

Polymers

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INTRODUCTION

Eras of civilization have frequently been named for materials discovered and subsequently used extensively by humans (e.g., the Stone Age, the Bronze Age, etc.). Toward that end, the 20th century might appropriately be labeled as the Plastics Age or, somewhat more broadly, the Polymer Age. Whereas biological polymers (e.g., DNA, proteins) have been present since the origins of life, the development of synthetic polymers and the realization that long-chain molecules could exist are relatively recent milestones on the materials calendar. Indeed, it was only in the 1920s that the concept of a polymer or macromolecule came to be grudgingly accepted, slowly displacing the colloid theory that suggested that macromolecules were nothing more than aggregates of small molecules. The subsequent two decades witnessed the rapid development of many types of synthetic fibers, plastics, and elastomers, including Dacron, nylon, and Spandex. Also, guiding principles for the successful linking of monomers into high-molecular-weight polymers were established. The remainder of the 20th century saw explosive growth in new polymers and their applications. Today, polymers are ubiquitous, from commodity plastics such as plumbing pipe, food wrap, and trash bags, to highly specialized and tailored materials for use in aircraft components, personal computers, and health care.

A key reason for the broad acceptance and appeal of polymers is that they are the most versatile of all materials, spanning the range of mechanical properties from soft gels and rubbers to extremely strong fibers. This versatility is a direct consequence of the great latitude conferred by design of the repeat-unit structure and control of chain length (or molecular weight) and chain architecture. While most polymers are based on carbon backbones, inorganic backbones (e.g., silicones) add yet another dimension to the tailoring of material properties. A key aim of this article is therefore to introduce basic ideas of how polymer structure affects properties. A short discussion of the implications of these ideas in the design of polymeric biomaterials will follow. Several examples of such materials are discussed in some detail in additional entries of the encyclopedia. This article concludes with a summary of opportunities

and challenges in polymer science for the next two decades and beyond.

INTRODUCTION TO STRUCTURE/PROPERTY RELATIONSHIPS

Small Organic Molecules

The properties of small organic molecules (melting point, for example) depend intimately on the structure of the molecule and principally on four factors: 1) size; 2) symmetry; 3) internal flexibility (presence or lack of bond rotations); and 4) strength of intermolecular forces. A consideration of how these dictate properties of small molecules is instructive in understanding structure/property relations in polymers. Melting (or fusion) is a first-order thermodynamic transition, and the melting temperature, T_m , depends on the ratio of the enthalpy and entropy of fusion:

$$T_m = \Delta H_m / \Delta S_m \quad (1)$$

Melting points typically increase with molecular size, as evidenced by tracking the properties (gas → liquid → grease → wax → resin) of n-alkanes as a function of carbon number. Highly flexible molecules that are reasonably symmetric crystallize readily because the conformation(s) required in the crystal (for example, the extended zig-zag conformation for n-alkanes) are easily adopted. Such materials have rather low melting points even at high molecular weights, since considerable entropy (translational and rotational) is gained on melting and thus ΔS_m is large. Branching can lower melting points by reducing the ability of a molecule to pack tightly into a crystal, thus lowering the enthalpy of fusion. Moreover, branching introduces asymmetry that can inhibit crystallization when the material is rapidly cooled, the result being an amorphous solid or glass. In cases where branching is extensive and does not lead to lack of symmetry, melting points can actually increase vs. linear counterparts due to loss of conformational flexibility and hence lower entropies of fusion. Rigid molecules such as anthracene tend to have high melting points due to a low entropy of fusion, as only translational entropy is

primarily gained on melting. Similarly, molecules with strong intermolecular forces (e.g., hydrogen bonds) have high melting points, usually not due to the need to overcome these forces on melting but rather as the result of their persistence in the molten state affording low entropies of fusion. For this reason, benzoic acid has a relatively high melting point for its molecular weight. These same four factors applied to polymer repeat units, along with chain orientation and extent of crosslinking, are the primary determinants of polymer properties. These points will be illustrated with polyethylene and vinyl polymers derived from mono-substituted ethylenes as examples, followed by a brief discussion of polyesters.

Glass Transition Temperature

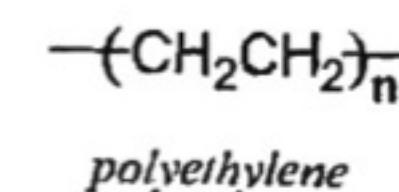
A glass is appropriately defined as material having the structural properties of a liquid, namely disorder, and the mechanical properties of a solid; it has a glass transition temperature, T_g , above which the material can flow. The idea of a melting point is easily appreciated but T_g is perhaps less familiar and thus deserves a brief discussion here. Cooling of a molten substance can lead to crystallization at T_m and is accompanied by a rapid drop in volume as shown in Fig. 1 (except for odd substances such as water). The crystalline substance will continue to drop in volume, albeit slowly, as determined by its coefficient of expansion. However, under certain circumstances it is possible to bypass T_m and form a supercooled liquid that

eventually forms a glass. This process, known as vitrification, can occur if cooling is rapid, the viscosity of the melt is very high, and/or the molecular structure of the substance is either asymmetric or large and difficult to pack into a crystal. At T_g , molecular motion effectively ceases. However, unlike T_m , the value of T_g depends upon the cooling rate, with rapid cooling "freezing-in" higher energy molecular conformations and organizations. Therefore, it is common to see T_g reported as ranges, and it is important to specify cooling or heating rates in measurements of T_g .

Polymers^[1,2]

Polyethylene and polymers from mono-substituted ethylenes

Consider first molecular weight, using the n-alkane series as an example with high molecular weight and linear or high-density polyethylene (HDPE) as the upper limit.



Several important points derive from inspection of samples of polyethylene and some lower-molecular-weight solid n-alkanes such as paraffin wax (roughly 30–40 carbons). The wax, a highly crystalline substance, is easily broken into small pieces with a fingernail, whereas the polymer resists such damage and is seen to be a very tough flexible material. Molten wax has a low viscosity in contrast to polyethylene. More significantly, and unlike the wax, fibers can be drawn from the molten polyethylene very easily. The reason is that the molecules of polyethylene are long enough to physically entangle with one another, thus supporting the ability to form fibers from the melt. The entanglement molecular weight is roughly the length of a molecule at which the properties of polymers begin to manifest themselves. It is dependent upon the chemical structure of the polymer, but most entanglement molecular weights are in the range of 2000 to 20,000 g/mol.

As expected, the viscosity of a molten polymer will rise dramatically with molecular weight since chain entanglements will inhibit the ability of molecules to move past one another. Many other properties such as melting point and tensile strength do not continue to increase with molecular weight but reach an asymptote. (However, the tensile strength can be increased substantially by chain orientation.) This is because, at long chain lengths, polymer chains behave as a collection of shorter independent segments. In the case of polyethylene, the

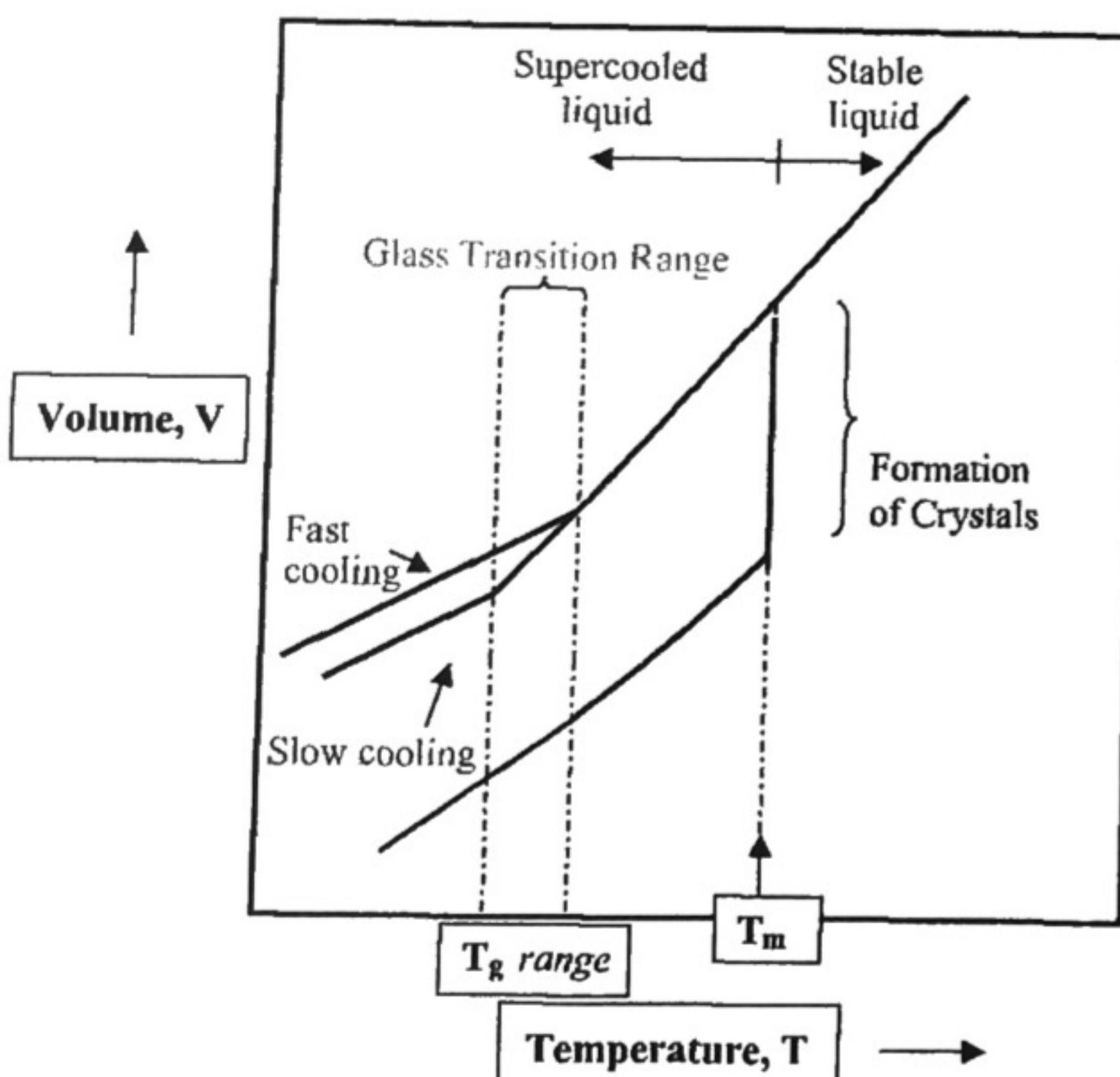


Fig. 1 Plot of specific volume vs. temperature, contrasting the formation of a glass vs. crystals from the melt. (View this art in color at www.dekker.com.)



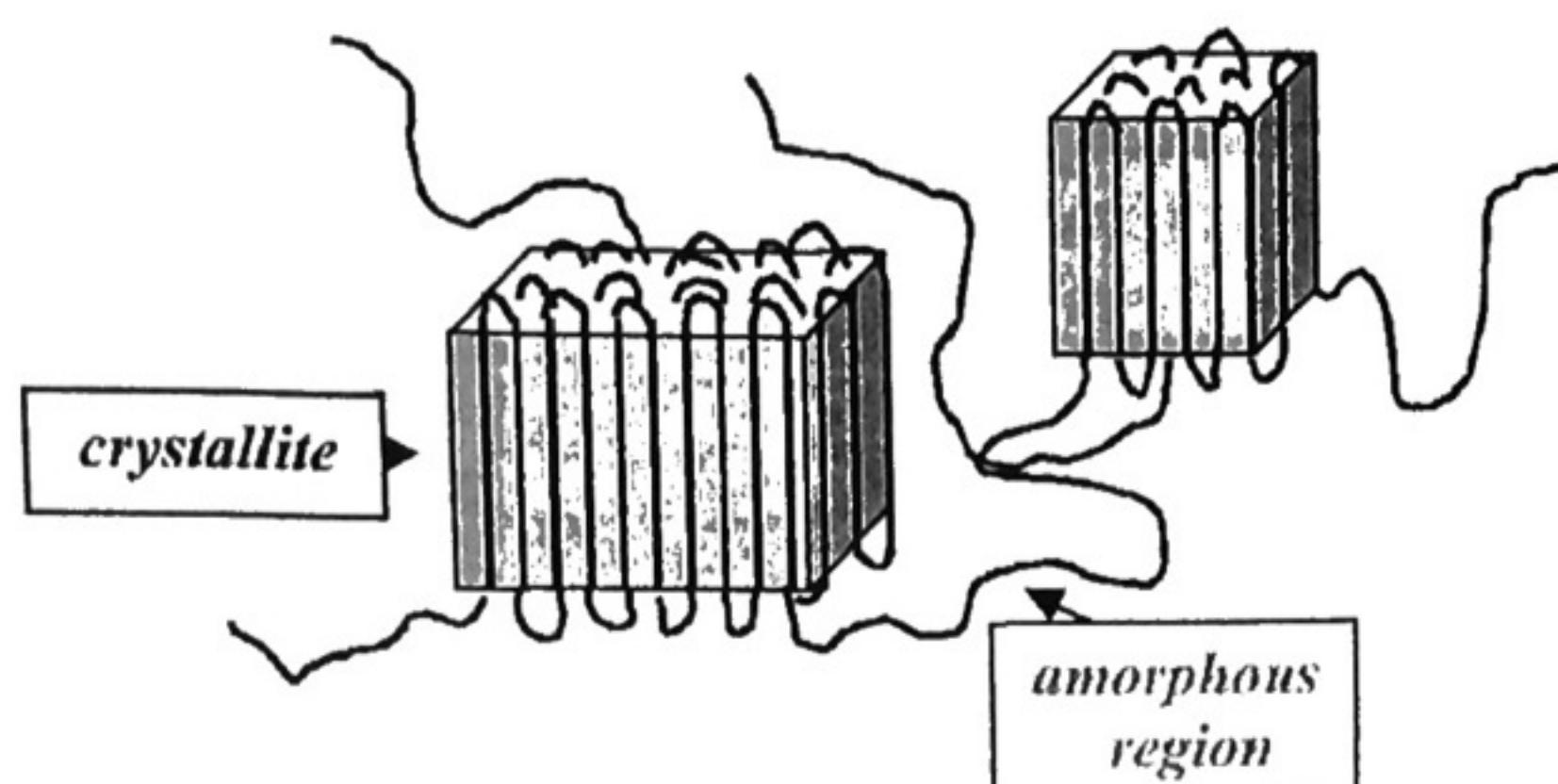


Fig. 2 Morphology of a typical semicrystalline polymer such as linear polyethylene. It is kinetically easier for the chains to fold on themselves during crystallization rather than form long extended structures. (*View this art in color at www.dekker.com.*)

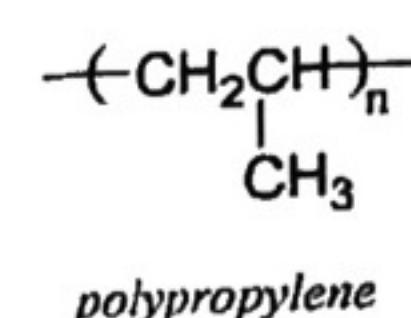
asymptotic limit for T_m is about 140°C . This relatively low temperature is the result of high chain flexibility and thus a high ΔS_m .

Polymers such as linear polyethylene crystallize easily due to the highly symmetric repeat unit and high chain flexibility. However, polymers rarely crystallize completely. Crystallization can begin at multiple points along a long polymer chain, eventually trapping segments of disordered or amorphous chains between crystallites. Therefore, materials such as HDPE are semicrystalline (Fig. 2), with a T_m for the crystalline component and a T_g for the amorphous regions, with the degree of crystallinity being about 70–80%. The T_g for polyethylene is approximately -50 to -90°C , and hence this polymer at room temperature is a composite of crystals and liquid-like amorphous regions. The toughness of polyethylene at room temperature is due to the ability of the amorphous regions above their T_g to absorb mechanical impact. Semicrystalline polymers are typically translucent due to light-scattering by the crystallites. Their solubilities can effectively be nil until temperatures rise to close to T_m , and this is why HDPE containers can be used to store gasoline even though a mixture of alkanes might be expected to dissolve the polymer readily at room temperature because of similar molecular structures.

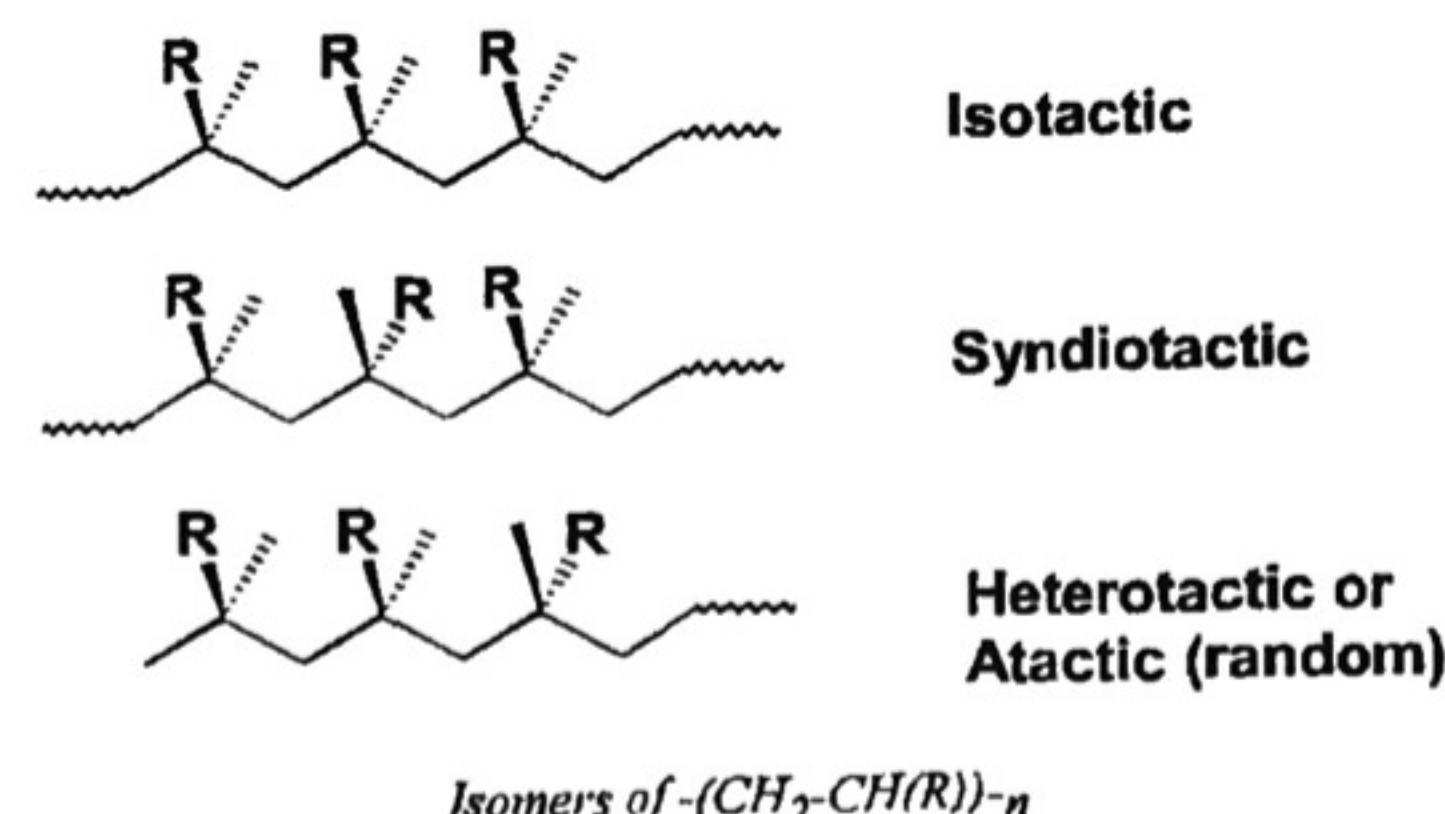
Mechanical extension of a semi-crystalline polymer typically leads to “necking-down” in the drawn region as chains are pulled out of crystallites and oriented in the stretch direction. Extensive orientation in gel-spun, ultra-high-molecular-weight HDPE affords fibers the tensile strengths of which exceed that of steel on a weight basis.

Molecular symmetry can affect both the melting point and the degree of crystallinity. Low-density polyethylene (LDPE) has occasional short alkyl branches that serve to disrupt chain packing and thus lower the degree of crystallinity to about 50% and the T_m to 105 – 110°C vs. about 140°C for the linear material. LDPE is softer (and tougher) than HDPE due to its lower crystallinity.

The effect of symmetry is particularly pronounced for polymers derived from mono-substituted ethylenes such as polypropylene.



This repeat unit as drawn is misleading in that there are two possible configurations at the methine carbon ($-\text{CH}-$) and the arrangement of these along a chain leads to three possible isomers (here $\text{R}=\text{methyl}$):



After polyethylene, polypropylene is the second most important polymer in terms of annual world production, and it is only the isotactic form of polypropylene that is produced. This material has a higher T_m (165 – 170°C) compared with HDPE, the principal reason being that the methyl groups reduce the conformational flexibility of the chain in the melt, affording a lower ΔS_m . Its T_g is about -10°C due again to restricted bond rotations, and hence, compared to polyethylene, it is not flexible at lower temperatures. Interestingly, the laboratory that discovered catalysts to produce HDPE many decades ago also produced isotactic polypropylene, but the material was ignored since it was not thought that a backbone with pendant methyl groups would have a higher melting point than polyethylene. As pointed out earlier in our discussion about small molecules, branching can lower T_m but that is principally if there is no regular placement of branches and no stereochemical control at the branch points. (This assumes that there are no strong intermolecular forces acting to depress the entropy of the melt; see the discussion on polylactide and polyglycolide.) Isotactic polypropylene has a very regular structure and its conformational flexibility dictates its thermal properties. The higher T_m makes this material useful in a variety of medical applications (e.g., plastic syringes and tubing) because it can be sterilized in an autoclave without coming too close to its T_m .





It is interesting to compare the structures of linear polyethylene and isotactic polypropylene in the crystalline regions. In polyethylene, the chains adopt a zig-zag conformation as is the case in crystals of small-molecule n-alkanes. In polypropylene, by contrast, the pendant methyl groups force the chains to be helical. An analogy exists with the secondary structure of polypeptides; for example, poly(glycine) prefers the β -sheet structure whereas polypeptides with bulky side chains adopt an α -helix.

Polystyrene is another important material derived from a mono-substituted ethylene where R is a benzene ring. Commercial polystyrene is exclusively the atactic form and, because this isomer is irregular, the polymer does not crystallize and therefore is transparent. This is an attractive property and accounts for the widespread use of polystyrene in petri dishes and related lab supplies. Its T_g is about 100°C due to restricted chain flexibility by virtue of the rather bulky phenyl substituents, and hence the material is rather brittle at room temperature. Like T_m , the T_g of a polymer reaches an asymptote with molecular weight, the 100°C value is the limiting T_g for atactic polystyrene.

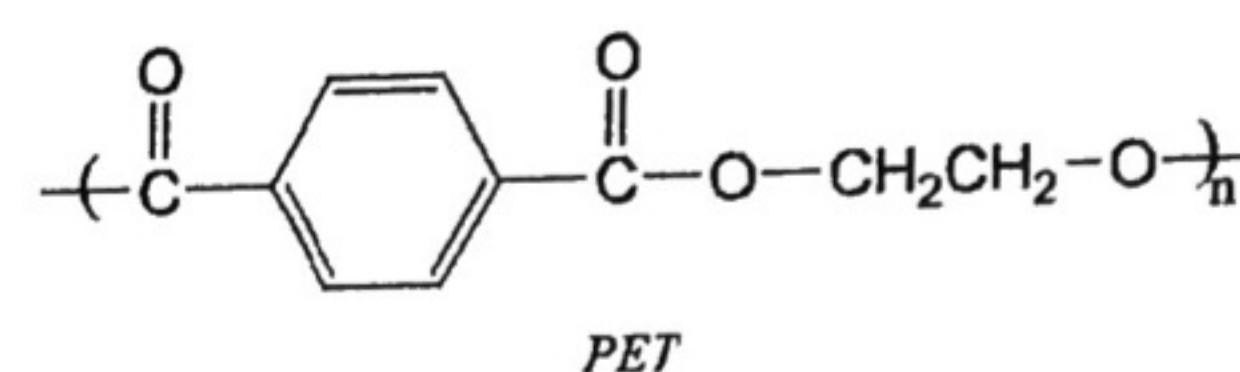
Poly(vinyl chloride) or PVC, where R=Cl, is another important atactic polymer. Besides its widespread use in plumbing pipe and connectors, it is a familiar lab staple in the form of flexible Tygon tubing. Tygon is PVC containing a plasticizer such as 2-diethylhexyl phthalate (DEHP). PVC has a T_g of about 85°C, significantly higher than that of polypropylene because of the slightly larger size of the pendant Cl but more significantly due to stronger intermolecular forces stemming from the polar C-Cl bond. At T_g , intermolecular forces need to be overcome to allow chain segments to move relative to one another. Addition of a plasticizer, which is typically a low-volatility liquid with good solubility in the polymer, serves to disrupt intermolecular forces and hence depress the T_g . In Tygon, the T_g is below room temperature. It is interesting that the material keeps its physical shape rather than forming a puddle of high-viscosity polymer plus plasticizer, and the explanation is that PVC contains a small amount of tiny crystallites (perhaps from short segments of syndiotactic repeat units) that act to hold the material together.

Another means of lowering T_g and thus increasing material flexibility is to copolymerize vinyl chloride with monomers such as vinyl acetate. At least some readers will recall long-playing phonograph records which were frequently made from such copolymers.

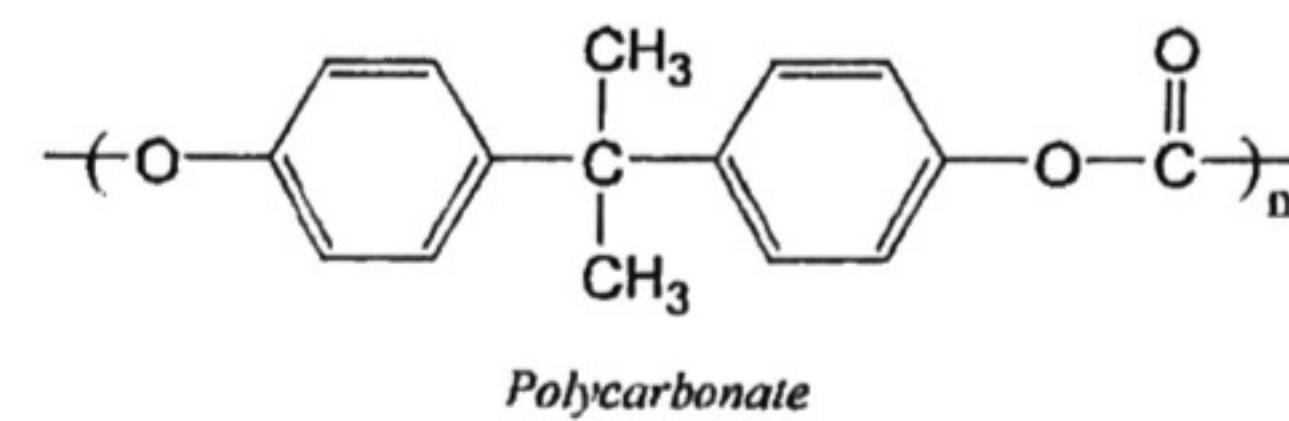
Polyesters

Polyesters represent an important class of materials with broad applications as biomaterials. Poly(ethylene tereph-

thalate), PET, is a ubiquitous material known as Mylar in film form and Dacron in fiber form. Woven Dacron mesh is used for large-diameter vascular grafts. PET, with its rather regular structure, is a semi-crystalline polymer with a T_m of about 265°C and a T_g near 85°C.

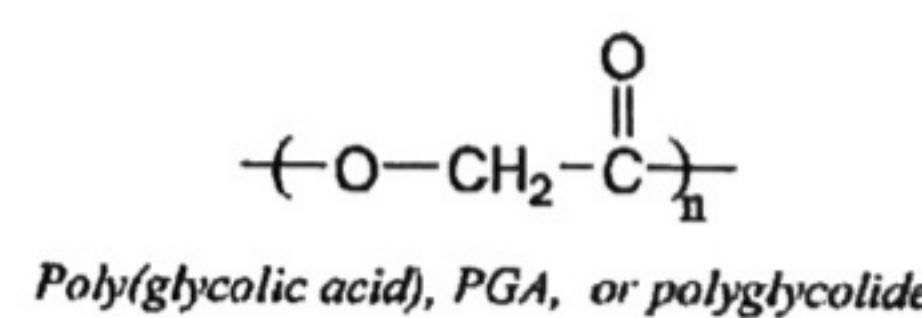


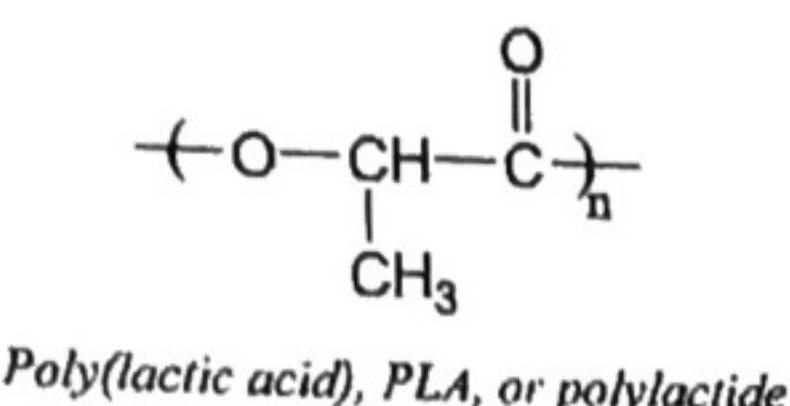
Polycarbonates are formally polyesters of carbonic acid, the most popular being the material with the trade names Lexan or Merlon. The repeat unit, which is symmetric, is more complex and less flexible than that of PET, and thus polycarbonate will typically form a glass (T_g ca. 150°C) on cooling; hence the polymer is transparent.



The polymer is rigid at room temperature, and it is tempting to think that all glassy polymers below their T_g might be brittle. Polycarbonate is remarkably resistant to impact vs., for example, glassy polystyrene, as evidenced by the properties of compact discs (polycarbonate) and their holders (polystyrene). Polycarbonate has sub- T_g short-range molecular motions associated with the flexible carbonate group that serve to absorb significant impact energy. Such energy-absorbing mechanisms are not available in polystyrene. Similar sub- T_g motions account for the flexibility of PET fibers and films at room temperature.

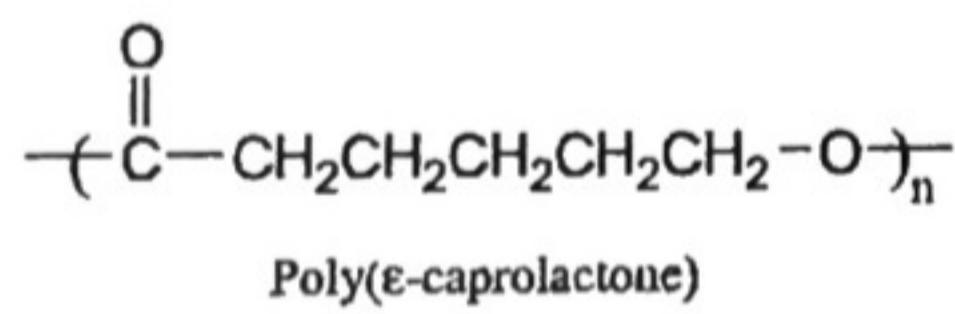
Both PET and polycarbonate hydrolyze very slowly and are not useful as biodegradable materials. However, simple aliphatic polyesters such as poly(glycolic acid) and poly(lactic acid) are well-known biodegradable polyesters. (They are sometimes referred to as polyglycolide and polylactide, respectively, because they are frequently prepared from dimers of the acids.)





PGA is semicrystalline (typically ca. 50% crystallinity) with a T_m of 225–230°C and a T_g of about 35–40°C. The small $-\text{CH}_2-$ group allows close packing in the crystal and strong dipole interactions among esters, and only rather unusual solvents such as fluorinated alcohols can dissolve the polymer. PLA, like polypropylene, has two possible configurations at the methine carbon. Since lactic acid is made naturally as the L-isomer, the pure (isotactic) polymer derived from it is called poly(L-lactic acid) or PLLA. This material is also semicrystalline (35–40%), but with a lower T_m (ca. 175°C) than PGA, presumably due to methyl groups acting to partially shield dipole-dipole interactions. The T_g of PLLA is around 60°C v 40°C for PGA, consistent with the idea that the methyl group increases rotational barriers along backbone bonds. Copolymers of the D and L isomers of lactic acid are readily made and these are amorphous as expected from their atactic structure. Also, copolymers of lactic and glycolic acids (PLGA) are of great interest because degradation rates can be controlled for a variety of applications in tissue engineering and drug delivery.

Dilution of the polar ester group by methylene units reduces intermolecular forces and thus lowers both T_g and T_m compared with PGA. An example is poly(ϵ -caprolactone), a semicrystalline polymer that has a T_m of 60°C and a T_g of about –60°C.



Cross-linking and Orientation

The molecular origins of structure/property relationships discussed above apply to both small molecules and polymers. However, two additional parameters affect polymers in unique ways. The first is cross-linking, which involves primary bonds (chemical cross-linking) or secondary bonds (physical cross-linking) and affords what are termed polymer networks. Light cross-linking of low- T_g polymers gives materials known as elastomers, and these have the typical properties of a rubber band. Cross-linking raises T_g , as chain motions are now restricted by network junction points. Heavy cross-linking can give very hard, brittle materials, as T_g will rise above room

temperature and molecular motions will be too restricted to contribute significantly to impact energy absorption (e.g., toughness). A biopolymer example is keratin, the major constituent of hair and fingernails. Keratin in hair is lightly cross-linked via disulfides from coupling of neighboring cystine amino acids, and the ability to introduce a “permanent wave” takes advantage of the reversibility of disulfide formation and cleavage via redox chemistry. Fingernails have a much higher disulfide cross-link density, and hence they are harder. (Tortoise shells are even more highly cross-linked.)

Polymer networks can be prepared by covalently linking chains into what is effectively a single molecule using high-energy radiation such as gamma rays, light, or a wide variety of chemical reactions (e.g., disulfide formation). It is also possible to exploit strong intermolecular interactions to afford materials with the properties of a polymer network, yet retaining the ability to reprocess the material upon heating. A classic example is the segmented polyurethanes, which contain a low- T_g block and are cross-linked via thermally labile hydrogen-bonded domains. These have the “snap” of a rubber band but are reprocessable, and are termed thermoplastic elastomers.

New Synthesis Strategies

Polymer chemists continue to explore and optimize polymerization reactions as well as discover new reaction schemes and catalysts that afford a tight molecular weight distribution (MWD), afford more precise control over backbone composition and repeat unit stereochemistry, and allow for the creation of novel chain architectures.

Particularly interesting advances have been made in the area of “living” polymerization, a term for a system where propagating chain ends remain active throughout the duration of the reaction. For example, it has long been thought that free radical polymerization would not be amenable to the characteristics of a living polymerization (e.g., a linear dependence of molecular weight with monomer conversion) due to the inherent high reactivity of radicals. However, it has been discovered over the last decade that it is indeed possible to achieve living polymerization character provided that the number of active radical species is very low at any given time. This can be done by reversibly capping active chain ends using stable nitroxide radicals, halides via redox chemistry with selected transition metals (called atom-transfer radical polymerization, or ATRP), or reversible addition-fragmentation polymerization (RAFT).^[3] On another front, it was believed about 15 years ago that polyethylene and polypropylene were mature technologies, although that has changed dramatically with the advent of new transition metal catalysts^[4] that, for example, afford fine





control of the extent of branching (and hence the degree of crystallinity) of polymers of ethylene and small amounts of α -olefins. The new catalysts are also producing old polymers with a high control of stereospecificity. One recent example is syndiotactic polystyrene.

Finally, polymerization reactions are being developed that yield polymers having interesting chain architectures, such as block and graft structures. Chain architecture is important in that compositionally different regions of a polymer chain can contribute different properties. For example, styrene-butadiene-styrene triblock polymer will self-assemble upon cooling from the melt into various thermodynamically stable morphologies depending on the relative lengths of, and thus volume fractions of, the blocks. At about 20 vol% polystyrene, the material is composed of a low- T_g polybutadiene continuous phase and small (ca. 20-nm diameter) spherical domains of atactic polystyrene (T_g of 100°C). The domains are interconnected by virtue of the block polymer chain structure, and hence this material behaves as an elastomer with cross-linking via the glassy polystyrene domains. Such a material is a thermoplastic elastomer, because it can flow if heated above the T_g of polystyrene.

Whereas block and graft copolymers have been known for some time, new polymerization methods such as ATRP are expanding the number of examples of these systems.

More complex architectures, such as multiarm stars and dendrimers,^[5] are being targeted as polymerization chemistry becomes more versatile. Star polymers (multi-arm structures emanating from a central core) are of interest principally for the large numbers of chain ends. For example, a 4-arm star polymer will typically have a lower T_g and a lower viscosity than a linear polymer of a similar total molecular weight. Dendrimers are a special class of star-like polymer that have regularly placed branched repeat units. Construction of such a polymer can begin with a core to which a monomer capable of branching is attached (divergent approach), or conversely by making highly branched arms and then connecting these to a core as a final step (convergent approach). Dendrimers typically have poor physical properties in the solid state due to the absence of chain entanglements. However, their interiors have open volume in which to bind drugs and an exterior with a very high concentration of functional groups due to the high degree of branching. These characteristics make dendrimers of great interest in medical applications, for example, as vehicles for delivery of genes to cells.

CHALLENGES AND OPPORTUNITIES: THE NEXT 20 YEARS

Polymer science and engineering will continue to be a key discipline for the design and development of new

classes of materials with new or improved applications in medicine. One snapshot of where the field might be heading is derived from a recent report focusing on similar challenges and opportunities for the Department of Defense,^[6] and a section of that report written by the author is amended here as it might apply to biomaterials development.

Modeling Will Be a Routine First Step

The creation of new polymers will begin with a broad evaluation of properties using high-level modeling and simulation to determine critical parameters (isomeric structure, molecular weight, degree of chain orientation) that influence a property of interest. In particular, modeling will be employed to predict complex organization of functional low-molar-mass molecules and polymers, as is beginning to be done for the difficult problem of predicting protein folding motifs. Modeling will also extend to synthesis routes to define the best approach, as well as to processing. Much guiding information will be in hand prior to doing "wet chemistry."

Synthesis and Processing Will Become Seamless

Synthesis and processing are typically separate operations. This will change over the next two decades as opportunities to carry out simultaneous synthesis and processing emerge. This idea is not new (e.g., reaction injection molding or chemical vapor deposition), but it will become more widespread. Of particular interest will be polymers and small molecules that self-assemble into ordered molecular structures (e.g., liquid crystals) or morphological structures (e.g., block copolymers). Combinatorial synthesis of polymers will become more routine, and the emergence of combinatorial processing approaches to rapidly identify conditions for fabricating polymers to achieve maximum properties is anticipated.

Polymer Synthesis Will Boast Sequence Control

Nature has evolved machinery to precisely control the sequence of amino acid additions and hence the primary structure of polypeptides. However, conventional polymerization techniques have limited opportunities for the control the sequence of addition of two or more monomers. Block copolymers are possible due to successive addition of monomer charges to active chain ends, and alternating copolymers can be obtained under special circumstances. However, there currently is no viable means to prepare, for example, vinyl-type copolymers with sequence control (e.g., poly[(monomerA)_n-(



(monomerB)_n). This is in stark contrast to peptide synthesis on ribosomes within biological cells, which employ a template to code for specific amino acids that are enzymatically linked. A major opportunity and challenge presents itself for the sequence-controlled polymerization of a wide variety of monomers using systems that mimic the functions of ribosomes. Template-directed polymerizations are energetically uphill due to the decrease in entropy resulting from monomer ordering, and in living systems the requisite energy is supplied by ATP. Electrochemical polymer synthesis is an attractive option in that properly patterned electrodes may simultaneously serve as solid templates for synthesis and as energy sources. Other lessons from biology, such as self-assembly and development of hierarchical structures, will continue to be borrowed and built upon.

The Definition of Structure in Polymers Will Rival That of Low Molar Mass Materials

Polymers are by their very nature complex materials, typically having a distribution of chain lengths, isomer content, degrees of orientation, and fractional crystallinity (if any). Thus, structure in polymeric materials is frequently ill-defined compared with small molecules. This difference will gradually disappear over the next two decades as long-chain molecules are synthesized with greater compositional and structural precision. The implications will be significant in that very precise structure/property relationships will be possible, and maximization of properties through the integration of modeling, synthesis, and processing will be realized.

The Impact on Nanotechnology

Many common examples exist of nanoscale (one dimension of <100 nm) materials, including block copolymer films and collagen fibers that function as scaffolds for tissues and organs. However, there will be an increasing push to exploit the properties of individual molecules, or very small aggregates of molecules, for the next generation of multifunctional biomaterials. For example, carbon nanotubes and collections of only a few organic molecules are being studied as components of diodes, transistors, and memory elements. The ability to create well-defined organic polymer structures and manipulate these to form complex and functional arrangements will drive a revolution in information storage and processing, sensing, and communications. This effort is predicted to impact biomaterials and biomedical devices in many

ways, including the design of surfaces with specific and predictable protein adsorption characteristics, and stable and reliable interfaces between cells and electronic materials, both inorganic and organic.

Hybrid Materials Systems Will Be Ubiquitous

Opportunities will continue to arise for the use of polymers as components in hybrid materials systems along with metals, ceramics, and/or electronic materials. Familiar composite material (e.g., graphite-reinforced epoxy) will see increased uses, but significant potential is seen for new materials combinations such as organic electroactive materials and silicon for hybrid electronic and optical devices in, for example, biosensors.

SUMMARY

Polymers represent the most versatile class of materials because of their adaptability to increasingly precise control of structure and properties. Thus, it is anticipated that polymers will continue to be exploited in many and, in some cases, highly specialized biomaterials applications.

ARTICLES OF FURTHER INTEREST

- Biofunctional Polymers*, p. 89
- Hydrogels*, p. 790
- Poly(Glycolic Acid)*, p. 1246
- Poly(lactic acid)s*, p. 1254
- Silicones*, p. 1348
- Ultra-High Molecular Weight Polyethylene (UHMWPE)*, p. 1690

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