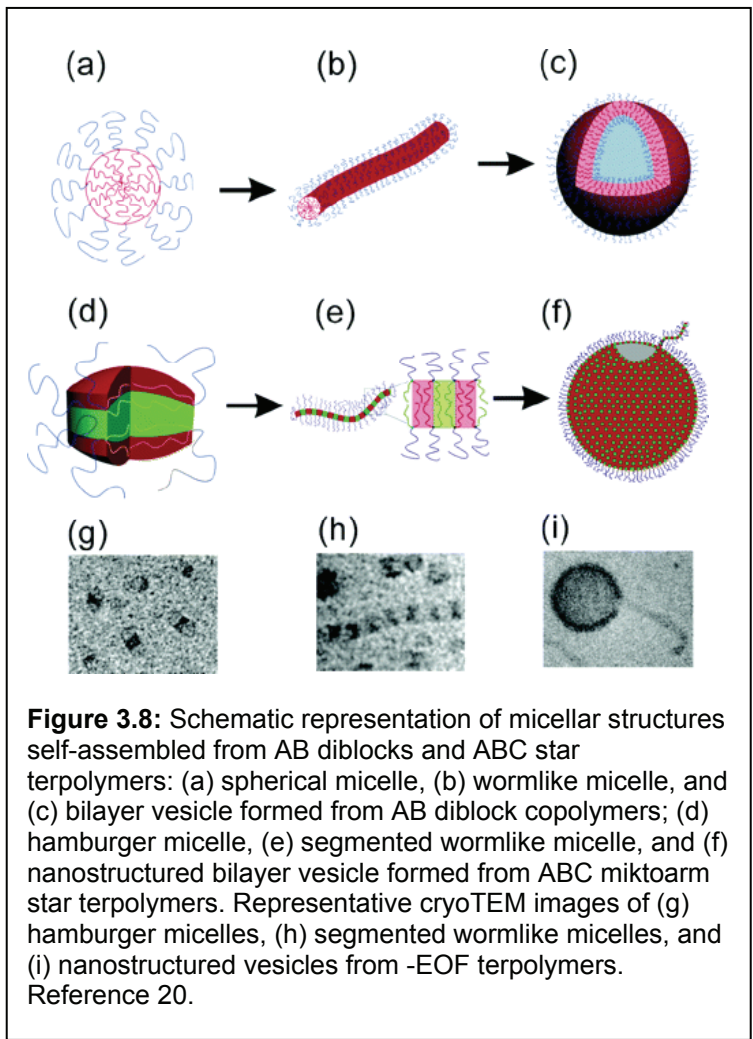
Ranging in scope from diatoms to humans, countless organisms shape inorganic materials into complex structures with the help of macromolecules. Despite a growing recognition of the widespread occurrence of nanoparticles in Nature, the control of their behavior in self-assembly (and disassembly) opens exciting pathways towards multifunctional polymeric hybrid materials. In particular, it has been suggested that entropy may play an important role in the assembly process of such materials, as corroborated by experimental studies. Since these considerations are applicable to a large number of nanoparticle-based mesostructures, they may have significant impact in a broad range of areas in which nanoscale structure and function are becoming increasingly important, such as microelectronics, power generation and storage, drug delivery, and separation and catalysis. For example, the ability to sequester inorganic nanoparticles into specific domains with nanoscale precision offers tremendous opportunities for the generation of materials with tailored properties. Emerging from these considerations is a vision that, by analogy to biological protein machinery, the monomer (block) sequence information of synthetic, non-natural macromolecules can be used to encode information about *molecular-level* structure and functionality of co-assemblies with dissimilar materials like ceramics and metals. This will lead to the design of entirely new classes of materials with properties that have no known analogues in the natural world.

3.44 Templates to generate complex systems

Advanced materials with complex micro- and nanostructures are important to many applications, including catalysis, lightweight structural materials, biomedical devices, photonics, and photovoltaics. Control of their structures, however, is non-trivial and primarily achieved by a top-down fabrication process. In contrast, bioorganisms often self-assemble into complex systems using precise control of size, shape, location,



orientation, and hierarchical organization. For example, biomineralization is a bottom-up process and biominerals, such as diatom exoskeletons, often exhibit hierarchical organization ranging from the nanometer- to macroscopic-length scales and possess remarkable optical, structural, and mechanical properties. Nature's control over biomineralization processes involves an intimate interaction with biomacromolecules, both as structured organic matrices and soluble additives. Learning from biological design and reformulating it into a synthetic context offers immediate benefits to the discovery of advanced organic-inorganic hybrid materials that will contribute toward the improvement of existing methods to assemble complex structures and develop new technology. Directing chemically-reactive processes onto structured polymer templates, and tuning the polymer-inorganic interactions at the molecular and macroscopic level using external fields, are exciting examples of means that can be utilized to create complex polymer systems, which demand critical research in these areas. New directions in templating of polymers and inorganic/organic complex systems include the achievement of finer control and nanometer-scale replication of templates via the use of controlled syntheses and processing methods that enable layering or vapor deposition schemes for the infiltration of fine features within a template. Issues to address include the maintenance of mechanical integrity in such systems, the control of surface characteristics within the structures, and the ability to generate such systems with order maintained over large scales. Additional advances include the potential for generating polymer systems that guide the templating of multiple inorganic or organic components or chemistries presented within the nanostructure.



3.45 Complex Systems as a Route to Fabricating Nanoscale Objects

As mentioned above, a number of complex polymer systems involve block copolymers or hybrid polymer systems that can arrange to form larger-scale isolated structures. Such systems range from crosslinked micelles, cylinders, and worms, to unusual shapes such as vesicular discs, oblate nanoparticles, and hollow tubes or containers. The ability to design polymeric systems

that can assemble in dilute solution has led to a wealth of new structures achieved with copolymers; furthermore, the ability to utilize ABC triblock copolymers or to introduce two assembling polymeric components with strong electrostatic or hydrogen bonding interaction has led to the ability to design a broad range of free-standing or isolated nano-scale objects that can be of use in biomedical applications such as drug and gene delivery, or in the development of templates for organic or inorganic nanosystems for imaging, photonics, or cellular engineering. Recent developments have shown that it is possible to generate micellar structures with multiple compartments yielding novel structures with uniquely arranged regions consisting of distinct polymer components—the potential to sequester different agents within each region could lead to unique multiple drug-delivery schemes or multi-component imaging and therapeutic agents.

New challenges in this area include achieving the means to control chemistry spatially on the surfaces of the nano-objects, the ability to achieve greater control of shape and shape dimensions, and the development of core-shell structures. The introduction of molecular recognition sites on spatially isolated regions of the particle surfaces, or on specific faces of the nano-object, could yield systems that act as assembly building blocks that can assemble or disassemble to create structures with unique responsiveness to the environment. Many incorporated functions can be also envisioned within the nano-particle, such as catalytic sites and magnetic properties. The development of such complex nanoparticles thus provides an open opportunity for innovative research towards the creation of new dynamic systems consisting of complex individual components that assemble into designed materials.

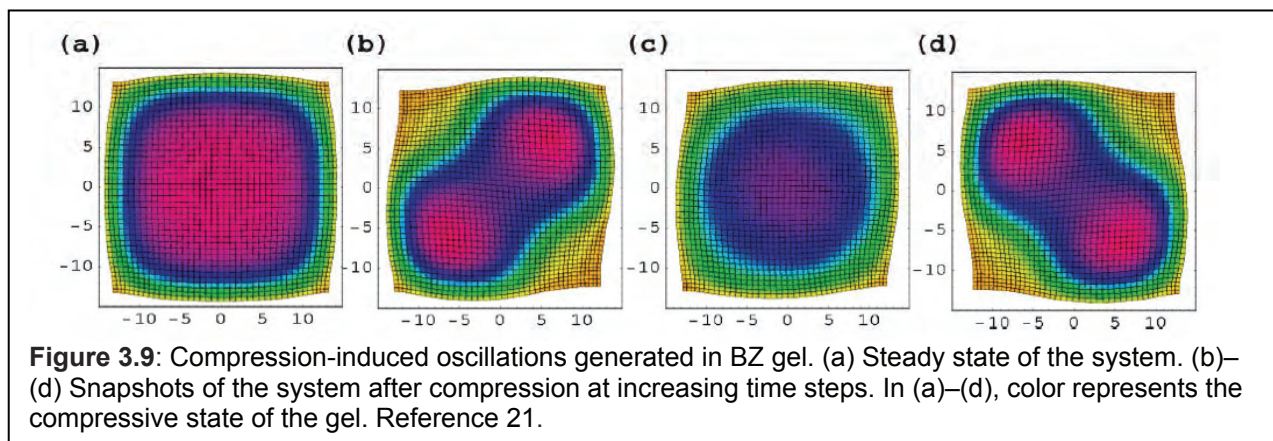
3.46 Reactive systems

There is a growing interest in the synthesis and preparation of reactive/responsive polymer systems. For example, the emerging field of small-scale robotics addresses the problem of developing micron-size or smaller machines capable of manipulating matter at a comparable scale. Hybrid devices driven by molecular motors operate only in an environment that is similar to conditions for cellular life, and therefore their functionality is quite limited. There are many potential advantages in using synthetic as opposed to biological macromolecules for such systems. Fully synthetic devices could work under a much wider range of environmental conditions, and could be easier to maintain and control. They are more robust, have faster response times, and can be readily incorporated into micro-electro-mechanical systems (MEMS). For example, recently a prototype position-controlled synthetic soft device has been demonstrated from thermosensitive polymer hydrogels by spatially controlling the propagation of the volume phase transition along the sample length, liquid crystalline elastomers have exhibited contractile motion upon switching from ordered to disordered states, and light induced reactions have been used to trigger a range of responsive behaviors. Recent predictions of a gel in which the components of the well-known oscillatory B-Z (Belousov-Zhabotinsky) reaction are imbedded can be used to design hybrid polymeric systems that respond to a single mechanical impulse with specific and well-defined mechanical oscillation. It can be anticipated that this and other emerging principles will be widely utilized in a variety of areas in biotechnology, actuators and responsive materials utilized for microfluidics, robotics, advanced prosthetics, membranes and drug delivery.

3.47 Hierarchical structures using charge

A large number of new and unique complex polymer systems can be achieved through the careful manipulation of electrostatic charge interactions. Generally charge has been used very effectively in Nature for the formation of stabilized cellular components, for example to modulate transport and engage biomolecular adhesion events. Charged electrostatic complexes exhibit among the largest non-covalent bond strengths (with bond enthalpies exceeding those of single bonds by as much as a factor of 10-20 in many cases), making them capable of creating assemblies with extremely large cohesive strengths. Furthermore, charge is a long range interaction, allowing the guidance of self-assembly processes from solution or bulk polymers with speed, consistency, and reliability. On the other hand, with few exceptions, the use of charge in self-assembly has been restricted primarily to the development of amphiphilic materials that stabilize objects in solution in the world of self-assembly. More recently charge has been used to append groups to polymer backbones, and perhaps the best example of this over the past decade has been the use of charge in the formation of polyelectrolyte multilayers, for which a sequential adsorption of oppositely charged polymers leads to the formation of nanocomposites that can have well defined thin-film architectures. Complex nanomaterials can also blend compositions that would otherwise be unachievable with uncharged elements, allowing specific placement of active elements along the thickness axis of a film.

A challenge in the use of charge in complex materials systems is the tendency toward aggregation and loss of structure that can occur due to the large binding forces that occur between positively and negatively charged species that often allow nonspecific and uncontrolled complexation in solution. By approaching this challenge with the use of charged groups that can be exposed or unsheathed on command to generate structure, by using the tuning of charge with ionic strength, pH, or other means, or by generating charge along macromolecular structures in a cascade or sequential fashion, complexes with high levels of order may be possible. The resulting structures would be highly stable to heat within a range of solvent and aqueous solution conditions, and could yield new and valuable tools with which to induce self-assembly. New frontiers in this area would enable the introduction and removal of charge by remote electrochemical or other means, thus allowing the triggering of materials assembly under a variety of conditions, including benign environmental conditions. Polymeric species are of particular interest and use in this area because of their multivalent nature, which generates very stable (in some cases, near-permanent) linkages, and for which entropic effects can be used to drive assembly even in the presence of small ions or charged molecules.



3.48 Controlled reversibility of assembly

One of the key aspects of complex polymer systems is their assembly—from solution or bulk state—into desired structures using non-covalent interactions. Because such interactions can, in many cases, be introduced or removed reversibly, such systems may be explored for adaptive capabilities or reversible assembly. Key areas in which such capabilities are needed include new biomedical materials for regeneration of tissues and manipulation of cellular behavior, responsive or adaptive membranes, etc. One example of an application along these lines is the development of elements that assemble into delivery vehicles that can travel through the bloodstream carrying assembled elements or components, but that spontaneously disassemble when taken up by cells. Materials that undergo assembly and disassembly at given temperatures could lead to clothing containing membranes that respond to the weather by insulating or generating channels that breathe to allow cooling. Similarly, electrostatic complexes for which charge can be modulated through the introduction of redox centers can be triggered to assemble into rigid mechanical structures that stiffen a mechanical element, and subsequently disassembled to enable reshaping of the element. Such possibilities could lead to numerous adaptive systems; however, many challenges remain in achieving the ability to control specific interactions with precision, to manipulate different complementary functions at different times, and to utilize far-ranging interactions that can drive assembly with accuracy even under dilute conditions. Indeed, reversibility, hysteresis of reversible behavior, and the ability to induce responsive behavior over multiple cycles challenge the development of such polymeric systems due to such issues as kinetic trapping, mechanical breakdown, and reproducibility; these issues must be addressed in the design of new materials that can be readily implemented in devices.

3.5 Critical Needs

Along with the key strategic areas described above, it is also necessary to have the appropriate tools available for the development of complex polymer systems. Because complex systems tend to exhibit nanometer-scale ordering, to consist of heterogeneous chemical compositions, and often exhibit supramolecular assembly into secondary or higher-level structures, specific tools and capabilities are required in order to generate and characterize them effectively.

- *New synthetic methods for the design of self-assembling polymer systems*

Control of monomer sequences remains one of the most fundamental unsolved problems in polymer synthesis, and indeed in all of polymer science and engineering. The full potential of self-assembly in complex polymer systems will require the development of new synthetic methods that afford improved control of chain sequences. In current synthetic methods, the statistical nature of polymerization processes limits control of molecular architecture, whereas biological synthesis enables exquisite control at the price of severely limited chemical diversity. Methods are needed that sacrifice neither control nor diversity.

- ***Advancements in Modeling of Complex Systems***

Advances in computational modeling and simulation will be crucial to the study of complex polymer systems—the presence of multiple levels of ordering, and the multiple types of potential interactions, lead to a large experimental parameter space which cannot be practically explored experimentally. Many of the methodologies that might be used to achieve new functional complex polymer systems, as described above, make modeling of complex systems extremely important for the prediction of materials structure. In such systems, indications of important directions in which to work in polymer composition and processing conditions achieved from simple models can be extremely illuminating. An area of key importance is the prediction of phase space for novel polymer architectures that reflect the new chemical synthetic capabilities. As indicated earlier, not only thermodynamic structures, but also kinetic structures achieved based on pathways to final conditions, are of particular interest. Furthermore, a greater ability to handle hydrogen bonding and ionic interactions in water will be extremely important to the development of supramolecular chemistry approaches to nanostructured materials. Advances in this area that make it possible to address such complexity in polyelectrolytes and other charged systems would lead to new developments guided by theoretical or mathematical models.

- ***Metrics and Imaging for Nanostructured Materials***

For regular nanostructured materials systems in ordered arrangements, research characterization tools are needed to determine the precise location of each element with an uncertainty of less than ~1 nm over macroscopic length scales. Metrics for order require a means to characterize defects in ordered arrays on the nanometer level over macroscopic distances rapidly and efficiently. The development of direct visualization tools for fabricated complex polymer systems will be a key to understanding the types of structures that are formed. Finally, the ability to observe equilibrium or metastable structures in a wet, controlled environment, with increased resolution, compositional mapping, and contrastive imaging at single nanometer-length scales requires sophisticated new tools.

- ***Evolution of microfluidic, MEMS, and NEMS tools for polymer processing and characterization.***

It will be critical to integrate synthetic tools with existing and evolving engineering tools, such as microfluidics, MEMS, and NEMS, which offer another dimension of control over the polymer assembly and processing at both the nano- and microscale. The creative use of microsystems and fluidic approaches make it possible to *simultaneously control multiple parameters of materials synthesis and processing with a high level of precision over multiple length scales.*

- ***Education of Future Researchers and the Public***

The development of complex polymer systems requires a large amount of cross-disciplinary study; thus, one of the greatest needs in this area is education that equips young people to learn about multiple areas of study, including a strong organic and physical chemistry background and a fundamental understanding of polymer physics. Because of the ever-increasing incorporation

of polymeric systems in a range of disciplines, from chemical and mechanical engineering to chemistry and biology, it will be increasingly important to introduce polymer educational components of appropriate depth into many more disciplines. Due to the breadth of training of those involved in polymer science research, it would be beneficial to develop more engaged and improved interfaces with other engineering/science/medical disciplines. In terms of encouraging research that continues to push the multidisciplinary boundaries, and will engage researchers to push the limits of our current understanding, it is important that funding agencies create more avenues for the funding of risky but transformational research.

To continue to achieve excellence in our fields, we must engage every aspect of our population in science and math education at the early stages. Diversity is an issue that must be faced by this nation by finding ways to encourage underrepresented minority students to investigate the field. Increasing awareness of polymers and accessing larger numbers of students may involve the training of the nation's teachers in research experiences with faculty in the polymer science area. Because polymers are ubiquitous in everyday life, and because the materials are highly accessible to all students, polymer science is a natural doorway to science education for young children. More programs must be developed that engage students at the K-12 level to increase exposure to the contributions of polymeric materials to society. Finally, the urgency and strong interest with which future scientists may approach environmental and energy issues can serve as an opportunity to attract more of the best students into the area of polymer science. Science demonstrations, design contests, and links to outreach organizations can all help to increase the visibility of the field.

Retention of undergraduates students within the field is also important; supplementary funding for undergraduates has made a difference and is encouraged; such endeavors should be specifically designed to ensure that undergraduates enjoy a rewarding research experience, and to give them an early idea of the possibilities of graduate school.

3.6 Recommendations:

Based on the technological and fundamental scientific challenges and frontiers in the development of complex polymer systems stated above, we recommend pursuit of the following objectives:

1. Integrating unique polymer function with inorganic or organic nanostructures.
2. Acquiring better understanding of charged polymers, polymer ionic complexes, and control of the supramolecular structures gained from polyion systems.
3. Deriving adaptive and complex systems utilizing assembly and disassembly, and controlled reversibility.
4. Controlling kinetic pathways in complex polymer and heterogeneous blend systems to gain specific structure, as well as directed structure through thermodynamic minima.
5. Generating and utilizing biological and synthetic templates for the derivation of controlled morphologies and hierarchical systems.
6. Designing and understanding the manipulation of complex polymer systems with designed interfaces that enable controlled transport.
7. Achieving significant advances in the computational modeling of complex polymer systems, their phase behavior, structure, and dynamics to guide the development of new complex and hierarchical polymer systems.

8. Developing more advanced metrics for the characterization of nanostructured complex materials.
9. Developing more engaged and improved cross-programs with other engineering/science/medical disciplines.
10. Funding agencies are encouraged to create more avenues for risky but transformational research to continue pushing multidisciplinary boundaries and expanding the limits of our current understanding.

Section 4: Macromolecular Processing and Assembly

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4.1 Introduction

Polymers share many characteristics with other classes of materials, but one respect in which they stand out is that they are used frequently, through advanced processing, in non-equilibrium structures, the vast majority of which are in metastable states. Processed either from the melt or solution, polymers can be shaped by molding, spun into fibers, or extruded as sheets or films, among many possible processing methods. Fiber spinning, one of the highest-volume uses of natural and synthetic polymers, produces fibers for textiles, non-wovens, and engineering and construction fabrics. The process of spinning fibers leads to molecular orientation and, if taken to the extreme, it can transform polymers from soft materials familiar to us when used in ordinary milk bottles to textiles capable of withstanding a bullet. Conventional fibers are tens to several hundred microns in diameter. Improved processing now enables the manufacture of microfibers less than 50 nm in size by electrospinning to form materials with characteristics that are considerably different from those exhibited by conventional textiles. The fact that simple processing can produce a wide range of distinct properties shows its importance as a critical aspect of polymer science and engineering. One of the most significant developments of the last decade of polymer research has been the dramatic increase in the number of methods available for fabricating or processing true nanostructures, that is, fibers, films, or processed forms only a few tens of nanometers in scale. A significant body of work has now developed that addresses how to precisely construct structures at dimensions not much greater than atomic-length scales.

For example, current film extrusion processes have progressed to the point that sophisticated multilayer films can be extruded to form dielectric mirrors. [22] Film extrusion technology

enables the creation of multiple layers of gradient thickness that are then drawn to enable formation of extraordinarily thin layers exhibiting variation in refractive index. By combining alternating layers of polymers with different refractive indices only ~100 nm thick, a dielectric stack is produced that can reflect infrared light and transmit optical wavelengths. Such films are being used as critical components of the light-transmitting system that is featured in liquid crystal displays. By means of sophisticated molecular design coupled with advanced processing it is possible to produce self-organizing liquid crystalline (LC) polymers in highly birefringent films. [23] At oblique viewing angles, LC displays have contrast and color distortion problems that prevent their widespread use. Increasingly, processing is coupled with tailored synthesis to achieve specific functional properties. To help solve the problem of overly

narrow viewing angle, specifically tailored polymer molecules with structures that are rigid, organo-soluble, and transparent have been developed that possess the anisotropic in-plane orientation needed to fabricate uniaxial negative birefringence films. When combined with novel film fabrication techniques to provide finer control over the negative birefringence, the viewing angle problem can be solved. Such negative birefringence films have a worldwide market are widely used in avionics, defense systems, micro-surgery, and large-screen LC televisions.

Unconventional bulk processing methods have also progressed. For example, electrospinning may be used to form a fiber with a diameter a few tens of nanometers in diameter by harnessing electrostatic forces. While process understanding and reproducibility can be improved, this process today enables the simple production of nanofibers that would be a challenge to produce by other means. The resulting fibers can be processed into a mat, or collected individually. The appeal of this process is that a broad range of polymer solutions, gels, melts, biomaterials, or hybrid mixtures can be processed in small quantities into nanofibers at low temperatures. Such fibers are being applied in a broad range of disciplines including tissue scaffolds, agricultural films, catalytic and selective membranes or as sacrificial channels for the manufacture of microfluidic devices.

Innovative processes for nanofabrication are being continuously developed, driven by the needs of the microelectronics industry. Advanced photoresists, used to produce the nanopatterns in ultrafast microprocessors made by the microelectronics industry, are based on subtle changes in polymer solubility to reveal miniature patterns. Some processes through which it is possible to create nanoscale structures such as nanoimprint lithography are instead based on ultrahigh-resolution thermal molding. Such processing methods are being seriously considered by manufacturers of hard drives since this approach not only yields extraordinarily small features (< 30 nm) but the shape can be arbitrary in form, in contrast to most self-assembly methods. Structures at this dimension now approach those of the molecular machinery of living cells and have only recently become possible. Other tools for operating at this size regime include step-and-flash lithography and dip pen lithography. Each is capable of forming structures as small as

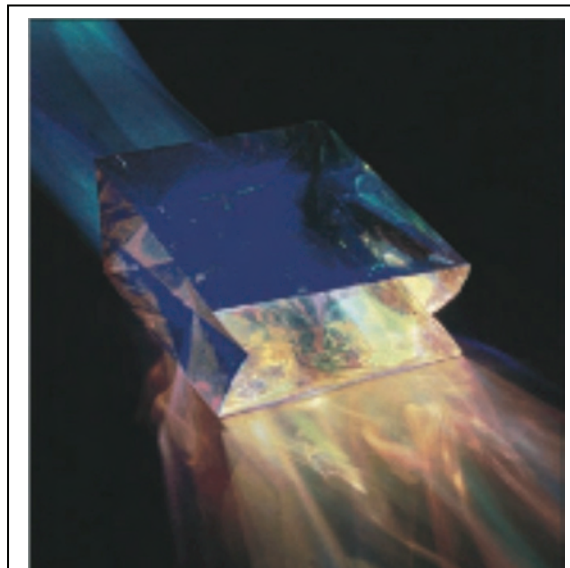
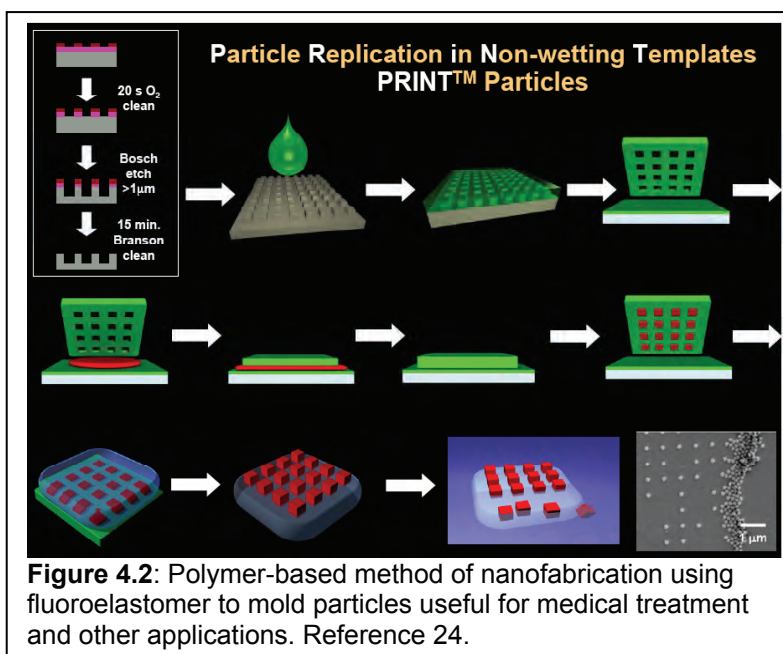
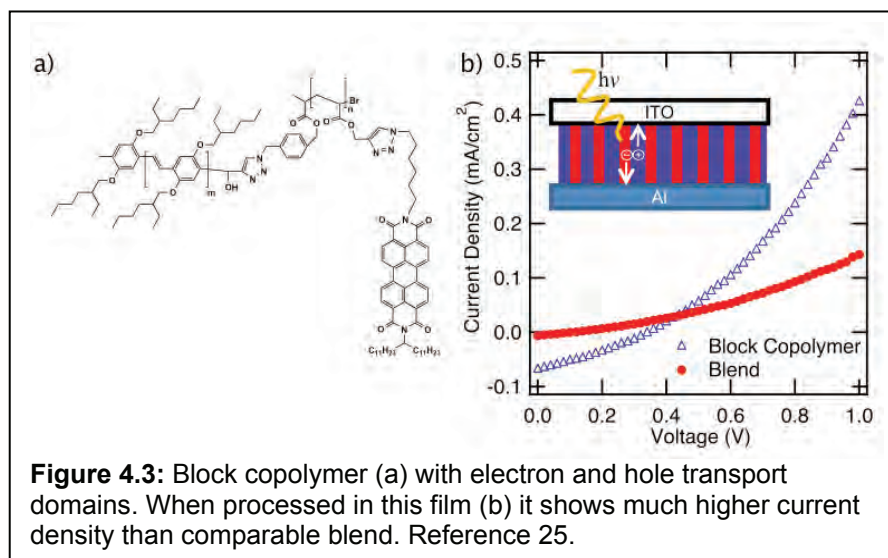


Figure 4.1: Multilayer photonic crystal film made via advanced extrusion methods. Reference 22.

ten nm in two and possibly three dimensions. In one case, by creating a negative image of a master in a fluoroelastomer, it is possible to mold other polymers, small molecules, or even pharmaceutical compounds into particles and nanoscale objects that are only a few tens of nanometers in size. Such methods are leading to new tools for therapeutics, labeling agents, and other bioactive agents as these particles can be easily taken up by living cells. While these new tools and techniques are showing great success, much fundamental work needs to be carried out.



In addition to these top-down processes that use techniques such as lithography and holography, a second, fundamentally different, approach colloquially known as “bottom-up” processing is being explored with monomers and polymers designed to self-assemble into various very-small-scale structures. The potential contributions of polymers to energy solutions through the fabrication of multilayer devices such as solar cells and fuel cells demand the processing of polymers into thin films through a variety of methods. Solvent-based coatings and films have long been used in many areas of science and engineering. Photographic films, photoreceptors for laser printing, and protective coatings, for example, all depend on the ability to coat a substrate at modest temperatures from a liquid phase. Typical solvent-based methods for processing polymers have been converted to water-soluble or water-dispersible systems in many applications, often with the consequence that a superior process is



developed. These new energy devices with their complex, sometimes delicate, electronic polymers will require the use of environmentally friendly, mild processes that provide superior performance. New developments in alternative solvents such as supercritical CO₂ may be required since many materials are water insoluble and typical dispersing agents may

seriously degrade device performance.

In addition, polymer processing should not be viewed in isolation. For example, it is likely that a switch to aqueous processing from solvent processing will require either modification of the polymer itself or the use of surfactants. Care should be taken to ensure that such changes are also environmentally friendly. In other words, all aspects of the total process must be assessed from the viewpoint of sustainability, resource consumption, and minimization of pollutants. Society will similarly benefit enormously from the development of sustainable technologies for processing polymers in an environmentally friendly manner. If all aspects of processing were examined from this perspective, massive savings in energy and other precious resources would be realized as well as improvements in worker and public safety.

4.2 Grand Challenges:

Within this context of rapidly developing processing strategies and materials needs, we have identified two grand challenges related to the processing and assembly of polymers, the first focused on processing methods that will provide extraordinary control over polymer structures, and the second focused on mild, environmentally friendly processing conditions. Such control will be needed to enable the development and sustainable manufacture of the cyberinfrastructure hardware, energy devices, and biomedical technologies needed for tomorrow.

4.21 Precision Fabrication with Giant Molecules

The ability to precisely form, shape, and fabricate macromolecules is becoming increasingly important as many current and future science and engineering developments demand precision at nanometer-length scales. This grand challenge encompasses the convergence of top-down and bottom-up processing to enable the development of hierarchical assembly at multiple length and time scales for directed structural control in both two and three dimensions. Today it is possible, using microfabrication methods, to create precise nanoscale, arbitrarily shaped thin-film structures. Self-assembly in contrast can produce thin films with somewhat smaller features but of a limited set as defined by the symmetries and interactions of the assembling molecules. There is now a growing need driven by problems in energy conversion, biology, and microelectronics to combine both microfabrication and self-assembly to enable greater control over 2D structure than is possible today.

Another important need is the engineering of robust molecular multifunctionality in these macromolecular systems. Using biology as an example of a field in which polymer science and engineering can have an enormous impact, we see a need to develop tools to temporally control the presentation of molecules. For example, spatial control of ligands to guide cell attachment and protein interactions is needed at multiple scales ranging from nanometers to tens of microns. Such control will lead to better mimics of the extracellular matrix and the *in vivo* environment. Solutions to these problems will no doubt produce processing tools that will impact a broad range of technical areas outside of biology.

There is also a growing need to be able to fabricate polymer materials at similar or smaller dimensions using strategies that will enable not only 2D but also true 3D control over both structure and function. Examples from cell biology reveal the very important role of the 3D structure in, for example, the extracellular matrix. Chemical composition and mechanical strength determine cell viability, growth, and function. At a smaller length scale, photovoltaics

require that exciton formation take place near an interface, and an easily processed, high-interface-area polymer device could catalyze the critical conversion efficiency improvement needed in organic systems. Furthermore, it has been speculated that microelectronics assembled in three rather than today's two dimensions would render Moore's Law obsolete and lead to microelectronics many orders of magnitude more powerful than current systems. To date, solutions to the goal of precision 3D fabrication remain elusive and should be pursued.

Finally, as an important aspect of this grand challenge, we note a need for custom small-volume processing, in the form of both new processes and new tools. This need stems from two important aspects: (i) Fundamental studies of new processing methods would benefit from the ability to work with small quantities of material and (ii) in many circumstances a new technology will require only a small amount of a very specific material placed in a precise location. In both cases the ability to work with small volumes of precisely fabricated materials would provide an important competitive advantage in terms of both technology development and manufacturing advantage. The growing development of microfluidics with its ability to mix small volumes of material, coupled with inkjet deposition or other mild deposition methods may offer remarkably effective possibilities for small-volume processing.

4.22 Ambient and Benign Processing Methods

A second grand challenge is based on the recognition that there is an increasing need for ambient-condition processing methods that make use of environmentally friendly, low-energy-use, zero-VOC (volatile organic compounds) processing methods. This need comes from several important developments. First, biologically active materials will increasingly be incorporated directly into functional polymers; second, to retain their functionality, low-temperature processing will be necessary. The high-temperatures of melt processing, certain solvents, and other conditions that are used for processing conventional polymers may all prove detrimental to retention of the function of these biological units. Success in this area will enable development of ambient processing methods for successful integration of biological functions into materials of uniform and controlled morphologies.

In another example, developments in flexible, printed electronics will make increasing use of processing methods such as inkjet printing or offset printing for rapid roll-to-roll processing and manufacture. Such methods will enable the rapid, low-cost production of flexible displays, flat-panel lighting, RFID tags, or solar cells. In many cases, high-temperature processing of the organic electronic materials will be deleterious to device performance. Traditional low-temperature fabrication uses large quantities of organic solvents. Industry has attempted to eliminate organic solvents and to replace them with water-based processes. While this is an excellent strategy for addressing current needs, it is unlikely that water will be suitable in all these new processes. Thus, there is also a growing need to improve sustainable or green processing methods for such polymers and devices. This convergence of needs requires new developments in processing methods, solvent choices, fabrication tools, and polymer processing (possibly hybrid) strategies that combine these attributes of ambient and benign processing methods.

4.3 Specific Challenges

4.3.1 Innovative Processing for Materials Structured at the nm-Length Scale

Polymer scientists and engineers need to create structured polymeric and complex materials with structure in controlled dimensions ranging from the nanoscale up to the microscale. (A structured material is one in which at least one of the components is ordered on a least one length scale or along one direction.) Such systems may be desired without defects or with particular types of features (purposeful defects), as well as preferred anisotropic structures and associated properties. Processing methods with which to achieve these structured polymers systems can include fiber spinning, extrusion, molding, lithographic patterning, and the use of self-assembly alone or in conjunction with other processing methods.

Most polymeric materials in commercial use undergo melt or solution processing, so that flow, directional cooling, or solvent evaporation can be used to impart orientation and resultant anisotropy to the forming structures. But current and future processing will need to go well

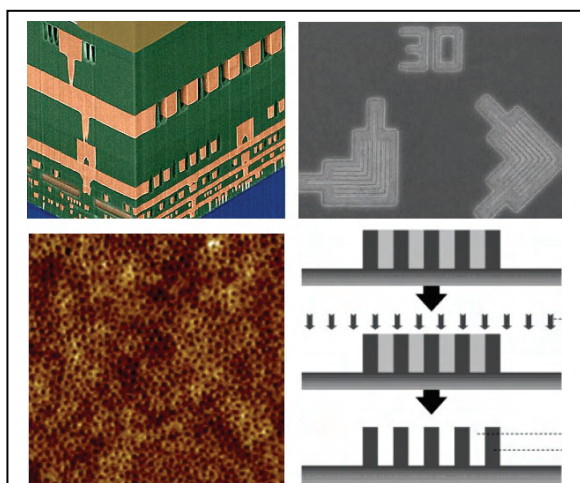


Figure 4.4: Photoresists, used to manufacture virtually every complex electronic micro-processor (upper left), are now capable of producing arbitrarily shaped structures as small as 30 nm, less than 1/1000th the size of a human hair (upper right). Self-assembly is enabling formation of even smaller structures 10 to 20 nm in size, as shown in the AFM image (lower left). The challenge will be to reduce process complexity and eliminate process steps such as shown schematically above (lower right). Reference 26.

beyond a homogeneous distribution of components or simple orientation at extremely small length scales. Lithography is arguably one of the most precise methods of fabrication developed to date. Using radiation-induced solubility changes in polymers, this method of pattern formation is employed by the microelectronics industry to create structures of arbitrary shape at dimensions of a few tens of nanometers. These structures, produced in high volume and with excellent fidelity, are less than 1/1000th the size of a human hair. Chemically amplified polymeric photoresists are now used to make virtually all the microprocessors worldwide and directly or indirectly affect most of the world's population. High-resolution photopatterning has enabled impressive developments in microelectronics and has become a key element in fields ranging from nanobiotechnology, microfluidics, and photonics. Even with these advanced capabilities, the semiconductor industry has plans to fabricate even smaller structures beyond those possible today using lithographic methods.

Companies such as IBM are currently pursuing the processing of polymers using “bottom-up” assembly of block copolymers to enable them to fabricate devices with critical dimensions of 20 nm when they cannot do this by other methods. Thus new designs for flash memory and air-gap low-k materials are being explored that use self-assembly methods. Like other processing methods, the success of self-assembly will depend on the creation of tailor-made materials, an improved understanding of the physical properties of these materials, and greater use of computational methods. Moreover, using

substrate templates to direct/guide self-organizing materials such as block copolymers, 2D patterned structures have been made with excellent long-range positional and orientational order. The manufacture of such materials and processes is in its infancy, but already block copolymers that form ordered 2D structures are being explored for microelectronics production, as new energy-conversion materials or nanoscale materials for biomolecular separations.

Novel processes and molecular architectures that incorporate and apply lessons and concepts learned from highly ordered self-assembled systems may be applied in turn to higher-volume, high-value-added polymeric materials. We note, for example, that block copolymers with the minimum level of dispersity still permit the formation of ordered materials. Such new materials would likely rely on existing monomers but would require new catalysts and synthetic mechanisms to achieve the target molecular architectures simply and economically. Despite recent successes, many aspects of self-assembly processing are to a great extent poorly understood. Knowledge of the key structure-property-processing relationships and insight into tolerances for distributions in the chain architecture and defects in the solid-state structure are essential to avoid the uncertain costs of trial-and-error approaches. While chemical tools exist for preparing many synthetic systems, we do not yet know the minimum level of synthetic perfection needed for the order required by new technological applications. While the corresponding theory is being developed, it is not yet providing reliable guidance to the researchers who are exploring and refining new structures, processes, and materials. The final form is a function of molecular structure and processing pathway. A key challenge therefore is to understand self-assembly processes from both a theoretical and an experimental perspective to control short- and long-range order and to determine the level of synthetic perfection necessary for advanced processing.

4.32 Precision Fabrication in Three Dimensions

As the sophistication of technology in fields such as microelectronics, energy systems, optics, and biology advances, control over structure is needed in not only one and two dimensions, but also in three dimensions. Several large-scale methods are under investigation for the production of complex structures using a variety of processing methods. For example, one form of 3D printing utilizes the construction of a scaffold in each dimension by serially scanning a temperature-controlled hollow tip or print head that delivers and sinters a polymer powder into a shape dictated by software control of stage motion. Another method that could be used for prototype production involves scanning a UV light beam across a bath of reactive, polymerizable monomer. Such methods enable rapid structure formation, but may lead to non-equilibrium, metastable structures. Repeatedly scanning and polymerizing layer after layer of monomer leads to the formation of a solid 3D object with features in the millimeter range. One advantage of serial processing is the ability it provides for creating complex, arbitrary shapes, including purposeful defects in otherwise periodic patterns (e.g., optical cavities in photonic crystals). A disadvantage is the rather slow nature of any serial process, such that only limited areas/volumes can be made.

In contrast, newer techniques such as interference lithography simultaneously and rapidly create periodic patterns over large (e.g., wafer size) areas by creating chemical changes using coherent light to change the solubility of a polymer (positive resist) or to crosslink a monomer into a polymer network (negative resist). Yet placing arbitrarily shaped features at precise locations within the periodic array remains a challenge, but one that is, however, being met by

other means. With the development of 2-photon lithography, it is possible to craft small-scale 3D structures only a few microns in size and introduce specific features to larger periodic objects. The technique, employing a laser-scanning confocal microscope as the scanning device and working at near-IR wavelengths, uses non-linearly absorbing dyes to trigger photochemical reactions only at the point of focus. Useful in a number of applications, it may for example be possible to create structures in the presence of living cells, thus making the method suitable for tissue scaffolds.

Yet there is a need to form 3D structures at much smaller length scales than is currently possible with these “top-down” methods. Three-dimensionally structured materials can be made by self-assembly using “bottom-up” approaches, but control of registration and orientation in 3D is rather primitive at present. Hybrid materials and other complex systems (see below) will offer choices in materials across an unrivalled range of mechanical, electrical, and optical properties. A key challenge of 2D and 3D processing will be to combine the ability of top-down fabrication methods to make precise, arbitrarily shaped structures with the ease and small dimensions of bottom-up self-assembly.

4.33 Processing of Complex, Organic/Inorganic Systems

Complex systems are becoming increasingly important in polymer science and engineering. While they are discussed in greater detail in another section of this report, we note here that they are expected increasingly to become the focus of processing and assembly efforts. Multicomponent polymer systems (block copolymers, blends, polymer-particle/plate hybrids) are characterized by structure at multiple length scales ($b_{\text{Kuhn}} - R_g$) and dynamics that can span many time scales (1 ns to hundreds of ms). These materials are termed ‘complex systems’ because their

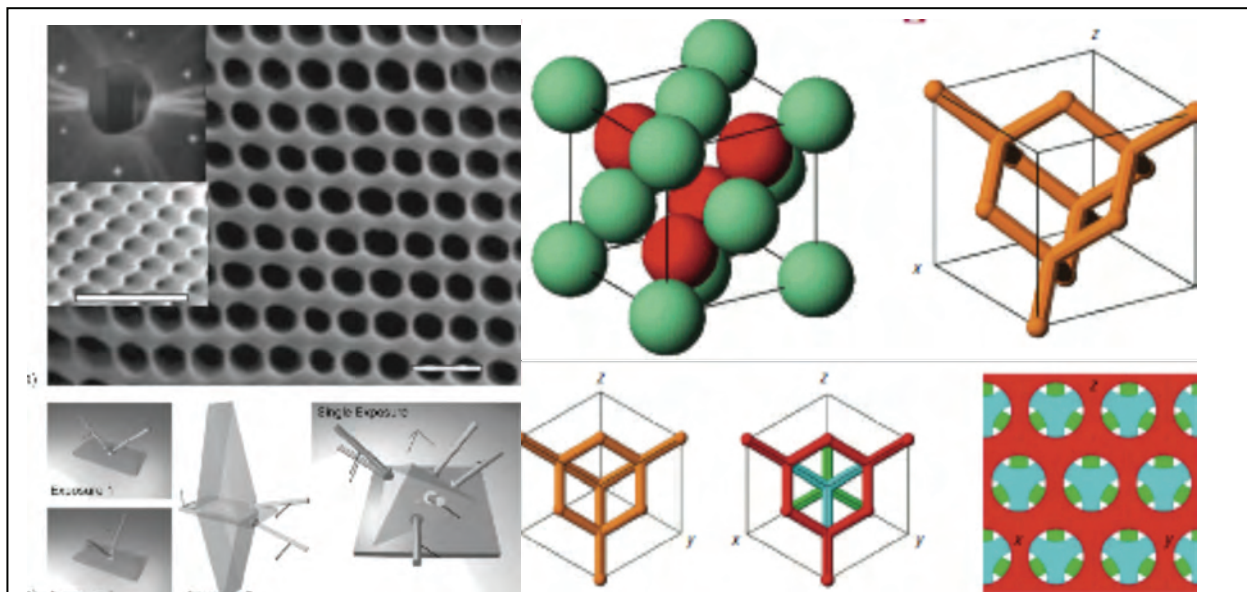


Figure 4.5: New methods of 3D microfabrication are enabling the formation of new optical structures as well as materials for biological assay. The left-hand figure shows micron-sized complex structures fabricated using interference lithography, Ref. 27a. (Reprinted with permission from ref. 27a. Copyright 2004, American Institute of Physics) The right-hand figure shows various diamond-like structures that have superior properties as optical crystals, Ref 27b. (Reprinted by permission from Macmillan Publishers Ltd: NATURE MATERIALS, ref 27b, copyright 2004.)

structure depends on both thermodynamics and their processing history. A key challenge for modern polymer science is therefore to understand and control local and polymer-scale interactions in complex systems in order to manipulate their structure, processing, and function.

To transform a complex polymer system into useful materials or devices, a shaping or assembly process is required. In this process the material is subjected to an external field (e.g., flow, an electric field) that defines the macroscopic shape of the object. The range of length and time scales typical of complex systems must be understood and controlled before these materials can be reliably processed. For example, heterogeneity in local chemical structure means that continuum variables such as the dielectric constant, conductivity, modulus, refractive index, etc., can be determined only by taking averages over the structure. The consequences of these effects are profound for both theory and applications. For example, coupling between a processing field and local structure can be used advantageously in some cases to superimpose processing-scale symmetries onto the smaller-scale structure (e.g., to align microphase domains into macroscopically ordered structures), or to create a string-phase of particles to reinforce a polymer-particle hybrid in a desired direction. Even in situations in which the coupling is imperfect, processing, particularly in confined geometries, can be used to align self-assembled materials in desirable ways. Additionally, theories capable of correctly predicting the processing of a complex system must presume that, although the processing field may be applied at the macroscopic scale, its influence is decidedly local. This means that calculations of the fluid properties required to predict processing requires an understanding of the local structure, which may in turn be a function of the field. It is therefore self-evident that these types of analyses require significant advances in the multiscale modeling of materials.

For example, introducing bulky side groups to an otherwise linear monomer unit will not only coarsen the local structure of a self-assembling copolymer but will also slow down the dynamics on all timescales. Likewise, the presence of polarizable groups, electrostatic charges, or the ability to form hydrogen bonds, can be used to profoundly alter local polymer structure, the symmetry of self-assembled phases, and to manipulate the distribution of another species (e.g., particles, additives, other polymers) in a host polymer. Improving our fundamental understanding of even a subset of these effects could be used to great advantage in manipulating the self-assembly and processing of polymer systems when researchers and engineers face issues that supersede currently complicated and poorly understood technologies.

4.34 Biomacromolecules as Models for or Components of Complex Polymers

Biological macromolecules achieve multiscale order and function through an exquisitely orchestrated ensemble of primarily weak interactions between molecules; in living systems, the coordination of these interactions results in well-organized materials with great mechanical strength (bone, skin, spider silk), biological specificity (antibodies, receptors), catalytic activity (enzymes), and energy-harvesting capability (photosynthesis). Similarly, polypeptides, block polypeptides, and polypeptide-polymer conjugates have been shown to form controlled self-assembled structures that have distinct features relative to structures formed from synthetic block polymers. Polypeptides have defined conformations (e.g., coil, helix), and the presence of these conformations has been shown to alter the types of assembled structures that can be formed from these materials. These conformations are sensitive to changes in temperature and solution conditions, so the structures assembled from these building blocks are therefore also similarly sensitive, and can form the basis of new classes of sensing and mechanically responsive

materials. Understanding the self-assembly behavior of biological molecules such as polypeptides as models for such behavior in complex polymers is a key step in generating the necessary understanding of synthetic materials.

As an additional functional difference in biomolecular assembly, proteins present functional groups in specific positions along the polymer chain, and this controlled group placement (monomer sequence) controls their folding behavior and directs their complex assembly. This functional group-placement control can also be used purposefully to direct the assembly behavior of the macromolecules; this potential advantage has not yet been exploited to its full extent in part due to current limitations in polymer synthesis (see the section on Polymer Synthesis). In contrast, advances in the biological synthesis of polypeptides have permitted the incorporation of novel chemical functionality in exact positions on the polymer chain, which will offer important opportunities to control the interactions that guide self-assembly, as well as to control the three-dimensional presentation of unique functional groups such as electron-transporting molecules and biological ligands in the final assembled materials.

Biologically based assembly mechanisms continue therefore to serve as compelling models for the production of well-ordered polymeric and biopolymeric materials that are able—on the basis of their controlled organization—to harvest energy, emit light, store information, and guide the functions of living cells. A key challenge will be to simultaneously develop the synthetic, theoretical, and processing capabilities needed to master the structural control that these new materials will make possible.

4.35 Low Temperature, Benign Processing

In many instances, it is desirable to incorporate the advantageous features of biological molecules—for example, their controlled structure and biological activity—into polymer fibers, films, and polymer objects. Potential applications include optical wave-guides, molecular wires new conducting assemblies, sensors for detecting toxins and pathogens, and wound-healing bandages. The processing of macromolecules in the biological environment occurs under mild aqueous conditions, in a sequence of well-defined steps that result in a final, controlled structure

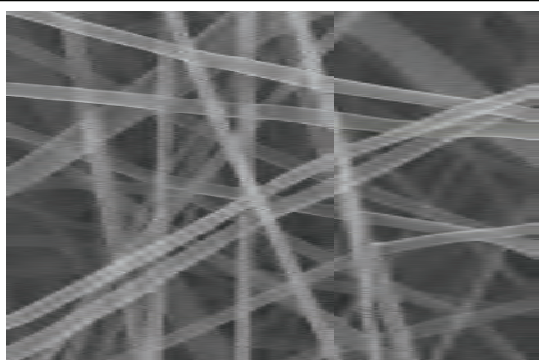


Figure 4.6: Electrospun fibers ~150 nm in diameter used to make water purification membranes for reverse osmosis. Reference 28.

with precisely tailored functions. In contrast, the processing of most synthetic polymers occurs under high temperature conditions, often with large shear, tensile or compressive forces or in the presence of organic solvents. Although these conditions are required to make the synthetic polymer processible, they are energy-intensive and may result in the emission of VOCs, with troublesome implications for natural resources and the environment. From a materials function perspective, standard harsh processing conditions may also be detrimental, because they preclude the incorporation of delicate biological motifs in synthetic hybrids that may otherwise offer unique

property sets. Thus these inter-related needs provide two complementary key challenges. Over the next decade, a challenge will be the development of efficient ambient processing protocols to

maintain the desired structures and functions of macromolecules. Another challenge in this connection will be to develop environmentally benign processing methods for all polymers.

Fiber-spinning methods, currently carried out in the melt or in some cases from solution, will require modification; such modifications should include the further development of small-scale methods that permit rapid evaluation and assessment of new polymer materials. Electrospinning, for example, exhibits many of these desirable features. Electrospinning protocols involve the application of voltage across the needle of a syringe and a grounded target; a variety of fiber diameters, mat sizes, and geometries are possible, including concentric, small-diameter tubes, and mats containing fibers oriented in controlled and multiple directions. With the appropriate choice of polymer/solvent mixtures, these processing methods are also conducted at room temperature, thereby reducing energy demand. New processing methods that combine these attributes are needed for progress in polymer science and engineering. The modification of existing fiber extrusion and film-processing methods (film casting, spin coating, etc.) will likely require the synthesis of new polymers that are soluble in water or flow at room temperature, but that form materials with sufficient mechanical integrity after processing, either via crystallization or molecular assembly, or upon post-processing modification such as crosslinking. Any of these processing advances should be applicable to a wide variety of polymer systems: biological polymers (e.g., proteins and peptides), synthetic polymers (commodity and high-performance), and composite mixtures (polymers/small molecules, polymers/particles, etc.).

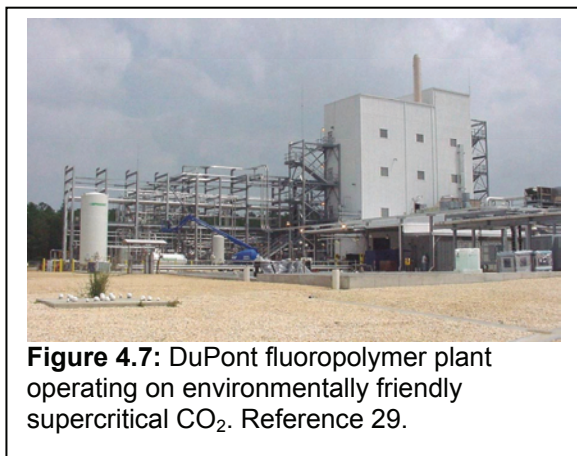


Figure 4.7: DuPont fluoropolymer plant operating on environmentally friendly supercritical CO₂. Reference 29.

At present it is still common to use organic solvents in the processing of many polymers. While solvent recovery is widely practiced, its energy requirements, the possibility of solvent release, material failure, or natural disasters all provide reasons to eliminate solvents. Where solventless processing appears impossible, aqueous-based methods should be explored. Processing should also be carried out at the lowest temperature possible to minimize energy utilization. A major goal in addressing these key challenges must be to eliminate the use of VOCs in processing of polymers. An example from

polymer manufacturing involves the construction of a new chemical plant for fluoropolymer synthesis that is based on environmentally friendly supercritical carbon dioxide (CO₂). This supercritical CO₂ would be recovered from power plants, recycled within the process and then sequestered if necessary. Using this approach, undesirable fluorochemicals are removed from the process and the environment.

Polymers offer the possibility of greater recycling. Today recycling of polymers is often hindered by the fact that they are used in complex mixtures or multilayer structures that hinder recycling by producing mixed plastic waste streams. Better reuse of these “resources” or the development of new polymer systems and processes that do not require such complex structures will greatly aid the application of polymers to existing or new technologies.

The processing of polymers is often made possible by a wide variety of so-called processing aids. Many of these are produced in an energy-intensive manner with little regard to sustainability or impact on the environment. Processors should be challenged to use only those materials whose production consumes the least energy, produces minimal by-products and waste

streams, and is derived from renewable resources. For example, one large sector of processing aids comprises the release agents that are used in various molding, extrusion, milling, and calendaring operations. Polyethylene waxes are commonly used but so are naturally-occurring carnauba wax and other naturally derived oils and waxes. The choice should be for the renewable, least energy-intensive alternative that does the job adequately.

4.36 In-situ, Real-Time Process Monitoring

Currently, there is an unmet need for monitoring how structure (and, ultimately, function) develops during the processing of polymers. If we are to succeed in the key challenges described above we will need to understand, monitor, and precisely control the processes used to fabricate complex, sophisticated polymer materials. Other areas of precision fabrication (such as microelectronics) routinely monitor the developing product throughout the process flow, using some combination of in-situ measurements and stage-by-stage examination. Although this is discussed as part of the section on Polymer Characterization, it is so important for advanced processing that it is discussed here. For polymers, the need becomes increasingly acute as our emphasis shifts towards “small-lot” processing of specialty, high-value-added materials, each of which processes somewhat uniquely. Unlike the high-volume continuous processes well known for polymers today (e.g., polyethylene film blowing), it will be impractical to spend days or weeks optimizing the processing conditions for the yield of a desired product whose production may last a day or less.

This need can be broadly separated into two key challenges: (i) the application of sophisticated tools to reveal the basic nature of a poorly understood structure-formation process and (ii) the development of instrumentation that can be used for routine diagnostics, enabling closed-loop feedback control. The latter will be especially important as small-scale custom processing becomes more prevalent.

In the first area, the application of sophisticated techniques (e.g., synchrotron x-ray scattering) to study established, high-volume, continuous processes (e.g., spatially resolved “down-line” measurements during fiber spinning, or during tape extrusion or film blowing) have already provided important insights into the operative complex structures (e.g., shish-kebabs) and processes (e.g., crystal nucleation), and how the combined stress and temperature fields can both produce different structures and accelerate these processes by orders of magnitude relative to the quiescent measurements accessible previously. But such methods rely on the quasistatic nature of these processes at steady-state; measurements for unsteady batch processes are considerably more challenging. Spin-coating is an excellent example: Although ubiquitous in microelectronics fabrication and specialty thin-film coating processes, spin-coating is extremely rapid, and the structures developed are nearly always out of equilibrium, especially for multicomponent coatings. Current methods used in assessing lateral structure (e.g., atomic-force microscopy), surface composition (e.g., x-ray photoelectron spectroscopy), and through-film structure (e.g., dynamic secondary-ion mass spectrometry) are *ex situ*, slow, and have not yet led to a general understanding (with predictive capability) of the process parameters that ultimately set the final structure. We need higher-throughput measurement capabilities with respect to both these quantities and other aspects of structure relevant to the end use (e.g., distribution of surface-chemical functionality for a material containing biomolecular components).

In the second area, we observe a need to develop simpler techniques capable of providing relevant on-line structural information; currently, the quantities measured and controlled in a

typical processing operation are temperature and perhaps a pressure or spinline stress, which are at best very indirect probes of structure, much less function. Robust probes, such as optical methods (e.g., birefringence, light scattering, ellipsometry) would be suitable; we need to know, however, how to relate the measured output to the desired quantity (structure/function) so that the process can be quickly and automatically brought under control when processing a small lot of a new material. Such on-line measurements will be essential tools in the agile manufacturing environment of the future, where custom-tailoring and facile, rapid product changes will be the heart of our competitive edge.

4.4 Theory, Modeling, and Cyber-Discovery

Throughout the workshop there was a call for improved theoretical understanding of polymer processing and other aspects of polymer science and engineering and for enhanced computational models that might guide research and lead to new discoveries (see section on Theory and Simulations). Current limitations include a lack of individuals trained in computational studies who can provide guidance and a lack of easy-to-use software to provide the desired information. One possible solution is the fostering of cross-disciplinary teams to tackle combined problems in processing, synthesis, characterization, and theory, or at least subsets of these problems. A possible outcome might be computational strategies that make it easier for scientists who are not trained in computational modeling to use simple software packages that provide the insights various groups are seeking. Another aspect of the solution to coupling theory to experiment would be to train individuals in computational tools and in the development of easier-to-use-tools. This development will require a concerted effort on the part of academics to break down traditional barriers and to consider computation as a core part of the current educational curriculum.

4.5 Education and Outreach

In order to accomplish these key challenges, we will need to train a new generation of polymer scientists and engineers. Part of the richness of polymer science is the breadth of academic backgrounds and the inherent academic diversity from which it is derived. We would like to both acknowledge the strengths that this diversity brings to our scientific culture and maintain this depth. This, however, also implies that a key challenge is incorporating the necessary fundamentals of polymer science and its interdisciplinary culture into a variety of curricula ranging from chemistry and chemical engineering to materials science and physics.

Plastics are familiar to everyone and, as a result, the study of polymers provides an excellent teaching tool. Having said this, we note that researchers in the field have too little time or training in early childhood education to develop both innovative and effective tools for outreach at this level. We suggest that, while a number of tools and modules for education (particularly at the elementary and middle school level) have been developed (usually in collaboration with teachers), the community as a whole does not have access to them. Furthermore, the standard for innovation in research is being applied to outreach within the proposal review process. A key challenge therefore is to develop new, simple, in-course tools and modules related to polymer processing and assembly that can be easily grasped by the student and teacher population.

We suggest that achieving the potential for effectiveness and impact would be a more valuable guideline in terms of educational outreach than is entailed by today's view. In keeping

with this sentiment, we realize that, in the outreach arena, real value could be achieved through the reinvention of demonstrations and modules on a broad scale and the availability of a centralized, updated resource of new and effective outreach and education ideas.

4.6 Global Competitiveness

Corresponding to the movement of large-volume commodity plastic manufacturing overseas, much of the low-margin, large-scale manufacturing and processing of polymer materials is also moving off shore. Therefore demand for the classical knowledge base associated with extrusion, fiber processing, and film forming is diminishing even as these techniques grow in importance in the developing world. There is, however, an important shift in the manufacturing of high-value-added polymer-based products as the biomedical, microelectronic, and energy sectors depend increasingly on the development of new materials with specifically tailored structure and properties. These new materials and devices have higher “information content” which is introduced by the use of complex polymers of increasing synthetic sophistication coupled to polymer processing. Polymer processing and assembly will play an increasingly important role in these developing technology areas as they represent high-value-added industries and it will be essential to ensure that we develop a knowledge base that is appropriate to these new science and technology areas.

To increase our competitiveness it will be essential to retain and enhance our leadership in the areas described in this report. As polymers play an increasingly important role in high-technology areas, the need for precision, small-scale, versatile custom processing will grow in importance. This evolution will be driven in part by the fact that polymers will be used increasingly to achieve extraordinarily precise functional properties (optical, electronic, and biological) instead of serving as simple low-cost replacements for other structural materials. The growth of bioinspired and complex materials will require an improved understanding of the role and effects of processing on their ultimate properties. Nanoscale and ultrasmall structures, and direct 3D assembly achieved both by processing only and processing coupled with self-assembly, will enable the advent of new devices and technologies. In short, new and sophisticated processing methods supported by the appropriate knowledge base will provide an important competitive advantage.

4.7 Recommendations

There are several areas in the processing and assembly of polymers that must be improved or developed to achieve the needed research, educational, and competitiveness goals of polymer science and engineering. These areas can be categorized as: (i) precision fabrication of polymers and (ii) processing under benign conditions. Both areas hold great promise for enabling the critical advances needed to solve many of humankind’s current challenges. It is important to keep in mind that these areas will develop only if processing and assembly is developed in combination with advances in polymer synthesis, polymer characterization, and polymer theory.

It is anticipated that self-assembling polymers and complex polymer systems will become increasingly important and that processing will play a critical role in their success. Understanding these materials, how they respond to applied fields, and the minimum level of structural and chemical perfection in both the polymer and in the control of order to achieve desirable structures will enable economical application of these new materials. Both 3D (bulk)

and 2D (thin films) processed with nm-scale precision will impact many areas of science and technology. To succeed in realizing these goals, it will be necessary to combine “bottom-up” with “top-down” processing. Processing these forms must be possible with greater precision than is achievable today. Successful processing will require the application of new analytical tools while real-time feedback will enable greater control of the process.

In order to gain greater insight into the self-assembly of biological molecules and to benefit from diverse molecular functionality, processing alone or as part of a larger synthetic system should be investigated. For these and other reasons, ambient processing methods must be much better understood to maintain the desired structures and functions of these fragile but important macromolecules. Coupled with this, it will be important to further develop environmentally benign processing methods and to eliminate all processing using volatile organic compounds.

These breakthroughs will require a workforce trained in new skills. To accomplish this we must introduce the concepts of polymer science and engineering into science curricula in high school and to enlarge it in undergraduate studies. A key element in this effort lies in creating new, simple, in-course tools and modules related to polymer processing to aid both students and teachers. Increased competitiveness will naturally come from accomplishing the key goals outlined below.

Finally, the following list provides a short synopsis of the key recommendations discussed above:

1. Understand, monitor, and precisely control processing methods used to shape polymer structure and functions in 2D and 3D
2. Develop in concert the synthetic, theoretical, and processing capabilities needed to master the structural control provided by new materials and processes
3. Systematically develop insight into tolerances non-equilibrium structures and for distributions of defects in the solid-state structure of self-organizing and complex polymers
4. Combine the ability of top-down fabrication methods to make precise, arbitrarily shaped structures with the ease and precision of bottom-up self-assembly
5. Evaluate and develop new small-volume processing methods
6. Develop efficient ambient processing protocols to retain the desired structures and functions of fragile but important bio/macromolecules
7. Develop environmentally benign processing methods for all polymers
8. Develop instrumentation that can be used in routine diagnostics, enabling closed-loop feedback control
9. Develop new, simple, in-course tools and modules related to polymer processing and assembly that can be easily grasped by the K-12 student and teacher populations for curricula ranging from chemistry and biology to materials science and physics
10. Foster international and industrial experiences to enhance the competitive skills of a diverse community of graduate students
11. Train a new generation of polymer scientists in advanced processing with knowledge of computation, synthesis, and analysis

Section 5: Characterization of Structure and Properties

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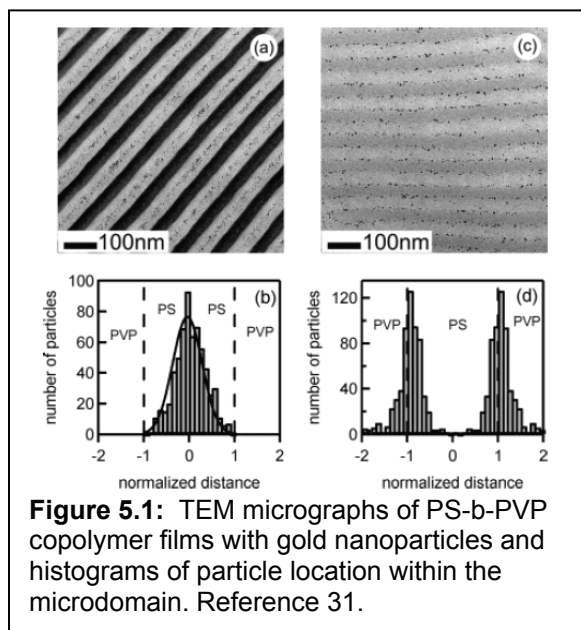
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5.1 Introduction

Many potential applications of polymers are limited today by our ability to understand their structure and dynamics at different length and time scales under easily accessible conditions. With the development of new polymer syntheses, new hybrid polymer materials and new polymer processing strategies we are now poised to produce new polymer materials with molecular level precision and as a result correspondingly sophisticated means to characterize them are needed. With the appropriate analytical tools we will be able to answer the scientifically inspiring question first posed by Richard Feynman: *What would the properties of materials be if we could arrange atoms precisely as we want them?* [30]

The characterization of polymer structure and properties was critical in the early days of polymer science beginning with the search for experimental evidence establishing the existence of long-chain molecules. Relating that long-chain connectivity to the properties it affects (e.g. melt viscosity) was a focus of the final quarter of the last century. Today it is evident that, to reap the practical benefits of these newly emerging polymer materials, a much deeper understanding of structure-dynamics-property relationships will be needed.

To accomplish this objective will require new methods and tools that push the limits of the spatial and temporal sensitivities and resolutions of current technologies. This will require the invention of new means of advanced characterization and the development of new methodologies for emerging materials and technologies. A particular challenge will be to develop real-time, high-throughput, non-destructive, *in situ*, multi-scale diagnostics that will enable rapid adjustments to materials and processes. The remainder of this section of this report outlines these needs in more detail and described areas of potential research focus.

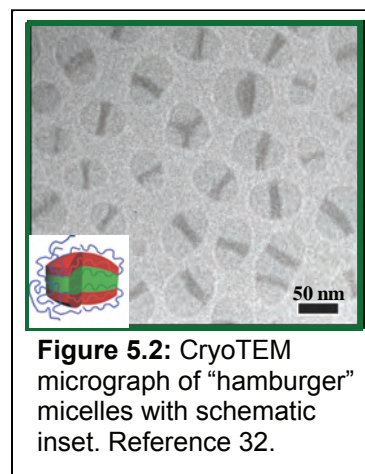


Polymers offer a uniquely general strategy for developing precisely tailored functional structures from the atomic up to the macroscopic scale. Polymer-based systems often display a rich hierarchy of structural features, from the size of the monomer unit (usually less than one nanometer) to the typical dimension of the chain itself (around several to tens of nanometers), up to the periodicity imposed by crystallization or block copolymer self-assembly (usually between several to several tens of nanometers), through the characteristic length scales of compatibilized blends and polymer nanocomposites (several tens to several hundred nanometers), and finally to the micron scale and beyond. The details of the resulting structures depend on a host of variables including the primary sequence of monomers along the chain; the molecular weight,

architecture, composition, and distribution with respect to each of these variables; interactions between monomers and among chains; the presence of multiple polymer components or of dispersed particles, sheets, and rods; and the processing strategy and thermal history.

In refining our ability to characterize polymer systems, we have encountered several unique opportunities that may not be seen in other fields. Two such examples shall be brought forth as novel, yet model, systems. The first is the incorporation of metal nanoparticles into a polymer matrix, specifically into the nanodomains created by block copolymer microphase separation. Recent work has shown that polymer-coated gold nanoparticles will preferentially segregate to the domain with similar composition. [31] The gold particles are coated with either polystyrene (PS) or poly(2-vinyl pyridine) (PVP) and blended with a PS-*b*-PVP copolymer. The mixture is solution-cast into a thin film and slowly dried to create the lamellar microstructure, as seen in Fig. 5.1. The coated nanoparticles selectively aggregate in the domain of the same polymer (PS coated in PS domains). This system provides a novel way to incorporate nanoparticles into structured arrays at small length scales for selective property manipulation, including electrical conductivity, permeability, and optical properties, among others.

A second area of interest is in block copolymer micelles. Micelles and block copolymer micelles have been studied for decades. Morphologies typical of micelles include spheres, rods, worm-like cylinders, vesicles, and lamella. Recently, a new area of micelles has emerged using miktoarm star triblock copolymers. [32] These systems exhibit a variety of new morphologies. Based on molecular architecture, chemical composition, and solvent conditions, segmented cores are formed creating a “hamburger”-like morphology (see Figure 5.2). These morphologies can have a single sandwiched structure or a periodic structure, creating a worm-like micelle, depending on the conditions. The micelles are characterized through a technique known as cryo-transmission electron microscopy (CryoTEM) to visualize the structure. This



method, developed by biologists, is today applied to water based systems and could benefit from adaptation to organic solvent-based media. Such micellar systems provide a unique way of transporting two different small molecules (e.g. pharmaceuticals) as opposed to a single molecule as designated by the simple diblock copolymer morphology. New methods that enable characterization of different ligands in specific regions of the nanoparticles would benefit both the understanding and application of these complex, new materials. These systems thus present unique opportunities with a corresponding need for progress in characterizing polymer structure in various environments.

Just as polymers inherently incorporate the potential for rich structural diversity, the range of time scales over which polymer motion takes place is immense. Local rearrangements at the monomer scale, which are central to such features as the glass transition, and of direct relevance to such technologically important processes as ionic and molecular transport, typically occur in the nanosecond regime. Conversely, relaxations at the scale of the entire polymer, which dictate the system's viscosity and are therefore central to liquid-state processing, often take place in time intervals ranging from milliseconds up to kiloseconds. Ongoing efforts to characterize both the structure and dynamics of polymers, as revealing as they have been, are just early steps in understanding these processes. There is still much work to be done in these areas to achieve the fundamental understanding needed for *a priori* prediction of properties.

Improvement in the physical properties of polymers such as elasticity, adhesion, and strength, resulting from an improved understanding of polymer science and engineering has raised standards of living for people across the globe. Emerging needs now exist in bio-medicine, communications, renewable energy, and environmental science that rely on a new set of physical, electronic, and optical properties. Again, the versatile and precisely tunable properties of polymers will provide an ideal platform for solving these new demands. However, in these new and emerging fields, tuning macromolecular structures over dimensions well beyond those between atoms will be required to achieve the necessary properties. The goal for polymer science and engineering is to precisely understand how polymeric structures and dynamics, when taken through a hierarchy of length and time scales, affect material properties.

To achieve our goals, we must learn both how to control structure and dynamics and how they relate to a polymer's properties at greater length and time scales than have been currently achieved in the bulk, and in lower dimensional spaces at surfaces, interfaces and defects. First, we need the absolute identification of chemical structures, sequences, and functionalities of polymers and macromolecules. Second, we require an understanding of single and multi-chain behavior passively and actively responding to different environments in different dimensions. Third, we need precise characterization of both polar and non-polar atomic and molecular physical interactions. Finally, we require accurate real-time, *in situ*, dynamic, structural, and morphological identification of complex systems at multiple length scales involving their formation in different environments. Accomplishing these goals will greatly benefit the bio-, nano-, electro-optical and environmental technology communities.

5.2 Grand Challenges

Development of polymer physics has always relied on novel phenomena observed by experiments, after which new theories are proposed based on experimental observations. We now recognize polymer physics as a core component of condensed-matter physics and solid-state physical chemistry because polymer physics generates new concepts to enhance our universal

understanding of these fields. The grand challenge for polymer physics is to develop a basic understanding of and characterization techniques for structure, dynamics, and properties as the materials' critical dimensions become increasingly smaller; we should realize, however, that in most cases our community does not develop experimental equipment but takes advantage of developments in other fields to accomplish our goals. We also need to design and develop polymers and macromolecules with specific structures and properties to connect with bio-, nano-, electrical, optical, and environmental technologies. Furthermore, we need to integrate the new experimental findings with theoretical developments, especially in the area of singularities of polymers and macromolecules at phase transitions. This requires us to push the limits of the spatial and temporal sensitivities and resolutions of current technologies, invent advanced characterization tools and methodologies for emerging materials and technologies, and develop real-time, high-throughput, non-destructive, *in situ*, multi-scale diagnostics in experimental methodologies.

5.3 Specific Challenge Areas

5.31 Chemical Structures, Sequences, and Functionalities

Key tasks in the characterization of designer polymers and macromolecules involve gathering information about their chemical composition, monomer sequence distribution, and architecture. This information must be collected as accurately as possible at the length scale of sub-nanometer to nanometers. Currently, we are capable of collecting information about some of the aspects but only at length scales ranging from millimeters down to a few tens of microns. For instance, chemical information can routinely be gathered by various spectroscopic methods or even imaging microscopies, and architecture can be estimated from viscosity, rheology, and scattering data. Determining sequence distribution in polymers, however, is quite challenging. There are few techniques available with which to facilitate direct measurement of this quantity. Some information can be obtained by nuclear magnetic resonance (NMR) spectroscopy—at least for monomers with sufficient chemical contrast between them—but only for limited sequences of consecutive monomers and not for the entire polymer chain. Other methods, typically based on measuring dipole moments and polarizabilities, may provide additional information. While most of these techniques were conceived of more than thirty years ago, they have not been as widely applied in polymers and macromolecules as they could be. Clearly, it is time for their revitalization.

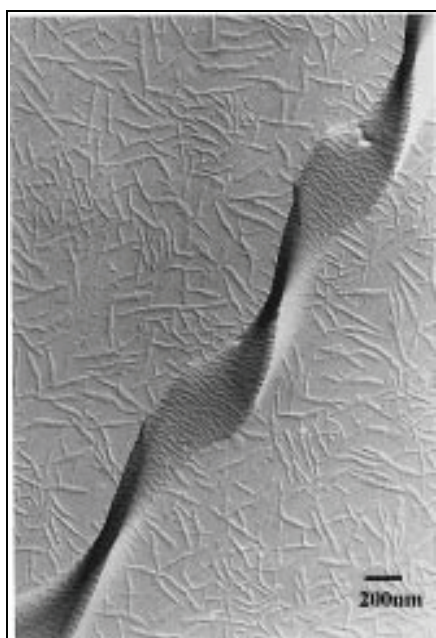
One characteristic that distinguishes designer polymers from biologically occurring polymers and macromolecules is their inherent polydispersity of properties, which results from imperfect control over the primary polymer sequence during synthesis. The polydispersities in question involve chemistry, length, and topography. While length polydispersities can be determined by several nearly routine means, including chromatography (SEC) and some spectroscopies (MALDI and its variants), gathering information about chemical polydispersity has proven to be the major challenge, and no methods at this moment can accurately provide this information. Yet, this polydispersity in properties will be an important parameter to address when discussing the application of such designer polymers and the relationship between performance and structure.

Obtaining information for systems at length scales smaller than a few microns and eventually going down to the single-coil dimension constitutes a formidable challenge. The primary

limitation is associated with the size of the probe used to gather this information. In principle, methods that probe longer length scales may be used to provide information about chemistry and architecture; it remains, however, to address the limit imposed by poor signal-to-noise ratio because of the drastically reduced amount of signal originating from the measurement at the shorter length scale. Thus, conventional methods may not always be able to help here, and new methodologies must be developed to overcome such obstacles. In recent years new techniques have been developed for determining the characteristics of single polymer coils. These include (but are not limited to) single-chain force spectroscopy and optical tweezer manipulation.

Our major goal is the development of molecular probes that will allow determination of chemistry and chemical distribution (functionality) at different locations on polymers and macromolecules. Current chromatographic and spectroscopic methods characterize the average response of the polymer system. If the detection size for these techniques can be reduced, it may be possible to utilize current methods for the study of individual molecules or monomers. Otherwise, new characterization tools that overcome existing detection limits must be developed to address these challenges. It is anticipated that this will require an orchestrated effort from the polymer physics and instrumentation communities. The next challenge will be to develop probes that will measure single macromolecules in complex yet similar environments.

5.32 Single-Chain and Multi-Chain Behaviors and Their Interactions



A single chain (and in many cases, a single particle) is the first level of the basic building blocks of self-assembled systems, and it is usually measurable at a length scale of a few to tens of nanometers. Although characterization of single chains in very dilute solutions has been successful for a long time using light-scattering techniques, there are limitations to the applicability of this technique. For instance, it is not useful in understanding chains near surfaces, under confined environments, or when the single chains or single particles are chemically or physically heterogeneous. Other scattering techniques such as x-ray or neutron scattering can be used in a grazing-incidence geometry to probe the structure and dynamics at a surface or interface. These methodologies provide a way of determining the state of the polymer or macromolecule outside of the bulk; however, they provide only an average picture of the system and typically include fitting algorithms to extract the physical information.

Precise characterization of atomic and molecular physical interactions, including both polar and non-polar interactions in a single chain or multiple chains in the bulk or solution, is important but difficult to obtain. With the increasing importance of non-chemical bonding in constructing chiral helical conformations *via* hydrogen bonding in bio- and bio-mimic polymers, the origin of chirality transfer and the amplification processes in these chiral polymers must be

Hierarchy	1 st Level Characteristics	2 nd Level Characteristics	3 rd Level Shape	4 th Level Shape
Scale	0.1 - 1 nm	nm - μ m	50nm - 100 μ m	> 1 μ m
Schematic Representations				
Examples	Acetylene	Polystyrene Chains	Helical Assembly, 1 st Moment	Assemblies of 3 rd Level Theory
Studying Methods	Polymerization	CD, X-ray	Microscopy, X-ray, Light Scattering	Microscopy, X-ray, Light Scattering

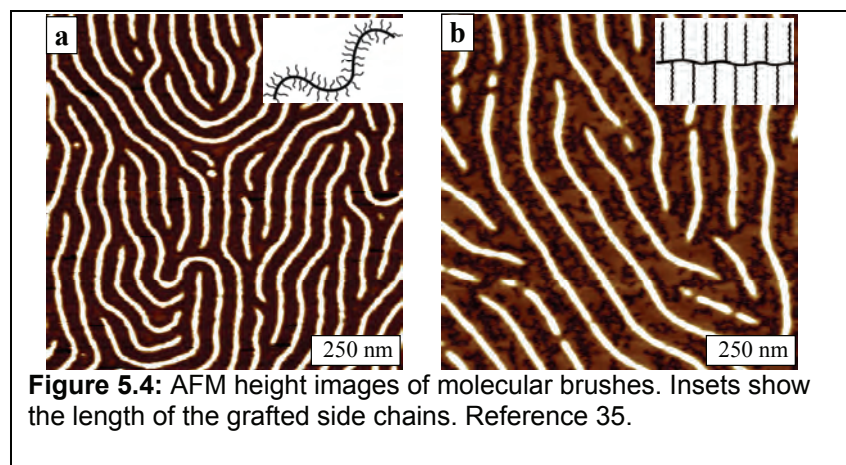
Figure 5.3: TEM of helical crystal of PET (R*)-9 with PE decoration. Table of hierarchical relationships. Reference 33, 34.

completely understood. In recent research, double-twisted helical single crystals have been obtained from a chiral polyester. [33, 34] These crystals are a crucial link in the hierarchical order of the atom-molecule-phase-object correlation. Figure 5.3 shows this relationship for the polyester from the chiral center to spherulites. This study provides a pathway over which to begin studying these interactions, but there is still much to learn. In biological systems, the exact chemical sequence is vital in determining the functionality of each macromolecule. The physical interactions within that sequence are intimately related to the functionality and activity of the molecule. Conformations in polyelectrolytes built up by electro-static interactions involving biopolymers also need to be precisely and carefully characterized. In order to reproduce and study the functionality of biomolecules and biopolymers, it is imperative to be able to characterize the physical interactions from the atomic scale up to that of intermolecular interactions.

In our case, the surface and internal physical structures must be characterized precisely. The response of interfacial regions to external stimuli represents its own set of challenges, as simultaneous detection of changes within interfacial regions as a function of temperature, pressure, flow, or other external conditions in time will be necessary. More broadly, the dynamics of interfacial regions and interfaces play a significant role in developing materials that function in complex environments. At the same time, it is integral to progress in the field to determine their chemical mappings at this length scale. The techniques utilized for physical characterization at surfaces or under confined environments require not only spatial resolution at the sub-nanometer scale, but also depth resolution at the nanometer scale. Unfortunately, chemical identification in both the spatial and depth resolutions at the same length scale is not available at this moment. It is important to resolve the characteristics of a single chain or particle to infer its role in the overall picture of the system's properties.

The second issue is how to monitor these single chains and single particles as they approach each other and assemble. The dynamics of single chains or single particles, in particular their diffusion and Brownian motion, at the same length scales on different surfaces, can be monitored using spectroscopic techniques and specific labeling; however, their applicability is also only in its infancy. These techniques meet with greater success in static measurements. When single chains and particles are in motion, the spatial and depth resolutions of the techniques, while still informative, are dramatically reduced. Furthermore, gathering information about polymer conformations at different time scales is a very difficult problem that we must address.

Currently, there are two techniques with which researchers have begun to address these issues, although they are designed for very specific cases. The first is the visualization of a single



chain using AFM. These chains are, however, molecular brushes, or single backbones with dense grafting of a second polymer along those backbones. [35] These molecules can be mapped using AFM, as seen in Figure 5.4. Due to their high grafting density, these specific chains are much larger than conventional polymer chains. The new

characterization techniques must be able to probe even smaller length scales to truly appreciate the physics of single chains.

The second technique in question involves using fluorescence to track the diffusion or Brownian motion of a single particle. One group has used two methods to study particle motion. [36] One employs optical microscopy and a tracking algorithm; the other is called MOON, for modulated optical nanoprobe. These fluorescent particles are coated on one half with a reflective metal to induce modulation in the fluorescence that makes it possible to track rotational motion. A CCD camera is used to capture images at small time-steps to monitor the diffusion of the particles. These images are then analyzed to locate particles (intensity) and track their displacement (the particle-tracking algorithm). Once the displacement is known, the diffusion coefficient can be calculated. This method, while it represents an important step in

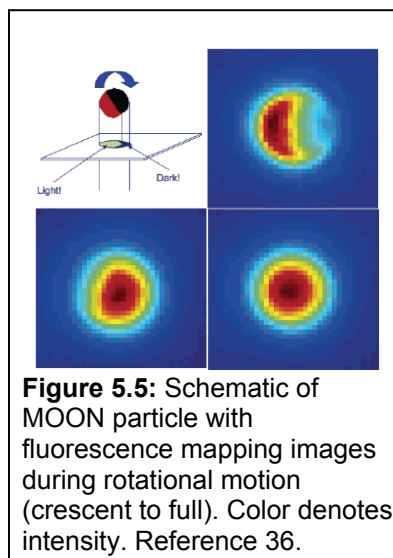


Figure 5.5: Schematic of MOON particle with fluorescence mapping images during rotational motion (crescent to full). Color denotes intensity. Reference 36.

monitoring single particles, does not provide the universality or absolute resolution needed to study polymeric systems. These particles cannot be monitored in some environments or without some variability in measurement.

Our major goal is to analyze the physical interactions of a single chain or particle directly and with precision to relate these interactions to microscopic conformations and macroscopic properties. The determination of the interactions at the atomic or molecular scale will help explain the differences found when comparing the chains in confined environments, near surfaces/interfaces, and in bulk. As with the chemical composition limitations, probes that are effective at the angstrom-to-nanometer scale must be developed to characterize these single entities. Current technologies, scattering techniques in particular, provide a direction in which to go in finding ways to move to the length scale desired; however, limitations in the

inherent physics may require the exploration of new characterization techniques.

5.33 Structure and Dynamics in Crystalline, Mesophase, and Amorphous Materials

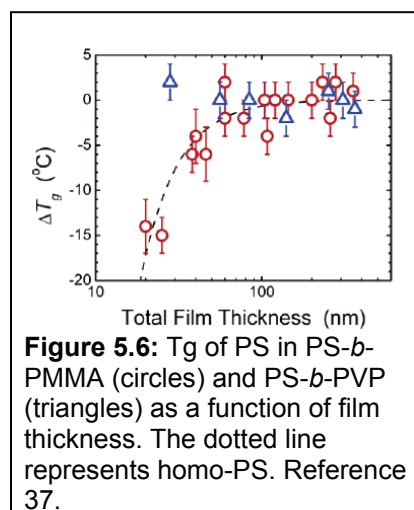
Polymers and macromolecules in condensed states are unique in exhibiting an unsurpassed range of interesting structures and dynamics. In each of their different condensed states, materials possess their own structure and dynamic characteristics, which largely determine the materials' applications. A wealth of characterization methods exist already, such as x-ray diffraction, dynamic mechanical analysis, and dielectric spectroscopy, but we still lack a coherent interpretation of the different structure and dynamic experiments that cover quite different length and time scales.

Most scientists view the structural aspects of experiments and theories as mature sciences and practices and, thus, they are classified as "traditional/conventional." However, their applications in polymers and macromolecules have been broader and deeper. The most representative example is polymer crystals. Although the methodology in determining crystal structures is well-established, crystal morphology, defects, and formation mechanisms, which have originated mostly due to the long-chain nature of polymers and thus are chain-folded and semi-crystalline in nature, remain under active investigation. In the same vein, the structural

determination of ordered structures in block copolymers and other self-assembled supra-structures have been endlessly utilized to elucidate the specific interactions as driving forces. When a state partially loses its long-range order in positional orientation, bond orientation, and molecular orientation, it becomes a mesophase. The precise structural determination of mesophases is also a challenge both experimentally and theoretically due to restrictions on the length- and time-scale of probes.

In principle, the tools for undertaking a comprehensive study of polymers and polymer-based materials dynamics, such as segmental relaxation where each repeating unit of a polymer first moves appreciably and as such is associated with the glass transition or the softening dispersion of the polymer, are available, using quasi-elastic neutron scattering (QENS) and neutron spin-echo (NSE—at the nanosecond time-scale), nuclear magnetic resonance (NMR—at the millisecond time-scale), and mechanical rheology (at time scales longer than that of segmental relaxation). Dielectric spectroscopy, which covers a very broad frequency range, can bind these experimental techniques together and be used to characterize not only polymer liquids (in the melt above the glass-transition temperature or in solutions), but also polymer networks and gels above their glass-transition temperatures; the amorphous phase of semi-crystalline polymers; polymers with dispersed nanoparticles; the soft phase of self-assembled structures; and others. The wide dynamic range of dielectric spectroscopy makes it possible to study how the QENS and NSE differences affect intermediate relaxation events and ultimately the segmental motion associated with the glass transition. Mechanical rheology can then be used to assess how those changes in segmental relaxation impact large-scale (longer-time) dynamics, providing a full picture of dynamics at all time- and length scales for polymers and polymer-based materials. It would be advantageous, however, to have a single technique with which to characterize the polymeric system across all of these length and time scales.

In order to begin to understand polymer dynamics under confinement, in different geometries, or on surfaces or at interfaces, work has been done on the glass-transition temperature of polymer thin films, patterned nanostructures, and nanocomposites. Here we will focus mainly on the characterization of thin films. [37] In this case, block copolymers of polystyrene and either poly(methyl methacrylate)—(PS-*b*-PMMA) or poly(2-vinyl pyridine)—(PS-*b*-PVP) were cast on a silicon substrate, and the lamellar morphology (period perpendicular



to substrate surface) was formed to create thin films under confinement. The T_g of the PS layer was measured, using steady-state fluorescence, as a function of thickness in both systems. The results can be seen in Figure 5.6. For the PMMA confinement, the PS exhibits a decrease in T_g that is similar to that of the homopolymer; however, for the PVP confinement, there is no change. This shows that the relaxation mechanism is different for each system although most parameters, other than the chemistry of the second block, are the same. This leads us to believe that further investigation into the relaxation processes of amorphous polymers is an area that is ripe for study. To really understand these phenomena, we must develop better characterization methods. In addition, it is well known that the value of T_g depends highly on the method used to obtain it; therefore, we need direct measurements, such as

dielectric spectroscopy, to determine these relaxations.

The major challenge of structural determination is in our understanding of these amorphous states. In particular, when an amorphous state is in its deep supercooled phase, a long-range correlation of density fluctuations in polymers with a length scale of up to several hundred nanometers can be observed based on scattering techniques. In addition, the characteristic length scale of several nanometers, which is nearly independent of the long-range correlation of density fluctuations, can be measured. The origins of these two correlations must represent distinct relaxation processes in polymer dynamics. Experimental techniques are needed to decouple these processes and study them in greater detail.

Entanglements pose another challenge in dynamics. While we cannot measure entanglements directly in the bulk, we can estimate their effect from independent rheological measurements. It is, however, very difficult to estimate the magnitude of entanglements at interfaces. Thus far, no experimental method has been conceived that would enable us to carry out such a measurement.

Our major goal is to determine the structure and dynamics over several orders of magnitude. While the coupling of various techniques has facilitated the sustainability of the field, new opportunities and further understanding lie in our ability to observe the material in varying environments with a single characterization technique. This will require exploratory research into promising non-traditional detection approaches that have not been explored in the past, followed by evaluation in terms of spatial resolution with the hope of achieving a single technique for the determination of dynamics over several time scales. We anticipate that combined detection methods, involving electromagnetic radiation, thermal, and other excitation processes, should be exploited as a starting point.

5.34 Defects, Impurities, and Heterogeneous Materials

As our ability to design polymer molecules and to guide their assembly grows, it is clear that the corresponding ability to accurately characterize structural details and dynamic processes will be severely challenged. As stated earlier, we are confronted with at least seven orders of magnitude in space and twelve orders of magnitude in time. From a physics standpoint, it is difficult to imagine a single technique that will access all of these scales. The picture is further enriched by the realization that the systems we are interested in can range from discrete nanometric particles to surface and thin-film structures to fully three-dimensional materials. Techniques that are powerful in one arena (e.g., atomic force microscopy for surface analysis) may be of little use in another (internal heterogeneity in a bulk material). On the other hand, our community does not usually develop its own tools, instead taking advantage of developments in other fields in order to accomplish our goals. Experimental measurement techniques such as scattering and imaging and spectroscopy have had a significant impact on developments in the field of polymers. The latest generation of scattering techniques (neutrons and synchrotron x-rays in national facilities), with improved flux and coherence, provide new opportunities to probe the structure and dynamics of materials at shorter length and time scales than has previously been possible. Scanning-probe techniques that measure topography, electrical properties, scanning near-field optical microscopies, and high-field nuclear magnetic resonance will play an increasingly important role in refining our ability to measure properties at smaller length scales.

A leading area of polymer research is in block copolymers. Microphase separation in block copolymers provides unique opportunities in lithography, filtration, and directed assembly or adsorption. One of the main drawbacks in transitioning the fundamental science to reflect technological advances is the presence of defects in the resulting structure. These defects can

prevent the system from providing the needed properties. AFM measurements have been made to study defects in block copolymer systems. [38] Figure 5.7 shows some images of defects and their time evolution. While this technique provides valuable identification of the defects in the system, it does not correlate their presence with the resultant properties. In addition, it can locate only local surface defects. To understand the role of defects in material properties completely, they must be characterized in a more efficient manner.

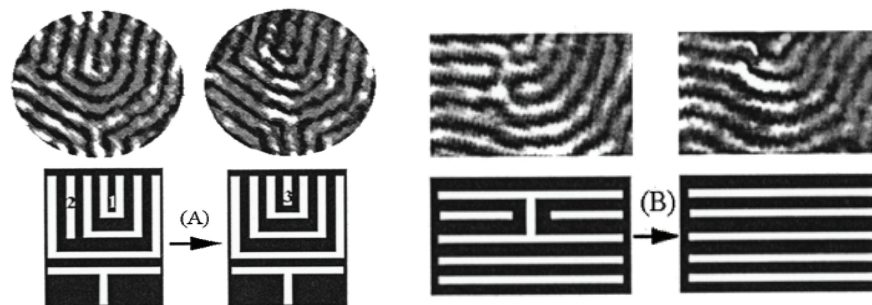


Figure 5.7: AFM images of cylinder morphology in a diblock copolymer with disclination defects. Both sets of images display the annihilation of the defects. The black and white figures provide a schematic representation of the annihilation. (Reprinted with permission from ref. 38. Copyright 2001, American Institute of Physics.) Reference 38.

As the core components of advanced technologies approach the nanoscale, impurities and defects will increasingly occur at the same length scale as the structures and devices of interest. While high-resolution imaging and analysis techniques such as electron microscopy and scanning probe measurements (e.g., scanning tunneling and atomic force microscopy) can probe a small fixed area to identify the presence of defects or impurities, they are incapable of identifying the location of a single defect on an integrated device at the length scale of a silicon wafer used in the production of devices in the semiconductor industry, nor are they readily amenable to production-line quality control. In applications such as filtration membranes or biohazard sensors that will use functional nanostructures, a single defect or impurity could result in catastrophic failure. It is therefore clear that characterization techniques capable of examining a large area on the order of millimeters to centimeters and identifying the density, or better still the location, of defects or impurities are critical to advancing the next generation of technologies.

Through various synthetic and processing strategies, materials wherein the structure and composition can be controlled over various length scales can be produced. In addition to three-dimensional bulk structures, thin films (two-dimensional), nano-wires (one-dimensional), and nano-crystals and nano-particles (“zero” dimensional) are readily available. These developments are vital in other interdisciplinary fields such as those treating systems that have structural and spatial heterogeneity (hybrids). Such systems, which include organic/inorganic composites, play an increasingly important role in various applications. The chemical and structural heterogeneity and spatial regularity of such systems, their structure and dynamics, and the means by which they manifest themselves across different length and time scales are often not well understood. It is also difficult to characterize the physics at or near the interface of these dispersions. Their size, shape, and interactions are essential to the state of the material. Indeed, we must answer a range of fundamental questions associated with the determination of the parameters in these systems, which vary in complexity.

Our main goal is to develop characterization techniques that will allow the detection of inhomogeneities, whether intended (hybrids) or unintended (defects), in a sample in order to relate their presence to macroscopic properties. Possible characterization techniques that could be developed to address these needs may include scattering-based techniques for determining the density of low levels of defects by increasing the sensitivity or contrast, e.g., by using an increased beam flux or functional probes. Also, employing existing imaging techniques, e.g., the fluorescence imaging techniques (photoactivated localization microscopy—PALM; PALM electron microscopy—see Figure 5.8; stochastic optical reconstruction microscopy—STORM; and stimulated emission depletion microscopy—STED) currently being developed and used in real-time monitoring of the presence of single protein molecules on a surface, [39] combined with specially designed probes that target the specific location of defects or impurities, could be an effective investment.

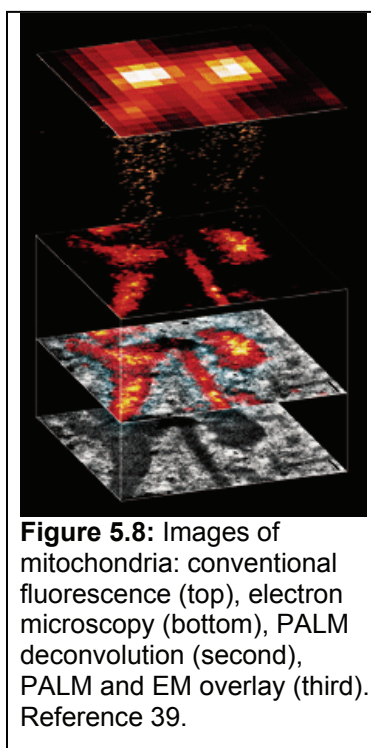


Figure 5.8: Images of mitochondria: conventional fluorescence (top), electron microscopy (bottom), PALM deconvolution (second), PALM and EM overlay (third). Reference 39.

5.35 Real-time, High-throughput, Non-destructive, In Situ, Multi-scale Monitoring Techniques for Structural Transformations

When we monitor changes in the structure and dynamics of polymers and macromolecules, we unavoidably meet the phase transformations at which the symmetry-breaking occurs or the dynamic behavior suddenly changes. One of the profound phenomena in polymer phase transformations is that polymers may possess several different pathways over which to reach their lowest free-energy states *via* different metastable states. The concept of metastable states in polymers has been associated with phase sizes and their formation kinetics and environment, providing a unique understanding of phase transformation mechanisms. Furthermore, metastable states in polymers can also occur at different length and time scales and lead to the linkage of those metastable states in multiple transition behaviors that coexist. Predicting these different pathways during phase transformations requires “new” experimental tools with which to monitor these metastable states, which are usually kinetically

trapped, short-lived processes with real-time, high-throughput, non-destructive, *in situ* measurements at multiple length and time scales that are utilized not only for the bulk, but also for lower-dimensional spaces.

The most extensively utilized experimental techniques for this purpose are synchrotron x-ray diffraction and scattering (XRD) and small-angle neutron scattering (SANS) to continuously monitor phase transformation processes. In the past twenty years, synchrotron x-ray experiments have been designed and developed with great sophistication. Due to high intensity sources, we have been able to use such methods to identify many new short-lived metastable states with unexpected structures, including different types of chain-folded crystals and various crystal orientation changes. Furthermore, this technique has also been used in continuous on-line fiber spinning or film extrusion studies to provide important structure development information as a function of processing conditions. The development of powerful new methods including the use of high intensity sources coupled to fast 2-dimensional detectors for simultaneous SAXS and

WAXS are revealing new insights into polymer behavior over broad length scales. Grazing incidence methods such as GISAXS are enabling a greatly improved understanding of structure in thin films, especially in self-assembling materials. Resonant soft X-ray scattering and reflectometry methods enable a broad range of materials to be explored. Soft X-ray absorption microscopy could also be exceptionally useful if the X-rays can be focused to less than the current 100 nm.

Neutron scattering experiments can provide information on the miscibility and structure of polymer blends. SANS provides similar advantages to those of synchrotron x-ray diffraction and scattering. SANS experiments are extraordinarily useful to identify the correlation length of the polymer components in a blend. This can show whether the polymer is miscible or if it has formed micro- or even nano-domains. In order to have a large enough neutron density contrast, one component must be deuterated, so the main challenge of this technique lies in the need for deuterium labeled samples. The new spallation neutron source at Oak Ridge National Laboratories will provide increased neutron intensity which will enable grazing incidence SANS studies of thin films or experiments on polymer solutions where solvents can be deuterated instead of polymers.

Parallel developments in real-time, *in situ* spectroscopic experiments have also been utilized. In the area of microscopy, environmental scanning electron microscopy (ESEM) provides some *in situ* observation capacity while atomic force microscopy (AFM) can partially follow structural and morphological developments on materials surfaces. Recent development of a new technique known as nano-Raman spectroscopy involves combining AFM and Raman spectroscopy. In nano-Raman spectroscopy, an AFM tip is coated with a gold or silver layer to enhance the Raman signal. A side-illumination geometry is also used to enhance the signal through polarization of the laser light and the ability to analyze transparent and nontransparent samples. A schematic of the experimental set-up can be seen in Figure 5.9. [40] The combination of AFM and Raman spectroscopy allows the user to determine chemical topology as well as physical topography. This is a prime example of the advantages that can be achieved by combining techniques to gather simultaneous information. We should continue exploring other method combinations to increase our ability to characterize polymeric systems. Although this technique is promising, it still remains that, in many cases, the monitoring of non-equilibrium, transient processes is considerably more challenging.

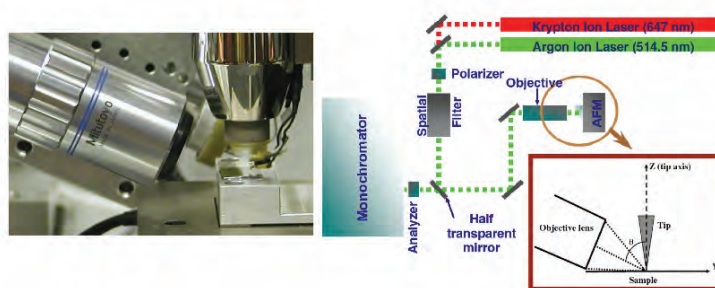


Figure 5.9: Experimental set-up of a nano-Raman instrument. On the left is a photo of the objective lens focused near the AFM tip. On the right is a schematic of the laser light path. Reference 40.

Many other techniques are unable to provide *in situ* or on-line information about structural evolutions. They are, at best, quasi-static. The limitations of these techniques hinder the study of polymeric systems at multiple length scales. If a broader understanding of polymer structure and dynamics is to be achieved, the pertinent information from both reciprocal space and real space must be obtained during real time. In addition, it is desirable to couple the structure and dynamics by pushing the limits of current techniques and the ability to measure multiple length scales simultaneously. The power of such combinations has been demonstrated recently. For example, a cone-plate rheometer has been successfully placed into a synchrotron scattering beamline for *in situ* measurement of the structure during shear measurements. In addition, Raman spectroscopy and light scattering have been integrated into microfluidic-based devices to characterize polymerization processes. New techniques should be developed to provide the most information available. By adjusting the length scale of detection, the signal-to-noise ratio increases. High-throughput analysis is essential to obtaining structural and dynamic properties.

The length scale issue is not the only one of importance. Many techniques require a certain minimum quantity to be utilized. These techniques will allow the use of small sample sizes or even single samples for various analytical experiments. Developing techniques that can use smaller sample sizes will benefit the characterization of low-yield, highly-specialized polymer samples. This point is intimately tied to the idea of simultaneous testing. If it is possible to preserve a sample's thermal history across multiple experiments, researchers can determine phase and structure without loss of information. Another essential element of current and new techniques is that they need to be non-destructive. As a complement to the previous comment on small-scale samples, we note here that it is important that characterization techniques do not damage samples. High-energy sources can provide high-throughput analysis; however, such sources may also be harmful to sample materials. It is important to note therefore that, without denying the superior efficiency of simultaneous analysis, we should simultaneously pursue new developments in non-destructive experimentation.

As polymer systems become increasingly complex, and our characterization tools become more sophisticated, the reliable analysis and interpretation of experimental data becomes correspondingly more challenging. This is an arena in which there is a huge need for modern theory and simulation tools to be made readily accessible to the experimenter. Although in certain cases sophisticated analysis packages exist, such as the Generalized Inverse Fourier Transform used to invert scattering data, and the inverse Laplace transform approaches in CONTIN and REPES to invert dynamic light-scattering correlation functions into particle-size distributions, their use still requires considerable expertise and experience. In many other situations, there are no widely distributed routines. For example, in scattering from dispersed polymer-coated nanoparticles (either in solution or in a bulk polymer), the data itself is not likely to be so precise or "feature-rich" that it can be interpreted in only one way. Yet, it is possible to make theoretical predictions about or simulations of segment concentration away from particle surfaces, under a wide variety of conditions (chain length, grafting density, surface curvature, solvent quality). In all of these examples, and many more that may be envisioned, creating a Web-based, cyber-accessible repository that includes downloadable, user-friendly analysis routines, user-friendly instruction manuals, and references to papers and experts who have experience with the technique and analysis in question should provide considerable utility to the polymer research community.

Our main goals for this area include the development of real-time, high-throughput, non-destructive, *in situ*, multi-scale techniques, as well as the streamlining of current techniques.

National facilities and laboratories should play a central and leading role in developing these monitoring techniques. The science and technology enterprise has benefited enormously from advances in characterization methods. While some of these advances have been motivated by the polymer community, most have been spurred by needs within other communities. It is the responsibility of the polymer community to ensure that advances in chemical, structural, dynamic, and property measurements be fully integrated into and adapted to issues within polymer science. These advances should move in conjunction with developments in simultaneous characterization techniques. In addition, it is our responsibility to facilitate the use of current techniques through education that conveys their availability, universality of use and analysis, and the application of real-time, current software for the analysis. Furthermore, wherever possible we must influence equipment manufacturers, national centers, and national laboratories to consider the need for advancement in the characterization of polymers.

5.4 Integration of Polymers with Emerging Technologies

Polymers are unique in terms of diversity of use across interdisciplinary fields. With that in mind, advancing technologies typically incorporate a variety of materials. The structures, properties, and processibility of polymers in these emerging technologies will typically be altered relative to a traditional all-polymer specimen because polymers have been subjected to the processing methods required to construct devices and integrated parts connected with metals, ceramics, glasses, and other materials. As polymers are integrated into a wide range of applications in bio-, nano-, electrical, optical, and environmental technologies, characterization techniques must be adapted to probe the structure and properties of polymers within these more complex environments. In some cases, signals from different materials exhibit differences of great magnitude, making the results difficult to resolve. Furthermore, multiple-material devices and assemblies feature a number and variety of interfaces. During the last few decades, numerous characterization tools (neutron and x-ray reflectivity, NEXAFS and NEXAFS depth profiling, ion beam methods, scanning-probe microscopy) have elucidated the structure of polymer surfaces and polymer-polymer interfaces. As polymers are increasingly incorporated as integral components in polymer/non-polymer devices, the characterization of their interfaces will become increasingly important.

To maximize the performance of polymers within advanced technologies, a polymer's structure and properties must be probed in its heterogeneous environment. For example, it is no longer sufficient to measure the electrical properties of a polymeric material, but rather these electrical properties must be evaluated within a device so as to grasp the importance of domain size and interfacial properties. In addition, the interplay between various materials in active electronic and optical devices is particularly interesting and might be integral to improving reliability and the lifetime of emerging technologies. Although using a polymer in a device may improve the device's performance, the performance of the polymer may change over time.

Usable lifetime is another important issue for polymer materials. Various chemical and physical environments lead to different material lifetimes. The aging process and the rate at which it occurs under certain environmental parameters becomes a critical issue. Polymeric materials undergo aging, wherein they experience structural changes across varying periods of time. Typically, aging occurs in the absence of visible physical evidence; however, the consequences of aging are manifested in changes involving density or mechanical and electrical properties, which can be catastrophic in systems such as airplanes and infrastructures where the

polymer may need to maintain its integrity for decades. For example, chemically robust polymers become susceptible to degradation when adjacent to certain metals, and metal nanoparticles that comprise the interface layer can diffuse into the polymer. In addition, the electrical properties of electro-active polymers can exhibit hysteresis as the polymer structure ages with voltage cycling, for example. In thin films, the aging process can be quite rapid compared with what occurs in bulk systems. The problems are exacerbated by interactions between chain segments and surfaces. Despite potentially devastating consequences, we still lack fundamental understanding of mechanisms in the aging process. Consequently, there remains a range of open questions pertaining to such phenomena as the non-equilibrium structure of glasses after processing, the effects of the environment on the aging process, prediction of the time-scale of aging, molecular level characterization of materials as they age, and development of appropriate accelerated aging experiments and theoretical models.

Finally, as polymer applications expand, the breadth of property measurements will necessarily expand as well. The polymer science community will need to provide standards (or at least expectations) for a broader range of properties. Expected areas for growth include electrical conductivity, thermal conductivity, biocompatibility, optical properties, and ion transport. In most cases, this expansion can be at least partially accomplished by borrowing extensively from other fields. These new requirements for property measurements also provide opportunities for simultaneous structure-property measurements.

5.5 Education and Outreach

From a broader perspective, education and academic issues are playing a very important role in our economic future. Polymer education has traditionally been intertwined with education in other science and engineering disciplines; therefore, at the undergraduate level, it receives little attention. In graduate schools, polymers are taught in a traditional sense with a focus on synthesis, physics, characterization, and technology. With the emergence of polymers in multidisciplinary research fields, however, how do we maintain our identity in polymer science and engineering, yet train our students to be open to other materials systems and the role of polymers in other disciplines? One of the key issues in this respect is: How do we balance education into fundamental knowledge against education in new-frontier disciplines? We need to continuously modify our curriculum to make sure that students learn at the frontier of polymer research.

We note several approaches to improving the educational experience for students and faculty in the area of physics and characterization. One is to focus on instrumentation and the availability of knowledge in that area. Students need to know the capabilities of current techniques and how they may best be utilized. This includes not only techniques that are prevalent in polymer science, such as spectroscopy, electron microscopy, scanning-probe microscopy, x-ray scattering and diffraction, and neutron scattering, but also techniques used in other disciplines such as the biological sciences. Several such techniques are available but are in limited use. These restrictions are due to the limited availability of tools as well as expertise. The development of a cyber-infrastructure to make information about current techniques and analysis easily accessible to new users is one way to address these issues. We can also look to the national labs and MRSEC centers to lead in educating new users about opportunities and utilization of experimental techniques. Polymer science has a long history of developing and providing gateway tools for structural biologists, particularly tools available at synchrotron X-ray

and neutron sources. At the student level, a key challenge is to bridge these communities by actively seeking to educate and extend our knowledge of these tools to new communities. We envision the utilization of workshops and summer schools that focus specifically on the use of these tools in soft matter analysis and characterization.

We should also focus on the collaboration of individuals in multidisciplinary fields of interest. Because it is difficult to maintain a strong foundation in fundamental polymer physics while delving into other fields such as biosciences or electronics and optics, one place to start would be to encourage the cooperation of groups in each area. Similar to collaborations between polymer chemists and physicists, intimate interaction between faculty and students will benefit the field and emerging technologies in a shorter time frame. To move forward in resolving hierarchical structure-dynamic-property relationships requires multidisciplinary effort on the part of synthetic chemists, physicists, and engineers to construct functionalized structures with different length scales, dimensions, and dynamics. In addition, the tools needed to evaluate the structures and dynamics and their effects on physical, electrical, and optical properties need to be developed in a joint effort. We should make a significant effort to create effective interdisciplinary research activities.

5.6 Global Competitiveness

Other issues we have faced with increasing difficulty are diversity and global competitiveness. Our field must improve the involvement of minority groups in the US. There are two approaches: One is to address the issue here, the other is to encourage international students and researchers to move to the US. In order to address the issue here, we must engage various age groups in educational activities. We must start outreach programs, science camps, and demonstrations for the K-12 demographic to expose them to sciences early. This should include both abstract and hands-on knowledge of polymers and their properties. We can, for example, demonstrate viscoelasticity (silly putty), light propagation and electrical conduction (OLED's), and structure-property relationships (Kevlar®). We can then hope that such involvement will spark young people's interest and encourage them to start careers in the sciences. By doing this, we can focus on both the young and those with varying ethnic and socio-economic backgrounds. Once they find an interest, we must have ongoing programs to support and nurture their desire to become the next generation of scientists.

In the second approach, collaboration and close interpersonal relationships with international researchers will help draw scientists from around the world to the US. The effects will be two-fold. First, through the exposure of these researchers to state-of-the-art, top-of-the-line experimental equipment during their experiences in this country, we will encourage them to enter the US job market. Second, following their involvement in a positive experience, visiting or residential scientists will encourage others to follow their lead. This will bring both current generations—through collaboration and word-of-mouth dissemination—and future generations—through advising and mentoring—into the American workforce.

With respect to all of these proposed methods, it is important to concentrate on recruiting a diverse group as well as those with the greatest potential. By engaging students who perform at the top of their classes in K-12 programs or top international researchers, we can strengthen our competitiveness on the global market. We must strive to be the leaders in fundamental research, technological and equipment development, and education. As we tackle the emerging trend of interdisciplinary studies in polymer physics, we must stay ahead of the curve and push the limits

of science and creativity. If we are to realize the goals set forth above for the characterization of new polymer systems and the intricacies of the old, we must continue to find bright, young minds that will someday measure the physics of a single polymer chain, study the intimate interfaces of heterogeneous materials, or develop new devices in biomedical and electro-optical technologies.

5.7 Recommendations

In summary, we should address several areas in the field of polymer physics and characterization. They fall under two main categories: length and time scales and equipment development. The structural characterization of polymers, both chemical and physical, at lengths from angstroms to nanometers, must be made with high precision to fully understand the fundamental science of polymers and macromolecules. The dynamics must be characterized over a wide frequency range, using a singular testing system to couple the dynamics and structural information. In addition, the geometry of a sample, whether three-dimensional (bulk), two-dimensional (thin films), or one-dimensional (rods), has a significant effect on these properties. The interaction of surfaces and interfaces in pure and hybrid samples is not well characterized, either. The intimate relationship of these parameters will define the ultimate properties of a sample.

Expansion of current experimental techniques is needed in order to realize these goals. The limits of the equipment and the probes must be pushed to observe phenomena at varying length and time scales. If we cannot probe the physics of single polymer chains, chains at curved interfaces, or defects in chemical or physical structure, our fundamental understanding of the correlation of structure with property will be incomplete. In addition to pushing detection limits, work must be done on combining techniques to create real-time, high-throughput, *in situ*, non-destructive testing methods. Because of the uniqueness of polymer thermodynamics and kinetics, transient states are important in the characterization of subsequent properties. Only with these combined techniques will it be possible to truly understand both. We must work together with the national labs and MRSEC centers to achieve these goals.

If the desired characterization goals cannot be reached with current instrumentation, new experimental techniques should be designed through collaborative efforts with those in other fields as well as the instrument manufacturers and designers. There are opportunities to adapt current techniques, especially in the biosciences, for use by polymer scientists. Educating our students and faculty in the application of these techniques will build a foundation on which future generations can become experts in their use. Also, given the uniqueness of polymers and polymer science, we should begin work to develop characterization techniques of our own with an explicit focus on obtaining information that is specific to polymers and macromolecules.

Finally, here is a short synopsis of the main goals discussed in the previous sections:

1. Develop molecular probes that will allow determination of chemistry and chemical distribution (functionality) at different locations on polymers and macromolecules
2. Analyze the physical interactions of a single chain or particle directly and with precision to relate these interactions to microscopic conformations and macroscopic properties
3. Determine the structure and dynamics over several orders of magnitude with a minimal number of characterization techniques

4. Develop characterization techniques that will allow the detection of inhomogeneities, whether intended (hybrids) or unintended (defects), in a sample in order to relate their presence to macroscopic properties
5. Develop real-time, high throughput, non-destructive, *in situ*, multi-scale techniques and streamline current techniques
6. Provide standards (or at least expectations) for a broader range of properties including, but not limited to, electrical conductivity, thermal conductivity, biocompatibility, optical properties, and ion transport
7. Educate current researchers in “traditional” experimental techniques and expose them to non-traditional ones with the development of new instrumentation
8. Educate individuals in and begin collaboration between multidisciplinary fields of interest, such as biosciences and electrical, optical, and environmental technologies
9. Create and enhance outreach and education programs for K-12 students to encourage and prepare future generations of polymer scientists with a focus on minority groups
10. Increase the quality and quantity of polymer science research and technological development to compete on the global market and become a world leader in these areas

By addressing these targets over the next 10 years, we can meet our grand challenge of improving quality of life through the manufacturing of novel polymeric materials for use in multidisciplinary fields.

Section 6: Theory and Simulations

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6.1 Introduction

When very small groups of atoms are connected together contiguously in a chain-like fashion, long strings, called polymers, form. Although polymers have constituted the stuff of life since its inception, only during the past century we have begun to harness the benefits of polymeric materials that are made in laboratories and in Nature. Polymers represent the unmatched promise of a myriad of new materials endowed with hierarchies of functional properties. Hybrids of relatively simple synthetic polymers and natural polymers, with richly endowed physicochemical properties, open up an infinitely wide horizon for the exploration of new materials to meet increasing societal demands regarding the environment, energy, and security. Furthermore, polymers are the basic materials [Fig. 6.1] behind the functioning of the multitude of life processes, including even consciousness. Fundamental research on polymeric materials is among our most daunting scientific and engineering challenges, comparable in degree of difficulty to the exploration of space or the discovery of life-saving medicines.



Figure 6.1: Inspiration from life processes. (a) Elastic Cartilage in the external ear, showing the wrapping of elastic fibers around chondracites [41]. (b) Rubber-like proteins in embryos [42]. (c) A neuron [43].

The fundamental forces, such as electrostatic and dispersion forces, that produce the diverse structures and functional properties of polymeric materials also hold all small molecules

together, but polymeric complexity poses unique problems. Although scientists understand well, for example, how table salt is organized into crystals and how molecules such as hydrogen, methane, and ethylene are stabilized, the nature of order in polymerized systems still continues to elude even the most advanced theories and microscopes. The challenge arises from the need to understand the systems at multiple scales of length and time, where the fundamental forces are manifest in primary, secondary, tertiary, quaternary, and mesoscopic structures. In addition, a rich variety of functional properties, in terms of their electromagnetic, mechanical, flow, chemical-reactivity, and biocompatibility behaviors, in turn depend on how the polymeric materials are processed. In view of the multiple scales being coupled into hierarchies of structures in both space and time, promulgation of fundamental principles that govern the assembly of hierarchical structures is itself a grand challenge. The central goal of research in polymer theory and simulations is to meet this challenge by facilitating an understanding of the fundamental principles behind the structure-function relations for polymeric systems under different processing conditions.

Thanks to the great conceptual advances made during the past six decades, researchers in polymer theory and simulations are well-positioned to facilitate the discovery of new concepts and phenomena for hierarchical polymeric materials. The key to these theoretical and simulation efforts lies in providing conceptual and mechanistic explanations of existing phenomena and to making predictions that are verifiable by experiments. We can also use simulations to validate assumptions and approximations invoked in analytical theories. Sustained efforts on the part of theorists and simulators will provide design rules for synthesizing polymers with tunable properties, methods for assembling polymeric structures at multiple length scales, and processing protocols (strategies) to enable low-cost production of novel polymeric materials.

With the emergence of new initiatives in cyber-enabled science, we have before us a crucial and timely opportunity for furthering research in polymer theory and simulations. Researchers in polymer science will take advantage of many platforms that will become available through cyberinfrastructure (CI) activities, for data-mining, data-sharing, using advanced algorithms for computing, achieving standardization between industrial and academic codes, and for maintaining polymer datasets.

Significant advances in the synthesis, characterization, and processing areas are being made at an ever-increasing pace, mainly through empirical testing. Empirical progress needs grounding in theory, however, so there remains a critical need to invest in theoretical work. Unfortunately, such progress has been made too slowly to keep pace with the needs of the polymer science community, a mark of the relatively meager support for polymer theory and simulation that has characterized the past decade. It became abundantly clear during this workshop that experimentalists are seeking design rules and fundamental conceptual understanding in meeting the grand challenges ahead, by collaborating with polymer theorists and simulators. Polymer theorists and simulators are, in turn, well positioned to work with experimentalists in achieving advances that make it possible to facilitate the synthesis and production of hierarchical and functional materials with which to enhance human life and secure American competitiveness through scientific and technological innovation.

6.2 Grand Challenges:

The grand challenge for Theory and Simulations is to provide **guiding principles** and **cyberscience tools** for understanding and predicting the occurrence of hierarchical and

functional polymeric structures with which we can address societal needs in energy, environmental sustainability, security, and human health. This challenge encompasses (a) the formulation of design rules through which to produce tailor-made polymer materials, including those for use in hybridization between biological and synthetic systems and hierarchical composites; (b) coming to a fundamental understanding of electronic-ionic transport in systems ranging from polymer-based batteries to sophisticated electronic, energy harvesting or sensing devices to living cells; and (c) the formulation of criteria for efficient processing to enable low-cost production of strategically significant polymeric materials.

We have an excellent chance of meeting this grand challenge successfully during the coming decade. With the availability of very fast computers, novel algorithms, and cyberscience initiatives, buttressed by the tremendous success seen during recent decades in understanding model polymer systems, modeling is at the center of polymer research. The various modeling techniques, including *ab initio* computations at one extreme and numerical solutions of macroscale constitutive equations at the other extreme, should make it possible to formulate, e.g., the designs of novel hybrid polymeric architectures and various assembly processes in solutions and bulk. With considerable effort we have largely succeeded in coming to understand the glass transition, crystallization, block-copolymer morphologies, polyelectrolytes, flow behaviors, and other important issues pertaining to both synthetic and natural polymers. As a result of this progress we are building an even stronger research platform that provides a basis for interdisciplinary research involving biology, nanoscience, materials science, and energy-generating devices. We are now able, on the basis of the fundamental theoretical concepts that have been cultivated in the past to understand complex polymers and the validation of such concepts by experimentation, use polymer theory to lay the foundation for systematically understanding how to custom manufacture polymeric systems. It will be through polymer theory that we learn about their ionic-, electronic-, and photonic-functions and the optimum processing conditions under which to achieve large-scale industrial production.

Such major advances in theory and simulation will, however, require (a) the promulgation of fundamental principles, by using statistical mechanics methodologies, in the contexts of assembly, phase behavior, transport, friction, adhesion, ionics, and electronics; (b) the development of quantum methods for polymers; (c) the development of new algorithms for multiscale modeling to cover classical phenomena over multiple length and time scales, (d) large-scale massive simulations; (e) tandem interaction with all experimental efforts; and (f) the networking of experimental and modeling data with the use of cyber-based tools. Modeling and theory will continue to play an integral part in polymer research at all levels of inquiry that include, for instance, polymer synthesis, biological-synthetic hybrids, physical assembly in solutions, membrane-polymer composites, nanocomposites, crystallization, glasses, gels, fuel cells, electronic sheets, and solar cells. In particular, characterization of the new materials that will be synthesized in polar media will be significantly aided by theory and modeling. The current success of the implementation of polymer theory in designing novel polymer architectures is expected to grow enormously in the newly emerging areas of research presented by the polymer community.

6.3 Specific Challenges

6.31 Electrically charged polymeric systems

Electrically charged polymeric systems pose an immense challenge to scientists seeking a fundamental understanding of their structure, dynamics, kinetics, and transport. The main difficulty lies in the inherent inhomogeneity of the dielectric function of the system. We have never captured the details pertaining to local electrical potential gradients that are involved when hydrophobic and hydrophilic domains are present in polar solvents. The theoretical elucidation of the structure of water and other polar solvents in the presence of charge-bearing macromolecules remains to be achieved. Furthermore, the spatial ranges of correlations for electrostatics and chain conformations are delicately matched, depending on the nature and extent of added simple electrolytes, which in turn are significantly modified by the hydrophobic components of the polymer molecules. There is ample experimental evidence for several nonuniversal roles played by the specificity of small ions that must be present along with the charged macromolecules to maintain the electroneutrality of the systems, but we have not yet explained them. Even the most fundamental determination of the net charge of an isolated polyelectrolyte molecule in an infinitely dilute salty solution has proved too elusive to be captured in quantitative measurements or to be modeled, due to the dielectric heterogeneity. It should also be recalled that biopolymers are heteropolymers with electrically charged monomers, and therefore understanding simple polyelectrolytes is a first step to be made in a systematic approach to the theoretical modeling of biological macromolecules. Still, a fundamental understanding of electrically charged polymers is crucial in many areas that are vital to meeting societal demands on energy, the environment, human health, and security.

A judicious control of electrostatic, hydrophobic, and hydrogen-bonding forces will make possible the fabrication of functional objects of controlled complexity. In fact, the realm of Life and biological macromolecules is separated by a wide chasm from the realm of synthetic polymer materials, so building a fundamental theory of polyelectrolytes will enable us to discover novel smart polymers and progress towards understanding living systems. Among the important specific challenges we must eventually surmount are learning how similarly charged and oppositely charged macromolecules interact with each other (accounting explicitly for solvent molecules and counterions), understanding coupling between the electrostatic and chain-connectivity correlations, revealing the roles of coupled electrostatic-hydrophobic forces in the kinetics and thermodynamics of self-assembled hierarchical structures, manipulating single molecules, understanding the mobility of large charged macromolecules in crowded environments, and mastering ion transport in polyelectrolytic gels and solids. Even without the additional complexity arising from the electrical charges on polymer assemblies and their behaviors, there are many significant specific challenges addressed below that must be overcome by the polymer community.

6.32 Nonequilibrium Properties and Processing

The unique properties of polymer-based materials derive in an essential way from their underlying nanoscale and mesoscale structures. Predicting the equilibrium structures of such materials is an important contribution to theory and simulation, and much progress has been made in this respect. Typically, however, polymeric materials as prepared do not reach their

equilibrium structure. For some applications, in which only the length-scale and general connectivity of the microstructure is essential (such as in membranes for fuel cells or substrates for battery electrolytes), this is not a critical limitation.

In other applications, however, such as nanopatterning templates for electronic device applications, perfection of the self-assembled structure is a key property to be provided [Fig.6.2]. It is therefore important to understand and observe the kinetic routes by which materials self-assemble, how defects emerge and evolve, and how external fields may be used to direct self-assembly towards the desired perfection. These fields may take many forms, depending on the application: We may use electric or magnetic fields, temperature or concentration gradients, physical deformation or flow, or a patterned substrate to encourage the formation of a desired self-assembled structure. Where competing metastable structures exist, it may be possible to kinetically trap highly ordered structures that are not the true equilibrium.

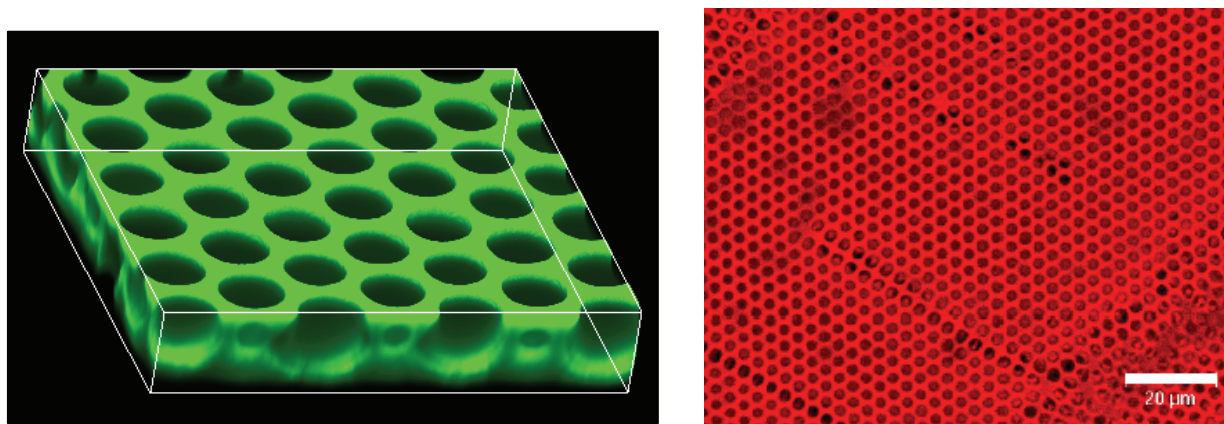


Figure 6.2: Left, 3-D image [44] of Poly(9,9-dioctylfluorene-co-benzothiadiazole) [F8BT] from CS₂. Right, emergence of defects at greater length scales [45].

In considering the theoretical challenges, it is important to recognize that, when we concern ourselves with nonequilibrium processes, the strong simplifying constraints of thermodynamic equilibrium are released, and no analogous unifying path to predicting behavior is available as a replacement. Progress therefore depends on recognizing the essential physics in dynamical processes of interest on a case-by-case basis. There are, of course, some patterns that emerge from previous work in this area, namely, that of the key role that is played by the dynamics of order parameters and defects. These phenomena may indeed be studied using a number of approaches in combination, including microscopic and coarse-grained simulations, as well as analytical theory.

Much progress in this area has been made on the general test bed of mesophases in diblock copolymers, though much remains to be done. As more exotic polymer-based nanostructured materials are developed to address materials challenges, we must sustain the continuing interplay between theory and modeling efforts and experimental characterization if we are to move forward in understanding how to achieve the desired structure in these materials that is inherent in the molecular design.

As the structures achieved by self-assembled polymeric materials depend on a proper appreciation of nonequilibrium phenomena, so too do the final functional properties of such materials in many applications depend on nonequilibrium properties. In essentially all

applications of polymeric materials, we are interested in more than the static structure.

Even for structural materials, the mechanical properties at finite deformation up to failure are key attributes. Progress has been made in achieving a mechanistic understanding of what makes polymeric materials special with regard to their deformation and failure properties in the area of glassy amorphous polymers, but much remains to be done even in the area of semicrystalline polymers. These materials are in some important ways analogous to nanocomposites of amorphous polymers, the crystalline lamellae playing a role similar to that of the nanofillers. A mechanistic understanding of the nonlinear mechanical behavior of such materials is needed to help optimize the design of a new generation of high-performance structural materials. With the combination of anticipated increases in computing resources and a strong emphasis on solving multiscale problems, this area may be ripe for theoretical progress in the next decade.

For many applications of polymeric materials, nonequilibrium phenomena, in the sense of transport properties, are key attributes. Of particular interest is electron, ion, or solute transport in conducting, charged, or polar polymers in various device applications. Addressing such transport properties represents a significant multiscale challenge because of the interplay between local Coulomb or polar interactions, larger-scale polymer configurations, and nanoscale structure. These problems require proper inclusion of chemical specificity at the local level, as well as coarse-graining—the classic signature of a challenging multiscale problem. To treat these problems, we must develop simulation methods through which we can work with inhomogeneous charged polymer systems, as well as in some cases with rare-event-driven scenarios involving the hopping of diffusants from one local free-energy minimum to another. Evidently solving these problems will require significant algorithm development as well as the use of large-scale computing resources. These are thus at the same time key obstacles that must be overcome to fulfill the promise of theoretical guidance for designing functional polymeric materials, but they are also rich and rewarding intellectual challenges. Scientists face the same challenges in other theoretical fields as well, and progress in polymer physics will guarantee similar progress in other areas of soft-matter physics.

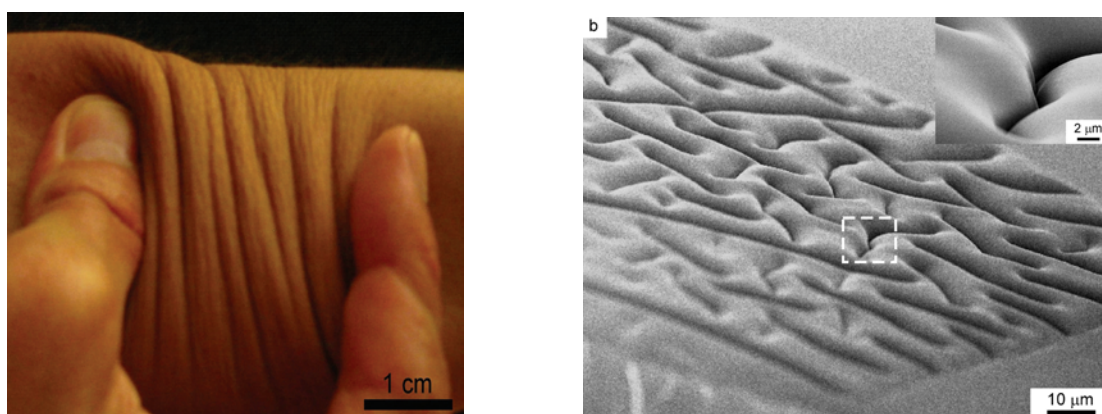


Figure 6.3: (a) Wrinkles formed upon compression of human skin [46]. (b) SEM micrographs of SiOx/PDMS surface wrinkles stabilized with a crosslinked poly(n-butyl acrylate) interpenetrating network [47].

Some examples of challenging topics that require additional fundamental understanding include (i) mechanical stability and fracture in solid polymers, (ii) polymeric glasses, (iii) mechanistic understanding of different polymer reactions under processing conditions, (iv)

structure and assembly kinetics in hybrid polymer/inorganic (such as nanoparticle) systems, and (v) control of structure in multicomponent systems under the influence of flow and surface forces. The industrially relevant area of adhesion of polymers at interfaces poses significant challenges for a fundamental understanding, due to nonequilibrium behaviors [Fig.6.3].

6.33 Self-assembly of hybrid and hierarchical structures as functional objects

There is a tremendous drive arising in the polymer synthesis community to synthesize versatile tailor-made supramolecular structures with precise compositional and structural control over primary, secondary, tertiary, and quaternary building blocks, and with capabilities pertaining to unconventional physicochemical properties at hierarchical length scales ranging from nanoscale to macroscale dimensions. It is a challenge to assemble particle systems with multiple functionalities that allow for sensing, targeting, delivery, and imaging. With a diverse set of building blocks the possible configurations and their functional properties constitute a vast parameter space. The exploration of this parameter space by permutations and combinations will consume considerable time and resources, as such a large parameter space cannot be practically explored experimentally. Advanced modeling will enable this work to converge on the most important parts of the parameter space. It is of utmost importance to develop theoretical methods that will allow the formulation of design rules for the fabrication of supramolecular structures. Such design rules will be needed to cover a combination of chemical synthesis and physical forces to assemble different moieties. The design of supramolecular structures depends on synergistic cooperativity among ionic, hydrophobic, and hydrogen-bonding forces, in addition to externally imposed electromagnetic and flow fields [Fig.6.4]. It is often observed that synthetic polymers with ions and dipoles have the tendency to indiscriminately aggregate and spoil the generation of the desired complex assembly. Again, the free-energy landscape is likely to be frustrated by local free-energy minima separated by huge barriers. It is necessary to devise strategies to navigate the time evolution of the self-assembling structures in their nonequilibrium states by providing external forces at opportune times. Theoretical advances should provide criteria for what is maximally possible by deriving boundaries for packaging different components together. We must learn how to organize gradient structures and partition polymer components into different functional domains and how to synthesize hierarchies with unconventional properties at different length and time scales.

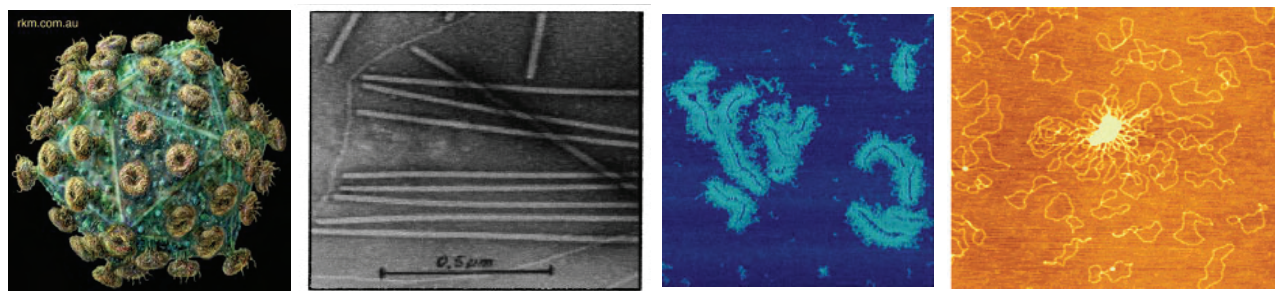


Figure 6.4: (a, b) Spontaneously assembled virus particles from proteins and DNA/RNA [48, 49]; (c) Interacting cationic bottle brushes [50a]; and (d) their complexes with DNA [50b].

Many organisms such as diatoms shape inorganic materials into complex structures with the templating abilities of polymers [Fig.6.5]. These complex structures are self-assembled with precise control over size, shape, and hierarchical organization. Understanding how polymers

template the growth of the complex systems is new territory into which we must venture without any molecular understanding. Key theoretical questions include: How do the polymer sequences, in terms of charged and uncharged monomers, control the nucleation barriers and further growth of inorganic crystals? How do the polymers adsorb at the various crystallographic planes of the inorganic crystallites? How can novel block copolymer architectures direct the growth of minerals? By mimicking the biominerals, we can create opportunities to discover many advanced organic-inorganic hybrid materials for many technological developments.

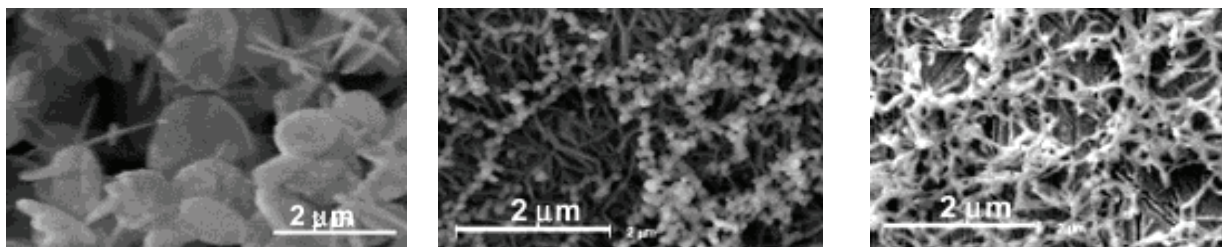


Figure 6.5: Scanning electron micrographs of polycation-mediated biosilicification [51].

We have seen excellent success in using diblock copolymers in forming well organized microstructures and highly controllable micelles. In addition, the ordering of block copolymers under confinement yields a panoply of morphologies that can be used as devices and nanoreactors [Fig.6.6]. The diversity of morphologies becomes much enhanced when even only one more new block is introduced to ABC copolymers. There is growing interest in synthesizing

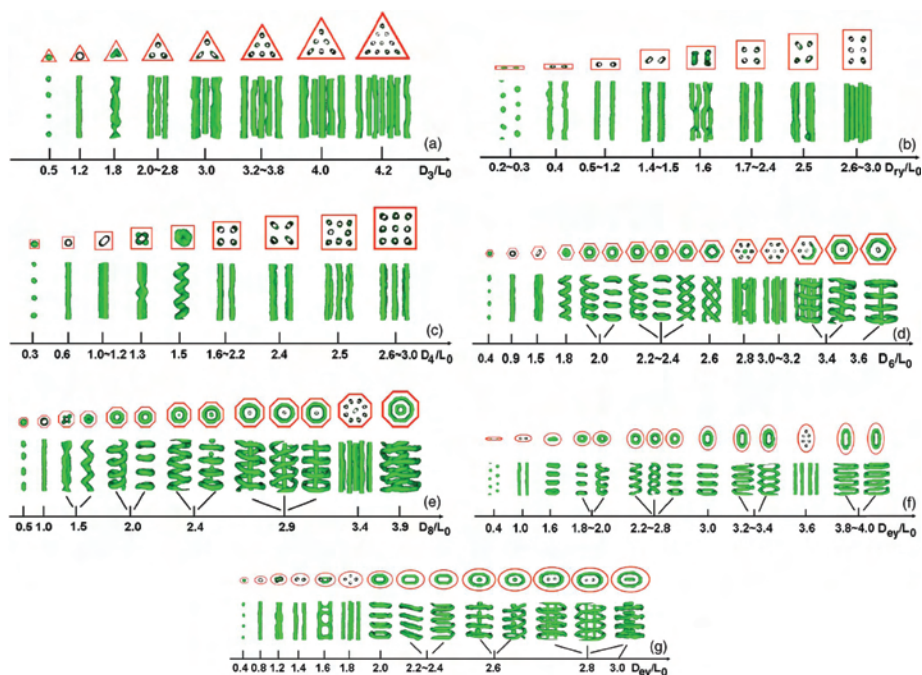


Figure 6.6: Morphologies of diblock copolymers under confinement in channels of different cross-sections [52].

block copolymers of four and higher components. The key question is, what kind of building blocks are needed to assemble a desired morphology and in what order do these blocks need to

be tethered together? Theoretical calculations, which have achieved considerable success in the arena of diblock copolymers, are needed in the formation of self-assembled structures from multicomponent multiblock copolymers. The kinetics of assembly of such structures is likely to suffer even more from nonequilibrium features and defects that are present even in the diblock systems. How do these morphologies respond to external stimuli such as exposure to small molecules and electromagnetic fields, or flow fields?

Once hybrid materials are made, we have a very significant opportunity to enhance their performance by dispersing other components such as nanoparticles, metal clusters and metal atoms, and other polymers. Interactions between polymers and specific additives are not yet sufficiently understood to guide the design and synthesis of desired new hybrid materials. It is not clear how polymers stabilize nanoparticles. We see a need to derive the mixing rules for the additives and polymers and the behavior of the resultant materials. How do we template patterns on polymer matrices to strategically position the additives? Theoretical work is critically needed in supporting the development of methods with which to control dispersions in these multicomponent systems precisely and to facilitate development of new materials with controllable transport and electromagnetic properties.

Additionally, we note substantial progress in synthesizing a variety of polymer gels that exhibit unique responsive behaviors under stimuli. The phenomenology of polyelectrolyte gels and related hydrogels exhibits amazing responsive properties under the influences of electromagnetic fields, flow fields, pH gradients, and tunable hydrophobicity/hydrophilicity variations. There is challenging theoretical work to be done with respect to these complex systems with a hierarchy of normal modes where certain intermediate degrees of freedom are quenched due to crosslinking. Yet, computational and theoretical research is necessary in view of the major role these systems play in biomedical applications.

6.34 Photonic/electronic/ionic materials

Inventing efficient new devices to harness energy from the Sun and new generations of batteries and fuel cells requires the control of photonic, electronic, and ionic properties of materials in dielectric media. We must develop a better theoretical understanding of mechanisms of electron, hydrogen, and oxygen transport and the optical properties of polymeric materials in order to make further progress in this area. The energy levels of electronic states of conjugated polymers provide the conduit for the transport of electrons in various electronic and photovoltaic polymer materials. We must undertake theoretical and computational research with the aim of predicting the electronic spectra and mobilities of electrons, holes, and excitons in polymeric materials. This is critically needed for facilitating precision design of electro-optic materials with enhanced stability of n-doped states, enhanced electronic mobility, and tailored electronic spectra. Accurate quantum calculations combining the electronic and vibrational states of repeat groups and the conformations of polymers are necessary in order to meet this vital challenge. These calculations should be geared towards resolving the key issue of improving the efficiency of polymeric photovoltaic cells. Furthermore, in realistic experimental systems, elaborate processing protocols are used in fabricating plastic photovoltaic devices. The optoelectronic properties of the morphologies that result from processing need to be computed. One of the theoretical challenges here is to understand how a mobile exciton is disrupted at an interface with an electron-withdrawing domain. The influence of microscopically imposed morphologies, as in copolymers with n-type and p-type blocks, and hybrid composites of polymeric and inorganic

matrices, on the optoelectronic properties is an additional theoretical challenge. Furthermore, calculations are necessary to quantify the robustness of the optoelectronic properties when subjected to various environmental pressures in order to enhance the commercial utility of polymeric photovoltaic cells. Finally, photonic band gap materials can be assembled via physical self-assembling processes [Fig. 6.7], and computational effort is needed in determining the dependence of optical spectra in terms of the morphological details of the synthetically assembled materials.

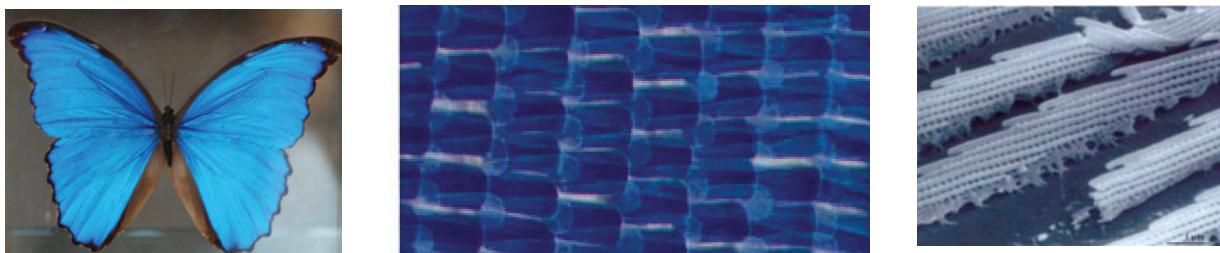


Figure 6.7: (a) Morpho butterfly [53]. (b) Wing scales of Morpho [54]. (c) Color is due to physical arrangements of lamellae and ridges (scale bar is 1 micron) [54].

Faced with the societal challenge of generating fuel cells that perform better than Nafion-based systems, we note a critical need in the area of designing [Fig.6.8] novel morphologies to be used in facilitating efficient transport of small ions and molecules. Theoretical modeling of the development of porous morphologies via micro- and macro-phase separations in heteropolymer assemblies and of the transport properties of ions through such morphologies needs to be performed, in collaboration with experimenters with expertise in synthesis and processing.

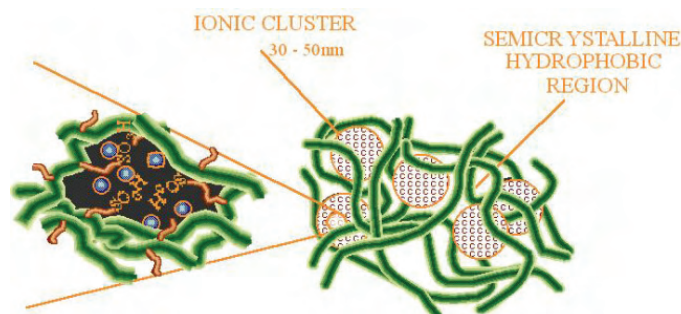


Figure 6.8: Sketch of a microphase-separated polar-nonpolar polymer [55]. Modeling of all aspects of structure, stability, and transport properties is key to designing efficient fuel cells.

Among the most serious global issues in the twenty-first century, one that affects both human health and national security, is that of sustaining a sufficient supply of pure water to a growing human population. While the formulation of new polymer-based ion-exchange columns for water purification will continue, the detection of toxic and hazardous macromolecular agents will become an increasingly significant challenge, due to growing concerns with security. A fundamental understanding of the transport properties of these agents and the mechanisms through which they interact with charged media is a critical step in ensuring the survivability of the planet.

6.35 Synthesis

Synthetic polymer chemistry is undergoing a revolution, creating a diverse host of new materials involving architectures, combination of synthetic and biological building blocks, and hybrids between organic and inorganic components. Work in this area would be greatly enhanced by a fundamental understanding of the behavior of the radicals and charged reactants in dielectric media that are becoming increasingly heterogeneous as reactions proceed. Furthermore, reactions are typically carried out under varying flow conditions, necessitating a fundamental understanding of reactants under nonequilibrium conditions. Accompanying the chemical process of polymerization, the physical consequences of phase separation and phase transformations, such as crystallization, often dictate the course of polymerizations. Except for the phenomenological kinetic equations used for polymerization, theoretical work in this area has been neglected. Reliable theoretical and computational work is needed in the quest for design rules that can be used in making customized polymer materials, combination of biological and synthetic systems, and hierarchical composites.

A tremendous effort is being invested in the synthesis community in the articulation of diverse architectures (such as multifunctional stars and bottle brushes); systematic variations on copolymer compositions in terms of gradients, blockiness, and randomized sequences; and in the creation of associating and self-healing polymeric gels. Such endeavors can be more easily facilitated by theoretical research, performed in collaboration with synthetic chemists, that encompasses atomistic details and macroscopic physical phenomena

Another focus of polymer synthesis is incorporation of unique monomers, such as ionic groups and dipolar groups, into polymer backbones at strategic locations. Reliable theoretical guidance is needed for the incorporation of polar monomers into polymer backbones. We must derive both the nature and the quantitative extent of this incorporation from theoretical modeling, in terms of their reactivity and the kinetics of polymerization. When these polar monomers are incorporated, the thermodynamic behaviors of their solutions are expected to be dramatically altered and it is necessary to derive the boundaries of thermodynamic stability against microphase separation, macrophase separation, and precipitation. What is the maximum tolerance level for growth when organic polymers as bioconjugates of biological polymers are controlled by thermodynamic considerations? Theorists and laboratory scientists should collaborate in exploring these issues. Theoretical work is also vital to the design of polymer-based therapeutics, in the context of responsive drug delivery, antimicrobial activity, and biocompatibility. What is the tolerance level for the incorporation of specific groups, needed for therapeutics, into the polymer backbone in terms of structure and function?

In light of environmental issues, serious efforts are also being mounted to perform polymer synthesis in nonvolatile and recyclable ionic liquids. Due to the diversity of possible cations and anions, there are, potentially, billions of multicomponent ionic liquids that could be used as solvents. Clearly, not all ionic liquids can be tested for polymerization processes. Computer modeling of polymerization in ionic liquids is a very fertile area of research that is needed to guide polymer synthesis in environmentally friendly media.

6.36 Crystalline and amorphous polymers

Computational efforts during the past decade have resulted in considerable progress in learning how polymer melts flow or become progressively frustrated upon cooling. The development of the reptation model of polymer dynamics in the melt state, along with its modifications, in combination with corroborative computer simulations, is clearly one of the greatest accomplishments in the field of polymer theory. Similarly, computer modeling of polymer glasses has revealed many insights into the ubiquity of this phenomenon that is prevalent in all complex systems [Fig.6.9]. There has also been considerable progress in our understanding of how the glass transition of polymers is influenced by confinement effects.

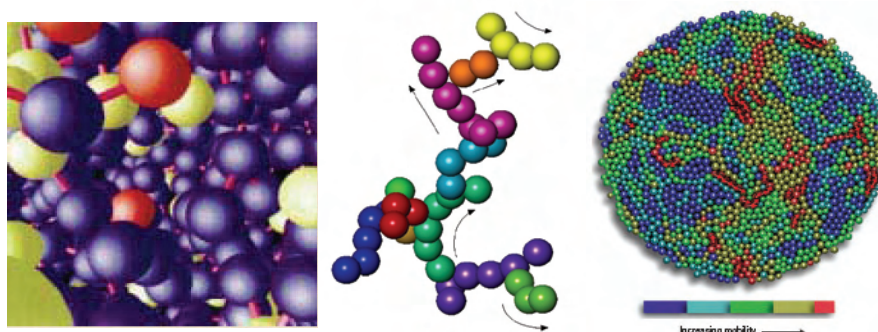


Figure 6.9: Local dynamics near the glass transition in polymers (left) share many features in common with molecular fluids (middle) and even granular materials (right), including dynamical heterogeneity and string-like correlated motion. Left: Computer simulation of a polymer melt approaching the glass transition [56, 57]. (Reprinted by permission from Macmillan Publishers Ltd: NATURE, Ref 56, copyright 1999.) String-like motion indicated by red and yellow spheres. Middle: String-like motion within a simulated bidisperse fluid [58, 59]. Right: Experimental data from an air-driven bidisperse system of steel spheres near the jamming transition [60]. (Reprinted by permission from Macmillan Publishers Ltd: NATURE Physics, Ref 60, copyright 2007.) Highly mobile spheres in red exhibit string-like motion.

However, many challenging questions still need to be understood in the context of technologically important viscoelasticity and the glassy behavior of polymers. While atomistic details control the local dynamics that are manifest in the glassy behavior, conformational details control the global dynamics in terms of the viscoelasticity. A fundamental understanding of how multiple length and time scales get coupled, and how the flow properties depend on the chemical details of monomers and the polymer architectures, is necessary for devising economically viable methods in the industrial production of commodity polymers. Theoretical understanding of the relations between the chemical structure and mechanical properties of (multicomponent) amorphous polymers is one of the challenges that further work should address, also taking the nonequilibrium processing conditions of these materials into account. Access to cyberscience tools provides an excellent opportunity to make significant progress in this important area.

The field of polymer crystallization is witnessing a renaissance, due primarily to the availability of modern experimental tools such as time-resolved synchrotron radiation and fine imaging techniques, as well as to significant efforts in computer modeling. Challenges remain, however, in learning how different growth sectors of lamellae form and grow in terms of the chemical details of the polymer chains [Fig.6.10]. We do not yet understand the molecular mechanisms of crystallization and melting, nor how these are altered by the branched

architectures of polymer chains. An additional theoretical challenge lies in understanding how flow fields, which are relevant to the industrial processing of commodity polymers, influence polymer crystallization. A concerted effort in multiscale modeling and reptation-like molecular theories needs to be mounted, in collaboration with experimenters.

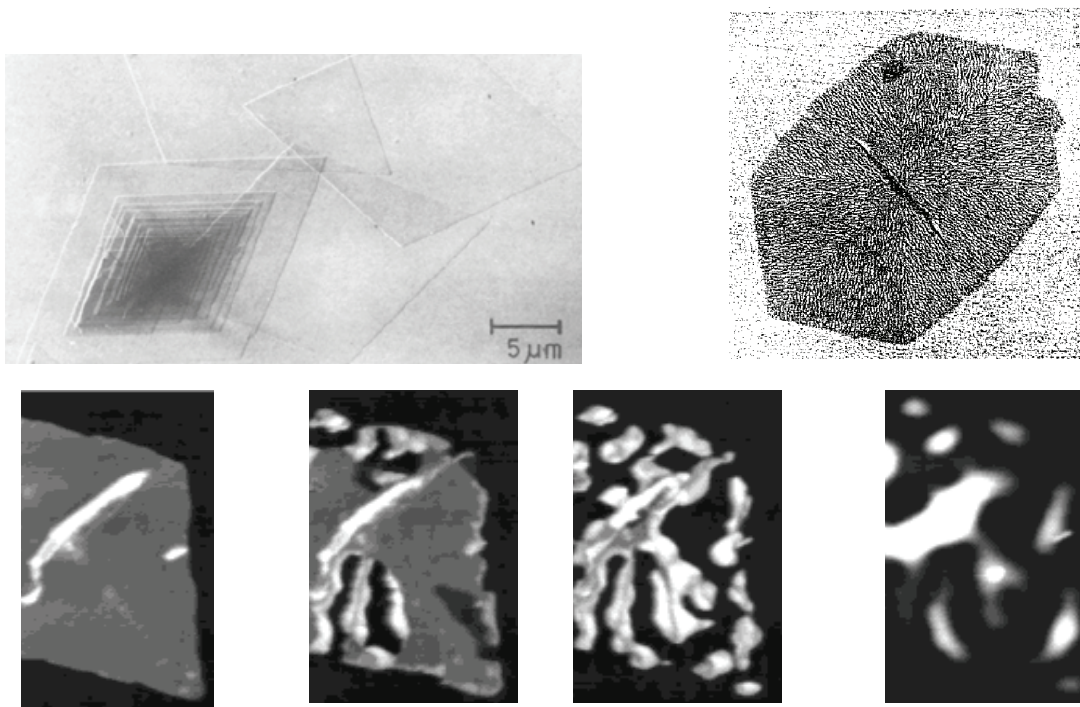


Figure 6.10: Top row: Electron micrographs of single lamellae and growth sectors [61]. Bottom row: AFM images of a lamella during melting [62].

6.4 Cyberinfrastructure

Computer simulations have contributed enormously to our understanding of polymer properties and processes. Parallel computer architectures, commodity cluster computing, and steadily increasing clock speeds have made possible simulations of polymer problems that were, for the most part, intractable just a decade ago. Examples of these successes include the prediction of the self-assembled equilibrium structures of polymer-nanoparticle composites; the dynamics of ultrathin, confined, and filled polymer films; and polymer crystallization. The era of petaflop computing is rapidly approaching, and this will bring with it the ability to simulate polymer materials at speeds that are more than 1000 times faster than is possible today. This increased power will allow for the faster prediction of, e.g., more complex polymer-based microstructures; the study of the kinetics of glassy systems and rare-event kinetics; and the design of complex, biomimetic, charged polymer architectures.

Petaflop computers are, it must be acknowledged, based on radically different architectures from those that typically run the applications we use today. Massively multicore chips (such as the 80-core Intel chip announced in early 2007) cannot be programmed efficiently using the now-standard Message Passing Interface (MPI) that is used for most parallel simulation codes. Instead, new parallelization paradigms will be needed in order to program these multicore chips. The same is true for graphical processing units, or GPUs, which drive the ultrafast computer

graphics on today's Xbox and Sony Playstation. These chips are ideal for linear algebra problems and molecular dynamics (MD) and, for simulating the MD of simple fluids, speed-ups of nearly 100 orders of magnitude have been reported. To date, however, the use of GPUs is rare within the scientific community, and there are no publicly-available polymer simulation codes for GPUs.

Terascale and petascale computers capable of simulating large polymer systems also make possible the generation of petabytes of useful data that may be mined for many applications. Yet the polymer community has made little use of mining tools that are presently used much more extensively in the genomics and proteomics communities. Community databases and digital libraries of federated datasets generated both by simulation and by experiment, along with mining and metadata-based smart-search cybertools, would make possible entirely new modes of research on polymer problems. Ultra-large datasets also require fast, flexible visualization tools capable of displaying real-time dynamics. Today's polymer visualization tools are insufficient to meet the demands of tomorrow's large simulations and datasets.

6.5 Perceived Barriers and Opportunities

The biggest barrier to continued progress in polymer theory is the need for algorithms to be used in multiscale modeling. Theorists must be able to build models in size scales that range across eleven orders of magnitude in size and time to explore nano- to meso- to macro-collective behavior. It is necessary to develop quantum mechanics packages for conformationally disordered systems, and force fields for systems undergoing dynamics. A quantitative description of the dielectric properties of highly inhomogeneous media such as polymeric materials will continue to pose a huge theoretical challenge. In addition, there is a critical need for efficient parallelization algorithms and memory distribution resources, which will perhaps be partially relieved by new cyber-based initiatives if the polymer simulation community seizes on these opportunities. The Division of Materials Research should partner with the Office of Cyberinfrastructure and CDI (Cyber-enabled Discovery and Innovation) to increase funding in this area. In addition, experimental data on model polymeric systems, to be used in validating theoretical models and algorithms, are scarcely available and efforts should be made to secure an adequate experimentally based database.

The advent of teraflop and petaflop computing will make possible the CPU-stressing computation of quantum effects in polymers for various conformations and for the simulation of rare events associated with energy landscapes and barrier crossing, in addition to the calculation of equations of state for condensed polymers with well defined molecular architectures.

We note also an increased need to bridge the gap between academic and commercial coding, and it is crucial in this connection to construct cyber infrastructure for flexible and shared software and algorithms. The time is ripe for creating and sustaining, over the long term, digital libraries that will function as repositories of data and codes to facilitate simulations. Such repositories must be created in response to the complexity of the challenging problems that remain to be addressed by theorists and experimentalists. In addition, digital libraries can act as repositories of data sets for polymer microstructures, thermodynamic data, phase diagrams, and rheological properties. Overcoming these barriers requires sustained and long-term support for force-field development, acceleration algorithms, model development, multiscale strategies, and new tools. Digital libraries, public domain tools, and codes must be supported both in their initial development phase as well as in subsequent phases of distribution and long-term maintenance.

6.6 Education

Simulations of polymers provide a unique opportunity to impart knowledge of polymers to undergraduate students and high school teachers. Since the student populations in high schools and undergraduate programs are increasingly familiar with computers, it should easily be feasible to expand their exposure to and generate greater excitement about the field of polymer modeling/simulation. Moreover, anecdotal evidence from faculty in polymer research clearly indicates that nurturing undergraduates with research opportunities in polymers is perhaps the best vehicle with which to attract talented students into the field. In order to facilitate such efforts, it is imperative to develop undergraduate courses that cover simulations of polymeric systems, in addition to introductory polymer theory courses. New cybertools such as wikis and blogs, which are well known to today's youth, can supplement traditional modes of teaching and provide novel opportunities for student engagement and peer-to-peer learning.

6.7 Recommendations

1. Develop a fundamental understanding of electrically charged polymeric systems by addressing dielectric inhomogeneity, electrostatics, hydrophobicity, hydrogen-bonding, and the structure of water in crowded environments
2. Develop an understanding of electronic-ionic transport in systems from polymer-based electronic devices to living cells
3. Develop a fundamental understanding of structure-function relations under nonequilibrium processing conditions
4. Develop methods that facilitate quantum mechanical computation for conformationally disordered systems
5. Establish an environment in which theory and simulations are performed in synergistic collaboration with research in synthesis, characterization, and processing
6. Force fields and algorithms need to be developed further, documented, and professionally maintained to enable simultaneous modeling of multiple scales from monomers to polymer structure and processing
7. Construct cyberinfrastructure for sharing modeling modules and simulation codes across the broader polymer community, and for creating smart, searchable, metadata-based digital libraries of extensive data on polymer systems
8. Develop codes for "grand-challenge" polymer-based applications for next-generation petaflop computers
9. Develop undergraduate courses in computational polymer science

Section 7: Responding to International Competition through Education and Outreach

The polymer industry is changing rapidly, marked by significant progress in the creation of specially tailored functional polymers that are needed for specific high-technology applications. This highly lucrative and rapidly growing value-added polymers business is extremely competitive globally. We *must* both *participate* in it and maintain a *leadership position*. A most effective way to respond to competition is to *train the next generation of global leaders in the frontiers of international polymer science*. It is this group of new science and engineering leaders who will accomplish the goals of the grand challenges laid out in this report by developing the new science and engineering breakthroughs we envision and, just as importantly, by continuing the leadership needed to maintain our competitive edge in the international marketplace of ideas.

We must therefore train a diverse set of the brightest students to be innovative, with skills valued by both academia and industry. This section of the report focuses on areas in which the educational mission of polymer science and engineering can be improved or enhanced. Here we discuss several important aspects of education in polymer science, including:

- Team-based research activities for graduate students
- Greater opportunities for international exchange
- An updated graduate and undergraduate curriculum
- Improved education in soft-knowledge-based activities such as entrepreneurship
- Increased use of computers as tools in education
- Grounding in the biological sciences
- Greater efforts to provide lifelong learning in polymer science
- Enhanced outreach that takes advantage of the ubiquity of polymers in our daily lives

7.1 Team-Based Research: Academia and Industry in Partnership

Increasingly, research in polymer science and engineering is not an individual effort but a collective effort requiring multiple skillsets to accomplish research goals. Industry and government laboratories commonly work in multidisciplinary teams, often led by scientists or engineers from diverse technical backgrounds. For example, advanced polymer research often involves chemists carrying out synthesis working with physicists who might be focused on specific materials characteristics or theorists who provide computational models and simulations. [63] Increasingly, biological applications require teams that incorporate skills in biomedical areas. Yet these collaborative skills are not always developed during an undergraduate or graduate education and they are certainly never taught in an organized way.

Team skills have been repeatedly shown in studies and emphasized by industrial researchers to be key elements in a successful career in advanced science and engineering. [64] As the contributions of polymer science and engineering to other disciplines expand, it will be critical for researchers of all backgrounds to be conversant in the language of and undertake collaborative activities with other disciplines. [65] Although it is not reasonable to expect researchers to master all topics, students should be trained to master specific skills and have sufficient breadth of knowledge to contribute to multidisciplinary research teams. In order to achieve this goal, and to meet the proposed grand challenges, there is a need for scientists and engineers to work together. To bring this about, funding agencies should foster the formation of

research teams that involve diverse polymer-related skills including computational modeling, synthesis, characterization, and processing. Interagency and interdivisional research activities that support interdisciplinary teams or centers should be strongly encouraged.

Partnerships and collaborative efforts with industry (ranging from established companies to startups) are also invaluable in providing researchers with needed skills to improve productivity and to increase the quality of research. [66] As industry changes its research strategy, we have observed a shift from higher-risk, long-term research to start-up companies and university collaborations. The collaboration of university and industry researchers is generally accepted as an important aspect of the US innovation system and many university researchers have had positive experiences with industrial research collaborations. We feel that opportunities for students to collaborate with industry (perhaps in the form of internships) should be encouraged, in part because many of the great industrial laboratories (e.g., Bell Laboratories) no longer provide the same opportunities for student collaboration they once did and also because this aspect of student education is not as readily available as it once was. These partnerships may also serve to compress the time to commercialization for polymer-based products.

7.2 Enhancing International Research Opportunities

We believe we must expose our students to international settings and research environments at the undergraduate, graduate, and postdoctoral levels. Such associations and collaborations greatly facilitate awareness and global exchange of fast-breaking developments in the field. [66] Given the nature of global competition, team-based collaboration will inevitably involve teams with international members. One of the great challenges of intellectual leadership is in staying in touch with developments around the globe. Multidisciplinary, international collaborations permit researchers to stay connected to new developments in areas in which the US research community might not be at the leading edge. Collaboration also facilitates rapid internalization of research breakthroughs. [67]

The education of our graduate students must be extended beyond classroom and local industry exposure—it must be augmented by a critical assimilation of global perspectives. It will be necessary that our graduates be prepared in essential languages, e.g., Chinese, Japanese, German, Spanish, etc., and be exposed to the cultural nuances of other parts of the world. Ideally, opportunities should be provided to students that would allow them to conduct part of their research activities elsewhere in the world in order to immerse them in non-US cultural and educational environments—experiences that are so critical to the development of a well rounded workforce.

While we are aware that several proposal-based programs exist (especially at the NSF) that primarily fund members of existing research groups (mostly graduate and postdoctoral students), we would like to see flexible student-driven fellowship/scholarship programs that allow individuals to pursue and participate in international internships and undergraduate research projects. Attracting and exposing the best students in the world to our culture and educational system is important for scientific, societal, and political reasons and the application of students to the US system is being hampered by a variety of rules and regulations. There is little doubt that this post-9/11 effect has reduced the number of outstanding international students coming to the US. [65] We encourage the pursuit of strategies that might lower these barriers. For example, by enhancing collaborative programs, especially those that bring students to the US, we can work to correct this negative impression, expose these students to our culture, and provide the type of technological exchange that benefits both sides. Expanding program offerings beyond those that

are available at the NSF Office of International Science and Engineering would go far in helping us to accomplish these goals.

7.3 Enhancing Polymer Education at Universities

The foundations for teaching polymer science and engineering were laid down by Flory in his book *Principles of Polymer Chemistry*. This has been followed by more recent books and curricula that focus on polymer physics and polymer engineering. However, much of the polymer curriculum was laid out on the old assumption that the polymer industry was going to be based in large chemical companies making vast quantities of a few high-performance polymers. With the shift within the industry to the production of small amounts of high-value-added polymers with specifically targeted property sets, the increasing off-shoring of high-volume polymer manufacturing, and tremendous growth in the biological and biomedical sciences that focus on polymers, there exists an opportunity to rethink the skills needed by students in polymer science and engineering.

- i) *Updated Curriculum and New Textbooks*: The past decade has brought with it an explosion of new synthetic methods that greatly enhance our ability to synthesize polymers with well controlled architecture. New methods of polymer characterization, particularly methods and tools that are based in large national facilities such as synchrotron X-ray sources, are making it possible to understand polymer structure, especially in self-organizing materials. New computational tools coupled with improved theories provide greater insight into the molecular mechanisms governing polymer behavior. Much of this new information has yet to find its way into the classroom. Greater effort to update the polymer curriculum at the graduate and undergraduate level needs therefore to be undertaken, especially in light of these cross-disciplinary activities. New textbooks are needed to address these important topics. Input from industrial scientists on the needs of this new curriculum would enable greater adaptability in changing job markets.
- ii) *Greater incorporation of computational methods in the curriculum*: The power of computation to predict and understand polymer behavior is at a critical juncture. It is poised to move from “experts-only” usage to more general use by the trained practitioner. This should considerably raise demand for new courses that prepare students for this change. In addition, more can be done to take advantage of the special attributes that computational teaching strategies enable. For example, we recommend the construction of cyberscience infrastructure and tools for sharing modeling modules across the broader polymer community. We also note a need for creating digital libraries of extensive data on polymer systems.
- iii) *Grounding in the life sciences*: Polymers are increasingly being used as tools that can be applied to biological and biomedical problems. With the convergence of the physical and biological sciences and with the central role of polymers in both, polymer scientists will need an educational grounding—in the classroom, through cross-disciplinary research programs, and appropriate internships—that spans the broad biological-physical interface. The polymer scientist of the future will need not only to be conversant in biological terms, but also to understand at a fundamental level the role that polymers can play in the life sciences. Enhanced curricula that

- include both synthetic and natural polymers as well as biology courses tailored to the needs of polymer scientists are encouraged.
- iv) *Combined degree programs for entrepreneurial careers:* We recognize that the science community needs to provide (in a deliberate fashion) intellectual knowledge and applied skills as well as “soft” abilities. Students should be able to communicate, lead, and participate effectively in *diverse* teams. This requires having the necessary skills in presentation, the selling of ideas through persuasive discourse, and language skills with which to communicate effectively in a global marketplace. Strong science or engineering training, culminating with a Ph.D., might be coupled with an M.B.A. or J.D. degree, which would be necessary for those wishing to pursue the entrepreneurial venture of a start-up company. For example, new programs that provide technical backgrounds in polymer science and a business focus on sustainable enterprise would provide students with invaluable skills in the start-up community. These start-up companies will be the lifeblood of the movement to develop new materials in the twenty-first century.
 - v) *Educational connections to industry:* Throughout a student’s educational career, it will be necessary to make available support mechanisms and educational opportunities to simultaneously fund and educate students for participating in the industrial way of life. The creation of industrial assistantships will fit that role as well as address the needs of the trade, particularly since the industrial enterprise is, in part, downsizing or retooling to meet new goals and directions. Such an assistantship program would go beyond a simple internship, providing an excellent opportunity to introduce students to industrial complexities; thus, when new job opportunities occur, students will already be trained to meet the industry’s needs because they will have taken courses with a business perspective in addition to courses in science and engineering. This training might engage students in innovation and entrepreneurship at an early stage, providing graduate students with the post-baccalaureate equivalent of an undergraduate work-study program. Additionally, the economic development of our communities will influence our graduates to stay in our local environments and expand the job base.
 - vi) *Developing opportunities for lifelong learning in polymer science and technology:* Given the dramatic and sometimes rapid changes that are occurring in the polymer industry, it will be important to identify methods for teaching new skills to mature scientists and engineers. This may involve developing new programs that enable technical staff to return to universities for short periods of a year or less. Such programs might be similar to an MBA in duration, but with a technical focus, involving the updating of technical skills with additional education in business and management. It may also be necessary to accommodate professionals in a university curriculum or craft new classes that provide just those skills needed by professionals.

7.4 Reaching out to students and educators

Polymer science and engineering touch virtually everyone’s life every day. Products with polymer-based components are ubiquitous. Thus, it is essential to expose K-16 students to a better understanding of polymers, to help them see that polymers are essential to our very existence. In fact, human bodies are made mostly of polymers (and a lot of water). Clothes, food,

and the majority of things around us are also derived from polymers. New polymers emit light, sense environmental changes, function as armor, and are extraordinarily strong. Students must be better educated early on about the importance of these indispensable materials through appropriate course content created specifically to meet this timely goal. Polymers are such easily grasped teaching concepts that we would like to see tools developed with which to incorporate polymers early in universal, core undergraduate curricula (e.g., basic polymer synthesis within an organic chemistry course, viscoelasticity within mechanics or transport phenomena courses, rubber elasticity and mixing theories in physical chemistry and statistical mechanics).

We suspect that our inability to attract as diverse a set of students to our field as there are in other fields such as biology may stem from our having not yet clearly articulated the inspiring questions of our field to demonstrate its immediate impact on society. We believe that this sort of immediate impact is inherent in our field, particularly as it relates to energy, the environment, sustainability, and biomedical and electronics applications. Furthermore, our own anecdotal evidence suggests that a new generation of bright students is looking for this level of interaction between their research efforts and society at large. We recommend creating new and enhancing existing outreach and education programs for K-12 students to encourage and prepare future generations of polymer scientists—with a special focus on minority groups

We also believe that expanding the diversity of the polymer science and engineering community hinges on early educational exposure to phenomena that generate excitement about science in general and polymer science in particular. We suspect that broader regulation of high school science education has made it more difficult for students to experience exciting (and perhaps dangerous) laboratory procedures. We therefore believe that outreach from our community, in the form of demonstrations and hands-on materials exploration, has the potential to attract a wide variety of students who do not currently choose our field. Because polymer science crosses all science and engineering disciplines, it should be introduced to all students as a core part of their education. Teaching modules that emphasize the importance of polymer science and engineering in an easily accessible manner should be encouraged.

7.5 Recommendations:

1. Encourage the development of new funding mechanisms through which scientists and engineers can work together more effectively in research teams involving computational modeling, synthesis, characterization, and processing
2. Encourage multidisciplinary teamwork to benefit research in general and students in particular
3. Encourage collaborations that provide graduate students with increased exposure to international and industrial experiences
4. Create a sound, multidisciplinary curriculum in polymer science and engineering
5. Evaluate polymer science and engineering curricula/courses in light of industrial and societal needs
6. Enhance cyberscience through initiatives that help scientists and engineers share modeling modules and create digital libraries of extensive data on polymer systems
7. Ground polymer science and engineering curricula in the biological sciences
8. Design new degree programs that are more in line with future career paths; consider implementing an MD/PhD or MBA-type science Ph.D. with industrial, legal, or political relevance and experience
9. Engage students in innovation and entrepreneurship at an early stage

10. Develop opportunities for lifelong learning of polymer science and engineering
11. Create and enhance outreach and education programs for K-12 students to encourage and prepare future generations of polymer scientists with a focus on increasing participation of women and underrepresented minorities
12. Introduce polymer science to all students as a core part of their science education

Section 8: Broadening Participation

8.1 Why Diversity?

The population of the United States is rapidly becoming more ethnically diverse. Traditionally underrepresented groups will likely become the majority within the next few decades. In order to maintain global competitiveness, it is imperative that the field of polymer science and engineering, and science and engineering in general, expose, mentor, support, and proactively recruit a diverse set of participants, particularly members of underrepresented minorities (URMs), to a degree that is at least reflective of the makeup of the larger society. Currently there is in this community a large pool of underutilized, untapped talent. If we do not include a diverse set of participants in the discipline, it will appear outdated and disconnected from the general public. A potentially large pool of students will be discouraged from participation and support, driving them to other disciplines, which will in turn lead science policymakers to decrease funding. Additionally, a considerable body of data shows that heterogeneous teams the members of which differ in culture, socioeconomic background, perspectives, etc., always outperform homogeneous teams in terms of innovation, creativity, and success. Several decades of increasing support for diversity have produced only modest advances. We need to adopt new approaches and programs.

In addition to considering the population of the United States, we must also be aware that international students, a traditional source of science and engineering talent, are becoming more likely to return to their home countries upon graduation since their countries are developing their own technological workforce opportunities. Therefore, building a diverse American workforce will decrease our reliance on international students and workers.

8.2 Strategies

In order to ensure that the United States remains a leader in the polymer science and engineering fields, it is essential to focus on recruiting and developing the American talent pool, particularly among URMs. This effort must include a pre-college outreach component in addition to retention efforts aimed at students who are already involved in these fields. In view of the many such outreach and retention programs now in place, we recommend as a first step the identification of currently known best practices. Once the best practices have been determined, the NSF and other funding agencies can play a key role in disseminating information to study and project proposers and grantees interested in developing such programs.

The pre-college outreach component should focus not only on the high school level, but also on middle school and even elementary school science programs. Previous research has shown that the younger the age at which students begin to see science and engineering as potential and exciting career choices, the greater is the chance that they will eventually enter those fields. This observation likely applies with even greater urgency to URMs because they are the least likely groups to choose science and engineering careers. This effort to attract younger students would carry the greatest impact if it were to involve undergraduate and graduate students, especially, again, those who are URMs, since they are nearest in age and sensibility to the pre-college students on whom we must focus. Here again we recommend identifying current best practices as a first step.

Pre-college teachers and counselors greatly influence the specific interests and career choices of students. However, many teachers and counselors know little about the exciting opportunities and rewards that we associate with careers in polymer science and engineering. New programs are needed to educate and train these key educators to give them the information they need to guide students in their career choices. Such an initiative might consist of simple informational brochures explaining what polymer scientists do and what they make (drug delivery systems, fuel cell membranes, components of microelectronic circuitry, etc.), courses with strong practical components designed to expose students to real-world research and manufacturing facilities, or active participation in research activities in polymer science and engineering. Existing programs, such as the large NSF-sponsored programs (MRSEC, STC, NSEC, etc) should be encouraged to incorporate more pre-college URM teachers into their summer offerings. Such programs could be designed to include teachers only or teacher/student pairs in summer research experiences. Currently, teachers at the pre-college level often work in jobs unrelated to science outside of the school year since they are driven to earn money during their non-teaching summer break. Small increases in the NSF center budgets could accommodate these educators in polymer-related fields and provide the excitement, motivation, and personal experience that would directly affect their outlook and influence many students to choose polymer science and engineering as a career.

Funding agencies also play a key role in these efforts because they are able to encourage grant requestors and recipients to seriously consider diversity and education in their proposals and reports. Such agencies could require that grant proposals include significant diversity and education components, as well as information about the current state of diversity in the requestor's department or institution. Additionally, funding agencies might require updates on the status of diversity in a grantee's progress report. If a given update indicates little change or effort, funding agencies might take this into account in determining whether the grant should be renewed. It is our perception that the NIH has done this successfully at many universities and this pressure has caused a significant enhancement of diversity at such universities.

Once students have successfully matriculated into polymer science and engineering degree programs, another key issue is to ensure that the courses they take are relevant and current in meeting foreseeable industrial and societal needs (see the section on education). This alignment will allow students to complete degree programs and enter the workforce as educated polymer science and engineering leaders, prepared to fill available jobs and support the technological workforce. Such preparation becomes critically important in considering the current workforce, since many senior technologists are nearing retirement and will soon be replaced with younger technologists. It is therefore essential that degree programs properly prepare their students and that employers formulate transition plans that will allow these younger employees to smoothly take over positions left by retiring workers.

In light of these considerations, we believe that it is essential that co-curricular opportunities be developed and encouraged to allow students to gain hands-on experience in polymer science and engineering. Some opportunities that can be promoted to undergraduates are international exchange programs, research opportunity programs, and cooperative education programs. Participating in these programs will allow American students to position themselves and this country for global technical workforce competitiveness, since graduates will be better prepared to work in the increasingly global marketplace. The NSF Office of International Science and Engineering, for example, already supports such international experiences, and these opportunities should be better publicized to current students. Best practices for such co-curricular

programs need to be identified and funding agencies can play a key role in disseminating such information.

Additional opportunities to promote diversity include programs that incorporate polymer science and engineering into entrepreneurial activities. Such opportunities enable students to better understand the interdisciplinary nature of technological fields and may excite students in a way that science and engineering alone will not. Some universities already promote entrepreneurship by sponsoring competitions. Encouraging the funding of additional competitions at universities may prove to be a very positive method of student recruitment and retention.

Finally, beyond initiating and supporting activities developed to bring pre-college and college students into polymer science and engineering, it is extremely important to develop outreach initiatives that target the general public, particularly members of URM. The general public and pre-college students have little or no access to traditional college-level texts. To increase the visibility of polymer science and engineering to the general public, new informational and “cool topic” modules aimed at a general audience should be developed that can be distributed via modern media such as YouTube, iPod/iTunes, and MP3 formats. Imagine the impact of a video showing the high-speed capture of a bullet inside a bullet-proof polycarbonate sample. These new media have an unprecedented ability to reach large numbers of people, especially young people, in the general public who have not been reached by traditional teaching methods. This appears to be an untapped method of educating the general public and younger students about polymer science, career opportunities, and the influence of polymers in everyday life. Additional modules could be developed that are aimed at specific groups of people such as policymakers. This would allow the polymer field to deliver key viewpoints and information relating to economic prosperity, job growth, and competitiveness in an effective, timely, and easily delivered method. Public outreach directed toward the families and communities of pre-college students will also increase their interest in and enhance the likelihood that they enter program in polymer science and engineering, since heightened community awareness of a field or career choice in lower-income and minority settings has been shown to impact a student’s desire to pursue that field.

8.3 Recommendations:

To broaden diversity, the polymer science and engineering community should:

1. Expose, mentor, support, and proactively recruit a diverse set of participants into polymer science and engineering
2. Recruit and develop the American talent pool, including a pre-college outreach component and identification of currently known best practices
3. Encourage undergraduate and graduate students to become involved in pre-college outreach
4. Enhance programs aimed at educating and training pre-college teachers and counselors by giving them added information to help guide student career choices
5. Incorporate more pre-college teachers into summer programs at NSF centers
6. Apply stricter and more visible diversity criteria to proposals and consider requiring updates on the status of diversity in a grantee’s progress report

7. Create a polymer science and engineering curriculum that is current and relevant to foreseeable industrial and societal needs
8. Further enhance co-curricular activities focused on polymer science and engineering, such as international exchange programs, research opportunity programs, and cooperative education programs
9. Incorporate polymer science and engineering education into entrepreneurial activities such as university-based entrepreneurship competitions
10. Develop outreach activities for the general public or policymakers, including informational modules that use modern means of dissemination such as podcasts and other electronic media

Section 9: Global Competitiveness

9.1 Introduction

Consistent with the goals and aspirations of the American Competitiveness Initiative, our competitive edge as a nation will require policies that accelerate our leadership position in polymeric materials science and engineering. Leadership in polymer science and engineering is essential to our capacity to drive the technologies that will underpin the industries of tomorrow as well as to support our nation's confidence in and growing dependence on polymeric materials usage in today's technologies. Such technologies include civil and military transportation and infrastructure; power generation, transmission, and storage; medical devices; telecommunications and computer hardware systems; healthcare; and securing the nation's food supply, sustainable farming, and the manufacture and use of renewable feedstock for the chemical industry. To increase our competitiveness, we need to create an environment in which universities can easily develop and translate technologies that will support the industries of tomorrow while at the same time train students to support the needs of US companies today.[66]

9.2 Investment in Science Pays Off

Long-term investment in science is the foundation of technology development. Areas needing increased and sustained investment to support polymer science and engineering include the design and synthesis of new materials, the development of new characterization tools and methodologies, materials informatics and cyberscience, the design and development of new process methodologies, and multiscale modeling. Because new discoveries are increasingly occurring at interdisciplinary interfaces, expertise in many disciplines is needed and more and more research is taking place in a multidisciplinary environment. [68] The complexity and sophistication of many necessary characterization methodologies have fostered the establishment

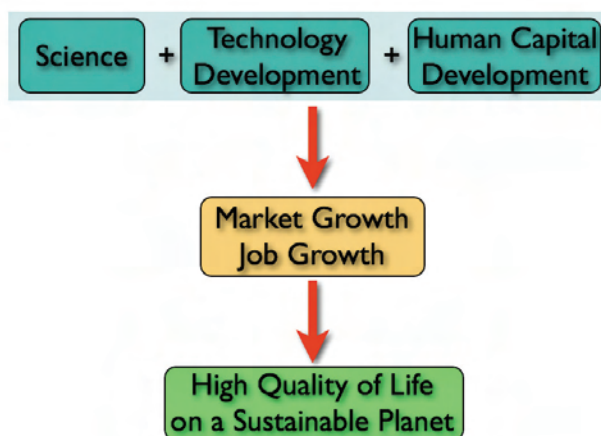


Fig. 9.1 Science and engineering, combined with technology development and training an outstanding workforce, form the foundation of an improving quality of life

of “centers of excellence” for particular techniques where the grouping of highly skilled researchers enables access to a wider segment of the research population.

This broad investment in science has led and will continue to lead to technology development. Notably, the polymer field has been at the forefront of entrepreneurship, with many start-up companies having grown from fundamental research conducted in universities. Five key areas impacted by these companies are electronics, security and defense, energy, health, and consumer products.

For instance, one company is developing low-cost, flexible polymeric solar cells to meet the nation’s future energy needs; a patented polymer technology is presently being used in an explosives sensor currently used to detect improvised explosive devices (IEDs) in Iraq. Another company is developing a fully dissolvable, drug-delivering, biodegradable stent made of polymeric materials that is now in clinical trials—it addresses problems associated with long-term in-dwelling of metal stents. Flexible displays based on organic materials are being developed by other companies. University research efforts have led to the development of green technologies for the production of fluoropolymers like Teflon®.

9.3 Investing in the Future

Looking at emerging trends, it is clear that developments in polymer technologies are moving away from commodity materials into high-value designer materials. Concerns about energy availability and environmental impact are driving industry from traditional petroleum-based products to renewable resources, and solvent-free, recyclable, and energy-efficient processes. Meaningful impact in this area will come not from incremental advances but from game-changing, disruptive innovations that feature a reduced carbon footprint. As our industries move away from traditional methods and materials into new, emerging fields, discoveries and innovations are increasingly coming out of highly cooperative groups rather than through individual efforts.

As new discoveries lead to marketable technologies, and with the availability of an educated workforce, we expect to see both market and job growth, which in turn will lead to a higher quality of life and a more sustainable planet. Some of the key challenges to our nation’s competitiveness revolve around:

- Impediments facing the rapid translation of technologies out of the university into the private sector
- Striking the right balance in university educational programs in polymeric materials sciences to enable the development of the exciting, disruptive technologies of tomorrow while still maintaining the faculty expertise needed to train employees to succeed in our current workforce
- Creating a government initiative to maintain a US presence and help companies to sustain US-based manufacturing to create the new industries of tomorrow

To succeed in these efforts, we must acknowledge and act on the need to support both emerging and traditional areas in research and education. We recognize that many of the above-listed technologies result in part from funding in new areas of polymer science; however, research in traditional areas, such as the reliability of structural composites and adhesives, is also important to maintain competitiveness because it allows us to sustain our strong position in today’s

industry. A meaningful example of this is the recent failure of the so-called Big Dig in Boston, Massachusetts. The tile that fell and killed a woman driving through the tunnel failed due to poor materials reliability. If we can't continue to improve today's materials, these industries will flee the US.

In order to maintain our leadership position and live up to the potential of polymer science and engineering outlined in this report, we need the strongest science and engineering community possible working closely with our nation's industrial sector. We need to train a diverse and well-educated workforce. We need flexible immigration policies that will enable the US to attract the best and brightest scientific minds from around the world. We need to facilitate university/industry collaborations and examine best practices on the sensitive topic of intellectual property. Finally, we need to encourage interdisciplinary team activities that may lead to new advanced technologies in ways that foster the creation of start-ups.

9.4 Recommendations:

1. Invest in science for the long term: Support fundamental studies related to the design and synthesis of new materials, the development of new characterization tools and methodologies, materials informatics, the design and development of new process methodologies, and multiscale modeling.
2. Invest in research aimed at the development of materials and process methodologies to transition polymer materials technologies from petroleum-based products to products derived from renewable resources.
3. Create and maintain flexible immigration policies: US science and engineering disciplines in general and polymer science and engineering in particular have benefited from the ability to attract highly qualified talent from outside the US. The US needs to continue to be able to attract the best and the brightest scientific minds from around the world. We should create immigration policies that will continue to allow these individuals to live and work in the US.
4. Develop and support flexible intellectual property practices that will allow timely translation of technologies developed in the academic sector to the commercial sector. With decreasing investment in research in the industrial sector, discoveries leading to the development of new technologies are increasingly being developed in academia. These technologies are then being transitioned into start-ups, new ventures, established industries, etc. We should develop IP practices that will facilitate the translation of new discoveries into the industries of tomorrow.
5. Continue to encourage interdisciplinary research activities: New discoveries are increasingly being made at the interfaces between disciplines. We need to continue to encourage and train students to work in an interdisciplinary environment and appreciate the value that different skillsets bring to the table.
6. Maintain an emphasis on diversity: Our nation is built on diversity—diversity of thought, diversity of interest, and ethnic diversity. We need to develop programs and policies that will attract underrepresented groups into science and engineering. This is a large under-utilized talent pool that we need to fully embrace.

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