

Rational Design and Synthesis of New Polymeric Materials

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Polymers constitute one of the four main areas of materials science. Modern research in polymers focuses on the ways in which tailored macromolecules organize themselves in the solid state and on materials design and synthesis at the interface between polymer science and the fields of ceramics, metals, and electroactive or electro-optical materials.

THE DISCOVERY AND DEVELOPMENT OF NEW SUBSTANCES can ultimately improve the quality of life. Indeed, this is the cornerstone of requests to the public by the scientific, medical, and engineering communities for the financial support of long-range research. Chemists in particular, with their strong track record of successes in the synthesis of new polymers and pharmaceuticals, often assume that the design and development of synthetic pathways to new materials is the key step in the advancement of both science and technology.

The purpose of this article is to explain the precepts and methodology by which new polymeric materials may be designed and synthesized and to provide the general reader with an understanding of the vital role that this process plays in the development of new technology.

Underlying Concepts

Materials science is one of the main connecting points between chemistry and engineering, and it is the principal area through which researchers in the chemical disciplines can influence technology. The field of materials is one of the broadest and most diverse disciplines in science, spanning the four critical areas of polymers, ceramics, metals, and a broad array of electroactive and optically useful solids (Fig. 1). These different areas have developed in almost total isolation from each other, and even today they have different cultures, nomenclatures, and approaches to the development of new materials. However, in recent years it has become increasingly clear that some of the most interesting and potentially useful new materials lie between these classical areas and can be viewed as hybrid systems that occupy the region that connects the classical disciplines (Fig. 1).

The rationale behind the design of hybrid materials is that each of the classical materials has different advantages and disadvantages. For example, many polymers are tough, lightweight, and easy to fabricate but lack stability at high temperatures and very few are biocompatible. Ceramics are stable at high temperatures but are heavy, brittle, and often difficult to fabricate. Metals are strong and

conduct electricity but are heavy and prone to corrosion. Many inorganic semiconductors and superconductors lack strength and are difficult to fabricate. The objective of modern materials synthesis is to find ways to generate new combinations of properties at three levels—at the molecular level, at the materials level, and at surfaces.

The need for rational design in this field cannot be overemphasized. The unplanned discovery of new and valuable materials will always be one of the most exciting aspects of science; but the main need is to construct predictive schemes that allow molecular, solid-state, or surface structural changes to be used predictably to generate tailored properties. The main influence by chemists on materials science has been through the design and preparation of synthetic polymers. The development of structure-property correlations has been an inherent part of polymer synthesis for the past 50 years, and this approach underlies most of the successes in this field. Many of the lessons learned by polymer chemists have a broad applicability to materials science in general.

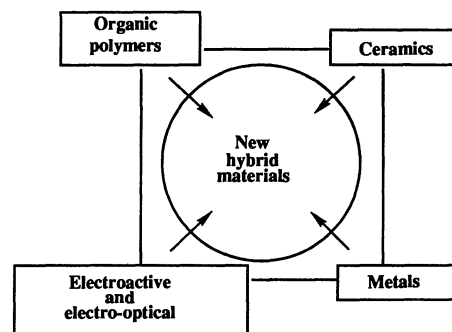
The Molecular Chemistry Approach

Principles. "Rational design" means that a knowledge of the relations between the properties and molecular structure of known molecules allows the scientist to design new molecules, with a fairly good expectation that the final product will have a predefined, tailored set of properties. These designs must, of course, be tempered by a knowledge of reaction chemistry and an awareness of the feasibility of developing new synthesis approaches. The principles of rational synthesis in polymer science are based on the following precepts.

1) Materials strength, toughness, or elasticity requires the presence of long macromolecular chains (typically at least 1000 atoms

Easily fabricated, strong, flexible, corrosion resistant, electrical insulating, and inexpensive, but thermo-oxidatively sensitive.

Inert, rigid, thermally stable, and often inexpensive, but heavy and brittle.



Vital for communications, but difficult to fabricate, and expensive.

Strong, usually inexpensive, and good electrical conductors, but heavy and prone to corrosion.

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Fig. 1. Advantages and disadvantages of types of materials.

per chain). Small molecules packed in crystals or randomly oriented in glasses do not provide these characteristics.

2) Changes in the side groups attached to a polymer chain bring about dramatic changes in materials properties. Thus, poly(vinyl alcohol) and poly(acrylic acid) are soluble in aqueous media, but polystyrene is not. Organic polymers with fluorine as a side group are generally more thermo-oxidatively stable, less soluble in common organic solvents, and more hydrophobic than their counterparts with hydrogen as a side unit, and so on. Enough experience has now been gained that reasonable predictions can be made of the properties of new polymers before they are synthesized, based on side-group-property correlations (1).

3) Changes in the backbone structure of an organic polymer bring about remarkable changes in properties. For example, replacement of the $-\text{CH}_2-\text{CH}_2-$ skeletal repeat structure in polyethylene by the $-\text{CH}=\text{CH}-$ structure in polyacetylene converts a colorless electrical insulator into a silver-colored conductive "polymeric metal." The replacement of aliphatic chain residues in a polymer by benzenoid rings increases the chain stiffness and leads to materials with high strength and dimensional stability (the so-called "engineering plastics") and may also generate electrical conductivity or nonlinear optical behavior. The presence of double-strand chains (ladder polymers) built from benzenoid or heterocyclic rings leads to high-temperature stability and high-strength materials. Finally, replacement of the $-\text{CH}_2-\text{CH}_2-$ structure in polyethylene by the $-\text{OCH}_2\text{C}(\text{O})-$ structure in poly(glycolic acid) sensitizes the system to hydrolysis and biological erosion and allows uses in synthetic surgical sutures and other medical devices.

4) The replacement of carbon as a skeletal element by inorganic elements such as silicon or phosphorus increases the thermo-oxidative stability, alters the chain flexibility and photolytic behavior, and leads to materials that form a halfway stage between classical polymers and ceramics or metals (2). Sulfur-nitrogen chains are metal-level electrical conductors at room temperature and are superconductors at <0.3 K. Polymers with silicon and carbon or silicon and nitrogen in the backbone are film- or fiber-forming precursors for pyrolysis to silicon carbide or silicon nitride ceramics.

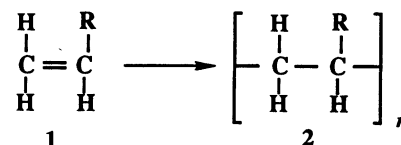
The examples of electroactive polymers, thermo-oxidatively resistant macromolecules, and preceramic polymers illustrate how experts in polymer synthesis, using structure-property correlations, have been edging across the central zone in Fig. 1 toward the fields of ceramics, metals, and semiconductors.

Polymer chemists now have an impressive database of molecular structure-property relations, so that it may seem that the development of new, precisely tailored polymers is a relatively straightforward exercise. However, it is much easier to design a new molecule than to find reaction pathways to its synthesis, and thereby lies the main hurdle that has to be overcome. The following examples illustrate two approaches to the rational synthesis of new polymers.

Rational polymer synthesis through choice of monomers. This is the classical method by which new polymers have been designed and synthesized since the 1940s. The approach is based on the knowledge that certain side groups generate specific solubility or solid-state properties. Small-molecule "monomers" can be produced from petrochemicals with specific property-generating groups attached to them, and the monomers are polymerized to macromolecules that bear these same groups as side units or as part of the main chain. This approach is illustrated most readily for polymers made by addition polymerization, although it applies equally well to those made by the two other main methods of condensation and ring-opening polymerization (1) (Scheme 1). Thus, the synthesis of an

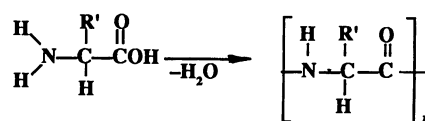
addition polymer begins with an unsaturated monomer, as shown in the conversion of 1 to 2. In 1 and 2, the side groups R can be varied from H (in polyethylene) to CH_3 (polypropylene), C_6H_5 (polystyrene), Cl [poly(vinyl chloride)], F, CN, COOH , $-\text{C}(\text{O})\text{OR}$, and so on.

Scheme 1
Addition polymerization

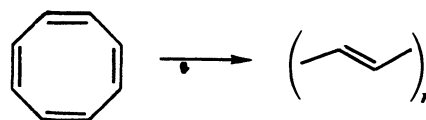


R includes H, CH_3 , C_6H_5 , F, Cl, $\text{C}\equiv\text{N}$, COOH , and COR'

Condensation polymerization



Ring-opening polymerization

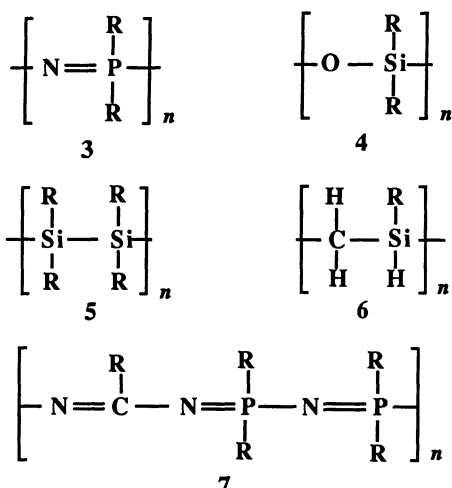


Thus, property variations in petrochemical polymers are achieved: (i) by changing the side groups in the monomer; (ii) by changing the type of monomer and the mode of polymerization to introduce backbone units that have different flexibilities, for example, by the introduction of $-\text{C}-\text{O}-$ or $-\text{C}(\text{O})-\text{N}-$ repeating units in place of $-\text{C}-\text{C}-$; (iii) by copolymerizing two or more different monomers to yield polymers with two or more different types of side groups; and (iv) by the use of polymerization catalysts (initiators) that yield polymers with specific chain lengths or precisely tailored side-group arrangements (3).

The success of this approach has been one of the major triumphs of the chemical sciences. It has had an enormous impact on technology and everyday life and should continue to do so. However, one of the main challenges is to devise new polymerization methods that yield polymers with precisely defined stereochemistries, comonomer arrangements, and chain lengths.

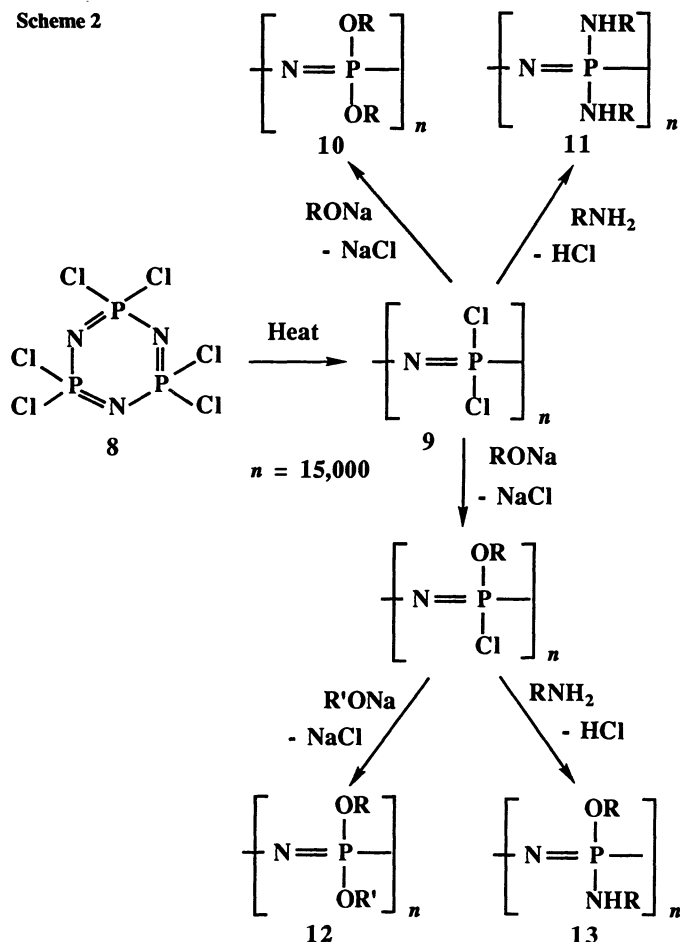
An inorganic polymer backbone with side group diversity generated by macromolecular substitution. An alternative approach to rational polymer synthesis is based on chemical reactions carried out on a preformed macromolecule. The most highly developed utilization of this method is in the relatively new field of polyphosphazenes, which are long chain polymers with a backbone of alternating phosphorus and nitrogen atoms and with two organic, organometallic, or inorganic side groups attached to each phosphorus (3). They form part of a growing class of hybrid inorganic-organic polymers, which includes the polysiloxanes (silicones) (4), polysilanes (5), poly(carbosilanes) (6), and poly(carbophosphazenes) (7).

The main method for the tailored synthesis of polyphosphazenes (10–13) is the pathway developed in my research group (4, 5) (Scheme 2). It involves first a ring-opening polymerization of a cyclic six-membered inorganic ring (8) to give a reactive macromolecular intermediate (9), followed by replacement of the chlorine atoms in 9 by reactions with a wide variety of organic, organome-



tallic, or inorganic reagents. Although macromolecular substitution reactions are known for classical organic backbone polymers, the very high reactivity of P-Cl bonds means that the reactions of **9** can be rapid and complete. Moreover, the macromolecular substitution step can take place in two stages (6-10), which allows combinations of two or more different side groups to be introduced into each polymer molecule.

Scheme 2



The main point to be emphasized is this: Changes in the side groups result in extensive changes in the materials properties. Because different side groups can be introduced so readily in this system without altering the nature of the chain or the length of the

backbone, broad opportunities exist for correlating molecular structure with properties and thereby for building a scheme for rational materials design. Approximately 300 different types of polyphosphazenes are now known, but only a few selected examples are mentioned here to illustrate general principles.

The introduction of aryloxy or fluoroalkoxy side groups generates microcrystalline materials not unlike polyethylene or polytetrafluoroethylene (Teflon) in properties, but resistant to burning and, in the case of the fluoroalkoxy derivatives, more readily fabricated into films or fibers than Teflon or related polymers. Polymers with mixtures of two or more of these side groups are oil- or flame-resistant elastomers, often with surprisingly high flexibility at low temperatures (6-10). Such elastomers are manufactured commercially for use in aerospace, medical, and other advanced applications (10). Polymers with inflexible polyaromatic or aromatic azo side units yield solids with liquid crystalline (11, 12) or nonlinear-optical properties (13), or with structurally tuneable refractive indexes (14).

Species with ferrocene side groups are electroactive solids (15). Polyphosphazenes with borazine side groups can be pyrolyzed to boron-nitrogen-phosphorus ceramics or to boron nitride. A wide range of phosphazene polymers show valuable properties as inert biomedical materials, hydrogels, microencapsulation materials for mammalian cells, or as bioerodible materials (16). The development of structure-property correlations in this system allows specific combinations of properties to be built into each polymer and forms the basis for rational materials design.

The Materials Processing Approach

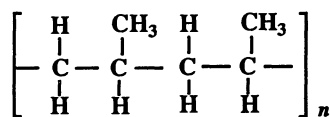
Materials science is really solid-state science. The approach of the polymer chemist revolves around the rational design and synthesis of molecules. However, the way in which those molecules are assembled in the solid state may have an equal or greater influence on the materials properties.

The materials processing approach has traditionally been the province of materials engineers, ceramics scientists, physicists, and metallurgists. For example, the properties of metal alloys or ceramics are highly dependent on domain structure, grain boundaries, and other phenomena of the solid state. Rational design is more difficult in this area because the simplifying factor of the discrete molecule no longer pertains, and aspects such as the thermal history of the material, pressure, or the exact sequence of the processing steps may alter the solid-state properties considerably.

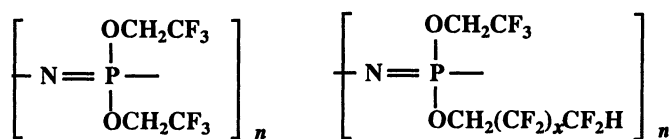
Perhaps the closest one can come at present to tailored synthesis at the materials level is by the incorporation of discrete, well-characterized molecules into solids, followed by an examination of the ways in which those molecules assemble into a solid-state structure, or how they react with each other in the solid or semisolid states. The following examples illustrate the way in which this applies to polymeric materials.

Materials structure and properties influenced by molecular self-assembly. An obvious example of materials character being controlled by molecular structure involves the way in which polymer chains and their side groups assemble themselves in the solid state. No reaction chemistry is involved—just an organization of the molecules based on nonbonding intermolecular forces. Amorphous polymeric materials are formed by the random entanglement of long polymer chains. Such materials may be elastomers or transparent glasses, depending on the flexibility of the polymer molecules. However, some macromolecules, especially those that bear side groups arrayed

in a highly regular manner along the backbone, may organize themselves into ordered parallel arrays in the form of microcrystallites. These polymers differ from their disordered counterparts in that they have less flexibility, higher load-bearing capacity, good fiber-forming qualities, opalescent or opaque optical properties, and sometimes electrical conductivity. This amorphous or crystalline character can be tailored into the system starting at the molecular level by the choice of monomer, the method of polymerization, or through macromolecular side group substitutions.



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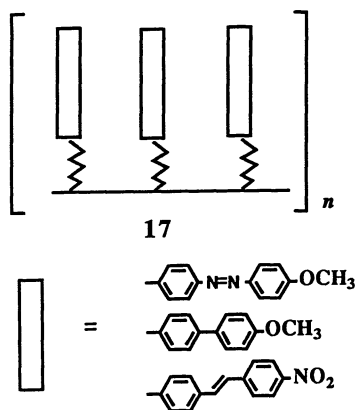


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16

Consider the case of polypropylene (14). The methyl side groups can occupy two different configurational positions along the chain—cis to the neighbors or trans (17). If they are all cis or all trans the polymer molecules have sufficient symmetry to allow ordered close packing of chains and the formation of microcrystallites. This is the case for commercial polypropylene, where the methyl groups are all cis. The modification with random cis and trans configurations is a gum. Similar principles hold for the polyphosphazenes shown as 15 and 16. Structure 15 has molecular symmetry and crystallizes in the solid state to give materials that are excellent formers of films and fibers. Modification 16, in which the presence of two different side groups disposed randomly along the chain prevents crystallization, is an amorphous, low-temperature elastomer.

The control of materials structure through the polymer side groups can be refined further. The linkage of rigid elongated or discoid side groups to a polymer chain is illustrated in structure 17.



17

If the polymer chain is sufficiently flexible, the side groups may form stacks in the solid state or in the quasi-melt and give rise to high levels of crystallinity or to liquid crystallinity (18). Again, design at the molecular level controls the solid-state structure. As an extension of this theme, rigid, polar, and polarizable side groups attached to a flexible polymer chain can be oriented in the rubbery or molten state by the application of a strong electric field ("poling" at ~10 kV) (19). Cooling or cross-linking of the polymer freezes the orientation

and allows the generation of nonlinear optical or ferroelectric effects.

The example of materials processing by poling of a polymer illustrates a key feature of macromolecular assembly processes—that external forces can "encourage" self-organization. The stretching of a semicrystalline polymeric material forces the polymer chains into colinear orientations that favor crystallization. For example, exceedingly strong fibers of polyethylene can be prepared by efficient orientation of the polymer chains. Special chain orientation techniques are also used to produce high-strength aramide fibers such as Kevlar. The application of external pressure may change the orientation of mesogenic side groups and alter the liquid crystallinity and, as mentioned above, a strong electric field may change the materials properties dramatically. All of these factors must be taken into consideration when designing a polymeric materials processing scheme.

One of the most important properties of polymer molecules is that they can be incorporated directly into "materials," often without further chemical reactions. However, this is not necessarily true of some of the systems to be discussed below.

Materials properties determined by cross-linking reactions. Cross-links between polymer chains affect the materials properties dramatically. Light cross-linking prevents materials flow or "creep" (the individual chains can no longer slip past each other). Heavy cross-linking generates rigidity, strength, load-bearing capacity, and thermal stability. Indeed, the epitome of heavily cross-linked materials is ceramics. This is a connecting point between polymer chemistry and ceramic science.

Sol-gel synthesis of ceramics is a now classical approach to the rational synthesis of materials through the hydrolysis of metalloid or metal alkoxides such as $\text{Si}(\text{OC}_2\text{H}_5)_4$ or $\text{Ti}(\text{OC}_2\text{H}_5)_4$ (20, 21). Hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ in water-ethanol media leads to the replacement of ethoxy groups by hydroxyl units. Molecules that bear Si-OH structures undergo facile reactions that lead to loss of water and the formation of Si-O-Si bonds. This condensation process links the small-molecule units together first to form clusters or branched polymers and later (because each silicon eventually bears four reactive hydroxyl groups) to generate a three-dimensional network that encompasses the whole reaction vessel. In the initial stages of molecular linkage the clusters and polymers are sufficiently small that they remain soluble in the medium (the "sol"). As the reaction proceeds, cross-linking occurs to form a "gel," and the shape of the monolith is now fixed. Further heating drives off water and ethanol from the interstices between the chains and cross-links and the material shrinks to form first silica gel and later silica. Thus, the shape of a final solid object is defined by the shape of the reaction vessel, and the final dimensions are controlled by the shrinkage that results from loss of the water and ethanol. One advantage of this process is that it provides a low-temperature route to shaped objects and to porous ceramics. A second advantage is that the process allows an intimate mixing of two or more different element-alkoxides, which permits a high level of rational design.

The sol-gel approach represents developments at the dividing line between polymer science and ceramic science. So too does a route to non-oxide ceramics through the pyrolytic cross-linking of polymers that contain inorganic elements (20–22). The objectives of this method are to use the molecular character of a polymer to define the ratio of its inorganic component elements and to use the materials processing advantages of the polymer to control the shape. Subsequent pyrolysis drives off the unwanted components of the polymer and simultaneously cross-links it to form a ceramic. An example of this approach, which is now a commercial process, is the conversion

of poly(carbosilanes) (6) to silicon carbide (22). As in sol-gel synthesis, the shape of the preceramic determines the shape of the final ceramic, although a volume contraction occurs due to the loss of the polymer side groups. Related processes are under development for the preparation of silicon nitride, boron nitride, aluminum nitride, and other high-temperature ceramics. The degree of predictability of the final ceramic composition from the structure of the polymer varies from system to system, but ideally this approach would allow the rational design of yet unsynthesized ceramics once the pyrolysis chemistry is understood.

Polymer composites, blends, and interpenetrating polymer networks. The preparation of metal alloys and ceramic composites has been an established part of inorganic materials science for a long time. These materials are two-, three-, or multicomponent systems, often with enhanced strength and mechanical and thermal shock resistance. The application of similar principles to macromolecular science is having a striking influence on the preparation of new polymeric materials.

The incorporation of inorganic fibers or fabric into a glass-like, cross-linked or uncross-linked organic polymer matrix provides another approach to the formation of hybrid organic-inorganic materials. This method is well established for the processing of rigid, tough engineering materials, especially those used in the automotive, aircraft, and marine industries. The underlying principle is to combine the heat stability and high strength of, for example, glass, carbon, or boron fiber with the ease of processing and fabrication of corrosion-resistant, lightweight organic polymers. A recent extension of these ideas is the development of ceramers, in which fibers of heat-stable organic polymers reinforce a glassy matrix of sol-gel-derived silica or other inorganic ceramics (23). In both types of composites the fibers strengthen the glasslike matrix by preventing the propagation of impact-induced cracks. These systems can be likened to the high-temperature inorganic-inorganic composites prepared by the incorporation of ceramic fibers into other ceramics or metals. Because of the dimensions of the reinforcement materials (0.01-mm-diameter glass fibers, for example), the properties of composites may depend heavily on surface effects at the interface between the two components. Thus the prediction of new materials properties in this area is exceedingly difficult because it depends on a knowledge of surface physics, surface chemistry, and adhesion, none of which are well understood for the components of most composite materials.

The classical organic-inorganic composite materials described above contain gross phase discontinuities at the macroscopic or microscopic levels. However, the principles involved can be extended down to the molecular level with an anticipated improvement in properties. Biomimetic composites are systems that may contain structural miniaturization down to the nanometer or molecular levels. Typically, a reinforcing organic polymer is dispersed at the molecular or multichain level within a crystalline mineralogical matrix. Again, the purpose of the polymer is to provide an impact-resistant matrix to increase toughness. Another objective is to use the organic polymer to define the dimensions of the final composite and to control the solid-state structure of the inorganic matrix, perhaps by epitaxial effects of the type found in biomineralization. Analogies with the structure and formation of bone are often used as a rationale for research in this field. Actually, the ideas inherent in virtually all areas of polymer composites can be traced back to analogies with biological skeletal systems, as enunciated many years ago in a classical popular volume by Gordon (24). In theory, the prospects for new materials design through bone or chitin biomimicry are attractive. In practice, only a limited database exists at present from which such rational syntheses may be developed.

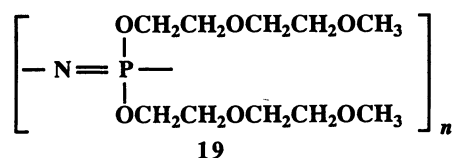
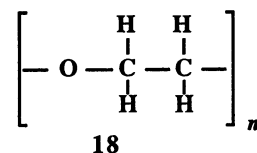
Polymer alloys or blends provide opportunities for rational design and synthesis at the level of intimate macromolecular mixtures. Polymer molecules that are "compatible" with each other (that is, they form homogeneous mixtures) can yield genuine alloys with materials properties that are some combination of those of the individual polymer systems. If the polymer molecules are incompatible, they segregate into domains, and here the analogy with ceramic structures or metal composites is most striking. Many modern commercial polymeric materials have this type of structure. It is possible to estimate which types of polymer structures may be compatible with each other, but simple theory or intuition may not be sufficient, and additional fundamental studies are needed.

Finally, the intimate mixing of polymer molecules in the solid state can be stabilized by the formation of interpenetrating polymer networks (IPNs), in which either one or both components of a polymer alloy are cross-linked to lock both polymers into a complex network (25). Some materials of this type have properties in common with living tissues. Again, a knowledge of polymer compatibilities and cross-linking mechanisms allows considerable scope for new materials design. This is an important field for the future development of high-technology and biomedical materials.

Electroactive polymeric materials. The development of electroactive polymers is another important and challenging field in which materials design plays a key role (26–28). As in the other areas, the molecular structure of the polymer provides a basis for generating an important property, but the materials structure and processing is essential for the manifestation of the phenomenon. Electroactive polymers fall into two groups—ionic and electronic conductors.

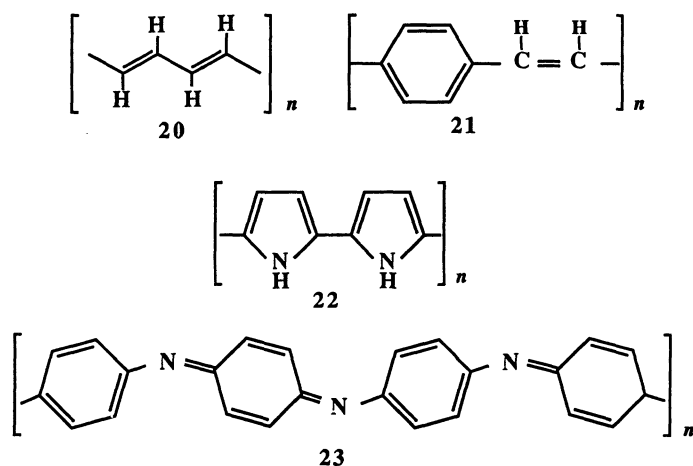
First, consider the field of solid polymeric ionic conductors (29). Certain polymers, especially those that possess highly flexible chains, function as solid solvents for salts such as lithium triflate. Coordination between the polymer and one or both of the ions favors ion-pair separation. Application of an electric current to the material causes ion migration through the solid polymer in a manner that is similar to the behavior of a salt dissolved in water. In the polymeric electrolyte the ions are passed in a hand-to-hand fashion from one polymer molecule to another as the chains twist and reptate under thermal activation. These materials are important because they offer the promise of liquid-free electrolytes for use in lightweight or large-scale energy storage devices, such as rechargeable lithium batteries.

Two polymers that behave in this way are shown as **18** and **19**. Both possess etheric oxygen units that coordinate weakly to the cations to favor ion-pair separation. The poly(ethylene oxide) system (**18**) is the most studied, but the pure polymer-salt system is a relatively poor conductor at room temperature because it is partly crystalline and the polymer crystallites impede ion migration (29). Random copolymers formed from ethylene oxide and propylene oxide apparently do not suffer from this defect. The phosphazene polymer **19** is noncrystalline, and amorphous solid solutions of



lithium triflate in this polymer show high room-temperature conductivities ($5 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ at 30°C) (30). In most of these polymer electrolyte systems the upper limits to the conductivity are defined by the amount of salt that can be dissolved in the polymer without stiffening the material and reducing ion migration. In systems derived from 19 this concentration corresponds to ~ 0.3 cations per polymer repeat unit. Materials design in this field involves the incorporation of etheric or other coordinative units into flexible polymers in order to optimize conductivity and dimensional stability while reducing chemical reactions at the electrode surfaces.

Finally, one of the most challenging objectives in polymeric materials science is the design of polymeric solids that conduct electricity by electronic mechanisms (26–28, 31). These may become easily fabricated alternatives to inorganic semiconductors, electrode materials, display panels, metals, and possibly superconductors. The available information suggests that materials design in these systems depends on five factors: (i) the need for an unsaturated polymer skeleton, as found in the structures shown in 20–23 or stacked side groups that facilitate electron migration; (ii) a solid-state structure



that generates a high degree of order, including parallel orientation of chains and crystalline matrices; (iii) a method for oxidizing or reducing the polymer by incorporation of “dopants” into the materials structure; (iv) the possibility of a multistep synthesis in which a precursor, saturated polymer is fabricated into the shape of a device and is then subjected to a final reaction that generates the needed unsaturation; and (v) the in situ polymerization of a monomer on a substrate that defines the shape of the material and avoids the need for subsequent fabrication. This usually involves electrochemical polymerization on the surface of an electrode.

It is obvious from the last two requirements that electronically conductive polymers are often difficult to fabricate into fibers, films, or devices because of their high degree of crystallinity or their insolubility. This, together with the requirement for efficient doping, means that the materials-processing aspects are often more challenging than the polymer synthesis. Thus, rational materials design in this field leans heavily on the development of materials-processing methods.

The Surface Modification Approach

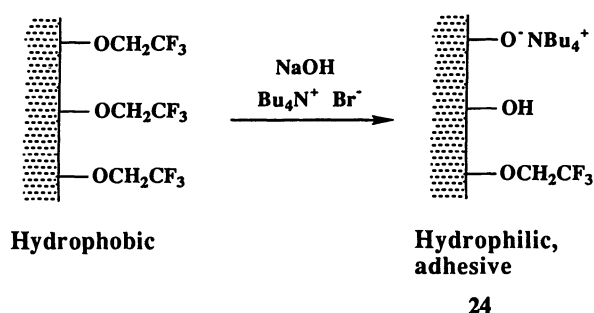
Many of the most critical properties of materials involve their surfaces. For example, the surface of a biomedical material determines its biocompatibility (32, 33). The surface lubricity of Teflon

underlies its use in bearings. The phenomenon of adhesion depends critically on surface character. The local surface character of a resist polymer that defines the patterning is obviously a key factor in the fabrication and function of an integrated circuit.

Only rarely does it happen that a material has valuable bulk properties and ideal surface properties for a particular application. For example, most of the elastomers that are candidates for use as heart pump or blood vessel prostheses have surface properties that favor protein deposition, trigger thrombus precipitation, and provide a foothold for bacterial colonization. This is why large areas of biomedical materials research revolve around the testing and retesting of five or six long-existing, off-the-shelf commercial polymers. In the absence of a better approach, materials scientists and biomedical engineers are constantly forced into a compromise in order to balance bulk materials advantages against unwanted surface characteristics.

Surface modification chemistry provides an answer to this dilemma. In this approach, a material is chosen for its bulk properties and the surface is then altered by reaction chemistry. In many ways, surface chemistry is a more complex process than solution chemistry. Factors such as the hydrophobic or hydrophilic interactions at the interface, or the tendency for certain side groups to concentrate at the surface, may play a controlling role in the reaction chemistry. Moreover, a change in surface structure generated by a chemical reaction in the outer few angstroms of the material may bring about only a temporary change in surface properties because the motions of polymer molecules may bury the new surface within minutes after exposure to air or to a different liquid medium. However, progress is being made in the development of an underlying understanding of these processes in ways that are likely to aid rational surface design in the future. The following examples illustrate a few of the principles involved.

Some of the earliest studies on the surface reactions of polymeric materials were the result of attempts to increase the adhesion of polymers to metals, ceramics, or other polymers or to change a hydrophobic surface to a hydrophilic one. For example, polyethylene can be surface oxidized by treatment with a solution of chromic acid and sulfuric acid to generate COOH and ketone groups in the surface layers (34). This treatment converts a hydrophobic surface to a hydrophilic one. Moreover, the hydrophilicity can be changed by “titrating” the surface with base to form COONa groups.



In my research program, surface reactions on polyphosphazenes have been used to generate adhesive, biocompatible and, in one case, antibacterial surfaces by simple chemical reactions. Consider the hydrophobic phosphazene polymer shown earlier as 15. This polymer and its mixed-substituent analogs have useful internal properties (flexibility and film- or fiber-forming properties, or elasticity). However, 15 is very hydrophobic and does not adhere to surfaces. A simple, rapid treatment of the surfaces of these polymers with an aqueous solution of NaOH and Bu_4NBr replaces surface fluoro-

alkoxy groups by OH groups (24) and generates a highly adhesive interface (35). Other reactions convert aryloxy surface groups to aryloxysulfonic acid, aryloxy-carboxylate, or aryloxy-amino units, and these not only yield hydrophilic surfaces but also provide footholds for the linkage of biologically active species, such as enzymes, other polypeptides, dopamine, blood anticoagulants, or hydrogels to the surface without affecting the bulk properties (16, 36). As an extension of these developments, specifically tailored polyphosphazene hydrogels are being used as surface coatings for the microencapsulation of mammalian cells for prospective uses in medicine and biotechnology (37, 38).

Final Observations

The three approaches to rational synthesis—at the molecular level, by materials processing, and by surface chemistry—cannot be separated from each other. Attempts to follow one approach while neglecting the others leads inevitably to disappointing progress. For this reason, future efforts in polymeric materials science require either (i) a willingness by individual research groups to pursue all three aspects or (ii) collaborations between specialist teams in the three different areas. This diversification and cooperation becomes even more critical as polymer materials research begins to overlap other materials areas such as ceramics, metals, and electroactive or electro-optical materials.

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