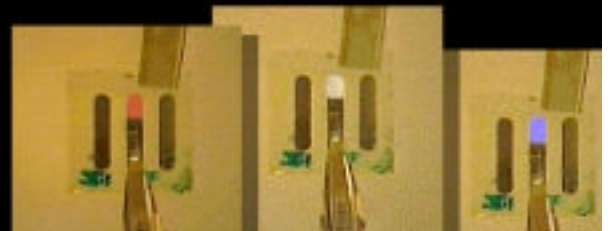
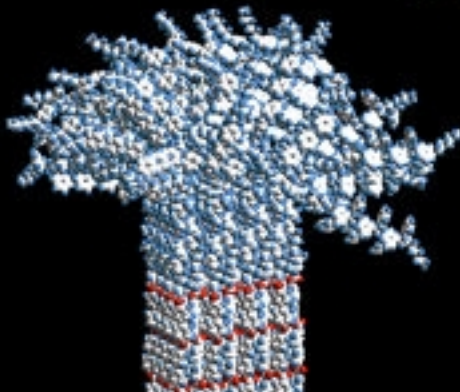
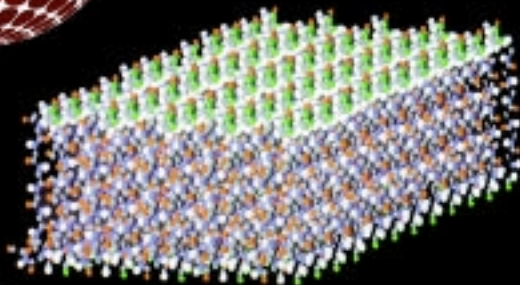
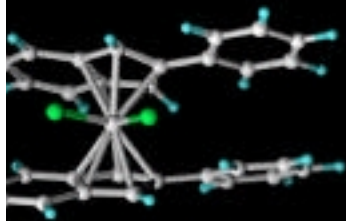
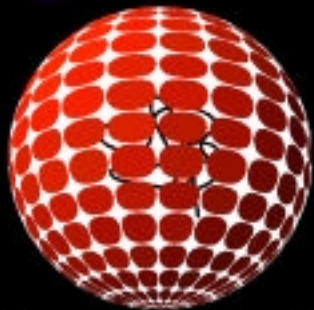


INTERDISCIPLINARY MACROMOLECULAR SCIENCE AND ENGINEERING



On the cover:

1 Human Repair. Courtesy of National Geographic and Corel Corporation.

2 Cell Membrane Interactions with Electronic Materials. Courtesy of Aaron Amstutz, Beckman Institute, Urbana, Illinois.

3 Genetically Modifiable Plants for Polymer Synthesis. Courtesy of Crop Sciences, University of Illinois.

4 Towering Blown Film. Courtesy of Chris Macosko, University of Minnesota and Rheometric Scientific.

5 Polymer Light-Emitting Diodes. Courtesy of Conjugated Polymer Group, Linköping University.

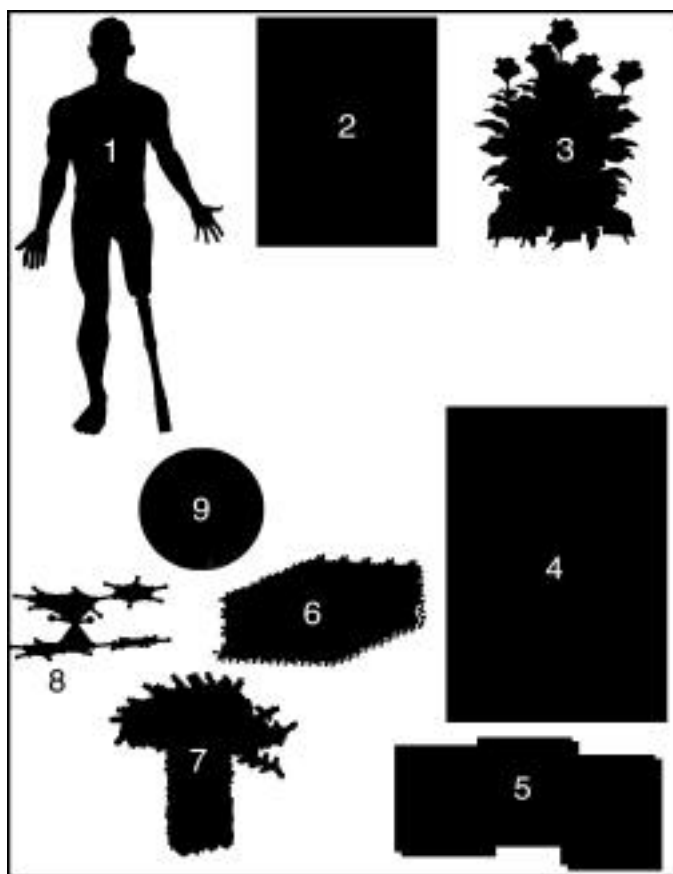
6 β -Sheet Assembly in Macromolecular Crystals. Courtesy of David Tirrell, University of Massachusetts.

7 Supramolecular Mushroom Nanostructure. Courtesy of Samuel Stupp and Aaron Amstutz, Beckman Institute, Urbana, Illinois.

8 Metallocene Catalyst. Courtesy of Robert Waymouth, Stanford University.

9 Self Assembly of Cone-Shaped Polymers into Nano-spheres.

Courtesy of Virgil Percec, Case Western Reserve University.



INTERDISCIPLINARY MACROMOLECULAR SCIENCE AND ENGINEERING

A WORKSHOP CO-SPONSORED BY

NATIONAL SCIENCE FOUNDATION
DEPARTMENT OF ENERGY

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UNIVERSITY OF ILLINOIS

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Preface

The Workshop on Interdisciplinary Macromolecular Science and Engineering (MMSE) was proposed by a Polymers Working Group formed at NSF in 1996 and chaired by Andrew Lovinger. A major objective of the workshop was to examine the emerging connections between macromolecular science and other areas of science and engineering, and identify exciting areas of opportunity in this context for the next decade. A second objective was to consider what approaches NSF could use to optimize, through research and education, the development of interdisciplinary MMSE. In the Fall of 1996, Andrew Lovinger approached me to chair the workshop and form an organizing committee. The first step was to solicit opinions from the community at large on what directions were perceived to be important and exciting. The solicitation to the community by electronic mail can be found in Appendix I of this report, and Appendix II lists the members of the community who responded to this request. Based on input from the community, the organizing committee formed five discussion groups for the workshop covering the following themes: Novel Macromolecular Structures: Synthesis and Function; Control of Properties through Innovative Processing; Solving Environmental Problems with Macromolecular Science and Engineering; Macromolecular Science Connections Between the Physical and Biological Sciences; and Translating Macromolecular Discoveries into Technologies. The selection of these particular topics for the workshop was not meant to exclude the vast number of other areas in macromolecular science and engineering that are scientifically and technically important. The topics of the workshop were selected because they were identified as exciting areas of opportunity with a high interdisciplinary content. The content of recommendations made by each discussion group varies; some emphasized research directions and others educational issues or funding procedures. These differences reflect the nature of each topic and also the specific concerns of individuals in the discussion group.

I take this opportunity to thank the other members of the organizing committee for their contributions to the workshop and to this report. I also express my gratitude to all the participants of the workshop, and members of the community at large who responded to my solicitation for feedback on the exciting areas of interdisciplinary macromolecular science and engineering. I am most grateful to NSF for the support of this workshop and to members of the NSF staff for their input, particularly the internal working group that suggested this workshop. In addition to the members of the NSF Working Group and the Inter-Agency Liaisons, a number of individuals have contributed to the success of this Workshop. For his introductory remarks at the Workshop, I would like to thank Dr. Joseph Bordogna, Acting Deputy Director of the National Science Foundation. For meeting with the Organizing Committee on a number of occasions, for helpful discussions, interest and support, we would like to thank the following individuals: In the Directorate for Mathematical and Physical Sciences, Dr. Robert A. Eisenstein (NSF Assistant Director), Dr. Adriaan M. De Graaf (Executive Officer), Dr. Henry M. Blount, III (Office of Multidisciplinary Activities), Dr. Thomas A. Weber (Director, Div. of Materials Research), Dr. W. Lance Haworth (Acting Executive Officer, Div. of Materials Research), Dr. Janet G. Osteryoung (Director, Div. of Chemistry), Dr. Donald M. Burland (Executive Officer, Div. of Chemistry), Dr. Donald J. Lewis (Director, Div. of Mathematical Sciences),

and Dr. John W. Lightbody (Acting Director, Div. of Physics.) In the Directorate for Engineering, Dr. Elbert L. Marsh (Acting Assistant Director), Dr. Joseph E. Hennessey (Acting Deputy Assistant Director), Dr. Gary W. Poehlein (Director, Div. of Chemical and Transport Systems), Dr. Janie M. Fouke (Director, Div. of Bioengineering and Environmental Systems), Dr. Bruce M. Kramer (Director, Div. of Design, Manufacturing, and Industrial Innovation), and Dr. Ronald L. Sack (Director, Div. of Civil and Mechanical Systems.) In the Directorate for Biological Sciences, Dr. Mary E. Clutter (NSF Assistant Director), Dr. James L. Edwards (Deputy Assistant Director), Dr. Maryanna P. Henkart (Director, Div. of Molecular and Cellular Biosciences), Dr. Bruce L. Umminger (Director, Div. of Integrative Biology and Neuroscience.) In the Directorate for Education and Human Resources, Dr. John B. Hunt (Deputy Assistant Director), Dr. Karolyn K. Eisenstein (Senior Staff Associate, Div. of Undergraduate Education), and Dr. Herbert H. Richtol (Program Director, Div. of Undergraduate Education.) In the Directorate for Social, Behavioral, and Economic Sciences, Dr. Norbert M. Bikales (Head, NSF Europe Office.) I apologize if I inadvertently left out anyone else. Most importantly, I am extremely thankful to Andrew Lovinger for his dedication and commitment to this project. Finally, I would like to acknowledge Verna Riley and Jeff Dalsin for their help in preparing this report.



Samuel I. Stupp
Workshop Chair

April 1998

Executive Summary

A very exciting new field of interdisciplinary macromolecular science and engineering (MMSE) is rapidly emerging, a field at the crossroads of materials science/polymer science, engineering disciplines, chemistry, physics, and biology. MMSE is the area of science and engineering that studies substances composed of very large molecules such as those found in common plastics but also in biological structures, including genes and proteins. The origin of the field is the narrower area of polymer science and engineering which grew over the past four decades around plastics technology. At the end of this century it is clear that our knowledge base in a number of disciplines including polymer science, chemistry, biology, and engineering is converging to initiate a new field that can exert a profound impact on the nation's economy and quality of life.

- The interdisciplinary field of MMSE will have a critical presence in 21st century chemical, pharmaceutical, biomedical, manufacturing, infrastructure, electronic, and information technologies. All new industries and businesses that will bridge information age technology and our rapidly growing knowledge base in biology require novel developments in MMSE. Interdisciplinary MMSE will also play a critical role in the development of nanotechnologies since macromolecules are themselves nano-sized objects that can have great structural diversity.
- Major molecular design achievements in macromolecular structures have occurred over the past decade in catalysis, molecular and cell biology, nanotechnology, and supramolecular materials science. Future exciting developments in MMSE are therefore expected at the interfaces of polymer science with the frontiers of other disciplines.
- New types of research and educational innovation are needed to translate recent and future macromolecular discoveries into technologies. The proactive role of NSF and other funding agencies is particularly critical at this time given the recent downsizing of industrial research infrastructure.
- Research and educational efforts in the following areas need to be strongly supported in order to develop frontier interdisciplinary MMSE in the U.S.

Biomaterials and Macromolecular Biology

- Connections between cells and computer hardware could deliver new types of environmental sensors, medical diagnostic equipment, and probes of biological objects such as viruses and bacteria. Macromolecules hold the key to create such connections because cell receptors are essentially polymers embedded in the cell membranes. Novel structures also need to be discovered to create contacts between synthetic and biological macromolecules.
- The ideal materials to repair humans have not been discovered yet and are not likely

to emerge from current health sciences research with strong clinical orientation alone. These ideal materials will be predominantly macromolecular in structure and will require very close collaboration among chemists, biologists, materials scientists, and processing engineers. NSF, NIH, and other agencies must spearhead the development of this critical field which cuts across many disciplines.

- Great frontiers in MMSE could emerge from research on the biological control of monomer sequences and molecular self assembly. This research should extend beyond proteins to other biological and even synthetic macromolecules.
- Advances in macromolecular technology based on lessons from biology offer the prospects of new catalysts for materials synthesis or environmental remediation, sensors for environmental monitoring or medical diagnostics, selective membranes, and chromatographic media for the purification of fine chemicals and pharmaceuticals.
- Revolutionary opportunities exist for creating new polymers with known monomers using novel catalysts such as the new generations of metallocenes. These catalysts could yield new breeds of engineering plastics because they offer unprecedented control over macromolecular architecture.
- Supramolecular chemistry of polymers is an emerging area bridging chemistry, biology, materials science, and engineering fields. It could yield self assembling materials that acquire multiple functions without the use of complex processing hardware. This area could also open spectacular horizons for unique nano-biotechnological systems. Especially promising is the study of macromolecular aggregates that form nanostructures not requiring the covalent bonds that characterize traditional polymers. Environmentally, these novel structures could be recycled indefinitely because their disassembly does not require breaking covalent bonds.
- It is important to support research on computer designed macromolecular substances in order to accelerate the search for new organic and biomolecular materials with novel properties. This will be critical not only to the rational design of functional macromolecular materials but also to our understanding of biological processes. Such efforts need to combine chemistry-based polymer theory and computer simulations. At the same time, development of new and improved characterization methodologies, and instrumentation is also needed in order to optimize the design and performance of novel macromolecular structures.

Environmental Macromolecular Science and Engineering

- Macromolecular science and engineering will have a great impact on future issues

involving the global environment.

- Research must be supported on the possibility of using plants or microbes to synthesize technologically useful macromolecules. It is also necessary to support research on benign processing and synthesis of macromolecules in water or carbon dioxide instead of organic solvents.
- Research must also be pursued in the use of macromolecular materials to assist in environmental remediation and cleanup. One example is macromolecules with high specificity to remove toxic metals from water.
- It is also important to study the interaction of polymers with ecosystems, covering the areas of toxicity, hormonal activity, and other health related effects.
- Because of recent advances in the synthesis of novel macromolecular architectures and supramolecular chemistry, there are new opportunities to be identified on biodegradable polymers. There are also new varieties of processing and new materials to be discovered that could withstand multiple exposures to recycling.

Innovative Fabrication of Macromolecular Products

- Processing innovation for macromolecular products is critically needed for the novel technologies that will involve self assembly and supramolecular chemistry. There is essentially no knowledge base in this area.
- Novel processing techniques will be needed for molecularly designed biomaterials, biomedical technologies, and for the new environmentally benign macromolecular compositions. Processing in fully benign environments will become an area of increasing interest.
- The great increase in polymer architectures made possible by recent synthetic advances requires a rational modeling approach to processing in order to take full advantage of the new diversity in structures and their relations to realistic processing flows. This modeling also needs to explore *in situ* correlations of microstructure development under flow conditions.
- Innovative polymer processing techniques must be developed to structure thin films, fibers, and foams by application of external electric/magnetic or substrate fields. New methods must also be developed to achieve rapid and precise microscale and nanoscale patterning of macromolecular products.

General Recommendations

The workshop participants hope that NSF and other agencies will insure optimal devel-

opment of this critical field of interdisciplinary MMSE in the U.S. by funding both research and educational initiatives that specifically target the areas mentioned above. These initiatives should include flexible modes of funding and proposal evaluation procedures to minimize the burden on the community.

- There is need to establish inter-agency agreements or initiatives to grow interdisciplinary MMSE programs that serve the missions of multiple agencies. One example would be a partnership between NSF and NIH in order to establish programs that target the area of novel biomaterials for the repair of human tissues.
- In order to promote development of macromolecular science related to environmental problems, biomaterials, and innovative manufacturing, a special effort must be made to enhance coordination among appropriate NSF programs in physical sciences, biological sciences, and engineering.
- In all scientific areas, education should be closely integrated with research. Creative educational approaches should be explored at all levels to train a new generation of interdisciplinary scientists who will need to be versed in the chemical, physical, biological, and engineering aspects of this field. The need to integrate these multiple aspects at all levels of education is particularly critical for the effective development of interdisciplinary MMSE.

Workshop Program

Tuesday, May 13

7:00 - 9:00pm Reception at the Arlington Hilton (sponsored by Dow Corning Corp.)

Remarks by Dr. Gordon Fearon (Dow Corning Corp.), Dr. Andrew Lovinger (NSF), Dr. Richard Kelley (DOE), Prof. Samuel Stupp (Workshop Chair)

Wednesday, May 14

Plenary Session

8:15 - 8:30 Sign-in

8:30 - 9:00 Welcoming remarks

Dr. Joseph Bordogna, Acting Deputy Director, NSF

Dr. Richard Kelley (substituting for Dr. Patricia Dehmer), DOE

Prof. Samuel Stupp, Workshop Chair

9:00 - 9:40 Prof. Pierre-Gilles de Gennes, "Polymers: Magicians, Witches and Illusions in the Quest of the Grail"

9:40 - 10:20 Prof. Gerhard Wegner, "Perspectives and Opportunities in Polymer Research in Europe: Recent Developments"

10:20 - 10:40 Coffee break

10:40 - 11:20 Prof. Robert Langer, "Polymers as Biomaterials"

11:20 - 12:00 Prof. Christopher Macosko, "Processing for Enhanced Polymer Properties"

12:00 - 1:00 Lunch

1:00 - 1:40 Prof. Samuel Stupp, "Expanding Macromolecular Function with New Monomer Alphabets"

1:40 - 2:20	Dr. Joseph Wirth, "Converting Polymer Science into Technology"
2:20 - 2:30	Coffee break
2:30 - 6:00	Subgroup discussions
6:00 - 7:30	Dinner
7:30 - 10:00	Subgroup discussions

Thursday, May 15

8:30 - 10:00	Subgroup discussions
10:00 - 10:20	Coffee break

Plenary Session, Samuel I. Stupp, Chair

10:20 - 10:45	Recommendations from Subgroup 1 and discussion, Prof. Robert Grubbs
10:45 - 11:10	Recommendations from Subgroup 2 and discussion, Dr. Scott Milner
11:10 - 11:35	Recommendations from Subgroup 3 and discussion, Prof. Lynn Jelinski
11:35 - 12:00	Recommendations from Subgroup 4 and discussion, Prof. David Tirrell
12:00 - 12:25	Recommendations from Subgroup 5 and discussion, Prof. Edwin Thomas
12:25 - 1:30	Lunch
1:30 - 5:00	Subgroup meetings to draft reports
5:00	Adjourn

Friday, May 16

8:30 - 10:00	Discussion of Workshop results by Organizing Committee
10:00 - 10:20	Coffee break

10:20 - 12:00	Meeting of Organizing Committee
12:00 - 1:00	Lunch
1:00 - 5:00	Meeting of Organizing Committee; draft of Report

BIOMATERIALS AND MACROMOLECULAR BIOLOGY

DISCUSSION LEADER: DAVID A. TIRRELL, UNIVERSITY OF MASSACHUSETTS

GROUP MEMBERS:

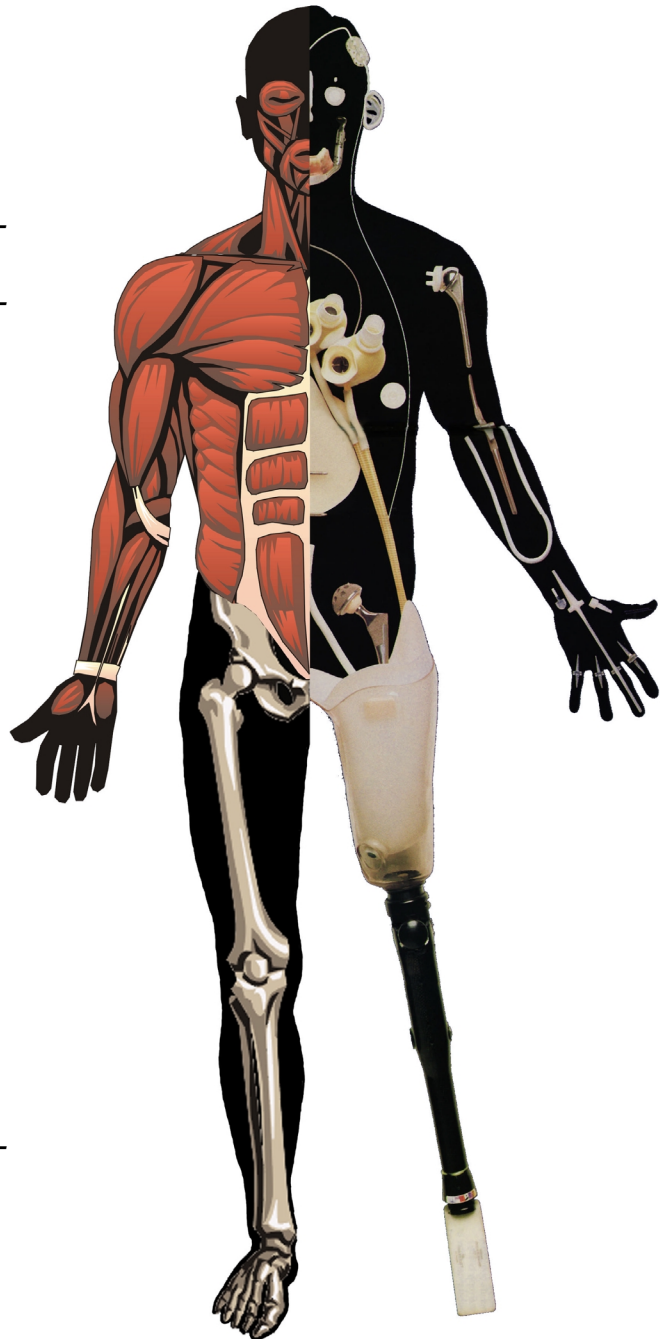
KENNETH DILL, UNIVERSITY OF CALIFORNIA, SAN FRANCISCO
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LINDA GRIFFITH, MASSACHUSETTS INSTITUTE OF TECHNOLOGY
JEFFREY HUBBELL, SWISS FEDERAL INSTITUTE OF TECHNOLOGY, ZÜRICH
BUDDY RATNER, UNIVERSITY OF WASHINGTON, SEATTLE
MATTHEW TIRRELL, UNIVERSITY OF MINNESOTA, MINNEAPOLIS-ST. PAUL

Summary

The forging of stronger connections among macromolecular science, bioengineering, and the biological sciences will return important rewards to each of these fields. Because macromolecules mediate virtually all biological processes, one expects many common elements in the behavior of biological and synthetic macromolecular systems. At the same time, there are profound differences such as the specificity of biological structures which has no parallel in the simple polymers used in technology at the present time. This dichotomy provides a basis for productive interaction at the interfaces between the disciplines. Research programs directed toward these interfaces will contribute in a significant way to the physical and economic health of the nation. Advances in macromolecular technology based on lessons learned from biology offer the prospect of new catalysts for materials synthesis or environmental remediation, sensors for environmental monitoring or medical diagnostics, selective membranes and chromatographic media for the purification of fine chemicals and pharmaceuticals, and new biomaterials for the treatment of injury and disease. New technological opportunities can emerge from molecular level coupling of cells to computer or sensor hardware, an interface which may require engineered contacts between biological and synthetic macromolecules. Many more advances are also envisioned in biomimetic synthesis and self assembly of macromolecules. All these interfacial areas will no doubt be synergistic with efforts to advance the field of molecular biology. Their development will be greatly enhanced by changes in educational curricula to address the junctions between biology, materials science, and engineering disciplines.

Human Repair

For decades macromolecules in many different forms have played a key role in human repair. Blood vessels have been repaired with fabrics woven from fibers made of poly(ethylene terephthalate) — the same polymer found in beverage bottles and magnetic tapes. In reconstructed hip and knee joints, the most technologically common plastic — polyethylene — is used as the low friction surface that allows patients to move their limbs without pain after surgery. Very recently macromolecular artificial skins that are partly biodegradable have been developed for victims of serious burns. Many other examples in current use could be cited. Novel concepts in human repair using macromolecules are being researched in laboratories around the world, and one interesting example is the tissue engineering approach to regenerate diseased or broken bones, torn cartilage in our knees, and other structures. This approach utilizes sponge-like materials made of biodegradable macromolecules that are seeded with cells and proteins that could, in principle, regenerate the tissue of interest. Through research the future could deliver much more sophisticated concepts in human repair using molecularly designed macromolecular materials that interact with tissues in the body in a pre-engineered way. These novel forms of macromolecular matter could be designed to form perfect junctions with natural tissues and function as ideal replacements for parts of the human body in need of repair. Other forms will be cell seeded and biodegradable in a prescribed time, and would be able to change size and shape predictably to make way to the regenerated tissues they template as scaffolds. The contact of cells with nanoscale features on the

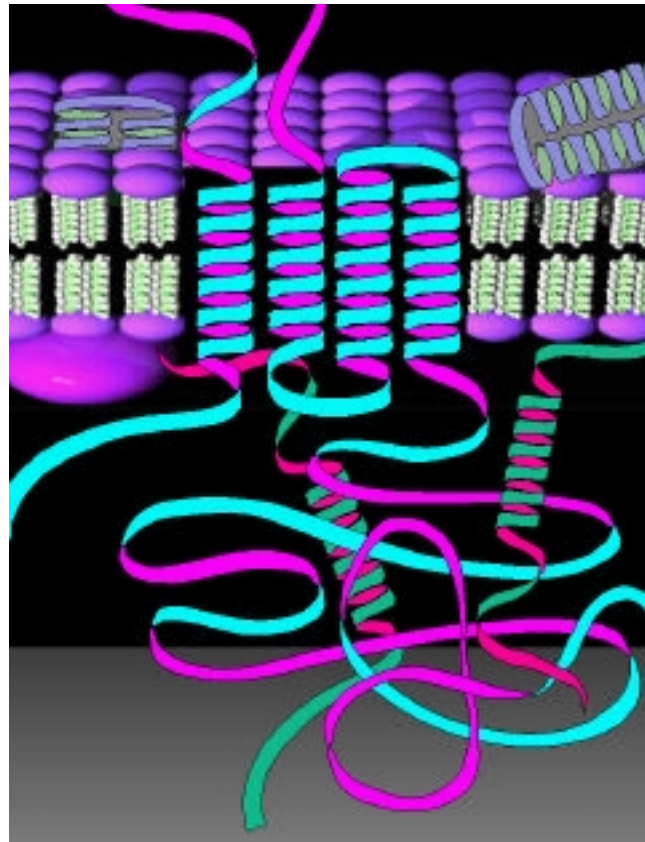


Human repair in the future will be done either with specially designed synthetic materials (right side) or with materials that will mediate the regeneration of tissues (left side.)

scaffolds could regulate some of their functions, thus curing diseases, dissolving tumors, and mediating the growth of missing tissues. Those advances will require nanoscale control of macromolecular structure, a deeper understanding of self assembly, advances in molecular biology, and access to genetically engineered proteins.

Intelligent Junctions between Cells and Computers

This past decade the information age has delivered amazing computer capabilities that impact our daily life. During the same decade we have seen great advances in our understanding of how the molecular machinery of cells works. The marriage of the fields of engineering and biology will generate many exciting possibilities to enhance the quality of human life. Macromolecules can be used to create the junctions between the hardware of computers and cells since many cellular functions are mediated by interactions between biopolymers embedded in cell membranes and molecules in their external environment. Thus, in order to talk to cells from silicon chips, designed macromolecules glued to semi-conductors could interact directly with biological macromolecules on cell membranes, an interaction that could be engineered with chemical specificity. These junctions could transmit signals to cells in order to identify their nature, instruct them to synthesize specific proteins, or cause them to multiply. Such capabilities could be used for medical diagnostics, for sensing the presence of other biological objects in the environment such as viruses and bacteria, or for transforming cells for therapeutic purposes. The hardware's function would be to control these processes spatially and temporally in complex devices taking advantage of molecular junction design. To make this happen we need to develop new chemistries to form polymers with specific shapes on the surfaces of electronic and photonic materials. Many exciting technologies for better quality of life will emerge from these computer-to-cell intelligent junctions.



Information may be retrieved or delivered to cells through junctions formed by synthetic macromolecules between biomembranes and electronic materials.

Bio-inspiration from Spider Silk

Why spider silk?

Spider silk is a protein fiber with unusually good mechanical properties. Single fibers of spider dragline silk, about 1/15 the diameter of a human hair, have a tensile strength that rivals that of steel, yet the fibers stretch to more than 10% elongation before breaking.

Spider silk also combines a reasonably high stiffness with a very large extension to break, so that the toughness — the energy required to cause a tensile failure — is very high. The initial modulus of the fiber is greater than that of nylon-6,6, and more importantly, the fiber does not fail in compression by kinking, a feature that makes spider silk in some ways superior to the highest performance human-made fibers.

In addition, the mechanical properties are achieved under extremely mild and environmentally benign processing conditions, and without extensive drawing of the fiber, unlike synthetic high performance fibers.

Finally, the spider system is ideal as a research vehicle because it represents a set of evolutionarily tailored fibrous materials. Most of these materials are poorly understood and hold many insights to be discovered regarding structure-function relationships and processing relevant to materials science.

Why now?

The tools of biotechnology now make it possible to produce genetically engineering silk-like proteins. Once the molecular basis for the excellent mechanical properties of silk is under-



Scientists are looking toward spider silks as a source of bio-inspiration for the production of a new class of high performance materials.

stood, we can produce synthetic DNA that codes for the correct sequences and express the proteins in bacteria or perhaps even in plants. There are still hurdles to overcome, though. One involves learning how the spider processes the fibers to produce a highly oriented material, and somehow imitating that process in the laboratory. Another involves understanding the effect that water has on the mechanical properties, and engineering out of the protein these deleterious effects.

Biomaterials and Macromolecular Biology

Introduction

The forging of stronger connections among macromolecular science, bioengineering, and the biological sciences will return important rewards to each of these fields. Because macromolecules mediate virtually all biological processes, one finds many common elements in the behavior of biological and macromolecular systems. Molecular flexibility, the capacity for motion, and the dominance of weak, collective intermolecular interactions, are common themes. At the same time, there are profound differences; for example, the complexity and specificity of biological structures and biological processes finds no direct parallel in the simpler polymers of materials science and technology. This dichotomy provides a firm foundation for productive interaction between the disciplines; communication is possible, yet each field brings fresh insights, new methods, and novel approaches to problems that lie at the multidisciplinary interfaces.

Research programs directed toward these interfaces will contribute in a significant way to the physical health of the nation. The marriage of biology and polymer science offers the prospect of new sensors for medical diagnostics, selective membranes and chromatographic media for the purification of fine chemicals and pharmaceuticals, new materials for the treatment of injury and disease, artificial muscles and even the creation of tissues and whole organs. Health care now represents a trillion-dollar industry in the United States, and biomaterials-based medical devices number in the thousands. Basic research agencies, in particular the National Science Foundation, have a clear role to play in supporting the fundamental science that underpins these technologies, a role complementary to the disease- and clinically-oriented mission of the National Institutes of Health.

The economic health of the nation will also be impacted. Advances in macromolecular technology based on lessons from biology offer the prospect of new catalysts for materials synthesis or environmental remediation, new sensors for environmental monitoring, and hierarchical materials that have improved performance by virtue of the hierarchy even though the starting materials are less than optimal. The 3 billion year old laboratory of evolution by natural selection is sure to suggest new routes to improved materials properties and performance.

Lessons from Biology: Polymers in the Biological and Materials Sciences

Among the most important polymers on earth are the biopolymers, including DNA, RNA, proteins, and polysaccharides. In their properties and functions, biopolymers are far more sophisticated than synthetic polymers, which are largely designed for structural, mechanical, and barrier functions. In contrast, proteins are catalysts for thousands of reactions; they are scaffolds; they are sensors of optical, electrical, mechanical, and chemical signals; they are regulators, as gates and channels in membranes; they transport ions, molecules, and electrons; they store information and energy; they repair and build other molecules; and they regulate the assembly of other molecules. While self-assembly among synthetic polymers means micelles and related structures that are

spheres or planes in solution, self-assembly in proteins means whole lifeforms that can walk and talk and think. What makes proteins so different from synthetic polymers?

Most of the more than 70 billion pounds of polymers produced in the U. S. each year are homopolymers, such as polyethylene, polypropylene, polystyrene, and polyvinylchloride. Such molecules carry no sequence information. "Information" in a sequence is the blueprint for folding, but could also include other directions for structure and properties. In contrast, proteins have those properties but they also have many other more sophisticated functions. Proteins are informational polymers: they have specific monomer sequences. The great power of biology is in its ability to create sequence-controlled heteropolymers. A fundamental goal in polymer chemistry is to find ways to create polymers having specific monomer sequences, using monomer sets that need not be biological in origin. About 15 papers since 1992 indicate that this is just now becoming possible.

The reason sequence control is so important is that it will lead to control of structure and function on atomic spatial and time scales. Biological polymers have capabilities that synthetic polymers do not have: They fold to specific structures, exhibit specificity in molecular recognition, and organize into hierarchical architectures where atomic structures are localized in space so precisely that multiple functionalities can be coupled to each other. Therefore proteins have the power of regulation: they can sense their environments, and act in accordance. Hierarchy is observed at all levels, from molecules to cells to organs to lifeforms. These are the capabilities that should be possible in sequence-controlled heteropolymers. An analogy is that ceramics and metallurgy, too, created only structural materials, like aluminum siding on houses, until advances in solid-state electronics and polymer lithography showed us how to control structures at the micron level. The result was a whole new industry, modern telecommunications.

How can we make materials, such as sequence-controlled heteropolymers, that capture some of the complexity and functionality of natural polymers? New methods of solid-phase synthesis are emerging. Some polymers are being produced by hijacking biological synthesis machinery in living cells and using it to create polymers of human-made designs. Some may be created by methods of combinatorial chemistry, a tool now being widely used in the pharmaceutical and biotechnology industries.

The ability to create sequence-controlled heteropolymers will require a parallel effort in computation and theory. The power to design creates a need to design. To tailor polymers that can fold requires an understanding of the principles of folding, and the ability to predict structure from monomer sequences. Much new work will be required before theory and computation can design the structures of foldable polymers.

Both polymer science and structural biology can benefit from the expertise of polymer theorists. Polymer theorists and simulators have an important role to play in understanding biomolecular conformational changes, including the folding of proteins and RNA, collapse and helix-coil transitions, the binding of ligands, self-assembly, motor protein action, adsorption, and the aggregation of proteins that are involved in "folding diseases," possibly including Alzheimer's and Mad Cow diseases. These are problems

for which polymer chemists' expertise in modeling polymer conformational changes can contribute unique and important insights into fundamental biochemistry.

Biology also makes use of intermolecular forces to order and organize molecules into aggregate structures. These precision molecular assemblies exploit cooperative interactions to form biological materials with outstanding combinations of physical properties and biological function. The potential to use self-assembly in synthetic materials has been demonstrated, but we still have much to learn to exploit with precision the full materials potential of biomolecules and related molecular building blocks.

Still another principle widely used by biology is the precision use of surfaces and interfaces. Biological surfaces deliver specific signals and recognition events with accuracy, while inhibiting non-specific interactions. Biology also uses well controlled degrees of mobility in its surface molecular units to enhance recognition interactions by easing some of the precise geometric requirements for docking events. Since surfaces are the communicators of biological signals, the potential exists to take today's synthetic polymeric materials, which have excellent mechanical and other physical properties, and modify only the surface zone to confer recognition and specificity. Issues of spatial control, precision chemistry and surface stability are the challenges here that confront the macromolecular science field in order to translate these biological ideas into useful technologies.

Two-Dimensional and Three-Dimensional Architectures for Cellular Control

The ability to accurately control cell processes offers myriad possibilities for medical implant materials, cell-based chemical production and biosensor technology. Advances in cell and molecular biology over the past 10 years have taught us about the mechanisms that cells use to receive signals from their external environment. Of particular relevance for macromolecular science are the possibilities for control of cells based on two- and three-dimensional polymer architectures.

Communicating to cells through their natural biological receptors offers rich possibilities for precise control. Receptors are protein machines that span the cell membrane, taking a signal from the outside and transmitting to the inner mechanisms of the cell. The receptor will have a chemically complementary structure (a ligand) that can induce a change in the conformation or state of association of the receptor. We must learn to tether ligands to surfaces or build those ligand structures within macromolecular surfaces. Furthermore, the spacing of ligands on surfaces may be essential to achieve proper control of cell behavior.

Cells also receive inputs mechanically. Stresses, confinement and cell-sized channels also send sharp messages to cells leading to changes in cell phenotype and function. These cell physiological changes can translate to production of specific metabolites and signaling agents. For example, enhanced healing for medical implants has been seen in porous polymers with "roundish" pores that are approximately the size of the cells. Thus, surface patterning technologies and control of pore sizes, pore interconnects and three-dimensional features suggest implementable strategies for the

manipulation of living cells. This area of endeavor brings together mechanical engineers, materials scientists, chemical engineers, polymer chemists and biologists to improve control of cell processes.

Instrumentation

Advances in both organic materials and biological sciences have often been made only after the development of new methods for measuring or characterizing structure and properties. Frequently, versions of the same methodologies have influenced both fields profoundly. Examples include high resolution x-ray diffraction, electron microscopy, molecular weight determination methods, nuclear magnetic resonance spectroscopies, measurement of intermolecular forces and scanning probe imaging techniques. Similarly, current instrumental challenges relevant to both fields include precise methods of sequencing heteropolymers, methods for imaging and mechanical testing of single molecules, determination of details of structure and organization in monolayer, bilayer and thin film assemblies, characterization of mobility on surfaces and membranes and quantitation of surface functionality and specific binding interactions.

Computation, as a special case of instrumentation, both to pursue the consequences of theory and to simulate complex structural or dynamic systems, continues to provide new levels of detailed understanding of structure and dynamics in the biological and materials sciences. The widespread complementarity and cross-disciplinary applicability of instrumentation and computational methods across these two broad areas is a result of the similar conditions and constraints that must be met in both. The lengthscales of the relevant structures, and also time scales of motional and relaxational processes, in biology and organic materials science are the same. In fact in both biology and polymer science, fundamentally important processes happen over extraordinarily broad scales - in space from atoms to life forms, and in time from femtoseconds to years. The circumstances of solvation (need to avoid drying or dehydration), fragility and need to avoid extreme temperatures are also recurrent themes in the two disciplines.

Clearly not all instruments in this class are perfectly adapted to a wide spectrum of simultaneous biological and materials science applications, but many are, and this should be exploited both for its efficiency and for the opportunities for cross-disciplinary research that might be engendered in this way.

Biological Activity as a Materials Science Objective

Many materials are optimized for “hard” properties such as high strength, toughness, stiffness, high temperature resistance, and so on. There is, however, an increasing need, especially at the interfaces with biology and medicine, for materials properties more appropriately characterized as “soft”, meaning responsive to weak external fields, adhesive, pliant, shape-adaptable and highly functionalized. Controlling interactions with biological systems is one of the most important objectives of this sub-field of materials science. Effective manipulation of biological interactions requires the construction of interfaces comprising multiple tethered functionalities, often consisting of both repulsive (to eliminate nonspecific adhesion) and specific, attractive, molecular and cellular recog-

nition sites. This tethering has to be done to allow flexibility, mobility, accessibility and mutual adaptability between ligand and receptor surfaces.

Synthesis of such multifunctional, responsive surfaces is a special challenge for macromolecular scientists, since a sequence of steps is necessary with detailed characterization along the way. Characterization of structure and responsiveness and mechanical characterization across the synthetic surface - cell membrane - tissue boundaries is also required. We view these activities to be appropriate activities of materials science, not fundamentally different from objectives of property optimization in other subareas of materials science.

Recommendations

- Research in the fields of biomaterials and macromolecular biology can lead to exciting new scientific and technical advances that will impact on the nation's economy and quality of life. Learning to connect the macromolecules of cells with information age devices, for example, is an enormous scientific challenge that will impact biosensor and medical diagnostic technologies. Also, the ideal materials to repair humans have not been discovered yet; it is therefore critical to direct frontier research in macromolecular science to this goal. Research in highly interdisciplinary areas such as nanobiotechnology and macromolecular biomimetics could bridge exciting areas such as biomaterials, macromolecular biology, and device bioengineering.
- Programs should be put in place to encourage a more thoroughly integrated approach to teaching in areas where biology and macromolecular science overlap, to enhance transfer of concepts and intellectual approaches between the two fields. Complementary areas include macromolecular synthesis, conformational properties of macromolecular systems, phase transition behavior, and many others. The panel recommends NSF support for curriculum development at all levels (K-Ph.D.)
- The National Institutes of Health and the National Science Foundation must re-examine, and perhaps redefine, their relationship. The current stance of the Foundation is predicated on the very reasonable decision to avoid overlap with the larger NIH; implementation of that decision has, however, created obstacles on the path to new materials technology of relevance to the health care industry. NSF and NIH are encouraged to work together to satisfy the needs of the research community at the interface between macromolecular science and biology at every level, including the role of biology in advancing macromolecular materials science. The panel recommends the establishment of joint NSF/NIH programs to promote complementarity in support of materials research that is relevant to the missions of both Agencies. Moreover, funding agencies at large are encouraged to explore these interfaces between macromolecular science and biology.
- Research priorities should be established in such a way that the materials and biological sciences communities are encouraged to embrace a "seamless" view of macromolecular science. This view must capture some of the complexity of biology, while at

the same time drawing on the methods and insights of polymer science to address phenomena such as conformational entropy, phase transitions, ligand binding, and self-assembly. The design and synthesis of sequence-controlled heteropolymers, the engineering of polymers for specificity in recognition, binding, and hierarchical ordering are great research opportunities, and could have great impact on nanotechnologies. The development of novel approaches to two- and three-dimensional cellular materials systems is also a specially promising opportunity.

- Mechanisms must be sought to allow joint development and shared use of instrumentation and computational tools of benefit to both the macromolecular materials and biological research communities. Current instrumental challenges relevant to both fields include precise methods of sequencing heteropolymers, methods for imaging and mechanical testing of single molecules, determination of details of structure and organization in monolayer, bilayer and thin film assemblies, characterization of mobility on surfaces and membranes and quantitation of surface functionality and specific binding interactions.

NOVEL MACROMOLECULAR STRUCTURES

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Summary

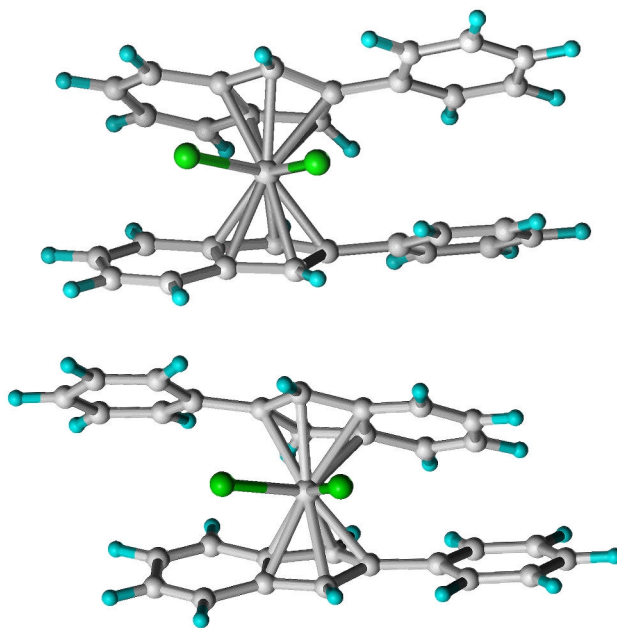
Less than a decade ago it was widely believed that all the important polymers had been made and all the low cost monomers had been converted into polymeric materials. Thus, the field of synthetic polymer chemistry for low cost materials was considered to be essentially complete. Today, the revolution in metallocene derived polyolefins proves this to be incorrect, and these materials may be the first of a complete new family of materials that are produced from old monomers put together in new ways with the aid of novel catalysts. It is also clear that completely novel polymeric structures can be accessed through noncovalent supramolecular design. This exploration may identify nanostructures that self assemble over multiple length scales into highly functional materials. For many reasons it may be desirable to form polymeric structures from monomers or small polymers that are joined through reversible, noncovalent interactions. The search for innovative covalent and supramolecular macromolecular structures must be accelerated based not only on synthetic chemistry but also guided increasingly by modeling and theory. The combination of theory and experiment will require innovation in the education of students at all levels. This area must also include research on instrumentation, as well as new and improved methodologies to characterize new structural features in macromolecules and polymeric assemblies.

Polyethylene

Ethylene gas is the simplest compound that can be turned into a polymer. The polymers made by hooking a large number of ethylene units can have a wide range of properties and applications. The key is how the units are assembled.

In the late 1930s, a group at British Petroleum was studying the fundamental properties of ethylene at high temperatures and high pressures and found that the gas became a waxy solid. This accidental discovery provided the material for the insulation of the wires required in the development of radar. This material is now most familiar as the clear plastic that is used as dry cleaner garment bags. While trying to develop an alternate source of petroleum products, German chemists were examining the reaction of ethylene with aluminum complexes which led to oils. An accidental contamination of one reaction with a transition metal resulted in the discovery of catalysts that allow a new form of polyethylene to be formed at low pressures and temperatures. This material is stronger, is opaque, and has many uses. Some of the most familiar are plastic milk bottles and shopping bags.

It is now understood that the difference between these two plastics, which are made from the same monomer, is the arrangement of the monomers in the long chains formed. The soft transparent material has many short branches which prevent the chains from packing tightly, resulting in a soft, easy-to-deform plastic. The materials formed with metal catalysts have mostly unbranched chains so that the long strands can pack into stiff crystals in the solid state. These crystalline regions result in a much stronger material.



Metallocene catalysts have been discovered recently that generate polymers with completely novel architectures and properties from common and inexpensive monomers.

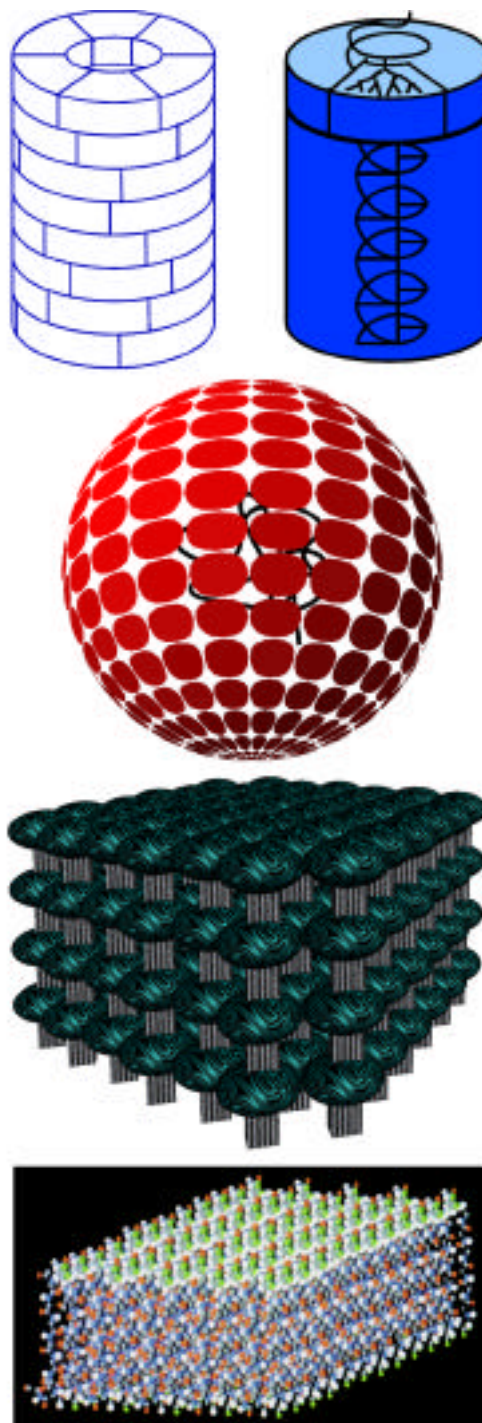
With a detailed understanding of the factors that control the properties of polyethylenes, new forms of the material have been recently produced. One new product results from the formation of very long linear chains of polyethylene using a metal catalyst, and then these materials are processed such that all the strands are lined up in a final fiber of solid. The resulting fibers can be woven into fabric strong enough to be used as bulletproof vests. Moving in the opposite direction, new metal catalysts called metallocenes, make polyethylenes that have very long branched structures. This form of polyethylene opens improved methods of fabrication and new applications.

Not all polyethylenes are created equal. Connect the chains in one way and it is a cheap, weak material used for protecting garments; assemble them in an alternate way and they will stop a bullet!

Designed Materials from Nano-Bricks

During the last half of this century we watched plastics technology develop to create the consumer goods and transportation vehicles that are critical in our daily lives. The macromolecules that make up these plastics fold into accordion-like shapes, entangle with each other as soft noodles, or orient parallel to each other as stiff strings. If we could have polymers that fold into specific and predictable shapes, or know how to form objects with specific shapes of the size of polymer molecules when large numbers of molecules aggregate, we would indeed develop a novel toolbox of nano-bricks to form exotic materials. Several discoveries have been made recently in research laboratories that indicate this goal is attainable with the possibility of huge pay-offs for new materials technologies. Cone-shaped polymers were synthesized that assemble into spheres, genetically engineered polymers were synthesized by bacteria and found to fold into specific shapes, and small molecules have been made that aggregate to form mushroom-shaped nano-bricks. The wedges and spheres could be used to turn materials into smart detectors or to change their surface properties. Artificial protein nano-bricks, on the other hand, could someday self organize to form artificial blood vessels that will save lives.

The mushroom bricks were recently found to stack on their own in a most unexpected stem-to-cap way, producing self organizing materials analogous to sticky tapes, with one very sticky side and a Teflon®-like opposite surface. For this reason the tapes they form by self assembly could keep airplane wings free of ice, protect metals from corrosion, or lubricate computer hard disks for improved performance. A nano-brick



Nano-sized polymers shaped as rounded bricks, cones, mushrooms, and plates have been prepared in laboratories and found to self assemble into tubular, spherical, layered, and lamellar constructs, respectively. These new types of polymers may eventually be useful in applications ranging from sophisticated sensors to de-icing agents.

materials technology involving self assembly could impact profoundly the manufacturing of sophisticated materials and their recycling as well. Genetic engineering of polymers, supramolecular chemistry, nanotechnology, and computational capabilities to predict polymer structure are all necessary elements to achieve this 21st century goal.

Novel Macromolecular Structures

Introduction

The search for novel macromolecular structures is at the core of innovation in interdisciplinary MMSE, and the future of this area requires the convergence of chemistry, physics, materials science, biology, and engineering disciplines. During the early development of polymer science the search for macromolecular structures involved polymerizing different monomers into linear chains and copolymer structures. The physical feedback in this search was offered by systematic studies of polymer properties important in technology. As polymer chemistry developed, this search expanded considerably covering the area of well defined homopolymers and copolymers made possible as a result of new catalysts or new polymerization methodologies. The technological benefit of many of these polymers is still being explored. In recent years we have witnessed an exponential growth in possibilities for macromolecular structure with discoveries in the areas of catalysis, macromolecular architecture, supramolecular chemistry, and macromolecular biosynthesis. Extremely exciting opportunities will emerge through the development of novel macromolecular structures as a result of these discoveries. To bring these possibilities to reality, it is critical to involve in this area theoreticians, computer scientists, engineers, and biologists. Taking the exploration for novel macromolecular structures beyond chemistry will help identify the systems that can have the most impact on environmental problems, better medicine, innovation in manufacturing, and greater human safety.

Linear polymer synthesis and monomer choice

Less than a decade ago it was widely believed that all the important polymers had been made because all of the commercially feasible monomers had been polymerized. The revolution in polyolefin materials made possible by the development of metallocene catalysts shows that this thinking was incorrect. In fact the spectacular technical and commercial success resulting from metallocene polyolefins suggests that they are just the first of a completely new family of materials that can be produced when old monomers are put together in new ways. The development of metallocene and other catalysts for polyolefins is a great demonstration of the role that NSF can play in fostering new technology. In most of the cases the catalysts that have been used in these advances were the result of fundamental research in organometallic chemistry. In many cases the work was directed toward fundamental questions and grew naturally and rapidly into commercial success. The lesson learned from this work is that controlled architectures will lead to new and improved properties and better commercial products. Thus, for the commodity monomers that exist today, emphasis must be placed on new polymerization methods that yield new properties through controlled macromolecular architecture.

When polymers are to be used in low-volume applications such as additives or thin films, an infinite variety of monomers is possible. In these cases only a small amount of material is required to produce the desired function. Furthermore, in these

cases the techniques used to assemble the monomers to the final structure can be reasonably complex. For example, it has been demonstrated that auxiliary groups can be placed on monomers to control the tacticity of the final polymer. Another example is the recent development of controlled radical polymerization that produces new topologies and structures from standard monomers. It is anticipated that new advances in this area will allow these techniques to be expanded for general use. In many cases, the principles required to design polymers with the desired property remain unknown and rapid means of synthesis and testing will be required. The techniques of combinatorial chemistry that are used in drug discovery could provide avenues for the development of polymers and materials for specific function. Of critical importance for this approach is the development of rapid assay techniques.

Branching

The importance of architecture in polymers has been amply demonstrated with commodity materials such as polyethylene obtained from certain metallocene catalysts, or thermoplastic elastomers such as the acrylonitrile-styrene-butadiene copolymers used to manufacture telephone housing and other shock-resistant, everyday plastics. While much effort has been devoted to the development and understanding of processes for the preparation of block copolymers, much less has been done with the very important family of branched polymers. Branching contributes not only to many physical and mechanical properties of polymers but also greatly facilitates processing. While the importance of branched architecture is now generally acknowledged, an understanding of the processes that control branching in most polymerization reactions is largely lacking. For example, a vast majority of the branched polymers that are prepared today are obtained via random chemical events leading to largely uncontrolled products. Examples include the preparation of polyethylene by radical or metallocene catalysis, or poly(vinyl acetate) by free-radical polymerization. With few exceptions fine control of branching is still elusive. A priority should therefore be the pursuit of fine control of polymer architecture with special emphasis on branched structures.

A totally new family of polymers with dendritic structures (both dendrimers and hyperbranched polymers) has appeared in recent years and been shown to possess unusual properties such as reduced viscosity. The study of these macromolecules is hampered by the limits imposed by current synthetic methods. A thorough exploration of more efficient procedures for the preparation of these interesting new polymers is recommended as is a comparative study of their properties with those of more classical linear polymers. For example, the gap between perfect dendritic structure obtained by tedious synthesis and the less defined structure of a hyperbranched polymer can probably be closed by a proper performance of the AB_x polymerization reaction. It has already been demonstrated that these highly branched structures show improved solubility compared to linear analogs, and the unique separation of space (interior vs. surface) provides the opportunity for the design of novel molecular level systems. For dendritic materials to be commercially important, new methods of synthesis will be required.

Supramolecular Polymer Chemistry

Supramolecular polymer chemistry can be considered at different levels, according to the size of the monomeric unit and whether the interactions are intra- or intermolecular. Inspired by the pioneering work of Jean-Marie Lehn, complementary bivalent small molecules can be designed to form supramolecular polymers through selective, directional interactions such as hydrogen bonds.

For many reasons it may be desirable to form polymeric structures from monomers that are joined through strong, yet reversible, non-covalent interactions. Through adjustment of temperature, concentration, solvent, and the strength of the non-covalent interactions, it should be possible to shift this monomer — polymer equilibrium. Consequently, it may be possible to have materials that behave like (easily processed) small molecules under certain conditions while spontaneously exhibiting polymer-like properties upon solidification — **materials with properties on demand**. Because of the reversible character of the supramolecular ordering process, it may be possible to design monomers that spontaneously achieve organizations that are impossible in kinetically formed covalent networks and linear macromolecules. The ability to switch from polymer to monomer without any molecular transformation offers great potential for monomer recyclability. Finally, intramolecular self-organization in a covalent macromolecule (folding) offers the possibility to create information-rich molecular surfaces that could be important in sophisticated catalysts and macromolecular assemblies.

Combination of synthetic strategies and methods as well as characterization methodologies at the molecular, macromolecular, and supramolecular levels should be elaborated for the preparation of polymeric building blocks and giant monomers with linear, cyclic, branched, hyperbranched, dendrimeric, and other complex architectures. Structure-shape dependence relationships for the design of these building blocks needs to be elaborated. Their self-assembly into ordered supramolecular nano-architectures followed by polymerization in ordered versus isotropic states should be investigated. The elucidation of the mechanism of polymerization and the development of polymerization processes for the controlled synthesis of giant monomers are required. By analogy with natural systems, self-assembly of shape-persistent molecular objects offers the potential for new macromolecular functional systems with novel properties. Alternatively, polymerization of giant monomers with well defined shape should be able to control backbone conformation from the random coil to the fully extended state. A fundamental understanding of order formation and universal relationships that exist between conventional lyotropic and thermotropic liquid crystals, block copolymers, blends, semi-crystalline polymers, and complex supramolecular systems needs to be pursued. Complex systems in which order is generated by thermodynamically and kinetically controlled processes need to be elaborated since they are complementary in understanding structure-property relationship in polymers.

Macromolecular Characterization, Theory, and Simulation

As methods develop to make new polymers with increasing control of the size, composition, architecture, and anisotropy, it becomes critical to be able to measure these

characteristics, relate them to properties, and understand how these properties can be tailored to new applications. It is therefore crucial that attention be given to the development and optimization of new analytical and characterization techniques that probe structure at an increasingly deeper level. This process will provide feedback to foster the development of new synthetic methods and advance our understanding of structure-property relationships.

The rapid synthesis and organization of ordered materials requires access to a variety of direct physical characterization methods. These can be divided into two categories: real space and reciprocal space. Real space methods are direct imaging methods such as optical microscopy, TEM, SEM, AFM, and STM, while X-ray, neutron, light, electron and other radiation scattering methods are reciprocal space methods. There are also a variety of indirect techniques that provide valuable information about the state of order in polymeric systems. These include: rheological (dynamic mechanical spectroscopy, shear alignment), thermal (calorimetric), NMR, optical (birefringence, dichroism), and dielectric spectroscopy.

Recommendations

- NSF needs to encourage development of new synthetic methods especially in catalysis, and for control of molecular weight and molecular weight distribution, sequence distribution, branching distribution, microstructure and incorporation of chemical functionality.
- The use of combinatorial chemistry for the preparations and evaluation of novel polymer architectures and compositions should be explored. The main target for such studies should include combinatorial syntheses and combinatorial assays of properties.
- Approaches need to be developed for the synthesis of sequence-specific heterocopolymers from nonbiological monomer sets. The invention of methods such as templated and self-regulated macromolecular syntheses should be encouraged. If such methods are discovered they will open the door to studies of folding in nonbiological macromolecules and this will have great impact on nanotechnology.
- Novel approaches are also needed to create supramolecular polymers from small molecules as nanostructures or as complex microstructures analogous to semi-crystalline polymers. Other supramolecular areas that need further development include, reversible networks, spontaneous polar order, and polymer aggregates.
- Development of new and improved characterization methodologies is needed for optimal understanding of macromolecular materials and of new complex architectures. In order for characterization techniques to have their greatest impact, synthetic polymer chemists must be educated in, and have access to, a broad range of physical characterization techniques.

- Development of novel theoretical and simulation methods of chemically predictive capability is greatly needed to help guide the rational design of functional macromolecular materials and also to achieve an understanding of biological processes. This requires work on chemistry-based polymer theory and simulation in which novel hybrid approaches synergistically combine statistical mechanical theory and computer simulation to attack complex supramolecular problems.

MACROMOLECULAR SCIENCE AND ENGINEERING AND THE ENVIRONMENT

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Summary

Macromolecular science and engineering will have a large impact on future issues involving the global environment. Major environmental applications of macromolecular science and engineering include energy reduction and production strategies such as fuel cells and electrolytes for batteries, as well as materials to assist in environmental remediation and cleanup. One of the most exciting future areas involves "green" chemical processes and products such as a shift to plant-produced macromolecules, microbe-synthesized polymers, and the development of biocatalysts for benign chemical transformations and polymerizations. Other areas of opportunity include the interaction of polymers and ecosystems covering the areas of toxicity, hormonal activity, and other health related effects. The area of biodegradable materials remains an important opportunity and would benefit from microscale processing methods for accelerated development of new systems. Many important questions remain with respect to macromolecules at the end of their useful life. These concern the relationship between macromolecular architecture and biodegradability, and the development of materials capable of withstanding multiple cycles of recycling.

Plastics from Plants

Plants have long been sources for biopolymers, including cellulose, starch, xanthan and guar gums, and lignin. These biopolymers have been used to make plastics; for example starch had been used to produce edible dinnerware, and potato waste has been converted into lactic acid, a starting material for biodegradable polymers.

Now scientists are looking to genetic engineering to cause plants to produce polymers such as the poly(3-hydroxy)alkanoates. These are natural polymers produced in bacteria and fungi. They are melt-processable polyesters, and have the added advantages that their production is environmentally benign and they are eventually biodegraded.

In a recent landmark paper it was shown that genes that encode poly(3-hydroxy)alkanoate production can be transferred into plants, and that plants can be induced to produce these polymers.

It will still be some time before this research comes to full fruition. However, much progress is being made to learn how to target the polymer to a specific tissue (e.g., the tubers of potatoes, rather than the leaves), and how to regulate the composition and sequence distribution of the polymers.



Scientists are looking to plants as alternative production sources for designer copolymers.



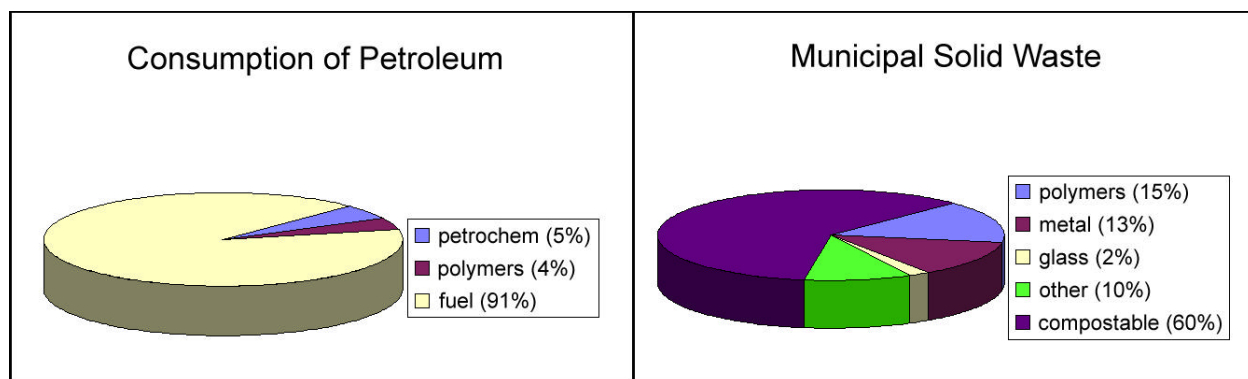
Genetically altered plantlets growing on an agar medium. Plants such as these may someday be used to produce biodegradable polymers.

Macromolecular Science and Engineering and the Environment

Introduction

New developments, discoveries, and knowledge in the field of macromolecular science and engineering will have a major impact on the quality of life, especially as global environmental concerns continue to increase. This section of the Workshop Report sets forth important research opportunities in macromolecular science and engineering as they pertain to environmental and energy issues. It then describes new approaches required for education at this interface, and suggests several infrastructure improvements to ensure that we have the fundamental knowledge base and capacity to effect progress.

Although polymers consume only about 3 - 4% of petroleum, plastics comprise about 15% by volume of municipal solid waste and present a very visible and long-lived disposal problem. Plastic litter on beaches, in rivers and lakes, and in parks has become a very serious problem. Not only does litter spoil the environment, but it also poses as a danger to wildlife, which can either mistake litter for food, or become entrapped in it. Consequently, there is a need for biodegradable materials and a need to develop strategies to deal with the end of the useful life of macromolecules.



Furthermore, it is becoming increasingly clear that bioscience will impact future materials synthesis. Biotechnological methods provide a wide range of tools that can produce new biodegradable materials, as well as more selective and perhaps more environmentally benign catalysts and processes. This progression is shown in the schematic below.



Finally, macromolecules can have an impact on energy and environmental issues through weight-savings and when employed as fuel cells or solid electrolytes, for energy storage devices. Polymers may also contribute to energy savings by providing improved insulation and more efficient means of energy transmission and use.

Green Chemical Processes and Products

One of the most exciting areas for the future involves "green" chemical processes and products — the development of benign chemical processes, biodegradable materials and plant- and microbe-produced macromolecules. This area covers themes such as, the development of *in vivo* and *in vitro* processes based on new types of catalysts for environmentally benign chemical syntheses and polymerization processes; polymerization either in the absence of solvent or in the presence of environmentally benign solvents; the synthesis of polymers by plants and microorganisms; and the development of biodegradable materials. Each of these areas is examined in more depth below.

Catalysts for More Efficient and Environmentally Benign Chemical Transformations

During the past several years there have been remarkable advances in our ability to produce new chemicals. It is worthwhile to explore directed evolution and combinatorial chemistry approaches to develop enzymes that can operate under extremes such as temperature, pH, and solvent. Such approaches may lead to process improvements; for example, a major breakthrough would be an array of enzymes and enzyme-mimics that could selectively and successively oxidize single components of benzene-toluene-xylene mixtures to provide aromatic diacids for important commercial polymers. Another opportunity would be the enzymatic synthesis of monomers such as lactones and epoxides, as well as the production of pre-polymers and polymers. The catalysts need not be biological. For example, there is a need for catalysts that work in less toxic solvents, use safer chemicals, and produce products that are safe for incineration, biodegradation, recycling, or reclamation. It is conceivable that enzymes could be tailored which would efficiently break down difficult-to-degrade consumer plastics into starting ingredients or other intermediates suitable for making virgin polymers. In the area of polymer synthesis, it is important to develop new preparations of important polymers either in the absence of solvent or in the presence of environmentally benign solvents. Water and such supercritical solvents as carbon dioxide are environmentally benign. There is the opportunity to continue to develop new initiator systems needed to synthesize some important polymers in such solvents, to develop new monomers, and to synthesize new polymers.

Synthesis of Polymers by Plants and Microorganisms

The industrial production of several polysaccharides (especially xanthan and guar gums), based on fermentation processes and intracellular bacterial polymerization reactions, is now well-established. The products of these processes are water-soluble polymers that are secreted by the cells in very large amounts. The bacterial production of cellulose in the form of microfibrils, is now being developed as a commercial process. Similarly, thermoplastics and thermoplastic elastomers with useful properties can be produced by bacteria as intracellular storage materials. Structurally, these materials are a family of melt-processable polyesters, the poly-3-hydroxyalkanoates, and among their most valuable materials properties are their biodegradability and bio-utilization by a wide variety of bacteria and fungi in natural environments.

Recent developments in both academia and industry have shown that it is possible to produce large amounts of these polymers by plants as well as microorganisms. In the bacterial production, amounts approaching 95% of product per dry weight of cells have been reported, and these approaches hold much promise for the commercially viable and environmentally sound production of biodegradable engineering macromolecules. These methods need to be extended to production of large amounts of protein polymers in bacteria and plants. With this success in hand for both routes, it is now essential to hone and improve our basic understanding of gene regulation and metabolic pathways involved in biosynthesis. For plant production, we must also develop mechanisms for targeting the product to specific tissues (e.g., tubers, rather than leaves). Furthermore, we have very little knowledge in and understanding of, polymerization processes for polysaccharides and polyesters. We also need to know the rates and mechanisms of reactions catalyzed by the polymerase and depolymerase enzymes, as well as their structures and properties. This area has "fallen within the cracks" because biochemists have shown very little interest in the specific polymerization reactions and enzymes involved in the biological synthesis of polysaccharides and polyesters, and polymer chemists have very little knowledge of these biological reactions and processes. We need to learn how to regulate molecular weight, repeat-unit composition, and sequence distribution in these natural polymers. It is recommended that cell-free and cellular work proceed in parallel, as it is essential to move rapidly from the current black box approaches to developing a firm fundamental understanding of the issues.

Proteins with unusual properties are being designed and produced in recombinant bacteria and yeast by constructing and inserting into the organism the genes that determine the composition and molecular weight of these polymers. The same opportunities are available for the synthesis of new polysaccharides and polyesters with specific structures and unusual properties, by both microorganisms and plants. For example, recent studies on the synthesis of poly-3-hydroxybutyrate (PHB) by a recombinant *E. coli* strain have shown that it is possible to obtain this polymer in incredibly high number average molecular weights, well above 10 million. This polymer could form materials with much better mechanical properties than the normal bacterial PHB, which crystallizes in a spherulitic morphology that generates brittle materials. The ultra-high molecular weight PHB may also be processable by gel-spinning methods to produce ultra-strong filaments in the same manner as ultra-high molecular weight polyethylene.

Development of Biodegradable Materials

Innovative ideas and new approaches are needed to develop biodegradable materials at reasonable cost. At the present time, this field is materials limited. For example, one may produce peptide-polymer hybrids with bio-active linkers or other sites where biodegradation could be initiated. Another example would be the design of switches or triggers into materials so that they will degrade to units sufficiently short for natural biodegradation processes to occur. Alternatively, the tools of biotechnology can produce biodegradable materials with precisely controlled molecular weights and composition (see above). Finally, it is important to recognize that it is not necessary for the entire material to biodegrade if special recovery processes are used. For example, it should be possible to produce a reinforced material in which the matrix degraded and

the reinforcing material could be reused, or alternatively, the reinforcing material could be degraded and the matrix material reclaimed. An example would be a cellulosic fiber reinforced polypropylene/polyethylene composite. In all of these areas, there is an underexplored opportunity to glean ideas from nature. The emphasis would be on the development of polymeric materials with linkages (ester, amide or ether) that are susceptible to attack by natural microorganisms, while managing the degree of crystallinity in the material to allow for complete biodegradation. Finally, rapid progress in biomaterials and biodegradable polymeric materials production will require developing micro-scale processing methodology. This will be important because of the cost involved in producing large amounts of genetically engineered materials and because of the very large parameter space that can be explored by random mutagenesis.

Macromolecules at the End of Their Useful Lives

One of the most important issues pertaining to macromolecules and the environment concerns the ultimate use of polymers at the end of their useful lives. The three most important strategies in waste management are biodegradation, recycling or reclamation into other products, and incineration.

Biodegradation as a Viable Strategy for Disposing of Polymers

Biodegradation of polymers occurs in two steps; the first step is an enzymatic hydrolysis of polymeric material into monomer and oligomers by the action of extracellular depolymerases produced by microorganisms, and the second step is a mineralization of enzymatically hydrolyzed products within cells of microorganisms. The first step involves the binding of enzyme molecules on the surface of materials. Because the size of enzyme molecules is generally 3 - 5 nm, the ability to characterize and regulate surface structures at nm length scales is an important research subject for the design of biodegradable polymers. In addition, we need to develop a better understanding of the mineralization of enzymatically hydrolyzed products.

There are many other fundamental aspects of biodegradation that are not well understood. Of particular interest is learning what the basic architectures (stereochemistry, sequence distribution, crystallinity, etc.) are that control biodegradability. For example, many different types of aliphatic polyesters will undergo enzymatic degradation by hydrolysis, but with a given microorganism or a given hydrolase enzyme, the rates of degradation can vary widely. We have no understanding why this should be so, but we know that many of the depolymerase enzymes have two types of sites: a binding site and a catalytic site. How each of these sites contributes to the specificity and activity of the enzyme in the degradation process for different polyesters is completely unknown at present. We also know that the amorphous regions of such polymers are degraded much faster than the crystalline regions. We know that biodegradation of crystals proceeds from the edges of crystals, rather than the surfaces, and the underlying explanation for this could be capitalized upon to enhance rates of biodegradation. Furthermore, the roles of different microorganisms or populations of microorganisms, that effect biodegradation, are not understood, nor are the actual enzymes or combinations of enzymes, as

discussed above. A highly desirable goal, for example, would be to design a microbial plasticide or a microorganism that used commercial polymers as its sole carbon source.

Examples of Macromolecular Impact on the Environment

New Ways to Use Natural Materials

We need to think seriously about all biomass. Natural materials such as cellulose, lignins, oils, proteins, and waxes have unique functional properties and all are inherently biodegradable. There is a need to develop new chemical transformations and new solvents. For example, is it possible to produce new nylon-like polymers using six-carbon diacids derived from starch? It is likely that chemically and/or biologically modified starches and celluloses and vegetable oils, which are annually renewable resources, will function as biodegradable thermoplastics or thermosets. Now that biotechnology makes it possible to tailor the fatty acid distributions produced in canola and other plants, it will be important to develop new chemical transformations and uses for these materials. Green plants typically contain a wide variety of saturated and unsaturated fatty acids and oils which show promise as intermediates for new hydrocarbon polymers with properties spanning the range of those of tough thermoplastics to rubbery elastomers. State-of-the-art materials science and molecular biology have shown that it is possible to reengineer Nature's macromolecules in ways that allow them to exhibit properties not found in evolutionary materials. For example, cellulose fibers with mechanical properties approaching those of commercial high performance fibers have been demonstrated in the last several years. It should be possible to accomplish similar transformations on other important biopolymers to produce better-than-natural performance characteristics while preserving other attractive natural attributes.

Macromolecules that Perform/Assist in Environmental Clean-Up and Remediation

More efficient biosurfactants, bioemulsifiers, and water absorbers are required and it is critical that these materials themselves be environmentally benign and that they degrade. Opportunities exist for producing novel systems; an example would be a catalytically active membrane.

Macromolecules for Energy Production, Storage, and Savings

Opportunities exist to employ macromolecules as fuel cells, solid electrolytes in batteries, and for weight reduction. An area in which research is needed involves the joining of metals and polymers. Furthermore, ionically conducting polymers with higher conductivity and greater temperature range for use are a possible area for research. This area becomes even more attractive if biopolymers or their derivatives can be developed for this purpose. Semiconducting and electronically conducting polymers may also be developed for use in batteries and fuel cells.

Interactions Between Polymers and Ecosystems

Much fundamental knowledge must be obtained concerning the degradation products of polymers and their fate in the environment. Of importance would be understanding and controlling fundamental biodegradation mechanisms in disposal systems such as composting, and understanding whether biodegradable polymers are affected or not affected. Furthermore, there are many ill-defined and unclear relationships concerning toxicity, hormonal activity, and other health-related effects of polymer precursors. Certain polymer chemicals, most notably phthalate esters, p-nonylphenol, styrene monomer, and bisphenol A monomer and derivatives, have recently been associated with endocrine modulation. These associations should be put on a scientific footing. Of particular interest are cell-polymer and enzyme-polymer interactions. Furthermore, there are specific shifts in microbial populations as biodegradation proceeds, and the impact of these shifts is unclear in relation to the types of degradation products formed and the utilization of the degradation products by the microorganisms. In that regard, the use of bacteria and plants for bioremediation of organic waste, especially toxic chemicals such as PCBs, is showing considerable promise. However, we know very little about the metabolic and cell processes involved in bioremediation and in the formation of secondary metabolites in such processes. There are substantial opportunities here for polymer science. For example, it has recently been shown that bacteria can convert toxic organics into poly-3-hydroxyalkanoates as the secondary metabolite.

Recommendations

- **There are many research directions in MMSE that must be pursued in order to access the sophisticated macromolecules that can solve the environments problems.** These include research exploring the possibility of using plants or microbes to synthesize technologically useful macromolecules. At the same time, we need research on synthesis and process in of macromolecules in water and carbon dioxide as opposed to organic solvents. The rapidly increasing sophistication in macromolecular architecture will also provide new directions in design and synthesis of structures that are highly specific for environmental remediation and cleanup processes that are tailored for pre-programmed biodegradation, or have the capacity to withstand multiple cycles of recycling.
- **We need more of a new breed of researcher.** Graduate and undergraduate education as it pertains to macromolecular science and the environment needs to become increasingly interdisciplinary, at the triple point between chemistry, engineering, and biological sciences. In addition, it is essential that the "traditional" students become acquainted with environmental issues. This could be accomplished by a number of means, including formal courses that integrate MMSE, biotechnology and polymer ecology, interdisciplinary postdoctoral fellowships, seminars, and even formal minors in environmental science, as well as education of professors through workshops and short courses.

- **K-12 education (and education of their parents) should be geared to allaying public misperceptions about macromolecules and the environment.** There is a need to address public misperceptions (e.g., the “paper or plastic?” controversy) through K-12 education. Possible mechanisms include highly leveraged activities such as workshops for teachers, widely distributed CD-ROMs, information on videos, and even biodegradation “kits” where children can experience, first-hand, biodegradation. In addition to educating in the schools, there is a need to have greater public awareness of problems relating to the environmental aspects of plastics. For this, members of the polymer community should be encouraged to give lectures to citizen groups and to distribute multimedia material to them. There is also a need for those in political office to be adequately informed so as to guide their formulation of legislation. The polymer community should be active in efforts to provide them with information.
- **How do we encourage looking at polymer/environment issues from a systems point of view?** It is clear that , in addition to the scientific drivers, other discipline such as economics, sociology, public policy, and law become important when considering environmental issues. Such interdependency argues for multidisciplinary centers, or for a “university without walls.” Finally, biotechnology must be brought into the polymer mainstream, either by education or through other infrastructure mechanisms.

INNOVATION IN POLYMER PROCESSING

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Summary

The final properties of polymeric materials depend crucially on processing history, that is on the temperatures, solvents, fields, and especially flows to which materials have been subjected. Furthermore, processability itself is a key material property in many applications. The great increase in available polymer architectures made possible by recent synthetic advances requires a rational design approach to processing in order to take full advantage of the new diversity in structures. This new synthetic control can also be used to generate appropriate model polymers. These model polymers can be combined with recent improvements in experimental tools for in-situ study of microstructure development in macromolecular materials under processing conditions. This is necessary to discover how processing of polymeric materials generates morphology and specific end-use properties, and what are the connections between polymer architecture and flow behavior, with an emphasis on realistic processing flows and predictive modeling of material behavior in these flows. Developing such a science base will be especially important for exploiting the new emerging classes of self-assembled supramolecular nanostructures, which are particularly sensitive to processing conditions because of the mesoscopic length scales and non-covalent nature of the interactions of such molecules. In addition, innovative polymer processing techniques are needed for improved control of the structure of thin films; for instance, external electric, magnetic or substrate fields can be applied to macromolecular materials to achieve microscale and nanoscale patterning for diverse applications (electronic or optical devices, barrier materials, cell/electronic interfaces).

Stopping the Bubble's Dance

Plastic film is mostly an unnoticed commonplace in our lives, serving as wrapping for everything from farm-fresh vegetables to disposable diapers. The majority of that film is made by a process called film-blowing, which takes advantage of the special flow properties of molten polymers.

Film-blowing is a continuous-feed process in which a thin-walled molten cylinder of plastic is extruded through a narrow circular die gap to form a molten bubble of polymer many feet tall. The cylindrical bubble is cooled by airflows, freezing several feet above the die into a solid film, which is pulled upward thereafter by a set of rollers and wound onto rolls. The molten film is 'drawn down' by a factor of about 50, made thinner as it is pulled upwards under tension by the takeup mechanism.

When this process works, it works wonderfully well, producing thin strong plastic film of uniform thickness, high clarity, at a high production rate and at low cost. But plastic film being the low-cost material that it is, and with the world-wide annual production of polyethylene blown film being worth about \$10B, there is always an incentive to produce thinner film at a higher rate. This would lower materials and production costs.

Unfortunately, when film producers try to run their equipment at too high a rate, or draw down the film too much, a scientifically delightful and technologically annoying phenomenon ruins the process: the steady, uniform bubble flow becomes unstable. Depending on operating conditions, the formerly stable bubble begins to perform one of a variety of slow, sinuous, periodic "dances", bulging



An unstable blown-film bubble, caught in the act.

first this way, then that way, then back again. These dances, while fascinating to watch, lead to an unusable film, which has frozen-in distorted shapes and thickness variations.

Similar hydrodynamic instabilities have been studied by fluid mechanics experts, and some rough guidelines can be guessed at for the conditions for stability of such drawing-down, stretching flows. The so-called non-Newtonian flow properties of the polymer melt can either promote or suppress the instabilities. In particular, a polymer melt that is “strain-hardening” — becoming more viscous, more resistant to thinning down under tension, at higher thinning rates — is expected to help to stabilize the flow. This strain-hardening behavior is expected to help keep thickness variations of the molten film, which arise from perturbation by the turbulent cooling air, from growing larger.

To design a polymer for better “operability”, then, it remains to say something about how to design in strain-hardening in stretching, extensional flows. Longstanding practical experience, as well as recent work on laboratory “model polymers” of well-defined architecture, gives some answers to this question. It appears that polymers with long branches can act as molecular “rubber bands” in a stretching flow; simply put, the branched polymers get caught up in the surrounding polymer melt and stretched by the flow, so that they resist further thinning of the molten film. Current industrial research in polyethylene film is focused on controlling the new generation of metallocene catalysts to produce the right amount of branched polymer architectures in commercial plastics, so as to give more strain-hardening and “operability” to these ubiquitous materials (see page 29).



A towering stable bubble of polymer film. New polymer architectures and realistic modeling will allow extremely rapid manufacturing of these films that avoid the bubble dance.

Innovation in Polymer Processing

Introduction

Essentially all polymer materials on their way from molecule to product undergo one or more processing steps (typified by such commercial processes as fiber spinning, blow molding, injection molding, extrusion, film blowing, solution casting, and reactive blending). Moreover, the final material properties (mechanical, optical, electrical, transport) can vary dramatically with processing history, that is, with the combined history of the temperature, solvent, fields, and especially flows to which the material has been subjected. The molecules in a polymeric material as synthesized by the chemist are only the beginning of the story as far as final properties are concerned, since microstructure in polymeric materials is so strongly affected by processing parameters. An increasing number of polymeric materials are compatibilized blends, the properties of which depend critically on their heterogeneous microstructure, which itself is generated by the processing flow. Indeed, the usefulness of a polymer in a given application is strongly determined by its processability and by the ability to control the microstructure during processing.

We believe that recent development of experimental tools to explore microstructure, of computational tools to simulate complex viscoelastic flows, and of growing understanding of the properties of multicomponent blends, have led to a point where an intensive research effort can lead to a predictive basis for major innovations in polymer processing and material design. The combination of increased synthetic control with an understanding of the connection between polymer architecture and final properties through processing promises an exciting new capability for rational design of polymeric materials. Indeed, the dramatic variety of new polymer structures that single-site catalysts make possible (see page 24) requires a rational design approach.

Commercial Trends

A brief summary of existing commercial polymers consumed in the U.S. reveals some important and surprising trends that must guide our recommendations for research opportunities. First, the quantity of polymers used is very large, growing at a rate faster than the GDP, approaching steel in mass, and amounting to some \$80 billion per year. Second, most of the applications of polymers are as structural and barrier materials, giving special importance to understanding their mechanical and transport properties. Third, over half of all polymers used are based on the simplest and cheapest monomer structures imaginable, namely, polyolefins. Predictions in the 1970s that higher-cost monomers used in engineering plastics would have a dominant market share by the 1990s have not come true.

While costly plastics for high technology applications have grown substantially by displacing non-plastic materials, the low cost and continuing improvements in properties of polyolefins have enabled them to maintain their market share and even to displace engineering plastics from some market segments. There are very substantial barriers to

the introduction of new monomers into wide commercial use. Indeed, the demand for polymers probably would not have grown nearly so fast if only more expensive polymers were available for use in new markets.

The improvement in properties of commodity polymers such as polyolefins came about in two basic and related ways: first, through developments in catalysis that offered improved control over polymer structure (i.e. comonomer content and macromolecular architecture), and second, through improvements in processing technology, mostly achieved through an "Edisonian" approach. Now, the sheer number of new polyolefin architectures means that continuing to design processing methods empirically threatens to negate the economic advantage conferred by their low-cost monomers. Advances in our understanding of polymer dynamics and the relationships between processing, structure, and polymer properties will enable a rational design of processing conditions and methods and produce large cost savings and improvements in material properties.

Experimental and theoretical insight into the dynamics of conformational relaxation, as well as the distortion and relaxation of phase-separated structures or nanoscale order provides the scientific foundation for designing macromolecules for enhanced processability, and the development of processing methods to achieve desired properties. Recent advances in synthetic capabilities combine with the development of powerful new methods to model, simulate, and experimentally observe dynamics on the molecular, mesoscopic, and microscopic scales. This progress opens exciting new opportunities for scientific discoveries in this dynamic and relevant field.

Processing Polymers with New Architectures

Now, there is a broad push across the polymer industry to commercialize a new generation of metallocene-catalyzed polyolefins. These catalysts make possible a new spectrum of materials, and a new degree of control of polymer architecture (i.e., comonomer content and placement, and chain length and location of long branches). This control can in principle be used to design the desired balance of mechanical and rheological properties for a given application, if the scientific understanding of the relation between molecular architecture and final properties exists --- and this relation depends crucially on understanding how processing affects final structure. The large variation of final properties with processing history, and the increased control of polyolefin architecture, both point to a critical need to supply the science base connecting molecular architecture to final properties through processing. To date there have been few fundamental investigations of the interplay of molecular architecture and applied flow in determining the dynamics of structure development in semicrystalline polymers. As both ease of processing and final properties are equally important attributes of the polymer, understanding is needed of both the melt rheology and the origin of final properties through molecular architecture and processing.

Some important progress has been made in recent years to understand the flow behavior of branched polymers of increasingly complex architecture, beginning with star polymers and progressing to multiply-branched structures and their blends. The most serious knowledge gap here is in the origin of the mechanical properties of semicrys-

talline polymers, and their dependence on flow history and polymer architecture. There was extensive research on semicrystalline polymers in the 1970s, but without an emphasis on the strong effect of flow, which can both greatly affect orientation of crystalline lamellae and change crystallization rates by orders of magnitude. There is a new opportunity to establish the molecular basis of these phenomena because polymers can now be prepared with uniform comonomer content and distribution that have relatively well-defined molecular weight and content of long-chain branches. Species of different length or branch content can be selectively labeled with deuterium to enable monitoring of their specific role in the dynamics of the whole system using in-situ infrared dichroism and neutron scattering.

At the same time, recent advances have dramatically improved the time-resolution and sensitivity of a whole arsenal of relevant experimental methods. Neutron scattering with time resolution of several tens of seconds, X-ray and light scattering on time intervals of several milliseconds, and polarimetry measurements on time scales of several microseconds can all be applied in situ, during flow and subsequent solidification. Thus, we now have both the synthetic capability to make appropriate model polymers and the experimental techniques to study the behavior of these materials in flow. The path is open to develop the scientific understanding of the combined effects of polymer architecture and processing on microstructure that is needed for control of material properties in semicrystalline polymers.

Multiphase Polymer Alloys

The next most prevalent class of polymer materials, which are higher value materials than simple polyolefins, are alloys of two immiscible polymers. These are typically "compatibilized blends" consisting of micron to sub-micron scale droplets of one polymer in another. Such materials can be thought of as composites in the sense that their properties are not some simple average of those of the constituents, but depend crucially on the microstructure. The most common examples are rubber-toughened glassy polymers, used to produce materials that resist high-speed impact damage.

The "compatibilization" is often provided by copolymers, either added as a third component, or produced during a mixing flow by reactive blending. The copolymers play several roles, helping to strengthen the interfaces between the droplets and the matrix, promoting break-up of the minority component into a fine dispersion and preventing coalescence of the dispersion once formed. Since development of new monomers is often prohibitively expensive, such blends afford a compelling way of generating new materials; and since nearly all pairs of polymers are immiscible at any reasonable molecular weight, the generation of compatibilized blends by processing is a generic problem. Nonetheless, the existing commercial blends are to a large extent the product of an empirical approach, rather than rationally designed materials.

The dynamical steady state under reactive blending and processing flow conditions, which leads to the morphologies present in the final material, and hence its unique final properties, has not been the subject of rigorous scientific study. And yet, the past decade has seen the emergence of powerful new experimental and theoretical tools that

could reveal much about the principles that govern the development of blend microstructure. The same issues apply to the connections between the morphology/ interfacial chemistry of the blend and its final mechanical properties. Progress has been made to understand some pieces of the puzzle, for example the rules for strengthening the interface between two glassy immiscible polymers with copolymers. The related rules for strengthening interfaces involving semicrystalline polyolefins however are of utmost importance given the developments noted above; these remain undiscovered but are now accessible using similar methods. A battery of experiments on "blends in progress" in well controlled flow fields would reveal much fundamental science but at the same time would help write the rules for developing new compatibilized blends. Likewise, new techniques for measuring the interaction parameter between immiscible polymers (e.g from the interfacial widths inferred from various scattering probe methods) would greatly aid in the design of such blends.

The reaction-induced formation of copolymers at phase boundaries can lead to large decreases in interfacial tension; in fact it is now clear that these decreases can be large enough to drive the tension of a flat interface negative leading it to become unstable, much like the instabilities that lead to the formation of oil-surfactant-water microemulsions. The resulting nanometer-scale blend morphologies, and properties that would result from these, should be explored. Investigations of the modes of these instabilities and their relation to the final morphology should prove fruitful. It seems likely that new connections between the physics of complex fluids and polymer science will develop as a result.

It has been long thought impossible to form well dispersed blends of inorganic and polymer materials on a nanometer scale, because of the supposed inherent thermodynamic instability of these materials. However recent experiments have shown that the conventional wisdom is wrong, at least in regard to organically modified layered silicates that can be produced very cheaply from clays. Such silicates have negatively charged layers that are charge compensated by organic cations. These organic cations can be thought of as the compatibilizer for these mixtures. A large number (but not all) polymers will intercalate between these layers in the melt to form layered structures with silicate layer spacings on the order of 3 to 5 nm or more. Fascinating questions about the science of these nanocomposites arise: Why do the polymers, which adopt a random coil structure in the bulk melt for entropic reasons, squeeze themselves into 2D pancakes between the silicate layers? Why is the motion of these polymers not significantly impeded by the much stiffer silicate layers? What new properties, e.g. mechanical (elastic and fracture), transport (molecules and ions) and rheological (flow), can one achieve with these layered polymer silicate systems? The prospect for low cost of both raw materials and processing should spark strong industrial interest in the answers to these questions.

Predictive Modeling of Processing Flows

The design of processing equipment itself is a major industrial undertaking. Each year in the U.S., for example, roughly 10,000 new designs for injection molds are made, in a trial-and-error process that involves 3-4 iterations at a total cost of roughly \$100,000

per design. The reason such molds cannot be designed more precisely is that adequate viscoelastic models of polymer rheology in complex flows, and their robust implementation in numerical computational schemes, are not in place. This represents an interdisciplinary challenge to the communities working on polymers, non-Newtonian fluid mechanics, and large-scale computing, which would have substantial economic returns.

If progress were made on this front, it would have consequences in a broad range of existing processing flows, including the origin of instabilities in extrusion, blown-film, and fiber-spinning flows that presently limit processing rates. If the origin of these instabilities and its relation to the flow properties of the polymer melts were better understood, and the connection between the polymer architecture, flow-induced changes in polymer structure and processing geometries were in hand, then the increased architectural control afforded by the new generation of catalysts could be used in conjunction with the predictive design of processing systems to allow control of end-use properties, as well as the realization of optimal processing rates. Because the economic advantage in such commodity polymers can depend on increments in performance or material usage, and the total market value is so large, the reward for improved processability would be great. Perhaps even more important to the long-term health of the U.S. polymer industry is the development of new high valued-added applications for polymeric materials. Such applications will require a level of predictability and reproducibility in physical properties and features of end-use products such as shape, that can best be achieved via a science-based and predictive approach to process and materials design.

A predictive approach for the design of processing schemes is an achievable goal with a modest but sustained level of support for the required basic research. The objective of predictive modeling of processing flows requires a commitment to research on three fronts: (1) characterization using newly developed experimental tools of the microstructure of polymer materials (including miscible and immiscible blends, semi-crystalline materials, branched and unbranched polymers) in complex flow geometries characteristic of processing systems; (2) models for the behavior of the same classes of materials and flow conditions, which must predict the material structure/morphology as well as velocities, pressures and stresses; and (3) computational techniques based upon these models for three-dimensional time-dependent flows at high shear or extension rates. These three fronts comprise a profound extension beyond the domain of conventional rheology, which studies a material in the simple well-characterized flows of a rheometer. Progress on these fronts will require an interdisciplinary, long-term approach to fundamental research involving polymer scientists, fluid dynamicists and computational scientists (with experience in numerical techniques for large, nonlinear systems).

Such integrated activities in this area of research are currently supported strongly in various European countries, and are also catalyzed by cooperative multinational research initiatives of the European Union in collaboration with polymer producers there. This represents an important challenge to the future competitiveness of the U.S. polymer industry that is currently being ignored.

Broader Definition of Processing

We can broaden our notion of processing away from conventional, commercial processing techniques, to encompass new ways that polymer morphology and hence properties can be controlled by the dynamical history to which the polymer has been subjected. This dynamical history may involve the application of various “fields” other than (or in addition to) flow to the material, including surface alignment, electric or magnetic fields, exposure to solvents, or novel flow geometries. Just as conventional processing gives wide variation in properties with an existing slate of monomers, so we expect that novel processing has the potential to generate qualitatively new and useful morphologies. The following are three illustrative examples:

Supercritical fluid swelling Some exciting work has begun in several groups to swell solid polymers with supercritical fluids, to introduce new monomers, nanoparticles, or other additive chemistry into surface layers. These foreign molecules can be trapped in the surface, crosslinked, or subjected to other chemistries, thus affording a versatile way to change the surface wetting, optical, or transport properties of a wide range of polymeric materials.

Structured thin films Thin films of polymers with novel optical or transport properties play an important role in a variety of technologies which range from organic light emitting diodes (LEDs) to transistors, lasers, or membranes. In many high-value-added technological applications the polymer serves an active component where it might be electrically active or it might serve as a host in which nano size particles are dispersed. There exists a variety of innovative ways to fabricate such thin polymer films of controlled microstructures (size, shape and distribution of pores, composition variation, monomeric alignment, etc). These include application of surface aligning fields, electric or magnetic fields, in combination with spreading or flow history, to achieve the desired microstructure.

Controlled flow geometries Simple oil-water-surfactant emulsions show surprising dynamical effects in controlled uniform shear flows. In recent experiments, a polydisperse droplet emulsion is made monodisperse enough by such a flow that the droplets stack in a crystalline array; the resulting sample actually Bragg-scatters light. This suggests a “finishing step” to be applied to compatibilized blends once preliminary mixing has taken place in a conventional mixer (where the applied flow is heterogeneous), in which uniformity in size of droplets is achieved by a uniform shear flow. This approach may provide a new degree of morphology control, and result in novel mechanical or optical properties.

Processing Supramolecular Systems

Recent progress in organic synthesis of supramolecular structures opens the door to a new class of supramolecular systems, in which molecules are designed to self-assemble into larger “polymeric” structures, which are held together by non-covalent interactions (see report on **novel macromolecular structures**). Fabricating products from these systems presents new technological and scientific challenges. These mate-

rials will exhibit unusual rheological properties because of the sensitivity to deformation of the self-assembly itself; such behavior is well known in self-assembling surfactant phases and solutions of associating polymer. The quiescent supramolecular structure may either be enhanced or destroyed by flow, or new flow-induced structures may emerge. Processing of these materials may thus require an additional "healing" step where the flow-induced microstructure is converted into the desired microstructure; or, some applications may be better served by the flow-induced morphology. In either case, processing issues should be considered at the beginning of the molecular design.

Conventional rheological tools for characterizing ordinary polymers may not be optimal for studying supramolecular materials. More sensitive devices with the ability of resolving very low stress levels may be needed. The development of probes of structure for monitoring structural changes during flow will be crucial. Novel design of "miniature rheometers" (e.g., employing diffusing-wave spectroscopy as a probe of thermal motion of small amounts of added colloid) will be important, because supramolecular materials are often the result of elaborate syntheses, and are initially only available in sub-gram quantities, at which point some rheological screening may be useful to select promising materials for further development.

Recommendations

- Innovative fabrication of macromolecular products, including future self-assembling and supramolecular systems, will require the support of research in a number of areas. It is critical to support work on a rational modeling approach to processing which also explores microstructure development under flow conditions. This type of work will allow us to take full advantage of the new diversity in macromolecular structure. Research targeting innovative polymer processing techniques for thin films, foams, and fibers is also extremely important, possibly involving the use of external electric/magnetic or substrate fields. Research on methods to achieve rapid microscale and nanoscale patterning is also of great importance for innovation.
- Because polymer processing is an interdisciplinary field of research, combining aspects of fluid mechanics, rheology, polymer chemistry, materials science, and condensed matter physics, there is no natural source within conventional academic departments for appropriately trained students to supply industrial needs. Within materials science departments, for example, fluid mechanics is not typically a part of the standard curriculum; within chemical engineering departments, heterogeneous solids and morphology-property relations are often not emphasized. Research in this area is crucial to underscore the importance of processing within polymer science and also to create a knowledge base in manufacturing and contribute to the training of needed professionals in this area.
- To foster communication of research results into the industrial setting and to give young academic researchers a close view of the nature and variety of applied problems faced by industrial polymer producers, some new mechanisms are needed for interaction between researchers and companies. One approach might be to emphasize "contin-

uing education” of industrial staff in the form of short courses. These short courses could communicate the emerging academic research picture to industry, at the same time providing much-needed informal contact between industry and young faculty struggling to define their research programs. The expenses associated with taking the short courses “on the road” could be borne by any companies interested in reaping the benefits of this approach to continuing education.

TRANSLATING MACROMOLECULAR DISCOVERIES INTO TECHNOLOGIES

DISCUSSION LEADER: EDWIN L. THOMAS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

GROUP MEMBERS:

ERIC BAER, CASE WESTERN RESERVE UNIVERSITY

GORDON FEARON, DOW CORNING CORP.

MARY GALVIN, LUCENT TECHNOLOGIES

DAVID MARTIN, UNIVERSITY OF MICHIGAN, ANN ARBOR

THOMAS SMITH, XEROX CORP.

RALPH NIELSEN, SYMYX TECHNOLOGIES

JOSEPH WIRTH, RAYCHEM CORPORATION

VALERIE SHEARES, IOWA STATE UNIVERSITY

Summary

Macromolecular science and engineering is the basis of an enormous portion of US and world industry, and new types of research as well as educational innovation are needed to translate recent developments in the field to commercial products. The industrial capabilities to pursue fundamental advances in macromolecular science and engineering have decreased substantially. Therefore, the next decade requires the involvement of NSF and other U.S. funding agencies in facilitating the transfer of newly synthesized macromolecular materials and novel polymer processing methods from their initial discovery into practical applications. Research advances are needed in macromolecular characterization and laboratory scale up methods. Furthermore, new methods are needed to screen effectively the large number of macromolecular substances being produced in order to establish which ones warrant further development.

LEDs

On a lighter note...

When we think of polymers in electronic devices, we normally expect that they will play secondary roles, e.g. providing electrical insulation for the wires or forming the “black box” that surrounds the interesting parts of the device. But polymers can do much more, and researchers are now exploring new classes of polymers that can carry electrical currents or even produce visible light when a voltage is applied. Recently it has been shown that such materials can be made to change color simply by varying the applied voltage, pointing the way to new kinds of color screens, cameras and displays.

Simple polymers like polyethylene or poly(vinyl chloride) are in fact widely used as electrical insulators, preventing passage of electrons from conducting metal wires to their surroundings. By controlling the chemical structure of the polymer, however, we can create organic semiconductors (e.g., transistors) with properties more like those of the silicon in computer chips than those of the polyethylene or poly(vinyl chloride) that insulates electrical wires. And because polymers are light in weight, flexible, and easily processed into useful shapes, they are very attractive as building blocks for all kinds of devices.

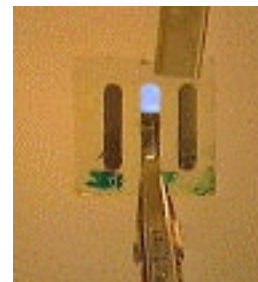
A particularly interesting device, called a light-emitting diode (LED), is shown in the figure. LEDs can be remarkably simple, consisting of a thin layer of polymer sandwiched between two electrical connectors. When a voltage is applied across the specially designed polymer layer, light is produced, and the color of the light can be varied



Voltage: 5V



Voltage: 10V



Voltage: 20V

Red light, yellow light, or blue light is produced by the same polymer exposed to different voltages.

from red to yellow to blue just by changing the voltage level.

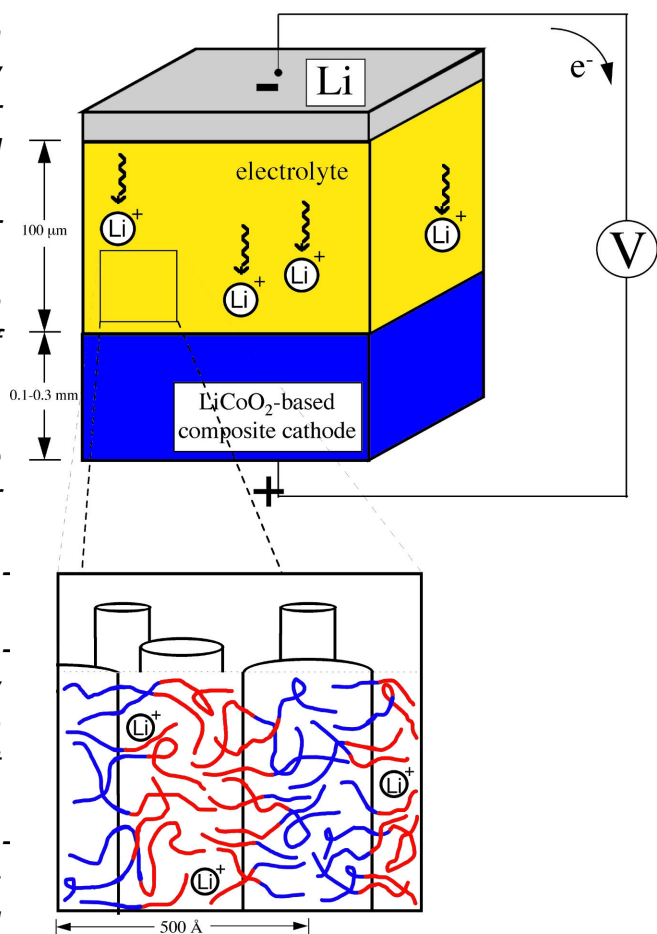
Why does this work? The key lies in using a mixture of polymers as the light-emitting layer. Because each polymer emits light of a different color, and because each “turns on” at a different applied voltage, increasing the voltage results in controlled and variable color mixing. Such polymer mixtures can be formed into regular arrays of tiny dots, each of which can be addressed individually, providing a means of forming precise color images and displays of various kinds. Such displays could be thin, lightweight, impact resistant, and perhaps even flexible, features that would allow many applications that are beyond the capabilities of current display technologies.

Powerful Polymers

We've all had to change batteries before. Whether it was the little button cell in your calculator, or the unwieldy lead-acid battery in your car, it was never convenient. Even the most advanced rechargeable batteries have to be recharged often, and any laptop owner can testify that they can be heavy to boot. Take heart--there are developments in our future which might alleviate some of these problems.

Lithium solid polymer electrolyte (SPE) batteries are being examined for applications in electric motor vehicles, portable electronics, personal communications and start-light ignition industries. The performance criteria for the applications mentioned above are extremely demanding. Why is SPE technology a prime candidate in these areas? What sets it apart from existing technologies, such as Ni-metal hydride or Ni-Cd systems? For one, lithium SPE batteries generate power superior to competing systems, and use lighter weight materials (density $\sim 1 \text{ g/cm}^3$). The result? Longer lasting batteries per unit weight. Moreover, the concept of a solid polymer electrolyte allows for an entirely solid-state device. Many current battery designs use a solvent-based liquid electrolyte which poses a leakage hazard to the environment. This risk is precluded in an SPE battery, since none of its "ingredients" flow. Lastly, polymers are generally low-cost, processable materials, offering potential long-term savings in production.

In the illustrated design, block copolymers form a novel means of solving simultaneously the electrical and mechanical requirements of an SPE battery. Block copolymers are advanta-



A lightweight polymer battery containing a block copolymer: the block copolymer self-organizes to make the battery more durable and powerful.

geous because the self-assemble, providing macroscopically solid-like behavior while preserving microscopic mobility of the polymer chains. This allows for an electrolytic membrane which is both highly conductive and mechanically robust.

Translating Macromolecular Discoveries into Technologies

Introduction

Emerging opportunities for future developments in macromolecular science and engineering have been discussed by the other focus groups at this workshop. Some of the products of these research activities have the potential to lead to dramatic benefits to society, but only if they can be translated rapidly into products. There is therefore a need to facilitate the transfer of, for example, newly synthesized macromolecular materials, processing methods, and characterization techniques from their initial discovery and development into practical applications to improve quality of life and economic competitiveness.

This need is further increased by current trends in industry over the last decade, where many large companies have been shrinking their research efforts. Strong academic-industrial ties will compensate for this to some degree. The extension of the industrial research base by coupling industry and academia is vital to the long-term health of this nation's economy.

This section of the Workshop Report identifies desirable links between academia and industry and explores ways in which these links can be nurtured and strengthened to enhance the impact that research has on society.

The Technology Transfer Interface Between Academia and Industry

People as the Link between Academia and Industry

A major component of the communication and transfer of technology between academia and industry involves the students and postdocs who are trained at universities and subsequently hired by companies. There is a need for undergraduate and postgraduate education to produce students with deep training in a discipline, but also with broader interdisciplinary experience, crossing the traditional domains such as chemistry, physics, materials science, theory, surface science, biology, electrical engineering, chemical engineering, and mechanical engineering. Such broad training will provide employees who can work well in teams, who speak the language of several disciplines, and who can effectively translate new discoveries into useful technology.

A less-emphasized mechanism linking academia and industry is the transfer of senior people. Because the current pace in industry makes it difficult for industrial researchers to undertake long-term sabbaticals at universities, shorter-term interactions need to be emphasized. These can be in the form of a mini-lecture series at a university, a short-term focused collaboration, or in the supervision of a shared student.

Industrial sabbaticals for academic researchers, or alternatively, summers spent working in industry, would aid in keeping professors connected to the state of the art

technology and help them become familiar with the patent literature (an often overlooked source for information and ideas). It would also re-acquaint them with important safety standards that too-often receive less emphasis in academia, and would reinforce the need for careful standards for documenting research and development which are crucial in an environment of industrial innovation. Such industrial sabbaticals would also improve and update the quality of career advice and professional guidance that professors are able to provide to students.

Technology as the Link between Academia and Industry

Intercommunication and exchange of ideas between academia and industry is facilitated by publications, patents, and the dissemination of research results at workshops and technical meetings. In addition, most universities have technology transfer and licensing offices, which are responsible for marketing university inventions to industry. It should be noted that the Bayh-Dole Act, which permits universities to hold the patents for federally-sponsored research, has had a major impact on how universities seek to protect and license the intellectual property that they have developed.

Another technology link between academia and industry involves the direct funding of specific research projects and contracts at universities. These take many forms; some are blanket grants or gifts to a department or a program, while others are highly focused scientist-to-scientist collaborations. No matter what the form, it is essential that the transfer of technology across this interface be as direct and as unencumbered as possible. To this end, some universities and some industries have developed standard intellectual property agreements that smooth this interface and make negotiations as efficient and timely as possible.

NSF has in place a number of programs that facilitate the technology link between academia and industry. These include programs such as the grant opportunities for academic liaison with industry (GOALI), and to some extent the faculty early career development award (CAREER).

Small Business Development as the Link between Academia and Industry

It is often the case that an invention or technology emanating from basic research at a university is at such an early stage as to be uninteresting or not sufficiently well-developed to garner the interest of large companies. It is sometimes possible to add value to the invention by additional research and development. Adding value can be as simple as producing a working prototype or a demonstration project. In other cases, one needs to make numerous measurements to test the robustness of the invention or technology. It is rare that a grant, originally for basic research, will cover the expenses of technology development.

In the past decade or so, the formation of small companies by graduate students, postdoctoral fellows, and/or professors has been an attempt to address this gap. Fueled by the small business technology transfer program (STTR), and small business innovation research (SBIR) grants, emerging companies have become a very effective means

to add value to important inventions and thereby increase the speed at which technology is transferred to society.

Recommendations

- **People as the Link.** We recommend that a workshop, survey, or some other information-gathering instrument or forum be designed and undertaken to define explicitly what industry foresees needing from academic training in macromolecular science and engineering in the coming decade or two. In light of these results, NSF may want to re-examine its training programs to ensure that the needs of industry are being adequately addressed.

We also recommend that NSF sponsor the design of new educational (nontraditional) experiments and programs aimed at industry. Ultimately paid-for by industry, such courses would be beneficial not only to students planning to enter industry but also to individuals in mid-career who seek short yet intensive exposure to the science and engineering of macromolecular systems.

We also recommend that NSF programs be created that will stimulate interactions between senior personnel in industry and academia. Such initiatives could include funding for adjunct professorships, introductions of new courses using industrial speakers and/or industrial perspectives, and co-directing thesis activities.

- **Technology as the Link.** In order to facilitate technological exchanges, we recommend that a small number of focussed workshops be held with co-sponsorship from NSF divisions and other agencies. These could also include foreign science foundations to take advantage of the considerable expertise in macromolecular science and engineering that resides in Western Europe, Eastern Europe, and Japan. Two examples of focused workshops include one on imaging and information storage and one on biomaterials and biomedical devices.

We also recommend that a project be undertaken to assemble "best practices" in the area of intellectual property agreements between industry and academia. A resource such as that would be of great utility to every university and to many industrial concerns, and would greatly speed the pace at which universities negotiate and sign research contracts with industry.

- **Small Business Development as the Link.** We recommend that NSF continue its very effective program of SBIR and STTR grants, which greatly enhance the way in which university innovations are transferred to industry for further development.

We furthermore recommend that NSF better-promote the success, impact, and effectiveness of its SBIR and STTR grants by providing vignettes of several successful businesses that owe their inception to the availability of an SBIR or STTR grant.

APPENDIX I**Letters to the Macromolecular-Related Communities, Soliciting Input**

December 1996

Dear colleagues:

Andy Lovinger of the NSF, serving as liaison for a recently formed NSF-wide working group interested in polymers, has asked me to organize a study of future directions and opportunities in polymer science and engineering. The study will include a workshop in Washington DC during the month of May and the publication of a report to NSF. Recommendations in this report could help to guide the Foundation's investment of research funds in our field over the next decade.

I am writing to solicit your thoughtful comments and suggestions on the important future directions of polymer science and engineering. In this era of shrinking resources for research, we all need to activate our imagination and prophetic powers to develop collectively a fresh vision of polymer science and engineering in the next decade. We need to ask what critical roles polymers could play in areas of science and technology that will be important to society in the next few decades. We also need to consider what new connections could be established between polymer science and other fields, and even question the very definition of a polymer in order to launch new explorations that could fall within the scope of our discipline. In thinking about the future of polymer science and engineering we also have to consider the new experimental and computation capabilities which may become available to us over the next few years. Finally, this NSF project also needs to consider the effectiveness of our current education of students and young faculty in the context of the new challenges to be faced in our field and its service to society.

It is critical for the community at large to offer its input. I therefore urge all of you to take the time to think about our future and offer your comments and suggestions. These will be considered by an organizing committee which I have convened in Washington DC February 7th to meet with NSF staff and plan the workshop. Depending on NSF funding, we may be able to invite 30 to 40 participants to attend the workshop and help prepare the final report. The participants will have to be selected to represent our community broadly and also to represent effectively the working areas identified for the workshop. Following the workshop, the organizing committee will finalize the report to NSF.

Your input would be most useful by email before February 1st, but feel free to write to me anytime before May 1st. Happy New Year

Sam Stupp

Summer 1997

Dear Colleagues:

Back in December I solicited input from you to identify future research opportunities in macromolecular science and engineering. This information was to be used in the organization of a workshop at NSF headquarters to be followed by the publication of a report. With this message, I would like to give a progress report on what has happened so far. In early February, the organizing committee (Bob Grubbs, Lynn Jelinski, Scott Milner, Sam Stupp (chair), Ned Thomas, and David Tirrell) met at NSF to organize a two-day workshop to initiate the preparation of a report to NSF. At this meeting we considered input received from members of the community as well as input from NSF staff to select the following five topics for the workshop:

1. Novel Macromolecular Structures: Synthesis and Function
Coordinators: Robert Grubbs, Samuel Stupp, Scott Milner
2. Control of Properties through Innovative Processing
Coordinators: Scott Milner, Edwin Thomas
3. Solving Environmental Problems with Macromolecular Science and Engineering
Coordinators: Lynn Jelinski, David Tirrell
4. Macromolecular Science Connections between the Physical and Biological Sciences
Coordinators: David Tirrell, Samuel Stupp, Lynn Jelinski
5. Translating Macromolecular Discoveries into Technologies
Coordinators: Edwin Thomas, Robert Grubbs, Samuel Stupp

After the February meeting, 41 participants were invited to attend the two-day workshop May 14th and 15th. The intent in this selection was to provide a balance in representation in all respects. It was a difficult process since we were obviously limited for both financial and practical reasons on the number of people we could invite. However, this workshop should be viewed as only one step in the preparation of a report to NSF. The selection of topics listed above does not identify these areas as the only ones of interest to NSF in the context of polymer science. These are simply topics selected to initiate discussion on possible future opportunities.

There is still ample time for any of you to provide more specific input to me or any member of the organizing committee, and I strongly encourage you to do that. During the recent APS and ACS meetings, I had very useful discussions with members of the community not attending the workshop.

I expect that the final report will be prepared over the next 6 to 9 months so please give us your additional input if you are interested. We will of course acknowledge your input in the final report. A participants list and titles of plenary talks will be available in my office if you wish to receive the information. Have a great summer.

Sam Stupp

APPENDIX II

List of Respondents to Messages in Appendix I

Prof. Jerome L. Ackerman	Department of Radiology, Harvard Medical School, Charlestown, MA
Prof. Robert Apfel	Yale University
Prof. Giovanni Astarita	University of Delaware/University of Naples, Italy
Dr. Norbert Bikales	Head, Europe Office, NSF
Prof. Bernhard Bluemich	Department of Macromolecular Chemistry, RWTH- Aachen
Prof. Frank D. Blum	Department of Chemistry, University of Missouri- Rolla
Prof. Paul Calvert	University of Arizona, Tucson
Prof. Gerard T. Caneba	Department of Chemical Engineering, Michigan Technological University, Houghton
Prof. Stephen H. Carr	Department of Materials Science and Engineering, Northwestern University
Prof. Stephen J. Clarson	Director, Polymer Research Center, University of Cincinnati
Prof. Benjamin Chu	Chemistry Department, SUNY, Stony Brook
Prof. Ralph H. Colby	Department of Materials Science and Engineering, Pennsylvania State University
Dr. Edmund A. Di Marzio	Polymers Division, NIST
Dr. Alan D. English	DuPont Co.
Prof. Yongli Gao	Department of Physics and Astronomy, University of Rochester
Prof. Murray Goodman	University of California, San Diego
Professor Fred Gornick	Professor Emeritus, University of Maryland
Prof. Mark Green	Polytechnic University
Dr. Peter Gregory	Editor, Advanced Materials
Prof. Eric Grulke	Chemical and Materials Engineering, University of Kentucky
Dr. Pete Halley	Department of Chemical Engineering, University of Queensland, Brisbane, Australia
Dr. Will Hawthorne	Editor, Trends in Polymer Science
Prof. Alan Heeger	Director, IPOS, University of California, Santa Barbara
Prof. Manfred Hennecke	Federal Institute for Materials Research and Testing, Berlin
Prof. Tom Horbett	Chemical Engineering Department, University of Washington
Dr. Michael Jaffe	Hoechst Celanese Co., Summit, NJ
Prof. Y. C. Jean	Chair, Chemistry Department, University of Missouri- Kansas City
Prof. Larry Katz	Visiting Professor, Rehabilitation Engineering Centre, Hong Kong Polytechnic University

Prof. Julie King	Chemical Engineering Department, Michigan Tech. University
Prof. Jeff Koberstein	Director, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs
Prof. Sonja Krause	Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY
Prof. Sam Krimm	Biophysics Research Division, University of Michigan, Ann Arbor
Prof. L. Gary Leal	University of California, Santa Barbara
Prof. Kalle Levon	Chair, Departments of Chemistry, Chemical Engineering, and Material Science, Polytechnic University
Dr. Wenguang Li	Yale University
Prof. Tim P. Lodge	Departments of Chemistry Chemical Engineering, and Material Science, University of Minnesota
Prof. Lon Mathias	Department of Polymer Science, University of Southern Mississippi, Hattiesburg
Prof. Phillip B. Messersmith	Department of Restorative Dentistry, University of Illinois at Chicago
Dr. A. B. Metzner	University of Delaware
Prof. W. E. Moerner	Department of Chemistry, UCSD, La Jolla, CA
Dr. Brian G. Morin	Milliken Research Corporation, Spartanburg, SC
Prof. Jeffrey S. Moore	Department of Chemistry, University of Illinois at Urbana-Champaign
Prof. Doug Neckers	Bowling Green State University
Prof. Joshua U. Otaigbe	Department of Materials Science and Engineering, Iowa State University
Professor Eli M. Pearce	Director, Polymer Research Institute, Polytechnic University
Prof. George Phillis	Department of Physics, Worcester Polytechnic Institute
Prof. Lisa Pruitt	Department of Mechanical Engineering, University of California, Berkeley
Prof. John Rabolt	Chair, Department of Materials Science, University of Delaware
Prof. Heidi R. Ries	Acting Director, Center for Materials Research, Norfolk State University
Prof. Subhash Risbud	University of California, Davis
Prof. David Royle	Massachusetts Institute of Technology
Prof. Michael Rubinstein	Department of Chemistry, University of North Carolina at Chapel Hill
Prof. Tom Russell	Polymer Science and Engineering Dept., University of Massachusetts, Amherst
Prof. Edward T. Samulski	Chair, Department of Chemistry, University of North Carolina at Chapel Hill
Prof. Dan Sandman	University of Massachusetts at Lowell
Dr. Nicholas Schlotter	SCCS Technologies, Colts Neck, NJ

Prof. Ken Schweizer	Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign
Prof. Kenneth R. Shull	Department of Materials Science and Engineering, Northwestern University
Prof. Richard Stein	Department of Polymer Science and Engineering, University of Massachusetts
Prof. Dotsevi Y. Sogah	Department of Chemistry, Cornell University
Prof. Leslie Sperling	Materials Research Center, Lehigh University, Bethlehem, PA
Prof. Nobuyuki Takahashi	Hokkaido University of Education, Hakodate
Dr. Vic Thalacker	3M Co., St. Paul, MN
Gary Wedlake	
Dr. Jeffrey A. Wesson	Medical College of Wisconsin, Milwaukee
Prof. George Whitesides	Department of Chemistry, Harvard University
Prof. Ward O. Winer	Chair, School of Mechanical Engineering, Georgia Institute of Technology
Prof. H. Henning Winter	Department of Chemical Engineering, University of Massachusetts, Amherst
Leonore Witchey-Lakshmanan	Schering-Plough Research Institute, Kenilworth, NJ
Prof. Thomas A. Witten	Department of Physics, University of Chicago
Prof. Fred Wudl	Department of Chemistry, University of California, Santa Barbara
Prof. Arun Yethiraj	Department of Chemistry, University of Wisconsin, Madison

