# Polymer Science and Engineering: Challenges, Needs, and Opportunities (1981)

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# POLYMER SCIENCE AND ENGINEERING:

## CHALLENGES, NEEDS, AND OPPORTUNITIES

AD HOC PANEL ON POLYMER SCIENCE AND ENGINEERING
COMMITTEE ON CHEMICAL SCIENCES
ASSEMBLY OF MATHEMATICAL AND PHYSICAL SCIENCES
NATIONAL RESEARCH COUNCIL

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Lord Todd, President of the Royal Society of London, during a recent interview was asked the question, "What do you think has been chemistry's biggest contribution to science, to society?"

His answer was, in part, "It's not easy to choose one thing alone. Some would say 'Look at the marvelous medical advances, the antibiotics and all those drugs that have come about. What a tremendous difference they have made to our lives.' That is one area where chemistry has had very big effects.

"I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has had the biggest effect on everyday life. The world would be a totally different place without artificial fibers, plastics, elastomers, etc. Even in the field of electronics, what would you do without insulation? And there you come back to polymers again."

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## AD HOC PANEL ON POLYMER SCIENCE AND ENGINEERING

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# I. INTRODUCTION

## A. BACKGROUND AND OVERVIEW OF THE STUDY

Polymer science and engineering deal with the chemistry, the molecular structure and physical properties, the applications and processing into useful forms, and the biological significance of materials consisting of large molecules--macromolecules--each containing from thousands to millions of atoms. Typically, the atoms are chemically linked in a sequence of repeating structural units derived from certain varieties of small molecules (monomers). The underlying structure of a polymeric molecule is thus a long chain that, in some polymers, may coil, branch, be chemically cross-linked to other chains, or take part in other orders of structural complexity.

The physical and chemical interactions among the atoms of a polymer are governed by the same laws that describe systems of small molecules, but extreme molecular size introduces a new realm of properties. The diversity of macromolecular structures represented by a given chemical composition increases enormously with the number of monomeric units present, and statistical considerations must enter the description of even the simplest polymer chain. The time scale for molecular adjustment to external stress is broadened vastly, leading to viscoelastic behavior not encountered with ordinary liquids and crystalline solids. The extreme length of macromolecular chains inhibits or even precludes their crystallization, so that diverse stable solid states occur that may be rubbery, glassy, or semicrystalline. New combinations of properties emerge, such as rubbery elasticity and strength, combined with flexibility and optical clarity. Fabrication methods available with polymeric materials facilitate their shaping into desired forms. Manmade polymers and their fabrication into finished products have become the basis of a major industry worldwide, which in the United States adds some $90 billion per year of value added by manufacture.

Life itself is grounded in the characteristics of large molecules. The remarkable adaptations of collagen and cellulose to structural functions, the specificity and efficiency of enzymes as catalysts, the subtle binding and release of oxygen by hemoglobin and myoglobin, and, ultimately, the encoding and manipulation of specific genetic information by the nucleic acids all have their origins in the polymeric nature of the molecules involved.

Polymer research is thus essentially interdisciplinary, with major contributions from chemistry, physics, several branches of engineering, biomedical science, and molecular biology. Unfortunately, this circumstance has not been conducive to support in many U.S. universities and research-funding agencies geared to traditional disciplines, and educational opportunities in basic polymer science have been neglected accordingly.

The study leading to this report was organized at the request of the National Science Foundation by an ad hoc panel of polymer research investigators commissioned jointly by the Committee on Chemical Sciences (CCS) and the Solid State Sciences Committee (SSSC) of the National Research Council, under the aegis of CCS. Its major purpose is to assess needs and opportunities in basic research pertaining to polymer science and engineering, particularly in the United States. No survey of this character has been conducted recently. Recent progress is reviewed as a background for assessing future needs. Promising areas of polymer research are highlighted, although the panel recognizes clearly the importance of major breakthroughs that are seldom foreseen but are fostered by a climate of vigorous encouragement of basic research by capable investigators. The report includes discussion of problems in securing the depth and variety of research and educational support needed to maintain leadership in this interdisciplinary field, which is not only of intense scientific and engineering interest but is of vital importance to the economy.

Section B of this chapter summarizes general conclusions and recommendations reached in this study and documented in subsequent chapters. Section C summarizes highlights of those chapters. Section D presents a brief historical survey of the field.

Chapter II is devoted to the main scientific and engineering content of the report, a state-of-the-art review of the field and of outstanding unsolved problems (as the Panel members perceive them). Four major areas are there reviewed: Part A, Polymer Chemistry and Synthesis; Part B, Physics and Physical Properties; Part C, Processing and Engineering Properties; Part D, Polymers of Biological and Medical Importance.

Chapter III describes the economic importance of polymers and the relevance of basic polymer research to meeting various categories of national needs.

Chapter IV addresses how polymer research can be supported most effectively, involving as it does the long-range interests of the universities, industry, and the public represented by the federal government.

Chapter V describes the related problem of securing a sounder base for education in polymer science and engineering, adequate to fulfill the perceived need, and of relating this interdisciplinary field more productively to the disciplines traditionally represented in the academic curriculum.

## B. GENERAL CONCLUSIONS AND RECOMMENDATIONS

### General Conclusions

- Polymers are essential in fulfilling a broad range of national needs, present and prospective, in such categories as energy, transportation, construction, agriculture and food processing, medicine, and national defense.

- The history of polymer science and engineering is replete with unforeseen discoveries of major consequence, and the future of the field is bright with promise. For example, the recent breakthroughs in understanding the structure and *in vivo* synthesis of biopolymers still have to make their major impact on synthetic polymers, and the theory and application of composite materials based on polymers are still in their infancy.

- Consideration of the various research opportunities indicates that certain areas of emphasis recur with some frequency. These include the synthesis of new materials that are usable in specially demanding environments; accelerated tests that can reliably predict long-term behavior; materials of extraordinary strength or strength-to-weight ratios; mechanisms of chemical degradation; theory underlying failure phenomena; multiple-phase systems, such as crystalline polymers, blends, and composites; and the three-dimensional structure of biopolymers.

- For a variety of reasons, some of them historic, university research in polymer science and engineering has been lagging in the United States compared with other advanced countries and in comparison with other disciplines. Also, support of long-term basic research in polymer science and engineering by American industry in recent years appears to be declining. These trends, if not offset, can be detrimental to future U.S. leadership in new ideas and new products.

- Federal support of basic polymer research at universities is fragmentary and in short supply, except perhaps in biopolymers and biomedical science. Although considerable academic interest exists, it is concentrated mainly in engineering colleges and a small number of materials science and polymer departments. Thus, there is an insufficiency of polymer-oriented faculty members--and consequently a lack of polymer teaching--in the chemistry and physics departments of most of the leading universities.

- Polymer science is particularly well suited to pioneer cooperative programs involving universities, government, and industry. Several such programs are already active.

## General Recommendations

- In view of the vitality and promising future of polymer science and engineering and the strong relevance to national needs, the Panel recommends increased commitment to basic polymer studies by the research funding agencies. The federal agencies should examine their programs in the light of this report to ensure that support of polymer science and engineering research is commensurate with agency goals and the major needs and opportunities that exist in this field.

- Further imaginative new programs should be sought to stimulate interest and provide funding in polymer research in order to enhance diversification and quality in this field, and to attract larger numbers of the more creative academic faculty and students. These programs should include various forms of cooperation involving universities, industry, and government, such as already exist in a few universities.

- Universities that are now lacking educational or research programs in polymer-related subjects should seriously consider the intellectual opportunities this field affords. It is essential that education in polymer science and engineering, related to the traditional disciplines, be more widely available in many more universities.

## C. SUMMARY HIGHLIGHTS

Many exciting areas for further research in polymer science and engineering are described in the body of this report. The primary purpose is to demonstrate the wide range of promising opportunities and to encourage new research in these and other opportune directions. This section illustrates some of the many opportunities and needs discussed in the following chapters by highlighting some major directions and citing representative specific examples.

## STATE OF THE ART AND RESEARCH OPPORTUNITIES (Chapter II)

Polymer Chemistry and Synthesis. The thrust of present-day polymer research is greatly influenced by the increased cost of energy and materials as well as by environmental considerations. Many specific research programs are motivated by these forces. To illustrate these opportunities and needs, a number of selected areas of research, more fully described in Chapter II, Part A, are listed below:

- New synthetic monomers derived from fossil sources or obtained by biological conversion.

- Polymers that possess increased durability and fill novel functions, e.g., unusually heat-stable polyimides and polybenzoxazoles, and superstrong fibers.
- Control of monomer sequencing through novel initiator chemistry, and synthesis and characterization of polymers and copolymers of precisely known structure and high purity for systematic structure-property studies.
- Improved polymer stabilization accomplished by attaching chemical stabilizer moieties to the chains either by grafting or by use of comonomers carrying the stabilizer group.

Physics and Physical Properties. An abundance of opportunities exists to improve understanding of the various condensed states of polymers, i.e., amorphous, crystalline, mesomorphic, solutions, blends, composites, and interfaces. The few examples below are only illustrative of the very many fundamental problems where progress to date promises fruitful areas for further advances.

- A much deeper understanding of the glassy state is needed, on both a molecular and an observational level, in phenomena such as crazing, yielding, diffusion of small molecules, and aging.
- Because of their profound effect on physical properties, further study is needed of such crystal phenomena as morphology, structure, nucleation, growth, molecular connection among crystals, nature of the fold surface, and deformation.
- The electrical properties of polymers (conduction, piezoelectricity, etc.) combined with other properties offer unique opportunities, that present many important research challenges.
- The tensile modulus and strength of polymers may be enhanced substantially by orientation, as in mesophases, by extrusion, and by shear. The fundamentals of such processes and systems (phase relations, effects of flow, effects of external fields, etc.) call for further study.
- The interface between a polymer and the surrounding medium can be studied by modern experimental methods, with major implications in problems of bonding, adhesion, coatings, etc.
- The achievement of new properties by blending, alloying, and reinforcing polymers offers many exciting opportunities.

Processing and Engineering Properties. Research on processing and engineering properties is an essential and integral part of polymer-related studies. Polymers, perhaps more than other materials, such as metals and ceramics, call for the interaction of many scientific and engineering disciplines. Among technology areas where specific research opportunities exist are the following:

- The enormous growth in computational power affords new opportunities for modeling the processing and performance of polymeric materials, taking account of the complexities of nonlinear behavior, orientation during flow, and chemical effects. Valid constitutive equations describing polymer behavior deserve early attention.

- Composite structures based on inorganic and organic fibers continue to evolve unique and exciting materials for high-technology applications, e.g., aircraft frame members and structural components of automobiles. Multilayer films are needed for a wide variety of applications, including packaging, fuel cell membranes, desalination cells, and solar hydrogen-generating cells.

- Microlithographic polymers (resists) sensitive to X-rays or ion beams are essential to processes for micromanufacturing electronic and optical systems used in computers, in communications, and in teaching and business machines.

- Polymeric systems are possible that will effectively couple or convert thermal, electrical, light (solar), mechanical, and, perhaps, other forms of energy.

- Techniques can be developed to generate unique properties through process-induced structures.

- Methodology is needed for prediction of service life. Attention should be directed at combined effects of multiple environmental variables and at nondestructive evaluation.

- New and diverse systems for polymer processing and fabrication are essential. Reaction-injection molding is a recent, energy-efficient method that invokes theory and practice of rapid mixing to achieve a new realm of processing capability.

Polymers of Biological and Biomedical Importance. Enormous strides have been made in the field of biopolymers since the discovery of the DNA double-helical structure in 1953. This was followed by numerous advances: the determination of the detailed sequence structure of nucleic acids and proteins, the recognition of nucleic acids as the carriers of heredity, and the solid-state synthesis of sizable protein molecules. Further progress has continued in many related areas, including such vital aspects as the three-dimensional structure of enzymes, its connection to binding of specific molecules, and thus its catalytic function. Following is a small sampling of the many promising possibilities for further work in this rapidly progressing science:

- New and improved methods for synthesis of biopolymers, solid-state synthesis of peptides and nucleic acids, and synthesis of oligosaccharides.
- Further advances in methods for sequencing and determination of three-dimensional structures by diffraction techniques (X-ray and neutron) and spectroscopy of many kinds (magnetic resonance, Raman, Fourier-transform infrared, vacuum ultraviolet).
- Theory of conformation of proteins and nucleic acids, with the aim of predicting the folding into three-dimensional structures.
- Synthesis of new biomedical polymers and polymeric drugs, and physiological action of such materials.
- Macromolecular interactions, especially as related to recognition processes.

## POLYMER RESEARCH AND NATIONAL NEEDS (Chapter III)

The production of polymers on a volume basis now exceeds that of steel, and its growth rate (8.5 percent per year) is four times that of steel and nonferrous metals. Polymer industries add $90 billion per year of value added by manufacture and employ 3.4 million people. Polymers also have a high-technology aspect that will be increasingly important in the future and may have a critical impact on fulfilling national needs. Examples of polymer-related research emphasis in selected categories of national needs are briefly outlined below:

Material Sources and Conservation. Although only a small amount of the oil consumed in the United States is converted to polymers, significant advances in conservation appear possible through production of monomers from coal or biological sources, through design of more durable polymeric materials to reduce the frequency of replacement, and through development of the technology of recyclable polymers.

Transportation. Reducing weight in airplanes and automobiles by replacing metals with high-performance, light-weight polymeric composites could translate into enormous savings in fuel. Research needs encompass the development of new matrix polymers, fibers, and adhesives for composites, as well as new fabrication techniques, including reactive systems that polymerize in the mold.

Construction. Polymers have been predicted to emerge as the major building materials of the twenty-first century. Growing applications include insulation, piping, roofing, and siding, as well as use in solar heating systems. Among outstanding research needs are the prediction of properties in long-term performance and the tailoring of polymeric materials for specific uses. Adhesion, reinforcement, stabilization, and flammability are important areas for study.

Agriculture and Food Production. Continued and growing impact of polymers is anticipated in agriculture and food production. A few examples are the controlled release of agricultural chemicals, the use of polymeric pipes and films for irrigation and water control, and the use of polymers in food packaging and preservation. Permeation through polymers, biodegradability, and coatings technology are research areas important to these applications.

Medicine. Polymers are already exceedingly important as materials in medicine and health care, and further dramatic impact is likely. A few directions for the future include controlled delivery systems for drugs, implants and prosthetic devices such as "synthetic organs," polymeric reagents for diagnosis, and the use of polymers in fertility and conception control.

National Defense. Polymers are key materials in national defense. Among specific needs that exemplify areas of current research interest are wide-temperature-range environmentally resistant elastomers, electronic encapsulants, solid-propellant binders, flame-resistant fabrics, and body armor.

High-Technology Applications. Important novel applications for polymers include membranes for water purification, for enhancing tertiary oil recovery, for use in optical fibers, and for photoresists for electronic microcircuits.

## POLYMER RESEARCH IN INDUSTRY, THE UNIVERSITIES, AND THE FEDERAL GOVERNMENT (Chapter IV)

Evidence is cited that industrial support of basic research in the United States appears to be in a decline, with worrisome implications for continuing leadership in polymer research and development.

The support of basic research on polymers at the universities is examined. Total funding is on the order of $20-$25 million (in 1979), of which about 60 percent comes from the federal government. This research is concentrated in a relatively small number of universities. Two of the 20 university Materials Research Laboratories supported by the National Science Foundation have research programs mainly in the field of polymers.

Industry-University Cooperative Research Programs in polymers, with start-up support from the National Science Foundation, are in place or in prospect at several universities. Other forms of industry-university cooperation on polymer research are cited.

## EDUCATION IN POLYMER SCIENCE AND ENGINEERING (Chapter V)

The Panel perceives opportunities in polymer education that go beyond existing patterns and that would reflect the large extent to which careers in science and engineering include work with macromolecules. The following statements summarize the Panel's views of how these opportunities can be appropriately met in U.S. colleges and universities:

Polymer concepts should be integrated into traditional courses in chemistry, biochemistry, and physics, as well as mechanical, materials, and chemical engineering. Teachers in these fields should consider how progress in polymer science and engineering has contributed to and been influenced by progress in their respective disciplines so that their courses may be enriched by examples drawn from this large and diverse field.

Introductory polymer courses should be included in chemistry, physics, chemical engineering, and materials science programs at the advanced undergraduate or beginning graduate level as an essential component of quality education for scientists and engineers.

Academic centers offering graduate concentration in polymer research need to be increased in number in order that prospective students will have better choices among different specializations, institutional styles, and geographical locations.

It recommended, through enhanced educational and research support, that an effort be made to introduce polymer-related subjects in the programs of the many universities that do not offer this important educational opportunity.

An increased commitment to basic polymer studies by the research funding agencies is urgently needed. The agencies should ensure that their support of polymer science and engineering is sufficient to meet their overall objectives and to take advantage of the great opportunities and to meet national needs in this field, as outlined in this report.

Polymer science and engineering are particularly amenable to imaginative new programs of funding, especially if they involve cooperation among universities, government, and industry, as is the case in several institutes that are already in place. Such cooperative ventures could stimulate creativity, diversification, and improved quality in polymer education and research.

## D. HISTORICAL BACKGROUND

Polymer science as a coherent subject is barely 50 years old. Prior to 1930, a number of natural products now recognized as polymers (e.g., cellulose, starch, proteins, rubber) had been studied with the relatively primitive instrumentation but highly ingenious methods of chemical experimentation and reasoning then available. Emil Fischer, after his classic researches on the sterochemistry and synthesis of the sugars, turned in 1899 to the linkage of the amino acids known to be combined in proteins. He succeeded not only in getting two amino acids to combine synthetically (as an amide), but by 1907 he had synthesized a polypeptide chain containing as many as 18 amino acid residues (amino acid molecules minus a water molecule eliminated by the reaction between each pair) linked in known linear sequence. His synthetic polypeptides proved to behave in every respect like corresponding natural intermediate products derived from the hydrolysis of proteins.

Important synthetic derivatives of natural polymers had been discovered, among them vulcanized rubber (C. Goodyear, 1839); cellulose nitrate (J. W. Hyatt, 1870); cellulose acetate (C. and H. Dreyfus, 1919); and even the first commercially successful class of entirely synthetic polymers, the thermosetting phenolic resins (L. H. Baekeland, 1909). The prevailing view of the structure of these amorphous, plastic, nonvolatile, slow-diffusing materials was that they consisted of micellar aggregates of small molecules--a colloidal "state"--cohering through intermolecular forces of nonchemical origin. There was a prejudice against believing that stable molecules of indefinitely large dimensions could exist.

The clear concept of macromolecules, and the term itself, are attributed to Hermann Staudinger, although others earlier had tentatively advanced chain structures to explain various observations. Staudinger's research during the 1920's, particularly on the chemistry of styrene, convinced him that the amorphous material this substance readily forms on standing or heating consists of styrene units covalently bonded sequentially in long chains through a chemical reaction involving opening of the vinylic double bond. He succeeded in preparing polystyrenes of varying degrees of polymerization (i.e., number of styrene units per chain), as reflected in their average molecular weights and molecular weight distributions, and he demonstrated a correlation of molecular size with the viscosity of their dilute solutions in suitable solvents. Although his views met with initial scepticism, newly developed experimental techniques, including the ultracentrifuge and X-ray diffraction, proved conclusive. Through the research of Staudinger, I. R. Katz, H. F. Mark, and others, the chain structure of rubber was firmly established, too. K. H. Meyer and others were then able to deduce theoretically that the unique elastic properties of rubber are to be expected of an amorphous system of cross-linked chain molecules. All this paved the way, ultimately, for the development, originating in Germany during the 1930's, of an increasingly sophisticated synthetic rubber industry. The systematic research of W. H. Carothers (1931) on the synthesis and characterization of numerous polyesters, polyamides, and vinyl and diene polymers (among them the commercially successful neoprene) clinched the argument for the macromolecular concept. Mark later (in 1944) founded the first university-affiliated institute for polymer research in the United States, at the Polytechnic Institute of Brooklyn.

The fundamental principles of vinyl polymerization were outlined in 1937 by Paul J. Flory in terms of a chain reaction sustained by a free-radical mechanism. He introduced the concept of hydrogen transfer as a chain-terminating and occasional chain-branching reaction operating according to laws of chance, and he also clarified the concept of cross-linking. He later developed a statistical mechanical theory of the coiled conformation prevailing when a long-chain molecule free of external constraints is subject to random thermally induced internal rotations about the covalent single bonds connecting atoms in the chain.

A landmark in polymer science and engineering was the commercial development in 1939 of nylon 66, discovered a few years earlier by Carothers. This entirely synthetic aliphatic polyamide, resembling natural silk but with controllable structural regularity and attendant desirable physical properties, proved to be a product for which a demand rapidly became evident. No small contribution to its commercial success was the engineering development of large-scale methods of manufacturing and processing the polymer in desired forms, particularly to secure fiber orientation and attendant strength through drawing. Following the Second World War, the synthetic fiber and textile industry burgeoned, and it has continued to expand as polymers with improved strength, durability, and special characteristics have been developed. A record 4.7 million metric tons of manmade fibers (including about 9 percent derived from cellulose) were produced in the United States in 1979.

C. S. Marvel pioneered in the organic chemistry of polymers and made outstanding contributions to polymer synthesis. His research on polymers stable at high temperatures and on polymers with heterocyclic structures has led to concepts and materials of major commercial significance.

An unexpected breakthrough in polymer research was achieved in 1955, when Karl Ziegler discovered polymerization catalysts based on various coordination compounds of transition metals. With such a catalyst, Ziegler found that polyethylene could be synthesized from ethylene rapidly at ambient temperature and pressure. Furthermore, this polyethylene was almost entirely linear, unlike the branched "low-density" polyethylene known since 1935, which is produced only at elevated temperatures and pressures in excess of a thousand atmospheres.

Giulio Natta then succeeded with catalysts of this type in polymerizing propylene and discovered the first synthetic stereospecific polymerization. Natural stereospecific reactions occur, of course, in the formation of proteins and other polymers of biological origin, such as rubber and gutta-percha (which are stereoisomers of each other). In polypropylene, all the propylene units are aligned "head to tail" (i.e., the pendant methyl groups occur at the same end of each unit), an orientation in the chain that is favored in general by the reaction kinetics, but they may assume either of two different mirror-image configurations depending on the orientation of the pendant methyl group about the chain. The Ziegler-Natta catalysts permit the synthesis at will of stereoregular polymers, in which the monomeric units have either the same or regularly alternating configurations, or the synthesis of isomeric randomly oriented polymers, which have quite different physical properties. Some stereoregular synthetic polymers may occur in a semicrystalline state; the randomly oriented polymers are always amorphous.

The Ziegler-Natta catalysts were used primarily to produce new forms of earlier polymers, rather than polymers of new chemical composition. This has been a major trend in more recent developments, i.e., existing polymer types have been vastly improved by chemical and physical modification. Examples include modification of polymer glasses to produce tough, impact-resistant materials; increase in the elastic modulus of polyethylene produced by extrusion; additives to preserve or fire-retard polymers; immobilization of enzymes by attachment to inert polymers; and many others, some of which are discussed in this report.

New possibilities opened by these discoveries are still being explored, contributing to the annual growth rate of 8.5 percent sustained in the production of synthetic polymers in the United States over the past two decades. Production in 1979 exceeded 23 million metric tons, corresponding to a volume of material greater than that of the combined production of steel and all other metals. High-performance synthetic polymers with various special properties have been developed as replacements for steel in belted tires, cables, and bullet-proof clothing, and they have been indispensable in the design of modern aircraft and spacecraft.

The development of molecular biology was greatly stimulated by the discovery of the double-helical structure of the DNA molecule (J. D. Watson and F. H. Crick, 1953). Molecular biology deals with biopolymers--macromolecules of biological origin and significance. General polymer science has contributed importantly, particularly in recent years, to the understanding of the structures and functions of biological polymers and in turn has been enriched by consideration of the problems and achievements in that field. A challenge exists in learning how to mimic with synthetic macromolecules some of the remarkable adaptations of biopolymers, such as the coding of genetic information and the efficiency and specificity of enzymes as catalysts. Also, a number of diseases have been found to involve minor variations or "errors" in the structures of specific biopolymers, and some progress has been made in coping with such diseases through basic understanding of their origins.

Aside from the intrinsic interest of biological macromolecules as polymers, interest exists in a wide variety of biological and biomedical problems where the specific chemical and physical properties of polymeric materials are adaptable to solutions. Biomedical implants, prostheses, and artificial organs come to mind, as well as polymeric or polymer-bound pesticides and drugs, and polymeric films, used in agriculture to protect young plants and to conserve moisture.

## GENERAL REFERENCES

H. R. Allcock and F. W. Lampe, Contemporary Polymer Chemistry, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1981.

F. W. Billmeyer, Jr., Textbook of Polymer Science, Wiley-Interscience, New York, 1971.

F. A. Bovey and F. H. Winslow, eds., Macromolecules. An Introduction to Polymer Science, Academic Press, New York, 1979.

P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y., 1953.

S. Middleman, Fundamentals of Polymer Processing, McGraw-Hill Book Co., New York, 1977.

"The Science of Macromolecules," Chapter 10, in Outlook for Science and Technology: The Next Five Years, National Research Council, 1981 (to be published by W. H. Freeman and Company, San Francisco, Calif).

# II. STATE OF THE ART AND RESEARCH OPPORTUNITIES

## A. POLYMER CHEMISTRY AND SYNTHESIS

Some of the early commercially successful polymer products were and are still made by chemical modification of existing polymers of natural origin (e.g., tanned leather, vulcanized rubber, cellulose acetate, cellulose nitrate). However, major interest in the chemistry of polymers is centered on synthesizing them from small molecules (monomers). To be incorporated into a polymer, a monomer molecule clearly must be capable of bonding to two or more other molecules of the same or of different species. This can be accomplished in three different ways: (1) by the opening of a double bond (as in vinyl and diene monomers), (2) by the opening of a ring, or (3) by linking through two or more reactive functional groups.

Polymerization by the opening of a double bond invariably proceeds by a chain reaction, sustained through a radical, an ionic, or a coordination catalytic mechanism by which monomer molecules add in succession to the live end of the growing polymer. Ring-opening polymerization, driven primarily by free energy resident in ring strain, is usually initiated by an ionic species (including coordinate ionic compounds such as Lewis acids) and also is propagated by addition of monomer molecules in succession to the live end of the growing polymer chain.

Monomers with reactive functional groups generally polymerize by step reactions in which the growing chains react with each other as well as with the monomer. One important class of step reactions is condensation polymerization in which water is eliminated, for example, between a diol and a dicarboxylic acid in the formation of a polyester, or between a diamine and a dicarboxylic acid in the formation of a polyamide. The reaction of a diisocyanate with a diol to form a polyurethane is an example of a step reaction that involves addition instead of condensation. Step-reaction polymerization can also take place with a single monomer bearing different reactive functional groups at each end, an amino acid or a hydroxyisocyanate, for example.

Whether produced by a chain reaction or, with different kinetics, by a step reaction, the polymer molecule, also known as a macromolecule, is in the form of a chain comprised of repeating monomeric links.

The chain may carry branches or be chemically cross-linked to other chains to constitute a network.

This part of Chapter II deals with the chemistry of polymers, present and prospective. Several subtopics have been identified to frame the discussion: (1) monomer sources, (2) polymerization, (3) polymer degradation and stabilization, (4) property modifications and correlations by synthesis, (5) specialty polymers, and (6) polymer characterization. The scientific and technological opportunities are suggested to indicate the vigor of polymer chemistry and the continuing need for innovative research. A representative list of major research challenges is found in the last section.

## 1. Monomer Sources

Synthetic polymers have stimulated the growth of a large petrochemical industry that produces many of the monomers needed. Compared with other uses of natural gas and petroleum (mainly for energy), the volume going into petrochemicals is not large--about 4 percent of the total consumption in the United States, of which 37 percent (in 1979) goes into the manufacture of polymers. However, the rapidly escalating price and recent uncertain availability of petroleum has put a premium on the development of alternative sources of monomers, chiefly other fossil fuels (coal) and renewable or biological sources.

Aside from commodity polymers produced from well-known monomers in large volume--polyethylene, polypropylene, polybutadiene, polystyrene, poly(vinyl chloride), and various acrylics, polyesters, polyamides, and polyurethanes--specialty polymers with unique capabilities of performing particular chemical, mechanical, or electrical tasks have attracted rapidly growing attention over the past decade. The ability to design such "custom-made" polymers (see chapter IIA, section 5) is a consequence of an accumulation of much experimental and theoretical knowledge gained through basic research. The present high level of research activity in this area and in many laboratories around the world attests to the value of the products. Specialty monomers that possess the desired functionality and can be either polymerized directly or copolymerized with available commodity monomers are the key to success in designing macromolecular architectures uniquely adapted to a myriad of new applications as well as to improved performance in existing ones.

## 2. Polymerization

Polymer synthesis is a distinct branch of chemistry, calling for specialized skills and tools. The goal is to obtain high polymers with controlled chemical structure, stereochemistry, and molecular weight. These requirements generally demand extraordinary precautions in purifying monomers and solvents and in maintaining specialized reaction conditions. Many technologically important polymers are copolymers in which two or more monomers are introduced to confer desired combinations of properties. The different monomers may be linked in either random or regular alternating sequence. Some copolymers are made with block or graft structures in which relatively long sequences of one repeating unit are attached to similar long sequences of another; the term "graft" usually refers to sequences of a second polymer attached as branches to a long sequence of another to form a comblike structure. The term "homopolymer" is used, where necessary, to distinguish a polymer consisting of a single monomer from a copolymer.

### a. Chain-reaction polymerization

i. *Free-radical polymerization.* Polymerization by way of chain reactions involving free radicals has played a central role in the development of polymer chemistry. It has proved to be convenient for the development of technical processes for practical synthesis on a large scale.

Radical polymerization starts with the generation of a free radical (X·), either directly from the monomer itself by exposure to heat, ultraviolet light, or high-energy radiation, or, more commonly, from decomposition of some other molecule, called an initiator (benzoyl peroxide is a familiar one), added in low concentration. The free radical reacts with a molecule of the monomer (typically on olefin or diene) to produce an activated species to which other monomer units add in succession, e.g., in the case of a vinyl monomer:

$$\mathrm{X\cdot + CH_2{=}CHR \longrightarrow X{-}CH_2{-}\dot{C}HR}$$

$$\mathrm{X{-}CH_2{-}\dot{C}HR + CH_2{=}CHR \longrightarrow X{-}CH_2{-}CHR{-}CH_2{-}\dot{C}HR}, \text{ etc.}$$

Chain termination may occur by either (1) combination of two chain radicals or (2) disproportionation via hydrogen transfer, e.g.,

$$\text{(1)} \qquad \mathrm{{-}CH_2{-}\dot{C}HR + RH\dot{C}{-}CH_2{-} \longrightarrow {-}CH_2{-}CHR{-}CHR{-}CH_2}$$

$$\text{(2)} \qquad \mathrm{{-}CH_2{-}\dot{C}HR + RH\dot{C}{-}CH_2{-} \longrightarrow {-}CH_2{-}CH_2R + RHC{=}CH{-}}.$$

Radical polymerization processes are versatile and may be applied to monomers in bulk, in solution, in suspension, or in emulsions. Thermoplastic resins are produced commercially on a large scale by free-radical processes; among them are polyethylene, poly(vinyl chloride), poly(vinyl acetate), polystyrene, poly(methyl methacrylate), acrylonitrile/butadiene/styrene (ABS) copolymer, and poly(tetrafluoroethylene). Free-radical polymerization is also used for synthesis of rubbers like styrene-butadiene and polychloroprene.

Important work is in progress on the development of more effective and more selective initiators for homopolymerization and for block and graft copolymerization. Continuing need exists for better understanding of initiator systems and for the development of new systems that can be used flexibly under various conditions of temperature, pressure, and environment. Among recent developments are bifunctional peroxy initiators that decompose in two stages (controlled by temperature or by selective electron-transfer mechanisms), a property particularly useful in the preparation of block copolymers. Graft copolymers have been prepared with polymeric peroxides as initiators.

The existence of "living" polymer radicals (i.e., long-lived by virtue of a low termination rate) has now been clearly demonstrated, and the technique is applied to the production of block copolymers. Under ideal conditions, emulsion polymerization favors "live" radical polymerization because it practically eliminates termination of the polymer radicals by combination. Specially designed block copolymers can be prepared by this means. Emulsion polymerization also permits high molecular weights to be achieved at relatively high rates of polymerization, compared to polymerization in bulk or in solution.

In emulsion copolymerization, the monomer composition can be varied during the course of the reaction, with attendant potentially useful variation of the polymer composition outward along the later particle radius. Many plastics and synthetic rubbers are prepared by coagulating or spray drying of the emulsions in which they are synthesized. In some cases, however, the latexes themselves are directly used, compounded with fillers, pigments, and other additives, to form coating dispersions and films.

"Nonaqueous dispersion" polymers are prepared in a nonpolar liquid that is a nonsolvent for the newly formed (polar) polymer but is miscible with the monomer. To stabilize the particles, a nonpolar soluble polymer is introduced, onto which the newly formed insoluble polymer is grafted.

Much research is in progress on specific catalysts for preparing copolymers in which the monomers are ordered in nonrandom fashion. An example is the copolymerization in solution of (1) vinyl acetate complexed with modified aluminum alkyls or Lewis acids and (2) ethylene to give an alternating copolymer. In another example, either random or alternating copolymers of vinyl acetate and methyl acrylate can be prepared by judicious selection of aluminum alkyls.

"Telechelic" polymers prepared by a free-radical mechanism have recently been investigated. These are end-reactive polymers of moderate molecular weight. Carboxyl or hydroxyl terminal groups are the most readily accessible. The polymers are prepared by controlling the radical polymerization to favor chain termination, for example, by means of excess initiator to further introduction of the terminal group by chain transfer, or alternatively by means of a solvent such as dimethylsulfoxide, which favors termination by combination of polymer radicals to the complete exclusion of disproportionation. Some uses of telechelic polymers are noted later (see chapter IIA, section 2d).

Further basic research is particularly needed in the determination of absolute rate constants (from nonsteady-state measurements) in solution polymerization at low conversions as well as at moderate to high conversions. Quantitative knowledge of rate constants for chain propagation and termination is generally insufficient and could be improved by direct measurements of radical concentrations during polymerization. Data for common monomers in selected solvents show much scatter, and they are even more scant and unreliable for other less commonly measured monomers. Comparison of reliable data from different laboratories would permit expansion of research on rates of polymerization to include effects of monomer structure, solvent polarity, viscosity, and other pertinent variables. Indeed, no generalizations exist at present that can predict the relative amounts of termination by combination and disproportionation. Other questions relate to the importance of primary radical termination, the rate constant for addition of initiator fragment to monomer, and low-level chain transfer to initiator.

Copolymerization kinetics also call for much additional research. Thousands of reactivity ratios have been determined, many of which require revision in the light of modern methods for their measurement. A general scheme utilizing all the reliable reactivity ratios for predictive purposes would also be valuable. Ternary and higher multicomponent polymerizations should be describable by linear combinations of the binary reactivity ratios. Although one may be able to describe a copolymerization in a conversion-composition framework, the absolute kinetics in terms of conversion (or composition) versus time cannot now be accurately predicted, even at low conversion before the gel effect sets in. Description (or prediction) of high-conversion behavior is a problem where very little progress has been made so far.

In bulk polymerizations at moderate conversions, the "gel" effect (also called Trommsdorff or Norrish-Smith effect) accelerates polymerization until a combination of monomer depletion and the onset of glassiness (at low enough temperatures) slows the polymerization to nearly zero rate. The effect is due to a decrease in the termination rate, which is controlled by the rate of diffusion of the polymeric radicals, as the viscosity of the medium increases with increasing conversion. The rate of diffusion of the small monomer molecules is affected much less until glassiness sets in. In some systems the polymerization rate is affected by the existence of a monomer-polymer equilibrium and/or by chain transfer to polymer. A few attempts at modeling some of these phenomena have been undertaken, but they are largely empirical and incomplete.

ii. Ionic polymerization. Research has dramatically expanded in the fields of anionic polymerization and, more recently, cationic polymerization, both with carbocations and with oxonium ions. Anionic addition polymerization is initiated by the addition of an anion, $X^-$, derived for example from an alkyl or aryl derivative of lithium, to the double bond of the monomer:

$$M^+X^- + CH_2{=}CHR \longrightarrow X{-}CH_2{-}CHR^-\ldots\ldots M^+$$

$$X{-}CH_2{-}CHR^- + CH_2{=}CHR \longrightarrow X{-}CH_2{-}CHR{-}CH_2{-}CHR^-, \text{ etc.}$$

As in free-radical polymerization (see above), anionic polymerization can lead to living polymers, i.e., to anionic end groups with very long lifetimes. This condition is made to order for the preparation of block copolymers, since, after the first monomer has been exhausted, the second can be introduced into the reaction mixture to continue adding to the anionic polymer chains. By this means styrene-isoprene and styrene-butadiene triblock copolymers of the type ABA have been prepared, where A represents a long sequence of styrene units and B a long sequence of isoprene or butadiene. These copolymers are commercially important because they have elastomeric properties without the need for vulcanization. Multiblock sequences of the type ABABAB, etc. can likewise be prepared.

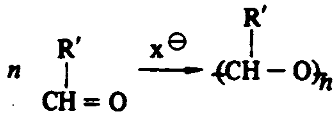
Anionic polymerization techniques have been applied to the synthesis of other remarkable well-defined block copolymers, star polymers, block-star graft blocks, and tapered blocks.

Anionic polymerization of styrene to polymers of relatively low molecular weight produces, by proper capping techniques, styrene-based "monomers" of molecular weight much higher than the usual monomers. A wide variety of microstructures of styrene-based high polymers and copolymers can be prepared by anionic polymerization of these monomers, with full understanding of the influence of counter-ions and solvent polarity.

Cationic addition polymerization of vinyl monomers is initiated by attack of an electrophilic agent (a Lewis acid or a strong protonic acid) on the double bond to produce a carbocation. Propagation takes place by successive additions of monomer molecules between the live end of the growing cationic chain and its counter ion. The rate of propagation is markedly dependent on the degree of association between the macrocation and its counter ion. Carbocation polymerization research is leading to detailed knowledge and control of the initiation mechanism. This permits the synthesis of rather simple macromolecules with controlled microstructures and is opening the way to new block and graft copolymers.

Methods have recently been developed to control termination by reducing chain transfer to monomer and so to extend propagation. Controlled termination permits the synthesis of numerous functional polymers.

In the polymerization of higher aliphatic aldehydes, carried out primarily with anionic initiators at low temperatures,



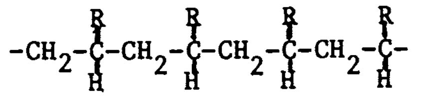
$$n\ \begin{matrix}R'\\|\\CH=O\end{matrix} \xrightarrow{X^{\ominus}} \left(\begin{matrix}R'\\|\\CH-O\end{matrix}\right)_n$$

crystalline isotactic polymers have been prepared that show the interesting phenomenon of side-chain crystallization. With short side chains, only the helical main chain contributes to the crystallinity; in the medium range ($C_4$ to $C_{10}$) both the main chain and side chains show a crystalline phase, while polyaldehydes with long side chains show only the crystallinity of the side chains.

Haloaldehydes such as trichloroacetaldehyde (chloral) are polymerized primarily with anionic initiators. Only isotactic polymers can be prepared. Studies in haloaldehyde polymers present an unusual opportunity to correlate size and bulk of the side group with the stereospecificity of the initiator, since the type of initiator has little if any influence on the stereospecificity of polymerization. Since these polymers are insoluble, a new technique of polymerization had to be developed that utilizes the concept of the ceiling temperature ($T_c$) of polymerization as its essential feature. Initiation is done above the $T_c$, where no propagation can occur, and polymerization then proceeds upon cooling (removing of the heat of polymerization). This technique, when used for casting the undiluted monomer, allows direct fabrication of solid polymer pieces and films. When used in combination with a subsequent polymerization of a second-addition monomer (sequential polymerization), it leads to the preparation of polymer blends and interpenetrating polymer networks.

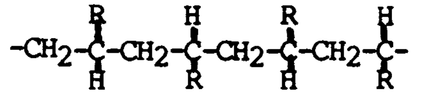
iii. Coordination polymerization. Polymerization promoted by coordination catalysts received powerful impetus from the discoveries in 1955 by Ziegler of a practical method for synthesis of linear polyethylene, and the discovery by Natta of isotactic polypropylene, the first manmade example of a stereospecific polymer synthesis. Stereoregular polybutadienes, as well as amorphous elastomeric ethylene-propylene copolymers, soon followed.

A simple vinyl monomer, $CH_2{=}CHR$, can be polymerized in several stereoisomeric forms having distinctive physical properties. Their three-dimensional structures may be represented schematically as follows:



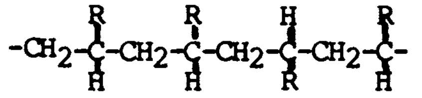
$$-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{R}{\underset{H}{C}}-$$

isotactic



$$-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{H}{\underset{R}{C}}-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{H}{\underset{R}{C}}-$$

syndiotactic



$$-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{R}{\underset{H}{C}}-CH_2-\overset{H}{\underset{R}{C}}-CH_2-\overset{R}{\underset{H}{C}}-$$

atactic

The first two are stereoregular, whereas the third is random and is the form generally obtained by free-radical or ionic addition polymerization. The "head-to-tail" alignment $-CH_2CHRCH_2CHR-$ implicit in the diagrams, rather than the head-to-head structure $-CH_2CHRCHRCH_2-$, is usually strongly favored by the kinetics of vinyl addition. The Ziegler-Natta catalysts, which are based on coordination compounds usually of a Group 4-8 transition metal halide (e.g., $TiCl_4$) combined with a Group 1-3 metal alkyl (e.g., aluminum triethyl), not only accelerate the polymerization--so that ethylene, for example, can be polymerized readily at ambient temperature and pressure--but may be capable of producing polymers in stereoregular form. Ethylene itself polymerizes in linear form, practically without branching (unlike the earlier polyethylene made by radical polymerization at high temperature and pressure). Polypropylene can be readily produced with the proper Ziegler-Natta catalyst in either isotactic or syndiotactic form, whereas the monomer cannot be polymerized at all by conventional free-radical or ionic procedures. Although extensive studies of the mechanism of coordination polymerization have been carried out, a complete basic understanding of the process has remained elusive.

Various solution and slurry processes for coordination polymerization were developed in the late 1960's and early 1970's. More recently, effort has gone into improving the efficiency of the catalysts to a point where their removal from the product is no longer necessary (with so-called high-yield or second-generation catalysts). The incentive has been to prepare polymers in the vapor phase (without solvent) and of particle size and bulk density suitable for direct utilization as pellets for extrusion or molding. A new process for the preparation of polyethylene utilizes conditions and initiators that can produce as much as 500,000 grams of polymer per gram of catalyst. It is essentially a vapor-phase process conducted on a fluidized-bed catalyst that is supported on and probably based on modified chromium oxides. The process is capable of preparing not only linear polyethylene but also polyethylene of controlled branching by copolymerization of ethylene with 1-butene. This polymer, with short ethyl branches along the chain, is quite different in physical properties from ordinary branched polyethylene prepared by high-pressure radical polymerization, which has not only short branches but also long branches randomly distributed. Ethylene-propylene copolymerization is carried out with soluble vanadium-based coordination catalysts in hydrocarbon solvents.

Research has been expanded substantially on novel methods of preparing crystalline polypropylene. The desired goal is isotacticity of more than 95 percent at a polymerization rate of about 20,000 grams of polymer per gram of catalyst per hour. The catalysts are based on titanium supported on various carriers, primarily magnesium chloride. Hydrocarbon solvents are used, and isotacticity of up to about 92 percent is commonly obtained. The ultimate aim is to carry out the polymerization either in the gas phase or in liquid propylene. Polymer prepared by any of these processes will have transition-metal content of less than 3 ppm, although the presence of chlorine as residue from the transition-metal compound presents a more serious problem, and halogen-free catalysts are relatively inactive.

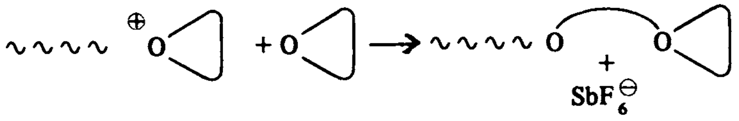
By means of iodide modification of Ziegler-Natta catalyst systems it is possible to control the cis/trans ratio of polybutadiene. By careful adjustment of the aluminum/titanium ratio in the catalysts, 2,3-dialkyl-substituted butadienes can be polymerized in either *cis* or *trans* configurations. Earlier work had shown that cobalt or nickel catalysts, especially when used as allyl complexes, can produce highly regular *cis*-polybutadiene. Recent work indicates that perhaps the best *cis*- 1,4-polybutadiene can be prepared with allyl compounds of uranium.

### b. Ring-opening polymerization

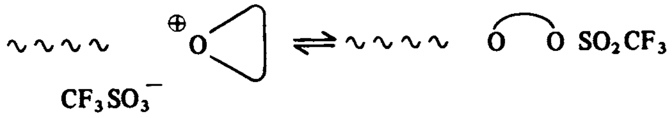
Ring-opening polymerization is the polymerization of cyclic compounds, usually having a hetero-atom in the ring, with anionic or cationic initiators.

Cationic ring-opening polymerization of cyclic ethers has been studied extensively. This polymerization may be initiated by proton acids or Lewis acids, either alone or with a promoter, which might be the actual initiating species. Special attention has been paid to organometallic compounds such as aluminum alkyls and zinc alkyls, modified with water, alcohols, or other compounds that can provide "active" hydrogen atoms. The "living" character of the polymerization of such systems as, for example, tetrahydrofuran or propylene oxide, has been clearly established kinetically, and block copolymers with blocks of narrow molecular weight distribution have been prepared.

Success of cationic ring-opening polymerization requires that the counter anion be nonnucleophilic, otherwise termination by recombination occurs. Such anions are normally derived from complex acids that often are not stable by themselves; e.g., $PF_6^{\ominus}$, $SbCl_6^{\ominus}$, and $SbF_6^{\ominus}$:



Complex oxygen acids such as $HClO_4$ and $H_2SO_4$ are also used. Triflic (trifluoromethyl sulfonic) acid has recently become popular because of its special effectiveness in cyclic-ether polymerization. However, the polymerization has been shown to involve an equilibrium between the ionic form and the triflic ester form of the propagating species:



A number of these equilibria have been studied for several monomers, and rate constants for propagation have been established for the two species (ionic and ester).

One of the main objectives in recent research on ring-opening polymerization is a clear understanding of the initiation steps. The mechanism of initiation was carefully studied in the polymerizations of 1,3-dioxolane and of tetrahydrofuran. Macromolecules, poly(vinyl chloride) for example, were also found to be useful as initiators, producing graft copolymers with poly(vinyl chloride) as the backbone and tetrahydrofuran chains as grafted side groups.

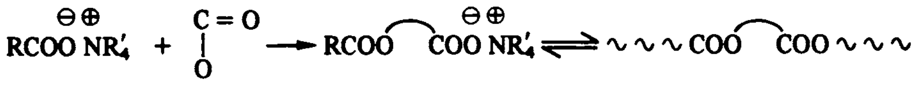
Another important development in ring-opening polymerization has demonstrated that epoxides-bearing functional groups such as ester groups can be polymerized with properly modified aluminum alkyl initiators, especially when the epoxide groups and the carboxylate group are separated by several methylene groups. Epoxides and cyclic ethers could be polymerized in the past only when the side groups were alkyl, chloroalkyl, or ether.

Special aziridine and oxazoline ring compounds can be polymerized with cationic initiators to polymers with secondary and tertiary amine groups in the polymer chain. Copolymerization of oxazoline with acrylic acid or similar acceptor monomers gives alternating copolymers, apparently by a noninitiator zwitterion mechanism. This principle has become the basis for preparing a number of alternating copolymers of cyclic compounds, with an oxazoline, cyclic phosphate, etc. as the nucleophilic monomer $M_N$ and acrylic acid, a sulfonic acid derivative, a lactone, etc. as the electrophilic monomer $M_E$:

$$\underline{n}M_N + \underline{n}M_E \qquad \left( M_N\ M_E \right)_{\underline{n}}$$

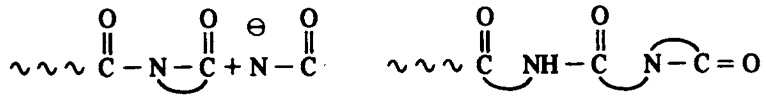
Anionic polymerization, normally associated with styrene or isoprene polymerization, is also effective for the polymerization of lactones, lactams, epoxides, episulfides, and aldehydes (considered here because of their similarity to epoxides in polymerization behavior).

Lactone polymerization has been studied in the preparation of polypivalolactone and other polymers of similary substituted propiolactones. They can readily be polymerized with ammonium salts of alkanoic acids as initiators,



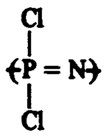
and show the interesting behavior of "living" polymers (similar to the behavior of some anionic styrene polymerizations). Consequently, various block copolymers have been prepared with well-defined block lengths, and their behavior has been studied. Some show interesting potential as biodegradable plastics. Other lactones such as ξ-caprolactone, polymerized with modified aluminum initiator systems, have become important as blending components with poly(vinyl chloride), as these blends have been shown to be completely miscible.

Aminoacid N-carboxy anhydrides (compounds with five-membered rings) have long been the subject of intensive investigation because they are starting materials for the synthesis of the simpler polypeptides. The polymerization mechanism has long been the subject of controversy. With new evidence being accumulated, this important problem may finally be solved. Lactams with seven--and five-membered rings have been investigated for the preparation of nylon 6 and nylon 4. These polymerizations are actually not anionic ring-opening polymerizations but take place by opening of the terminal ring of a growing polymeric imide, which propagates by attack of the anionic $O{=}C{-}N^{-}$ species (the actual mononer) on the carbonyl group of this ring:



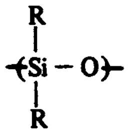
Epoxy and episulfide polymerization, particularly with substituents on one or both carbon atoms, has been studied from the points of view of stereospecificity, stereoselectivity, and stereoelectivity of polymerization, and the direct preparation of optically active polymers. Anionic copolymerization of propylene episulfide with sulfur has given rise to copolymers with sulfur content exceeding 90 percent.

Certain "inorganic" polymers are prepared by the polymerization of their cyclic trimers and/or tetramers. These include the polydichlorophosphazines:



$$\left( \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}} = N \right)$$

and silicones:



$$\left( \overset{\displaystyle R}{\underset{\displaystyle R}{\mathrm{Si}}} - \mathrm{O} \right)$$

The polymerization kinetics and mechanisms are not clearly understood and require additional study.

### c. Condensation polymers

Condensation polymers include polyesters, polyamides, polyisocyanates, aromatic polyethers, and other polymers obtained by electrophilic or nucleophilic substitution reactions.

Aliphatic polyesters of moderate molecular weight that bear terminal OH groups are prepared by normal polyesterification reactions from glycols and aliphatic dicarboxylic acids; they are used primarily as glycol components for polyurethanes. The properties of polycarbonates prepared from bisphenols and phosgene have been significantly improved over their earlier values. Polycarbonates, as well as copolyesters, have been prepared with rigid bisphenols in place of the 2,2-propane linkages used for conventional polycarbonates. With these bisphenols, polymers with glass transition temperatures, $T_g$, above $200^{\circ}$C can be prepared. A number of hindered bisphenols produce polycarbonates and polyesters with increased stability towards hydrolysis.

Poly(ethylene terephthalate), PET, has generally been prepared by transesterification of ethylene glycol with dimethyl terephthalate. The trend now is to replace dimethyl terephthalate with terephthalic acid because improved oxidation techniques for preparing terephthalic acid from *p*-xylene have made it readily available in high purity. PET crystallizes slowly when injection molded, whereas poly(butylene terephthalate) crystallizes rapidly, and this is an advantage when the polymer is used as a molding compound. Much effort has gone into increasing the crystallization rate of PET, and rapidly crystallizing grades have recently been introduced. Progress has been made in understanding the mechanism of the polymerization process, and this has led to catalysts based on transition metals, such as germanium compounds, in addition to the titanium-based catalysts normally used for transesterification. In the area of highly aromatic polyesters, the interest has been primarily directed toward the preparation of materials that can be melt-fabricated. A most exciting development is the incorporation of 60-80 percent *p*-hydroxybenzoic acid in PET to form polymers with significant liquid crystal regions in the polymer melt, affording the promise of oriented, high-strength polyesters (see chapter IIB, section 3).

Polyamides (nylons), aliphatic and aromatic, with higher glass transition temperatures have been prepared. Much of the research has been concentrated in the development of aromatic polyamides such as linear poly(p-phenylene terephthalamide). These linear polymers give liquid crystal solutions in polar solvents and even in sulfuric acid that can be spun to yield fibers notable for their exceptionally high strength and elastic modulus (see chapter IIB, section 3). High-performance polyamides with relatively low crystallinity, including aromatic/aliphatic and alicyclic polymers, are finding applications as hot-melt adhesives and as insulation where crystallinity and orientation are not as important as availability, price, and fabricability.

Novel and improved polyurethanes have been prepared from diisocyanates although no practical alternatives to polyether glycol and polyester glycol as flexible segments have been found. Linear polymers from diisocyanates have also been made, in which the isocyanate group forms linkages other than urethane, e.g., polyoxazolidones, polyquinazolinediones, polybenzoxazinediones, poly(parabanic acids), and poly(barbituric acids). The cyclotrimerization of diisocyanates and nitriles on the ends of polymer chains has been applied to the formation of cross-links in laminating resins for use in high-performance composites.

Research on oxidative coupling of phenols to form polyethers has continued. Only the polymer from 2,6-dimethylphenol has been commercialized. Completely aromatic poly(phenylene ethers) have been prepared that tend to crystallize rapidly and can be made into fibers and films. Other polymers and copolymers with less tendency to crystallize are also being investigated. Advances in polyquinoxaline and polyquinoline chemistry have been rapid, but activity in this area is now decreasing.

New high-performance aromatic polysulfones have recently been introduced and aromatic polyketones and other polymers prepared by nucleophilic substitution reactions are under development.

General problems exist in the demand for high-performance polymeric materials. Polymers are now known that approach the ultimate that can be expected in thermal and oxidative capability for organic materials. The best-known polymers for high-temperature use are the polyimides prepared from bisanhydrides and aromatic amines via the poly(amide acids). A new route to polyimides uses isocyanates and anhydrides as starting materials.

Because of their low solubility in conventional solvents, two of the most important classes of high-temperature polymers, polybenzoxazoles and polybenzthiazoles, have to be prepared by polymerization in polyphosphoric acid in order to obtain high molecular weights. Since fabrication also involves solutions in strong acids, their use in forms other than fibers remains problematic. A milder method for the facile preparation of polybenzimidazole has recently been developed by utilizing bis-orthoesters instead of phenol esters.

### d. Network polymers

Network polymers are highly cross-linked polymers, exemplified by most rubbery polymers (see also chapter IIB, section le, and chapter IIC, section 2c). Much additional research is needed for better understanding of networks, particularly on reaction variables related to effective functionality, mechanisms of cross-linking, and rates of reaction. With the more sophisticated instrumentation that is becoming available, such as solid-state NMR, many of these factors can now be studied more effectively.

An important development in network polymers is the availability of telechelic polymers (see chapter IIA, section 2a), which can be used to prepare networks of carefully controlled topology. Polymerization reactions are also sought that will yield polymer networks of appropriate properties but with less shrinkage than that normally encountered in going directly from a vinyl monomer to the corresponding polymer.

Functional and postreactive polymers useful for forming networks include not only hydroxyl-terminated species for polyurethane formation and acrylate-terminated ones for curing by ultraviolet radiation, but also novel epoxy- and isocyanate-terminated intermediates which, when combined with hydroxyl-terminated ones, form the basis for the new, rapidly developing fabrication technique of reaction injection molding (RIM) (see chapter IIC, section 3a). Reactions such as RIM that are rapid and require low energy for processing will become increasingly important for their energy-saving and other processing advantages.

## 3. Polymer Degradation and Stabilization

Advances in understanding polymer degradation and stabilization represent a key way in which polymer science can contribute to the nation's need for conservation of natural resources. The most important destructive agents for polymers are heat, oxygen, ozone, UV light, moisture, and microbial action. In practice, the effects of these agents are retarded by designing more stable polymer structures and by adding appropriate antioxidants, UV screening agents, peroxide decomposers, antimicrobial agents, flame retardants, and the like. While much has been accomplished, as evidenced by the ever increasing use of polymeric engineering materials in severe environments, this area of science can be expected to show great progress in the future. Because each polymer system presents a unique chemical problem and because this facet is crucial to the usefulness of polymeric materials, the research is pursued mainly in industrial laboratories and has not received the attention in university laboratories that its intrinsic interest merits.

When polymers are exposed to the environment, they undergo gradual chemical and physical changes which may impair usefulness or even result in failure of the material. Some of these effects are due to thermal oxidation and photooxidation. Thermal oxidation may start in the melt during the processing step at high temperature with very low oxygen levels and continue slowly at or near ambient temperature in air.

Antioxidants are needed for fabrication and long-term use of most polymers. Although not yet accepted, polymeric antioxidants have great potential because they will not readily migrate out of the polymer system and will most likely be better able than small-molecule antioxidants to meet developing safety and health requirements. Polymers of

4-vinyl-2,6-di-tert-butylphenol and of 4-propenyl-2,6-di-tert-butylphenol are examples. Polymeric phenolic antioxidants have also been developed as food additives; one example consists of condensation products of p-cresol, hydroxyanisole, tert-butylphenol, and hydroquinone, with some divinylbenzene as cross-linking agent.

Photochemical reaction occurring in polymers on exposure to solar radiation also can damage the physical and mechanical properties and the appearance of the polymer. Polymers for use outdoors are usually protected by added UV stabilizers to absorb most of the damaging radiation. UV absorbing compounds of low molecular weight are used for this purpose. The most effective UV stabilizers are salicylates, 2,4-dihydroxybenzophenones, 2-(2-hydroxyphenyl)benzotriazoles, and certain other, more complex compounds that do not discolor.

The UV stabilizers can be lost by exudation, volatilization, and solvent extraction during fabrication, and also by processes occurring under end use conditions. The problem is most severe for articles with a high surface-to-volume ratio, such as fibers and films. It was initially believed that low-molecular-weight stabilizers together with appropriate compatibilizing groups would be sufficient or even advantageous to protect the polymers, especially because they are primarily present in, and consequently effective in, the amorphous fraction of the polymer. Recent experiments with stabilizers grafted onto rubber have shown that the stabilizing group can be incorporated into the polymer without diminishing its effectiveness.

Most past efforts in this direction have centered on the preparation of stabilizer monomers by relatively simple reactions on stabilizers already formed. This has not always provided stabilizer systems easily incorporated into polymers by copolymerization. Recently, new UV stabilizers have been prepared with the polymerizable vinyl group directly attached to the phenyl ring of the stabilizer, as in the antioxidants mentioned above. These monomeric stabilizers are thus styrene derivatives, and they are readily homopolymerized or copolymerized by means of azobisisobutyronitrile (AIBN) and similar common radical initiators. They copolymerize readily with ordinary vinyl monomers by radical polymerization and can function as grafting agents. Copolymers of 2-(5-vinyl-2-hydroxyphenyl)benzotriazole with methyl methacrylate so prepared have shown outstanding UV stability in accelerated tests equivalent to almost twenty years of outdoor exposure.

More sensitive and more accurate accelerated aging tests are needed. Present methods are quite time consuming and often do not accurately predict behavior under actual conditions of use. This is especially true of accelerated outdoor weathering procedures. Ultrasensitive techniques, such as chemiluminescence, now permit measurement of rates of oxidation at or near actual exposure temperatures. The development and refinement of such methods would be invaluable to the study and control of polymer stabilization.

Better understanding is needed of the pathways by which polymers are degraded. The increased sensitivity of modern analytical techniques such as FTIR, ESR, and $^{13}C$ NMR spectroscopy should allow study of the degradative process in sufficient depth to provide a rational basis for improvements in stabilizer systems and for the design of more stable polymers.

Polymer degradation can be utilized positively in several problem areas: (1) recycling, when a polymer is converted to useful chemicals after its initial use, e.g., hydrolysis of polyurethanes from automotive foams to monomers; (2) controlled degradation, so that the polymer does not become an ecological waste problem, e.g., polyethylene incorporating ketone groups that make waste packaging materials susceptible to UV degradation, or filled black agricultural polyethylene which becomes quite brittle and decomposes after controlled time intervals; and (3) drug or chemical delivery systems based on chemical erosion of a polymer, e.g., delivery of contraceptive drugs from a poly(lactic acid) medium which degrades hydrolytically in the body. The factors controlling such positive uses of polymer degradation are incompletely understood, and further research on degradation mechanisms is needed to lay the base for design of appropriate systems.

The mechanism of stabilizer action is poorly understood, e.g., the efficacy of hindered cyclic amines as thermal and photo stabilizers, the secondary oxidation products of hindered phenolic antioxidants, and antioxidant synergism such as between hindered phenols and thiodipropionates or phosphites at elevated temperatures (150°C). The roles of various stabilizers in the initiation, propagation, and termination of polymerization need study. The negative influence of many mineral fillers and additives on antioxidants is not understood, nor has the mechanism of phosphorus-based antioxidants been fully explained. For example, how do phosphites prevent thermally induced chain cleavage in saturated polymers? More efficient stabilizers such as catalytic peroxide decomposers are needed. More effective and longer-lasting antimicrobial and antifungal agents would be valuable additives in antifouling paints for ships and in polymers for use in humid environments.

Polymers are known to degrade faster under mechanical stress; the chemical reason for this is uncertain. The degradation mechanism involved in the friction and wear of rubbing polymer surfaces and the role of fillers in this phenomenon are likewise not well defined. The effects of such physical phenomena as solubility, diffusivity, microscopic distribution, and miscibility on the effectiveness of stabilizer action are only partially known.

In photodegradation the relative importance of light intensity and wavelength on product distribution and quantum yields needs systematic study. The importance of the oxygen charge transfer phenomenon and singlet oxygen is presently not clear, nor is the influence of energy transfer mechanisms and quenching phenomena in the photodegradation of commercial polymers.

A better understanding of polymer flammability and combustion is needed. The usual approaches--incorporation of chlorine, bromine, and/or phosphorus compounds as additives--may impair mechanical properties and increase potential safety and health hazards. Polymeric versions of these additive types have taken on increased significance. Moreover, polymer systems are being investigated that do not contain extraneous elements but produce unusual degrees of cross-linking and aromatization in the condensed phase at high temperature. This leads to high char or residue formation, with reduced formation of volatiles necessary for combustion. The mechanisms of these high-temperature processes require much additional study and should have a bearing on the understanding of problems associated with smoke and soot formation.

### 4. Property Modifications and Correlations by Synthesis

In general, approaches to structure-property correlations have been limited to readily available polymers. This limits confidence in the extension of the concepts beyond those structures that are available and may cause difficulties in interpretation because the history and preparation of the samples may be unknown.

Many excellent techniques have been developed for the characterization and evaluation of structure-property relationships. Structures with known or zero chemical defects are needed for these studies, which will call for new or modified synthetic approaches. For example, current studies are under way to prepare and evaluate head-to-head structures of vinyl polymers (see chapter IIA, section 2a,iii). Another example is the preparation of samples with known defects, such as occur in standard polymerizations (e.g., melt polymerization in making nylon-66), in order to study their effects on a number of basic properties. The synthesis of chemical structure modifications in a systematic way also can be used to develop and quantify basic correlations.

Property enhancement, as well as possible environmental and health effects due to migration, toxicity, etc., make it necessary to consider polymeric plasticizers and additives in greater detail. Plasticizers and such additives as antioxidants and UV stabilizers have generally been of relatively low molecular weight, each additive serving a particular function or property modification. The development of polymeric additives naturally extends to the synthesis of "multifunctional" additives.

Chemical surface modifications of polymers have received study in the past, and improvements of a number of properties have been made, although the chemistry associated with these changes is not completely understood. The advent of sophisticated tools for surface characterization now allows more complete investigation of the chemistry at the surface. New organic reactions, plasma reactions, and metal-atom chemistry are among potential areas for study.

Modifications of polymer systems by further reaction have been studied and utilized for some time, but the correlations and knowledge of the chemistry, physical effects, and properties of these systems have been inadequate. New techniques provide the opportunity to improve understanding and control of the preparation of materials with new and improved properties from the base polymers.

### 5. Specialty Polymers

An especially attractive area for research is that of specialty polymers--polymers tailored for specific useful functions, many of which require innovation in design and synthesis. Examples currently under research and development include polymeric delivery systems for drugs and pesticides, polymeric catalysts for chemical processes, and chemical separation systems. A few specialty areas are selected here for discussion. Biologically related specialty polymers are discussed in chapter IID.

Coatings and adhesives technology depends heavily on specialty polymers. Continual research is in progress in these areas to seek improved products through new monomers and the polymers derived from them. At present, three classes of organic functional groups characterize the most widely used monomers: carboxylic acids, amines, and alcohols.

Carboxylic acid monomers, incorporated into polymers and copolymers, are widely used. Paper-pigment binders and carpet-backing adhesives are made from vinyl acetate/acrylic acid and styrene/butadiene/itaconic acid copolymers. Poly(acrylic acid) is used in cosmetics, printing inks, and coatings on nylon and polyester fibers. Polyacrylates copolymerized with some acrylic acid are used in automobile, home laundry, and exterior can coatings. FDA-approved coatings for heat-sealing polyethylene food-packaging films are available from a copolymer of crotonic acid and vinyl acetate.

Amino monomers and polymers are widely used in adhesives. Synthetic tire cord is bonded to styrene-butadiene rubber (SBR) by means of a copolymer of SBR with vinylpyridine. Amines are broadly used to cure epoxides and isocyanates in a wealth of adhesive and coating formulations. Copolymers of acrylamide with unsaturated tertiary amines are produced as flocculants for the paper-making industry.

Hydroxyl monomers are exemplified by hydroxyethyl acrylate, which, when copolymerized with other acrylates and styrene, yields coatings cross-linkable with melamine resins. Vinyl acetate/hydroxyalkyl acrylate copolymers are good adhesives. Copolymers of monomers containing long-chain alkyl groups with hydroxyethyl acrylates are good dispersing agents.

Specialty monomers can be designed to produce polymers of unique electrical, magnetic, and photoresponsive properties. For example, substantial effort is in progress to develop a class of electrically conductive polymers. Photosensitive functional groups attached to polymerizable monomers have yielded photoresists--light-initiated polymers selectively either sensitive or insensitive to removal by solvent action or other further chemical or physical treatment--which permit the imprinting of the electronic and microelectronic circuits so pervasive today. Monomers of still higher photosensitivity would permit even closer packing of components in the next generation of submicroelectronic devices.

Photography itself, through most of its modern lifetime, has been supported by natural polymers or their derivatives. In recent years, particularly with the advent of instant photography, new synthetic polymers have been developed to accomplish specialized tasks, such as dye mordanting, base neutralization, and timing. A multilayered photographic element takes particular advantage of the relative immobility of macromolecules, which allows a chemical function to be localized in a single layer without major loss in reactivity. Many such compositions exist as polymeric couplers, dyes, developers, stabilizers, hardeners, etc., to accomplish this end.

The dominant role of gelatin as the principal vehicle for silver halide emulsion making and coating is still unchallenged in spite of decades of work with synthetic polymers. In principle the limitless flexibility available in synthetic polymer design should allow the chemist to prepare a gelatin equivalent, and indeed this has been accomplished to a considerable extent. Synthetic emulsifiers and vehicles have been refined to a state such that, on occasion, equivalent photographic effects, but no startling discontinuities, have been obtained. This outcome, coupled with the unusual physical properties of gelatin in the fluid and swollen state, has sustained the traditional method. At present, only the possibility of a shortage of raw material is likely to stimulate renewed activity in this field, although increasing physical and chemical demands on the matrix have suggested that gelatin may not always be adequate. In nontraditional photography involving nonsilver light-sensitivity and nonaqueous coating, synthetic polymers have been extensively used as vehicles and as chemical agents.

Photoconductive polymeric materials have passed from the stage of being laboratory curiosities to commercial exploitation by the electrophotographic industry in the United States, Japan, and Europe. Significant progress has been achieved in the past decade in tailoring the photoelectronic and physical properties to meet specific application requirements and to make the polymeric systems competitive with the more established inorganic systems. The phenomena of molecular structure controlling the photogeneration, transport, and trapping of electronic charges in organic polymeric systems are reasonably well understood. Further improvements in photosensitivity and transport properties, particularly at low applied-electric fields, could enable these materials to penetrate other technologies such as microimaging, electro-optics, and solar cells.

Polymeric materials exhibiting dark electronic conductivity are now known and used over the entire range of insulators, semiconductors, and conductors. The recent discovery of metallic conductivity in doped polyacetylenes has stimulated search for other classes of conducting polymers with improved stability and processability. Such polymers as the polypyrroles, polyphenylenes, and poly(phenylene chalcogenides) exhibit some of these improved properties. Further understanding of the molecular and structural parameters determining and controlling conduction in amorphous disordered polymeric solids would be highly desirable. The ability to combine functional electrical response with unusual mechanical properties (e.g., flexibility) in a polymer material could create new opportunities in the microelectronics industry.

Polyelectrolytes also exhibit significant levels of dark conductivity. These materials have cationic and/or anionic charges distributed along the polymer molecules, and conduct electricity by virtue of counter-ion mobility. Polyelectrolytes are generally freely soluble in appropriate solvents and thus can be cast and fabricated into many useful articles. Applications as conductive layers for electrographic papers and as antistatic agents for insulating plastic surfaces have been highly successful. Since the mobility of an ion normally depends on solvation by water, the conductivity of ion-containing polymers is a direct function of relative humidity. This humidity dependence is detrimental to some applications. Therefore, a present research goal is to design polymeric materials that can transport ions without the benefit of water. Polymers have recently been discovered in which ions are solvated to the extent that conduction independent of humidity is observed. This development should greatly extend the utility of polyelectrolytes as conductors.

Since the development of solid-phase polypeptide synthesis in the 1960's, research on polymeric reagents has burgeoned, and many specific contributions have been made in organic synthesis, biochemistry, catalysis, and separation technology. Several potential advantages are realized by attaching a reagent to a polymer. First, polymeric reagents are easily separated from compounds of low molecular weight by simple filtration or membrane techniques. This also permits the ready regeneration and reuse of the reagent. Second, the polymer microenvironment can enhance the stability of labile reagents during storage and handling. Linking a reagent to a polymer often lowers reactivity, but in some cases the activity towards a specific substrate of interest can be enhanced. In fact, the possibility of synthetic enzymes is being actively explored, and polyelectrolyte effects can accelerate interionic reactions by several orders of magnitude. Finally, polymeric reagents are nonvolatile and generally less toxic than their analogs of low molecular weight.

Current challenges in polymeric reagent technology include the identification and development of applications which possess advantages over conventional techniques. Many opportunities also exist in optimizing the polymer carrier itself. Much of the previous research has involved polystyrene, but significant improvements in the rate and specificity of reactions can be expected by the careful design of the steric and polar characteristics of the polymer microenvironment.

Polymer-bound catalysts afford a fertile field for future research. Attachment of precious metal catalysts to cross-linkable polymers can both improve the economics of current chemical processes and greatly aid in product isolation and purification. The attachment of enzymes to polymeric supports has already met with some success (see chapter IID, section 2b) and can be expected to find application in the fermentation and drug industries.

Photoresists for the semiconductor industry have been mentioned above. Their improvement through research has facilitated the extraordinary reduction in the size of circuit geometries of semiconductor devices. The device-manufacturing process requires that the polymer coatings be accurately imaged by light, X-ray, or electron-beam exposure. Classical light-exposing systems will produce processed images with linear dimensions in the range of 2 to 5 μm, short UV and special optics allow dimension reduction down to 1 to 2 μm, and electron-beam and X-ray exposure allow images to be formed with dimensions below 1 μm Various trade-offs, such as capital expense, process time, and labor costs, make the choice between short UV, X-ray, and electron-beam exposure dependent on needs of individual manufacturers.

The physical properties of the polymers determine their performance in this application to the manufacture of printed microcircuits. On exposure, a major change in solubility must occur, such that the images can be solvent developed. The polymers must stand up to wet chemical corrosive etchants such as HF solutions. They must also resist dry etchants, gases containing free radicals, and ions that are generated in plasmas, ion beams, etc. Typical use demands soluble, coatable polymers that are imageable and will stand up to etchants, yet remain sufficiently soluble or swellable to be readily stripped. These are conflicting properties requiring close control of polymer variables for optimum performance. Among types of materials in current use are: (1) poly(vinyl cinnamate)-based resists, (2) photopolymerizable materials in precoated form, (3) cyclized polyisoprene-azide liquid resists, and (4) positive-working resists based on diazoketone-polymer combinations. Special polymers for use with X-ray and electron-beam systems are available, both in the United States and in Japan.

The industry presently can produce resists that respond to light anywhere in the range of 200 to 600 nm. Resist-polymer systems can easily be manufactured that provide coated films with glass-transitions temperatures from -50°C to +300°C and with effectively controlled solubility characteristics. The solvents range from hydrocarbons and chlorinated hydrocarbons to water.

For future progress, basic research is needed on negative-working, water-processable polymers adaptable to imaging systems; chemical-resistant and heat-resistant polymers; plasma-resistant imageable polymers; and, ideally, polymers that could be developed by plasma, survive plasma etching, and ultimately be plasma-stripped--all controlled by temperature and plasma composition. Polymers are also needed that show increased sensitivity to specific energy sources (short UV, X-ray, and electron-beam) yet have a good shelf life.

Specialty polymers are needed in many energy-related applications (see chapter IIIC). For example, elastomeric and plastic materials that will withstand conditions of high temperature and corrosive environments will find use in geothermal drilling, solar energy recovery, and oil recovery. In the last category, much effort has been concentrated on just two water soluble polymer systems, one based on acrylamide and the other based on guar, and the field is open to innovative approaches based on other systems.

## 6. Polymer Characterization

### a. General

Knowledge of the detailed structures of homopolymers and copolymers is necessary for advances in understanding structure-property relationships, advances in synthesis of polymers with particular properties, and improvements in the useful lifetimes of polymeric materials. Powerful and versatile instrumental techniques have become available in recent years that permit many problems of polymer characterization to be handled almost routinely, if not automatically. The increasingly detailed information about polymer structure so obtained has led to more and more sophisticated research on polymer synthesis and properties.

Nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), and laser Raman spectroscopy, together with gel permeation chromatography (GPC), are used extensively for polymer characterization. NMR spectroscopy in particular has undergone continuous development. Large superconducting magnets now permit proton resonance to be studied in homogeneous fields at 360 to 600 MHz, providing a more than tenfold increase in resolution and sensitivity over those of fifteen years ago. The development of pulse NMR spectrometers has increased the sensitivity sufficiently for nuclei present in low isotopic abundance, such as $^{13}C$, to be studied routinely. The pulse techniques for recording polymer NMR spectra also provide information about the dynamics of polymer chain motions in solution and in bulk, which is valuable in studies of the mechanical properties of polymers.

Size-exclusion chromatography, also called gel-permeation chromatography (GPC), has been developed as a rapid method of separating the components of a soluble polymer according to molecular size in dilute solution. When coupled with detectors to determine the concentration (by differential refractometry or light-absorption methods), the average molecular weight (from small-angle light scattering), and viscosity, the method affords a means of characterizing the distribution of molecular weight and, in favorable cases, the distribution of long-chain branching. By use of multiple detectors (refractive index, UV, visible and infrared absorption) on the eluate, one could also in principle elucidate the composition of copolymers as a function of chain length.

Additional structural information can be obtained by intensity-fluctuation light scattering (or dynamic light scattering) methods, which measure a hydrodynamic property. Comparison of these data with molecular dimensions derived from absolute-intensity light scattering and from the viscosity in dilute solution can aid in the characterization of the overall chain conformation, i.e., the extent to which the chain behaves like a flexible coil, a rigid rod, or something intermediate. In this context, an important need is to extend small-angle light-scattering detectors to make scattering measurements simultaneously at a number of angles.

### b. Polymer compositions.

Specific problems of structure characterization will now be considered. The compositions of polymers containing several structural features must be known for most studies. For example, in polymers derived from dienes, the relative amounts of *cis*-1,4, *trans*-1,4, and 1,2 or 3,4 units need to be known. When the diene is not symmetrical, as in isoprene, the relative proportion of linkages containing diene units enchained in 1,4 versus 4,1 or 1,2 versus 2,1 fashion (i.e., head-to-head versus head-to-tail) should be defined, and when the polymers contain large proportions of 1,2 or 4,3 units, the stereochemistry of placements involving these units should be defined. For example, 1,2 placements can have meso or racemic configurations.

Much progress has been made during the past decade in procedures for analyzing polymers derived from dienes. High-field $^{13}C$ NMR spectroscopy has been invaluable for these analyses, especially when the dienes and their hydrogenated counterparts can be studied together. Unfortunately, only a few spectrometers capable of performing these analyses are available to the polymer research community. Information provided from such analyses is particular useful for fundamental studies of anionic polymerization because the structures of polymers derived from dienes are much affected by polymerization conditions.

In general, NMR and infrared spectroscopy can handle most of the problems encountered in measuring the gross compositions of soluble polymers and copolymers. Characterization of the compositions of insoluble polymers, such as phenolic resins, epoxy resins, urethane resins, cross-linked rubbers, polyimides, polypyrroles, polyacetylenes, and ion-exchange and reagent resins, is often a much more difficult matter. Techniques appropriate for such analyses include infrared and Raman spectroscopy, pyrolysis-chromatography, thermogravimetric analysis (TGA), differential scanning calorimetry, and surface analysis methods such as ESCA and Auger spectroscopy. Much research is needed in this area. The general structure of these polymers can be inferred from the method of synthesis, but the extent of reaction obtained, the nature and amount of chain ends present, the presence of structures derived from unknown side reactions, and other features are often not known. As an example, moldable polyimides and quinoxalines containing reactive end groups can be cured by heating, but the actual chemistry involved does not seem to have been defined. Any new knowledge obtained in this area is certain to have immediate practical and theoretical consequences.

### c. Polymer stereochemistry

Information about the relative proportions of monomer units of different steric configurations in polymer chains and how they are distributed along the chains is needed in a number of contexts: the mechanisms of vinyl polymerization; the properties of partially stereoregular polymers; and stereoselection in ring-opening polymerization of oxiranes, thiatanes, aziridines, lactones, lactams, and N-carboxyanhydrides. NMR spectroscopy has been effective for such studies, especially when shift reagents can be employed. Polymers derived from aromatic vinyl monomers represent one of the few remaining classes of materials whose characterization has not yielded to this technique, but this situation is close to being rectified.

### d. Monomer sequence distribution in copolymers

The properties of copolymers are dependent not only on their compositions, but also on how the monomer units are arranged in sequence along the chains. This is especially true of copolymers in which long enough sequences of one of the monomer units can crystallize. Knowledge of copolymer structure is necessary for studies of copolymerization mechanisms and for studies of polymer modification reactions. When diads (pairs of monomer units) can have any of several configurations (meso, racemic), the stereochemical structure of the copolymer needs to be analyzed as well as its segmental structure. This can be a very difficult problem. NMR spectroscopy, especially $^{13}C$, has been useful for this task. Progress in the analysis of copolymers has been substantial over the past decade, so that many characterizations can now be done routinely. However, methods are still lacking for accurately determining block and graft lengths, branch lengths, and branch points in polymers.

### e. Compositional distribution of copolymers

A problem that has scarcely been studied is the determination of the distribution of compositions among copolymer chains in a given sample. This information, coupled with the molecular weight distribution, is necessary for the proper characterization of any copolymer. Convenient fractionation procedures based on composition must be developed. Some progress in this direction has been made by thin-layer chromatography, but much more is needed. Further progress will benefit research on the synthesis of block and graft copolymers, on polymer modification reactions, and on characterization of commercial polymers.

### f. Fine structure

Fine structural features present in polymers, such as end groups, branch sites, cross-links, and imperfections, often need to be identified and measured. A dynamic range problem is associated with the determination of these features by conventional spectroscopy, but it can be solved by means of internal standards, by reference of NMR signals to $^{13}C$ NMR satellite signals, or by use of chemical techniques. For example, OH end groups in polymers can be converted to $-O-SiR_3$ or $-O-CO-CF_3$ groups. The latter can be characterized by $^{19}F$ NMR spectroscopy. Because of the importance of end group analyses in polymer synthesis, many sensitive procedures have been developed, among them dye absorption methods.

The characterization of branching in such polymers as polyethylene, poly(vinyl chloride), and poly(vinyl acetate) is an important problem. Carbon 13 NMR spectroscopy has been effective in studies on polyethylene and hydrogenated poly(vinyl chloride), but much remains to be done on poly(vinyl acetate) systems.

Cross-linking in polymers is generally determined at present by physical methods such as equilibrium swelling or determinations of elastic modulus. These are not very satisfactory; if better methods for characterizing cross-links could be developed, significant improvements in the properties of cross-linked elastomers and resins should follow. Some progress was made in the analysis of sulfur-containing cross-links in elastomers during the 1970's, but little has happened since. The use of "magic angle" NMR spectroscopy is promising. This new technique appears to be the first since the advent of infrared to provide detailed molecular information for insoluble materials.

Closely related to the problems of characterizing branching and cross-linking in polymers is the problem of monitoring the course of multifunctional condensation reactions (phenol-formaldehyde, epoxy resin, etc.) to and past the gel point. A better understanding is needed of the detailed chemistry of these reactions and the structures of the products.

### g. Impurities

Impurities will be defined as those materials present in polymer samples that are external to the polymer chains. They include moisture, catalyst residues, plasticizers, stabilizers, and residual monomers. Small amounts of these materials can have important effects on physical properties, stability, and suitability of polymers for applications requiring FDA approval. For instance, small amounts of moisture cause unusual transitions in polystyrene. Because a number of monomers, e.g., vinyl chloride and acrylonitrile, are considered to be carcinogens, sensitive procedures for determination of residual monomers have been developed. Catalyst residues can be determined at low levels by ashing followed by atomic absorption spectroscopy measurements. Identification of polymer additives by extraction followed by thin-layer chromatography, mass spectrometry, infrared spectroscopy, or NMR spectroscopy is quite routine, with much background information now available to assist the analyses. Computer searching devices are commercially available to assist in identification of unknown species.

The use of labels on polymers represents another front where considerable progress is being made. Instead of studying the polymer of interest, one attaches to the macromolecule another chemical group more easily observed experimentally. The label may fluoresce, it may quench electronic excitation, it may form detectable pairs (excimers), or it may have a spin detectable by ESR. Perhaps the simplest labels are isotopes. Deuterium, replacing hydrogen, gives the molecule enhanced elastic neutron scattering capability. No doubt the use of this technique will increase after the national neutron and synchrotron facilities become fully operational. Carbon 13 is distinctive in NMR experiments. The research challenge is threefold. How can one use labeling techniques to learn more about polymers? What significant new labels can be developed? How closely do the properties of the labeled polymer resemble those of the unlabeled?

### h. Current problems and future needs

Many new applications developed for polymeric materials in recent years will generate a need for new methods of characterization. Certainly the purity of polymers used in microelectronics or medical applications needs to be assessed to a high degree of accuracy. Improved methods are needed to characterize polymer surfaces and insoluble polymers because of the importance of polymers as supports for catalysts, immobilized enzymes, reagents, and chromatography columns. Ability to characterize surfaces more completely would considerably benefit the field of adhesives. Instruments and methods for characterizing the conformations of polymers in solution are much needed, particularly for biopolymers. This information can be obtained from NMR coupling constants, contact shifts, and optical rotatory dispersion measurements, and, perhaps at a coarser level, from rheological studies. Since conformation has been successfully predicted theoretically for synthetic polypeptides and certain other polymers, it would be gratifying to verify such predictions with precise experimental data.

## 7. *Major Challenges**

a. *Monomers.* Basic research on catalysis of organic reactions for monomer syntheses and in biological conversion can provide new or improved processes, as well as new monomers that can lead to new polymers.

b. *Polymerization initiation.* Better understanding of the initiation process and development of new initiators would allow the preparation of polymers of specific architecture.

c. *Polymerization rates.* Quantitative knowledge of absolute rate constants and mechanisms would allow better control of the molecular weight and structure of polymers.

d. *Polmerization methods.* New methods are needed for *in situ* formation of high-performance polymers and for polymerizing directly into useful shapes.

e. *Specialty polymers.* Syntheses need to be worked out for specialty polymers which are, for instance, photoconductive, piezoelectric, electrically conducting, chemically resistant, chemical reagents, or flocculants.

f. *Stabilization.* Better understanding of oxidative, thermal, and light-initiated degradation of polymers can lead to stabler polymers through modified polymer structures or specific inhibitors.

g. *Accelerated aging.* Reliable accelerated aging methods are needed to predict the useful life of polymers.

h. *Synthesis and characterization.* A major effort is needed to synthesize well-characterized polymers and copolymers of known structure and high purity for systematic structure-property studies.

i. *Chemistry of the interface.* There is a need for selective chemical modification of the interface. New and improved analytical techniques now or soon to be generally available (NMR, ESCA, FTIR, photoacoustic spectroscopy, etc.) will afford detailed information particularly of the chemistry at the interface.

j. *Environmental.* New processes are needed in monomer and polymer synthesis to eliminate environmental problems (solvents, toxic reagents, etc.) and to reduce energy consumption. Processes are also needed that utilize renewable raw materials.

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*Not in priority order.

## B. PHYSICS AND PHYSICAL PROPERTIES

The study of condensed polymeric states deals with complexities inherent in the long-chain nature of the macromolecule. These complexities involve an array of unique and fascinating properties whose description calls for broadening of the familiar concepts applicable to ordinary liquids and solids comprised of small molecules. As an illustration, the crystalline state of polymers displays locally the usual regular packing of atoms, but in at least one direction the crystal rarely extends beyond tens of nanometers. Moreover, polymer crystallites are in a nonequilibrium state at the very edge of stability, formed even considerably below the melting point by the fastest rather than the most stable route. Polymeric materials commonly labelled as crystalline generally contain a significant fraction of amorphous phase. Many crystalline properties thus depend on the history of the sample.

The amorphous state affords other illustrations of the broad range of polymeric phenomena. For small molecules, "amorphous state" normally signifies a fluid or "liquid" state characterized, for example, by viscous shear flow. Polymer melts can be fluid, but because of the large molecular size and entanglements among molecules, they show high viscosity and significant viscoelastic behavior, with an "elastic modulus" even at low frequencies. Furthermore, with little change in local structure, the topological change associated with cross-linking produces a rubber, which is a viscoelastic solid rather than a fluid. Finally, an extremely important form of amorphous polymers is the glassy state, a nonequilibrium condition assumed also by small molecules but less commonly.

The gaseous state is of no significance for polymers since macromolecules cannot get into this tenuous form of organization without chemical breakdown. The closest analogue of a gas is a dilute solution, in which the polymer molecules are separated from each other but not from the solvent. Given the large number of repeating units tied together in a single macromolecule, one can dilute a solution to the point where the local concentration of polymeric material is so low that interactions among chains have little effect; thus the mean configuration and properties of the macromolecule can be studied effectively in isolation. Moreover, the presence of the solvent can be turned to advantage, so that by judicious choice of solvent composition and temperature (Flory theta conditions) the net polymer-polymer interactions can be brought to zero, analogous to the balanced molecular interactions in a gas at the Boyle point.

States of order intermediate between crystalline and amorphous can exist for macromolecules consisting of stiff chains dispersed in concentrated solutions. Such "liquid crystal" or mesophases are mobile but anisotropic. From them one can form anisotropic solids with mechanical properties of considerable interest.

Some of the most interesting polymeric materials are blends or composites. Blends may be mixtures in the thermodynamic sense or fine dispersions. A mixture or heterophase system may combine beneficial aspects of its components. For instance, brittle glasses can be rendered resistant to impact if rubbery inclusions with dimensions on the order of a micrometer are incorporated.

The surfaces and interfaces of polymers have properties interesting in their own right. These regions frequently differ chemically and physically from the phase interiors. Such differences may be inherent in the material, may be induced purposefully, or may be the inadvertent result of deterioration. Surface studies are central to the problems of adhesion.

Throughout the following sections examples of physical concepts and phenomena are described that are either unique to polymers or more important in these materials than in others: crazing, semidilute solutions, block copolymers, chain-folded crystal surfaces, tie molecules, conformational entropy, and the type of motion picturesquely called reptation. Yet, the familiarity of the methods of investigation is also noteworthy: light-scattering measurements, IR and NMR spectroscopy, rheology, relaxation rates, crystal morphology, and phase diagrams.

## 1. Amorphous State

### a. Introduction

Almost all polymers and their concentrated solutions form an amorphous state in which long-range three-dimensional order is absent. Moreover, almost all polymers with regions of crystalline order also contain (nearly) amorphous domains. The predominant feature of the amorphous state is the extensive intertwining of the coillike polymer chains, with no intermolecular order save the liquidlike short-range orientations of closely positioned repeating units. Amorphous polymers find important and widespread use as elastomers and plastics; crystallizable polymers are almost always processed in the amorphous state above their melting temperatures. Despite a substantial body of literature on the physics and chemistry of amorphous polymers, the complexity required of theory and experiment has left many aspects of the amorphous state at only a qualitative level of understanding. As should be expected, new developments and materials often raise questions heretofore unasked.

It is convenient to separate the behavior of amorphous chains into (1) phenomena dominated by short-range interactions among molecular fragments located in some relatively small element of volume (containing, say, a few repeating units of neighboring chains), and (2) phenomena dominated by long-range interactions involving the contiguity of the polymer molecule, whether it is a linear or a branched chain, or a network formed by cross-linking. The former group of phenomena involves concepts and methods similar to those encountered in studies of ordinary fluids of low molecular weight, with additional complexities owing to the enforced local asymmetry of segmental interactions because of the connected-chain nature of the macromolecule. The second group of phenomena, involving interactions among segments far removed from each other along the chain, presents a range of properties unique to polymeric materials. An example of this distinction is the factorization of the viscosity of an amorphous linear polymer into a term dependent predominantly on the molecular weight M but nearly independent of temperature T and a term dependent predominantly on $T-T_g$, where $T_g$ is the glass transition temperature (see below), but otherwise nearly independent of M (except for the variation of $T_g$ itself with M for low values of M).

As the preceding statement suggests, rheological properties of amorphous polymers are of considerable interest. They include linear viscoelastic behavior at low stress or strain and nonlinear behavior under large applied stress or strain.

### b. The coiled polymer chain

The coiled nature of long-chain polymers is important to many of their properties in the amorphous state. Indeed, it is important also in the kinetics of crystallization and in disordered domains of otherwise crystalline polymers. Experiment and theory agree on the overall coiled conformation prevailing at equilibrium when the macromolecules are isolated in dilute solutions, the coiled nature being a statistical effect of the rotational states independently available to each of the numerous segments comprising the backbone. Although the absence of long-range order in the bulk amorphous state, predicted theoretically in the 1950's, was challenged by some dark-field electron microscopy results in the 1960's, more recent dark-field electron microscopy and neutron-scattering measurements of particle shape have confirmed the correctness of the earlier view. Thus, insofar as long-range structure is concerned, the chain adopts (nearly) the same mean shape in the amorphous state (either undiluted or in concentrated solutions) as in dilute solutions (at the Flory theta temperature). However, local short-range segmental orientations are to be expected. These are enhanced by the asymmetry of the repeating unit (which must after all be connected at each end to the remainder of the chain). Spectroscopic and depolarized-light-scattering studies may help to elucidate the effects of local orientation.

Questions of the dynamics of chain motion are likely to be prominent in further studies of the isolated chain. The connectivity of the chain complicates application of the large body of information on internal rotations of small molecules to the dynamics of macromolecules. Improved methods are needed to investigate chain dynamics either by experiment on polymers in solution or by simulation with digital computers. Experimental methods spanning a range of time scales include nuclear magnetic relaxation, special spectroscopic probes such as fluorescent tags, dielectric methods, and fluctuations of scattered light intensity. Related problems of the equilibrium chain conformation will call for study by neutron scattering, depolarized light scattering, and fluorescence spectroscopy.

### c. The glassy state

Most polymers will form a glassy state in preference to a crystalline state when the temperature is lowered under appropriate conditions, and most polymers lacking regularity in the geometric arrangement of their repeating units never crystallize. Of course, nonpolymeric fluids can form glasses as well. In either case, the onset of the glassy state is characterized by a rather abrupt change in the slope of some temperature-dependent thermodynamic variables (volume, energy, or entropy) at "the" glass transition temperature $\underline{T_g}$. However, glass temperatures so determined depend on the time scale of the experiment. This observation is closely related to the temperature dependence of molecular relaxation times, one of the most important areas for further research. At a given temperature the molecular relaxations governing useful mechanical properties typically span a time range of 10 to 20 powers of ten. This fact emphasizes the need for experimental methods covering a wide range of time. Usually, dynamic and transient mechanical methods must be combined to obtain the necessary range.

Reliable rheological data on glassy polymers are still sparse, but the relaxation spectrum appears to be not much affected by temperature variation for $\underline{T}$ above $\underline{T_g}$, except that it is shifted toward longer times as $\underline{T}$ decreases. Thus, the factorization of the viscosity, mentioned above, into terms dependent on $\underline{M}$ and on $\underline{T-T_g}$ is useful, because each of the many relaxation times involved in polymer dynamics increases in nearly the same way as $\underline{T}$ is lowered toward $\underline{T_g}$. This particularly simple behavior has given rise to the highly useful principle of time-temperature equivalence: time-dependent linear viscoelastic properties at two temperatures can be correlated through properly reduced time scales. Materials with such behavior are termed "thermorheologically simple."

By contrast, the relaxation spectrum may change as $\underline{T}$ is lowered to $\underline{T_g}$ and below, giving rise to thermorheologically complex behavior. Precise knowledge of the spectrum as $\underline{T}$ approaches $\underline{T_g}$ is necessary to explain the effect of long-term annealing on the mechanical properties of glasses or the response to nonlinear deformations, such as may play a role in the formation of crazes and in cold forming methods increasingly used in industry. The experimental methods for studying such effects must extend over wide ranges of time and temperature; isochronal experiments are not adequate. Besides studies of the relaxation spectrum through its effects on rheological properties, other methods can provide useful information on dynamic processes in glassy polymers: neutron diffraction studies of chain conformations, infrared spectroscopy to examine the population of rotational states, heat capacity measurements, light-scattering intensity fluctuations, and dielectric relaxation.

The individual roles of temperature and, say, volume (or energy or entropy) on the spectrum of relaxation times for $\underline{T}$ near $\underline{T_g}$ are still largely not understood and should be studied to elucidate the sources of variation of the relaxation spectrum near $\underline{T_g}$. Such studies are especially important near $\underline{T_g}$, because of the long relaxation times characteristic of glasses. For example, the properties of a glassy polymer may change gradually as its volume relaxes isothermally. It is important to distinguish whether mechanical properties vary directly with the volume or are explicitly dependent on the temperature. Such questions bear on the changes that occur in a glass during annealing, an important but poorly understood process.

The dynamic behavior of a glassy polymer can be studied as a diluent is added, with $T$ held close to $T_g$ of the concentrated solution so formed. Besides the general bearing on molecular dynamics in the glassy state, the data bear directly on the technologically important question of the diffusion of small molecules in a glassy polymeric material. Diffusion of this sort is important in many applications involving the use of polymer films (see below).

The preceding remarks have emphasized the importance of understanding how the relaxation spectrum behaves as $T$ is lowered through $T_g$. From such understanding, an improved theory of the glassy state should follow. Interest will likely continue in whether a glass transition can be observed at equilibrium. That is, does an equilibrium process exist with properly defined (excess) entropies, enthalpies, etc., indicating a second-order transition temperature $T_2$? This theoretically important question has practical import, even if the equilibrium state cannot be achieved. For example, such a thermodynamic transition might correlate with the extrapolated temperature $T_0$ at which relaxations that are dominant above $T_g$ appear to become infinitely slow (this is typically about 50 K below $T_g$). Furthermore, insight might be provided on methods of estimating $T_g$ from the chemical structure of a polymer by the use of approximate contributions for each moiety in the repeating unit of the chain.

The important problem of crazing in glassy polymers will be considered in the following section.

### d. Flow properties

The rheological properties of polymers relate to their deformation and flow, usually in response to an external stress. Such behavior underlies the technology of forming polymers into useful shapes and the performance of the material in use. The flow properties are dominated by intertwining of the long polymer chains, as mentioned above. An interesting possibility for studying this effect will be neutron scattering to determine the molecular shape of a polymer under an external stress.

The intermolecular interactions described as entanglements greatly inhibit chain motion. This inhibition is locally asymmetric, motion lateral to a chain contour being more effectively inhibited than motion along the chain contour. The result, according to one model, is a snake-like motion termed "reptation." One well-known manifestation of entanglements is a dependence of the viscosity on the 3.4 power of $M$ for $M$ greater than a critical value. The impact of the reptation model has not yet been fully developed theoretically or explored experimentally. The rheological behavior of branched chains is not well understood at present, and work on such polymers may prove valuable in assessing the virtues and shortcomings of the reptation model. Limited observations have shown that branched chains can exhibit far greater shear viscosity at low shear rate than their linear homologs of the same molecular weight. These studies should be expanded to provide a deeper understanding of the deformation process at the molecular level. Some properties are especially sensitive to the molecular weight distribution, and these effects also call for further study.

The nonlinear rheological behavior of polymers will receive continued study. It is an important subject technologically, impinging directly on the processing and use of polymers, and its understanding will permit critical assessment of such molecular models of polymer flow and deformation as the reptation model. The nonlinear response depends on the strain history in a way that is not yet fully understood. Studies of nonlinear behavior must include not only steady-state properties but also a variety of transient measurements covering a wide range of strain histories. Instrumentation is needed that is capable of precise measurements of the pertinent variables (e.g., strain rate, total strain, stress, stress frequency). Optical rheological measurements such as flow birefringence and dichroism would also be informative.

The mechanisms of extensive localized deformations also need much more study. For example, the rheological response to a suddenly applied large stress controls the impact strength, a property that calls for further elucidation at a fundamental level. Near the glass transition temperature the time scales for molecular response (slow) and applied stress (fast) are greatly mismatched, giving rise to failure mechanisms. Thus, at temperatures well below $\underline{T_g}$, many polymer glasses develop crazes, in which polymer is pulled to bridge the two halves of a nascent crack. This process can greatly affect the material properties, for example, by absorbing energy in a glassy polymer without catastrophic failure. The processes leading to crazing and the effect of solvent on craze formation, as well as other forms of failure (such as yielding) need much additional study. The role of small molecules (including gases) on craze formation, the morphology of the crazed domain, and the effect of strain and thermal history on the development of crazes all should be included in future studies. This will call for sophisticated application of electron microscopy, low-angle X-ray or neutron scattering, and rheological measurements.

### e. Cross-linked polymers

In many applications of polymers, all the chains are joined by chemical cross-links to form one giant molecule. An early triumph in polymer science of the 1930-40's was the prediction that the elasticity of such a system should be controlled primarily by entropic factors and be proportional to the number of strands available between cross-links to support an applied stress. Deviations from the simple theory may be due to neglected chain interactions, such as those described as entanglements in the absence of cross-links, or may result from imperfect characterization of the topology of the cross-linked network. Despite long-term interest in the subject, continued theoretical and experimental work is needed to elucidate the equilibrium mechanical properties of cross-linked polymers.

Newer methods of network formation utilize cross-linking reactions involving only chain ends. This permits the use of shorter precursor chains and better control of the network topology, including its heterogeneity, the number of free ends, and the extent of interchain entanglements. Better methods are needed to characterize these aspects of the network and to predict their effects on the equilibrium mechanical properties. Such information may be especially important for highly cross-linked polymers, such as many of the thermosetting polymers. With some systems, the deformation can be studied at the molecular level by neutron scattering for comparison with the macroscopic deformation. Thus, the molecular conformation from neutron scattering can be observed under conditions of equilibrium swelling or under great strain. The latter condition may permit evaluation of the relative contribution of finite chain extensibility and of crystallization to the mechanical behavior of networks at great strain.

The time-dependent properties of cross-linked polymers merit further study. For example, detailed understanding of the molecular or topological factors influencing the mechanical loss of elastomeric polymers would be helpful in the design of materials with lower energy loss under cyclic stressing.

The ultimate properties of network polymers under great strains require further systematic study. With elastomers, it is clear that the shorter strands rupture first, leading to progressive failure with increasing strain. The detailed role of network topology in this process requires more study. With many polymers, great strain induces local crystallization, resulting in a composite structure that may exhibit enhanced ultimate properties.

### f. Diffusion in amorphous polymers

Diffusion of molecules through any polymer occurs almost exclusively through amorphous regions, because crystalline regions are essentially impermeable barriers to all but the smallest molecules. The diffusion rate depends on the free volume available in the amorphous polymer; diffusion measurements therefore afford a sensitive probe of polymer structure. Further details on the crystalline state are described in section 2f.

Above their glass transition temperatures, diffusion in rubbery polymers largely follows Fick's law and can be understood on a free-volume basis. The principal problem lies in the action of penetrants that strongly swell the polymer and thereby affect the diffusion kinetics of all species.

Below their glass transition, i.e., in glassy polymers, much more fundamental work is needed on the mechanisms of transport for small molecules. Sorption data for many gases in glassy polymers have been successfully interpreted by a dual-site model, and other supporting evidence such as differing NMR relaxation times suggests that the diffusing molecules are sensitive to different environments. The validity and consequences of these views should be explored more fully.

The self-diffusion of macromolecules and the diffusion of polymeric solutes in a compatible polymeric solvent require additional study. Theoretical treatments have described such diffusion by models in which the macromolecule diffuses by reptation along its own length. Experimental methods to study such effects are still difficult and have to be tailored to each case. Additional effort is needed to establish the dependence of diffusion on chain length, concentration, chain branching, etc. Such data will be helpful not only for testing of the theoretical reptation model, but also for understanding the nature of blends and for treating problems arising in the application of coatings and adhesives.

### g. Polymers in solution

Polymer molecules widely separated from each other in solution are in a state in which some of their characteristics can be most reliably measured. Much of the basic physics of chain molecules, applicable to other forms of aggregation, has been derived from studies of polymers in solution. Although such studies were undertaken systematically more than twenty years ago, modern theoretical and experimental methods show that the subject is more intricate than had been supposed, though not beyond representation by useful universal laws. The phenomena occurring in polymer solutions are characterized by large fluctuations. Therefore, they are akin to critical phase-transition phenomena. Recent major breakthroughs in the theory of critical phenomena may be fruitfully brought to bear. In fact, polymer solutions may prove to be the best systems for studying the critical state. Such oddities as tricritical points and crossovers occur, and critical fluctuations are observed over a wide range of controllable variables such as molecular weight, concentration, solvent quality, chain stiffness, and cross-link density.

An individual polymer chain in dilute solution behaves as a loose, random coil permeated with solvent. The mean chain conformation may be essentially unperturbed by long-range interactions. This condition is achieved experimentally by choosing a rather poor solvent whose tendency to permeate the polymer is exactly balanced by energetic forces driving it out of the region occupied by the polymer. This state of effective cancellation of interactions between pairs of distant polymer segments is called the "Flory theta condition." On the other hand, in a good solvent the polymer coil expands to relieve the net repulsive interactions. The description of the polymer conformations now requires "excluded volume" statistics, a problem still not wholly solved, especially for branched macromolecules. Many problems call for the consideration of interactions between distinct segments of a coiled chain or section of chain that is too short to be treated by the asymptotic laws of the excluded-volume theory. This case is described as in a so-called "crossover" regime.

When a polymer is slightly more concentrated in a solvent, which generally means at less than a few percent by weight, a condition known as a semidilute solution develops. It is unique to polymers. Since any one segment of the polymer may be considered to have an effective force-field range of less than a nanometer, few other segments are within its range at these concentrations. In this sense the segments are dilute. However, the whole coil spreads over many nanometers. Thus each macromolecule overlaps many others, creating the conditions typical of a concentrated collection of molecules. The situation is described in terms of a screening distance beyond which intermolecular contacts mask intramolecular excluded-volume interactions. Crossover phenomena, i.e., those characteristic of concentrations between the dilute and the concentrated regimes, abound in this situation because any particular experiment may be probing phenomena involving distances of the order of the screening length, or may be effectively in a range between theta and good solvent. Theoretical and experimental description of these intermediate types of behavior is needed. New problems enter when one considers nonequilibrium phenomena, such as the role of entanglements in hydrodynamic interactions.

In poor solvents phase separation occurs, and many of the phase diagrams are quite unusual. Phase separation on heating, as well as on cooling, is common. A system of a solvent and two polymers (or two different degrees of polymerization of the same polymer) may form three coexistent phases. A remarkable condition may occur in extremely dilute solution when the quality of the solvent is made poorer, as by varying the temperature: as the polymer phase separates, the individual coils may collapse, forming separate globules. This reversible transition, which also occurs in DNA and gels, may have important biological implications.

Progress has been made, but much remains to be done, on predicting the solvating power of solvents for polymers, either theoretically or by semiempirical cataloguing. The problem is especially difficult for complex solvent molecules, in which many types of forces are in effect, and for mixed solvents. The concept of additive group properties has shown some promise.

Polyelectrolytes form a class of polymers whose properties in solution deserve special mention both because of the role they play in life processes and because of the growing interest in water soluble polymers. The long-range Coulomb repulsion between like charges along the polyelectrolyte chain can effectively stiffen it. However, this effect can be screened by adding salt or reduced by decreasing the degree of ionization through adjustment of the pH. The response of the macroions and their small-ion atmospheres to external fields (electrical, acoustic, or strain) needs further study.

### h. Outstanding problems

1. The behavior of the relaxation spectrum as the temperature is lowered through the glass temperature $\underline{T_g}$ (e.g., assessment of the time-temperature superposition principle).
2. Experimental evidence on the roles of (free) volume and temperature on the properties of annealed glassy polymers.
3. Methods to characterize the molecular structure of highly cross-linked polymers for correlation with mechanical properties.
4. An understanding at the molecular level of nonlinear rheological behavior of polymers and their concentrated solutions, including branched polymer chains.
5. An understanding of failure mechanisms, such as crazing, yielding, at the molecular level.

6. The rheological properties of ionizable polymers, both undiluted and in concentrated solutions.
7. A unified understanding of the intramolecular and intermolecular effects that control the properties of polymers in moderately concentrated solutions.
8. Fundamental study of the mechanism of transport of small molecules in glassy polymers.

## 2. The Crystalline State

### a. Introduction

The fundamental feature governing the ability of polymers to undergo crystallization is the microstructure of the chain molecules: to crystallize, the chains must have predominantly regular chemical and geometrical structures. Polymers with occasional structural imperfections also may undergo crystallization. The number of such imperfections compatible with crystallization is limited, however.

Polymers exhibit a diversity of morphologies varying with the conditions of crystallization. For example, crystallization from dilute solutions usually results in the formation of microscopic lamellar single crystals, of the order of several micrometers on a side, the thickness (5-20 nm) of which increases with the crystallization temperature. The molecules repeatedly traverse the lamellae from one face to the other, fold, and return. The segments between successive folds have been observed to be oriented either at right angles or at angles up to 45° to the surface of the lamellae. The crystalline lamellar character and chain folding are closely associated. The lamellae can be flat, hollow pyramidal, or curved. They may exhibit either "regular" (well defined polygonal) lateral growth habits, reflecting the symmetry of the unit cell, or "irregular" lateral habits (with rounded or finely serrated edges).

Upon cooling from the molten state, polymers crystallize over a wide temperature range, usually in spherulitic form. The spherulites typically exhibit diameters in the range 1-100 μm and evolve from simpler, single, crystallike lamellar precursors. Spherulites consist of a radiating array of long, narrow, and thin lamellar structural units the thickness (approximately 10-100 nm) of which rises with the crystallization temperature. Lamellar width also tends to be greater the higher the crystallization temperature. The molecules are oriented as in solution-grown crystals. Available evidence indicates the presence of tie molecules bridging neighboring lamellae.

A feature distinguishing crystalline polymers from other crystalline materials is that even in what would be expected to be the most favorable cases, i.e., solution-grown single crystals, the density is usually much lower than that calculated from the structure of the unit cell. Consequently, the overall degree of order in polymer samples has been characterized customarily in terms of the degree of crystallinity, $\underline{x}$. The values of $\underline{x}$ depend on the crystallization history as well as on the nature of the polymer. For single crystals of polyethylene grown from solution, $\underline{x}$ is at most 0.9. In bulk polychlorotrifluoroethylene and polypropylene, values from 0.4 to 0.8 can be obtained, depending on thermal treatment. In some polymers (e.g., nylon 66), $\underline{x}$ has never been found to exceed 0.6. Accordingly, important aspects of the morphology of crystalline polymers are the nature of the disordered regions in them and the disposition of these regions relative to the ordered (crystalline) ones. Other important questions center on the nature of the interface between the two regions and the validity of the simplest two-phase model.

Crystalline polymers can be formed into ordered fibers or films upon stretching. In fibers the chain molecules in the crystalline regions are oriented preferentially, parallel to the fiber axis. The fibers consist of microfibrillar structural units (∿100 nm long and of the order of 10 nm in diameter) interconnected by interfibril tie molecules. In the microfibrils crystalline and disordered regions alternate along the axis with a periodicity on the order of 10 nm. The chains in the crystalline regions of the microfibrils are apparently folded or partially folded and are connected to the adjoining disordered regions by taut intrafibrillar tie molecules. The same type of fine structure prevails in uniaxially stretched films. A whole spectrum of different morphologies, however, occurs in films produced by biaxial stretching. When the stretching along the two directions is the same, the crystalline regions tend to be oriented with the chain molecules parallel to the surface of the film and with one particular set of crystal planes also oriented parallel to the surface. The orientation of the crystallites is otherwise random. In some such films there is evidence for domains consisting of alternating ordered and disordered regions. However, the nature of the interdomain regions remains obscure and is an important problem.

### b. Structure and morphology

A factor determining many trends in research on morphology and crystallization and on the relationships between fine structure and physical properties has been the availability of new and improved experimental tools. Small-angle neutron scattering, Raman and FTIR vibrational spectroscopy, $^{13}$C NMR, synchrotron X-ray sources, one- and two-dimensional position-sensitive detectors for recording diffraction patterns, ultrasonic microscopes, and scanning transmission electron microscopes are among these techniques. Some of the areas of research in which these tools have been used or offer promise will be indicated below.

A feature of central interest is chain folding--in particular the details of its manifestation in the growth of crystals both from solution and from the melt. A fundamental aspect being addressed experimentally and theoretically is the extent of adjacent reentry relative to nonadjacent reentry of the molecules at the edges of growing lamellae. Views range from rather complete to nearly negligible adjacent reentry. Other questions concern the number of interlamellar tie molecules and the number of molecular cilia (loose ends). Neutron scattering and IR spectroscopic measurements on isotopic mixtures of deuterium-substituted and ordinary polyethylene crystallized from solution and the melt have been carried out in connection with these questions.

Neutron scattering studies have been carried out also on isotopic mixtures of deuterium-substituted and ordinary isotactic polypropylene and isotactic polystyrene. Although these techniques are specifically sensitive to details of the conformation of the chain molecules of the one isotopic species in a crystalline matrix of molecules of the other, the analysis and interpretation of the data with respect to chain folding is strongly debated.

In the theory of polymer crystallization, recent developments include differing analyses of the role played by entanglements and/or self-diffusion (including reptation) in crystallization from the melt. A key question concerns the rate of self-diffusion compared to the rate of advance of the crystal growth front. Monte Carlo computer calculations show promise as a means of determining answers to questions concerning adjacent reentry, tie molecules, and cilia. Other efforts address the nature of crystallization under extensional flow and of the crystallization of copolymers.

Research on crystallization habit and fine structure has been somewhat lagging because of the complexities of the problems. There have been significant advances, however. Detailed studies have been performed of the influence of molecular weight on the morphology and kinetics of crystal and spherulite growth of polyethylene, and the results have been analyzed in the light of current theories. New light has been shed on the shapes and mode of propagation of the constituent lamellae in spherulites by combining chemical etching techniques with electron microscope examination of either microtomed sections of the etched polymer or replicas of its etched surfaces. Besides confirming that amorphous regions representing disorder occur at the surfaces of lamellae and are sandwiched between overlapping lamellae, the study demonstrated that the lamellae had either tentlike or curved S-like cross sections, depending on crystallization temperature and molecular weight. These results provide a fresh basis for pursuing one of the unresolved problems of polymer morphology, the origins of the "twisting" orientation in spherulites of polyethylene and some other polymers. Other active research is concerned with the relationship between morphology and the temperature dependence of the associated crystallization kinetics.

A promising development applicable to the study of morphology is the commercial electron microscope operating in a scanning transmission mode. A limiting factor in ordinary electron microscopy has been the susceptibility of polymers to irradiation by electrons. The scanning transmission electron microscope (STEM), however, can enhance brightness and contrast electronically, enabling the examination of crystals at an acceptable low level of beam damage. An additional advantage is that diffraction patterns can be obtained from extremely small areas ($10^2 \times 10^2$ nm), so that the mosaic or domain structure of the crystals can be studied in detail.

Much experimental research has addressed oriented fibers and films. The goal has been to attain extensional moduli in the fiber axis direction that approach the limiting value characteristic of the crystal lattice. A variety of methods to produce such fibers has been investigated, including stretching at elevated temperatures, extension in the solid state, and crystallization from solution or from the melt under the influence of hydrodynamic flow. Polyethylene fibers having an extensional modulus as high as 100 GPa have been produced, this elastic strength comparing favorably with the lattice elastic constants determined by spectroscopic techniques. Fibrous, highly crystalline polymers can also be produced in some special cases by solid-state polymerization. Important contributing opportunities exist in *ab initio* quantum mechanical calculations of the lattice modulus. Other important problems concerning the use of such fibers are creep under tension and fibrillation under twisting or bending. Research aimed at determining how the fine structure can be modified to improve resistance to these effects is certainly called for.

As pointed out in the introductory remarks, important aspects of the fine structure of biaxially stretched films remain to be elucidated. There is considerable interest in the structure-property relationships of these materials. There is also much interest in the theory of crystallization under deformation. Research in these areas should be encouraged.

Time-resolved X-ray diffraction studies are now possible, based on intense sources of X-rays (synchrotron) coupled with position-sensitive (array) detectors. They afford promise of real-time experiments on the dynamics of crystallization and the development of orientation in polymers subjected to stretching. Recent advances in NMR permit high-resolution spectra to be obtained from polymeric materials undergoing deformation, providing further insight on structure-property relationships. Ultrasonic microscopy also can reveal regions of differing mechanical modulus, often associated with chain reorientation.

### c. Electrical properties

A significant property of many polymers is their ability to withstand high electric fields with negligible conduction. This property, coupled with the favorable mechanical and processing characteristics, makes polymeric insulation the material of choice in a wide range of applications. The absence of conductivity is due to large energy differences between localized valence electronic states and the conduction band. But these initially excellent insulating properties deteriorate with time. Such aging and failure is usually linked to morphological defects, which may originate in particulate impurities, aggregation of antioxidant or chemical cross-linking additives, and lamellar or interspherulitic boundary regions. Both the theory of electrical aging and the experimental techniques to detect it are of major importance to improved energy storage and transmission systems. Dielectric loss in polymer insulation is another important area of concern, especially in superconducting cable and magnets. Proton tunnelling mechanisms at low temperatures and dipolar mobility at high temperatures must also be better understood and controlled.

Recently, controlled conduction in polymers, both ionic and electronic, has been receiving increased scientific and technical attention. An electrolyzer for hydrogen generation is being developed in the United States with a solid polymeric ion-exchange membrane. The polymer promises considerable increase in efficiency over liquid electrolytes. Batteries with solid polymeric electrolytes offer a considerable advantage in energy-to-weight ratios over batteries of other types. The scientific problems are in understanding the interaction of charged ions with solid polymers and the relationship between polymer structure and ion selectivity and mobility.

Electronic mobility in polymers is greatly enhanced along a polymer molecule with conjugated bonds. Instead of the typical insulator value of $< 10^{-14}$ $(\Omega \cdot \mathrm{cm})^{-1}$, the conductivity may be in the range of $10^{-5}$ to $10^{-9}$ $(\Omega \cdot \mathrm{cm})^{-1}$. When such a solid polymer is doped with electron donors or acceptors, it becomes highly metallike in conduction and appearance, with conductivities of the order of $10^3$ $(\Omega \cdot \mathrm{cm})^{-1}$. Extensive applications are thought to be possible for these materials if problems of stability and fabrication can be overcome. The questions of how carriers are generated and how conduction takes place in polymers are poorly understood, and conducting polymers, whether ionic or electronic, are generally developed on an empirical basis. Quantum mechanical theories are needed in this area. Greater understanding of the conduction process is highly desirable and will probably require the cooperation of solid-state physicists, physical chemists, and synthetic chemists.

The coupling between the electrical properties of polymers and their mechanical and thermal properties has led to important transducer applications. Poly(vinylidene fluoride), which has acceptably large piezo- and pyroelectric activity and desirable mechanical and fabrication properties, has been developed commercially for use in a variety of devices. This polymer is crystalline with a relatively large dipole moment per unit cell. A theory based on fundamental properties has been developed for the electrical activity and for the ferroelectric switching properties. Better understanding of these properties should lead to an expanded range of active polymers.

### d. Mechanical properties

The dependence of the mechanical properties on chemical and physical structure and on time is a fundamental aspect of current and future research on polymers. Much of the discussion about mechanical properties of glassy polymers and composites is valid for crystalline polymers as well. Mechanical behavior can be categorized in two distinct regimes: (1) linear, where the time dependence can be described in terms of the Boltzmann superposition principle to yield the various moduli uniquely as functions of time or frequency, and (2) nonlinear, where the response to stress, dependent on deformation history, becomes complicated, and present phenomenological theories are only approximations of what happens.

In high-density polyethylene a linear response in extension can be obtained at strains as great as one tenth of one percent, while the linear regime in torsion is confined to strains two orders of magnitude smaller. Why? In simple extension many crystalline polymers show the phenomenon of "necking." A proper description of the nonlinear behavior is lacking and is needed.

Although much is known about the dependence of uniaxial tensile properties on structure, serious gaps remain in the knowledge of deformation under biaxial conditions and of molecular mechanisms associated with degradation of mechanical properties. As noted previously, a primary structural feature of crystalline polymers is the quasiperiodic alternation of crystalline and amorphous layers. The crystals have an extremely high elastic modulus in the chain direction if the chain is fully extended (for polyethylene, $\underline{E}_c\|$ $\cong$ 320 GPa) and a substantially lower modulus if the chain has a helical coil conformation (for polypropylene, $\underline{E}_c\|$ $\cong$ 90 GPa). The elastic modulus perpendicular to the chain direction, $\underline{E}_c\perp$, is much smaller, about 5 GPa. Because the chains are anchored in the adjacent lamellae, the amorphous regions are not in all cases fully disordered. Furthermore, in some cases the lamellae are so wide that the amorphous material must expand on stretching (i.e., they have a Poisson ratio less than 0.5), and the tensile modulus must be replaced by the bulk compressibility modulus, which is substantially larger. For both reasons the elastic modulus in the amorphous region, $\underline{E}_a$, is about 0.5 GPa, and even in the rubbery state the modulus is 10 to 1,000 times higher than one would expect for a rubber. Below the glass transition temperature this value increases to between 5 and 10 GPa.

The alternation of crystalline and amorphous layers yields a low elastic modulus for the bulk polymer, $\underline{E} \sim 10$ GPa. Orientation *per se* does not help much, as the values for the modulus of the crystalline and amorphous components indicate, but any fully extended chains connecting the crystals through amorphous layers increase the elastic modulus in the direction of their orientation. The mechanism of creation for such chains is a subject of some discussion. One view is that drawing activates slip mechanisms, which yield highly oriented, long narrow microfibrils composed of alternating blocks of folded chains (with lateral dimensions between 10 and 20 nm) and amorphous layers bridged by numerous taut tie molecules. The other view is that the mechanism involves strong disordering and recrystallization. Kinetic studies of birefringence, together with small-angle and wide-angle X-ray studies of polymers under various stresses, would be helpful. Theoretical studies are also needed. In any event, the process yields fibrous material with an axial elastic modulus of more than 100 GPa for polyethylene and 30 GPa for polypropylene. Exceptionally high moduli (130 GPa) are obtained with fibers of rodlike polyarylamide molecules such as Kevlar$^R$. Clearly, further research could lead to fibers with modulus values closer to the theoretical limits.

Annealing a fibrous crystalline structure reduces the elastic modulus. Possibly the annealing process transforms the taut tie molecules between the crystalline domains into lax molecules. If annealing is performed with fixed fiber length, the elastic modulus recovers in time at room temperature. Recent $^{13}C$ NMR measurements suggest that the axially aligned, more mobile tie molecules crystallize during elastic recovery, whereas the amount of nonaligned material remains constant. These phenomena invite further investigation.

In a fibrous structure the microfibrils with many taut tie molecules are strong. However, the axial connection by taut tie molecules falls off sharply at the ends. Holes with diameters between 10 and 20 nm form there and concentrate the stress on adjacent microfibrils, which fail sooner than those in the bulk of the sample. The coalescence and growth of such microholes thus leads to a critical crack, which makes the entire sample fail. The prevention of failure depends on either reducing the defects or increasing the strength by introducing more taut tie molecules to bridge the amorphous layer at the end of the microfibril. This can be achieved with highly drawn material of high molecular weight.

Mechanical failure has been treated in the context of fracture mechanics, which studies the growth of flaws. While many aspects of failure can be treated within the context of linear fracture mechanics, there is a major need to account for nonlinearities introduced at the crack tip and for the inherent time-dependent nature of polymers. Furthermore, since spectroscopic and mechanical measurements indicate that failure is associated with skeletal bond ruptures and their coalescence into microvoids, more study is evidently needed of the events that lead to flow initiation.

In spherulitic samples of polyethylene, cracking can occur at low strains, either under an environmental stress or under a low load for a long time. Theoretical and experimental investigations of the mechanisms involved in environmental stress cracking and long-time brittle failure should be expanded.

Stress relaxation at a fixed and recoverable elongation has a fast and a slow component. The former is reasonably well accounted for by the viscosity that controls the reorientation of molecules in the amorphous area, while the latter is related more to the deformation of crystals. An important research opportunity is presented by the molecular and morphological mechanisms of relaxation effects. These can be pursued effectively through dynamic X-ray and light scattering experiments with synchrotron and laser radiation sources.

The wear resistance of a polymer sample generally increases with the molecular weight. The supercrystalline morphology may also play a role. Very few systematic investigations have been performed on these correlations, and even rudimentary knowledge of wear mechanisms is limited.

### e. Thermal properties

Crystalline polymers exhibit a melting temperature that increases tens of degrees with increasing lamella thickness. This effect is relatively well understood in terms of the high surface energy of the fold surface for thin lamellae. A molecular model is less well developed. Less understood is the several-fold thickening of the lamellae when annealed at temperatures close to but below the melting temperature. Possibly this process lowers the energy of the crystal by allowing it to proceed toward the equilibrium shape. Theoretical models based on nucleation and on irreversible thermodynamics have been advanced. However, a better understanding is needed. A key question concerns possible mechanisms by which the molecule within the crystal translates along its axis. Pair-potential calculations hold promise for analyzing this self-diffusion as well as lateral self-diffusion by vacancy diffusion. Other theoretical and computational opportunities lie in various crystal-crystal transitions that occur. Calorimetric measurements, spectroscopic measurements, and theoretical calculations have been brought to bear on the heat capacity of crystalline polymers and have afforded considerable insight into this property.

### f. Transport properties

The sorption or desorption of a penetrant molecule associated with diffusion is usually, at least in the beginning, proportional to the square root of time (Fick's law). Some glasses and crystalline polymers, even when the amorphous component of the latter is above its glass transition temperature, exhibit a change in sorption proportional to $t^n$ with $n$ between 1/2 and 1 (non-Fickian or Type II diffusion). This effect occurs above a critical penetrant concentration at which the penetrant transforms the glass into a much more permeable gel. The kinetics of this transformation can have a significant effect on the diffusion, as can the presence of other species in either the polymer or the penetrant. The details of sorption and diffusion in glasses are understood primarily in semiempirical terms. More research is needed to describe in quantitative terms the mechanism of these processes, which influence many of the uses of polymers.

Practically all the material transport in a semicrystalline polymer is through the amorphous component, the crystals acting as impermeable barriers. Hence the diffusion coefficient as determined from the initial time dependence of the sorption is reduced by tortuosity and blocking factors. The tortuosity factor represents the fact that the impermeable crystals force the penetrant to travel a longer path than in a uniform amorphous material. The blocking factor accounts for the fact that some passages of the amorphous layers are too narrow to admit the larger penetrant molecules. Field-gradient NMR should prove to be a rapid and convenient technique for measuring diffusion in polymers.

In recoverably deformed samples the sorption increases with the immediately recoverable portion of the deformation and remains practically constant in the slowly recoverable portion This can be understood if the slowly recoverable portion of the deformation is actually a recoverable plastic deformation which does not change the specific volume, i.e., the fractional free volume (ffv), of the amorphous component. On the other hand, in samples that are purely plastically deformed, the sorption drops quite drastically because of the increased density of the amorphous component that reduces its ffv. According to this same concept, the diffusion coefficient is an exponential function of the negative inverse ffv. Investigations of these effects should reveal much about the diffusion process, as well as details of the mechanism of polymer deformation.

A substantial help in the prediction of the barrier properties of a polymer is the power law $D'=KD^m$ where $D'$ and $D$ are the diffusion coefficients of the same penetrant in two polymers, and the constants $K$ and $m$ being properties exclusively of the two polymers, independent of the penetrant. In particular, m can be identified with the ratio of the fractional free volumes of the two polymers. Use of this relationship can quantify changes in ffv by means of diffusion measurements as a probe of structures. This relationship can also contribute to the understanding and prediction of the diffusion of larger molecules, such as the important protective additives.

### g. Outstanding problems

Morphology, Crystallization, Melting, Annealing:

1. The influence of entanglements and/or self-diffusion, molecular weight, comonomers, and deformation on crystallization and morphology.
2. The nature of the surface, domain, and mosaic structure of crystals.
3. Molecular models of mechanisms of lamellar thickening during annealing, crystal transitions, and melting.
4. The mechanism of transition from crystal nucleus to spherulite, and the origin of curved crystals and of "twisting" of lamellae in spherulites.
5. The fine structure of biaxially oriented polymers.

Mechanical Properties:

6. *Ab initio* calculations of modulus and strength limits and the development of polymers approaching those limits.
7. Description of nonlinear mechanical behavior.
8. Molecular mechanisms of aging and failure, and lifetime predictions.
9. The mechanisms by which spherulites deform and form fibers.
10. Theoretical and experimental investigations of environmental stress cracking, crack initiation, and wear and fracture mechanics, and including time-dependent materials.

Other Properties:

11. The elementary nature of carrier generation and conduction processes for electrons and ions.
12. Electrical aging and failure mechanisms; and lifetime predictions.
13. Theories of the coupling between electrical, mechanical, and thermal properties.
14. Morphological and molecular base for the influence of the crystals, amorphous components, and deformation on diffusion and sorption.

## 3. The Mesomorphic State

### a. Introduction

Liquid crystals formed by certain substances consisting of small molecules illustrate a liquid mesomorphic state in which molecular organization is neither absent (except for short-range orientations), as in a normal unordered fluid, nor well-developed in three dimensions, as with crystals. These so-called mesogenic small molecules tend to have an asymmetric molecular structure (e.g., one molecular axis much longer than the other two), and the mesomorphic state is characterized by long-range order of the long axes.

A limited class of mesogenic macromolecules, characterized by a backbone chain with a rodlike configuration, will form ordered liquid crystalline solutions. Despite the relative immaturity of the physics and chemistry of mesogenic polymer solutions, it is known that such solutions may be used to fabricate well-oriented solids with enhanced mechanical properties, including high elastic modulus and strength. The possible attainment of such properties in organic polymers with low density, compared to metallic alternatives, has prompted some of the current interest in synthetic mesogenic polymers, as has the similarity between the mesophases of these synthetic macromolecules and those of biological polymers.

With most mesogenic synthetic polymers, the mesophase is nematic, although a cholesteric mesophase has been reported for some. In the nematic mesophase, the rodlike macromolecules tend to be locally ordered in domains, the rod axes being (nearly) parallel within the domain. Within the domains of a cholesteric mesophase, the chains are organized in planes in which the molecular axes are parallel, but the direction of the axes twists in a regular way between adjacent planes. In unoriented liquid crystals, there is no relation between the direction of the molecular axes in neighboring domains, but they are fluid and may be oriented by imposition of suitable external fields. Of course, this orientation is more sluggish for liquid crystals of macromolecules than for small molecules.

Mesogenic polymers include polymers with para-catenated aromatic backbone residues and chains with long sequences in helicoidal conformation. The thermodynamics of the mesophase transformation from the disordered isotropic solution to the ordered mesophase depends on chain length, temperature, and solvent. Even moderately concentrated solutions of mesogenic polymers exhibit interesting and complex rheological properties that are as yet incompletely characterized and imperfectly understood. This is especially true of ordered solutions, but is also the case with isotropic solutions near the phase boundary. The molecular dynamics of such solutions remains largely unexplored.

The following discussion treats the mesophase in the absence of external fields (except temperature and pressure), the effects of external fields (stress, electric, magnetic, surface tension, etc.), the mechanical properties of undiluted polymers derived from mesogenic solutions, and some aspects of the synthesis and characterization of mesogenic polymers. Although this discussion of the mesomorphic state is lengthy, much has had to be omitted. For example, the kinetics of polymerization in such a state and possible effects on the molecular weight distribution deserve attention. The properties of solutions prepared with mesogenic polymers dissolved in mesogenic solvents have not been explored. The methods of characterizing mesogenic rodlike and semiflexible chains in dilute solution require attention, especially because of the tendency for intermolecular association.

### b. Behavior in the absence of external fields

i. Chains with a rodlike or helicoidal configuration. Polymers with an overall rodlike structure are an important class of mesogenic polymers. Examples include helicoidal polymers, such as poly($\gamma$-benzyl-L-glutamate), and chains with para-catenated aromatic residues, such as aromatic polyamides, aromatic polybenzoxazoles, and the commercial Kevlar® fiber. The thermodynamic properties of mesogenic solutions of rodlike polymers have been the subject of experimental and theoretical study, which focused on the effects of polymer chain length and concentration on the equilibrium phase diagram. The major features of this dependence are reasonably understood well. The influence of orientation-dependent intermolecular interactions, however, is far less well characterized or understood. These interactions are important in understanding the effects of temperature, solute-solvent interactions, and solute-solute interactions (including electrostatic interactions). The latter are particularly pertinent since many mesogenic polymers are soluble only as positively charged protonated species in strong acid solvents (e.g., sulfuric acid). Order-order transitions of the mesomorphic state have not yet received much attention, although there is some evidence for their existence. Neither has the supramolecular structure of the ordered state received much investigation. Some features of the cholesteric mesophases have not been elucidated, nor have the kinetics of the order-disorder phase transformation and the kinetics of domain reorganization in the ordered state.

In studies of rodlike polymers investigators have relied on a variety of experimental methods (polarized microscopy, light scattering, nuclear magnetic resonance) to investigate phase diagrams and molecular organization in the ordered state. The effects of molecular weight and molecular weight distribution on the phase equilibrium will continue to be of interest, along with possible fractionation according to chain length when a heterodisperse polymer forms two phases in equilibrium. As more mesogenic rodlike polymers become available, investigation of the effect of intermolecular interactions on the phase equilibrium will advance, permitting, for example, a better understanding of the effect of temperature on the phase transformation. Methods for studing molecular dynamics in the ordered state have scarcely been initiated, and new efforts can be anticipated. Intensity-fluctuation (or dynamic) light-scattering methods are possible, along with fluorescence probes, NMR bandwidth measurements, and dynamic mechanical methods.

In dealing with mesogenic polymers, one is faced with the difficult problem of nonequilibrium (metastable) behavior caused by intermolecular aggregation. The severely diminished number of molecular conformations available to the rigid chains often makes the dissolution process slow and uncertain. Because of the extreme anisotropy of the molecular configurations, even relatively weak attractive interactions between chain elements may act collectively to inhibit dissolution, making it necessary to use such strongly interacting solvents as protonic acids to solvate the polymer and effect solution. The presence of metastable intermolecular aggregates vitiates interpretation of experimental data and can prohibit attainment of the expected mesomorphic transition. Methods to identify and study interchain association deserve attention.

ii. Chains with accessible rotational isomeric states (semiflexible chains). The preceding description treated macromolecules that have a rodlike configuration. It has been predicted that certain types of semiflexible chains with a coillike conformation in dilute solution might form nematic solutions with the molecules assuming an extended rodlike conformation under appropriate conditions of concentration and chain length. This mesogenic characteristic is not observed with most coiling polymers, but may obtain if the rotational states available to each repeating unit are severely restricted so that, above some limiting solute concentration, the free energy of mixing of the coillike chains becomes unfavorable compared with the formation of the nematic state. Certain cellulosic polymers have been reported to exhibit mesogenic behavior of this kind. The possibility that semiflexible chains might exhibit mesogenic behavior is especially interesting since these might exhibit better solubility in the isotropic state than rodlike chains.

As emphasized elsewhere, theoretical considerations and experiment agree that for coillike chains, the population of rotational isomers is not much affected by solute concentration in the absence of phase transformations. Thus the conformation of mesogenic semiflexible chains is expected to be nearly independent of concentration (with the possible exception of so-called excluded volume effects at very low concentration) up to the concentration for mesophase formation. This aspect of mesophase formation with semiflexible chains will likely receive further attention since it bears directly on the assessment of which chain structures should be expected to exhibit mesogenic behavior. As with nonmesogenic flexible chain polymers, it can be expected that neutron, X-ray, and light scattering methods will be employed to elucidate this behavior.

The variables of solute molecular weight and molecular weight distribution, as well as the effects of solute-solute and solute-solvent interactions, will form the frame for most of the theoretical and experimental studies on mesophase transformation with semiflexible chains. Currently available preliminary reports have scarcely begun to probe the effects of these variables. The necessary systematic studies should be part of future work. Similarly, as semiflexible polymers that form mesogenic solutions are identified, investigations can commence on the kinetics of the phase transformation, the domain structure, and molecular dynamics in the ordered phase.

As with solutions of rodlike chains, the possibility of metastable intermolecular association is an important problem with solutions of semiflexible chains. For example, it is known that cellulose esters can exhibit substantial intermolecular association even in very dilute solutions. Association of this sort could prevent formation of the equilibrium mesophase, and so lead to incorrect interpretation of experimental data if ignored.

iii. Mixtures of rodlike and flexible or semiflexible coils. Solutions containing both rodlike and flexible or semiflexible coils are predicted to exhibit mesogenic behavior, with separation into an ordered phase rich in the coillike component. Fragmentary reports consistent with this expected behavior have appeared, and systematic studies should be a major part of future programs on solutions of such mesogenic mixtures. The anticipated phase separation provides interesting possibilities for the formation of a "composite" structure on a molecular scale comprising domains of ordered rodlike chains with a high modulus dispersed in an amorphous matrix. The domain size and stability will likely be kinetically controlled because the high viscosity of the phase rich in the flexible coils.

### c. Effects of external fields

i. Effects on the phase diagram. Since mesomorphic solutions are fluids, the application of external fields can effect long-range molecular orientation. The principal interest with mesogenic solutions of macromolecules is the application of stress fields, which can be used to produce well-oriented states that have direct application in solution-processing technology. With mesogenic fluids of low molecular weight, the use of magnetic fields has played an important role in the study of mesomorphic single crystals created by the action of surface forces. It has been demonstrated theoretically and experimentally that elongational flow fields can augment the mesomorphic transition for a given solute. Similar effects may be possible with uniform magnetic and electric fields, but the extent of the effect may be small for materials with typical anisotropy of the pertinent susceptibilities. The effects of external fields on the phase diagram will probably be of theoretical and experimental interest in future studies.

ii. Rheological properties and molecular dynamics. One of the earliest rheological features noted for mesogenic solutions of macromolecules was the pronounced maximum in the shear viscosity with increasing solute concentration, the maximum occurring near the concentration for the onset of the phase transformation. Studies have now reached the stage where some features of the rheological properties of isotropic nematogenic solutions of rodlike polymers are understood, but even with isotropic solutions much remains to be done. The strong dependence of the viscosity on solute concentration and chain length of such isotropic solutions is attributed to the same sort of geometric repulsive interaction that is implicated in the mesophase transformation. A crude model for the dependence of some rheological properties on the rate of steady-state deformation in shear is available, but more systematic data are needed. The all-important time-dependent rheological properties have received scant attention, and this deficiency should be redressed in future work. In addition to the ordinary rheological studies of creep, recovery, or deformation under a stress varying sinusoidally in time, which have found wide application in studies of coillike polymers, rheooptical methods should be particularly attractive with nematogenic solutions of rodlike chains because the principal axes of the refractive index, absorption, and fluorescence emission tensors should be well defined in terms of the molecular axis. Thus, for example, the investigations should include flow birefringence and dichroism. Intensity-fluctuation light-scattering should also be informative in the study of molecular dynamics in such fluids.

The rheological properties of ordered mesogenic polymer solutions have received some attention, and a number of unusual features have been noted. The studies are bound to be complicated by the effects of ordered domains, which may have sizes comparable to the critical dimensions of the instrument or the gradients in the shear field. Optical experiments are further complicated by the turbidity of the mesophase. The subject is presently in a primitive state and should receive more attention in the future. The rheological behavior determined, for example, by cone-and-plate rheometry has been shown to be complex and nonlinear even for small and/or slow deformations. Moreover, it is not yet firmly established whether the time-temperature equivalence principle that is so useful with coillike polymers will have similar application to mesophases over a wide range of the time variable. The molecular dynamics of the ordered state and, particularly, of the oriented ordered state have received little attention despite their obvious importance. The domain structure and size can be expected to play a role in such properties. Considerable theoretical and experimental work is needed on the rheological properties of ordered mesogenic polymer solutions before those properties can be understood.

iii. Continuum foundations of the rheological properties of the nematic state. Continuum theories can provide a foundation for study of the rheological properties mentioned above. Appreciable work has been done on continuum theories for mesogenic fluids consisting of small molecules, but almost no attention has been given to the continuum mechanics of mesogenic polymer solutions with their long-term memory effects. As is well known, memory effects dominate the properties of coillike polymers, and presently available data suggest that the same will be true of mesogenic polymers. This difficult subject deserves, and will probably receive, more attention as the rheological properties become better characterized phenomenologically.

### d. Mechanical properties

Mesogenic polymer solutions form oriented or unoriented ordered solids.

The mechanical properties of the latter will be anisotropic, and the differences in different directions will probably be large. For example, with uniaxial (fiberlike) orientation the modulus may be large in the direction along the fiber axis but small in the transverse direction. Only fragmentary data are presently available; theoretical estimates of the mechanical properties to be expected; and the effects of various imperfections are undeveloped. In fact, the problems are similar to those discussed in section 2b in connection with the properties of well oriented fibers of crystalline polymers.

Some aromatic polyesters have been reported to form a nematic solid when cooled from a disordered melt. The morphology and anisotropic mechanical properties of such materials deserve careful study. One can anticipate that the relatively low molecular mobility in the melt may impede full development of the equilibrium order in such thermotropic polymers.

Mixtures of rodlike and coillike chains forming a phase-separated system of ordered and disordered components offer a method of preparing interesting "composite" systems in which the dispersed component may be small and show anisotropic mechanical properties. The preparation and study of such systems represents a broad subject in itself, offering numerous possibilities of achieving enhanced mechanical properties.

### e. Outstanding problems

1. The rheological properties of nematic solutions of rodlike chains, including the orientation of the chains in a flow field.
2. The phase equilibria of mixtures of rodlike and coiled polymer chains in solution.
3. The possibility of a nematic phase transition of suitable polymers that have a coillike conformation in very dilute solution.
4. The effects of interchain interaction (especially electrostatic) on the phase equilibria of nematogenic polymer solutions.
5. The limiting modulus and ultimate properties to be expected with well-oriented rodlike chains in the solid state.
6. The effects of external fields other than flow fields on molecular orientation of nematic solutions.

## 4. Microphase-Heterogeneous Systems

A heterogeneous system shall be considered here as consisting of more than a single phase at dispersion greater than molecular (1.0 nm) but less than macroscopic (0.1 mm). The morphology is often determined by kinetic rather than thermodynamic factors. Such systems often exhibit unique mechanical, thermal, electrical, or transport properties not readily attainable in a homogeneous system.

### a. Block and graft copolymers

Block and graft copolymers consist of two or more chain segments of different repeat units in sequences usually greater than a few monomer units. In block copolymers the sequences occur within the main chain, and the polymer may be classified as diblock (a chain consisting of two parts, one of each type of sequence), triblock (three parts), or multiblock. Graft copolymers consist of main chains of a given type to which one or more side chains of a different type are appended. If the chain sequences of block or graft copolymers are sufficiently different chemically and sufficiently long, phase separation occurs. However, it is usually a "microphase" because its size is limited by the length of the molecular sequence that may be involved.

i. Morphology: Evidence for phase separation. Random copolymers have glass transition temperatures ($T_g$) intermediate between those of the homopolymer components. On the other hand, phase-separated block or graft copolymers often exhibit separate $T_g$'s characteristic of each component. If their block length is short, leading to small domain size, the $T_g$ will differ from that of a macrophase polymer in a manner dependent upon the ratio of surface area to volume of the domain. Glass transition temperatures may be observed by conventional methods (calorimetric, dynamic mechanical, dilatometric) with varying degrees of sensitivity, so this criterion for phase separation depends on the method used.

If one component of a block or graft copolymer is crystallizable, the melting point depression associated with a finite crystal size provides a measure of domain size. The depression will be less than for a random copolymer. Crystallization rates of sequences in block or graft copolymers are usually significantly less than those for homopolymers, indicating that degree of crystallinity and morphology are often controlled by kinetic factors.

Because phase dimensions are often in the range of 1-100 nm, they may be most readily studied by transmission electron microscopy on cast or microtomed thin films. It is usually necessary to augment contrast by staining one of the phases with an electron-dense material (for example, $OsO_4$ for unsaturated polymers). Finding suitable staining agents to provide contrast between phases for microscopy or scattering experiments, however, is often difficult. A new technique is to use neutron scattering in which contrast is developed by isotopic substitution of deuterium for hydrogen in one of the phases.

Phase morphologies may be idealized as spherical, cylindrical, or lamellar depending upon relative lengths of chain sequences (see below). These microphases sometimes develop a macrolattice structure that can cause X-ray or optical diffraction. Depending upon relative lengths of sequences, one or the other component may be the dispersed or the continuous phase, or there may be two interpenetrating phases. More complex systems may involve blends of block or graft copolymers with homopolymers. A promising possibility is the study of neutron scattering from isotopically labeled systems, in which the label is selectively located on one of the blocks or at the junction between them.

ii. Effect of casting and molding conditions. Solid samples of block or graft copolymers may be prepared by casting from the melt or from solution. In solvent casting, the morphology often depends upon the choice of solvent. If a solvent-cast sample is heated above the $T_g$ of both components, as in processing, the morphology may change. Under these conditions, phase separation may or may not occur in the melt. Such phase transitions in the melt call for experimental and theoretical characterization, and better understanding of their effect upon rheology. If the melt is phase-separated, morphology will be affected by rheological factors in a manner dependent upon processing geometry, sequence lengths of phases, and temperature. At normal cooling rates, specimens often adopt a morphology dependent upon kinetics.

iii. Orientation. Shearing or stretching of a phase-separated melt, particularly with cylindrical or lamellar morphology, can lead to orientation of phase boundaries (as may be demonstrated by microscopy or diffraction) or to molecular orientation within phases (as may be demonstrated by IR dichroism). Such oriented systems often have highly anisotropic mechanical properties.

iv. Domain boundaries. As theoretically predicted (see below) and experimentally measured, the boundaries between microphases have finite widths (in the range of 0.5-5 nm). This is qualitatively observed by electron microscopy and small-angle X-ray scattering. Boundary regions having a thickness dependent upon the molecular weights of the blocks and upon differences in cohesive energy density may represent a significant volume fraction of the system and may thus appreciably affect properties.

v. Thermodynamics and statistical mechanics. Phase separation equilibria are described by minimization of free energy, taking into account entropic elasticity of polymer chains, density uniformity, and cohesive energy density. Thermodynamic theories are capable of predicting the most favorable domain size and shape (sphere, cylinder, lamellar), which is dependent upon temperature and the molecular weights of block segments. Predictions of boundary layer thicknesses are moderately successful but depend on knowledge of molecular parameters (interaction coefficients). Theories have been extended to blends of block copolymers with homopolymers, in which thermodynamics, morphology, and boundary properties depend upon molecular-weight matching between components as well as upon interaction coefficients.

In dilute solution, two models of the conformation of diblock copolymers are the dumbbell model and the shell-core model, which differ in the relative location of the two blocks. In the latter the locations of components in the shell and the core depend upon the relative interaction of the two components with the solvents. Neutron scattering studies of block copolymers with deuterium-labelled blocks have served to decide between these models.

vi. Rheology. The melt viscosity of phase-separated systems above $T_g$ is generally greater than for homophase systems of comparable molecular weight. This occurs because of (1) the "filler effect" of a separated phase, (2) the increase in surface area arising from the deformation of dispersed phases, and (3) the increase in energy associated with pulling a block of a particular type through a phase of differing cohesive energy density. Since the morphology is perturbed by flow, nonlinear rheology is often observed.

The viscoelasticity of block copolymers has been called "thermorheologically complex" in that such polymers do not obey time-temperature superposition with a single temperature-dependent shift factor. There are at least two separate $T_g$'s, each of which would be associated with a different shift factor in the viscosity-time-temperature relationship.

vii. Mechanical properties. Phase-separated block copolymers often have the properties of thermoplastic rubbers in a temperature range above the $T_g$ of one block but below that of the other (the hard block). This property is most evident in triblock (ABA) copolymers where A is the hard block. These A regions soften and permit flow on heating. Above $T_g$ of A, the material is melt-processable, but below it behaves like a cross-linked rubber. Since the thermoplastic cross-link is often not as stable as a chemical cross-link, creep and relaxation phenomena are seen even below the $T_g$ of A. To reduce this effect, continued efforts are needed to synthesize copolymers which either have hard blocks of higher $T_g$ or are crystalline.

Multiblock copolymers, such as segmented polyurethanes, often exhibit incomplete phase separation. Phases may become compatible at high temperatures and separate upon cooling. This phase separation is often time dependent, leading to time-dependent $T_g$'s or mechanical loss peaks. This phenomenon has also been studied by free-induction-decay NMR and by observation of the time dependence of intensities of small-angle X-ray scattering.

Stress-strain curves of interconnected microphase sytems often exhibit hysteresis arising from rupture of one of the phases, which leads to an increase in interphase surface area and in free energy. With time, healing occurs, accentuated by elevated temperature. Healing may be observed microscopically and by optical scattering, and it results in recovery of mechanical properties.

Block or graft copolymers in which the rubbery component is the minor one have properties of high-impact-strength glassy polymers. The dispersed rubbery microphases serve as crack stoppers and craze initiators, leading to greater resistance to failure under impact conditions.

### b. Ionomers

Ionomers are a special type of block or graft copolymer in which a component has an ionizable group such as COOH or $SO_3H$. They may exist in an acid or a salt form. The salts have enhanced mechanical properties such as toughness and low heat distortion that have been associated with phase separation of ionic regions.

Evidence for microphase separation is seen in a small-angle X-ray peak observed for salts but not acids, and in viscoelastic and dielectric studies. A new loss-peak is observed corresponding to the onset of motion in the more tightly bonded ionic regions. Indirect evidence also comes from infrared observation of the perturbations of frequencies and intensities of bands. Preliminary electron microspcopic observations indicate the existence of electron-dense phase-separation regions.

For ionomers based upon a crystalline parent polymer, e.g., poly(ethylene-co-methacrylic acid) (Surlyn®), ionization results in decreased crystallinity and crystallization rate. Spherulite formation is suppressed, leading to enhanced optical clarity.

X-ray radial distribution-function analysis and quantitative integrated intensity measurements provide information about the size, concentration, and electron density of ionic clusters. The existence of scattering maxima requires a periodicity of electron density. Models to account for this are intercluster (paracrystalline lattice) or intracluster (shell-core, lamellar). Quantitative considerations favor the latter. Scattering maxima are suppressed by water absorption, indicating a break-up of intracluster order.

The theory of cluster formation has been developed in a manner similar to that for phase separation in block copolymers, but with the additional inclusion of coulombic contributions to the free energy. Depending upon their size, ionic aggregates may be classified as isolated ion pairs, multiplets, or clusters, the relative concentrations being dependent upon the concentration and degree of ionization of the ionizable groups.

The formation of ion aggregates in ionomer solutions leads to enhanced viscosity and nonlinear effects. Especially with polyvalent cations, precipitation and insolubility occur. The inclusion of ionic groups within an amorphous phase of a bulk polymer leads to an increase in its $\underline{T_g}$. As previously indicated, the formation of a phase-separated ionic domain may lead to a separate transition temperature and viscoelastic or dielectric loss peaks. The material becomes thermorheologically complex. Creep and relaxation are suppressed and heat distortion temperatures are increased. The enhanced "toughness" of the material is of obvious commercial significance. Rheooptical studies may distinguish between the responses of structures within and outside of the ionic domains.

### c. Blends

Blends are mixtures of two or more different polymers (or different molecular-weight species of a single polymer). Compatible blends are single-phase systems in which components mix on a molecular level. Because of the low entropy of mixing between polymers, these are the exception and most polymer mixtures show phase separation. An important problem is to determine conditions leading to compatibility. The morphology of such blends is often kinetically determined, and the existence of microphases is common.

i. Evidence for compatibility. The evidence for compatibility in blends is similar to that previously stated for block and graft copolymers: (1) the existence of a single $T_g$, (2) absence of X-ray or neutron scattering characteristic of microphases greater than molecular in size, and (3) examination by microscopy. With blends, dispersion sizes of phases are not limited by molecular factors, as they are with block copolymers. Phases may grow to sizes that scatter visible light to a great degree and can be seen with the optical microscope. In fact, at equilibrium, macroscopic phase separation should occur for incompatible systems. The optical turbidity of an incompatible blend depends on both the domain size and the difference of refractive index between components.

Additional evidence for compatibilty can come from studies of volume changes upon mixing. For incompatible blends $\Delta \underline{V} = 0$; for compatible blends there is often a volume decrease. Similarly, there is usually a negative enthalpy of mixing for compatible blends, although its direct measurement is difficult.

Further evidence for compatibility may come from spectroscopic techniques. For a phase-separated blend, the molecular mobility within each phase should be different, as can be determined by NMR-measured relaxation times or by fluorescence depolarization. Infrared or Raman frequencies of components of incompatible blends should be unperturbed, whereas compatible systems should show frequency or intensity changes characteristic of interaction between components. Studies of additivity of spectra of components in blends by the FTIR technique have proved useful for this purpose.

Another optical method is based upon fluorescence spectroscopy. Nonradiative energy transfer may occur between compatible species. For blends with a crystallizable component, there will be a depression of the melting point of crystals if the one component is compatible with the amorphous phase of the other. The amount is predictable by standard thermodynamics from the molecular weights of the components and the interaction parameter $\underline{X}_{12}$ between them. If both components may crystallize, melting-point depressions of both should be observed; an eutectic mixture should occur, although its observation is difficult because of kinetic limitations. This assumes that the components do not form crystalline solutions, as is usually the case.

ii. Morphology. Compatible amorphous blends are homogeneous at the molecular level and exhibit no discernible morphology. Molecular weights and dimensions of molecules within the blend (as might be measured, for example, by neutron scattering with a deuterium-labeled component) are characteristic of those of a single molecule and comparable with values found in solution in a low-molecular-weight solvent. Second virial coefficients are zero or positive. Aggregates exist with phase-separated blends, the size determined by either (1) the kinetics of phase separation if the incompatible blend arises from phase separation from a compatible mixture (see "Kinetics" below), or (2) melt blending of components, in which case the morphology will depend upon mixing geometry, power input, time, and component rheology.

Sizes of dispersion and degrees of phase separation may be measured microscopically or characterized by X-ray, neutron, or light scattering techniques depending upon domain size and contrast between components. For blends with crystalline components, degrees of crystallinity, unit cell structures, and crystal sizes may be analyzed by conventional X-ray diffraction techniques. A problem arises in location of the noncrystalline component. Interlamellar location is indicated by an increase in interlamellar distance with content of the amorphous component. Spherulitic structure is observable microscopically or may be studied by small-angle light scattering. If the content of the noncrystalline component of the blend is not large (less than 20-30 percent), the spherulitic structure is preserved and the noncrystalline component resides within the spherulite.

iii. Phase diagrams and thermodynamics. As with systems of low molecular weight, equilibrium compatibility of polymer blends may be expressed as phase diagrams that specify the range of concentrations and temperatures over which compatibility occurs. The experimental determination of such phase diagrams (for example, by the observation of cloud points) is difficult because of kinetic limitations. For this reason measurements are often made on three-component systems consisting of two polymers and a solvent, and phase equilibrium is represented on a triangular diagram. Approach to equilibrium becomes slow as $\underline{T}_g$ is approached.

Upper and lower critical solution temperatures are frequently observed, below and above which compatible blends become incompatible. Conventional constant-volume theories predict the existence of an upper critical solution temperature at a position dependent upon molecular weights of components and the interaction between them. Lower critical solution temperatures are predicted by an equation of state or by theories in which volume of mixing differs from zero (lattices with holes). Predictability of transition temperatures and compatibility is hindered by the lack of information about interaction parameters, volume-of-mixing data, and their dependence on composition and temperature. Research emphasis in these areas is desirable.

Because of the low entropy of mixing, compatibility is most dependent on a negative enthalpy of mixing, related to attractive interaction energy between components. Predictions of this from calorimetric studies on model compounds of low molecular weight have met with some success. Predictions based upon solubility parameters of components have not been so successful because the requisite negative $\Delta \underline{H}$ usually arises from specific interactions between components.

iv. Kinetics and phase separation. Polymer blends are often processed at temperatures at which phase separation occurs. In such cases the understanding of phase-separation kinetics is important. Phase diagrams are characterized by the existence of the binodal and spinodal lines of metastability and absolute stability of phases. In the metastable region phase separation occurs through statistical fluctuation to produce a nucleus of critical size, the probability of which depends on the degree of overcooling or undercooling and on the interfacial energy. The nucleated domain then grows at a rate limited by diffusion. In the region of absolute stability, small fluctuations in composition may grow according to spinodal mechanisms. This leads to fluctuations in composition of approximately constant wavelength, but growing amplitude. The resulting phase-separated regions may subsequently grow by "Ostwald ripening" so as to decrease interfacial area. Desired morphologies may be optimized through understanding of phase-separation kinetics.

v. Mechanical and rheological properties. Molecular interaction occurring in compatible blends often leads to enhanced mechanical properties (elastic modulus, tensile strength). The rheology of a compatible blend is like that of a homopolymer of comparable average molecular weight, entanglement spacing, and $T_g$. Means are needed to predict these quantities in terms of properties of the components. The use of blends of rubbers to enhance rheological and processing characteristics is still an art, and scientific understanding is desirable. Blends of polymers having low $T_g$ and high $T_g$ serve as polymeric plasticizers that do not suffer loss by evaporation or extraction as with plasticizers of low molecular weight.

Phase-separated blends behave as composites. The relationships between composition and properties depends upon morphology. The bounds on properties are those given by series and parallel models. Well-defined morphologies (dispersed spheres, arrays of cylinders, or lamallae) can be described in terms of composite theory. Prediction of elastic modulus is easier than prediction of ultimate properties. Failure is often localized at phase separation boundaries and is related to the degree of interphase adhesion and to the diffuseness of the boundary. Interphase adhesion may often be promoted through use of block copolymers as surfactants. A high modulus or high $T_g$ polymer dispersed in a softer matrix serves as a filler, enhancing the modulus. Dispersions of low $T_g$ polymer (rubbers) in a high $T_g$ matrix (glasses) are used for enhancement of impact resistance, with interphase binding being promoted through grafting and use of block copolymers. Without such improvement, the performance of many glassy polymers would be unsatisfactory. Rubbery polymers are sometimes blended with crystalline polymers (e.g., ethylene-propylene copolymer with polypropylene) to enhance their impact properties. In this case bonding may be enhanced by cocrystallization of segments of the copolymer with the matrix. The morphology of incompatible blends may be affected by deformation, leading, for example, to strain softening.

The rheology of incompatible blends may be modelled in terms of assumptions regarding the morphology. Non-Newtonian phenomena are common because of the perturbation of morphology by flow.

vi. Transport properties. Transport through incompatible blends is also treatable by composite theory. The tortuosity of the path taken by a diffusing molecule is highly dependent on morphology. Transport changes abruptly with phase inversion and is strongly dependent on whether the phase with higher diffusion rate is continuous or disperse. Transport properties in oriented systems are obviously anisotropic. Application of the modern approaches of percolation theory to these problems is important.

### d. Outstanding problems

1. Development of thermodynamic theories of block copolymers and blends.
2. Measurements and theories of interface widths of block copolymers and blends.
3. Development of theories interrelating morphology, mechanical properties, and rheological properties of microphase-separated systems.
4. Means to predict the compatibility of blends in terms of the properties of components.
5. Theories of the kinetics of phase separation of blends.

## 5. Polymer Surfaces and Interfaces

### a. Introduction

A polymer surface is the face the polymer presents to the outside world. The utility of a polymer may depend on such outward properties as durability, inertness, electrical behavior, friction, appearance, compatibility with life processes, and ability to bond to other materials. The properties relate to the fundamental science of the surface, a fascinating subject receiving increasing attention today.

Some of the features of polymer surfaces and interfaces are common to other substances, but many arise uniquely from the macromolecular character. For instance, when a polymer chain approaches a boundary layer it must turn and direct itself back into its own phase, a requirement not imposed on small, rigid molecules.

A surface is often dramatically different from an interior. For instance, polymer crystals may take on a unique morphology and orientation as a result of special nucleation processes on the substrate. Even when the material is amorphous, the molecules statistically orient themselves in a special way at the surface to facilitate the turning back, to minimize interaction contacts missing at a surface, or to maximize contacts at a high-energy interface. If the material is a copolymer or blend, the less interactive units are preferentially drawn to the outer layer. In the case of an interface between two polymers, the bulk of each phase may be quite pure, but the interface consists of a region, frequently several nanometers thick, where extensive mixing occurs. The origins of all these phenomena are clear, but their measurement and prediction is limited, especially in complex systems.

### b. Modified surfaces

The differences between surface and bulk properties cited so far have been inherent ones, but much research is centered on modified surfaces. Great success has been achieved in tailoring surfaces to satisfy special needs. The most common technique involves coating, but even here new twists such as plasma polymerization, grafting, and sputtering metal onto polymers are being developed. An interesting coating, specific to polymers, involves the formation of a topologically inseparable interpenetrating polymer network of one polymer on another.

Surfaces are often changed by mixing the bulk material with a chemical that concentrates at the surface; when this surfactant is polymeric it will not evaporate. A surface may also be altered by a chemical reaction--polyfluorocarbons may be etched with sodium, or polyethylene may be treated with fluorine, each producing outer layers more suitable for bonding. Surfaces can be strengthened by cross linking induced through exposure to inert-gas plasmas. The value of surface modification is so great, the possibilities so manifold, and the resulting structures so intriguing, that this subject should continue to attract increasing attention and inventiveness.

Not all surface modification is deliberate or desirable. With aging, environmental attack, or abrasion, physical and chemical changes occur. How to prevent this degradation or alleviate its detrimental effects are important problems. The primary steps, though, are the identification and measurement of deterioration processes.

### c. Fundamental studies

Mastery of the surface conditions of polymers must be built on a foundation of systematically acquired scientific knowledge. Experimental probes capable of distinguishing the outer region from the interior must be developed. In the past few years many such instruments have come forth. Scanning electron microscopes now have been developed with increased power with less radiation damage to the sample. The faint infrared and Raman reflectance spectra attributable to the small surface region can be detected by the Fourier-transform interferometric technique. The newest types of probes are exemplified by X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), secondary-ion mass spectra (SIMS), and Auger spectroscopy. In each the material is bombarded by electromagnetic radiation or ions, and the electron or ion emission from the outer layers is interpreted in terms of structure and composition. Compilation of spectral patterns for functional groups, now begun, will facilitate interpretation. Finally, low-energy electron diffraction (LEED) studies have been tried, but this technique has not yet proved to be as important with polymers as with inorganic crystals.

Spectral tools complement the traditional studies of surfaces, based on observation of area, composition, thermodynamics, energetics, and rheology. Surface and interfacial tension are not easily measured for polymers, because of their complex rheology. Difficult to determine, too, is the surface free energy of a solid polymer (more should be known about the meaning of critical surface tension). This difficulty has resulted in a paucity of essential data. The available interfacial energies have been interpreted in terms of contributions from dispersive, dipolar, acid-base, and hydrogen-bonding terms. The results are useful and widely employed, but the theoretical foundation is weak. The limits of applicability are not well recognized or understood.

Another traditional study, that of adsorption phenomena, is also incomplete. One concern is the adsorption of small molecules onto polymers: how they arrange, the energetics, the adsorption isotherm. Another process for study is the adsorption of polymers, generally from solution, onto solid surfaces. The kinetics of desorption pose problems because of the many points at which each macromolecule can attach. Ellipsometry remains a powerful tool for characterizing thin polymer layers.

The dynamical behavior of polymers at interfaces is an important subject. How are the modes of motion of macromolecules modified by the surface? Attention focuses also on two aspects of the dynamics of adhesive bonding and coating. One is the making of good contact between polymer and substrate, which depends on film spreading and the flow into surface irregularities. Descriptions of these processes based on Stokes' equation are inadequate. The other is the mechanics of adhesive detachment. Frequently the mechanical strength of a joint exceeds the free energy of adhesion. This can be attributed to two factors: (1) the energy required to separate units of the two surfaces is thought to be an activation energy, rather than the energy difference between the initial (bonded) and final (unbonded) states, but the kinetic path, on a microscopic basis, has not been specified; and (2) the mechanical energy put in is dissipated in viscoelastic deformation of the polymer in advance of a fracture tip. The mechanics of interfacial fracture are particularly difficult when one surface has been treated with a coupling agent, such as siloxane on glass, but this represents a key problem in understanding the strength of fiber-reinforced composites.

Much of the study of polymer surface properties is inspired by a desire to achieve a basic understanding of adhesives, coatings, and composites. The fundamental laws emerge from consideration of simple model systems, but one must bear in mind the highly complex factors that affect real systems. The polymers involved are frequently unusual materials with many rings in the backbone to provide thermal stability. Typically there are fillers, fibers, plasticizers, antioxidants, etc. The polymers may be blends, or they may contain block copolymers (the value of which is well documented but poorly understood). The state after application generally differs substantially from the initial state: For instance, the polymer may become highly cross-linked, it may chemically attach to the substrate directly or through a coupling agent, and solvent may evaporate. Progress is being made by isolating each of these factors.

### d. Conclusions

Polymer surfaces and interfaces are likely to be a lively subject of research in the future for a number of reasons: (1) Surface science is a tremendously active area in all branches of materials science. The techniques, insights, and interest thus generated, and the investigators drawing, can be expected to enlighten the polymer field. (2)

Technology is generating questions that call for basic research and, at the same time, is quickly utilizing fundamental advances, as in the incorporation of block copolymers in adhesives and the adaption of research instruments to monitoring production. (3) Interfacial properties impinge on other areas, such as the properties of blends and composites. Finally, (4) opportunities exist for fundamental contributions in an engrossing research area.

### e. Outstanding problems

1. The role of coupling agents in enhancing bonding between polymers and substrates, particularly with respect to impact and peel strength, resistance to stress induced by differential thermal expansion, and solvent induced debonding.
2. The development of means of modifying polymer surfaces to achieve desired changes of surface properties.
3. The refinement of techniques to analyze thermodynamics, composition, and organization of surface and interfacial regions of polymers.
4. The development of laws describing the rheology of polymer layers on inpenetrable substrates.

## 6. Concluding Remarks

The study of the condensed phases of polymers poses challenging problems. Fortunately, some of the newest techniques hold out great promise for facilitating advancement of our knowledge. Small angle neutron scattering is particularly promising in providing information about single-chain conformations in the condensed state, information which is relevant to our understanding of amorphous polymers, blends, block copolymers, and crystalline polymers. This technique also allows one to obtain much needed information about interaction between polymeric species in the melt. New techniques of examining surfaces, such as X-ray photoelectron spectroscopy, will permit the determination of concentrations and orientations of surface species and enable us to better understand surface energies. The structure of diffuse interfaces is being studied using the high angle portion of small angle X-ray scattering. Dynamics at the molecular level is being probed by inelastic and quasielastic light and neutron scattering techniques. Methods such as time-dependent X-ray diffraction, use of high energy sources such as synchrotrons, and time resolved FTIR spectroscopy, show promise of probing the dynamics of larger structures. Employing the most modern methods to improve the resolution of NMR, as in magic angle spinning, yields a bounty of new results. Morphology is being elucidated by new electron microscopy techniques along with scattering methods. Advanced methods involving STEM microscopy and new approaches for producing contrast through selective staining permit the study of structures in phase-separated and crystalline polymers, and their changes during deformation. Motion and structure in polymers is being studied through large-scale computer simulations.

Finally, it is worthwhile to comment on the important role which theory has played in cutting through the apparent complexity of certain polymer problems, sometimes reducing them to utter simplicity (at least as a first approximation). Examples are the elegant theory of rubber elasticity, the concept of Rouse modes, and the idea of kinetic control of crystal properties. The role of theory is as strong today as ever: witness the picture of polymer dynamics which emerges from reptation theory, and the unified approach to uncovering a myriad of solution laws which emerge upon application of scaling concepts.

## C. PROCESSING AND ENGINEERING PROPERTIES

### 1. Introduction

The history of mankind is often divided into eras defined by materials. The "stone age," the "bronze age," and the enduring "iron age" are terms conveying the aura of dependence on the characteristic material in use. In this context mankind can be said to be moving rapidly into the "plastics age" (even though the term plastics is inadequate to cover the many important classes of macromolecular substances). The revolutionary pace of this development is evident in the fact that synthetic macromolecular materials have exceeded the volume of steel production only a few decades after their introduction. The trend to increased use of macromolecular materials undoubtedly will continue.

#### a. Polymers as materials

Macromolecular substances exist in many forms, differing not only on a molecular level but also in the macroscopic properties that govern their suitability in various applications. The presence of a chain structure is the single unifying theme underlying this class of materials. Differences within the class arise through variations in chain length, chemical composition, chain branching, cross-linking, and compositional heterogeneity. The range of structural options is enormous, and the diversity of properties and applications has not approached any identifiable limits.

The polymer or base macromolecular resin is compounded with various other substances, which may or may not be polymeric, to form a material of commerce. The material is then processed, in one or more operations, to form the final product, which may be anything from an automobile spring to a food package. It is important to realize that polymer-based materials can be produced with properties that compare favorably with those of other classes of structural materials. The public image of plastics as cheap substitutes for superior materials is outmoded and refers only to one extreme of the spectrum of uses. Plastic materials already offer superior combinations of properties and significant processing advantages in many applications, and recent advances give promise of even greater superiority.

Polymers, perhaps more than the other major material systems (metals and ceramics), involve the interaction of many disciplines.

In the sequence from monomer production to finished product the macromolecular material undergoes irreversible changes. Each step is affected by all the previous ones and will influence the later ones and, hence, the properties of the finished product. The purity of the monomer affects the mechanisms and kinetics of polymerization; the conditions of polymerization control the characteristics of the polymer; the compounding method and formulation affect the structure and morphology; the fabrication procedure affects the application properties; and, therefore, the design of the product depends on all that has gone before.

Polymerization involves the disciplines of chemistry and chemical engineering; characterization has to do with physics and physical chemistry; fabrication and product design depend on mechanical and chemical engineering. It is essential to have an appreciation and understanding of the contributions from all the disciplines involved.

### b. Supply, production, and characterization of polymers

The supply of monomer is intimately related to the total demands of the chemical industry. Because at present raw material for polymers comes primarily from petroleum, the changing demands on the petrochemical industry strongly influence the availability of monomers. While there is a great need for fuel, the societal and economic benefits of polymeric materials require an adequate monomer supply.

Polymer production involves polymer chemistry and chemical engineering. It has been said that the field of polymer chemistry has been explored to the point of diminishing returns. Nevertheless, the flow of new and unanticipated breakthroughs has continued, as in effecting the low-pressure polymerization of olefins.

The large-scale production of polymers uses the discipline of chemical engineering. To go from the test tube to a plant with the capacity to produce several hundred thousand metric tons per year involves complex considerations of kinetics, as well as heat and mass transport. Relatively little exists in published literature on practical methods of this type of scale-up, and documentation of such information deserves strong support.

As they come from the reactor macromolecules require much more characterization than materials of low molecular weight for which purity is the only essential property. In polymers molecular weight and its distribution are of fundamental importance. In addition, such molecular characteristics as chain stiffness, branching, end groups, degradation, cross-linking, reactivity, and transitions are equally significant. Characterization is not the domain of any single discipline, but rather involves organic chemistry, physical chemistry, physics, and mechanics to produce understanding of the structure-property relationships.

### c. Compounding

Few if any polymers are used in pure form. For good and practical reasons, formulations contain many additives (antioxidants, stabilizers, fillers, pigments, flame retardants, plasticizers, lubricants, coupling agents) besides other polymers for "alloying" or "blending." Specialists ranging from economists, scientists, and engineers to fire marshals are involved.

Ease of fabrication has been the single most important factor in the growth of the polymer industry. After Goodyear discovered vulcanization, Hyatt discovered plasticization, and Baekeland discovered filler reinforcing, their materials would have been of little value without the development of compression molding and extrusion. Injection molding (introduced in the 1930's) made possible the large-scale production of millions of complex shapes rapidly and with modest capital investment.

All elements of the field are important. The development of fabrication methods by engineers would be of little value without the development by chemists of materials with unique properties; conversely, the synthesis of a material that cannot be fabricated would be of little value.

The selection of a material for a specific application requires consideration of many factors: strength, stiffness, thermal stability, chemical resistance, radiation resistance, electrical resistance, ease of fabrication, and economics. For polymers in particular another factor must be considered: The properties of the product depend on and can be controlled by the process used in its fabrication. Among the possible variables are uniaxial and biaxial orientation, configurational volume strains, internal stress, crystalline morphology, and degree of crystallinity. Equally important are cycle time and dimensional control.

### d. Feedback loops

All too frequently problems arising through the misuse of polymers have resulted from lack of experience and knowledge of polymers' special characteristics on the part of processing and design engineers. Part of the problem is the dearth of basic data and design methods; another is unreasonable expectations. Apparently needed is a systems approach in which an overall framework provides for interaction among disciplines and functions to allow for optimization or replacement decisions.

The materials scientist and materials engineer can usually deal with questions of synthesis, formulation, and properties. A critical link to the design and processing engineers is a useful quantitative material description. This may be a rheological equation of state and/or a quantified fracture criterion. In addition, some information on basic physical properties is needed, such as the thermal expansion coefficient, thermal diffusivity, and density. In all cases the information passed from one function to the other is expressed in tables of data or in mathematics, the common languages of science and engineering.

The relationships of polymer structure to material properties are topics of ongoing research in many laboratories. It would seem quite natural, therefore, that if a particular change in a material property were called for by the designer, the polymer scientist might design a material to meet the requirement or suggest an available one. A process somewhat like this occurs quite often in industrial laboratories. The deficiencies are many, however. The designer may be trained or experienced in metals, and therefore may not know what to ask for; and the polymer scientist may not be familiar with engineering and thus may not know how to respond.

For effective feedback, two essential elements must be present: an understandable framework for the total process (system) and a common language. An understandable framework implies that each participant in the process is familiar at some minimal level with all functions and realizes the impact his function has on the ultimate outcome. Mathematics and quantified data have already been suggested as the common language.

A design method is diagrammed in figure II-1. It is generalized to the extent that it applies to a structural design application. It provides an example of the formalized feedback process.

## 2. Classes of Polymer Engineering Materials

### a. Thermoplastics

Thermoplastics are macromolecular substances whose shapes can be changed repeatedly by heating and mechanical deformation. Thermoplastics consist of linear and branched chains comprising large individual molecules, but no pervasive network extends throughout macroscopic regions. Large-scale deformation implies molecular rearrangement without appreciable alteration of the chemical bond structure. In the solid phase thermoplastics may be amorphous, glassy, or partially crystalline. Above the crystalline melting point and the glass transition temperature, thermoplastics are viscous melts that are viscoelastic because of the long relaxation times associated with molecular reorganization. For most crystalline polymers, there is a temperature range in which the disordered regions are above their glass transition but the crystalline regions are below their melting point. This range of temperature may be large, and it encompasses the useful state in many applications.

Polyethylene is one of the oldest, structurally simplest, and most important of the thermoplastics. It is produced in enormous quantities--over five million metric tons per year in the United States--and is employed in a wide range of applications. The material is relatively inexpensive, chemically inert, easily processed, and possessed of attractive mechanical and electrical properties. Commercial grades of polyethylene are remarkably pure, approaching purity levels associated with semiconductor materials.

On a molecular scale polyethylene achieves its diversity through variations in chain branching. Early materials had adventitious branches that led to soft low-density grades. In the 1950's, catalyst systems were discovered that led to tougher high-density linear polyolefins. Recently, in a new burst of process and catalyst activity, polyethylenes have become available with controlled branching and a

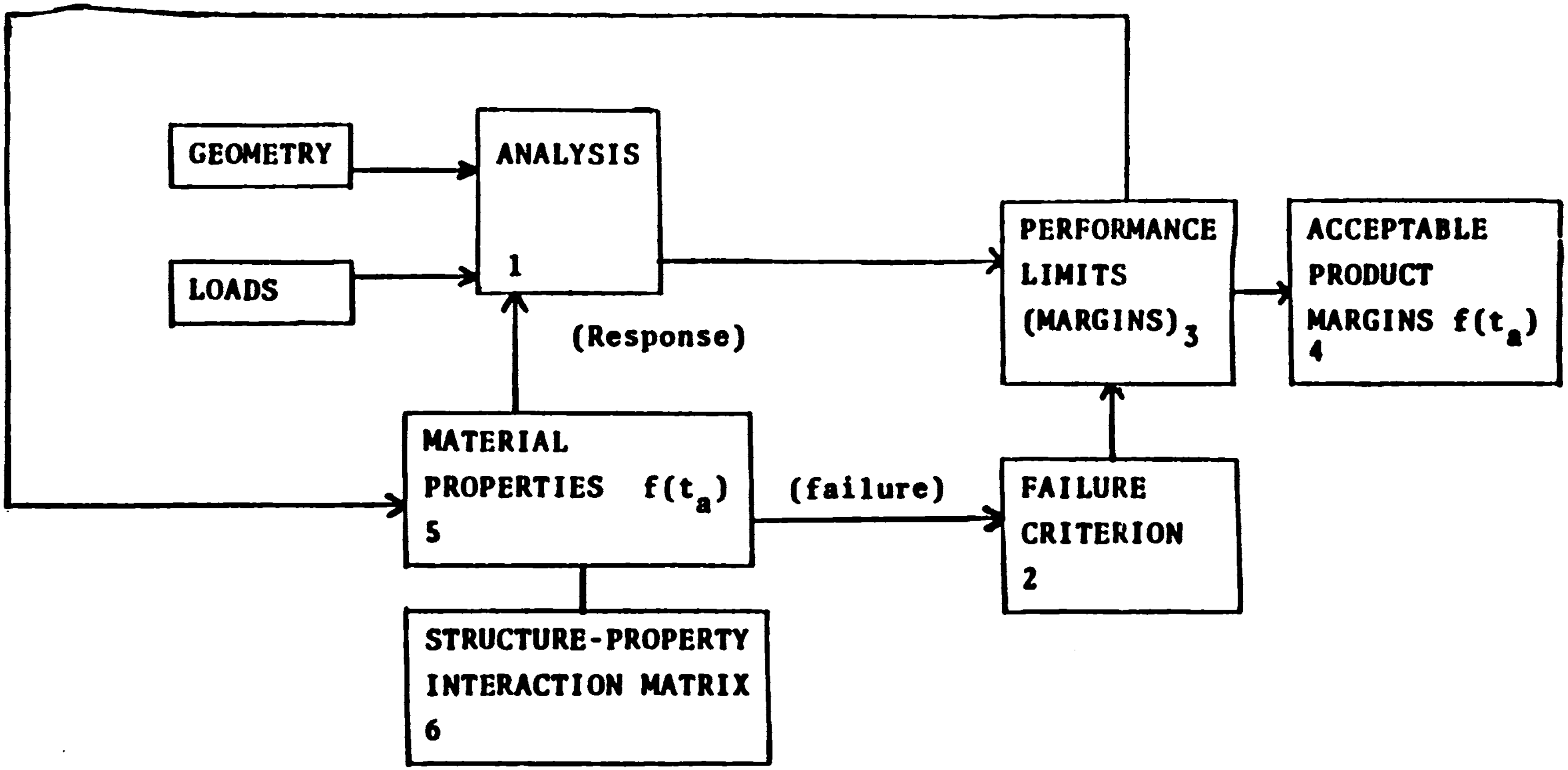


FIGURE II-1. Design method diagram.

combination of some of the favorable properties of high- and low-density polyethylene.

Applications of polyethylene include bottles, drums, tanks, pails, toys, housewares, pipe, film, sheet, wire insulation, cable sheathing, crates, pallets, and packaging. Low cost is a factor, but this should not draw attention from the unique physical properties of this material. For example, polyethylene exhibits extremely low dielectric loss and is the premium material available for many critical electrical applications.

Polypropylene and other polyolefins became available for use as a result of catalyst systems (see chapter IIA, section 2a) discovered in the 1950's. These systems control the stereochemistry of the polymerization addition reaction. Regularity in molecular structure favors crystallization and improved mechanical properties. Stereoregular polypropylene competes with polyethylene in many applications, and its position may become economically favored as feedstocks shift from natural gas to oil.

Poly(vinyl chloride) ("vinyl" or PVC) is another well-established commodity polymer, with United States production approaching three million metric tons annually. Poly(vinyl chloride), which is often mixed with plasticizers, stabilizers, and other additives, is used for flooring, apparel, building construction, automobile tops, mats and seat covers, packaging, conduit, pipe, wire insulation, cable sheathing, and a host of other applications. Its toughness, weatherability, and resistance to flammability combine with low cost to make this polymer one of the most important materials of commerce. Improved formulations continue to be introduced that expand its useful range. Processing instability remains an important, unsolved chemical problem on which future research is indicated.

A number of high-performance polymers are included in the category of engineering plastics. Polyamides, polycarbonates, polyacetals, and acrylonitrile-butadiene-styrene copolymer (ABS) are examples of materials exhibiting mechanical properties so attractive that designers are willing to pay premium prices. ABS exemplifies the application of basic knowledge to the engineering of a new material. Copolymers of styrene and acrylonitrile are brittle and thus have limited applications. The impact strength is greatly improved through the addition of rubber particles that provide a mechanism for dissipating mechanical shock without fracturing the material. The improvement is enhanced by matching the rubber-matrix interface with matrix polymer chemically grafted onto the particles before mixing. The result is a material with the high bulk modulus characteristic of a glassy polymer but a capacity for absorbing mechanical shock characteristic of softer materials. Advances are still being made in improving the impact strength of thermoplastics through the close cooperation of chemists and mechanical engineering researchers.

Specialty polymers are diverse, and only three examples will be mentioned here. Poly(vinylidene fluoride) was found to be piezoelectric about a decade ago; already it is widely used in acoustic devices. The combination of high electromechanical coupling, low density, easy formability, and mechanical integrity make this material ideal for use in microphones, loud speakers, strain gauges, etc. Further understanding of the molecular basis of the piezoelectricity is needed, and active research continues on this problem. The uniqueness of the electromechanical coupling of poly(vinylidene fluoride) is interesting in itself.

Polytetrafluoroethylene (PTFE) is a polymer structurally similar to polyethylene (with fluorine in place of hydrogen), but it is very different in application. PTFE is expensive and relatively difficult to process. Consequently it is favored only in a limited number of applications. Among its unique and useful properties are low friction, low dielectric permittivity and loss, and virtual inflammability. Steady improvement in processing characteristics through modifications of molecular structure can be expected.

Lithographic resist chemicals comprise another class of thermoplastic polymers. Advanced representatives of this class are used to define the patterns in manufacturing microcircuitry. The mechanism of pattern development depends on chemical changes induced in the polymer by radiation projected through a pattern mask. As circuit dimensions become smaller, the use of near ultraviolet radiation is compromised by diffraction effects. Thus, new polymers have been developed that are sensitive to far ultraviolet radiation, X-rays, or electron beams. Sulfones and glycidyl acrylates are examples of such radiation-sensitive materials. The polymers form a vital component at the forefront of the electronics revolution, and research in this area is being vigorously pursued (see also chapter IIA, section 5).

### b. Thermosets

Thermosets are a broad class of materials in which three-dimensional polymeric networks of indefinite extent are formed from reactive species of relatively low molecular weight. Network formation may take place by addition reactions, as in the cross-linking of unsaturated polyester resins with styrene monomer, or by condensation reactions, as with epoxides, phenol-formaldehyde (phenolics), silicone resins, urethanes, or melamine-formaldehyde. Thermoset polymers in the cured (cross-linked) state are insoluble and cannot be reprocessed. They find extremely diverse applications in adhesives, coatings, molded parts, and the primary continuous phase in composites with either fibrous or particulate reinforcements. They may be fabricated by essentially all known methods and, in general, the reactions involving network formation are carried out during the fabrication process. Highly cross-linked systems are generally amorphous (noncrystalline) because of their lack of regularity.

Classically, networks have been viewed as continua, possessing an average composition and average properties. For elastomeric (rubbery) networks, this approach has led to an understanding of such characteristics as elastic modulus, birefringence, swelling by solvents, and thermoelasticity. However, most polymer networks are inhomogeneous and contain a variety of defects at various structural levels--chain loops, pendent chains, nonuniformity of chain length, fluctuations in cross-link density, and highly cross-linked sparsely connected domains.

A better understanding of networks, in the glassy state as well as in the rubbery state, requires a refined analysis of inhomogeneities on the molecular, microscopic, and macroscopic levels. Such treatment is particularly relevant for relating structure and chemical composition to elasticity and strength. Few experimental methods exist for studying the irregular nature of highly cross-linked systems; however, low-angle X-ray scattering and nuclear magnetic resonance appear to be useful and deserve further attention in the investigation of the nature of defects in these amorphous solids.

Substantial efforts have also been directed toward development of new chemical compositions and cross-linking reaction mechanisms to achieve improved properties. The efforts by government and industrial laboratories to improve the upper temperature limits of thermosets for structural composites illustrate this undertaking. The development of thermosetting polyimides derived by addition copolymerization of three monomers have extended the temperature capabilities of composites to 260°C. Acetylene-terminated sulfones, quinoxalines, and phthalocyanines are other complex (generally nitrogen-bearing) materials used for producing high-temperature specialty polymers.

New commodity resins exhibiting rapid cure and/or improved temperature and fatigue characteristics have also been under development for mass markets. They include reaction injection-molded urethanes and caprolactam, modified polyester and epoxide systems, and interpenetrating networks (networks of one composition dispersed in a second network matrix polymer). Generally, however, comprehension of the interrelation of network chemistry, morphology, and properties in use is inadequate. Finally, most thermosetting resins shrink on curing, and new chemical reactions or other mechanisms are needed that lead to low and controllable shrinkage in order to achieve improved set shape and dimensional stability. (For network polymers, see also chapter IIA, section 1d and chapter IIB, section 1e.)

### c. Rubbers and elastomers

Severe reversible deformation is the unique property that characterizes rubbers and elastomers. This property is developed by chemical or physical cross-linking of linear macromolecules to form infinite networks. Such materials are used at temperatures above their glass transition temperatures.

In recent years macromolecular systems with physical cross-links, such as segmented polyurethanes, styrene-butadiene block structures, and ionomers, have received considerable attention because the network is formed by simple quenching (conventional melt processing), rather than by chemical cross-linking, as in vulcanization. Continuing research will refine understanding of the minute nodular structures that serve as physical cross-links. This research should encompass the mechanism, kinetics, and thermodynamics of nodule formation. The process is a gelation of the condensed state, and analogies derived from solution gels may prove revealing.

While great improvements have been achieved in the strength, durability, and environmental resistance of elastomers, further advances can be anticipated. Resistance to solvents and heat exposure has been greatly increased over that of the original hydrocarbon elastomers (natural rubber and styrene-butadiene rubber) by introducing inorganic substituents--first chlorine (neoprene) or nitrogen (butadiene-acrylonitrile), and then fluorine in partially fluorinated carbon main-chain polymers (vinylidene fluoride polymers), or silicon in organic substituted silicon-oxygen main-chain polymers (polysiloxanes). Now the industry has advanced to fully fluorinated carbon main-chain elastomers as well as polymers with a completely inorganic main chain (polyphosphazenes), both capable of functioning as elastomers. Further progress toward even more resistant elastomeric materials is needed for high-technology applications. This will require synthesis of more esoteric polymers and, more importantly, study of the mechanisms of deterioration under aggressive conditions.

The more conventional cross-linked rubbers will be improved, particularly against wear and fracture. The molecular origins of "green strength" (a technological term for the dimensional stability and tear resistance of unvulcanized rubbers) should continue to be a major area of study. Strain crystallization, topological constraints by long chain-branching, and reinforcement by particulate fillers all contribute to final properties, but also have a considerable influence on ease of processing. Empirical studies have been under way for many years, but the complexities of behavior of rubberlike materials, coupled with the need for efficient processing, provide a significant scientific challenge. Self-adhesion or "tack" of filled synthetic elastomers is a technologically important subject about which little systematic scientific knowledge exists.

The application of fracture mechanics to viscoelastic materials is in a primitive state, yet an unambiguous measure of strength will depend on progress in this area. Fatigue, cut growth, abrasive wear, and friction are major concerns in many elastomer applications, and environmentally induced deterioration with respect to these effects requires fundamental understanding in order to improve aging stability as well as to predict service life.

Conventional rubber processing is energy intensive. Large amounts of energy are expended in forcing viscous materials of high molecular weight through channels into the mold and then heating the mold while cross-linking is accomplished. Furthermore, scrap material cannot be reprocessed. Thermoplastic elastomers are based on thermally reversible physical cross-links and can be processed with much less expenditure of energy because their melts can be less viscous, their molding time quite brief, and their scrap reusable. This is why thermoplastic elastomers have become such an important, rapidly growing sector of the elastomer industry.

### d. Fibers

Virtually all synthetic macromolecules can be oriented into the fibrillar state, which is strongly anisotropic. Few technological discoveries have had such a profound impact as Carothers' discovery of nylon.

The scientific concepts and industrial developments that followed are among the outstanding achievements of the twentieth century.

Techniques are now being developed to produce fibers of stiffness and strength aproaching the theoretical limits of the covalent bond. Also, fibers of remarkable thermal stability are being produced by orientation from an ordered liquid-crystalline state (as described in chapter IIB, section 3) and simultaneous reaction to a chemically inert and mechanically intractable state.

In the future renewed attention to the science of natural fibers such as cellulose, fibrous proteins, wool, and cotton will emphasize the role of morphology and the control of hierarchical organization. By understanding and controlling similar hierarchical levels in synthetic materials, unique textures may be developed to mimic the unique features of natural products.

### e. Paints, coatings, and adhesives

Almost all materials are subject to degradation and chemical attack brought about or accelerated by such environmental factors as water, salt, industrial gases, ultraviolet light, oxygen, and ozone. Paints and coatings, therefore, play an immensely important role in protecting all kinds of equipment and structures, from electronic devices to bridges. The use and application of coating systems calls upon remarkably diverse disciplines to provide organic polymers (thermosets and thermoplastics) that can be applied readily, adhere strongly to particular surfaces, tolerate various environmental conditions, and meet suitable strength and durability requirements.

Recently, as a consequence of pressures to reduce energy consumption in oven-baked coatings (e.g, on automobiles) and to minimize the emission of volatile solvents into the atmosphere, substantial efforts have been expended to develop systems which (a) contain a higher content of solids (fewer volatiles), (b) utilize water as the medium to carry the polymer and pigment, (c) are in a dry, powdery state, contain no solvents, and can be applied to metal surfaces electrostatically, and (d) can be cured at lower temperatures. The use of thin metallic coatings to reduce the consumption of expensive metals and the electrodeposition of organic polymeric primers on metal surfaces are additional developments of great interest. These efforts require not only synthesis of novel polymers, but also a deep understanding of such phenomena as wetting, adhesion, coalescence, film formation, and degradation mechanisms and kinetics.

Adhesives play an equally important role for assembling everything from books to major aircraft structures. Here, too, the approach is interdisciplinary, calling upon sophisticated polymer synthesis along with a wide range of physicochemical and mechanical studies. As with coatings, a profound knowledge of the mechanism of wetting of one material by another and of maintaining the integrity of the interface under environmental attack are fundamental issues to be addressed.

Because adhesives are becoming more widely used in place of mechanical attachment techniques, it is becoming increasingly important for design analysis to understand the mechanical behavior of bonded joints. Test methods, particularly nondestructive ones, are needed to judge adhesive bond integrity and to predict bond-joint life under complex mechanical stresses combined with aggressive environmental conditions.

### f. Composites

The past few decades have witnessed a continuing revolution in the development of lightweight composite materials to replace metals and other construction materials in aircraft, aerospace vehicles, automobiles, marine vessels, appliances, etc. Discussion here is confined to two-phase systems consisting of a matrix phase, generally a thermosetting polymer, and a disperse phase of a high-strength fiber such as glass, carbon, or aromatic polyamide. For brevity, the broad class of important composites with particulate mineral fillers is omitted.

Fabrication technology for fiber-reinforced composites varies drastically from one industrial sector to another, depending on cost, productivity, and engineering performance requirements. Maximum strength and/or stiffness-to-weight ratios have dictated the use of laminate construction by the aerospace industry. Here, structural components are fabricated by forming stacks of a number of resin-fiber layers in the form of tapes or sheets. Where layers contain continuous, unidirectional fibers, a particular sequencing of fiber orientation of the various layers is required through the total stack. The resulting sandwich of layers is then "cured" slowly under heat and pressure to consolidate the structure and to complete polymerization and cross-linking of the polymer phase. The automobile industry, however, for mass markets, has explored other methods of higher productivity and lower cost, such as injection molding and rapid compression molding of composite materials in sheet form with fast-cure thermosetting resins. Still other methods are currently under study, such as high-speed winding of complex shapes with continuous fiber and wet resin, as well as pulling of continuous fiber and/or fabric and resin through forming dies (pultrusion).

Each of these methods poses fundamental chemical and engineering problems. For example, a better understanding is required of heat transfer and temperature profiles through a material during compression molding as affected by the heated platens of the molding press and the heat generated (exotherm) during the cure process. Such factors influence residual stresses and the strength of the resulting part. Further, the flow of materials during a molding cycle must be understood sufficiently to quantify prediction of the interaction of flow with fiber orientation and final properties in all directions. Besides residual stresses and fiber orientation effects, a host of other features and defects may arise during molding, including voids, nonuniform fiber and resin concentrations, polymer degradation from excessive local heat, inadequate cure, and "knit" lines arising from the meeting of two flow fronts. The mechanism by which of these undesired features are formed must be understood in order to control their occurrence and location.

The major limiting factor in the application of fiber-reinforced composites in the aerospace industry is the matrix material. Epoxy resins are the workhorse of that industry, but these polymers have severe limitations in upper use temperature and moisture cycling under load. Sophisticated organic chemical investigations are in progress to generate new polymer systems free of these limitations, subject to more rapid cure, and free from producing void-forming volatiles. (See chapter IIC, section 2b.)

A vast mathematical language has been constructed to describe the elastic and strength properties of fiber-reinforced composites. The purpose of this engineering development has been to relate the properties of the constituent fiber and matrix to properties of the final part. Such data are required to study design, failure mode, fatigue behavior, notch or flaw sensitivity, impact properties, heat and moisture sensitivity, etc. All problems must be analyzed for all types of loading conditions, such as tensile, shear, and compressive stress. The overall problem is severely complicated by the either grossly or locally anisotropic nature of composite materials. Efforts are sorely needed to improve the speed and reliability of analytical and predictive computations.

A third "phase" is invariably present in a two-phase fiber composite--the interfacial zone between fiber and matrix including the region of the matrix near the interface where the properties are altered. This factor profoundly affects interfacial adhesion and local properties and, consequently, influences most properties in use. Better methods are needed to characterize the interfacial region. Chemical and mechanical means of inserting inner layers of controlled properties between matrix and fiber also merit investigation.

Finally, many physicochemical methods are required (1) to provide rapid determination of resin properties, fiber characteristics, manufacturing reliability, and final part properties to assure quality control and process uniformity and (2) to predict field performance.

An innovative concept of mixing rigid-rod polymer molecules with a chemically similar matrix of flexible molecules to produce a true "molecular composite" is in an early stage of development. Research on polymers resistant to high temperature has led to para-catenated aromatic backbone structures produced by condensation polymerization, resulting in a broad range of semiflexible and rigid-rod molecules. Materials of extremely high strength have been formed with these polymers in fibers and films, but the potential for useful combinations at the molecular level is enormous. The principal challenges are to increase the length (molecular weight) of rodlike molecules and to achieve uniform dispersions in the flexible matrix by reasonable processing conditions.

### g. Films and membranes

Most polymeric films are used for packaging everything from garbage to frozen food. A vast spectrum of applications obviously exists. Such films, usually less than 80 μm thick, are either uniaxially or biaxially oriented in order to increase their toughness.

High-performance films must have a unique balance of surface properties (gloss, printability, good friction, nontackiness) and bulk properties (haze, stiffness, impact and tear resistance, barrier behavior). There are many examples of multilayered films designed to obtain a unique balance of properties that cannot be obtained in a single layer.

The resistance of polymeric materials to penetration and attack by gases, vapors, and liquids is a primary factor determining their use in many applications. Low permeability to moisture, oxygen, carbon dioxide, and corrosive substances is essential when polymers are employed as packaging films. Such polymeric films play a vital role in the preservation and transportation of food. Polymers can be designed as layered structures with optimum transport, mechanical, and optical properties; and, by means of coaxial extrusion technology, multilayered films and packages can be economically manufactured.

## 3. Production and Processing

### a. Physical aspects

The processing of polymeric materials into finished products is complex, and many of its aspects are far from being understood in a quantitative way. Even so, the flexibility and ease of processing contribute strongly to the competitive position of the industry.

Processing polymers involves producing, formulating, mixing, compounding, and fabricating them into finished products. In most processes, these steps are carried out in separate sequential operations, but in a few cases the raw polymer as received from the polymerization reactor is converted into the final product in a single operation.

In the majority of processing operations compounding and fabricating are carried out in the melt state. Hence an understanding of the nature and properties of the melt underlies most processing procedures. Polymer melts exhibit both viscous (liquidlike) and elastic (solidlike) behavior and are therefore called "viscoelastic" materials.

Many fundamental research studies have been carried out to obtain melt characteristics for optimizing the design and operation of processing systems. Much of this work is not directly applicable to the practical purpose for which it was intended because of simplifying assumptions and the ideal experimental conditions of the laboratory. Research is badly needed on polymer melts under the conditions involved in actual processing practice, including high pressure and great strain.

Processing equipment is usually developed by machinery manufacturers whose background and interest center in mechanical engineering machine design and not the melt rheology of polymers. Greater interaction is needed between scientists and engineers familiar with melt properties and the manufacturers of process machinery. A great challenge and opportunity exists in the development of systems utilizing process-induced structures that optimize properties in finished products. In other words the properties of polymers can be changed in a desired way not only by changing chemical structure through synthesis, but also by process-induced orientation and morphology. Fundamental studies in this area have tremendous potential.

i. Physical factors in polymerization. Production of polymers requires the large-scale polymerization of monomers, which involves not only the chemistry of reaction, but also the coupled interaction of kinetics, heat, and mass transport. Macromolecules are unique in that not only chemical structure but also molecular size and size distribution must be controlled. The details of most practical polymerization processes are considered to be proprietary. The problems are complex and have not been presented in a complete or systematic way in the published literature. The following discussion will serve only to point out the many factors involved.

Heat transfer becomes an increasingly difficult problem as reactor volume is increased because, for a given reactor shape, the surface-to-volume ratio decreases as the volume increases. Thus, removal of reaction heat becomes a major design parameter for large-scale production units. A consequence of scaling up is thus increased departure from uniform temperature conditions, and this can lead to heterogeneity of the product.

Mixing of reactants is also a major engineering problem. Agitation is needed to achieve uniform reaction conditions and to aid in the removal of reaction heat. As polymerization progresses, particularly in bulk polymerization, the viscosity of the medium increases, and more and more energy is required to maintain a given level of uniformity. At high conversion the stirring process itself may contribute to heating and chain scission.

In addition to thermal transfer and mixing problems, scale-up considerations must include metering of raw materials, temperature control, separation of polymer from the reaction medium (i.e., solvents or unreacted monomer), gel or side-product buildup, reactor corrosion, and catalyst recovery. Design mistakes in large-scale production can be extremely costly, and extensive planning and modeling are justified.

The total polymerization process is exceedingly complex, and mathematical modeling has involved significant oversimplification. The present surge in power and convenience of computation will have an enormous impact on the engineering of polymer production facilities. Planning and design will be greatly facilitated by advances in modeling capability, and plant operation will be increasingly controlled by computers. Further rapid progress can be expected in the expanding application of computers to polymer production.

ii. Extrusion. Extrusion is the process of melting and pumping materials through a forming die. Concurrent mixing, compounding, homogenizing, and devolatilizing may also be accomplished. The vast majority of all thermoplastic polymers go through an extrusion operation at least once (to be pelletized), and in most cases twice or even three times during the production of finished products. For this reason, it is possibly the most important processing operation.

In screw extrusion the raw polymer feed falls from a hopper reservoir into the flights of a rotating screw which transports the material through a heated barrel or tube. The material picks up heat from the barrel, melts, and is compacted. The contours of the flights of the screw are such that, after the polymer melts, a high pressure develops that pushes the material through an outlet die to form a continuous extrudate of the desired cross-section. Such products as pipe, wire insulation, film, fiber, and a multitude of special shapes are produced in this manner.

The state of the art is advanced enough today so that the portion of the screw transporting the melt through the die (the pumping zone) can be well designed to achieve the desired throughput rate at the desired pressure and temperature. This is not the case, however, with the other parts of the screw. Recently some progress has been made in understanding the interaction of the properties of the individual polymer with the shape of the portion of the screw where the polymer is melted and compacted (the compression zone), but the state of knowledge on how to design the portion where the cold new material is transported by the screw (the feed zone) is not very far advanced.

At present extruder screws are designed by using a combination of practical experience and computer programs in which many, but not all, of the interactions with the material parameters are considered. It is unfortunate that so little attention is paid to such important material fundamentals as the effect of pressure on viscosity and melting characteristics.

It is well recognized that each material requires a different screw design for optimum efficiency. The greatest unsolved problem concerns the surging or fluctuations in the output rate. The present approach uses feedback circuits with computerized adaptive control. But there is a risk that this approach will not optimize energy efficiency because it involves continual changes of energy input and removal.

More than 90 percent of all extrusion is carried out by screw extrusion, but in certain cases it is necessary to use ram extrusion. The process involves heating the polymer in a closed container and pushing it through an extrusion die with a ram or piston. The process usually is a batch or intermittent operation, but it can be made continuous by means of two or more units coupled to operate alternately. Growing interest exists in ram extrusion for the highly filled materials used in the production of bulk molding compounds.

iii. Molding. Molding involves forming the raw material, usually in pellet form, into the desired finished shape. Different types of molding systems are used, depending on the nature of the materials to be formed and the product. All involve melting and flow, and thus viscoelastic behavior is critical to all of them. The following discussion provides some examples of molding processes.

Compression molding involves placing the material (sometimes preformed) into a heated mold cavity, closing the mold with a mating piece, and forcing the entrapped polymer to flow and conform to the shape of the cavity by pushing the two parts of the mold together in a press. The process is essentially used only for thermosetting materials because less time-consuming methods are available for thermoplastics, which have to be cooled before removal from the mold.

Injection molding involves heating the material in a cylinder, injecting it into a closed cooled mold cavity, allowing the material to cool, then opening the mold, and ejecting the finished part. The fact that all this can be done at a rapid rate (cycle times as brief as a few seconds) makes possible the mass production of large numbers of complex shapes with a minimum of investment and time. The heating of the material is carried out either in a cylinder equipped with a ram or in a screw extruder in which the screw reciprocates back and forth to accomplish the injection.

Injection molding is the most common method of fabricating thermoplastics, but is also used for thermosetting materials because, compared to compression molding, much shorter cycle times can be achieved if elaborate controls are used to prevent premature reaction.

Reaction injection molding involves the rapidly mixing liquid prepolymers and curing agents and then injecting them into a closed cavity where polymerization and/or cross-linking takes place. Advantages include the elimination of heating or melting prior to injection and, since the materials are of relatively low viscosity, the need for only moderate pressures in the injection process, which eliminates the necessity for strong, expensive molds and mold-clamping systems. This processing system is relatively new, and its development is being extended to the production of large parts. Economic factors dictate efforts to reduce cycle time, which involves an interaction of the time required for mixing and the rate of reaction. Complete mixing of the reactants is required, and improved mixing technology is evolving. Highly reactive ingredients are necessary, and urethane polymers have been most successfully processed thus far. Considerable interest exists in other systems, and progress has been made with epoxies and polyamides.

The term "cold forming" is used for processes in which the finished item is fabricated either at room temperature or at an elevated temperature below the melting point. The objective is to shorten cycle times by using metal pressing and stamping techniques, avoiding a heating and cooling cycle. Although it has long been known that polymers can be cold formed, only recently has this process been found to be economically viable for the production of such items as packaged food containers. The flow characteristics of polymers below their melting points are the fundamental material properties that need to be known.

iv. Coating. The coating of substrates with polymers is carried out by several different systems. The fundamental principles of adhesion, coalescence, and fusion are involved.

In solvent coating the polymer is dissolved in a solvent, the solution is applied to a surface, and the solvent is then removed by evaporation. This process is becoming less desirable because of the cost of solvents and the atmospheric contamination they cause.

In emulsion coating the polymer is dispersed in very fine particle form in a water and applied to a surface. The water then evaporates and the polymer particles coalesce to form a continuous film. The solvent problem is avoided.

In sintering the polymer is in very fine particle form and is applied by air spraying, tumbling, or fluidized bed techniques to a heated surface. The polymer melts and fuses to form a coating and is then cooled.

In plastisol coating the polymer is again in very fine particle form and is dispersed in a mixture of plasticizers and solvents. A surface is then coated with the mixture and heated. The polymer goes into solution and gels to form the coating.

In melt coating the polymer is melt-extruded as a thin sheet, which is then pressed in the melt state against the substrate to be coated. It fuses to the substrate and is cooled.

v. Fiber spinning. Synthetic fibers are produced by three spinning processes: wet, dry, and melt. Material fundamentals include elongational or tensile viscosity, orientation effects on crystallization, heat transfer, and solvent diffusion.

In wet spinning the polymer, dissolved in a solvent, is forced under pressure through a spinneret containing a multiplicity of tiny holes (more than 1000 in some cases) into a nonsolvent and there precipitates as a fiber.

Dry spinning is similar to wet spinning; but instead of going into a nonsolvent, the fiber goes through a heated chamber where the solvent is evaporated.

In melt spinning the most important spinning process, the polymer is melted and then pushed through a spinneret into an air cooling tower where it solidifies as a fiber.

vi. Film blowing. The vast majority of film is produced by the blowing process. The polymer is melted and then pumped through an extruder out of a ring die to form a thin-walled tube. The tube is pulled longitudinally and concurrently blown out by internal air pressure. The combination of increasing surface area and air cooling solidifies the film, which is taken up on rolls and then cut to the desired width.

By controlling the conditions of blowing, biaxially oriented film can be produced. Many variations of the basic process exist to produce film of special desired properties.

vii. Fundamental problems. It is often said that polymer processing has evolved as an art rather than as a science. Many different processes are involved, each with its own characteristics and problems. To attempt fundamental studies of each process would be a tremendous undertaking. Fortunately it is possible to identify fundamentals common to all processing operations. Mastery of these fundamentals should facilitate problem solving and optimization of the individual processes.

In all processing operations the polymer material flows. The greater the understanding of the flow properties of polymers, the greater the opportunity to solve processing problems. Because flow under the conditions encountered in polymer processing is far from simple, but a realistic approach involves considerating all the pertinent variables; the problems cannot be solved by making simplifying assumptions. For example, melt viscosity is not simply a function of shear rate, temperature, and pressure; in the practical situation of processing, the response of polymers is also highly dependent on the previous history or sequence of experiences that the material has been through.

As indicated in the above description of the processing methods, material fundamentals are the common theme. Realistic basic studies are the paramount need.

### b. Continuum mechanics

Engineering analysis of polymer processing problems requires the mathematical description of transport operations, i.e., transfer of mass, momentum, and energy. The relevant equations of such transport phenomena are the balance equations, which express conservation of mass (continuity equation), momentum (equation of motion), and energy, and constitutive equations for the polymer. Constitutive equations describe the response of a material to a stimulus forcing it out of its equilibrium state. Balance equations are usually written as field equations in differential form applicable at every point in the medium. Their solution in conjunction with appropriate constitutive equations embodies the work of the researcher, who models or simulates polymer flow in geometric situations of interest, such as in processing equipment or rheometers.

Two principal problem areas have occupied the attention of researchers in continuum mechanics applied to polymer processing. These are (1) the formulation of constitutive equations capable of describing the behavior of polymer fluids in a variety of deformational, temperature, and pressure fields, and (2) the solution of boundary and initial value problems associated with processing geometries.

The response of a polymer to severe applied deformation is not currently predictable from molecular information. Therefore constitutive equations for polymers are generally empirical, though they may be based in part on molecular models. Linear constitutive equations, such as Newton's law of viscosity, generally do not apply to polymer fluids; rather, the rheological parameters describing polymers are found to depend upon the applied stimulus or deformational response and, therefore, the equations become nonlinear. Furthermore these parameters are found to be time dependent in nonsteady-state situations and dependent upon the prior history of the applied stimulus or deformation. These characteristics associated with the long-range molecular interactions (entanglements) and chain dynamics of polymers have greatly complicated analysis of engineering flows.

Constitutive equations have been developed that describe quite well the response of polymers in steady, simple shearing flows. These equations fit viscosity and elastic normal stress behavior with varying deformation rates, and also describe some unsteady-state flows, such as onset of steady shearing ("steady overshoot") and cessation of steady shearing (stress relaxation). However, these same equations usually fail to describe correctly fluid response in more complex flow fields--e.g., extentional flows in converging dies, fiber spinning, and extrudate swell at die exit--nor do they deal with more complex flow histories, such as flow through an extruder or injection molding machine. Constitutive equations with more universal applicability need to be developed so that actual polymer operations can be modeled.

The solution of boundary and initial value problems in polymer processing is complicated by complex geometry and nonlinearities in the relevant systems of balance and constitutive equations. Such problems cause much expended effort on the part of researchers in polymer processing. Powerful, though complex, tools of modern analysis, resting heavily on computational methods, are available, however. This effort needs to be continued, and coupled with improved constitutive description. Some of the problem areas deserving attention are flow instabilities leading to surface defects in extrusion or coating flows, mixing and blending operations, flow fields with chemical reaction (polymerization, cross-linking, chain scission), conveying and melting of solids in processing equipment, and flow around objects and corners. Finally, the description of the state of stress in a polymer fluid as the polymer undergoes solidification in a processing operation is of great importance in determining its properties in the solid state.

### c. Chemical aspects

Chemical reactions important in processing polymeric materials may be divided into two broad categories. One involves the buildup of polymer molecular structures through gelation or chain-linking reactions (as in thermosetting resins); the other involves the breakdown of molecular structures (as in the chemically aided mastication of rubber). A basic understanding of the kinetics and mechanisms of such reactions is necessary for the sensible control of processing conditions. Control may be realized through thermal and/or catalytic methods and by the reactant mixing process.

Needs and opportunities in basic research include the search for new reactions involving well-defined chain-linking reactions that produce structures with high levels of hydrolytic and thermooxidative stability. These reactions normally should not release volatile products, which could lead to bubbles and voids in the cured material (except when deliberately required, as in foamed products). Many constraints limit the practical application of reactive polymer systems--cost, availability, environmental acceptability, etc--but the processing issues focus primarily on control and through-put. Apart from the basic polymerization reactions that produce the polymer from monomers, useful products may be obtained. from functional oligomers which flow readily to meet the required geometric and/or wetting conditions and then react conveniently to reach the final state with a minimum of residence time in the mold. Cure shrinkage and residual stresses may be minimized by proper control of material and processing variables if they are understood.

Opportunities exist for innovative synthetic approaches to incorporating reactive moieties in the polymer chain structures, whether placed at chain ends or positioned along the backbone. While chain-linking reactions are most common for producing materials with desirable mechanical properties and dimensional stability, possibilities exist for chain-stiffening reactions that engage backbone segments in ring formation. The proximity of reactive groups along the same chain allows intramolecular rather than intermolecular reaction, with advantages for certain applications.

Liquid polymer approaches based on reactive oligomers have achieved widespread use, yet some applications have not yielded the potential benefits. A desired objective for some time has been the castable automobile tire. Conventional methods for tire building are quite complex. The energy- and labor-intensive breakdown, mixing, building, and vulcanization steps could be replaced by a simpler casting process. Studies are needed of stable linking reactions and of resultant reinforcement, adhesion, friction, abrasive wear, and dynamic response.

Radiation cross-linking is an alternative to chemical curing and in some cases is particularly suited to continuous processes. In particular, where coatings, adhesives, wire insulation, and thin sections are involved, high-energy radiation has advantages. Other radiant energy sources, such as microwave and dielectric heating, have seen only limited use, yet they have such appealing features as uniformity of exposure throughout a bulk component. Research is needed on the reaction mechanisms for both cross-linking and degradation processes in order to regulate the energy spectrum, flux, and total dose. Incorporation of particular chemical species in the molecular structure of polymers responding to the radiant energy by undergoing chain-linking is a particularly promising area of research.

Degradation during processing may be detrimental to the process itself and to the final product, so a detailed knowledge of oxidation, pyrolysis, hydrolysis, and mechanical fatigue is important. In some cases, competing buildup and breakdown reactions are occurring simultaneously, producing changes in branch structure, molecular weight, and molecular-weight distribution that significantly affect rheological properties. Where degradation is desirable, as in rubber mastication or in recycling of polymer products, many challenges remain for optimizing both properties and product at each stage of the process. The principal needs, once again, are in basic understanding of the underlying reaction mechanisms and kinetics, as well as of resulting structure-property relationships.

## 4. Performance and Properties

### a. Environmental exposure

Exposure of polymers to various environments is often categorized according to types of stresses: mechanical, chemical, electrical, or radiation. Certainly, the growing use of polymers in place of traditional materials such as metals, glass, wood, and stone has led to concern, especially for long-term durability. Environments range from the radiation-vacuum-thermal conditions of space, through a wide range of atmospheric pollutant, chemical, moisture, and oxygen environments experienced on the earth's surface, to the demanding high-temperature, high-pressure, reductive, and hydrolytic conditions associated with geothermal energy recovery. The imposed mechanical loads may be static or repetitive, and the various chemical environments must be examined as they interact with them. As polymers come into wider use for structural materials in highly loaded applications such as aircraft primary structures, the distinction between chemical deterioration and mechanical aging (multiple flaw initiation and growth) must be recognized, and coupled effects need to be understood.

Two areas of research are immediately suggested, one covering the deterioration processes themselves (chain scission, depolymerization, cross-linking) and the other dealing with the stabilization process effected through incorporation of stabilizing structures in the chain or as additives. Other changes may occur that do not necessarily involve chemical reactions, including loss of plasticizer, change in morphology or chain orientation, volume relaxation, and swelling. The two objectives, understanding material deterioration and stabilization, are compatible in the broader sense. By gaining a more complete understanding of the processes, appropriate modifications may be suggested.

Most polymer systems are susceptible to oxidation, which in many cases leads to lower molecular weight and consequent impairment of physical properties. Through understanding of the chemical mechanisms involved, it is often possible to retard oxidation effectively by adding small quantities of stabilizers. For example, thermal oxidation of hydrocarbons occurs by way of a radical chain mechanism, and the chain reaction can be interrupted by substances that form stable radicals. Addition of hindered phenols at a level of 0.1 percent can retard oxidative embrittlement by more than an order of magnitude in time, and this practice is standard where thermal oxidation is the primary effect.

Other oxidative mechanisms come into play on exposure to ultraviolet light. Ultraviolet absorbers and other stabilizers are commonly used to protect polymers, particularly for outdoor use.

Oxidation processes are strongly affected by catalysts that may occur inadvertently in the polymer. Specific additives can be used to reduce or eliminate the known or expected catalytic effect. For example, chelating agents are effective in poisoning the catalytic oxidative effects of copper in hydrocarbon polymers.

Ozone is a special problem for unsaturated polymers such as polymerized dienes. This oxidant poses an important problem for the rubber industry, and stabilizing additives are used extensively. Countermeasures have been studied for many years, and although an extensive literature exists, this field of research remains active.

Polyamides, polyesters, and certain other polymers are susceptible to hydrolysis, which can lead to mechanical weakness through reduced molecular weight. The detailed mechanisms of the hydrolysis reactions call for further study, and strategies are needed for stabilization against their effects.

All polymers show some degree of thermal instability, decomposing spontaneously at sufficiently high temperature even in the absence of oxygen, ozone, water, or other reagents. Some materials return to monomer, as does poly(methyl methacrylate); some decompose by liberating chain fragments of varying size, e.g., polyethylene and others decompose in specific ways, e.g., dehydrochlorination of poly(vinyl chloride) to yield polyenes. The design of chain structures stable at high temperatures is an active field of study.

A greater challenge lies in prediction of long-term service life. Performance requirements imposed upon an article manufactured from a given material may exclude many stabilizing approaches. Especially in high-performance applications, the lifetime for operation within specified conditions of performance must be known, and so too the conditions that lead to catastrophic failure.

While endurance tests are commonly carried out under thermal, mechanical, or radiation loads to accelerate deterioration and gain an early estimate of durability, a notable lack of correlation has been observed between short-term accelerated tests and long-term performance. Many of the reasons for poor correlation are well recognized, such as the varying activation energies for many simultaneous processes, which may be accelerated accordingly at different rates. Laboratory studies embodying isolated environments cannot normally be combined to match the real environments in operation.

The greatest opportunity for progress in service-life prediction remains in improved understanding of structure-property relationships. The performance properties of interest are, after all, the primary indicators of when useful life has ended. A definitive study is needed of structural changes that are produced by single or combined environments and are directly related to performance. Quantitative criteria of failure are needed as well. Statistical analysis of both material and environmental variations might be applied to yield service life in terms of probability of failure within a population, but the basic quantitative data on deterioration mechanisms and kinetics needed for even the simplest polymers are unavailable. Furthermore, the necessary development of instrumentation and of characterization techniques is not in hand, particularly for engineering polymers.

Degradation of surfaces and interfaces calls for special mention because these regions are often critical to performance. Mechanical abrasion and wear may be the life-limiting mechanisms in many applications. Frictional properties can change through surface oxidation or solvent absorption. Biological activity may cause surface deterioration. Adhesive bonding is itself a surface phenomenon. Finally, the "interphase," a thin region of transition between matrix and reinforcement in composite materials, is an area of growing research interest.

### b. Material response

Objects made of polymeric materials are subject to physical and chemical stresses throughout their service lives, and the design engineer must understand how the material responds to the stresses if he is to make rational predictions. An object's useful life may end in a variety of ways determined by its specific purpose. It may break in a brittle fashion, distort with or without external stress, discolor, burn, or develop a disagreeable odor. This section deals briefly with some of the modes of material response that can be analyzed.

Elastic response implies that all mechanical energy put into the body is recoverable upon the release of the stress. The stress-strain relationship may be described in terms of a free-energy increase as the body is elastically deformed, equilibrium conditions being maintained throughout. The change in free energy may be resolved into contributions from changes in internal energy and in entropy. The internal energy change resides in changes in the interatomic and intermolecular potentials under strain, while entropy changes arise from changes in the number of available molecular conformations or in distribution of lattice defects.

In a lightly cross-linked rubbery solid, the molecules orient under strain and the entropy decreases. The internal energy changes mainly in accordance with the energy differences between different rotational states of the chains. These changes may be significant or small, positive or negative, depending on the chemical structure of the chain. Unlike a simple elastic body conforming to Hooke's linear stress-strain law, the rubbery body exhibits nonlinear behavior--i.e., its Young's modulus varies with strain. However, thermodynamic theory has enjoyed some success in predicting equilibrium behavior from molecular structure, at least at small deformations.

Mechanical behavior of many kinds of metals under stress is described by linear elastic or Hookean response under small strains and by plastic response beyond a certain material-dependent stress level, called the yield point. The plastic region is characterized by increasing deformation under a constant stress, but without reference to the dependence of the deformation rate on the stress. Experimentally, the yield-stress level in aluminum depends on the rate of strain, so that, even for metals, the elastic-plastic description is an unsatisfactory model. However, the concept of <u>critical</u> stress or strain at which the material begins to flow is a useful one. Some of the criteria proposed include those of von Mises, which specifie the maximum deviatoric (shape-changing, rather than volume-changing) stress, the critical strain-energy criterion, the critical strain criterion, and other completely empirical measures.

When the fluidlike viscous response is combined with the elastic response, the time or strain-rate dependence of mechanical behavior can be predicted. A solution of polymer molecules in a nonassociative solvent behaves in a manner that can be described as linear viscoelastic--i.e., the elastic response is that of an entropic spring, and the viscous response is that of a Newtonian fluid.

Molecular theories have been constructed in which the solvent flowing past the polymer molecules undergoes drag as the polymer molecules are deformed, resulting in partial dissipation and partial storage of the mechanical energy. Since polymer molecules can exhibit many modes of motion with a wide range of associated time constants, the viscoelastic behavior is described by the superposition of many relaxation processes, leading to a distribution of relaxation times, or a relaxation spectrum, ranging over many decades of time. For polymer molecules with sizes exceeding a critical value dependent on the chain flexibility, interactions occur also among whole molecules, further extending the relaxation spectrum by a few decades. This intermolecular association is known as the "entanglement phenomenon."

The linear viscoelastic model has been empirically applied to concentrated solutions as well as to polymers in the molten state. The temperature dependence of viscoelastic behavior of polymer solutions and melts has been described by a combination of free volume and the thermally activated energy process. At low temperature the free volume dominates the control of the process, while at higher temperatures a process with constant activation energy predominates.

Even for polymer solutions and polymer melts the linear viscoelasticity model is limited to small strains. The flow behavior at a constant flow rate, for example, cannot be treated as linear viscoelastic behavior since the viscosity progressively decreases with increasing flow rate. For glassy and crystalline polymers the constitutive equations become more complex. Since they are highly nonlinear even under strains of the order of only one percent, no linear model can be sufficiently useful. One alternative has been to introduce an empirical curve, such as a power law with a stochastically fitted exponent depending on the polymer. While useful, such an equation cannot, in principle, be applied outside the range of the experimental data unless it can be supported by structural or thermodynamic arguments.

The glassy state is one in which the molecular conformational rearrangements have become so sluggish that, on the ordinary experimental time scale, the polymer behaves like a stable elastic solid. However, the entropy and the free-volume fraction of a glass have been found to decrease with time, and this process is accompanied by an increase in the relaxation time and the elastic modulus.

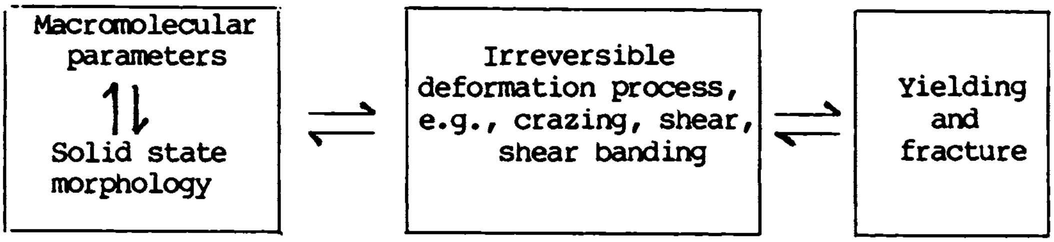
Crystalline and semicrystalline polymers can be described up to the yield point in a manner similar to that used for glasses. Above the yield point crystalline polymers typically undergo morphological transformation, which ultimately leads to a highly oriented form of fiber or film. Thus, the stress frequently rises again after yield.

Examples of linear and nonlinear responses have been cited in the preceding paragraphs. Nonlinear response is clearly the general law, and linear behavior is limited to special cases involving small strains. When the response is nonlinear, the principle of superposing stresses and strains cannot be considered applicable a priori. This presents a difficulty in deriving one stress-strain function from another for the same body. Therefore, the constitutive equation for a nonlinear viscoelastic body is difficult to obtain. Various schemes have been introduced to circumvent this difficulty, and some have given encouraging results.

### c. Mechanical failure and fatigue

Fracture in polymeric materials is usually preceded by localized irreversible deformations which occur in tension (crazing) or in shear. Crazing refers to the formation of localized, "spongy" regions of highly deformed polymer. These micromechanical processes absorb considerable amounts of energy, and the resistance of a polymeric material to fracture is strongly dependent on their stability and intensity.

The mechanisms of craze and of shear-band formation and growth are only partially understood. Further basic research is strongly needed to determine the effects of such parameters as molecular weight distribution and intermolecular interaction (cohesion). Furthermore, since crazes and shear bands occur in amorphous as well as in crystalline polymeric materials, solid-state structure and morphology play equally important roles in the control and development of these irreversible deformation processes. The diagram below classifies schematically the needed development of interrelationships:



Once the relationships between molecular and solid-state structure are established, the variables that control crazing and shear banding can be determined. These variables are essential to understanding the ultimate properties of bulk yielding and fracture. Particular emphasis must also be placed on the following subjects.

All polymeric materials behave mechanically as time- and temperature-dependent solids under stress. Attempts to describe these irreversible mechanical processes must utilize quantitative concepts combining the contributions of viscosity with elasticity or plasticity. Correlations of primary and secondary mechanical transitions (dispersion maxima) in dynamic experiments with toughness should be attempted to elucidate the segmental molecular motions that control and influence irreversible deformations.

Yield and fracture processes must be studied under simple and complex stress conditions and also with the methodology of solid-state mechanics. The material property parameters emerging from these studies may then be related to the molecular mechanisms controlling irreversible mechanical deformations. Also, since polymeric materials are highly compressible solids, unique and practical information can be obtained by studying yield and fracture phenomena under pressure. Naturally, if pressure, temperature, and thermal parameters can be defined and measured, attempts to apply thermodynamics and irreversible thermodynamics to failure processes should be strongly encouraged.

Recent work on the effects of the environment has shown that nearly all liquids and even some gases are potential stress-cracking agents, particularly if the polymeric material is under complex stresses. However, the mechanisms and dynamics of environmental stress cracking need considerable attention in the future because virtually all engineering components must be capable of performing or of being stable in liquid environments. No one knows, for instance, whether large stresses "activate" liquid diffusion or whether cracking because of environmental stress intensification simply occurs from the surface. Furthermore, since nonswelling liquids can also cause environmental cracking, new combined mechano-chemical concepts may emerge from a fundamental analysis of these problems.

Fatigue in polymeric materials and composites deserves particular attention because structural parts are often subjected to repeated stresses below the short-term ultimate strength threshold of the material. Failure ultimately occurs as the result of the accumulation of damage (irreversible localized deformation). Fatigue failure is exhibited by most materials; it has been studied extensively in metals, but much less in polymers and composites. The detailed microscopic processes leading to fatigue failure in polymers and composites differ considerably from those in metals, but there are strong analogies in the phenomenological description.

Often, localized damage occurs at stresses that are relatively low compared to the failure strength, and disproportionately large amounts of damage may occur in the first few cycles of stress or strain. Damage is progressive and occurs throughout the stressed region, although the material may survive for as many as $10^4$-$10^6$ cycles after the first signs of damage are evident. The inhibition of crack growth by various crack blunting mechanisms, particularly in polymer composites, accounts along with other factors for the generally high fatigue endurance limits normally experienced with these materials.

Fatigue endurance limits in composites depend on a large number of material and test factors such as: (1) fiber geometry and orientation; (2) resin properties; (3) resin-fiber interface adhesion; (4) fiber composition as in hybrids, e.g., carbon-glass; (5) composition fluctuations; (6) mode of testing (tensile, flexural, shear, or combined loading); (7) stacking sequence in laminates; (8) environmental effects of temperature and humidity; (9) presence of holes, notches, and flaws; and (10) frequency of cycic loading.

A major effort has been made to establish the micromechanics of crack initiation and propagation through the resin and the fiber, as well as the relation of crack growth processes to gross failure of the composite part. However, much remains to be learned. Interface adhesion, resin structure near the interface, resin deformation processes on a molecular level, and the influence of special additives (such as dispersed rubber particles) exemplify the many variable factors to be considered in studying this critical type of behavior.

Recently, efforts have been expended on developing analytic methods to monitor and identify microscopic processes occurring in fatigue tests. Such methods as acoustic emission and ultrasonic attenuation are examples. The possibility exists of utilizing these and other nondestructive techniques to predict fatigue life under prescribed conditions.

## 5. Major Research Opportunities*

1. Catalyst systems and procedures for polymerization that provide greater control over molecular structure and consequent improvement of properties.
2. New poly(vinyl chlorides) with enhanced processing and service stability.
3. Polymeric systems that will effectively couple or convert thermal, electrical, light (solar), mechanical, and perhaps other forms of energy. Poly(vinylidene fluoride) is a specific example that has exciting applications now but is also worthy of further investigations.
4. Advances in processing methods to realize the advantages of polymers that are difficult to process--e.g., fluorocarbons and polyimides.
5. Microlithographic polymers (resists) sensitive to X-rays or ion beams that are needed as essential features of micromanufacturing processes. Electronic and optical systems derived from this technology that can be used in computers, in communications, and in teaching and business machines.
6. Control and characterization of highly cross-linked (thermoset) networks and their relation to performance.
7. The structural basis of the performance of thermoplastic rubbers.
8. The spinning of fibers from ordered liquids to produce materials of high modulus and strength.
9. Nonpolluting and low-energy paint systems using water-based, high-solid, nonsolvent, and powder coatings.
10. More emphasis on matrix and interface materials and processes for new high-strength. Fracture mechanics of composites needs study.
11. Multilayer films for a wide variety of applications, including packaging, fuel cell membranes, battery separators, desalination cells, and solar hydrogen-generation cells.
12. Modeling the processing and performance of polymeric materials. Complexities of nonlinear behavior, orientation in flow, and thermal chemistry have been too difficult in the past, but there is now a reasonable expectation of rapid progress. Constitutive equations deserve early attention.
13. Techniques for generating unique properties through process-induced structures.
14. New and diverse chemical systems to expand the use of this reaction injection molding. Techniques for rapid mixing should receive research attention.
15. Methodology for prediction of service life. Attention should be directed at combined effects of multiple environmental variables and nondestructive evaluation.

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*Order of listing does not suggest priority.

16. New methods for the structural study of thermoset and other cross-linked materials.
17. The kinetics and mechanisms of the development of cross-linked networks.
18. Replacement of metals by composites, new polymer blends, and "alloys" based on new monomers.

## D. POLYMERS OF BIOLOGICAL AND MEDICAL IMPORTANCE

### 1. Natural Biopolymers

#### a. Introduction

Polymers form the basis of life. They store information and transmit it from generation to generation; they provide enzymes which catalyze and regulate the manifold metabolic interconversions of all living systems; they form the three-dimensional frameworks of organisms; they transport small molecules within organisms and across cell membranes; they provide the basis for movement; they allow organisms to recognize their own unique individuality; they serve as the structural fibers of plants. For many of these purposes a precise sequence of monomeric units is essential (as in DNA and RNA, responsible for information storage and transmission, and in proteins, responsible for catalysis, transport, and generating motion). Polymers with less precisely determined structures (e.g., certain structural proteins of animals and cellulose in plant fibers) fulfill other important roles. The challenge is to learn the structures of biopolymers in three-dimensional detail, how their functions derive from their structures; and, from such knowledge, how to use them not only to satisfy man's needs for various materials, but also how to manipulate the biological processes themselves so as to cure disease and enhance human health. Phenomenal progress has been made toward these goals in the recent past, and this justifies great optimism for the near future.

A central canon of present-day molecular biology is that one-dimensional information in the genetic material (deoxyribonucleic acid or DNA) uniquely specifies the three-dimensional structures of all biological molecules and consequently all of their physical and chemical properties. One of the major challenges of modern molecular biology is why a specific sequence of amino acids in a polyamide chain folds only into the protein with the three-dimensional structure and catalytic properties of, say, the enzyme ribonuclease. Polymer chemistry contributes importantly to understanding this vital link by providing synthetic macromolecular systems which, because of their relative simplicity compared to natural proteins, allow systematic study and deeper understanding of the molecular forces that determine structure and function in real biological macromolecules. Accordingly, considerable present effort is, and should continue to be, devoted to studies of homopolymers and of random, regular sequence, and block copolymers of amino acids, nucleotides, saccharides, and lipids. Recent advances in techniques for synthesis of such model polymers and of natural polymers, coupled with advances in instrumentation and theory for investigating their properties, promise continuing progress in this effort.

Advances in the chemical synthesis of polynucleotides with specific base sequences, together with the biological techniques of recombinant DNA, open wide vistas for the preparation of both natural and modified polypeptides* and proteins in essentially limitless quantities for use in medicine. The direct chemical synthesis of polypeptides likewise holds great promise for generating pharmaceutical agents with highly specific biological functions and other properties, such as stability, that will enhance their therapeutic utility.

The use of immobilized proteins is a special and important field of investigation dating back to pioneering research in the 1950's on attachment of enzymes to insoluble polymer matrices. Initial interest stemmed from a growing awareness of the potential of insoluble enzymes both as industrial catalysts and as model systems for the investigation of isolated aspects of complex biological processes. More recently, research has also emphasized opportunities for dealing with diseases involving enzyme deficiency or enzyme imbalance. Enzyme modification by covalent attachment to water-soluble polymers has evolved for drug applications as well as for simplified diagnostic clinical analyses.

Enzymes immobilized on or within a solid matrix by conjugation with native or synthetic water-insoluble polymeric supports can serve in the laboratory as reusable and removable highly specific catalysts that often possess excellent storage and operational stability. Continuous large-scale processes can also be carried out in immobilized-enzyme reactors. Immobilized enzymes in conjunction with detectors have led to the development of highly specific electrode systems and new analytical and monitoring devices. They are also being developed in the form of extracorporeal shunts or microcapsules for use in clinical medicine. Moreover, the clarification of some of the principles underlying the kinetic behavior of immobilized enzyme systems (i.e., effects of the microenvironment imposed by the chemical nature of the supporting polymer material, and the effects of diffusional restrictions on the translocation of substrate and product) makes possible, in principle, the modulation of the properties of a bound enzyme by utilizing a support of predetermined chemical and physical characteristics.

Polymeric materials have been used for decades in many medical applications, including surgical implants, tissue and vascular prostheses, and dental work. Because physicians will continue to use polymeric materials in a rather empirical fashion, extensive studies of the fundamental aspects of polymer molecular structure and physical properties (especially surface phenomena in the physiological environment of the human body) will be required of polymer scientists and engineers in order to guide successful applications.

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*The term "polypeptide" was introduced by Emil Fischer to designate a polyamide of $\alpha$-aminocarboxylic acids, particularly, of the 20 or so that constitute natural proteins.

Polymeric drugs are another area where polymer research has made and can continue to make important contributions. This infant field yields both new therapeutic agents and new insights into the etiology of disease and the relevant pharmacology.

Finally, agriculture benefits greatly from polymeric pesticides and from polymeric films to reduce water loss and keep down weeds. Further developments hold promise of polymer-bound growth hormones and growth stimulants. Polymers in agriculture and food production are discussed in chapter III, section F.

### b. Information storage and expression: DNA/RNA

The fundamental mechanism by which genetic information can be passed down the generations with exceptional fidelity was discovered in 1953 in the double helical structure of DNA and the unique complementarity of the base sequence in one strand relative to the other. Subsequent discoveries have revealed many aspects of how information stored in DNA is translated into the functioning agents of life processes, the proteins. However, the strategies used by living systems to control the expression within specific cells of the appropriate genetic information so that differentiation can proceed to produce cells of heart, muscle, liver, skin, or nerves are just beginning to be understood. Major progress is now being made in learning how information is processed during differentiation--for example in some aspects of the immune response and of the switching between different types of hemoglobins that occurs during embryonic and fetal life. Exciting opportunities beckon for understanding this central aspect of cell differentiation and developmental biology.

Translation of DNA into protein requires mediation by other forms of nucleic acid: ribonucleic acid as messenger RNA, transfer RNA, and ribosomal RNA. Protein is synthesized within the living cell on a ribosome, a complex entity composed of many polypeptide subunits together with its own ribosomal RNA. Considerable progress has recently been made on the structure of this complex entity by innovative use of neutron diffraction studies of ribosomes, some of whose subunits were constructed from deuterated amino acids. Though the observed accuracy in translating a sequence of bases in DNA into a unique sequence of amino acids in a protein is beginning to be understood, the detailed mechanism remains a future challenge. For example, what is the molecular basis for the editing that occurs in the high-fidelity charging of a particular transfer RNA with a specific amino acid?

The biological behavior of nucleic acids (both DNA and RNA) depends fundamentally on their biophysical properties as polymers and, in this area particularly, physical techniques for study of synthetic polymers have been fruitfully applied. However, new surprises in DNA structure are still encountered, as in the recently discovered left-handed, or Z, form of DNA; the significance of such structural elements in the biological function of DNA remains unknown.

For the DNA of the genes and for messenger RNA (mRNA), the main structural feature is the linear sequence of bases which encodes the message. A present mystery concerns the occurrence, within a gene that specifies a single polypeptide chain, of intervening sequences of DNA that never themselves become expressed in the eventual protein. During translation these regions are spliced out in the formation of mRNA used as the template for protein synthesis in the ribosome. What role, if any, these intervening sequences may play, or may have played, in evolution and in the control of gene expression awaits further research. Other forms of RNA, such as transfer RNA (tRNA), have a complex three-dimensional structure, which has recently been determined and is essential for biological function. In tRNA, as in proteins discussed later (chapter IID, section 1d), the linear one-dimensional sequence of ribonucleotides (or of amino acids in proteins) determines uniquely the three-dimensional structure. One of the great challenges of the future is to be able to specify this three-dimensional structure from a knowledge of only the linear sequence of bases.

### c. Recombinant DNA

In a more immediately practical sense, progress in understanding the structure and function of DNA has given rise to the manipulation of genetic material within bacteria so that, in the short-term future, it should be possible to cause microorganisms to synthesize any desired protein. New techniques for the synthesis of polynucleotides, probably utilizing solid-phase procedures, will allow the rapid creation of the information necessary to direct the synthesis of a protein with the amino acid sequence (and hence three-dimensional structure) of any enzyme, peptide hormone, central nervous system agent, transport protein, cytoskeletal element, or muscle. Such synthetic techniques will also allow the creation of essentially any amino acid sequence and will open the way to the production of specifically designed polypeptides. The DNA sequence, once synthesized, can be cloned in microorganisms that can, in turn, serve as factories for the biosynthesis of essentially limitless quantities of the protein encoded in the synthetic DNA. The impact of these developments has recently received considerable attention in the production of human insulin, interferon, somatostatin, thymosin alpha-1, and growth hormone.

Synthetic polynucleotides also have great promise as probes for isolating a particular piece of genetic message from a cell containing thousands of different genes. Such probes have been productively utilized in many of the recent isolations of the genes for various human interferons.

### d. Proteins

i. Amino acid sequence and three-dimensional structure. Considerable effort has been devoted to understanding how noncovalent interatomic forces cause a given sequence of amino acids to generate a given three-dimensional structure, and the general principles now seem fairly clear. Further research is needed on the pathway by which a nascent polypeptide chain folds to give the final structure. To be able to predict the three-dimensional structure of a protein from only its amino acid sequence stands as one of the great present challenges in biopolymers.

ii. Catalysts and metabolic control. In a living organism virtually every chemical conversion is promoted by specific catalysis by a particular enzyme. Great strides have been made in understanding the mechanisms of biological catalysis by a few selected enzymes (for example, ribonuclease, lysozyme, serine proteases, and dihydrofolate reductase). Such knowledge of protein function provides a rational basis for design of potentially useful therapeutic agents (for example, methotrexate and other antimetabolite anticancer drugs). In understanding enzyme catalysts much still has to be learned about how the chemical reactivity of various catalytic functional groups is modulated by the environment provided for them within the protein. Such understanding offers the possibility of designing powerful catalysts for many industrial processes, and these will probably be most useful when attached to solid supports. Thus, one can envision the design of specific polypeptides with desired catalytic activities, some of which quite possibly have not previously been encountered in living systems. Such polypeptide catalysts could be produced in appropriate quantities by the cloning and recombinant DNA techniques discussed earlier.

In general, enzymes show a precise specificity for their substrates. This specificity of the enzymes operating at any given moment within a cell accounts largely for the metabolic control that is an essential aspect of all living systems. Though the mechanisms of some individual enzymatic processes are beginning to be understood, how they are integrated to provide the far more complex metabolism of an intact cell represents a major challenge for future research.

iii. Multisubunit proteins and cooperative interactions. Many proteins of great physiological importance (hemoglobin, acetylcholine receptor, aspartate transcarbamylase, fatty acid synthetase, the protein coat of a virus or a bacteriophage) are composed of several subunits, each of which is a single polypeptide chain. The cooperative interactions of subunits in these proteins provide possibilities for functional aspects not available to a protein composed of a single chain. The efficient take-up of oxygen in the lungs and its release in the tissues depends on interactions of four subunits of the hemoglobin molecule, as well as on effects of physiological agents other than oxygen. Recent years have seen enormous progress in understanding the structure and function of hemoglobin. Though hemoglobin serves as a useful paradigm for cooperative interaction, much further research is needed to unravel how cooperative proteins function in such important and complex biological processes as conduction of nerve impulses, metabolic control, the immune response, the assembly of cytoskeletal structures, and cell division.

iv. Polypeptide hormones. Many polypeptides carry messages from place to place within organisms and thereby control important physiological processes. Such polypeptide hormones, accordingly, present possible means of intervention in disease processes by administration of the polypeptide either with its native structure or with its structure altered to emphasize one and suppress another aspect of the function of the native hormone. The use of insulin in the treatment of diabetes mellitus is the classical example of such therapy. Other real and potential examples would now include somatostatin, growth hormone, enkaphalins, dynorphin, and interferon. Almost limitless possibilities are in prospect for beneficial modification of the functioning of an organism by the use of recombinant DNA techniques and cloning, the ability to prepare artificial DNA sequences that will direct the synthesis of virtually any polypeptide, and the further ability to synthesize chemically polypeptide hormone analogs composed partly of natural L-amino acids and partly of other units. Moreover, new techniques for isolation, purification, and structural determination on minute samples afford promise of revealing additional natural polypeptides with profound physiological roles.

v. Cell-surface proteins. Lipid bilayer membranes separate the inside of a cell from its external environment and separate the interior of a eukaryotic cell into a wide variety of subcellular organelles: nucleus, mitochondria, lysozomes, secretory granules, Golgi apparatus, and endoplasmic reticulum. Proteins embedded in, or associated with the surface of, such membranes perform many crucial functions: they transport specific substances from the environment into the cell; they receive signals from the environment, which they transduce into a cellular response; they transform the energy released in oxidation into chemical energy; they control the release of calcium in muscle contraction; and, by their specific structures, certain proteins distinguish the cells of one individual from virtually all others, thereby performing a central role in the recognition of self as distinguished from nonself in the immune response. In this regard polysaccharides attached to proteins can significantly modulate recognition monitored by immune surveillance (see section e following).

Because membrane proteins are difficult to manipulate in aqueous media, knowledge of their structures and mechanisms of action has lagged behind that of soluble proteins. Today, however, progress has become rapid, and possibly no area of inquiry into protein structure or function holds more promise of exciting new discoveries. For example, the structure of bacteriorhodopsin, the light-sensitive protein in the purple membrane of halobacterium, has been analyzed by innovative techniques that allow the determination of three-dimensional structure of protein molecules organized in a two-dimensional array in lipid bilayers. Among other membrane proteins whose structures and functions are becoming increasingly well understood are the acetylcholine receptor of the muscle end plate, which interacts with acetylcholine causing depolarization and contraction of the muscle; LDL receptor, which binds with low-density lipoprotein, a cholesterol carrier of the serum, transports it into a cell such as a fibroblast, and thus plays a central role in cholesterol metabolism and atherosclerosis; and the insulin receptor, present in the surface membranes of many cell types, whose malfunction contributes importantly to diabetes.

vi. Muscle. Muscles turn chemical energy directly into work. The various protein constituents of vertebrate muscle have been characterized, and their assembly into an intact skeletal muscle is now fairly well understood, as are the outlines of the mechanism of contraction. A present challenge is to learn the fundamental principles of polymer contractability and its application to muscle contraction. For example, poly(acrylic acid) polymers can be caused to contract by the electrochemical generation of acid, as can synthetic fibers of collagen in response to electrolyte balance. However, these processes occur far more slowly than physiological muscle contraction, and this presents a challenge both in understanding the physiological process and in duplicating it in synthetic models.

vii. Structural proteins. Many polypeptides serve essential structural roles both outside and within cells. Collagen plays the major role in construction outside the cell in animals; it is the most abundant animal protein (25 percent of the total), constituting the main fibrous elements of skin, bone, tendon, cartilage, and teeth. After initial biosynthesis on ribosomes, the protein is processed extensively within the cell before being secreted into the interstitium where further chemical changes occur, including extensive cross-linking of the individual protein molecules. (Such cross-linking is entirely analagous to the cross-linking of individual polymer chains in curing an enamel or an elastomer.) At least five genetically distinct types of collagen molecules have been identified. Though the functional significance of such molecular diversity is not yet well understood, abnormalities of collagen in many human diseases focus continuing attention on this protein in medical research. Of particular importance in this regard is the molecular basis for aging, which has quite probably, been programmed into the genetic information every person acquires at conception, but which also involves "aging" in many structural components of the body; for example, collagen of connective tissue becomes more cross-linked and less flexible with age. How these undesirable processes might be forestalled requires a clear understanding of the molecular alterations that occur with both age and pathological insults, and an understanding of the biochemical processes that mediate them.

Other extracellular structural proteins also serve important functions. Elastin, for instance, is found in most connective tissues in conjunction with collagen. Elastin is the major component of elastic fibers that can stretch to several times their length and then rapidly return to their original size and shape when tension is released. Such behavior may have important relationships to elasticity in synthetic elastomers.

Keratin serves as a major structural protein of hair, skin, and nails. The chemical manipulation of the disulfide cross-links between individual polypeptide chains provides the basis of permanent-wave technology.

Many other proteins function outside the cell in quasi-structural roles. For example, hemostasis relies importantly on fibrinogen, which in the final step of a complex cascade of events is converted to fibrin in a blood clot. Fundamental knowledge of polymer gelation has been applied to understanding the formation of blood clots and their properties. To comprehend the formation and properties of infarcts, one must understand the interaction of fibrin with tissues. The interaction of fibrin with surfaces is particularly important in artificial prosthetic devices inserted in the circulatory system.

Disorders in clotting cause such diverse problems as, on the one hand, hemophilia, in which the blood fails to clot when it should, and on the other, infarcts where blood clots plug essential circulatory pathways. Recombinant DNA technology has the potential to make a major contribution to treatment of hemophilia by providing a source of factor VIII, the absence of which is the underlying cause in many cases of this inherited condition. However, considerably more work is essential to understand all the underlying features that play significant roles in the formation of infarcts. Such understanding may be the key to forestalling potentially catastrophic cardiovascular accidents, such as heart attacks and strokes.

Within the cell several different types of cytoskeletal elements have been identified and partially characterized in recent years--microtubules, microfilaments, and intermediate filaments, for example. These structural elements, essential features of almost all cells, arise from the spontaneous self-assembly of individual polypeptide units; but as yet neither the molecular structure of the proteins is known nor the mechanisms by which they function. Actin and myosin, the major proteins of skeletal muscle, are also found within many other cell types. This entire area of skeletal elements within cells, their structure and function, is one of the liveliest in cell biology today.

viii. Immunoglobulins. The recognition of individuality relies heavily on immunoglobulins (antibodies) that are produced by plasma cells and circulate in the serum. Other analogous molecules are important components of the surface membranes of other cell types involved in the immune response. These molecules recognize a widely diverse array of foreign substances with an exquisite specificity. Important advances in elucidating the genetic origins of immunoglobulin diversity have been made, especially in the past few years. These advances reflect an aspect of the rapidly growing knowledge of gene structure and expression made possible, in part, through the new techniques of recombinant DNA and cloning. Structural studies of immunoglobulins have yielded further insights into the origins of antibody specificity. Great opportunities exist for understanding the many complex interactions in the immune response of soluble proteins with other proteins in solution or on cell surfaces, and of cell-cell interactions mediated by membrane proteins. Such knowledge will have enormous impact on a variety of diseases known to involve the immune system directly: arthritis, collagen vascular diseases, systemic lupus erythematosus, some hemolytic anemias, allergies, and others such as cancer in which the role of the immune system is presently less well documented.

Because of their high specificity, antibodies play an increasingly important role in medical diagnosis through such techniques as radioimmune assay. In this regard especially, homogeneous antibodies from hybridomas will play a vital role. When attached to solid supports, antibodies have the potential for selective removal of toxic substances (or even, possibly, undesirable cells) from blood, which can be treated outside the patient by an extracorporeal shunt. Considerable progress in both fundamental understanding of the immune response and practical applications to specific medical programs can be expected through continuing research.

### e. Polysaccharides

Traditional chemical interest in polysaccharides has focused on the industrial and commercial applications of the major species of plant origin: cellulose and its deriatives; the starches; plant gums such as guar, karaya, and arabic; the pectins; and the polymers of algal origin--algin, agarose, and carrageenan. In recent years several polysaccharides produced by microbial fermentation have achieved limited commercial importance, among them dextran from *Leuconostoc mesenteroides* and xanthan from *Xanthomonas campestris*. Perhaps the most prominent line of investigation in the past decade has been fiber X-ray diffraction analysis for a wide array of partially crystalline polysaccharides. Polysaccharide conformation in solution and in the gel state has also received considerable attention.

Biochemical interest in the polysaccharides has revived as newer techniques of chemical analysis have been brought to bear on the structural characteristics of the microbial polysaccharides and, especially, the oligosaccharide components of cell-surface glycoproteins and glycolipids. Suggestions that conformational characteristics of the cell-surface carbohydrates may be important in cellular recognition, adhesion, and information transfer have stimulated interest in analysis of the conformational preferences of these species. Substantial progress has also been recorded in understanding the structure-function relationships among the mucopolysaccharides (proteoglycans) of skeletal and connective tissue in animals.

i. Cellulose and cellulose derivatives. The crystal structure of cellulose continues to be a subject of investigation, including both X-ray and electron diffraction studies, although significant progress has been made in recent years in understanding how the cellulose molecules are arranged in the crystallites. Because cellulose dissolves only in solvents with which it undergoes chemical reaction or strong complex formation, characterization of its properties in solution has been restricted largely to its derivatives, some of which are polymers of great commercial importance (cellulose acetate, cellulose nitrate). Interest in renewable resources has stimulated studies of the chemical, microbial, and enzymatic degradation of waste cellulose to glucose, and efforts in this area hold promise of producing a commercially viable degradation scheme.

ii. Starch (amylose, amylopectin). As with cellulose, enzymatic degradation of starch has been a major topic of interest in recent years; the production of sweeteners has been the primary objective. Fundamental theoretical considerations of the conformation of polysaccharides in solution have been productive in studies of amylose, and experimental investigations of this polymer continue. Both theoretical and chiroptical methods of studying polysaccharide conformation can be expected to continue as topics of active interest in the near future.

iii. Algal polysaccharides: algin, carrageenan, agarose. Experimental and theoretical investigations of these industrially important polyeletrolytes have occurred over the past decade. Fiber diffraction studies suggest a double helical interaction of carrageenan and of agarose chains in their respective crystalline solid states, and these interactions have been implicated as network junction points in the native polymer gels. The alginates and pectinates also form gels important to their commercial applications, and efforts have been made to elucidate the nature of the intermolecular interactions stabilizing the gel state. The configurations of both algin and carrageenan in solution have been investigated with realistic chain models by means of statistical mechanical theory.

iv. Bacterial polysaccharides. The most important recent developments in commercial and technical uses of polysaccharides involve the extracellular microbial carbohydrate polymers. Among these, dextran has been employed for various pharmaceutical purposes, including use as an anticoagulant, the action of which mimics that of heparin. Suitably cross-linked dextran constitutes the starting material for producing a widely used group of chromatographic packings (sephadex) for gel permeation, ion exchange, and affinity chromatography. The extracellular polysaccharide xanthan has been approved by the FDA for human consumption as a component of various food products. A great many nonfood uses have also been identified for xanthan; among these, its application in oil-field technology has attracted particular attention. A third microbial polysaccharide, Pullularia pullulans, is being developed commercially in Japan for a number of applications in the packaging and food industries. A Japanese firm is also investigating the commercial potential of the gel-forming $\beta$-1,3-glucan produced by Alcaligenes faecalis var. myxogenes. The great range of chemical and structural features available among the extracellular microbial polysaccharides potentially obtainable through "genetic engineering" or through fermentation from inexpensive feedstocks makes these substances increasingly important items of commerce and technology.

v. Cell-surface carbohydrates. Biochemical interest in carbohydrate polymers focuses largely on their role when associated with cell surfaces. Among the prokaryotes, the cell-surface carbohydrate material is largely polymeric. In contrast, components of the eukaryotic cell surface are normally oligomeric, rather than polymeric, and usually occur in covalent association (glycoconjugates) with protein (glycoprotein) and lipid (glycolipid) components of the cell membrane. Such cell-surface carbohydrates determine the classical blood groups (A,B,O), for example. A more complete understanding of the role of carbohydrates in biological recognition will greatly advance many aspects of cellular biology.

vi. Mucopolysaccharides (proteoglycans). This class of polysaccharides occurs in animal connective tissue, predominantly in the intercellular matrix or "ground substance" and usually in close association with protein. Because abnormalities in polysaccharide distribution are associated with a number of serious metabolic disorders, they have been studied intensively, and a relatively clear description of their molecular and supramolecular structural characteristics has begun to emerge. The several distinguishable polymers of this class include hyaluronic acid, the chondrotin sulfates, dermatan sulfate, heparin, heparan sulfate, and keratan sulfate. All appear to possess a disaccharide repeating unit, one member of which is always a hexosamine and the other a nonnitrogenous uronic acid. Ester- and amide-linked sulfate groups are present in most of the species. Within the past five years a more complete picture has emerged of the covalent and noncovalent interactions of the polysaccharide chains (glycosaminoglycans) with the associated protein constituents to form the proteoglycan aggregates believed to exist in the native tissue. The next several years should see an increasing understanding of the structural details and function of these aggregates, importantly associated with medical and biological concerns.

vii. Lignin. Nearly 25 percent of the dry weight of wood is lignin, a polymer of aromatic alcohols. The main present fate of lignin is its removal by chemical treatment of wood pulp in the production of cellulose. More productive uses of this abundant natural resource would be most welcome.

viii. Isoprenoids. Plants use the branched five-carbon isoprene unit as the basic building block for terpenes of low molecular weight and for polymers of considerable importance--natural rubber and gutta percha, for example. The properties of natural rubber have been closely matched, and indeed improved upon, by the creation of synthetic elastomers. A large body of theoretical and experimental work has provided deep insights into the fundamental characteristics of elastic behavior in both natural and synthetic elastomers. These fundamental insights have greatly assisted the development of synthetic elastomers which display a broad variety of specific properties and are widely used in modern industrial societies. (Aspects of this vast and commercially important group of polymers are discussed in chapter IIC, section 2c.)

## 2. Synthetic Biopolymers

### a. Synthetic analogues of natural biopolymers.

Polypeptides, as basic structural and catalytic macromolecules in all life processes (in the form of proteins, enzymes, antibodies, hormones, etc.), have been exhaustively studied throughout this century with the aim of understanding how these complex polymeric structures generate biological activity. Chemical synthesis has played an important role in these structure-function investigations by providing large quantities of well-characterized molecules and numerous structural analogs for study. Examples include the extensive study of bradykinin and the angiotensins during which thousands of analogs have been synthesized and their biological activities evaluated. Additionally, synthetic accomplishments in this field have afforded commercial quantities of polypeptides for therapeutic and analytical use, including such materials as oxytocin, calcitonin, and human corticotropin.

The concept of polypeptide synthesis on insoluble polymer supports (styrene-divinylbenzene beads) was conceived by Merrifield in the early 1960's. This method automates the sequence of chemical reactions involved in chain growth of the polypeptide, with easy purification at each step. It was a turning point in polypeptide studies and a singularly important example of polymer control in biopolymer synthesis. Widespread adaptation of the method has now yielded thousands of bioactive polypeptides. The total synthesis of ribonuclease A was in fact a milestone, not only in enzyme chemistry but also in polymer science more generally because it established unequivocally that a biologically active enzyme conformation might be naturally assumed by a long-chain polypeptide built simply with the appropriate amino acid sequence.

Although syntheses using polymer support have achieved spectacular successes, this is by no means the final word in biopolymer synthesis. Serious problems in sequence development, which may have both physical and chemical aspects, are found with this method. Recent work indicates that the fundamental organic chemistry of coupling reactions used in this and other polypeptide syntheses needs much further emphasis, with the prospect of dramatic improvements in reliable synthesis of long polypeptide chains. Innovation in this field is still likely and offers many important opportunities. Furthermore, the synthesis of polynucleotides, polysaccharides, and mixed or uniquely sequenced biopolymer structures not available in nature affords exciting possibilities with future implications.

Nucleic acids, as carriers of genetic information, offer a major challenge to polymer chemistry and physics. Steric control of structure and preparation of different charged analogs is of paramount interest since the major factors guiding nucleic acid structure and function are their polyanionic and stereoregular character. Recent studies with polymers derived from vinyl analogs of nucleic acids represent one direction for further researh. The tailoring of structure, sequence, and ionicity of polynucleotides is now ripe for important future work. The implications of such research for genetic engineering are clear.

The preparation of wholly synthetic enzymelike polymers is another area of biopolymer synthesis deserving attention. Progress has been made in achieving enzyme-mimicking properties by modifications of polymer structure in the direction of balanced hydrophilic and hydrophobic character combined with appropriate ionicity and catalytic sites on synthetic chains, e.g., based on poly(ethylene imine). These preliminary studies offer numerous directions for future work of general interest to biological science and to the field of catalysis.

Finally, altered or controlled biological synthesis of biopolymers, such as recently developed hybridoma technology for production of specific monoclonal antibodies, represents a new field bridging the traditional ones of polymer synthesis and microbiology. Future research here offers promise of new antibody preparations for diagnostic and therapeutic applications as well as for fundamental studies of biochemical pathways.

### b. Immobilized enzymes

i. Immobilization techniques. Enzymes can be immobilized by matrix entrapment, by microencapsulation, by physical or ionic adsorption, by covalent binding to organic or inorganic polymeric carriers, or by whole-cell immobilization. Particularly impressive is the great number of chemical reactions developed for the covalent binding of enzymes to inorganic carriers such as glass, to natural polymers such as cellulose or agarose, and to synthetic polymers such as polyamides, polyacrylamide, and other vinyl polymers and copolymers possessing reactive chemical groups. The parallel field of affinity chromatography, which involves covalent binding of proteins or enzyme substrates to chromatographic matrices, has contributed much new coupling chemistry of value to studies of immobilized enzymes. Cyanogen bromide, carbodiimide, and periodate oxidation are just a few of the methods developed for coupling hydroxyl, amino, and carboxyl functions on proteins to polymer matrices. Unfortunately such covalent attachments lead as a rule to nonspecific binding. The preparation and characterization of well-defined carrier-enzyme conjugates requires the development of highly specific reactions by which an enzyme can be attached precisely to functional groups on a carrier. This is an important area for future study.

Immobilized enzymes are often more stable to denaturation by heat, chemical denaturing agents, or organic solvents, than the corresponding native enzymes. The reasons for this effect are still not fully understood, and a thorough analysis of the conformation, ease of denaturation, and conformational fluctuations of immobilized enzymes should be undertaken.

ii. Effect of microenvironment on kinetic behavior. Considerable progress has been made in elucidating the influence of the enzyme-polymer microenvironment (such as electric charge, dielectric constant, and lipophilic or hydrophilic nature), and of external and internal diffusion, on the activity of immobilized enzymes. These factors have been considered in deriving expressions for the kinetic behavior of immobilized enzymes treated as simple heterogeneous catalysts. Substantial changes have been observed in apparent pH optima and substrate specificity which are important to basic studies as well as applications. For example, the 5.5 pH optima in solution for amyloglucosidase and glucose oxidase are altered to 4.9 and 6.5, respectively, when the enzymes are bound to an insoluble polymer carrier.

Further progress on the mechanism of action and kinetics of immobilized enzymes will require both theoretical and experimental studies of more complex enzyme systems. Of particular interest will be the study of the highly specific interactions between an enzyme embedded in a native membrane and adjacent molecules of high or low molecular weight. Multiple bound-enzyme systems will also be of basic and practical interest.

iii. Enzyme membrane. Enzymatic reactions in nature occur most often in membranes or on membrane surfaces. Studies of synthetic enzyme membranes are therefore relevant to understanding the biological processes. Enzyme membranes have been prepared by surface adsorption or impregnation of natural or synthetic membranes. Enzyme membranes may be stabilized by covalently attaching adsorbed protein to the membrane or by cross-linking the protein (for instance, with glutaraldehyde).

One special class of enzyme membranes is that of polymer-encapsulated enzymes where control of substrate and product diffusion through the capsular membrane may control the kinetics. Such compositions begin to mimic natural cell properties crudely and suggest future opportunities for the synthesis of "synthetic cells" with highly specialized biochemical functions.

iv. Immobilized coenzymes and enzyme cascades. Many enzymes require the participation of dissociable coenzymes for catalytic activity. The use of coenzymes to activate immobilized enzymes on a large scale is hampered by their relatively low stability and high cost. Accordingly, attempts are being made to stabilize the coenzymes and to find suitable means for their continuous regeneration. The principal approach has been to attach a coenzyme covalently to a polymeric water-soluble matrix, thus making the coenzyme, like the enzyme, potentially reusable.

In nature different enzymes may carry out a sequence of consecutive reactions. Such enzymes are often specifically associated in multienzyme complexes. Studies of the characteristics of artificially produced multienzyme complexes and cascade reactions, accordingly, hold both theoretical and practical interest.

v. Immobilized cells and synthetic organs. The immobilization of microbial cells under conditions in which enzymatic activity remains but the normal metabolic processes cease represents a novel technique for enzyme immobilization.

Within the past decade procedures have been developed for immobilization of microbial cells by entrapment in such matrices as collagen, gelatin, agar, cellulose triacetate, alginate, K-carrageenan, polyacrylamide, and polystyrene. For example, Streptomyces phalochromogenes has been incorporated into thin collagen films treated with glutaraldehyde, with retention of good glucose isomerase activity. The effect of the matrix on the metabolically inactive cells is still not understood. Accumulation of experience and information should lead to practical guidelines for choosing the most suitable matrices for entrapment and the best conditions for immobilization.

Possibilities even exist for artificial organs based upon composite structures of polymer and cells. One example is a combination of living rat-liver cells with semipermeable hollow polymer fibers to carry on artificial liver functions (e.g., bilirubin breakdown). Another artificial organ of rat pancreatic cells in hollow fibers mimics the pancreas in insulin production. These are still primitive modified cell-culture systems, but they suggest intriguing opportunities for future development.

vi. Applications. Immobilized enzymes and immobilized cells are now employed as specific heterogeneous catalysts by several chemical companies. Aminoacylase electrostatically bound to DEAE-sephadex is used for the production of L-amino acids from the corresponding racemic acetyl DL-amino acids prepared synthetically. Penicillin acylase (penicillin amidase) immobilized by adsorption or covalent binding on organic or inorganic carriers is used for the production of 6-aminopenicillanic acid (6APA) from penicillin G. Immobilized glucose isomerase is used extensively in the United States, Japan, and Europe for production of high-fructose syrups by partial isomerization of glucose. L-Aspartic acid is being produced continuously from ammonium fumarate in columns packed with immobilized E. coli.

Enzyme immobilization has facilitated development of enzyme electrodes and of novel enzyme-based automated analytical methods. Specific enzyme electrodes combine an enzyme membrane and ion-selective electrode, and their use is expanding. Enzyme columns are now part of many automated clinical analyses.

Soluble enzyme-polymer compositions have also found increasing use, especially for enzyme therapy. Uricase binding to poly(ethylene glycol), for example, provides a more metabolically stable and less antigenic uricase possibly useful for uric acid detoxification. Many other stable, active, nonimmunogenic, soluble conjugates of enzymes with hydrophilic polymers may have important future roles in enzyme therapy and diagnostic medicine.

### c. Synthetic polymers of medical importance

i. Polymers for implants and prosthetics. This enormously important and complex field works with both basic scientific and technological aspects of soft and hard tissue biocompatibility and blood compatibility. Tangential aspects include (1) bioadhesion phenomena and cell binding to damaged tissue and to polymer surfaces, which may have implications for bacterial or viral infections, and (2) tissue damage in surgical procedures that may lead to numerous unsuspected postoperative complications. The physical and chemical factors that lead to good long-term acceptance of vascular implants, soft or hard tissue implants, and the materials used in various in vivo or ex vivo devices constitute a major area for further investigation.

Of many possible applications for polymeric materials in surgical reconstruction and replacement of hard and soft tissue, particularly widespread interest focuses on heart and vascular prostheses, functional implants such as intraocular lenses and pacemakers, and implants for tissue reconstruction, especially for cosmetic surgery, following disease or accident. Basic underlying questions concerning tissue "biocompatibility" remain essentially unanswered. We do not yet understand the many complex relationships between the physiological environment and basic polymer characteristics such as structure and purity, surface structure and properties (ionicity, hydrophilicity, surface energy, surface morphology, surface roughness or texture), mechanical properties, diffusion of fluids, and stability toward chemical or enzymatic degradation.

Although surface energy and chemical inertness of polymers have long been considered important factors in blood compatibility, only recently has serious attention also been focused on matching the mechanical properties of implants to those of tissue (e.g., to the elastic molulus for vascular prosthesis) or on evaluating the effects of surface roughness and texture. Furthermore, polymers that exhibit good bioacceptance in soft or hard tissue (e.g., acrylics) may prove disastrous in a situation involving contact with blood. Experiments involving injected polymer microcapsules to probe bioacceptance in various organs and tissues clearly show that even different locations in the same organ may impose widely varying environmental constraints on implanted materials.

The problems are further complicated by highly variable tissue trauma that normally occurs in surgery and that may produce widespread, insidious, and serious problems involving both materials and procedures. Tissue protection with polymer coatings prior to surgical manipulation, and alteration of the surfaces of surgical gloves, sponges, and instruments may therefore be a challenging, promising, and difficult new area of research.

Related to questions of tissue damage are bioadhesion phenomena or "sticking" of tissue or cell surfaces to foreign materials. In the field of blood-compatible polymers, blood-cell (platelet) and metabolite (protein) adsorption have been widely recognized as important. However, the role of such interfacial phenomena in tissue damage and in viral or bacterial adherence (and subsequent infection) is less clearly appreciated.

ii. Ex vivo blood contacting devices. Dialysis membranes and associated instrumentation, other extracorporeal blood-shunt devices and pumps for detoxification and surgical assist, and blood bags and tubing are applications imposing less stringent requirements than long-term implants. Nonetheless, lack of insight into basic polymer science has sometimes led to marginal serviceability, poor quality control, and frequent complications and failures. Plasticized PVC, for example, has been in widespread use for blood handling, but has given rise to problems of plasticizer leaching.

Fundamental knowledge of function-property-structure relationships and of the influence of fabrication processes is essential for improved safety and reliability of such devices. The major breakthrough in cellulose acetate membranes for dialysis, for example, came from film casting studies. These studies, aimed at modification of thin-film structure, yielded a unique kind of thin solid skin with a thick porous substructure, combining good transport and good mechanical properties. One might expect further that block copolymer research could lead to tailored films with unusual diffusional, metal chelating, and mechanical properties. Evidence for this possibility is afforded by polycarbonate-poly(ethylene oxide) block copolymers that display superior strength plus excellent dialysis performance.

Despite significant success with blood dialysis, blood oxygenation, blood pumping, and blood handling, serious difficulties with current materials and devices remain. Smaller, simpler, less costly, less blood-damaging, and more routinely reliable instrumentation is needed and could follow from progress in the synthesis of new polymer compositions as well as in new fabrication methods and in engineering design.

iii. Polymers for temporary in-dwelling devices. Virtually all major surgical procedures require temporary in-dwelling devices made of polymeric materials, such as vascular and urethral catheters, wound-drainage tubes, and trachea tubes. Current devices display important deficiencies. Secondary infections following wound drainage and urinary catheterization are much too common. Tracheal tissue damage and related complications (including postoperative bacterial pneumonia) may be traced to tracheal tubes used in anesthesia. Highly compliant tracheal "cuff" elastomers of lower modulus, which would seal the irregular trachea at low pressures, coupled with modified surfaces to reduce tissue damage, would greatly improve current practice. Vascular and urethral catheterization with PVC, silicone, Teflon®, or rubber latex catheters results in too high an incidence of damage to the urethral mucosa or vascular endothelium. Knowledge is needed of the events at specific tissue-polymer surfaces that lead to mechanical, physical, or chemical changes, or that may affect bacterial adherence and growth on polymer surfaces.

iv. Dental polymers and composites. Progress in the development of polymers, composites, and adhesives for dental applications has been significant during the past three decades, and polymers now play an indispensible role in dentistry. For dental fillings and prostheses fixed to teeth or to other hard tissue, interfacial phenomena again dominate the outcome. Indeed, a clear distinction is difficult to make between mechanical failure and problems of biocompatibility at the interface. Although mechanical strength and modulus may be tailored for dental polymers, adhesion is one of the most challenging problem areas. Bonding to dentine is particularly difficult because acid etching techniques cannot be used. Secondary caries and prosthetic failures most often occur because of percolation of microorganisms, liquid, and other matter into marginal unfilled areas. The development of improved interfacial bonding polymers, such as covalently reactive acrylics, will lead to simpler dental procedures (with less etching and grinding) and inhibition of subsequent caries. Additionally, opportunities exist for new fissure sealants to act as plaque barriers and to minimize harmful deposition of calculus. The advent of improved polymer prostheses and cements combining environmental stability, desired strength, bone-matching thermal expansion behavior, and, most importantly, genuine adhesive bonding at the interface remains a clear but elusive target. Further fundamental physical and chemical studies at the hard tissue-polymer interface are, therefore, crucial in this field.

A fruitful and extensive area of research on dental materials involves the development of improved composites from which new products appear frequently. These materials, like amalgams, may be formed and cured in the mouth without the need for dental laboratory facilities. Dental composites consist of a reinforcing filler of small inorganic particles (usually quartz or glass) imbedded in a matrix of organic polymer. A currently popular matrix constituent is bisphenol A-glycidal methacrylate (bis-GMA). Because this dimethacrylate monomer is difunctional, cross-linking and polymerization occur simultaneously, producing the hard durable material required for occlusive applications.

The areas of importance in research on composites are manifold. Physical and chemical properties are enhanced by appropriate modifications of the matrix components--monomer, initiator, amine, inhibitor, diluent, and coupling agent.

Since most current dental materials are reasonably durable, meaningful selective clinical evaluations require about three years. Several laboratories are developing accelerated _in vitro_ wear tests with the aim of obtaining reliable data to assess the _in vivo_ durability of these materials. A complementary activity is analysis of subsurface wear for microdefects to compare _in vivo_ and _in vitro_ damage on worn dental composite specimens. Matching the wear mechanisms is necessary to obtain a reliable correlation between laboratory and clinical tests. This problem of correlating clinical experience and laboratory data is indeed a major issue in all biomedical polymer research.

v. _New polymers and polymer modifications for medical devices._ Each specific medical device or prosthesis demands a special balance of properties. Physical and chemical requirements for a degradable suture material, for example, are quite different from properties that a heart valve or bone prosthesis must have. Most often, adaptation of available materials has been the rule, although there has been increasing effort to synthesize new polymers or devise new composites or surface modifications. Fluorocarbons, silicones, rubber latex, poly(vinyl chloride), poly(methyl methacrylate), polyethylene, and polypropylene have all found use. However, hydrophilic acrylic "hydrogels," such as poly(hydroxethyl methacrylate) (HEMA), have been specifically prepared for ophthalmic applications (and now find broader use); elastomeric urethane block copolymers and urethane-silicone blends have been prepared for blood-contacting cardiovascular devices; and chemically reactive acrylics have been synthesized for bone and tooth cements. The need for new synthetic biomedical polymers far exceeds the effort devoted to such research to date.

Attention in the future must focus especially on surface modification by chemical reaction or irradiation grafting to alter hydrophilicity, ionicity, mechanical behavior, and texture. New medical polymers may be synthesized to have special bioinert or bioactive properties (for instance, to stimulate or retard adjacent cell growth) or to have tissue-binding behavior through controlled porosity and/or incorporation of ionic sites and diffusable ions such as calcium.

vi. Polymers for biological separations and analyses. This area includes such topics as polymers applicable to separations by gel and affinity chromatography, and membranes for ultrafiltration and dialysis. Although research emphasis may be upon biological separations and clinical analysis, there are therapeutic aspects as well. The widespread application of gel, affinity, and electrophoretic separations which rely upon polymer carriers and columns foreshadows the future importance of work in this field. Polyacrylamide gels and cross-linked polysaccharides have become a routine part of all biochemical and biophysical research. However, new chemical modifications of chromatographic polymers to alter binding properties are now being actively investigated, with the prospect of improvements for all types of chromatography.

Similarly, affinity chromatography, which involves covalent attachment of biospecific complexing ligands to a polymer gel for efficient separation of specific binding molecules, has emerged since the mid-1960's as one of the most powerful tools for bioanalytical work. Here too, many basic problems require attention--ligand-binding chemistry, polymer-ligand stability, binding specificity. New substrate polymers and new elution methods will offer faster, simpler, and more reliable methods of clinical analysis, and there is a great need today for improvement of the reliability and cost of diagnostic analyses.

The advent of polymeric membranes for more precise control of dialysis and ultrafiltration is another accomplishment of great value, and the prospect of advancing this "art" by creation of superior membranes and microcapsule adsorbents is clear.

### d. Polymers and drugs

Polymer drugs are synthetic polymers with biologically active functional groups. They include any agent either curative or prophylactic that upon introduction into a living system, causes a physiological response. This highly fertile infant field of polymer research is yielding new therapeutic agents as well as new insights into disease etiology and pharmacology; it deserves further cultivation.

Development of new drugs has two highly desirable objectives: enhancing drug specificity and increasing the duration of the drug action. Enhanced specificity produces an increase in the therapeutic effect of the drug without a proportionate increase in toxic side effects. Long-term delivery in appropriate quantities to a particular organ or tissue presents one of the major challenges in pharmacology. With most soluble drugs of low molecular weight, the entire body becomes infused with the drug and maintenance of the required level at the desired site may lead to side effects because of undesirably high concentrations elsewhere. An increase in the duration of drug action can be accomplished by slow delivery through slow dissolution from a crystalline depot; through diffusion from, or dissolution of, a matrix material; or through cleavage of the drug from a carrier molecule.

Two basic types of polymer drugs can be considered: (1) the polymer itself acts as the drug (polymeric drugs); (2) a drug ligant is chemically attached to a polymer which functions as a carrier (polymer-bound drugs).

i. Polymeric drugs. Many polymers have been tested for biological activity, and some have been found that are antibacterial, antifungal, interferon inducing, antiviral, or antiparasitic. Polymeric materials having gastro-intestinal, dermatological, or antiulcer activities have also been studied, as have polymers that affect the immune response or act as suppressors of inflammation. Other polymers may be anthelminthic, narcotic, antitussive, hypotensive, antihistaminic, hypnotic, tranquilizing, analgesic, antisecretory, antispasmodic, antineoplastic, appetite suppressing, motor activity depressing, or muscle relaxing. Polymers have also been discovered that are useful in treating circulatory, cardiac, and blood diseases. Some specific examples include: plasma extenders, such as poly(vinylpyrrolidone) and poly(vinylpyridine-N-oxide); synthetic analogs of heparin; and various polyanions, such as synthetic polyanionic copolymers of pyran, which have proved useful in inducing interferon and thus have antiviral properties. Polymers also inhibit mitosis and neoplastic processes, though adverse side effects have halted clinical trials of them as antitumor agents.

ii. Polymer-bound drugs. When known drug structures are present either in the chain backbone or as pendent groups, the polymer itself may exhibit biological activity and need not be degraded to release low-molecular-weight species.

Hydrophilic polymers covalently bound to drug or other natural ligands with biological activity, such as enzymes, hormones, and antibodies, may show properties quite distinct from those of the ligand itself. In this regard, such polymers as poly(vinylpyrrolidone), poly(glutamic acid), polylysine and poly(ethylene glycol) have produced unusual conjugates with antitumor drugs and with enzymes. Such combinations act as new drugs with significantly altered and potentially highly desirable pharmacological properties, including reduced toxicity for antitumor agents, increased metabolic stability for drugs and enzymes, reduced immunogenicity for poly(ethylene glycol) conjugates, and significant alteration of polymer-bound protein ionicity (perhaps by hydrophilic shielding as evidenced by large changes in electrophoretic mobility and ion-exchange properties). Research to date suggests exciting opportunities to create entirely new classes of drugs with macromolecular structures as a key factor in their function. Most obvious is the opportunity to tailor properties, such as tissue diffusion, specific cell-receptor binding, endocytic cell uptake, plasma serum albumin complexation, and renal clearance, by relatively simple alterations in molecular weight and structure.

Noncovalent polymer-drug complexes can also have useful pharmacological characteristics. Among examples are ionic complexes of negatively charged polymers and basic drugs, such as complexes of carboxymethylcellulose with quinine, procaine, diphenylhydramine, and tripelennamine (pyribenzamine) or salts and complexes of the antitumor drug adriamycin with DNA or polyglutamic acid.

Some drugs have themselves been polymerized with a suitable reagent, such as formaldehyde, which reacts with many drugs of aromatic structure to form copolymers. Examples include many sulfonamides, tropolones, and aromatic steroids. Quaternary ammonium salts containing a lipophilic group having 8-28 carbon atoms are known to be effective germicides. Polymeric quaternary ammonium salts with antibacterial and fungicidal properties have been described. Polyionenes, in which the quaternary ammonium groups are located along the polymer chain, have been shown to have bactericidal properties.

Penicillin, the first and most important antibiotic, has been incorporated into both natural and synthetic polymers--for instance, with vinyl amine and vinyl alcohol copolymers. These polymers have the same activity as the parent drugs in clinical studies. Primaquine, a potent antimalarial drug, has been attached to a polyepichlorohydrin.

Studies on polymers of various vinylsalicylic acids have demonstrated that the specificity of a given biological agent may be altered through derivatization (acetylation) or copolymerization with a suitable but inactive comonomer, implying the possibility of designing new biological agents of high specificity by using appropriate combinations of drug and comonomer. Some polymeric derivatives of vinylsalicylic acids have been found active against Gram-negative and Gram-positive bacteria.

iii. Controlled release and physical localization. This class of polymeric drugs includes both soluble and insoluble polymer carrier compositions in which: (a) drugs are covalently attached to a polymeric carrier but released by hydrolytic, enzymatic, or ozidative means; and (b) noncovalent polymer-drug complexes exist, such as ionic complexes of negatively charged polymers and basic drugs; or (c) drugs are physically trapped in polymer matrices or encapsulated in polymer barrier coatings requiring diffusion or polymer degradation for drug release.

In this area, very important practical results have been achieved. Intrauterine contraceptive devices that release hormone locally and in this way avoid systemic side effects have been commercially developed. These devices are based on controlled diffusion through membranes or from silicone-hormone mixtures. Such physical localization may involve biostable polymers, or removable wafers or rings (in the case of contraception). Biodegradable polymers, such as polylactic acid in the form of pellets or capsules, can dispense a drug for prolonged periods from a "depot" implant site, then degrade and disappear. Administration of narcotic antagonists (e.g., methadone) has been studied in detail with this type of localized delivery system. Research has also focused on the use of bioinert or degradable membranes as depots for localizing and controlling release of simple molecules, large molecules, and even polymers. Such membrane systems for release of macromolecules have been explored with considerable promise for delivery of immunization and antitumor agents.

Polymers with biologically active groups in the main chain are desirable when they can be hydrolyzed to the active component and inactive small molecules. Primary candidates in this category include polyesters, especially polycarbonates and polyphosphates because their hydrolysis leads to the formation of the active molecule and carbon dioxide or phosphate only.

Polymers with active groups attached through a hydrolyzable or degradable link to the polymer chain, either directly or via a spacer group, are the most extensively studied release agents. In this case the polymer main chain is not attacked and remains as a polymer fragment. Such agents have found extensive use in agriculture as controlled-release pesticides, herbicides, insecticides, and fungicides.

iv. Specific targeting of drugs. Soluble polymeric drugs can be targeted or localized to specific tissues, organs, or metabolic pathways by means of attached ligands that bind to specific proteins or cell surface receptors. Antibody-antigen, enzyme-substrate, and hormone-receptor are examples of such biospecific interactions. Although only limited success has been achieved to date, this approach offers in principle an exceedingly attractive way of avoiding the often severe side effects of conventional administration of systemic drugs. Site-specific targeting with polymer-bound drugs that bind to tissue by virtue of attached complexing or chemically reactive functionality is also of interest for direct injection into organs or diseased tissue, for instance with intratumor chemotherapy.

## 3. Structure-Function Relationships

### a. Sequence analysis

For many years the amino acid sequences of proteins have been determined by increasingly sophisticated technology. Today one can automatically determine the N-terminal sequence for up to 60 residues on as little as $10^{-8}$ mole of protein, and even more sensitive procedures are being developed. New methods have also allowed the determination of nucleotide sequences in DNA and RNA. Indeed, if the gene for a given protein has been identified and isolated, it is now probably easier to learn the amino acid sequence by determining the base sequence in the DNA which codes for the particular protein than to determine the amino acid sequence directly (although the recently discovered intervening sequences, mentioned in chapter IID, section 1b, may complicate this DNA-protein relationship). Information about such sequences can then be applied in synthesis, in determination of the relation of amino acid sequence to three-dimensional structure and biological properties, and in genetic and evolutionary studies.

Advances in techniques for separation and purification, such as chromatography and density-gradient ultracentrifugation, have provided polymeric materials of the purity required for proper sequence analysis. Advanced techniques of applying mass spectroscopy should contribute further to the ease and efficiency of sequencing even smaller quantities of biological macromolecules.

With the sequence determined, many synthetic methods become available (and are still being developed) to synthesize large polypeptides and polynucleotides with specific sequences (see chapter IID, section 2a).

### b. Instrumentation

Advances in instrumentation have led to characterization of natural and synthetic biopolymers of many chemical constitutions. X-ray and neutron diffraction of single crystals, fibers, films, and even ribosomes have provided information about static structures. Recently, dynamic information has also been obtained from studies at low temperatures.

A new technique that provides information about the three-dimensional structure of membrane-bound proteins from two-dimensional ordered arrays has been applied to bacterial rhodopsin. Other methods that yield structural information about both the solid state and gels include neutron scattering, electron microscopy (with and without fluorescent antibodies), and mechanochemical techniques. Further development of the relatively new technique of solid-state NMR should add a powerful tool for studying structure and function of biopolymers in gels, in membranes, and in the solid state.

The properties of solutions of macromolecules have been investigated by thermodynamic, hydrodynamic, and spectroscopic methods. Calorimetry of various kinds, and osmotic pressure and potentiometric titration measurements have provided thermodynamic data on charged and uncharged macromolecular systems. Molecular weights and molecular weight distributions have been obtained by measurements of osmotic pressure, light scattering, sedimentation equilibrium, and the combination of sedimentation velocity with diffusion. Information about the size and shape of macromolecules has been deduced from light scattering, low-angle X-ray scattering, and a variety of hydrodynamic measurements, including viscosity, translational diffusion, flow birefringence, and dielectric dispersion (the latter technique also yields information about dipole moments). Details of the electronic configurations and internal structure of biopolymers have come from a variety of spectroscopic methods: NMR, ESR (with spin labels attached), infrared, Raman, ultraviolet and visible, linear and circular dichroism, and fluorescence.

Instrumental methods have also fostered the application of other techniques to structural problems of biopolymers. Various relaxation methods have been applied to study the kinetics of fast biological processes. Instrumentation has also made possible the study of the rates of exchange of labile hydrogen for deuterium or tritium, which leads to information about internal structure and flexibility. Flash photolysis has been successfully applied to probe the surfaces of biopolymers and membranes. Recently, radio-immunoassays and fluorescently labelled antibodies have been used to probe the surface structure of biopolymers. Future advances in the development of homogeneous monoclonal antibodies will greatly expand the utility of this technique.

Further dramatic advances, particularly in real-time studies of biochemical dynamics, can be expected through more advanced instrumentation now in prospect, such as improved X-ray sources and detectors, increased neutron fluxes, vacuum ultraviolet, Fourier-transform infrared, higher-field NMR spectrometers, and improved lasers (tunable in the ultraviolet) for resonance Raman spectroscopy and light scattering. Increases in the speed of spectroscopic techniques will open up new time ranges in studies of the kinetics of fast reactions and may provide a deeper understanding, for example, of the processes involved in vision.

### c. Theory

Many of the advances in instrumentation could come about only because of developments in the underlying theory, carried out in many cases by polymer scientists motivated by the need to apply these various techniques to polymer problems. Furthermore, quantum mechanical, statistical mechanical, and thermodynamic treatments have been developed to account for various properties of biopolymers, such as circular dichroism, phase transitions, equilibria in multicomponent systems, contractility in multicomponent systems, and conformations of polymer chains (including folding of natural biopolymers). Molecular dynamic and Monte Carlo methods have also been used to investigate the conformational properties of polymers in solution. These theoretical developments have depended largely on the availability of computers, and further advances in computer technology can be expected to foster a better understanding of the liquid state and the influence of solvation on the three-dimensional structures and properties of biopolymers.

### d. Interfacial phenomena

Increasing attention is being paid to interfacial phenomena, which play an important role whenever two phases come into contact. Problems of biological interest often involve contact of a polymer with a physiological environment, and it is essential to understand the surface properties of the materials involved.

One important need is for more sensitive methods of surface characterization with higher spatial resolution. This is of special importance for heterogeneous "mosaic" surfaces often encountered in biological systems. For example, contact angle measurements to determine critical surface tension are widely applied but are of questionable merit when surface heterogeneity and domain morphology approach molecular dimensions. Combinations of transmission and scanning electron microscopy; electron spectroscopy applied to chemical analysis (ESCA); Auger, NMR, and FTIR spectroscopy; and optical microscopy and zeta-potential measurements afford a wealth of data and have substantially improved the exploration of surface properties. However, the complex and dynamic events affecting a surface *in vivo* are exceedingly difficult to monitor and even more difficult to relate to functional performance. New surface analytical methods, especially for *in vivo* kinetic and dynamic structural characterization, are vitally needed for progress in this area.

## 4. Current Areas of Biopolymer Research

Changes in the conformations of biopolymers (denaturation) have been investigated to determine the nature of the interactions that hold a natural biopolymer in its native structure. With the availability of computers further advances may be expected in resolving the interactions in a native biopolymer and the steps in the pathway from newly synthesized chain to ultimate biologically active native structure (i.e., to answer the question of how one-dimensional sequence information determines three-dimensional structure). The availability of so many known protein sequences provides an excellent opportunity for developing methodology to solve this problem.

Much has been learned about the interaction between macromolecules and ligands, and about polymer-polymer interactions. Such information will be crucial to understanding the molecular processes involved in cell-cell and antigen-antibody recognition.

Recent advances in mechanochemistry and the underlying biochemistry can be expected to provide information about the basic nature of muscle contractility.

Chemical modifications and cross-linking experiments and the application of various instrumental techniques can be expected to elucidate structure-function relations in general and, in particular, the structural features of viruses, chromatin, and ribosomes, and the role of the latter in protein synthesis. Experiments with complexes of synthetic polypeptides and synthetic polynucleotides will be of help in elucidating the interactions in such nucleoprotein complexes, interactions which influence the conformation of both the polynucleotide and the polypeptide (for instance, see the discussion of Z-DNA in chapter IID, section 1b).

Development of aqueous solution chemistry at low temperatures, under which molecular motions and reaction rates are greatly slowed, can be expected to allow X-ray studies with reduced thermal-motion effects and spectroscopic studies of the mechanism of enzyme action.

Recent advances in general techniques for studying interfaces should lead to increased knowledge about the surface chemistry and physics of biopolymers.

Synthetic RNA messengers and cell-free protein-synthesizing systems should permit study of the molecular basis of ribosome-mediated protein synthesis.

## 5. Major Research Opportunities*

### Group I

1. Improved methods for structural characterization of natural biopolymers. These include improved sequencing technology and experimental determination of three-dimensional structure, and involves physical techniques such as X-ray and neutron diffraction; magnetic resonance spectroscopy; and resonance Raman, FTIR, and vacuum UV spectroscopy.
2. Improved methods for synthesis of biopolymers. These include solid-state synthesis of polypeptides, synthesis of polynucleotides (including automated, solid-state procedures), and synthesis of specific oligosaccharides and their attachment to specific residues of polypeptides.
3. Conformational theory of protein and nucleic acid folding to find how sequence determines three-dimensional structure.
4. Interfacial science. The aim is to establish fundamental principles of interaction between polymers and biological fluids and tissues.

### Group II

1. Synthesis and pharmacological properties of polymeric drugs.
2. Pharmacology of synthetic polymers, and investigation of the physiological response (including immune system) to soluble and insoluble polymers.
3. Relation between three-dimensional structure and biological function.

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* Order within the group is not significant.

# III. POLYMER RESEARCH AND NATIONAL NEEDS

In the seven decades since Baekeland introduced the first commercially successful plastic produced entirely by the reaction of small molecules, synthetic polymers have come to fill an overwhelming number of needs, many generated by the very availability of these extraordinary new materials. The increase in production and use has been spectacular. The average annual growth rate of about 8.5 percent sustained over the past two decades is three to four times that of other materials[1] (see figure III-1). The production of synthetic polymers in the United States reached an all-time high of 23 million metric tons in 1979,[2] corresponding to a volume of material exceeding that of steel[3] (see figure III-2). This production formed the basis for about $90 billion of value added by manufacture (a measure of the relative economic importance of manufacturing among industries) and for the employment of 3.4 million people.[4,5] Clearly, polymers represent a large, rapidly expanding, and economically important class of materials.

The commodity polymers now being produced in such large volumes reflect the science of an earlier period. Polymers also have a critical high-technology aspect that does not show in tonnage figures but will become increasingly important in the future. In many applications they have unusual leverage in that small quantities may be capable of yielding large returns. For example, weight reduction in airplanes and automobiles through replacement of metal components by polymers provides improvements in operating efficiency that can translate into enormous savings in fuel. Resistance of polymers to specific forms of corrosion can drastically reduce replacement costs of components that are subject to a variety of hostile environments, and can lessen national dependence on critical materials such as chromium and manganese. Milligram quantities of advanced polymers consumed in the production of each electronic microcircuit are indispensable in that industry.

This chapter records how polymer research bears on fulfilling selected categories of national needs, identified under the following headings:

A. Polymeric Materials: Sources, Conservation, and Disposal
B. Polymeric Materials: Capabilities, Limitations, and Special Applications

C. Polymers and Energy
D. Polymers in Transportation
E. Polymers in Construction
F. Polymers in Agriculture and Food Production
G. Polymers in Medicine
H. Polymers in National Defense

The treatment is brief but will suggest the wide scope of perceived national needs on which polymer research impinges.

Preservation of the preeminent position of the United States in polymer science and engineering is itself a vital national need. Vigorous pursuit of long-range basic research is essential to maintaining that position, particularly in the face of strong challenges from other industrialized nations. An industry dependent on imported technology and imported processed materials is a national liability in that it can lower the standard of living through an unfavorable balance of payments. Sustaining and improving the quality of polymer research in the United States is a primary objective in preparing this report, and some specific proposals are discussed in chapters IV and V following.

## References

1. 1979 U.S. Industrial Outlook, (Washington, D.C.: U.S. Department of Commerce, 1979); Statistical Abstract of the United States, (Washington, D.C.: U.S. Department of Commerce, 1979); Facts and Figures of the Plastics Industry, (Soc. Plastics Ind., 1978). The data vary somewhat with the years and sources of information, but the relationships among the different materials are similar and reasonably represented by the averages given here.
2. "Facts and Figures for the Chemical Industry", C&EN News, 57, 33 (1980).
3. Metal Statistics 1979, (American Metal Market, Fairchild Publications); Historical Statistics of the United States: Colonial Times to 1970, (Washington, D.C.: Department of Commerce).
4. 1980 U.S. Industrial Outlook for 200 Industries with Projections for 1984, (Washington, D.C.: U.S. Department of Commerce, 1980).
5. Table 2 of 1977 Census of Manufactures, (Washington, D.C.: U.S. Department of Commerce, 1979).

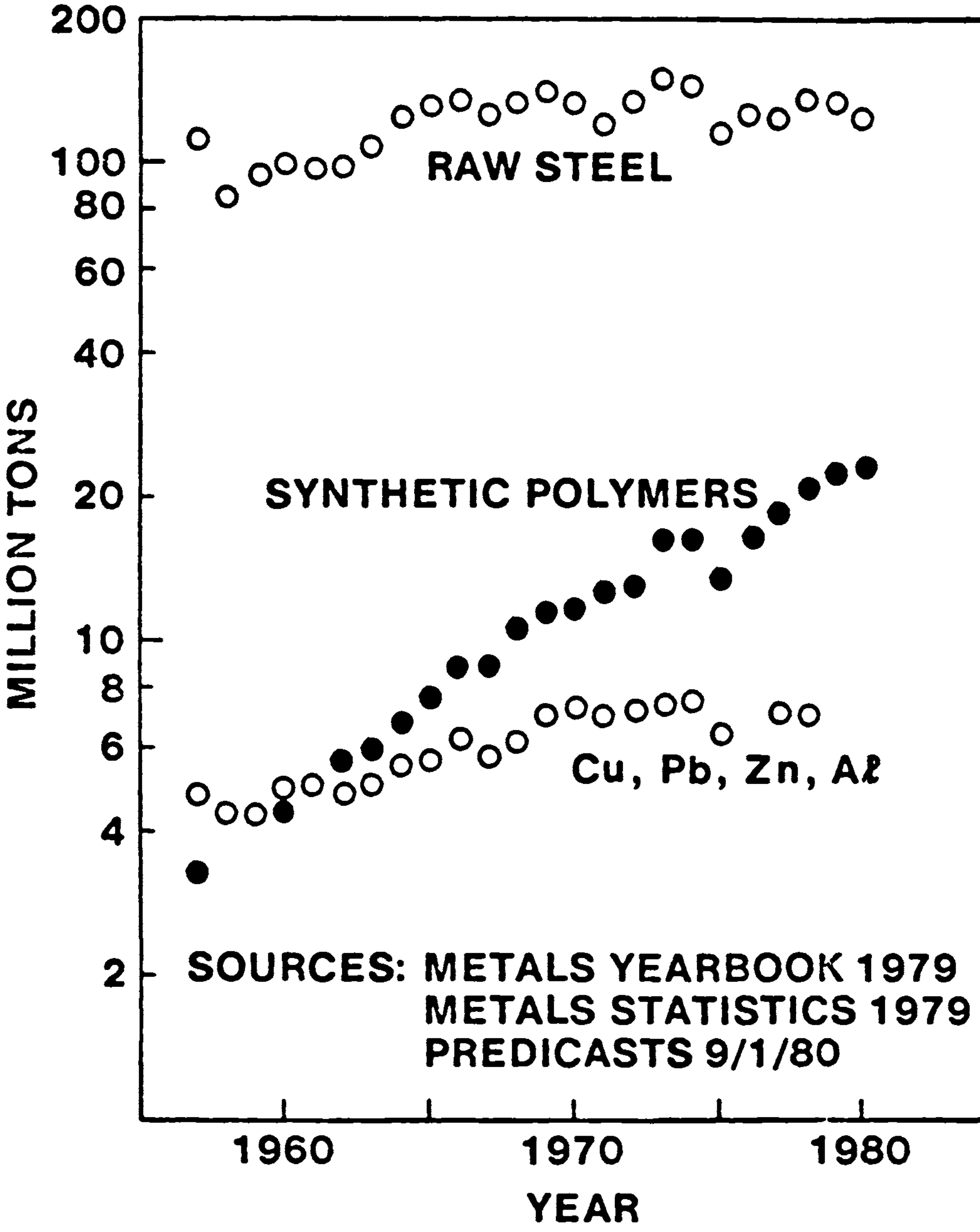

FIGURE III-1. Production of steel, nonferrous metals, and synthetic polymers in the United States.

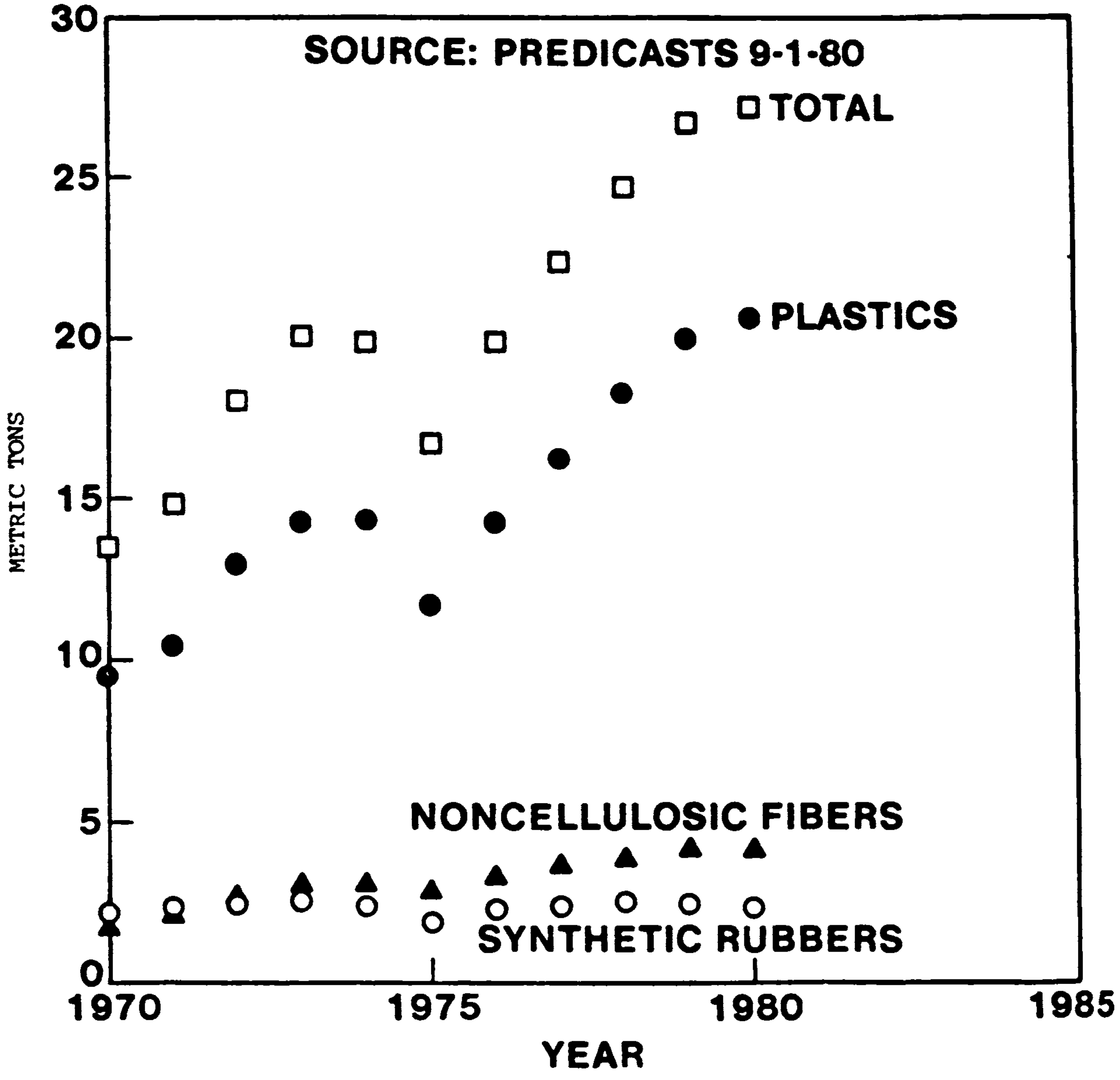

FIGURE III-2. Volume of production of synthetic polymers and steel in the United States.

## A. POLYMERIC MATERIALS: SOURCES, CONSERVATION, AND DISPOSAL

### 1. Sources

Polymeric materials are now derived principally from oil and, to some extent, natural gas. In spite of the enormous quantities of synthetic polymers produced, only 2 percent of the oil consumed in the United States goes into polymers, very little compared to the 95 percent used for energy. This small fraction for polymers may grow during the years ahead, but the growth will probably not be dramatic. However, in the competition for hydrocarbon feedstocks, polymer production is in a favored position relative to fuel uses because of greater manufacturing value added and greater impact upon employment. During the embargo period of 1974-1975, polymer feedstocks were not curtailed, although costs began to escalate. World stocks of oil will be rapidly depleted over the next decades if present rates of growth in the demand for energy continue; however, these reserves would be more than ample for the chemical industry in the foreseeable future if they were devoted largely to chemical use. It is hoped that alternative sources of energy can be developed so that this invaluable resource of raw materials is not destroyed.

As a result of extensive research over the past forty years oil and natural gas are scientifically and technologically well understood. The polymer industry would encounter no fundamental problems in converting from oil to gas or vice versa, although all process changes are costly. Shale oil, tar sands, and other heavy crudes are also likely to qualify as chemical feedstocks with some preprocessing. The overall economic viability of these alternative sources is under study but is not yet established. At present petroleum price levels the heavy crudes are unattractive, even for use as low-grade fuel.

Coal is a term that encompasses a variety of solid carbonaceous substances containing from zero to about 10 percent hydrogen. Conversion of coal to liquid hydrocarbons or synthetic natural gas can be accomplished by means of known technology. This route is not presently cost-competitive with oil and natural gas, but the margin is not great. For example, coal is attractive in South Africa where political factors unsettle petroleum supplies. Large capital investment, long lead times, environmental concerns, and political problems will complicate the development of large-scale coal conversion in the United States. However, with continued escalation of petroleum prices, coal seems an inescapable major source of hydrocarbons within the next several decades.

Although the basic technology for coal conversion is established and proved, the processes can be significantly improved from both cost and environmental standpoints. Research utilizing powerful new analytical techniques to learn more about the molecular structure, morphology, and composition of classes of coal should yield important technological benefits. Conversion processes are also under study and may be improved. Underground processing to avoid the necessity for mining is an intriguing idea and encouraging experiments have been carried out, although control over the operating conditions remains a formidable problem to be solved.

Plant and animal sources also provide abundant organic materials. Wood, rubber, cotton, and wool are among the natural macromolecular substances of importance. The conversion of cellulose to rayon is well known, and cellulose esters have long been employed as plastics. These conversions of biomass to synthetic macromolecules involve chemical reactions of natural polymers to produce the desired synthetic polymer. Reduction to monomer is not necessary. Alternatively, monomers may be synthesized from biomass and then polymerized to the desired final products. A good example is the production of ethanol by fermentation, followed by its conversion to ethylene.

Utilization of materials that are available but of little present value (i.e., normally regarded as waste) continues to present opportunities even though there has been considerable research activity over the years without a major success. For example, a practical process for producing useful macromolecules from lignin has been sought for several decades.

## 2. Conservation and Recycling

Conservation of macromolecules has become increasingly important as the finite character of hydrocarbon reserves has emerged and the capricious nature of feedstock supply has aroused concern. In fact, polymers or plastics have been identified with the "throw-away society," and this image lingers. Even so, the importance of conservation is gaining recognition. Generally, conservation must be a design feature of polymeric products if it is to be effective.

One approach to conservation is the development of compositions that retain their physical characteristics for longer times and thus do not require frequent replacement. A great deal is known about polymer degradation and the mechanisms of failure, and chemical strategies for prolonging polymer life have been developed for many systems. Long life leads to material and monetary savings through extended replacement schedules, lowered maintenance costs, and enhanced performance. Research motivated by these considerations underlies knowledge in this area, but much remains to be done.

To cite a specific example, hydrocarbon polymers are known to oxidize thermally by a radical mechanism that is understood on a qualitative level. This chain reaction can be interrupted by small quantities of "antioxidants," and significant extension of polymer life can be achieved by means of such additives. Cable insulation and sheathing for power and communication lines are protected in this way, and the quantity of polymer thereby conserved amounts to several thousand tons annually. Other additives stabilize polyolefins exposed to ultraviolet light. Hydrolysis and ozonolysis are further examples of chemical processes that lead to failure of macromolecules in service. Indeed, many polymers would degrade quickly in service (if not in processing) if they were not stabilized by ingenious additives.

Conservation can also be achieved through improved mechanical design of products. Additional material is often used to ensure mechanical integrity, whereas the same or superior result may be accomplished by careful elimination of stress concentrations in the design. In addition, the processing details (for instance, flow patterns in a mold) can confer enhanced mechanical strength in critical regions. A thorough understanding of these design factors is badly needed. Complex structural and rheological analyses are implied.

The reuse of polymers contributes to conservation. The motivations for recycling have not been strong in the past because of difficulties in collection and separation, along with the low cost of virgin materials. As feedstock costs have risen, however, the incentives to recycle have increased accordingly.

Recycling of polymeric materials within factories has been practiced for some time. In-house reuse of factory scrap (extruder purgings, sprues and runners from molding operations, unacceptable products, etc.) presents only minor problems of collection, separation, and transportation. This material is usually blended with virgin material and may be used in less critical products if deterioration has occurred in the first processing.

Recycling of polymers at the end of a product's life is a difficult problem and near-term utilization will occur primarily in special situations. Scrap generated after consumer use is generally widely dispersed geographically and consists of an unknown mixture of polymers and other materials. Special situations exist in which recycling of such postconsumer scrap is favorable. For example, power and communication cables are collected for highly profitable recycling of metal as they are removed from service. Thus, the polymeric components are carried along and the economics of polymer recycling is relieved of a large fraction of collection, transportation, chopping, and separation costs. Even so, this process is only now becoming economically attractive, partly because of the influence of environmental constraints on burning and dumping the used polymer. The recycling of polyester bottles for soft drinks is another example of a special situation. In some states the bottles are returned for deposit, and recycling is being actively pursued. On the other hand, the recycling of the increasing volume of automobile plastics has been studied and does not appear to be attractive at this time.

## 3. Disposal

The disposal of polymeric materials is often particularly complicated and difficult. When landfills are used, it is hoped that the material will ultimately be degraded by means of chemical processes or the action of microorganisms. But most polymers are resistant to the action of microorganisms, and many have been designed to resist chemical degradation. The success in developing long-lived polymers for superior products is at cross-purposes with the need to have materials that degrade readily on disposal. For some applications it may be desirable to develop short-lived polymers.

Incineration has been employed in the disposal of polymeric materials. Many are flammable and almost all will burn in the presence of more flammable materials or fuel. However, the engineering of incineration facilities is not an easy matter, and research in this area could well be increased. Ideally, the incineration heat should be utilized effectively, but this is not always economically feasible in practice.

The frustrations associated with disposal may be illustrated by considering poly(vinyl chloride). In landfills the material degrades slowly and yields highly acid ground water. On combustion, hydrogen chloride and noxious organic compounds are produced in abundance. Such problems are of increasing importance to society. Their solution will require a strong commitment to research.

## B. POLYMERIC MATERIALS: CAPABILITIES, LIMITATIONS, AND SPECIAL APPLICATIONS

Polymeric materials play an important and often vital role in areas of technology that are of fundamental importance in modern society. Because material behavior is at the core of the discussions, it will be helpful to recapitulate the principal characteristics of polymers as materials and to highlight their utility as substitutes for traditional materials. Important gaps in understanding the behavior of macromolecular substances will be pointed out.

### 1. Properties of Polymeric Materials

Chapter II presented topics now at the forefront of research in polymer science and engineering. Materials spanning a wide range of technological properties and uses were described. Research on polymeric systems (including homogeneous polymers, composites and blends, anisotropic polymeric fluids and solids, and others) can be expected to lead to materials with an even wider range of useful properties. Blends of amorphous polymers result in materials displaying various combinations of toughness, flexibility, and impact strength. Composites provide a wide range of special flow properties, stiffness, and strength. Crystalline or well-oriented polymers provide tensile strength needed in textile fibers and in materials of construction. Table III-1 presents tensile properties of several important polymeric systems compared to those of other representative engineering materials. Because of the low density of organic polymers, the specific property (property value divided by density), which has engineering importance, is often favorable for polymeric systems. For a few specially prepared, well-oriented polymers, and under certain conditions, the tensile modulus and tensile strength themselves can exceed the limits met with metals. It must be emphasized that the information listed in table III-1 would be incomplete for engineering design purposes, since the properties of organic polymers often depend markedly on temperature and environment, and exhibit time-dependent failure modes (discussed in the following section). Similar effects with metal are usually less pronounced.

Theoretical estimates of the tensile modulus and strength have been made with simplified models. As table III-1 shows, the theoretical limits can be approached with well-oriented materials. Theoret-

## TABLE III-1

### Tensile Properties for Polymers and Other Materials

| | | Property | | Specific Property[a] | |
|---|---|---|---|---|---|
| | | E, Tensile Modulus (GPa) | TS, Tensile Strength (GPa) | E/pg, Sp.Tensile Modulus (km) | TS/pg, Sp.Tensile Strength (km) |
| **Isotropic Material** | | | | | |
| Polystyrene | | 2 | 0.04 | 200 | 4 |
| Polycarbonate | | 2.5 | 0.06 | 150 | 6 |
| Polyethylene (high density) | | 1.5 | 0.025 | - | 2.5 |
| Graphite | | 72 | 1.5 | - | - |
| Glass | | 72 | 1.5 | 3,000 | 64 |
| Steel (carbon) | | 200 | 0.45 | 2,500 | 6 |
| Aluminum | | 70 | 0.4 | 2,600 | 15 |
| **Oriented Material** | | | | | |
| Polyethylene; single crystal theoretical | $E_{\parallel}$ | 180-360 | - | - | - |
| | $E_{\perp}$ | 2-10 | - | - | - |
| Polyethylene; submicroscopic crystallite, exptl. | $E_{\parallel}$ | 240-360 | - | - | - |
| | $E_{\perp}$ | 2-6 | - | - | - |
| Polyethylene (ultra-oriented) | 300K<br>77K | 140 | 3 | 14,000 | 300 |
| Polyaramid (Kevlar®-49) | | 130 | 3.8 | 9,000 | 270 |
| Flax, native | | 100 | 1 | 7,000 | 70 |
| **Composite Material** | | | | | |
| Random fiberglass/vinylester (65 wt percent glass) | | 16 | 0.20 | 850 | 10 |
| Unidirectional fiberglass/-vinylester (75 wt percent glass) | $E_{\parallel}$ | 38 | 0.55 | 1,900 | 30 |

[a] g = standard acceleration of gravity; p = density.

ical estimates of the modulus are less certain for unoriented materials. Comparison of theoretical and experimental tensile strengths is hampered by the effects of flaws in the material; with composite materials, the failure to reach anticipated property values can often be traced to adhesion problems at the interface of the components.

Finally, the properties of polymeric systems can be varied over a wide range by modifications that can be introduced at various stages in their preparation and processing. Thus, several design criteria often can be met simultaneously. For example, ease of fabrication, cost, failure properties, or environmental resistance can be adjusted by control of molecular weight distribution, branching, copolymerization, crystallization, orientation, added components, and other techniques.

### a. Special design considerations

Light, strong, durable materials are needed in place of metals for many applications. The variety of properties that can be achieved with polymers offers the opportunity to meet a number of these needs. The range of properties that can be achieved with composites, blends, and imposed anisotropy provides the design engineer with materials for a wide range of applications, but also makes necessary a working understanding of the advantages and limitations of such materials. For example, some types of well-oriented polymers may exhibit tensile modulus and strength in the preferred direction that approach theoretical limits, while having inferior properties in the transverse direction (see the values of $E_{\parallel}$ and $E_{\perp}$ entered in table III-1). In other cases, a polymer may provide the needed properties and have advantages of processing and cost, but may be unsuitable unless the design engineer is aware of failure modes that might involve crazing, long-term creep, or chemical instability in an adverse environment (see chapter IIC, section 4c). The polymer processor and user alike must be aware of the special structural and rheological features of blends, composites, and other formulations, in order to use them most effectively.

Improved understanding of failure modes and predictive failure criteria are needed. In its present state of development fracture mechanics has had some success, but further research is called for. The time-dependent viscoelastic properties of polymers result in a complex interplay between failure involving yield behavior and mechanisms involving crazing. Much is known about craze phenomena, but predictive criteria and methods to control crazing are still undeveloped.

Among the important problems in the use of composites is adhesion between the polymeric matrix and the dispersed filler. This adhesion problem calls for new approaches if the full advantage of composite materials is to be realized in practice. The problem may be attacked through chemistry (by surface modification of the filler or use of reactive components in the matrix) or through better understanding and control of the rheological effects near the interface.

In many applications the replacement of metals and other materials by polymers results in an overall energy saving despite the dependence on petrochemical feedstocks. Such savings may result not only from efficient polymerization and fabrication methods, but also from product durability and efficient operations. The use of lightweight substitutes for metals comes immediately to mind, and this benefit is described in section 2 following. In some cases the use of biodegradable or photodegradable polymers can help to reduce environmental problems associated with disposal of waste wrappings, containers, and so forth.

### b. Process freedom and opportunities

The varied properties of polymeric systems present many opportunities to develop improved methods for processing and fabrication, such as solid-state forming methods, powder sintering, reactive processing, the use of ordered (mesomorphic) fluids, and electrodeposition of coatings. Exploitation of these and other new developments will result in faster processing methods, with consequent increase in productivity, and often at lower energy cost and with less use of trouble some solvents.

Reactive processing permits the rapid formation of shaped objects at low pressure through the use of in situ reactions of rapidly mixed reagents. Advantage is taken of the low viscosity of the reactants and the exothermal nature of the process to minimize energy consumption. To broaden the range of applicability, reseach is needed on suitable reactions and on properties of the final products (see chapter IIC, section 3).

Developments in high-speed fiber formation from the melt, solid-state forming, and powder sintering can result in greater productivity from increased througnput at lower energy cost with elimination of succeeding processing steps. To develop these technologies, one must understand the time-dependent rheological properties of the materials involved and the morphological features of the polymers. The unavailability of constitutive equations applicable to each process presently limits engineering design in many circumstances.

Processing methods based on the mesomorphic liquid crystalline state (see chapter IIB, section 3d) offer advantages in preparing well-oriented solids with elimination of intermediate processing steps. Applications beyond those with special performance requirements will call for developments in polymers that can be fabricated directly from the melt or from solutions with less corrosive solvents than those in current use.

The electrodeposition of coatings from suspensions involves a complex mixture of colloid chemistry, electrochemistry, polymer physical chemistry, and rheology. Ecological advantages that accrue from the use of aqueous solvents indicate the need for further developments in understanding the entire process.

## 2. Substitutes for Metals and Other Materials

### a. Categories and incentives

The displacement of natural rubber and textile fibers by synthetic polymers almost symbolizes 20th century science and technology. Mankind and the world economy have profoundly benefitted from these material developments. The process of substituting age-old natural materials by synthetic macromolecular materials is ongoing and, in fact, so commonplace that it is taken as a matter of course by the general public. The potential for this material revolution is founded, as outlined above, on the remarkable and growing versatility of properties and manufacturing methods available with polymer-based materials. Many mechanical, physical, and chemical properties are called into play; but underlying the success of these efforts is the cohesive strength of macromolecular systems and their stability towards environmental conditions.

The incentives for substitution are legion, and the list in table III-2 merely illustrates some of the many considerations motivating the ongoing changes. Additional incentives include the reduction of our dependence on cobalt, chromium, manganese, and other critical elements, as well as the economic advantages of polymers. However, polymeric substitutes possess limitations of their own that offer opportunities for further research and refinement.

Apart from material substitutions of the kind illustrated in table III-2, plastics can be replaced by other plastics as new or modified materials are continually developed. Polyethylene, with its unique dielectric loss properties, has emerged as the material of choice for many electrical applications; urethanes have replaced rubber in such foamed applications as seat cushions, because of its ozone resistance and ease of fabrication; ABS, a rubber-modified copolymer of polystyrene, has replaced polystyrene in many applications because of its enhanced toughness (as in refrigerator liners). The list is nearly endless and will continue as the utility of polymeric materials is extended by chemical changes and increased control of molecular and supramolecular structure. It is often useful to combine traditional with polymeric materials to exploit advantages of both, as in metal-plastic laminates, blends of natural and synthetic fibers, and blends of natural and synthetic rubbers.

### b. Novel opportunities

Polymeric materials lend themselves to a variety of novel uses both as substitutes and as unique materials for which there may be no other workable alternatives. Several of these uses are listed below to illustrate the range of applicability (other specific applications are treated in more systematic fashion elsewhere in chapter III):

- drag reducers in pumping of water and other fluids
- viscosity modifiers in tertiary oil recovery
- agricultural mulches
- membranes for purification of waste liquids
- anchor cables for oil rigs
- modifiers in concrete for improved strength
- energy absorbing foams for vehicle bumpers
- composites for metal replacement in marine hulls and recreational equipment

## TABLE III-2

### Incentives for Material Substitution

| Traditional Material/Usage | Some Reasons for Substitutions | Factors Limiting the Utility of Polymer Substitutions |
|---|---|---|
| 1. Glass: windows and nonreturnable containers | High energy consumption in manufacture; low impact resistance and safety | Surface hardness; solvent resistance; leachable components; ultraviolet stability |
| 2. Aluminum | High energy consumption in manufacture; economics | Upper use temperature; moisture sensitivity |
| 3. Steel | Corrosion; need for weight reduction | Upper use temperature; elastic modulus; more complex design issues |
| 4. Natural Rubber | Limited availability, lack of versatility | "Green" strength (before vulcanization); hysteresis |
| 5. Paper: food packaging | Cost and availability of wood | Repairability |
| 6. Concrete (without polymeric additives) | Need for improved compressive strength and freeze-thaw stability | ----- |
| 7. Fish and Animal Glues | Restricted use temperature and adhesive strength | ----- |
| 8. Cotton, Wool, Silk | Need for enhanced abrasion resistance, strength, durability, launderability, versatility; cost; large land usage | Comfort; dyeability |
| 9. Leather | Limited availability, nonuniformity, property limitations | Moisture permeability, comfort |

Over the past several years research programs have been actively working to develop and evaluate high-efficiency flywheels as energy storage devices. Flywheels combined with the transmission of an internal combustion engine could permit the engine to operate at peak efficiency for improved fuel economy in passenger cars, buses, and urban subways. By taking advantage of more efficient engine operation as well as regenerative braking, a theoretical improvement of 100 percent in passenger car fuel mileage has been shown feasible. Additionally, flywheels might be employed to store energy generated by solar or wind power, or even a utility's off-peak production. Storage of useful amounts of energy in a small space requires high speed, however, which creates high centrifugal forces that may cause wheel failure. Polymer composites containing graphite, glass, and high-strength polymeric fibers appear to offer special advantages because of their high strength-to-density ratios (see figure III-3).

Because vehicle weight in military aircraft is critical to load carrying capacity and other performance requirements, major efforts have been made to replace aluminum, titanium, and other metals by lighter-weight, fiber-reinforced composites of advanced design, such as graphite/epoxy (see chapter IIC, section 2). This effort has generated sufficient confidence in the long-term reliability and performance of these materials to warrant their use in commercial aircraft. Significant amounts of such materials may be used by aircraft manufacturers to improve fuel economy.

Of greater immediate relevance to the consumer is the substitution of lightweight composites for metals in the automotive industry. Recent projections suggest that the use of composites may increase from 1 to 8 percent of the dry vehicle weight during the period 1980-1990. When account is taken of the declining average automotive vehicle weight, such increase corresponds to about 70 kilograms of composite materials per vehicle. Further discussion of polymers in transportation will be found in part D of this chapter.

### c. Technological and economic limitations

Material substitution for any of a variety of incentives is often retarded and even prevented by technical and economic considerations. Replacement of steel and aluminum by advanced composites in structural components of aircraft or passenger vehicles, for instance, requires the development of new design concepts adapted to the particular properties of composites. Entirely new manufacturing methods and facilities are needed, requiring major allocations of engineering effort over long periods of time. Even a relatively simple substitution of one plastic material by another in a conventional injection molding process may require a new tool to match the mold shrinkage characteristics of the new material.

Aside from research and development costs, new facilities are needed, which means major capital investments and obsolescence of older facilities. These considerations must be ultimately factored into product cost and carefully examined in view of anticipated

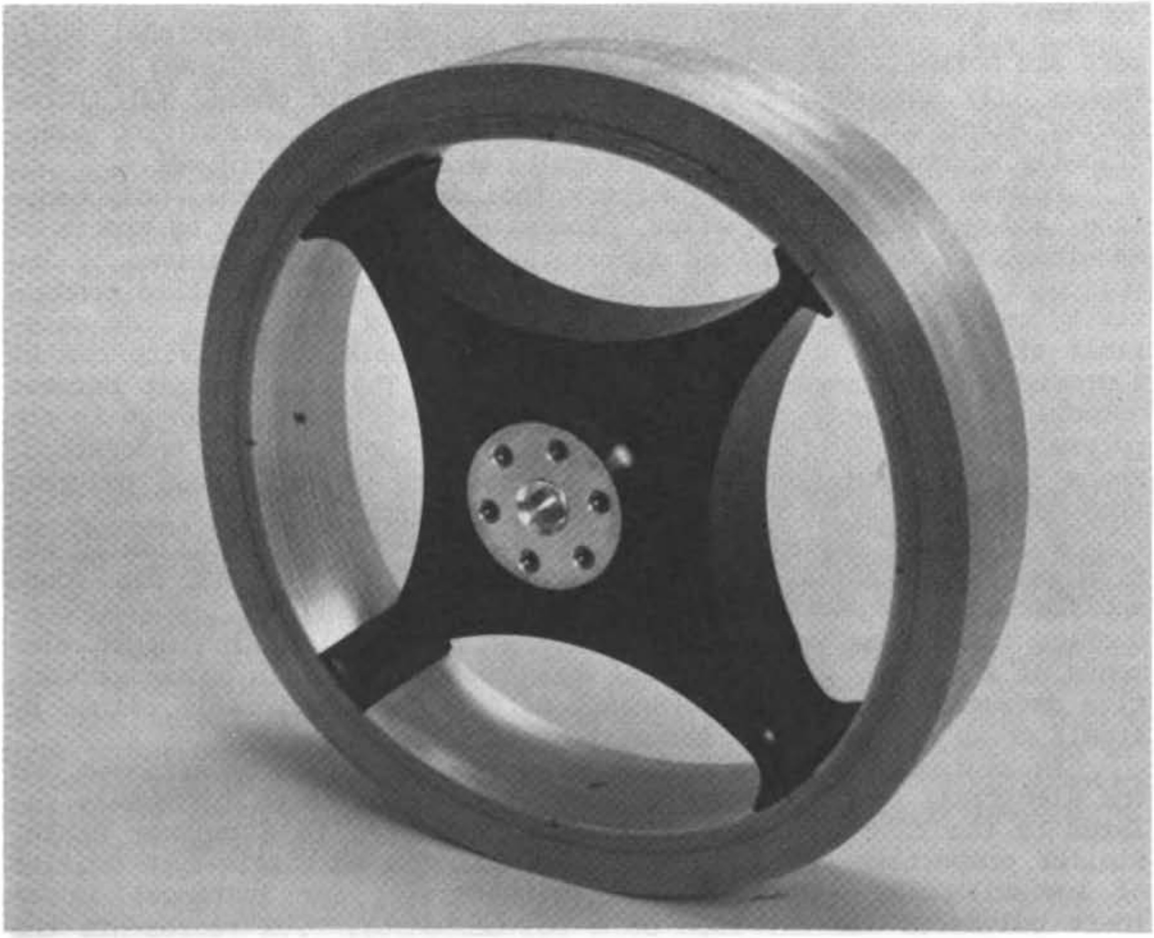

FIGURE III-3. Composite multi-rim flywheel-rotor assembly developed by the Garrett AiResearch Manufacturing Company of California. The rim consists of glass and armid fibers in epoxy resin. (Photograph curtesy of T.M. Barlow, Lawrence Livermore National Laboratory.)

benefits. Thus, only the most rewarding efforts can be sensibly supported.

## 3. Polymers with Unique Properties

Reference has been made to the fact that polymer-based materials possess unique properties and, therefore, may offer solutions to problems for which there are no other viable solutions. Exploitation of these properties is likely to foster the growth of new enterprises to meet material needs. A few such cases, relevant mostly to the communications, electrical, and electronic industries and not specifically considered elsewhere in this chapter, are discussed here.

### a. Electrical applications

i. Electrically conductive polymers. Conventional polymers are normally nonconductive. Conductivity may be achieved by three means: (1) introducing delocalization in the main chain, (2) introducing electrically active pendent groups, and (3) dissolving electrically active species of low molecular weight in the polymer.

Polymers in the first category include polyacetylene, polyphenylene, and polyphenylene sulfide. Increase in conductivity by orders of magnitude can be achieved by doping the polymer with additives of low molecular weight, leading to materials that approach metallic conductivity but suffer from sensitivity to oxygen and moisture. Some materials are fibrous and of low density, and their conductivity can be improved through compaction and orientation. The relationship between morphology and electrical properties and the effects of changes in the polymerization conditions and additives are not clearly understood. Means for encapsulation must be developed to protect these polymers from deterioration through environmental interaction.

A principal representative of a polymer with an electrically active pendent group is poly(N-vinylcarbazole) (PVK). PVK has found application as a photoconductor, normally insulating but rendered conductive through excitation by light. In combination with other elements of a system, it can replace amorphous selenium in photoreproductive devices. It has the advantage of being manufacturable either by itself or as a laminate in large flexible sheets.

In amorphous PVK the carbazole groups are randomly arranged and the electrical properties therefore do not appear to be intimately related to the fact that these groups are attached to a polymer chain. Similar properties are achievable by dissolving carbazole-type moities of low molecular weight (N-isopropylcarbazole, for instance) in an inert polymeric matrix, such as a polycarbonate. PVK represents the third category of electrically active polymers mentioned above. Other active species utilized are tri-p-tolyl-amine and trinitrofluorenone. The phase behavior of such solutions and the relationship of morphology to electrical properties deserve further study.

ii. Piezoelectric polymers. Polymers may serve as transducers to convert mechanical deformation into an electrical signal or vice versa. While polymers do not exhibit piezoelectric coefficients as large as those of the best materials of low molecular weight, they possess the advantage of being processable as relatively inexpensive flexible films of large area. These films find uses in microphones, loudspeakers, and devices sensitive to heat and pressure, such as push buttons and burglar alarms. The polymer by far the most extensively used for this purpose is poly(vinylidene fluoride). Important studies are in progress on polymer blends to maximize mechanical and electrical properties. Understanding of the piezoelectric effect may lead to other polymer systems with superior properties.

iii. Dielectric polymers. Polymers can be dielectric materials of either low or high dielectric constant. The former are desirable in cables for the transmission of high-frequency signals and the choice is polymers of low polarity, such as hydrocarbons. However, the dielectric constant is often affected by impurity content, such as polar groups, which may be caused, for example, by inadvertent oxidation during processing.

Appreciable economic advantages accrue if processing conditions can be achieved that lead to polymers of low dielectric constant; the distance between repeaters in submarine cables can be increased, for instance. High dielectric constants can be achieved by incorporating ionic groups within phase-separated polymers. Salt-containing polymers have been utilized for this purpose. The polymers find application in small capacitors of high capacitance. Studies of relationships between morphology and dielectric properties for such systems are needed.

iv. Insulators and electrical breakdown. Electrical insulation requires polymers having no mobile conductors. But ionic impurities such as catalyst fragments remaining from polymerization are often present. Minimizing these impurities obviously calls for careful purification. It is also desirable to eliminate ionizable (carboxyl) or hygroscopic (hydroxyl) groups. Minimizing the mobility of carriers leads to low conductivity. Thus glassy polymers having a high glass transition temperature are advantageous.

Dielectric breakdown arises from ionization, so that for high dielectric strength, polymers without easily ionizable atoms or groups are desirable. Breakdown arises from local high electric field gradients which occur at structural heterogenities; thus, formulation of polymers with highly homogeneous structures is desirable. High elastic modulus is another desirable attribute because it hinders deformation of the polymer in a high field gradient.

### b. Optical applications

i. Polymer fibers for communication. Optical fibers should exhibit low attenuation of transmitted light. Attenuation usually results from scattering, either from impurities dispersed in the fiber or from frozen-in density fluctuations. The former can be minimized through purification; the latter are inherently greater for a polymer than for silica glass fiber. Consequently, it will never be possible to produce a polymeric optical fiber with as low an attenuation as glass fiber, and glass fibers will predominate in long-distance communication. However, for certain applications in which short distances are involved and in which light weight is important (as in aircraft and missiles, and for intra-building communication), polymeric fibers have advantages. For this application, polymers are needed that are noncrystalline, homogeneous, and incompressible. They must be obtainable in exceptionally pure form.

ii. Polymer-clad glass fibers. Glass optical fibers transmit light by total internal reflection of rays striking the surface at a glancing angle. A ray that is not totally reflected escapes from the glass and results in attenuation of the light. The maximum angle to the surface at which total reflection occurs depends on the refractive index gradient of the glass.

Glass fibers are often coated with polymeric or other materials for mechanical protection. Such a coating must adhere strongly to the glass and preserve its mechanical integrity.

iii. Photoresists and integrated circuits. The preparation of integrated circuits involves producing microcircuit patterns on a silicon wafer. One method of accomplishing this uses a photolithographic process based on photoresists. These are generally polymer films that may be cross-linked (negative photoresist) or degraded (positive photoresist) upon exposure to UV light, electrons, or X-rays in a predetermined pattern. Electron-beam lithography has the advantage that the generation pattern may be computer controlled, eliminating the need for masking. Positive electron photoresists are either polysulfones or modified poly(methyl methacrylates), while negative ones are copolymers of glycidyl acrylates, polystyrene, polysiloxanes, or epoxidized polybutadiene. After exposure, uncross-linked or degraded parts of the resist are removed by solvent treatment, leaving the uncovered part of the silicon wafer available for solution or plasma etching. New photoresist systems are needed with improved radiation sensitivity, solubility properties, and resistance to etchants.

## C. POLYMERS AND ENERGY

Connections between polymers and energy are pervasive and extremely complex. They can be categorized, somewhat arbitrarily, as (1) commonality of fuels and polymer feedstocks, (2) contributions of polymers to the production of energy, and (3) contributions of polymers to the conservation of energy. A systematic development of the confluence of energy and macromolecules, both synergistic and antagonistic, would be beyond the scope of this report. More appropriately, the report is focused generally on macromolecules, and energy appears abundantly as a ubiquitous accompaniment. Thus, the present section is restricted to a brief summary of polymer-energy ties, with no attempt to engage such detailed discussions as are presented elsewhere in the report. Moreover, a report is available from the Department of Energy, Polymer Materials: Basic Research Needs for Energy Applications, (CONF-780643, UC-25), presenting the proceedings of a workshop on the subject, held in August 1978, to which the reader is referred for further information.

## 1. Feedstocks

Most polymers are manufactured from raw materials that are used primarily as fuels. In consequence, the production of macromolecules is intrinsically enmeshed with the problems that have plagued energy production in recent years. In view of the relatively small volume of material consumed by the polymer industry and the relatively large value added, polymer and fuel applications are not competing for resources in the ordinary sense. Nevertheless, cost and availability are dominated by fuel usage.

It is generally accepted that the world is within a few decades of substantial depletion of petroleum and natural gas. Alternative fuels and feedstocks can be expected to become increasingly important, and coal must be considered the most obvious choice in terms of availability, costs, and demonstrated technology. Even so, the conversion of coal to liquid and gaseous fuels and to polymer feedstocks presents challenging problems. Tar sands and shale oil may also be developed to fill some fraction of the fuel/feedstock supply. Plant and animal sources and supplies are more difficult to project. Biological materials are frequently polymeric, and the opportunity exists to produce desired materials by processes that do not involve reduction to monomer and repolymerization, as, for instance, in natural rubber and rayon. Plants may well be developed to produce larger yields of desirable materials.

Polymer developments can contribute favorably to feedstock supply. For example, conventional petroleum pumping methods obtain only a portion of the oil in a given pool. Displacement fluids based on water-soluble polymers may allow recovery of much larger yields and thus alleviate or delay the expected shortages resulting from depletion. Polymers also contribute to undersea drilling technology through the use of noncorroding, high-strength, high-modulus fiber support cables.

## 2. Generation, Distribution, and Storage of Energy

Present power-generating systems depend heavily on polymeric materials. Excellent structural and electrical properties coupled with ease of fabrication will ensure that polymers retain a central role in power-generating equipment. Many of these uses are highly demanding in terms of ultimate properties, service life, and reliability. Environmental stresses include high voltage, elevated temperature, high energy radiation, and aggressive chemicals. As the requirements become progressively more stringent, the need for understanding the relationships between polymer structure and properties increases.

Conventional generators require insulation that permits close windings and freedom from electrical breakdown. Nuclear reactors have critical components exposed to high levels of ionizing radiation. Fuel cell design calls for membranes that are stable in strongly reactive chemical environments. Solar energy systems rely heavily upon polymeric components as mirror backings, needed in large-area low cost arrays. Fabrication advantages are a key consideration here, but the needed long-term stability in strong sunlight presents a challenging problem for the polymer engineer. Fusion reactors and other exotic generation schemes will offer further novel opportunities for polymer research and applications.

Cables used for power distribution are insulated with high-quality polymeric insulation. The mechanical and electrical integrities of the insulation are essential to this application, and polymeric materials are uniquely able to meet the demands. Transformer construction is another area where the fabrication techniques available with polymers are important. Cure must be achieved with such low shrinkage that voids, which can initiate treeing, arcing, and breakdown, are not formed. Epoxy formulations are often used for this purpose.

Polymers are extensively used in energy storage devices, for which their resistance to corrosive chemicals is an advantage. Electrochemical cells (batteries) require plate separators, while fuel cells incorporate polymeric membranes. Polymeric cases are used for batteries, fuel cells, and passive solar devices involving salt hydrates.

New polymers are emerging that display electrical activity, and these materials may well contribute in future to solving energy problems. Polymers with electrical conductivity in the range of metals have recently been synthesized. Semiconducting systems responsive to doping are also known. It would be premature to predict specific applications of these research materials, but they seem likely to find a place in energy technology. Piezoelectric and pyroelectric polymers are now in use as transducers and thermal detectors, and such materials will surely stimulate further research bearing on energy-related applications.

### 3. Conservation of Energy

Important contributions to solving the nation's energy problems are coming from the effort to conserve energy, and polymeric materials have a role. Modern refrigerators employ polymeric foam thermal insulation, which is superior to all competitive material systems for the purpose. These premium insulating materials are used also in homes and other buildings, with enormous long-term savings in energy.

In transportation, which is discussed in detail in section D following, vehicle weight is a major factor in energy consumption; the substitution of polymers for metal is a leading strategy in conserving energy. Polymeric materials are being introduced in a wide range of automotive applications, from decorative trim to the most demanding structural parts. An engine composed substantially of polymeric material may be feasible. Weight reduction is even more rewarding in aircraft, and the aircraft industry has played a leading part in the introduction of high-technology polymeric materials and structures.

The need for a complete understanding of materials properties and polymeric structure is particularly marked in transportation applications. Composite structures are used abundantly, and their properties are sensitive to the details of the fabrication technique. Much remains to be learned in this area, and it is an active field of inquiry.

Conservation in the use of polymers can reduce the demand for energy consumed in their manufacture, as well as for hydrocarbon feedstocks. Design efficiency, taking into account structure-property relationships, can be an important contributor to conservation. Many plastic articles are overdesigned; it will be wise energy policy to reduce wall thicknesses and other design parameters. Polymer use can also be reduced through the introduction of fillers and foams. It is often economically rewarding to pursue this option, because material properties often improve with the use of inexpensive, abundantly available fillers. An example is the improved abrasion resistance of vehicle tire treads when they include carbon black.

A major contribution to reduced usage can be achieved through extending the service life of polymers. This is a large and active field involving studies of the mechanisms of material failure, the methodology of life testing, studies of aging and fatigue, and associated testing and development of life-extending additives and other strategies. Here again, economic rewards accompany conservation.

Polymer processing involves significant expenditure of energy because of the viscous nature of polymer melts. As the cost of energy increases, new energy-efficient processing methods will become critically important. Reaction injection molding is a promising technology that affords more efficient use of energy through employment of low-viscosity reactants. Radiation processing--i.e., the generation of cross-links after forming--may also turn out to be an energy-efficient technology; it is already in substantial use.

As the foregoing examples illustrate, many important relationships exist between energy development and polymer science and engineering. All aspects of energy technology will benefit from developments in the field of polymers. Polymer research is essential to the future of energy systems.

## D. POLYMERS IN TRANSPORTATION

The oil embargo of 1973-1974 and the passage of the Energy Policy and Conservation Act of 1975 raised the issue of energy conservation and vehicle fuel economy to national attention. These events, combined with the rapidly rising cost of fuel, have profoundly affected the transportation industry, especially with regard to materials in use. Thus, weight reduction by downgrading vehicle size and substituting light-weight materials, such as plastics, composites, aluminum alloys, and high-strength steels, has become a cornerstone of the automobile manufacturers' strategy to meet increasingly stringent standards of fuel economy. Lack of experience in manufacturing, design, and application technology has inhibited the use of these materials, and national programs are under consideration to increase the information base available to innovative manufacturers through research in materials science and processing.

This section deals principally with the passenger car because: (1) it is the predominant mode of personal transportation, (2) enormous quantities of materials, including polymers, elastomers, and fiber-reinforced composites, are used in its manufacture, and (3) automobile manufacturers need high-productivity technology to satisfy a huge market. Many of the observations will be relevant, however, to other modes of transportation, especially aircraft, to which a number of references will be made. Particular attention is devoted to materials substitution, its relation to national goals, and areas of research necessary to its support.

## 1. Fuel Economy Requirements and Weight Reduction

The U.S. government legislated mileage requirements for passenger car fleets beginning in 1978. The schedule required a fleet average of 18 miles per gallon (mpg) in 1978, rising to 27.5 mpg in 1985. Many means are being taken to meet these objectives: improved engine efficiency, reduced aerodynamic drag, reduced vehicle weight. The relationship between fuel economy and vehicle weight is complex and depends on the vehicle inertia weight class, driving conditions, and other factors; nevertheless, as an approximation, fuel consumption is reduced by 0.001 gallon per mile per 100 pounds of vehicle weight reduction.* To the energy-conscious nation this means 0.91 gallon of gasoline saved for each pound saved over the vehicle lifetime of ten years (100,000 miles). Taking 100 pounds out of every vehicle would result in savings of about 1 billion gallons per year, roughly one percent of current passenger car consumption.

Vehicle weight reduction is being accomplished by a combination of size reduction and materials substitution. Since the former utilizes known and generally familiar engineering practice, it has been the predominant mode of weight reduction. Materials substitution frequently requires new design and manufacturing technology, additional facilities, development of reliability-assurance techniques, and historical experience; it therefore represents a more protracted process. In the long term, as vehicle size reduction reaches its practical limits, the role of light-weight materials will increase in importance.

In either case the lifetime saving in fuel should be taken into account in assessing the benefit of weight reduction by any method. The benefit must reflect the rising cost of fuel. At present fuel costs, it appears that a penalty of one to two dollars per pound of weight saved may be cost effective for certain weight-reduction problems. On this basis automobile manufacturers will continue their support for efforts directed at weight reduction by materials substitution.

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* A typical 2500 lb car may consume 0.041 gal/mile. A reduction of 0.001 gal/mile results in a change in fuel economy from 24.39 to 25.00 mpg.

## 2. Changing Patterns of Materials Usage

Petroleum and natural gas liquids are the primary sources (70 percent) of raw material for the synthetic plastics industry today. This use represents roughly two percent of the total U.S. consumption of oil. The remainder of the plastics raw material (30 percent) is obtained from natural gas and coal. Thus, there appears to be no present lack of availability of plastic-based materials for the automotive industry. As feedstocks become less accessible, however, the energy requirement and resulting dollar cost are expected to rise, as will be the case also for steel and aluminum. It is noteworthy that rising costs of plastic finished parts in constant dollars over the last decade have been offset to a large extent by improved productivity and new chemical manufacturing technology.

At current levels of use, the total consumption of polymers in the U.S. automotive industry is on the order of 1.5 billion pounds annually. The economic impact on the chemical industry is large, particularly for those materials that are utilized extensively, such as polypropylene, poly(vinyl chloride), polyurethanes, and unsaturated polyesters (for composites). About 50 percent of the total rubber output of the United States is utilized for automobile tires. Table III-3 presents a breakdown of plastic materials other than rubber used in U.S. automobiles in 1977 and projected to 1988. On the average the amounts form a small percentage of total U.S. consumption. Nevertheless, the total absolute amount is substantial, and the amounts for specific polymers do represent sizable fractions of total consumption. Besides a broad spectrum of low-cost commodity plastics, substantial amounts of higher cost, so-called "engineering" plastics also find specialized use in vehicles. This diversity reflects the remarkably different mechanical and physical requirements for particular parts, from highly stressed leaf springs to durable soft goods such as poly(vinyl chloride) sheet for upholstery and polyurethane foam for seating.

While vehicle size reduction may be expected to lower the total quantity of all materials used, the use of plastic materials is expected to increase. A recent forecast of U.S. automotive industry trends by A. Andersen and Co. and the University of Michigan predicts that the average weight of cars will drop by 25 percent in the decade of the 1980's and that steel usage will directly reflect this change.* Plastics usage, however, will rise from 175-195 pounds per car in 1978 to 250-290 pounds per car in 1985, an increase of about 50 percent. The use of polymer-based composites as a class is projected to grow more dramatically than other plastic materials, from 35 pounds per car in 1980 to 100 pounds per car by 1985. Fiber-reinforced composites, a special class of composites, will be used increasingly for exterior

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* An increasing fraction of the total steel content is expected to consist of high-strength, rather than mild steel.

## TABLE III-3

### Projected 1988 Demand for Automotive Plastics

| | Total U.S. Consumption | | | U.S. Automotive Consumption | | |
|---|---|---|---|---|---|---|
| | 1977 $10^3$ metric tons/year | 1988 | Effective Growth Rate (percent) | 1977 $10^3$ metric tons/year | 1988 | Effective Growth Rate (percent) |
| ABS | 468 | 1,000 | 6.5 | 70 | 125 | 5.0 |
| Acrylic | 240 | 400 | 4.3 | 20 | 70 | 11.0 |
| Cellulosic | 67 | 54 | ( 1.8) | 7 | 6 | ( 1.3) |
| Nylon | 110 | 310 | 9.0 | 20 | 60 | 9.6 |
| Phenolic M.P. | 158 | 260 | 4.2 | 22 | 20-40 | 0-5 |
| Polyacetal | 42 | 75 | 5.0 | 10 | 15 | 6.6 |
| Polycarbonate | 57 | 210 | 11.5 | 3 | 10 | 7.9 |
| Polyethylene, H.D. | 1,620 | 5,000 | 9.8 | 24 | 80 | 10.6 |
| Polyethylene, L.D. | 2,939 | 7,000 | 7.5 | 1 | 1 | 0 |
| Polypropylene | 1,247 | 4,000 | 10.2 | 140 | 400 | 9.1 |
| Polystyrene | 2,010 | 3,000 | 3.4 | 2 | 1 | ( 5.6) |
| Polyurethane | 811 | 1,800 | 6.9 | 182 | 400 | 6.8 |
| Poly(vinyl chloride) | 2,380 | 4,900 | 6.2 | 135 | 260 | 5.6 |
| Unsaturated polyester | 477 | 1,100 | 7.2 | 72 | 350 | 14.1 |
| Thermoplastic polyester | 21 | 120 | 18.6 | 9 | 49 | 15.2 |
| SAN | 50 | 100 | 5.9 | 4 | 5 | 1.9 |
| Total Plastics* | 14,791 | 35,000 | 7.4 | 736 | 2,200 | 9.5 |

* Includes others.

Source: H.H. Aerospace Design Company, Bedford, Massachusetts, August 1978.

panels, and are likely to find their way into a variety of structural components such as leaf springs for vehicle suspension systems. Increasing the usage of composites by 50 pounds per car translates to a volume of production worth about $500 million in the Inited States. For an overview of the growth pattern of composites versus automotive as well as other transportation modes, see table III-4.

## 3. Materials and Energy Consumption in Manufacture

It is of further interest to comment on the effect of materials usage on energy consumption in the manufacture of components. An important study by the Owens-Corning Fiberglass Company in 1975 presented energy needs for the manufacture of plastic components versus steel and aluminum, taking account of all factors. Because design enters into the analysis, the comparison was made on the basis of a total product rather than simply on a basis of energy per mass or per volume. Using a passenger car hood as an example of an exterior panel, the results shown in table III-5 were obtained.

A modest energy saving is indicated for fiber-reinforced plastics (FRP) vs. steel, and a severe energy penalty for aluminum. These calculations do not take into account energy savings due to improved fuel economy over the car's lifetime, which could amount to about 5 x $10^6$ BTU for the one-piece hood in FRP vs. mild steel. Further energy savings could be realized by recovery of the energy content of scrapped FRP materials, perhaps by incineration. This amounts to about 0.17 x $10^6$ BTU for the one-piece hood. Analogous savings are realized in the reuse of metals. (See chapter IIA for a discussion of recycling of materials.)

A leaf spring serves as another illustration of cost-weight efficiency. As part of a suspension system on a passenger car or light truck, the spring must possess appropriate stiffness and strength to meet fatigue, ride quality, and load-carrying requirements. Fiberglass-reinforced composites consisting of essentially continuous, unidirectional fibers possess an excellent combination of design strength, stiffness, and fatigue life relative to steel. General Motors Corporation has recently announced that it will substitute for the steel spring (44 lb) in the 1980 Corvette a composite spring (7.5 lb) in 1981, a net saving of 36.5 lb. This transverse rear spring is shown in figure III-4.

In these substitution efforts full account must be taken of the intimate interrelationships among the various factors of design, material, manufacturing, and performance. Design technology must be innovative to take maximum advantage of the performance characteristics of plastic materials. At the same time a choice of particular design and material must be made that will promote high-speed manufacturing without compromise of quality and reliability. Manufacturing science and technology appear to be in a more primitive state at present than other technical elements in the development and utilization of polymers in transportation. As a consequence, the importance and relevance of processing and fabrication cannot be overemphasized as fundamental to future innovations in vehicle materials technology.

## TABLE III-4

### Reinforced Plastic Composites in Transportation*
1978-1985
(million pounds)

| Year | Polymers | Aircraft | Automotive | Marine | Rail | Total |
|---|---|---|---|---|---|---|
| 1978 | Thermosets | -- | -- | -- | -- | 1,021 |
| | Thermoplastics | -- | -- | -- | -- | 178 |
| | TOTAL | 3 | 708 | 481 | 7 | 1,199 |
| 1979 | Thermosets | -- | -- | -- | -- | 1,007 |
| | Thermoplastics | -- | -- | -- | -- | 177 |
| | TOTAL | 3 | 673 | 501 | 7 | 1,184 |
| 1980 | Thermosets | -- | -- | -- | -- | 715 |
| | Thermoplastics | -- | -- | -- | -- | 125 |
| | TOTAL | 3 | 528 | 301 | 8 | 840 |
| 1985 | Thermosets | -- | -- | -- | -- | 1,565 |
| | Thermoplastics | -- | -- | -- | -- | 389 |
| | TOTAL | 6 | 1,388 | 551 | 9 | 1,954 |

* TPC Business Research Group, Westport, Connecticut

## TABLE III-5

### Energy Comparisons for Manufacturing a Car Hood

| | Part Weight (lb) | Material Energy Need (BTU/lb) | Part Energy Need ($10^6$ BTU/hood) |
|---|---|---|---|
| Steel | 75 | 28,000 | 2.1 |
| Aluminum | 36.7 | 108,300 | 3.98 |
| *FRP (2 piece) | 47 | 40,100 | 1.89 |
| *FRP (1 piece) | 34 | 40,100 | 1.36 |

* Fiber-reinforced plastic composite consisting of 30 percent resin and 70 percent fiberglass and mineral filler.

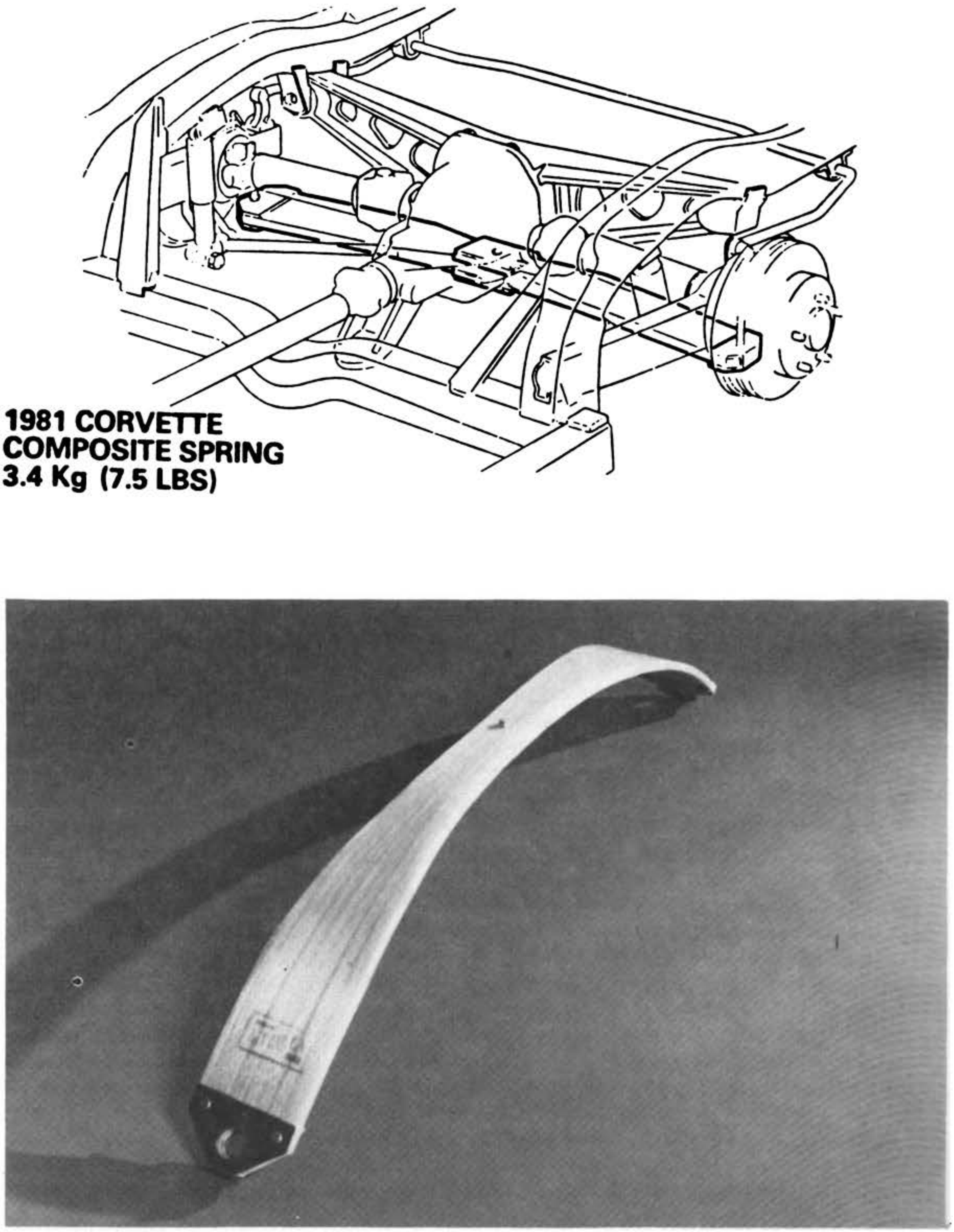

FIGURE III-4. 1981 Corvette composite spring.

### 4. Energy Storage and Fuel Economy

Fiber-reinforced composite flywheels as energy storage devices in buses and other vehicles are briefly discussed in chapter IIIB, section 2.

### 5. Component Weight Savings and Cost

The weight-saving potential of substituting materials in a vehicle component depends on the nature of the application, the size and function of the component, whether the performance is related to stiffness or strength, and the suitability of isotropic versus anisotropic behavior. Weight savings depend also on whether the substitution is in a vehicle of existing or of new design. Substitutions in new vehicle designs are more efficient because they provide opportunity for taking advantage of secondary effects, such as smaller tires or smaller engines. Some typical weight savings are presented in table III-6; only 10 out of a total of 600 plastic parts per car are represented. No simple rules can be given as to the direct cost of substituting fiber-reinforced plastic components for metal. Cost penalties or savings may be realized, depending on component function, choice of material, manufacturing efficiency, and design complexity. Generally speaking, a cost saving is to be expected when the weight reduction is large and/or when a single plastic-based component is substituted for a metal part fabricated from a number of subassemblies involving a multiplicity of operations, as, for instance, in welding and machining. Current automotive development efforts are directed at substitution programs entailing either a cost saving or a modest cost penalty.

### 6. Aircraft

In the aircraft industry weight savings profoundly influence cargo carrying capacity and fuel economy; substantially larger cost penalties (in excess of $100 per pound of weight saved on commercial aircraft) are therefore tolerable in materials substitution efforts. Consequently that industry has made more extensive use of costly composites based on graphite and/or polyaramide fibers (see chapter IIC, section 2f).

For example, the Lear Fan Jet manufactured by Lear Fan Corporation achieves substantial fuel savings through weight reduction by fabricating the entire structure of the airplane, including fuselage, wings, frame, tail fin, and control surfaces, from epoxy/graphite composites. The total weight of the airplane (without engines) is 1,250 pounds. The fuselage is made of seven molded parts bonded together at their maximum breadth. The main wing spar, for instance, is a 39-foot, 80-pound I beam made of 85 layers of graphite.

Extensive use of polyaramide and graphite fibers is planned for a number of commercial, crop dusting, and military aircraft in such other parts as engine cowling covers, leading edges of wings, radomes, pontoons, and helicopter rotor blades. In each instance the saving in component weight by substituting plastic materials is about 40 percent of the weight of the metal part replaced.

## TABLE III-6

### Typical Weight Savings by Materials Substitution in Vehicle Components

| Metal Part | Substitution Material | Potential Weight Saved (lb) |
|---|---|---|
| Wheel | Fiberglass composite | 6 |
| Light truck single leaf spring | Fiberglass composite | 20-30 |
| Hood | Fiberglass composite | 6 |
| Transmission support crossmember | Fiberglass composite | 3 |
| Deck lid | Fiberglass composite | 8 |
| Bumper | Fiberglass composite | 12 |
| Tailgate | Fiberglass composite | 14 |
| Seat | Thermoplastic | 5 |
| Fuel tank | Thermoplastic | 9 |
| Connecting rod (engine) | Graphite-fiber composite | 1 |

## 7. Science and Technology Needs

Future innovation in vehicle design rests heavily on potential developments on several fronts: (1) synthesis and preparation of materials, (2) fabrication science and technology, (3) interrelationships of structure, properties, and performance, (4) engineering design and product durabilility, and (5) recycling and/or disposal of materials. All of these factors impinge on one another and therefore must be simultaneously taken into consideration in any material substitution endeavor.

Following is a list of specific areas in which research on plastic-based materials is needed to foster energy conservation, safety, reliability, and productivity in the transportation industry, particularly in passenger vehicles. The list is not exhaustive and, of course, does not anticipate new ideas that will be forthcoming from investigators in the polymer and transportation fields.

### a. Design data base

- Design data base particularly with regard to long-term performance under various service conditions--temperature, moisture, solvents, ultraviolet light, aging--especially in combination with stress.
- Design methodology and rapid, readily performed calculation methods for stress analysis and failure prediction.

### b. Destructive and nondestructive evaluation

- Nondestructive evaluation methods that can be performed reliably at high rates and low cost, and be consistent with manufacturing speeds.
- Correlation of defects with end-use performance.
- Failure prediction capability, particularly under static and cyclic stresses; failure mode analysis.
- Reliable test procedures for better interlaboratory consistency.

### c. Manufacturing technology

- Kinetics of cure reactions and faster-cure thermoset systems.
- On-line processing controls--for degree of cure.
- Rheology of flow in molds.
- Automation technology and hardware.
- Reduced variability and freedom from defects. Mechanisms of defect formation, both internal and at surfaces.
- Reactive process technology for direct conversion of monomer to shaped polymer, especially for a broad range of materials.

- Repair methods; techniques for determining repair reliability.
- Higher-speed process technology; new process methods--curved pultrusion, pull-forming; alternative heating methods.
- Prediction of part performance based on composition and morphology--fiber orientation distribution. Prediction and control of morphology and structure as it is determined by fabrication parameters; modeling of molding and forming processes.
- Heat transfer relationships in molding.

d. Materials

- Synthesis of polymer systems with higher thermal stability.
- Fiber surface treatment and control of fiber-resin interface properties.
- Chemistry of thermosets as it relates to cross-link density distribution and mechanical properties.
- Development of reaction-injection moldable polymers.
- Structure-property-morphology relationships of polymer blends.
- Polymers of high surface hardness to replace glass.
- Polymers with reduced flammability and with less toxic by-products induced by heat (especially for aircraft interiors).

e. Bonding and joining

- Bonding of plastics to plastics and metals.
- Automated high-speed adhesives application technology.
- Adhesive chemistry development for improved suitability to particular applications.
- Nondestructive evaluation for bond strength assessment.

f. Impact

- Energy absorption of designed plastic structures for impact strength, crash worthiness of small vehicles, resistance to damage from flying stones and reduction of injury to vehicle and occupant on collision.

g. Energy storage

- Materials, design, and manufacturing technology for high-efficiency flywheels.

h. Coatings

- Low-temperature, nontoxic, low emission paint systems.

### i. Recyclability

- Efficient methods for recovery of energy and materials from rubber tires and plastics (see chapter IIIA).

## E. POLYMERS AS MATERIALS OF CONSTRUCTION

### 1. Applications of Polymeric Materials in Construction

In 1979, the nation spent $230 billion on buildings and other construction. This was about 10 percent of the gross national product. Polymeric materials find many uses in buildings, and their use is increasing rapidly as they open up new design possibilities not available with conventional materials. They can contribute substantially to improvements in productivity and energy conservation. Besides helping to meet the increasing need for housing in the United States, they also offer opportunities for improving international trade through export of low-cost, lightweight building components.

A recent article* stated, "If the construction industry continues to use them at the present rate, plastics could emerge as the major building material of the 21st century."[1] This statement is indicative of the optimism towards the future role of polymers in construction. The growing number of both load-bearing and nonload-bearing applications for polymers in construction is one reason for the optimism. For example, polymers are used in exterior cladding (siding), windows and doors and their frames, piping, thermal insulation, electrical insulation, roofing, bathroom components and modules, surface coatings, joint sealants, flooring, lighting fixtures, vapor barriers, decorative items, structural sandwich panels, and other elements such as those made of polymer impregnated concrete. Another reason for the optimism is the rate of growth of polymer consumption in construction. The use of resins in construction has increased from 1 million metric tons in 1972 to over 3 million in 1977. By 1985 the figure is expected to reach 4 million metric tons. Table III-7 shows the amounts of plastics used for some building applications in 1977 and 1978.[2] About $5-6 billion is spent each year on protective coatings (excluding the cost of applying the coatings), and a recent forecast estimates that by 1985 half of all architects and builders will specify builder-applied structural adhesives.[3]

Foam insulation and vinyl siding are other areas of rapid growth. From 1976 to 1978 the amount of urethane foam used increased by approximately 50 percent. Nearly 1 million homes are now clad with vinyl siding. The amount of poly(vinyl chloride) (PVC) siding installed each year is predicted to increase by a factor of five from 1975 to 1985.[4]

An important new energy-related application for polymers is in solar heating and cooling systems for buildings. Polymers are used in

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* Superscripts refer to citations at the end of chapter IIIE.

## TABLE III-7

### Use of Plastics in Building Applications in 1977 and 1978[a]

| Application/Material | $10^3$ metric tons<br>1977 | 1978 |
|---|---|---|
| Decorative laminates | | |
| Phenolic | 17 | 18 |
| Urea and melamine | 14 | 15 |
| Flooring[b] | | |
| Epoxy (including paving) | 6 | 7 |
| Poly(vinyl chloride) | 135 | 132 |
| Urethane foam (rug underlay) | 50 | 54 |
| Glazing and skylights | | |
| Acrylic | 28 | 29 |
| Reinforced polyester[c] | 12 | 14 |
| Polycarbonate | 24 | 30 |
| Insulation | | |
| Phenolic (binder) | 96 | 112 |
| Polystyrene foam | 46 | 51 |
| Urethane foam (rigid) | 81 | 99 |
| Light fixtures | | |
| Acrylic | 9 | 9 |
| Cellulosics | 2 | 2 |
| Polycarbonate | 5 | 5 |
| Polystyrene | 11 | 11 |
| Poly(vinyl chloride) | 5 | 6 |
| Panels and siding | | |
| Acrylic | 5 | 5 |
| Butyrate | 2 | 2 |
| Poly(vinyl chloride) | 41 | 55 |
| Reinforced polyester[c] | 53 | 59 |
| Pipe, fittings, conduit | | |
| ABS | 126 | 119 |
| Epoxy (coatings) | 3 | 4 |
| High-density polyethylene | 166 | 206 |
| Low-density polyethylene | 11 | 10 |
| Polypropylene | 6 | 8 |
| Polystyrene | 5 | 5 |
| Poly(vinyl chloride) | 778 | 886 |
| Reinforced polyester[c] | 81 | 87 |
| Profile extrusions[d] | | |
| Poly(vinyl chloride) (including foam) | 57 | 60 |
| Polyethylene | 3 | 3 |
| Plumbing[e] | | |
| Acrylic | 10 | 10 |
| Polyacetal | 7 | 8 |
| Polyester, thermoplastic | 3 | 3 |

TABLE III-7 continued

| Application/Material | $10^3$ metric tons<br>1977 | <br>1978 |
|---|---|---|
| Plumbing (continued) | | |
| Polystyrene | 2 | 2 |
| Reinforced polyester[c] | 43 | 50 |
| Resin-bonded woods | | |
| Phenolic | 164 | 176 |
| Urea and melamine | 315 | 347 |
| Vapor barriers | | |
| Low-density polyethylene | 69 | 72 |
| Poly(vinyl chloride)[f] | 15 | 16 |
| Wall coverings | | |
| Polystyrene | 2 | 3 |
| Poly(vinyl chloride) | 43 | 51 |
| TOTAL | 2,551 | 2,841 |

[a] From Modern Plastics, 56(1), 45 (1979).
[b] Excluding bonding or adhesive materials.
[c] Including reinforcements.
[d] Including windows, rainwater systems, etc.
[e] Excluding pipe. Plumbing pipe is included under "Pipe" category.
[f] Including swimming pool liners.

cover plates, thermal insulation, absorptive coatings, sealants, gaskets, and hoses of solar collectors,[5] as well as in heat storage and heat transport subsystems.

In a recent seven-year study for the Department of Housing and Urban Development, Bernhardt expresses the opinion that the efficiency of the mobile home industry (such as mass-production techniques and use of lightweight building elements) must be transferred to other segments of the building industry if shelter producers are to respond adequately to the needs of the U.S. market for affordable construction.[6] Such a trend in construction is likely to lead to increased demands for new, lightweight materials, particularly for load-bearing applications. Developments are now in progress on modular building components, structural wall panels, air-supported structures, and foam structures. Polymers will have a major role in these changing construction practices.

Through innovative design utilization of the potentialities of polymeric materials, the aesthetics of buildings can also be improved, which will help in achieving public acceptance.

## 2. Measurement Technology

### a. Prediction of service life

To be widely and successfully used in buildings, polymers or any new materials must offer advantages over traditional materials. Such advantages include availability; strength-to-weight ratio; ease of installation, maintenance, serviceability, and productivity; and first and life-cycle costs. Furthermore, the materials must be capable of performing their intended functions both when initially installed and when subjected to in-service environments for extended periods of time. Assessment of the ability of polymers to perform their intended functions requires not only identification of the necessary levels of performance but also tools to evaluate those levels. Thus, measurement technology is essential to gaining acceptance of polymers in new building applications. Currently, engineering data for plastics and other polymeric building materials are either inadequate or nonexistent, largely because of gaps in measurement technology.

The lack of adequate measurement techniques for predicting the service life of new materials and components is a major barrier to the acceptance of polymeric materials. Reliable service-life tests have been sought for many years. Although short-term tests designed to accelerate the degradation processes have been developed for many building materials,[7] these tests are seldom adequate for more than ranking the performance of materials under a single set of conditions that may produce the same effects as some service conditions. Misapplication of data has led to skepticism about the value of short-term tests; this scepticism must be overcome if innovation in the use of materials is to be encouraged. The inadequacies of accelerated tests stem from the difficulty of relating them to in-service conditions. At least three reasons exist for the problems experienced in interpreting the data. First, mechanisms by which polymeric materials degrade are complex and often not well understood. For short-term tests to be useful in predicting service life, the induced degradation mechanisms must be the same as those occurring in actual use in buildings. If the mechanisms are not well characterized, uncertainty is bound to affect even the most meaningful accelerated tests. Second, the factors affecting service life (see table III-8) are numerous and difficult to quantify. Many existing tests do not include all factors of importance, and thequantitative relationships between the factors that are included and in-service exposure factors are seldom known. Third, the materials are usually tested in configurations different from those used in service, thereby increasing the uncertainties about the relationships between the results of accelerated tests and in-service performance.

A systematic approach to improving the technology of service life prediction has led to the development of ASTM E632, "Recommended Practice for Developing Short-Term Accelerated Tests for Prediction of the Service Life of Building Components and Materials."[8,9]

### b. Performance of systems

A second measurement-technology barrier to the use of polymers in buildings stems from the lack of knowledge of "systems" as opposed to materials comprising the systems. In the case of low-slope roofing, for example, it is important to assess performance of the entire system, including the deck, thermal insulation, and waterproofing membrane, rather than a single material such as an elastomeric membrane. The need to consider a system as a whole frequently leads to increased complexity in evaluating performance as well as to more costly testing.

### c. Flammability

Flammability of building materials is of concern from at least three points of view: (1) increased fire load, (2) generation of smoke and toxic materials upon burning, and (3) rapid loss of load-bearing capacity upon burning. The flammability characteristics of polymers are a barrier to their increased use in buildings. For example, the increased emphasis on upgrading thermal insulation in buildings has led to increased interest in plastic foams; but, although these materials provide excellent thermal insulation, the question of fire safety has limited their use. Acceptance of plastic piping for drain, waste, and vent applications has been slowed by the same concern.

For structural (load-bearing) sandwich panel construction using polymers such as fiber-reinforced polyesters, intumescent coatings have been applied to reduce flammability. Questions remain regarding the effectiveness and durability of these coatings.

### d. Durability of polymers

In the past, polymers often have been viewed with suspicion when pro-

## TABLE III-8

## Degradation Factors Affecting the Service Life of Building Components and Materials

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I. WEATHERING FACTORS

- A. Solar radiation
- B. Temperature
- C. Water
- D. Normal air constitutents
- E. Air contaminants
- F. Freeze-thaw
- G. Wind

II. BIOLOGICAL FACTORS

- A. Microorganisms
- B. Fungi
- C. Bacteria

III. STRESS FACTORS

- A. Stress, sustained
- B. Stress, periodic

IV. INCOMPATIBILITY FACTORS

- A. Chemical
- B. Physical

V. USE FACTORS

- A. Design system
- B. Installation and maintenance procedures
- C. Normal wear and tear
- D. Abuse by the user

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posed for new building or construction applications, largely because of a widely held belief that polymers are unreliable and susceptible to rapid degradation. This view is changing.

While polymer durability has improved in recent years, exposure to ultraviolet radiation, heat, moisture, and other environmental factors can rapidly degrade some materials used in buildings. As polymers increasingly come to be applied in load-bearing applications, the development of more durable polymers becomes particularly important, along with effective criteria for selecting them. For example, a recent study indicates that a major reason for the reluctance of builders to use structural adhesives stems from the lack of documented data on adhesive properties and performance (durability).[3]

### e. Building codes and standards

Building codes and stardards are typically written around traditional materials and frequently exist at many levels of government. It is usually difficult to introduce new materials not specifically approved by the codes. For polymeric building materials to be developed to their full potential, it would be helpful if code requirements were based upon level of performance required rather, than on specific materials.

## 3. Research Needs

The research needed to increase the use of polymers as materials of construction falls into two main areas: (1) the prediction of properties and long-term performance in construction applications and (2) the tailoring of polymers and polymer composites to meet particular requirements.

### a. Degradation of polymers

Research is needed on the mechanisms by which polymeric materials are degraded under the influence of environmental and other imposed stresses. Mechanistic data on degradation are essential (1) in identifying possible stabilization processes to slow degradation and (2) in developing short-term methodologies for predicting service life.

### b. Relationships between microstructure and performance

A better understanding of the relationships between microstructural composition and performance of polymers must be developed. For example, performance-related properties such as creep and strength are likely to be important in end-use building application, but little understanding has been developed on how the microstructure and its changes affect the performance properties of interest.

### c. Probabilistic approaches to prediction of service life

Research is needed on probabilistic techniques to predict the service life of building materials. Although such techniques have been developed for limited application to materials used in the aerospace industry, they do not exist for building materials.

### d. Adhesion

An improved understanding of adhesion is essential. Most materials used in buildings are joined to other materials, and frequently the bond depends upon forces of adhesion. Examples include joint sealants, adhesives, paints and coatings, and roofing membranes. Moreover, the components of materials, such as glass fibers and resins in fiber-reinforced plastics, as well as the pigment and binder in coatings, are joined by forces of adhesion. Degradation or failure of materials is frequently associated with loss of adhesion.

### e. Flammability

The flammability hazards of polymers used in construction must be reduced. Areas for research include effects of microstructure on flammability, mechanisms of combustion and the reduction of smoke or toxic by-products, and effectiveness of protective barriers, such as coatings.

### f. Reinforcement of polymers

Research is needed on mechanisms to improve the strength of polymeric materials through reinforcement to form composites. Reinforcement is particularly important for polymers used in load-bearing applications. While glass-fiber-reinforced laminates have been used in buildings, degradation from such factors as moisture, ultraviolet radiation, and fatigue has been noted. As the demand increases for building components with high ratios of strength to weight, new and improved reinforcement techniques will be needed, including fabrication technology that will maximize desirable attributes at a cost competitive with that of conventional materials.

## References

[1] "Plastics in Construction: Coming on Strong in 1978," Plastics Engineering, vol. 34, no. 7 (July 1978).

[2] Modern Plastics, vol. 56, no. 1 (January 1979).

[3] G. M. Estes, A Delphi Forecast: The Future of the Adhesive Industry, (Wilmington, Del.:E.I. du Pont de Nemours and Co., 1974.)

[4] "Vinyl Dresses up for a New Era in Siding," Modern Plastics, vol. 53, no. 6 (June 1976).

[5] L. F. Skoda and L. W. Masters, Solar Energy Systems-Survey of Materials Performance (NBSIR 77-1314; October 1977).

[6] A. D. Bernhardt, Building Tomorrow: The Mobile/Manufactured Housing Industry (Boston: Massachusetts Institute of Technology, 1980).

[7] L. W. Masters et al., Durability and Related Tests for Elements and Materials Used in the Exterior Envelopes of Buildings (NBSIR 75-955; December 1975).

[8] L. W. Masters, "An Approach to the Development of Predictive Service Life Tests for Building Components and Materials," paper presented at Proceedings of the RILEM/ASTM/CIB Symposium on Performance of External Vertical Surfaces of Buildings, Otaniemi, Finland, August 1977).

[9] G. Frohnsdorff, and L. W. Masters, "Durability of Building Materials and Components: The Meaning of Durability Prediction", (paper presented at Proceedings of the First International Conference on Durability of Building Materials and Components, Ottawa, Canada, August, 1978).

## F. POLYMERS IN AGRICULTURE AND FOOD PRODUCTION

### 1. Agriculture

Agriculture represents one of the key areas of national needs on which polymer science can and will have an enormous future impact. Although agriculture for food production may be more obviously important to health, nutrition, and economic development, environmental and energy considerations may be of equal importance. The need for raw materials for the plastics industry, as well as growing interest in solar energy via biomass intermediates, lends high priority to improvements in agricultural technology.

Early polymer science was grounded in the study of cellulosic materials. It is fitting, therefore, that cellulose once again looms as a major basic raw material. Cellulose may be converted by hydrolytic and fermentative processes into ethanol, single-cell proteins, amino acids, vitamins, and many other products. Another material, lignin, derived from cellulosic waste products, can yield solid fuel, synthetic gas, various organic chemicals, and even soil-binding agents. Terpene fractions obtained from forest waste products have potential value in automotive fuels and can serve as raw materials in the production of other chemical and medicinal agents. Leaf protein also has much potentential for use in animal and even human foods. The proteins from softwood trees may be especially valuable because of their high content of the amino acid lysine.

The key issue in maximum utilization of agricultural and forest biomass products is an integrated strategy of use. Of course, many plants besides those of the forest (which have been emphasized because trees constitute the major portion of the world's biomass) are excellent, fast-growing solar energy collectors; among them are sugar cane and arid land plants of the euphorbiaceae type. Some plants and trees produce an abundance of isoprene-like metabolic products, such as natural rubber and are natural sources of hydrocarbons. If genetic manipulation of plants could succeed in enhancing hydrocarbon production, a major direct resource for converting solar energy to hydrocarbon production on a short time cycle would be available.

### a. Wood and "biomass"

Nature does superbly in capturing and storing solar energy. Each of the billions of conifer trees in our nation is a relatively inexpensive solar collector, often adapted to land that may not be suitable for other purposes. Indeed, a national program of tree planting on a grand scale could easily be justified for many valid reasons, including esthetics, recreation, air purification (with special emphasis on removing carbon dioxide from the atmosphere), soil stabilization, improved water shed performance, production of high quality water, and wood products for energy and structural materials.

Wherever wood is available in the world it is "the poor man's oil," representing a principal source of fuel for heating and cooking. Unfortunately, as the population grows in underdeveloped nations the forests are rapidly destroyed because of fuel needs, logging, and land clearance. Therefore, a key problem calling for research and development is that of producing fast growth cycles for trees and other vegetative resources. Polymer-bound pesticides, herbicides, and growth stimulants, as well as genetic manipulation, have major potential here.

Wood may be regarded as a natural "composite polymer" and is still the most widely used raw material in the United States, surpassing in weight the use of metals combined. Unlike the situation in many other countries, wood is not being depleted in the United States. More than 1.5 million acres of forest land are planted annually, and substantially more could be planted. Unfortunately, because of loss through planting shock, disease, and competitive vegetation such plantings do not necessarily improve wood supply. Solutions to these problems lie in selective application of hormones, herbicides, and pesticides in polymeric delivery systems. In some cases even wood chips and cellulosic by-products may be economic substrates for admixtures of chemical and appropriate biological agents in such controlled delivery.

### b. Polymeric controlled release agents: herbicides, pesticides, and growth stimulants

The ability to effect profound changes in growth patterns by the application of minute quantities of biologically active compounds has led to the development of today's multimillion dollar pest-control industry. Although this development may have been regarded as the ultimate weaponry in the war against weeds and agricultural predators, the indiscriminate use of herbicides and pesticides in their present forms is now recognized as a mixed blessing. The undesirable side effects of highly successful agents that are toxic in the environment have resulted in severe restrictions, but excessive application still often extends these side effects beyond the target area. And, depending on the method of application and climatic conditions, as much as 90 percent of applied pesticides never reach their objective. Furthermore, effective concentrations are significantly reduced by leaching and soil erosion after application. On the other hand, development of short-lived, easily degraded, biologically active agents has been economically discouraging because they degrade too rapidly upon application. An important solution to such problems lies in the use of polymer compositions that fix hazardous agents in place and continue release of biodegradable pesticides at effective levels over a desired period of time. These polymer compositions may involve either chemical attachment, with release of the pesticides upon subsequent degradation, or physical admixture, with release by diffusion or by erosion of the polymeric composition. Besides synthetic polymers with precisely controlled properties, wood chips and wood bark can serve as viable "polymeric" substrates for combination with agricultural chemicals. Considerable attention has been focused on combinations of auxin herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxybutyric acid (2,4-DB) with natural polymers such as cellulose and lignin. These are designed to break down slowly in the soil to release the herbicide.

Although polymeric herbicide and pesticide systems are increasingly important for all types of agriculture, research in growth stimulants has also produced remarkable results and represents a major area for future emphasis. The application of cytokinins to stimulate tomato and orange growth is well known, as are the applications of auxin-type regulators to stimulate root development and gibberellic acid to stimulate grape growth. There is growing evidence that very low doses of certain herbicides can greatly enhance growth rates, especially when administered in a precisely controlled fashion. The effect has been demonstrated for fir and pine trees, and encourages investigation of polymer-bound agents for this purpose.

### c. Polymeric coatings for seeds, leaves, and roots

The coating of seeds with polymers has been studied because of the potential for (1) mechanical protection during handling and storage, (2) enhanced stability, improved germination, and improved yield, (3) incorporation of nutrients or protective pesticides, and (4) enlargement of the seeds to facilitate handling and automated mechanical planting. Although coated seeds have not yet been widely adopted commercially, many specialty crops have been planted in pellet form, including lettuce, beets, onions, cabbage, and celery. Polymers used for encapsulation are of both hydrophilic and hydrophobic types, including such natural polymers as gum arabic, sodium alginate, and methylcellulose, and such synthetic polymers as poly(vinyl chloride), poly(vinyl acetate), polyurethanes, and acrylics. Fillers and additives--clay, flour, and porous vermiculite, for example--have been often used in such polymer coating mixtures with considerable promise.

Polymer coatings offer promise also as protective and semipermeable barriers applied to leaves and roots. Permanent or semipermanent coatings of insect-resistant polymer films could substantially improve agricultural production. Coatings to leaves that would allow normal gaseous diffusion and metabolism of plant life, and yet minimize loss of water, could have a major impact on water control and irrigation, particularly in tropical and semitropical arid lands.

### d. Water control and irrigation

Plastic films and pipe are widely used in agricultural irrigation and water control. Lightweight, low-cost, easily installed pipe made of poly(vinyl chloride) has already had a large impact on irrigation practices, and plastic film, such as polyethylene, is extensively used throughout the world as ground cover for weed control, water control, and seedling protection. Improvements in such agricultural film to control light transmission and biodegradation will be of considerable importance.

Water purification of otherwise brackish and saline sources looms as an everimportant necessity in the future and will certainly be heavily based on polymeric devices utilizing membrane technology. Polymeric films for use as water-retaining linings in ponds and ditches are also of growing importance in farming. Soilbinding and consolidating agents, such as those based upon polyacrylamides, have shown potential in agriculture to alter the basic character of soils in order to achieve better resistance to weather and erosion.

### e. Agricultural machinery

All types of land management and harvesting equipment can benefit from the use of lightweight, low-cost plastics. Fast, gentle, and efficient plastic devices for harvesting have considerable merit for improving efficiency and yields. Automated planting equipment is becoming increasingly important and may be used in combination with polymer coatings and other innovative methods of packaging seeds.

### f. Genetic engineering of plants and trees

Possibilities for genetic manipulation have been described in chapter IID, section 1c. The potential impact upon normal life cycles, growth rates, food quality, and energy utilization is revolutionary.

## 2. Food Production

Polymer research is contributing importantly to solving many of the problems encountered in the production and distribution of food. Some of the problem areas are briefly highligted here.

### a. Food distribution

Tremendous losses occur in the packaging, transporting, handling, and distributing of food products. Poor shelf life and spoilage may be improved through the use of new and safer polymer-modified stabilizing agents. Specialized and inexpensive packaging for transporting fragile products, such as fruits and vegetables, can be readily molded from plastics, and provides not only protection but lightweight containers for shipment and display. Lightweight plastic jars and bottles are resistant to damage and economical to transport.

### b. Packaging materials

In this nation the development of protective plastic films and containers has revolutionized the distribution and esthetic presentation of food products for sale. Polymers are finding increasing use as packaging materials of all varieties. The advantages of polymeric materials include selective vapor-barrier properties, excellent mechanical strength, and versatile fabrication.

### c. Food processing

Few food processing plants today do not utilize plastics extensively in automated equipment for handling fluids and solids in high volume with maximum cleanliness and safety. The equipment benefits from the optical transparency of plastics, the ease of cleaning and sterilization, the light weight for easy handling, and the versatility with which plastics can be fabricated into complex components with great precision. The toughness and strength attainable in plastic materials also contributes to their growing use in food processing machinery. Important too are improvements in water handling and purification made possible by ultrafiltration devices using polymeric components for filter membranes and housings.

### d. Polymeric additives: colorants and preservatives

Polymers may play an innovative role in food production as additives to provide flavoring, color, and spoilage resistance without the toxic properties attributed to many chemical additives in current use. Polymer-bound food colorants, antioxidants, and preservatives can afford excellent functional properties without adverse biological effects because they can be designed to be stable in the human digestive tract and thus be eliminated without entering into tissue or the circulatory system. Similarly polymer-bound flavoring agents and sweeteners may be developed to provide enhanced appeal without the metabolic drawbacks of the small molecules they would replace. Polymeric sweeteners, for example, could be noncaloric and yet free of the health hazards suspected in some of the artificial sweetening agents now in use. Continued research in this field of food additives could also lead to enhanced quality of synthetic foods derived from nutritious but relatively tasteless materials, such as bacterial proteins.

## G. POLYMERS IN MEDICINE

There are few areas of national need in which polymer science and engineering have contributed so influentially as in health care and the biomedical sciences. Further prospects for dramatic contributions are truly exciting. Polymeric materials and basic polymer science impinge on virtually every aspect of medical treatment. In the operating room, not even a simple surgical procedure is accomplished without the use of plastic and elastomeric instruments and devices in the form of endotracheal tubes for anesthesia, blood bags and tubing for transfusions, syringes for injections, surgical gloves and sponges, dressings, sutures, bandages, tapes, catheters, and all types of equipment for intravenous feeding, blood handling, and clinical analyses. The advent of plastics in medical care has brought an ever growing array of disposable products and novel packaging that have simplified sterilization procedures and improved patient safety. Further development of disposable instruments, devices, and packaging will continue to be a most important contribution in future.

The requirements for biomedical materials and devices are exceptionally demanding. Physical, mechanical, and chemical properties range from the compliant elastomers considered for replacement of skin or soft tissue to hard, durable plastics for bone and joint prostheses. Adequate chemical stability (survival for many years or for the life of the patient without appreciable degradation in the hostile biological environment) is, however, difficult to achieve for implant materials.

The science of "biocompatibility" is still at an early stage, but with much promise, however, for outstanding future achievements. Different requirements exist for vascular catheters and urethral catheters or dialysis membranes, which require relatively short periods of exposure to blood or tissue. In some cases, such as with surgical sutures or controlled drug delivery, rapid biodegradation to nontoxic products may even be desired. Immune reactions and blood or tissue damage are all important factors complicating the development of drugs and devices based on polymeric materials. Despite these formidable problems, a broad variety of plastics and elastomers has found important applications. They include silicones, acrylics, urethanes, fluorocarbons, polyethylene, polypropylene, polycarbonates, and many others. In this area alone, the NIH, through the Heart, Lung, and Blood Institute, supports studies of polymer materials to an estimated extent of $3 million per year.

In view of the enormous variety of specific applications that might be discussed, the brief discussion provided here is confined to several topics sufficient to highlight the importance of polymers in medicine. Further information on research in progress is presented in chapter IID, sections 2c and 2e.

### 1. Genetic Engineering

The great potential for genetic engineering and manipulation in health care is evident. Polymer science has an important role in the synthesis and separation of macromolecules crucial to the transfer and control of genetic information. The research includes modeling and studying the coding and sequencing of natural genetic molecular structures, as well as achieving new synthetic and synthetic-natural biopolymer structures that may lead to control of serious genetic diseases and to the production of valuable biochemicals such as insulin.

## 2. Polymeric Drugs

Great opportunities exist in the development of new drugs and drug modifications based on polymers, not only for new therapeutic treatments but for more sophisticated delivery procedures. Most important are efforts aimed at drug localization and controlled delivery for long periods of time with minimal harmful side effects. Such drugs would have obvious potential for safer and more effective cancer chemotherapy and immunotherapy, for prophylactic and therapeutic treatment of cardiovascular disease, and for treatment of enzyme deficiencies and genetic diseases.

## 3. Functional and Cosmetic Implants and Prostheses

Accomplishments with implants and prostheses are already important, but future achievements can be still more impressive. Hard and soft plastic contact lenses as well as dental adhesives and prosthestics, are now widely available. Yet, further improvements for safety and functional performance are needed. Synthetic organs, such as ventricular assists, dialysis machines, and blood oxygenators, utilize plastics as essential materials. One can envision synthetic organs of greater sophistication and simplicity on a miniature scale, and perhaps involving polymeric microtubules combined with living cells as composite synthetic-living systems.

## 4. Surgical and Dental Materials and Devices

As already noted, numerous types of catheters, syringes, sponges, and biodegradable implant suture materials are increasingly significant in health care. Such devices as the heart-lung machine have made astonishing surgical feats possible, including the repair and transplant of human organs. Heart valve replacement and heart by-pass procedures are now routine and widely used. Instrumentation based on numerous polymeric components is utilized in intensive care units and has had lifesaving value in countless situations. Kidney dialysis using polymer membranes is a major medical effort supported by a billion dollar federal program. Dialysis and hemoperfusion devices improved by new materials and engineering will lead to many more lifesaving achievements. Polymers have made remarkable contributions to better dental health through improved materials.

### 5. Diagnostic and Analytical Methods and Instrumentation

Polymer-bound or immobilized enzymes, antibodies, polysaccharides, polynucleotides, and various polymeric compositions for biological separations in gel or affinity chromatography columns and in electrophoresis are basic to biological analyses and diagnosis. These materials are subject to continuing research in the effort to devise ever simpler, more reliable, and more rapid clinical analyses for diagnostic use.

### 6. Public Health and Environmental Safety

Sanitation and waste disposal based on plastic pipes, valves, and tubing, as well as polymeric membranes for ultrafiltration and water purification, are important areas of polymer utilization. The development of polymers for solventless coatings and water-based paints has contributed to health and safety by eliminating the use of hazardous and flammable solvents. The management of radioactive waste represents yet another area to which polymer technology can contribute. Chemical corrosion and mechanical problems, as well as fabrication difficulties associated with metal or ceramic encapsulation of radioactive waste, may make polymer-based composite structures attractive.

### 7. Learning, Memory, Mental Health

Although a large body of information has been gathered concerning brain structure and function, the physiological basis for long-term or short-term memory is not understood, much less the biochemical factors that influence mood and emotional behavior. However, there is reason to believe that memory and learning occur through biochemical switching mechanisms involving macromolecules such as polypeptides. Indeed, a major new field has been established by discoveries of polypeptide neurohormones that function like neurotransmitters, diffusing from the site of release to surrounding cells. These polypeptides may be important in general changes in mood, alertness, sleep, and mental illness. Some neuropeptides, for instance, endorphins and enkephalins, bind to the same nerve receptors as opiates and seem to be the natural physiological polymeric agents of which drugs such as morphine are analogs. A new field of biopolymer investigation is therefore emerging, involving what might be termed neuropolymers such as the neuropolypeptides, which can switch and alter brain function and thereby play a major role in mental health as well as in education.

### 8. Population Control

Population growth may be regarded as the single most important biomedical and social dilemma. Despite significant technological progress in this nation and in the many industrialized nations of the world, the many social problems concerned with energy, health, food, defense, housing, and transportation are derivatives of too rapid growth. Individual, group, and national desires in a society or world with rapidly increasing population must often be at odds with the general welfare. There are consequent limitations on individual freedoms in the expression of personal tastes and in achievement of individual objectives. The governments and societies that best cope with population growth and attendant social problems will achieve most for their people and will probably be most successful in surviving.

World population has increased 75 percent in 30 years, from 2.5 billion in 1950 to 4.4 billion in 1980. The United States and the Soviet Union grew at about the same rate during this period, slightly less than 50 percent. Furthermore, in 1950 one third of the population lived in the industrialized nations (in Europe, North America, USSR, Japan, and Australia) whereas two thirds lived in developing or underdeveloped nations. These latter nations have continued to grow much faster in both numbers and rate, their populations almost doubling from 1.7 billion in 1950 to 3.3 billion in 1980. Reasonable projections suggest that population growth will slow during the next 20 years in all parts of the world except Africa. By the year 2000 a population increase of perhaps 12 percent for developed countries and 50 percent for the developing nations may be expected.

United Nations data on world population trends project a population of about 6.2 billion by the year 2000 and an asymptotic world population of between 8.5 and 13.5 billion within 100 years as a result of an overall decline in fertility. There is no real consensus, however, as to when fertility will begin to decline, and at what rate in the most rapidly growing areas; nor can there be any good consensus at this time as to what the world population will be when growth ceases. A plateau of around 10 billion would not be an unreasonable guess. Even in such a rapidly growing country as India, there is unmistakable evidence that fertility has decreased significantly during the past 15 years, from a birth rate of about 45 per 1000 population to a current level of 36 per 1000.

Major factors involved in declining birth rates are complex. However, there seems little doubt that simple, reliable, and safe contraceptive methods have an important role to play in achieving a stable and balanced population density in the world. As a high-technology nation, the United States is in an important position to advance the requisite technology. The most important consequences, however, are likely to be seen in the rest of the world. It is here that polymer science and engineering can make a most significant contribution through development of vastly improved contraceptive drugs and devices. Since advances in health care in years to come may ironically be considered counterproductive in achieving population stability, advances in fertility control assume even further significance. Polymer science and contraceptive development will therefore be emphasized here.

Control of conception and the use of antifertility prophylactic measures require substantial improvement. Undesirable and hazardous side effects plus unreliable use associated with orally administered contraceptive hormones emphasize the need for new methods, most of which involve sustained and localized release of hormones or spermicides. Polymer-based research has achieved considerable success in developing controlled-release, polymer-steroid devices. Intrauterine devices providing steroid diffusion through polymeric membranes, such as silicones, have afforded long-term contraception (for periods of up to one year) without the risks of systemic adverse hormone reactions. Extensive clinical evaluations in the United States and abroad have demonstrated the safety and efficacy of such products. However, further research and development are needed to produce polymeric compositions and devices with maximum safety, reliability, and simplicity of use. One important problem is that the pharmaceutical industry in the highly developed nations, including the United States, has reduced its research in the contraceptive field, especially on methods more appropriate in less developed countries, for instance, long-lasting injectable steroid contraceptives. As a consequence, special projects of the World Health Organization (through its Program of Research in Human Reproduction) and the National Institute of Child Health and Human Development of NIH (through its Center for Population Research) have assumed an increasing role in support of research on polymers for contraceptive purposes.

This research includes studies, for example, of microcapsules of the biodegradable polymer poly(D,L-lactic acid) containing norethisterone, which can be administered by intramuscular injection to provide uniform release of the hormone at a rate sufficient to inhibit ovulation for a period of six months. This type of system eliminates fluctuations in hormone blood levels and also minimizes exposure of the gastrointestinal and hepatic systems to the hormone. One of the greatest benefits, especially important in underdeveloped nations, is elimination of the need to remember to take a daily pill. Various other nontoxic, biodegradable polymer mixtures with steroids, including those based on a-butyrolactone, polyesters and polyacetals, and glutamic acid containing polypeptides (which hydrolize and degrade *in vivo*), have been shown to provide sustained long-term hormone release. Typical hormones that have been studied extensively include norethindrone, ethynylestradiol, and levonorgestrel.

Nondegradable vaginal barrier devices based on acidic hydrogel polymers that take advantage of the spermicidal activity of polyacid copolymers have received attention, as have vaginal rings made of silicone rubber and hormone compositions. The vaginal silicone ring releases steroids for prolonged periods and can be utilized without a physician's assistance. This polymeric contraceptive device appears to be simple and versatile. It is being evaluated extensively abroad, but curiously has not been of much interest in the United States.

Because of health hazards and problems of reliable use associated with hormone pills, the development of safer and more effective polymeric contraceptic systems represents a key area of biomedical research involving polymers. To the extent that this line of research is successful in producing a simple contraceptive technology widely acceptable throughout the world, some of the hunger, suffering, poverty, and other social problems that stem from rapid uncontrolled population growth may be alleviated, especially in those nations where the need is most critical.

## H. POLYMERS IN NATIONAL DEFENSE

### 1. Organization and Sources

The Department of Defense (DOD) has maintained an active research and development program on polymers for many years, by supporting investigators at various academic institutions and research organizations as well as at its in-house laboratories. The needs are diverse, but in general they stress performance and durability, often exceeding the limits for existing materials. The separate army, navy, and air force missions suggest polymer applications that may differ substantially, yet the fundamental research goals show many similarities of interest, as might be expected.

In recent years the DOD's program has emphasized principally the utilization of known materials, with only a relatively small amount of research aimed at the discovery of new materials. Because the expenditure involved in basic research on new materials is only a small percentage of the total involved in bringing a new material to the marketplace, some industrial companies are reluctant to undertake government funded work in which they would not be allowed to maintain a proprietary position to justify the major expenditures incurred in the latter phases of the innovation cycle. Requirements for materials with specialized functions, for which the DOD or National Aeronautics and Space Administration (NASA) are the only users initially, lead to challenging research, often stimulating new concepts for later commercial use.

About $3-4 million per year is directed by DOD to the synthesis of new polymeric materials. Among them are high-temperature elastomers for use in strong oxidizing environments, such as propellants; environmentally resistant fluorinated coatings; electrically conducting polymers derived from polyacetylene; and antifouling coatings based on organometallic polymers.

The army is currently seeking understanding of the fundamental interactions of liquids and vapors with polymeric materials related to chemical defense. Properties of coatings, clothing, and protective materials of all kinds that would lead to low contamination levels, such as self-cleaning characteristics, are important.

### 2. Needs

Apart from the variety of polymers purchased directly from commercial sources, requirements for polymers by the DOD include such materials as wide-temperature-range, environmentally resistant elastomers; structural resins; electronic encapsulants; coatings; and adhesives. Specific components with highly specialized functions must also be considered. These include aircraft windshield interlayers, solid-propellant binders, fibers for reinforcement, flame-resistant fabrics, parachute deployment, and body armor.

In addition to the development of polymers to be used in the various material forms suggested above, a principal concern is the control of processing, design, and manufacturing necessary to meet, or sometimes to set, stringent military specifications. High-performance applications, in which flight safety or mission performance and exceptional reliability are demanded, often require methods of testing and analysis beyond those of normal experience with commercial applications of polymers.

Each of the branches of the DOD and NASA are currently pursuing research to improve the properties, processing, and durability of structural resins for fiber-reinforced composites and adhesively bonded structures. Objectives include lower cure temperatures, moisture resistance, controlled fiber interface bonding, and higher working temperatures. Uniformity of product is stressed, with emphasis on chemical composition and effects of processing on final properties. Efforts to produce new resin compositions and curing reactions are being undertaken to find materials with advantages over the current epoxy-matrix resins. Acetylene-terminated polymers are expected to provide improved high-temperature capabilities in thermosetting materials. A scientific basis is sought for processing polymers from bulk or prepolymer form to the final configurations, including kinetic, rheological, and structure-property correlations.

The DOD and NASA have similar interests in polymer research for space applications. Advanced fiber-reinforced plastics offer attractive possibilities for stiff, lightweight satellite structures, and good, dimensional control over wide temperature ranges for optical, antenna, and sensor platforms. There is interest in behavior of matrix polymers and structural adhesives at cryogenic temperatures. Of particular importance is the concern for stability of materials in the combined vacuum/thermal/radiation environment of space, where not only the performance of polymeric components must be maintained, but any outgassing of these materials must be minimized. In space, condensation of low-molecular-weight fragments on sensitive detectors, lenses, or thermal control surfaces limits the operational life of the satellites. Polymer-based fabrics and films are used as thermal protection coverings, often with reflective metallized coatings. Electronic devices make use of conformal coatings which encapsulate and protect sensitive components. Again, stable polymers with low outgassing are needed, but with the additional requirement of transparency at the appropriate wavelengths for photovoltaic and photoconductive devices.

Durability studies, including both physical and chemical deterioration, are needed as part of an overall methodology for predicting in-service life. A wide range of environments, which may include the conditions of space, the severe cold of the polar regions, or perhaps the high pressure and saline conditions under the sea, must be considered.

The following list of current needs suggests the scope of the defense agencies' primary interests in polymer research:

- Piezoelectric polymers for underwater acoustic sensing; flexible, reproducible, at reduced cost. (navy)

- Electroactive polymers for a variety of applications, including electrooptical systems. (all forces)
- Improved damping polymers that may be subjected to small temperature changes (0-35°C), but large pressure changes ( $\sim 10^4$ kPa), for underwater vessel applications. (navy)
- Flameproof materials for shipboard clothing and equipment. (navy)
- Compliant coatings for drag reduction in the sea. (navy)
- Antipolluting-antifouling coatings. New approaches are needed for understanding of leaching and solid-state diffusion. (navy)
- New high-strength, tough fibers for composites. (all forces)
- Polymers resistant to moisture, UV, bacterial attack, and long-term degradation, for weapons, packaging, etc. (army)
- Materials resistant to chemical attack for storage of hazardous chemicals and explosives. (army)
- Transparent materials that are impact and abrasion resistant for face plates, canopies. (army, air force)
- New polymeric fibers and textiles for chemical/biological protection and weather protection that can be easily decontaminated. Flame-retardant fire protection fabrics. Mechanism of flame retardation, char formation, efflorescence, and intumescence. (army)
- Photochromic materials for flash protection. (army)
- Polymeric foams for thermal and blast protection, and lightweight structures. (army)
- New electrode materials; diaphragms for quiet, efficient power sources with low thermal emission. (army)
- Energetic plasticizers and binders for propellants and explosives. Synthesis and characterization of nitro compounds, nitrogen-fluorine compounds, and other fluorine-containing oxidizers. (all forces)
- Rapid, thorough means to destroy chemical agents and other contaminants by catalysis at fiber or thin-film interfaces. (army)
- Development of highly compressible fluids, which maintain high compressibility down to -65°F, for damping the recoil forces in artillery. (army)
- Research on understanding and compositional control of elastomeric sealants with high adhesion, fuel compatibility, and tailored rheological properties for use in aircraft wing and fuselage joints. The integral fuel tank concept utilizes internal space in the aircraft structure, and employs curable liquid polymers as joint sealants. Some sealants are injected into mating surface channels as well. (air force)
- Elastomers with wide temperature range (-65 to > 450°F) for hydraulic system seals, compatible with advanced hydraulic fluids and resistant to abrasion and cuts. (air force)

- Coatings, films, fabrics for spacecraft use, negligible outgassing under vacuum conditions, resistant to radiation. (air force)
- Elastomeric interlayers for aircraft windshields resistant to bird impact. Good adhesion, wide useful temperature range, and optical clarity. Emphasis on processability. (air force)
- New structural polymers with high strength/density and stiffness/density. Innovative approaches are needed including oriented rodlike polymers and molecular composites. (all forces)
- High-temperature, moisture-resistant resins for composites and adhesives. New cure mechanisms are needed for stable structures processed at room temperature. (all forces)

# IV. POLYMER RESEARCH IN INDUSTRY, THE UNIVERSITIES, AND THE FEDERAL GOVERNMENT

## 1. Introduction

The United States is losing its worldwide competitive technological edge, and there is a widespread perception that this is due in part to a decrease in research and development. Innovation spans the cycle from conception of an idea through commercialization of the new product or process. The striking coincidence of new ideas often emerging simultaneously from different parts of the nation or of the world strongly supports the thesis that they originate in basic research, the results of which are widely promulgated throughout the scientific community in journals, meetings, and correspondence. The presumed decrease in basic research, therefore, is cause for particular concern. The trends have been summarized in a recent paper by G.F. Mechlin and D. Berg ("Evaluating Research - ROI is not enough," *Harvard Business Review*, September-October 1980, p. 93). In the decade ending in 1978:

- R&D as a fraction of GNP had decreased 20 percent.
- Basic research as a fraction of GNP had decreased 24 percent.
- The proportion of scientists and engineers in the labor force who are engaged in R&D had dropped 13 percent.
- Industrial investment in basic research as a fraction of net sales had declined 32 percent.

In 1956 industry performed 38 percent of the basic research in the United States; in 1976 just 16 percent.

The general trends in international science and technology have been summarized in *Science Indicators 1978* (National Science Board, 1979). Two especially relevant points raised are:

- U.S. investment in research and development is much greater than in most countries, in terms both of expenditures and of scientific and technical personnel. However, Japan and West Germany have been increasing their R&D investments more rapidly than the United States.
- U.S. universities and colleges have made a significant contribution to the building of world scientific and technical

> capabilities. They have contributed to the development of foreign universities and have also assumed the role of training many foreign scientists and engineers. Almost 60 percent of all foreign students in the United States are studying in scientific and technical fields; about 15 percent of the scientific and engineering doctoral degrees were awarded to foreign citizens in the United States in the mid-1970's, and 32 percent of the U.S. postdoctoral appointments in science and engineering fields in 1977 were held by noncitizens.

Section 2, immediately following, describes trends in R&D on polymers in selected developed countries. The status of basic research in polymer science and engineering in industry and in universities is discussed in sections 3 and 4. A brief discussion of patents follows in section 5, and a brief summary of university-industry relationships in section 6 concludes this chapter.

## 2. Polymer Research in Selected Nations

From 1967 to 1979 the number of abstracts concerning polymer studies appearing in Chemical Abstracts increased by 2.9 percent annually for papers and 3.2 percent annually for patents. The percentage of the total number ofabstracts in nonpatents varies by research category, as shown in table IV-1. Property studies tend overall to be more basic in character thanstudies related to synthesis which can lead directly to new or improved proprietary materials and processes.

Obviously no quality judgment is made by adding up total numbers of papers and patents abstracted; however, some indication of the amount of activity in the area is realized. The USSR. leads the world by a wide margin in total numbers of papers published in polymer science and engineering (table IV-2). About twice as many papers are published there annually as in the United States. Japan is now essentially equivalent to the United States in number of papers published. In the category of research on polymerization, Japan exceeds the United States by a significant margin; we have gone from 17 percent of the total in this category in 1972 to 14 percent in 1978. The United States continued to exceed Japan in the category of properties.

The USSR is not a major factor in worldwide patents, but the number in the field of plastics has been gradually increasing; in 1978 it was 40 percent of the number originating in the United States (figure IV-1). The most startling numbers are those for Japan, which was essentially equivalent to the United States in 1972 but has dramatically increased its patent activity in this area while the number of U.S. patents has decreased. In 1978 Japan issued worldwide almost two and one-half times as many patents as the United States. In 1978, 49.7 percent of the worldwide patents on plastics originated in Japan, compared with 19.6 percent in the United States.

These statistics are misleading because of differences in patenting procedures in the different countries. A more realistic assessment can be obtained by looking at U.S. patents in the area solely of plas-

## TABLE IV-1

### Percentage of Nonpatent Abstracts in Categories of Polymer Research, 1972-1978

| | Percent Nonpatents |
|---|---|
| Polymerization | 54 |
| Stabilization | 45 |
| Analysis | 98 |
| Monomer | 63 |
| Properties | 86 |

### TABLE IV-2

### Percentage of Worldwide Publishing by Categories of Polymer Research

| | U.S. (percent) | | Japan (percent) | | U.S.S.R. (percent) | |
|---|---|---|---|---|---|---|
| | 1972 | 1978 | 1972 | 1978 | 1972 | 1978 |
| Polymerization | 17 | 14 | 19 | 17 | 32 | 24 |
| Monomer | 20 | 18 | 15 | 14 | 32 | 20 |
| Stabilization | 12 | 15 | 4 | 3 | 50 | 33 |
| Analysis | 24 | 26 | 13 | 10 | 22 | 16 |
| Properties | 18 | 15 | 10 | 9 | 43 | 32 |

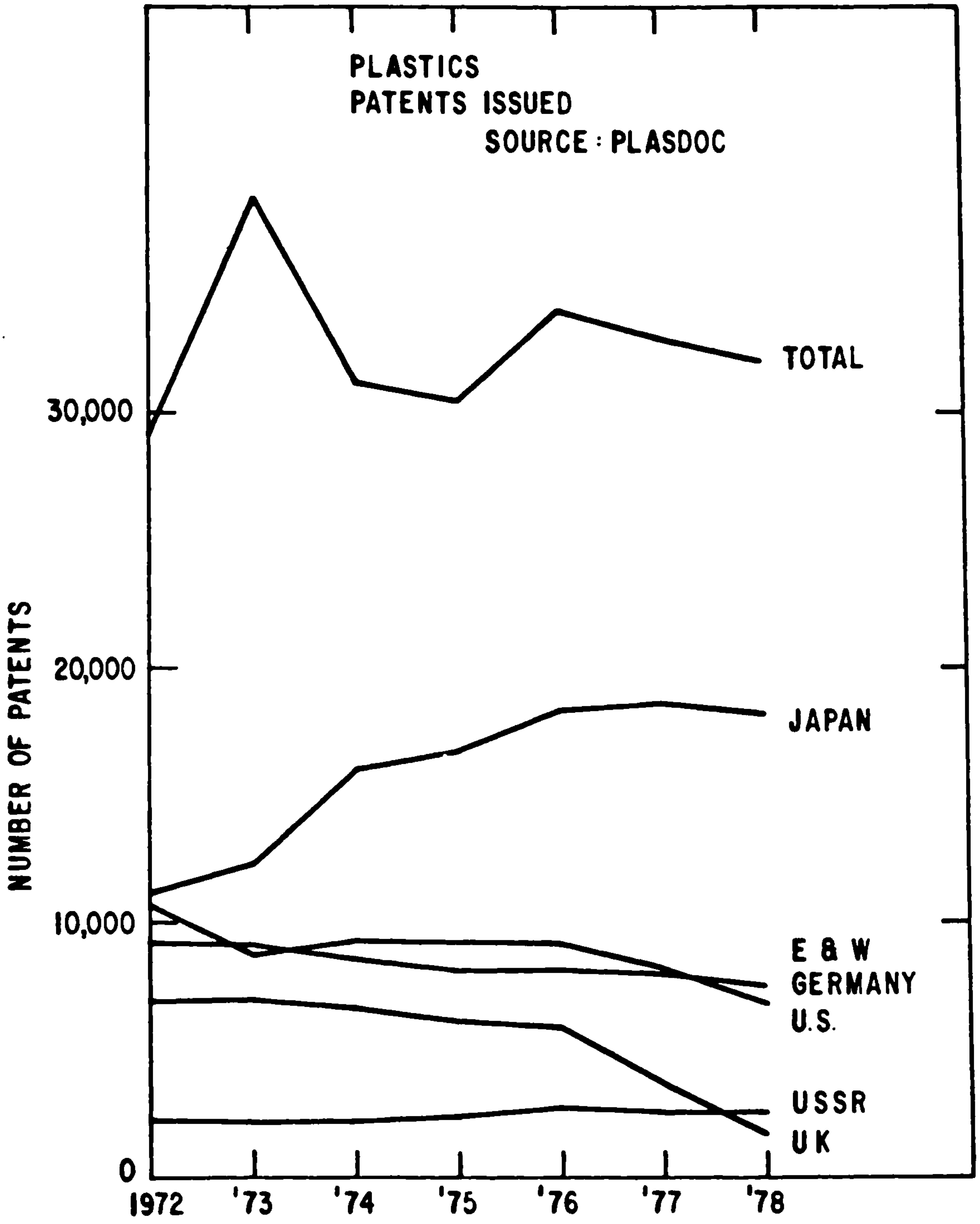


FIGURE IV-1. Patents issued in the field of plastics.

tic materials and synthetic resins (figure IV-2). The U.S. share has decreased from 77 percent in 1966 to 59 percent in 1979, while patents originating from Germany and Japan have increased from 8 and 3 percent to 12 and 14 percent, respectively. One can only conclude from these statistics on publications and patents that the United States is no longer the dominant force in worldwide polymer activity. Japan is now at least equivalent to and probably exceeds the United States in the total amount of activity in this area.

Japan is also a major producer of plastics. In 1979 the United States and Japan produced 29.7 and 16.4 billion pounds, respectively. On a per capita basis, this amounted to 141 pounds per person in Japan and 135 pounds per person in the United States.

S. F. Adler ("Patents and Innovation in the Chemical Industry," Research Management, July 1980, p. 30) has analyzed patents issuing from the major U.S. and European companies. From 1967 to 1976 the combined annual production of patents from the top twelve U.S. chemical companies declined about 25 percent. During this period, there was a 50 percent increase from the eight largest European companies.

An analysis of papers published in the three leading U.S. polymer journals (Journal of Polymer Science, Macromolecules, and Polymer Engineering and Science) shows a dramatic drop in the percentage of papers from industry versus universities over the past 10-15 years and an increase in the number of papers originating outside the United States in particular from Japan (figures IV-3 through IV-6).

### 3. Basic Research in Industry

All of the previously cited statistics indicate a substantial shift in the balance of R&D work in industry towards more applied work. Adler, in the study referred to previously, Alder has pointed out that during the period 1967 to 1976 a more dramatic decrease occurred in scientific publications than in patents from the twelve largest chemical companies (figure IV-7).

In a recent article R. H. Hayes and W. J. Abernathy have also addressed this question ("Managing Our Way to Economic Decline," Harvard Business Review, July-August 1980, p. 67):

> By its very nature, innovative design is, as Joseph Schumpeter observed a long time ago, initially destructive of capital--whether in the form of labor skills, management systems, technological processes, or capital equipment. It tends to make obsolete existing investments in both marketing and manufacturing organizations. For the managers concerned it represents the choice of uncertainty (about economic returns, timing, etc.) over relative predictability, exchanging the reasonable expectation of current income against the promise of high future value. It is the choice of the gambler, the person willing to risk much to gain even more. Conditioned by a market-driven strategy and held closely to account by a 'results now' ROI-oriented control system, American managers have increasingly refused

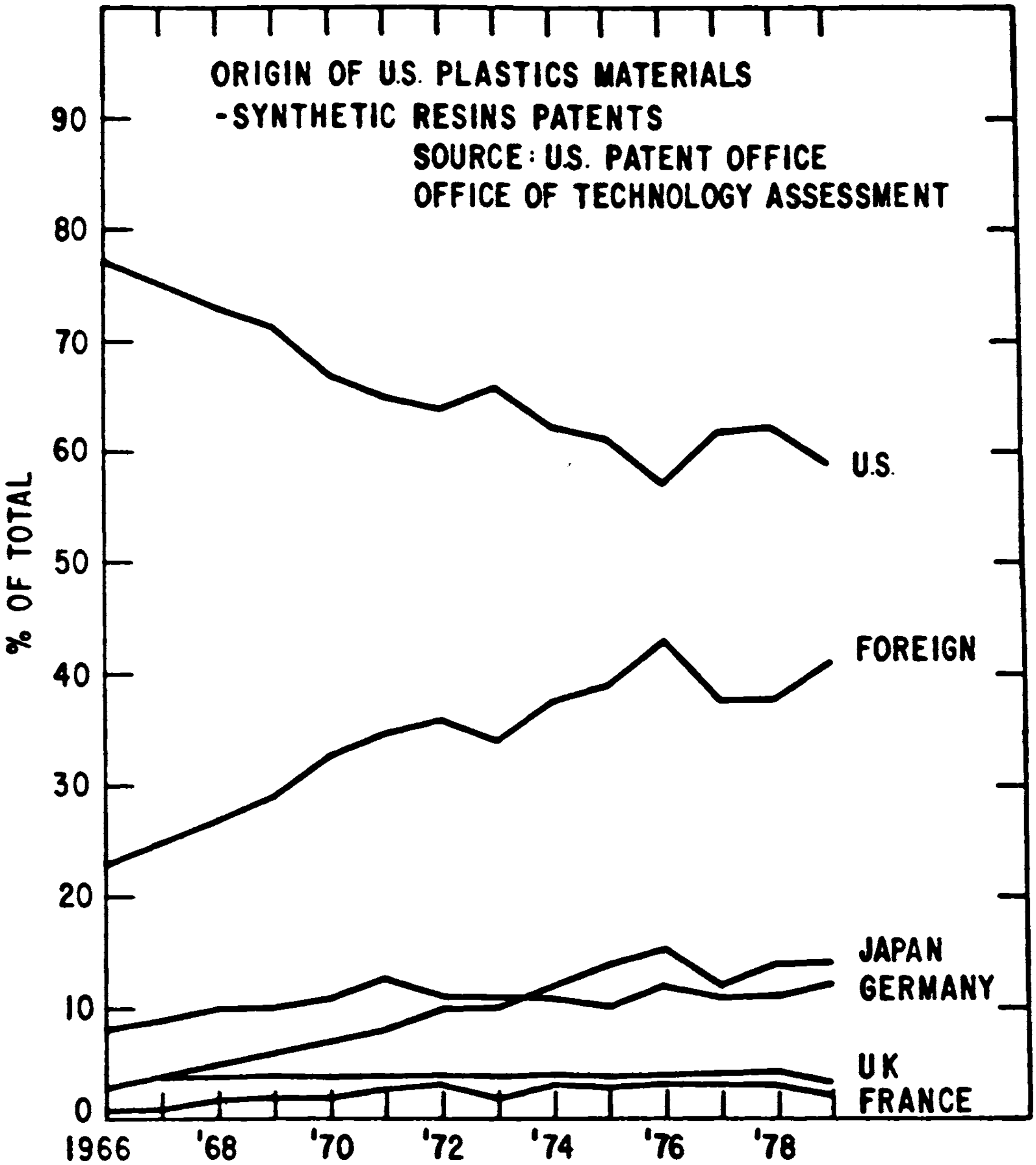


FIGURE IV-2. Origin of U.S. patents on plastic materials and synthetic resins.

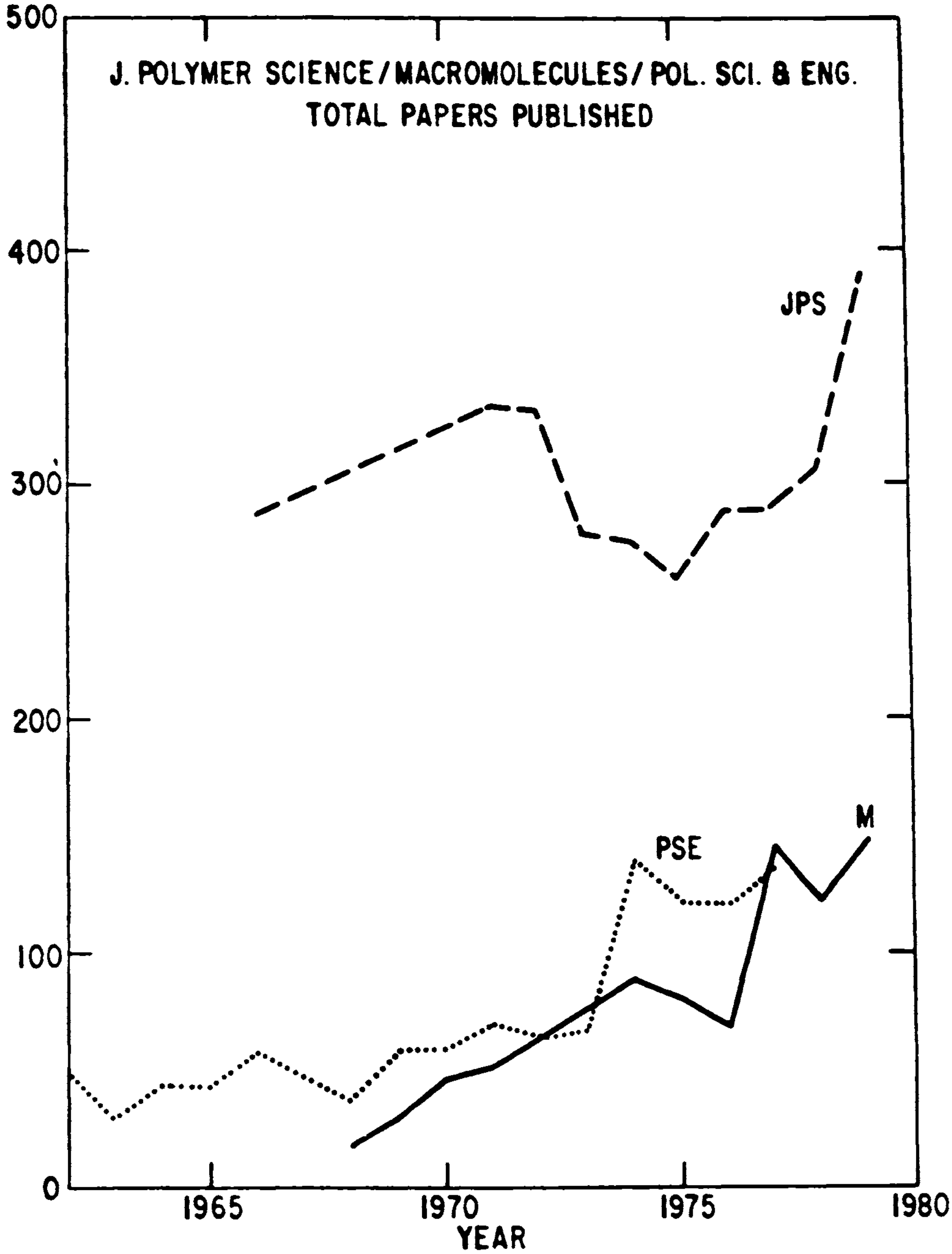


FIGURE IV-3. Total numbers of papers published per year in the *Journal of Polymer Science*, in *Macromolecules*, and in *Polymer Science and Engineering*.

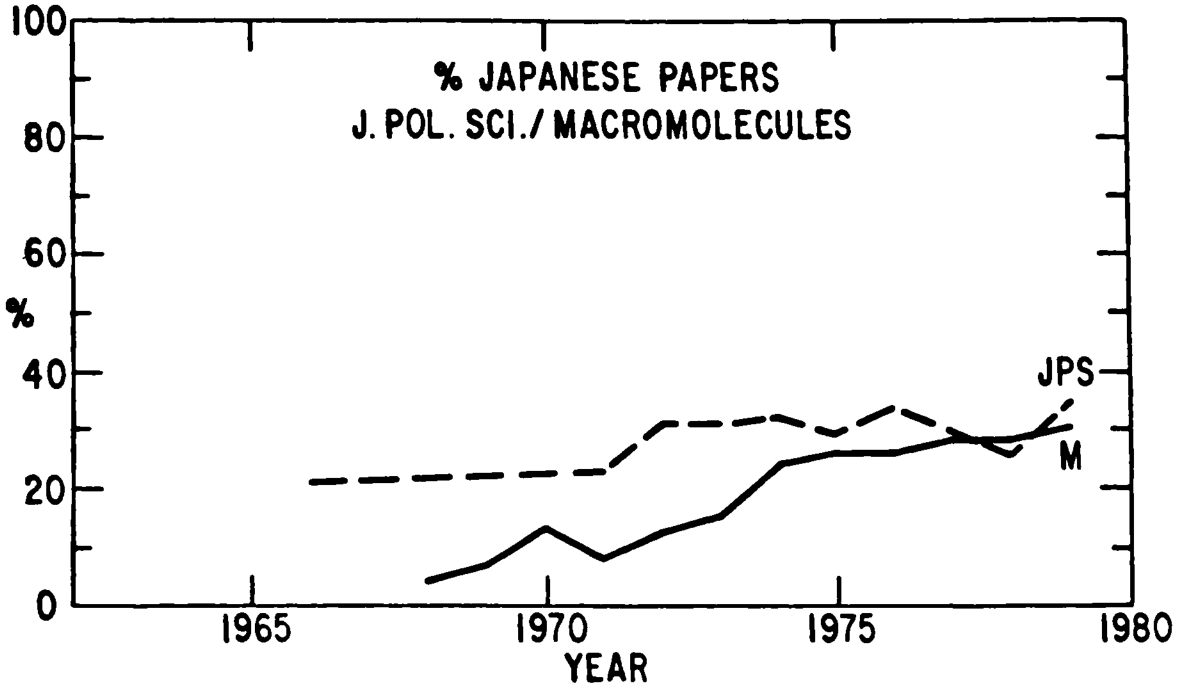
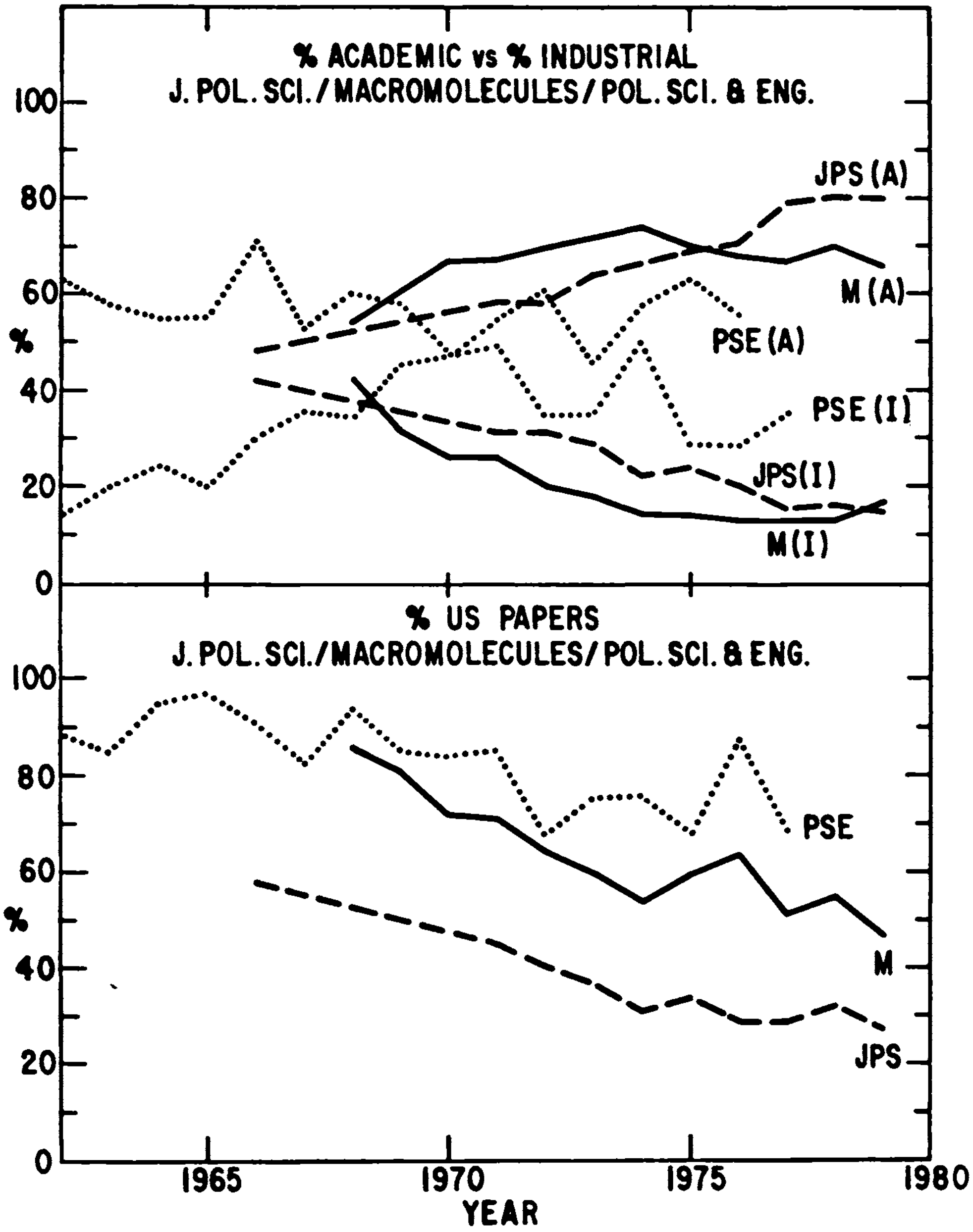


FIGURE IV-4. Percent of Japanese papers in *Journal of Polymer Science* and *Macromolecules*.



FIGURES IV-5 and IV-6. Percent of papers published--academic versus industrial--and percent of U.S. papers published.

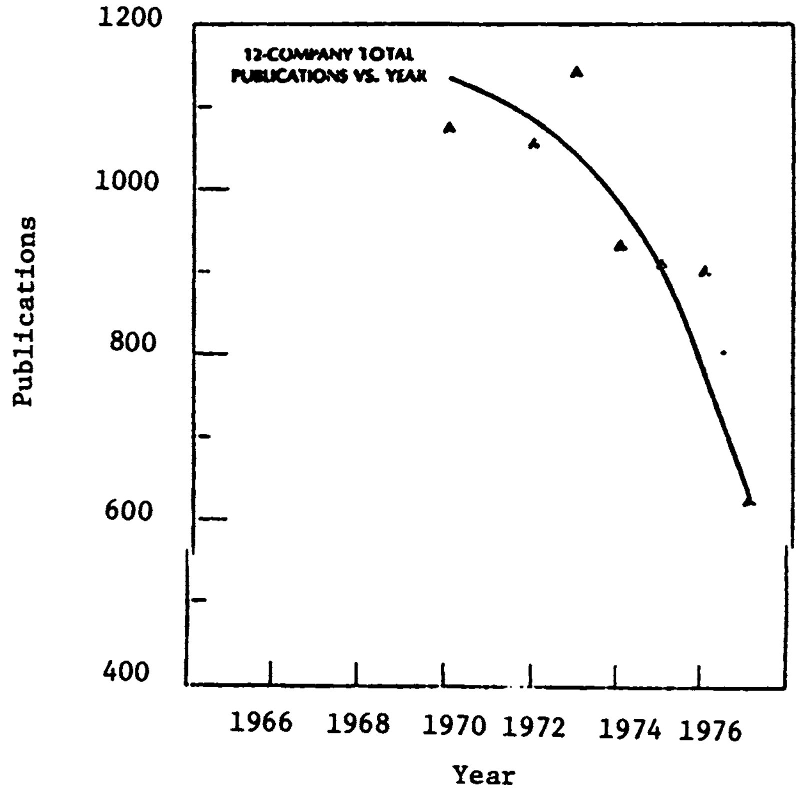


FIGURE IV-7. Scientific publications from twelve largest U.S. chemical companies.

> to take the chance on innovative product/market development. As one of them confesses: 'In the last year on the basis of high capital risk, I turned down new products at a rate at least twice what I did a year ago. But in every case I tell my people to go back and bring me some new product ideas.' In truth, they have learned caution so well that many are in danger of forgetting that market-driven, follow-the-leader companies usually end up following the rest of the pack as well.

They also commented on the different attitudes of the European and Japanese managers:

> Gaining competitive success through technological superiority is a skill much valued by the seasoned European (and Japanese) managers with whom we talked. Although we were able to locate few hard statistics on their actual practice, our extensive investigations of more than 20 companies convinced us that European managers do indeed tend to differ significantly from their American counterparts. In fact, we found that many of them were able to articulate these differences quite clearly.
>
> In the first place, European managers think themselves more pointedly concerned with how to survive over the long run under intensely competitive conditions. Few markets, of course, generate price competition as fierce as in the United States, but European companies face the remorseless necessity of exporting to other national markets or perishing.

A. Gerstenfeld and A. Sumiyoshi ("The Management of Innovation in Japan - Seven Forces that Make the Difference," Research Management, January 1980, p. 30) have discussed the different management approach in Japan. They point out a different risk-reward structure in Japan where decision making and hence risks are shared; unions in the United States and Europe are opposed to innovation, whereas in Japan they are enthusiastic and cooperative. In Japan there is much government-industry cooperation in contrast to the adversary relationship that exists in the United States.

## 4. University Research in Polymers

N. M. Bikales, Director of the Polymers Program for the National Science Foundation (NSF), has attempted to estimate the size of the U.S. research effort in polymers ("Current Status and Trends in Polymer Science in the United States," 10th National Colloquium of the Groupe Francais des Polymeres, Paris, November 15, 1979). The number of academic scientists and engineers interested in polymers is estimated to be about 625, of whom somewhat less than 250-300 are actively engaged in research. Total federal funding for basic research in polymers (exclusive of biopolymers and biomedical research) is estimated to be about $13 million for FY 1979, the average size of a grant being $50 thousand (see table V-2, chapter V). About two thirds of this support comes from NSF.

The federal government is expected to provide about 70 percent of all U.S. basic research funds in 1980 (table IV-3). An additional 15 percent is likely to come from industry sources and 10 percent from universities and colleges. The universities are estimated to account for 52 percent of all basic research funded, industry 16 percent, and the federal government (in-house) 15 percent.

A brief questionnaire was sent to twenty universities that have among the largest polymer science and engineering programs. Responses were received from seventeen (table IV-4). They average 11.2 faculty members involved in teaching and/or research in polymer science and engineering, with average numbers of about 35 graduate and twelve postdoctoral students. Detailed funding information was obtained from 12 of these institutions. Total funding for polymer research was $14.3 million, of which 60 percent came from the federal government. The total number of faculty members in polymer science and engineering at the 12 universities is 146, so that the average funding per member is $98,000. Bikales has estimated that the federal agencies provided about $13 million in funding for basic research in polymer science and engineering in FY 1979 (see table V-2, chapter V). If this represents 60 percent of the total funding, an estimate of $20 million is indicated for the total funding. Most of the academic research is taken to be basic.

Four of the schools responding have separate departments of polymer science and/or engineering; but the most common arrangement is an interdepartmental collaboration among faculty members, which in some cases is organized as an institute. Seven of the schools have an industrial associates program, and most of them have a definite patent policy in force. Six schools indicated plans for a substantial increase in the size of their polymer programs over the next few years.

The major concerns expressed and difficulties faced in the universities are:

- Inadequate funding for facilities, equipment/instrument maintenance, and replacement.
- Inadequate funding of research; federal funding often has narrow objectives and industrial funding is very limited.
- Shortage of high-quality graduate students, U.S. citizens in particular.

In recent years the National Science Foundation has created several mechanisms for encouraging cooperation between universities and industry. Industry/University Cooperative Research Grants provide support for joint research of academic and industrial investigators. The research must focus on fundamental scientific questions of a basic or applied nature. The criteria for selection of projects are the same as for other proposals in science and engineering. More than half a dozen projects of this type had been initiated in polymer science as of the end of 1980, including a substantial one at the University of Delaware.

TABLE IV-3

## Funds for Basic Research by Categories of Sources and Performers, FY 1980 (Estimated)

| | Performers | | | | | | |
|---|---|---|---|---|---|---|---|
| Sources of funds | Federal government | Industry | Universities and colleges | Associated FFRDC's+ | Other nonprofit institutions | Total | Percent distri- sources |
| Federal government | $ 1,210 | $ 325 | $ 3,100 | $ 650 | $ 450 | $ 5,735 | 69.7 |
| Industry | -- | 1,000 | 125 | -- | 95 | 1,220 | 14.8 |
| Universities and colleges | -- | -- | 785 | -- | -- | 785 | 9.9 |
| Other nonprofit institutions | -- | -- | 265 | -- | 225 | 490 | 6.0 |
| TOTAL | $ 1,210 | $ 1,325 | $ 4,275 | $ 650 | $ 770 | $8,230 | |
| Percent distribution, performers | 14.7 | 16.1 | 51.9 | 7.9 | 9.4 | | 100.0 |

+ Federally funded research and development centers.

Source: *National Patterns of Science and Technology 1980*, NSF 80-308.

## TABLE IV-4

Universities Responding to Questionnaire on Polymer Program

---

Akron, University of
Carnegie-Mellon University
Case Western Reserve University
Cincinnati, University of
Delaware, University of
Florida, University of
Lowell, University of
Massachusetts, University of
Massachusetts Institute of Technology
Michigan, University of
Pennsylvania State University
Polytechnic Institute of New York
Princeton University
Rensselaer Polytechnic Institute
Southern Mississippi, University of
Utah, University of
Virginia Polytechnic Institute

TABLE IV-5

U.S. Contributions to Polymer Preprints, 1979-1980

| Industrial | Academic | Institute | Government | Other | Total |
|---|---|---|---|---|---|
| 206 | 307 | 36 | 29 | 6 | 584 |

### TABLE IV-6

### Numbers of Papers Presented at the Annual Meeting of The Society of Polymer Science, Japan

(Percentages of totals in parentheses)

| | 1968 | 1972 | 1975 | 1978 |
|---|---|---|---|---|
| Major national universities | 212 ( 36) | 209 ( 33) | 195 ( 32) | 245 ( 32) |
| Other national universities | 112 ( 19) | 152 ( 24) | 198 ( 33) | 226 ( 30) |
| Private universities | 60 ( 10) | 82 ( 13) | 74 ( 12) | 96 ( 13) |
| Municipal universities | 23 ( 4) | 18 ( 3) | 19 ( 3) | 30 ( 4) |
| National government institutions | 57 ( 10) | 72 ( 11) | 60 ( 10) | 59 ( 8) |
| Private corporations | 124 ( 21) | 92 ( 14) | 58 ( 10) | 73 ( 9) |
| Foreign universities | 3 (0.5) | 3 (0.5) | 3 (0.5) | 21 ( 3) |
| Vocational colleges | 1 (0.2) | 7 (1.1) | 2 (0.3) | 11 (1.5) |
| TOTAL | 592 (100) | 635 (100) | 609 (100) | 761 (100) |

TABLE IV-7

Attendance at Polymer-Related Gordon Research Conferences, 1979

| | Percent of total | | |
|---|---|---|---|
| | Academic | Government | Industry |
| Polymer colloids | 33.7 | 0 | 66.3 |
| Polymers (Eastern Conference) | 30.6 | 6.9 | 62.5 |
| Fiber science | 26.8 | 3.1 | 70.1 |
| Ion-containing polymers | 25.8 | 3.9 | 70.3 |
| Polymers (Western Conference) | 24.7 | 17.8 | 57.5 |
| Elastomers | 21.1 | 2.6 | 76.3 |
| Coatings and fibers | 13.6 | 2.9 | 83.5 |

Another mechanism provides university-industry linkage through Cooperative Research Centers. The Centers generally involve a single university, with six to twelve private-sector companies acting as cosponsors of the research. Among the centers that have been established in the polymer field is one at Massachusetts Institute of Technology, dealing with polymer processing programs, and one at the Center of University of Massachusetts--Industry Research in Polymers, dealing with the preparations and properties of solid polymers. Case Western Reserve University, with NSF financial assistance, is studying the establishment of another such center in polymer science or engineering.

The University of Michigan has a Macromolecular Research Center with research support from twenty-six industrial sponsors, besides research funding of individual faculty projects by federal and private agencies. The University of Akron and the Polytechnic Institute of New York are among other institutions with long histories of support from, and strong interaction with, industry in polymer research.

It is difficult to judge the magnitude of the basic research effort on polymers in industry. If judged by the number of publications, the effort must be relatively small. Table IV-5, however, shows a survey of Polymer Reprints of the American Chemical Society's Division of Polymer Science for 1979 and 1980. Thirty-five percent of the papers presented were from industry.

In Japan one must conclude that almost all the basic research on polymers is performed in universities, because only nine percent of the papers presented at the annual meeting of the Society of Polymer Science, in 1978 were from industry (table IV-6).

It is also instructive to look at the attendance at polymer-related Gordon Research Conferences (table IV-7). Although a high percentage of the speakers at these conferences come from universities, the attendance figures indicate an interaction between academic and industrial polymer scientists and engineers considerably above that indicated by the average attendance from industry at the conferences in many other fields.

## 5. Patents

Innovation takes in the complete gamut of activities from inception of a new idea through commercialization of the new material or process. The chemical industry is particularly sensitive to the issue of proprietary rights because of the large sums of money that must be spent in commercialization--in development and plant investment. A company is not likely to proceed into commercial development unless it has proprietary rights to the material or process.

Therefore, if a discovery of potential commercial significance were made in the course of a basic research investigation, it would probably not be pursued far enough to demonstrate commercial viability if the company did not have proprietary rights to the invention. This situation accounts in large part for the singular lack of success in commercializing chemical inventions that are in the public domain. It also presents a barrier to interactions between industry and the universities. Where joint programs do exist, they tend to be in fundamental areas not likely to generate new products in the near term. An important exception, possibly, is the case of a small company specializing in high technology. Here only a small industrial R&D organization and facilities may be required if augmented with university-supported research and analytical facilities. A university patent policy giving such small companies at least first-refusal rights to licensing might go far towards fostering basic research that could be mutually beneficial.

## 6. Types of Industry-University Interactions

A recent article by D. Prager and G. Ommen, "Research, Innovation, and University-Industry Linkages," Science, vol. 207 (1980), p. 379, has summarized the types of university-industry relationships (table IV-8).

The point is made that the industrial share of basic research spending has declined and the proportion of in-house R&D budgets allocated to basic research has dropped dramatically. Since the key to effective interaction between universities and industry is scientist-to-scientist contact on research matters of common interest, the gradual decline in industrially performed basic research has probably decreased such contacts and impeded university-industry relations.

In polymer science and engineering, the university-industry relationship started at a much higher level than in chemistry, for example. Apparently this interaction is still much higher than the norm for industry and is now increasing.

## TABLE IV-8

## Types of University-Industry Relationships

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### CORPORATE CONTRIBUTIONS TO UNIVERSITY

Undirected corporate gifts to university fund.

Capital contributions: gifts to specific departments, centers, or laboratories for construction, renovation, equipment.

Industrial fellowships: contributions to specific departments, centers, laboratories as fellowships for graduate students.

### PROCUREMENT OF SERVICES

By university from industry: prototype development, fabrication, testing; on-the-job training and experience for students; thesis topics and advisers; specialized training.

By industry from university: education and training of employees (degree programs, specialized training, continuing education); contract research and testing; consulting services on specific technical management problems.

Industrial associates: single university; usually multiple companies; industry pays fee to university to have access to total resources of university.

### COOPERATIVE RESEARCH

Cooperative research projects: direct cooperation between university and industry scientists on project of mutual interest; usually basic, non-proprietary research. No money changes hands; each sector pays salaries of own scientists. May involve temporary transfers of personnel for conduct of reseach.

Cooperative research programs: industry support of portion of university research project (balance paid by university, private foundation, government); results of special interest to company; variable amount of actual interaction.

Research consortia: single university, multiple companies; basic and applied research on generic problem of special interest to entire industry; industry receives special reports, briefings, and access to facilities, for example.

### RESEARCH PARTNERSHIPS

Joint planning, implementation and evaluation of significant, long-term research program of mutual interest and benefit: specific, detailed contractual arrangement governing relationship; both parties contribute substantively to research enterprise.

# V. EDUCATION IN POLYMER SCIENCE AND ENGINEERING

In view of the impact of polymers on the economy, health, and daily life, and in view of the strong intellectual basis of progress in this field, the Panel perceives opportunities in education regarding the nature of polymers that go beyond existing patterns and programs. The careers of many professional scientists and engineers include work with large molecules. Formal education in the concepts and methods of this broad field should, therefore, be a significant aspect of their training.

Have these scientific challenges, national concerns, and professional requirements been adequately recognized in the academic community? Academic institutions are increasingly accepting this young field. However, given its vitality, much greater incorporation and emphasis seems appropriate. The Panel is concerned about the adequacy of the present role of U.S. universities in disseminating knowledge relating to polymers, in training sufficient numbers of scientists and engineers with broad knowledge of the field, and in supporting polymer research.

In this chapter the educational and academic research picture will be described more fully. There are areas in which progress can be reported. Academic engineering programs have included polymer topics, courses, and research,[1] and biochemistry programs naturally deal with biopolymers and associated polymer concepts. On the other hand, students of chemistry and physics at many leading universities receive little or no exposure to polymer science. The Panel considers this situation to be of serious national concern. Modest and attainable steps are proposed to stimulate progress in securing a proper balance.

## 1. Polymer Education at American Universities

In the United States the study of synthetic polymers generally started in industry, and the industrial contribution remains strong today. Universities began to be involved in the late 1940's, with teaching and research activities clustered around a few renowned individuals. University interest has grown steadily, but has not kept pace with the rapid development of the field. In a 1980 survey the Plastics Institute of America summarized polymer-related curricula in thirty-nine U.S. universities that offer undergraduate and/or graduate majors in polymer science and engineering.[2] Many other universities have courses, research, and faculty members concerned partly or entirely with polymers. Even so, the acceptance of polymer science as an academic field of study has been uneven, and much remains to be accomplished, particularly in chemistry and physics departments.

Some impediments to acceptance in universities may be noted. Nucleation of any new activity to form a viable program is difficult. Uncertainty and risk are involved, and faculty may not be available from traditional university sources (i.e., other universities). Furthermore, the great technical strides made with polymers in industry created a large body of unpublished knowledge, much of it proprietary, which may have impeded entry into the field by established faculty members.

The multidisciplinary aspect of the field has also inhibited university focus. The science of polymers is connected with chemistry; physics; biochemistry and molecular biology; and chemical, materials, and mechanical engineering. This diversity leaves unclear the natural place of polymers in the academic curriculum. The various scientific and engineering disciplines bring different orientations to the field--continuum vs. molecular approaches, complex vs. simple molecules, laboratory vs. industrial scale--and these complement each other. Thus, it is desirable to have investigators from different disciplines converge on the problems of macromolecules, rather than to have all polymer workers trained in the same manner.

Polymer education and research have received attention in American universitiesin complex ways. The study of macromolecules has been incorporated into the fabric of biochemistry and molecular biology. Modern research techniques have provided a growing understanding of the size, structure, and specificity of reaction of biologically important molecules. These developments have fostered increased interaction among the biological chemists with the organic and inorganic chemists who synthesize large molecules, and the physical chemists who characterize their structures and rationalize their properties. Courses in biochemistry deal routinely with aspects of polymer science, and research on polymers of biological interest is conducted at many universities.

Because of their bearing on biomedical research, biochemistry and molecular biology are generally funded at much higher levels than polymer science and engineering. This circumstance results in support for biomedically related polymer studies, but little support for other polymer studies. Thus, it is important that a balance be maintained at the universities in the emphasis on the biological and synthetic branches of the polymer field. Communication between these branches must also be encouraged.

Chemical engineering departments evidence a healthy interest in polymers, especially during the past 15 years. A 1980 survey by Peppas[1] shows that 73 percent of 94 departments replying offer at least one course in the polymer area, and these courses are attracting students. The chemical engineering departments average 2.2 faculty members doing research on polymers and 1.8 teaching courses in this field. Unfortunately, the polymer field shares in the general shortage of chemical engineers, especially Ph.D.'s.

Other engineering departments are also devoting some attention to rheology and strength of polymers, strength of composites, and related topics. Departments of mechanical engineering, metallurgical engineering, theoretical and applied mechanics, materials engineering, and ceramic engineering can be found that offer courses and research in polymers.

Materials science departments now exist on many university campuses. It is beyond the scope of this report to recapitulate the history of these departments, which have developed rapidly over the past two decades. It is fair to say, however, that materials science today places strong emphasis on metallurgy and the inorganic solid state. One may still achieve an advanced degree in some departments of materials science with virtually no exposure to polymer science. Materials science textbooks usually treat polymers superficially. However, there is a trend, which should be encouraged, towards more balanced metal-ceramic-polymer materials science programs and departments.

Materials Research Laboratories at twenty universities comprise a group of interdisciplinary research centers established with federal support beginning in the 1960's. They do not usually grant specialized degrees. Although basic polymer research is the major activity at two of these laboratories (at the University of Massachusetts and at Case Western Reserve University), polymer funding is only a small fraction of the total. Of the approximately $20 million budgeted in FY 1980 by the National Science Foundation for direct support of the Materials Research Laboratories, about 10 percent was in support of polymer research. The support from outside of NSF is not expected to be more favorable. The Panel believes that Materials Research Laboratory funding is seriously out of balance in regard to polymer research.

Multidisciplinary fields are creating much excitement among physical scientists, and the field of polymers is among these. Conducting polymers, glasses, and theory of polymer behavior, in particular, have stimulated growing interest in polymers in the physics community. Though the trend is encouraging, the total involvement of physicists with polymers is still minute in comparison with what they might contribute to this branch of condensed state physics. The earlier lack ofattention of physicists to large and complex molecules may account for the fact that studies of conducting polymers and of neutron scattering from polymers have only recently burgeoned.

A basic component of the mix of disciplines entering into the study of polymers is chemistry. The synthesis, reactions, and stability of these materials, emphasized in chapter II, part A, are almost exclusively the province of organic chemists. Training in physical chemistry is called for in attacking many of the structure-property problems described in chapter II, part B. The extent to which chemists contribute to university polymer research is suggested in table V-1, which shows that about 40 percent of NSF Polymers Program grants go to principal investigators in chemistry departments. Yet polymers represent only a small fraction of academic chemistry research and

## TABLE V-1

### Department Affiliation of Principal Investigator for NSF Polymers Program* Grants to Universities (1980)

| Department | Percentage of Total |
|---|---|
| Chemistry | 40 |
| Polymer Science | 19 |
| Materials Science | 16 |
| Chemical Engineering | 14 |
| Physics | 3 |
| Others | 8 |

* The Polymers Program is providing about 44 percent of the total NSF support for research in polymer science and engineering.

education, mainly concentrated at a few universities. Most chemistry departments do not offer any course in polymers at any level.

To document the situation in chemistry departments, the Panel has surveyed research interest in polymers as indicated in the American Chemical Society's Directory of Graduate Research, 1979.[3] Only 3 percent of the chemistry department members listed include polymers among their research interests, and two-thirds of the departments have not a single member expressing interest in that field. About 17 percent of the chemical engineering department members indicate interest in polymer research.

Among the 20 highest rated graduate chemistry departments, according to The Gourman Report,[4] including 666 full-time faculty members and awarding 34 percent of the Ph.D. degrees in chemistry in 1978-1979, the figures are even more depressing. Only 12 (1.8 percent) of their faculty members express research interest in synthetic polymers, and 15 of the departments have no member interested in nonbiological macromolecules. A further 63 members (9.5 percent) express research interest in the biochemical field with emphasis on biopolymers. Of course, this field is covered by independent biochemistry departments as well. Admittedly, in a few of the universities involved, synthetic polymers are included in the curricula of other departments; but the contribution to polymer research and education by the leading chemistry departments is singularly deficient.

To complete the picture of the current state of academic polymer research and education, special note must be taken of the role played by a number of institutions that have developed major programs in polymer science and engineering and grant special degrees either within traditional departments or through a polymer department. Much fundamental research flows from this source, and Table V-1 shows that 19 percent of the NSF Polymers Program grants have principal investigators in polymer science departments.

Representation of polymer education in U.S. universities thus spans a wide spectrum. In a few the faculty has been organized into a group or department with responsibility for doctoral programs in the polymer field; alternatively, an academic polymer program may be fostered by interdisciplinary exchange. Seventeen universities offer Ph.D. programs in polymer science. At the other extreme some major universities have no faculty members involved in polymer teaching or research. In between are universities with one or a few faculty members interested and active in polymer studies, but without a formal program, and the Ph.D. degree may be identified with one of the traditional disciplines. Courses on polymer topics are usually offered in these intermediate situations.

The structure appropriate to a given university depends on the nature and goals of the institution, the inclinations and personalities of the faculty, and the social environment of the area. The Panel does not recommend any particular format, but wishes to record some of the advantages cited by advocates of the various forms of association.

An organization of faculty provides a means of exchanging ideas, sharing major instrumental resources, and attracting distinguished visitors and lecturers. It also helps convey to the student the multidisciplinary nature of polymer studies, and perhaps may encourage taking courses in other departments. On a given campus, where the nucleus of faculty members active in polymer research is small, some form of association with neighboring schools may prove valuable. Industrial laboratories could be considered for participation. An independent, degree-granting department can offer the advantages of autonomy in finances, selection of faculty, and program development. Further advantages claimed are nucleation of a superior faculty, enhanced interactions among the professors and among their students, an educational program balanced between general and polymer subjects, and recognition of the multidisciplinary aspect of the field, even within a single course.

On the other hand, different advantages are claimed for the distribution of polymer studies in the traditional disciplines. This provides a greater opportunity to attract into the polymer area students who have not made that commitment before entering graduate school. It trains students in greater depth in a conventional discipline, which they can then bring to bear on polymer problems. With conventional departmental structure, faculty interactions with other subdisciplines are enhanced, and the techniques being developed by a colleague may suggest polymer applications. Fellow departmental members may be attracted to turn a part of their talents toward macromolecular problems, possibly cooperatively; and, in general, a person with diverse interests can move easily into and out of the polymer area.

Some chemistry faculties have perceived the importance of macromolecular science and sought to acquire qualified members, only to find that candidates are difficult to locate and attract. This is a serious problem for which the Panel sees no solution within existing university procedures. The universities with strong traditional programs tend to attract the best students, and new faculty members tend to be drawn from a select subgroup of these individuals as they graduate. Since polymer work is weakly represented, there are few candidates to break into the pattern. A further limitation arises in fierce competition from industry to employ the most gifted graduates in the polymer field. Many feel that industry is "consuming its own seed corn" in this area.

A strong case can be made for polymer education. In recent reports many authors have noted that large fractions of chemists and chemical engineers affiliated with industry are working on polymer-related problems.[5] It is not easy to obtain a precise figure because of the lack of data base, and the difficulty of categorizing professional activity. In an effort to provide some quantitative measure, we have counted in American Men and Women of Science[6] all chemists who list research activities strongly related to polymers. Of the 14,461 chemists in industry, 30 percent work in the polymer field. We regard this as a lower limit of all industrial chemists, because American Men and Women of Science tends to deemphasize certain development and production activities in which polymer chemists are heavily engaged. The clear conclusion is that a very significant fraction of industrial chemists (and probably chemical engineers) work in polymer areas. (A parallel study of academic chemists shows that 8.4 percent of 10,462 work on polymer problems.)

Graduates with a background in polymers are in very strong demand. At the National Clearing Houses held at American Chemical Society meetings, polymers chemists are widely sought; along with analytical and organic chemistry, they lead the list of subdisciplines.

One hears the proposition that a scientist or engineer with a sound grounding in the fundamentals of his or her subject can readily adapt to work in the polymer field. But as can be seen from chapter II, there are many aspects of the polymer subject today that are neither included nor sufficiently emphasized in the core curricula--the stabilization of organic molecules, the glassy state, viscoelastic materials, and the mechanisms of protein folding--to name only a few topics. Many of these topics are of interest beyond the polymer field, and today could well be considered as proper material for the core curricula. They are subjects difficult to master by self-study, particularly because of the interdisciplinary aspect of macromolecular studies.

Much research and development involving macromolecules is carried out in industry. Because of a scarcity of graduates with training in polymer science, industry seeks additional training for a rather large number of people. In response to this need many short courses have been created by professional societies, universities, and private enterprises. For example, of the 60 current American Chemical Society short courses, 11 deal directly with polymers. The Plastics Institute of America offers 20 short courses, while the Society of Plastics Engineers offers 41. Standard university courses are also open to nonmatriculating students from industry. Although these efforts are laudable, they do not meet the exigency for more general, broadly based training, in which macromolecular science is recognized as an active component of contemporary physical science and engineering.

The pros and cons here delineated will never be resolved in an inclusive way; a multiplicity of approaches is implied. The Panel is unanimous, however, on the need for programs and actions that will augment the present representation of polymer studies in the universities and enhance their quality. The intellectual challenges and practical dividends treated at length in chapter II and the relevance of polymers to national needs summarized in chapter III warrant attention by the academic community and interest on the part of the funding agencies.

## 2. Polymer Education in Other Nations

Education in polymer science and engineering in other nations is varied and the science aspect is most prominent.[7] In the technologically highly developed nations of Western Europe, Japan, the Soviet Union, and Israel, good educational programs exist in polymer science. It can be stated, with some valid exceptions, that in the United States more emphasis is placed on education "in breadth," while in Europe and Japan there is more emphasis on education "in depth."

Probably the most comprehensive polymer education program is in the Soviet Union. In Eastern Europe some form of polymer science is a compulsory feature of chemical education. During the past 20 years, most chemistry departments in the USSR have had an obligation to include theory and application of polymer science in their curricula on a level with other subdisciplines. The Lomonosoff Moscow State University provides probably the most comprehensive education in polymer science and technology, not only through lecture courses but also through good laboratory courses. Polymer training is also available in a number of Academy Institutes in Moscow, Leningrad, and elsewhere. As further evidence of recognition, four polymer scientists in the main stream of research are now full members, and a number of others are corresponding members, of the Soviet Academy of Sciences. The situation in polymer rheology and engineering is comparable, with a number of specific chairs in these disciplines, too.

In West Germany the historical tradition associated with the birth of polymer science is still felt. Training in polymers is primarily through research, such as the large program at Mainz-Darmstadt, involving over 200 scientists. There are full chairs at about nine institutions. Polymer physics is a recognized and active discipline. This came about, as Kausch and Bonart write, when it was recognized that "considering the industrial needs and the technological importance of polymeric materials, there was until the early 1960's a definite numerical underrepresentation of polymer physics in the universities. Then, a successful campaign led to the establishment of polymer groups at one-half of the 26 existing and at some 10 newly founded schools."[8]

In France there are at least six universities with a major component of polymer science, especially in those where a Laboratory of the National Center of Scientific Research is attached to the university or is located adjacent to University Institutes. Here again, the education is by supervision of graduate students in polymer chemistry and/or polymer physics, with relatively less emphasis on the polymer engineering aspects. In at least one case a school of high polymers is attached to a university where students are trained in chemical engineering. The strength of polymer studies in France is perhaps associated with the renown of its scientists in this field, and spectacular successes in small-angle neutron scattering and theory have sparked a broad interest.

In the United Kingdom polymer science education is diversified in chemistry, physics, engineering, and polymer departments, again primarily on the graduate level. Education is by graduate student supervision, sometimes with graduate level courses backing up this effort. The development of schools of training in polymer science depends much on the interests of individual professors, who on retirement may or may not be replaced by a person active in polymer science. It is worth noting that the last two chairmen of the Science Research Council have been polymer scientists.

Some concern about the general dissemination of polymer education was expressed in a 1978 report of the UNESCO European Experts Committee on Polymer Science, Industry, and Environment, where it is noted that:

> ....in Western Europe, many, if not most, chemists can graduate without receiving any formal education in polymer science. It was recognized that the greater part of the chemical industry throughout Europe is concerned with the manufacture and processing of polymers, and moreover that the rapidly developing life-sciences are increasingly involved with the elucidation of processes in which macromolecules are of vital importance. For these reasons, it was unanimously agreed that it is essential to include polymer science in the undergraduate curriculum for all students of chemistry and chemical engineering. The committee therefore recommends to the relevant authorities and to UNESCO that at least 40 hours of lectures should be dedicated to polymer science for all such students and that the syllabus should comprise:
>
> 1) Polymer synthesis and reactions
> 2) Polymer characterization (in the solid state and in solution)
> 3) Physical and mechanical properties of polymers.[9]

The development of polymer education in Japan was sparked by the Education Act of 1949, when the education system was reorganized and polymer science and technology received a prominent place. The subject typically enters the chemistry syllabus in the third and fourth year. Several institutions have international reputations, including Kyoto, Kyushu, Nagoya, Osaka, Sapporo, Tohuku, and Tokyo Universities as well as the Institutes of Technology at Tokyo and Nagoya. At Kyoto at least sixteen professors are identified with polymer interests, and at Sapporo seventeen electives are offered in the polymer field. Polymer training is carried out primarily in the research group, in which advanced undergraduates and graduate students work together under supervision of Instructors and Assistant Professors. Through the professor, university research groups in Japan cooperate closely with industry. Industry frequently accepts scientists with master's degrees, dispatching promising people to the University to complete their doctoral degrees.

## 3. A Program for Education in Polymers

The Panel suggests that education in polymer science and engineering should address two needs: dissemination of knowledge about the nature of polymers to science and engineering students in general, and wider opportunity for specialization in the polymer field.

In view of the relevance of macromolecules to biochemistry; molecular biology; chemical, mechanical, and materials engineering; chemistry; and physics, it is important that all students in these fields have some familiarity with polymers at the undergraduate level. A significant step in this direction would be to incorporate polymeric topics into the basic curricula as sections of traditional courses: stereospecific polymerization in organic chemistry, viscoelastic rheology in fluid dynamics, the glassy state in materials science and physical chemistry, polymer crystals in solid state physics, and so on. In addition, polymer concepts can be naturally introduced in examples and assigned problems: e.g., the temperature rise of a rubber band on stretching, the opening of double bonds in polymerization, and polymer conformations as examples of random walks.

Beyond the incorporation of polymer topics in existing core curricula, the Panel recommends that an introductory polymer course be made available as an advanced undergraduate option in universities that offer major programs in chemistry, physics, biochemistry, and materials or chemical engineering. The Panel reemphasizes here the message of chapter II: polymer research includes a large body of good science and engineering knowledge that goes considerably beyond the usual subject matter of traditional curricula, yet is quite fundamental and important. For help in constructing such a course, several excellent videotaped series are available, one being an innovative computer package offered by the American Chemical Society that includes simulated experiments.[10] Additional texts and other teaching materials would be useful. Furthermore, the Joint Education Committee of the American Chemical Society's Division of Polymer Chemistry and Division of Organic Coatings and Plastics Chemistry will send representatives to any institution to work with the faculty to incorporate polymer courses or topics into the curriculum. At the American Chemical Society's 181st National Meeting, March 29-April 3, 1981, in Atlanta, Georgia, a three-day Symposium, on "State of the Art for Chemical Educators: Polymer Chemistry," was organized jointly by the Division of Chemical Education, Inc., and the Division of Polymer Chemistry, Inc. The papers presented are to be published in a forthcoming special issue of the Journal of Chemical Education.

The American Chemical Society's Committee on Professional Training has recognized polymer chemistry in its guidelines, "Undergraduate Professional Education in Chemistry: Criteria and Evaluations Procedures."[11] After defining a recommended core of eight semesters of introductory, inorganic, organic, physical, and instrumental chemistry, the Committee goes on to speak about advanced electives as follows:

> In view of the current importance of inorganic chemistry, biochemistry, and polymer chemistry, advanced courses in these areas are especially recommended and students should be strongly encouraged to take one or more of them. Furthermore, the basic aspects of these three important areas should be included at some place in the core material.

The figures presented earlier indicate that the response to the polymer portion of this recommendation is not yet widespread. The Panel feels that major chemistry departments, in which a wide variety of electives at the senior-graduate level are taught, should offer all three recommended electives.

The course of action proposed herein requires adequately trained teachers. Specialists in the polymer field are the most obvious solution but suitable candidates may not be available or additional faculty openings may not exist. The Panel suggests that most faculty members can become qualified through self-instruction; the teaching aids previously mentioned are available. The problem of already crowded curricula is also difficult. The Panel suggests that polymer course offerings will compete well with other options if the interest and unique opportunities of the field are conveyed in earlier, standard courses.

Many students may wish to concentrate in polymer science or engineering at the graduate level, either to do thesis research on polymers or to prepare otherwise for employment in the polymer field. They should have a reasonable range of choices among universities at different locations, with different standards and styles. Proper preparation requires that they be able to take at least one graduate level course. A more adequate program would provide a variety of courses, possibly offered in several departments. Laboratory courses should not be ignored.

### 4. Funding of Polymer Research at the Universities

Research is an essential feature of graduate education, and a large art of the financial support for this activity comes the federal government. An estimate of $13.2 million in federal support for basic polymer research in universities in FY 1979 by various agencies is indicated in table V-2.

The Polymers Program of NSF is lodged in the Division of Materials Research, as is the program providing funds for the Materials Research Laboratories, mentioned previously. The Division's entire budget for FY 1979 was about $64 million. The budget for the polymers program in FY 1979 was $3.85 million. Additional support for basic polymer research of about $5 million was provided by other NSF programs. For comparison, federal support of basic research in chemistry at universities and colleges in FY 1979 was estimated to be about $114 million,[12] exclusive of industrial, and other support.

Academic research on polymers of biomedical interest receives further support, particularly from NIH. NIH support of basic polymer and biopolymer studies is difficult to estimate, but probably exceeds $5-6 million per year. This contributes importantly to progress in the field, as the discussion in Chapter II, section D, makes clear; but it does not compensate for a paucity of opportunity for students to acquire graduate education and research experience in more general aspects of polymer science and engineering.

In view of the importance of basic polymer reseach to national needs for which the various federal agencies are responsible (as outlined in chapter III), the Panel proposes that the funding agencies expand their programs to attract reasonable numbers of creative academic scientists and their students to work in that field. It is essential that polymer science and engineering be represented in many more universities where its relevance to the traditional disciplines is not now recognized. The future of this vital field in the United States is at stake.

TABLE V-2

Estimate of Federal Funds for Basic Polymer Research in Universities, 1979*

| Agency | $ in millions | Number of grants |
|---|---|---|
| National Science Foundation | 8.8 | 162 |
| Department of Defense | 3.4 | 73 |
| Department of Energy | 0.2 | 5 |
| Others (NASA, NIH, EPA, etc.) | 0.8 | 20 |
| TOTAL | 13.2 | 260 |

* N.M. Bikales, Director, Polymers Program, NSF; estimate does not include biopolymer and molecular biology research.

## 5. Conclusions and Recommendations

- Polymer concepts should be integrated into traditional courses in chemistry, biochemistry, physics, and mechanical, materials, and chemical engineering. Teachers in these fields should consider how progress in polymer science and engineering has contributed to, and been influenced by, progress in their respective disciplines, in order that their courses may be enriched by examples drawn from this large and diverse field.
- Introductory polymer courses should be included in chemistry, physics, chemical engineering, and materials science programs at the advanced undergraduate or beginning graduate level as an essential component of quality education for scientists and engineers.
- Academic centers offering graduate concentration in polymer research need to be increased in number in order that prospective students will have better choices among different specializations, institutional styles, and geographical locations.
- An effort is recommended, through enhanced educational and research support, to introduce polymer-related subjects in the programs of the many universities that do not offer this important educational opportunity.
- The Panel is unanimous in recognizing the urgency of increased commitment to basic polymer studies by the funding agencies. It recommends that the agencies examine their programs in the light of this report to ensure that their polymer science and engineering activities are commensurate with agency goals and the major needs and opportunities that exist in this field.
- Imaginative new programs of funding should be welcomed to stimulate diversification and enhanced quality in polymer education and research. These could include various forms of cooperation involving universities, industry, and government.

### References

[1] N. A. Peppas, "Teaching of Polymer Science and Engineering in Chemical Engineering Departments," (paper deliverd at American Institute of Chemical Engineers Meeting, Chicago, November 1980: to be published in *Chemical Engineering Education*.

[2] *Catalogue of Polymer Science and Engineering Programs, 1980-81*, Hoboken, NJ: Plastics Institute of America, 1980).

[3] *Directory of Graduate Research, 1979* (Washington, DC: American Chemical Society, 1979).

[4] J. Gourman, *The Gourman Report, Rating of Graduate and Professional Programs in American and International Universities* (National Education Standards, 1980).

[5] W. Bailey, *J. Chem. Ed.*, *45*, 500 (1968); C. Winding and P. Brodsky, *SPE J.*, *24*, 31 (1968); M. Morton, *Chem. Eng. News*, Aug. 14, 1972, p. 498; D. Chaney, "Employment Opportunities for Textile, Fiber, and Polymer Chemists," Amer. Chem. Soc. 164th Meeting, Aug. 28, 1972; P. Lindenmeyer, *Chem. Eng. News*, Nov. 18, 1974, p. 4; R. Deanin, *Plast. Eng.*, *30* (5), 55 (1974); R. L. Rawls, *Chem. Eng. News*, May 23, 1977, p. 19.

[6] *American Men and Women of Science*, ed. by Jaques Cattell Press (New York: R. R. Bowker Co., 1979)..R. Bowker Co., New York, 1979).

[7] Some information for this section was drawn from R. P. Sheldon, Education and Training in Polymer Science and Technology," report to the IUPAC Macromolecular Division, 1979, which contains greater detail.

[8] H. H. Kausch and R. Bonart, *J. Polym. Sci., Polym. Lett.*, *14*, 565 (1976).

[9] *Report of the European Experts Committee on Polymer Science, Industry, and Environment* , meeting organized by UNESCO and the University of Leuven, Leuven, Belgium, November 8-10, 1978.

[10] J. Pochan, H. Gibson, and S. Smith, *Introduction to Polymer Chemistry: An ACS Computer-Based Course* (Washington, DC: American Chemical Society.

[11] *Undergraduate Professional Education in Chemistry: Criteria and Evaluation Procedures*, (Washington, DC: American Chemical Society, 1977).

[12] *Federal Funds for Research and Development*,(Washington, DC: National Science Foundation, 1979).

# APPENDIX A

# CONTRIBUTORS

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