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Polymers for the 21st Century

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POLYMERS FOR THE 21ST CENTURY

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ABSTRACT

In the 21st century, polymers will be even more in demand for our modern societal needs than they are today. From the high volume *commodity plastics* to the highly sophisticated, highly priced, and specially designed low volume *functional specialty polymers*, an entire rainbow of needs and application possibilities awaits the polymers of the future. In some cases new and improved manufacturing techniques or improvements in the life cycle of these materials will be needed. In other cases completely new polymer structures and their morphologies will have to be developed.

PREFACE

Few scientific endeavors have had a greater impact on mankind than those focused in the polymer science area [1]. The discovery of reliable polymerization methods combined with significant advances in the theory, physics, and engineering of macromolecules earlier in this century helped to launch a materials revolution that is still underway today. Initial efforts in this field resulted in the rapid commercialization of so-called commodity plastics like polystyrene, polyethylene, nylon, and other high volume, relatively low cost materials. During this period, polymer production was perfected, monomer syntheses were optimized, and the availability of commercially important chemical feedstock was secured.

The arrival of the late 1960s witnessed a substantial shift in the direction of polymer science. Research efforts were broadened to encompass the synthesis of materials possessing a higher degree of sophistication, including polymers with novel molecular architectures, high performance polymers, and other "specialty" materials [2]. These efforts fostered the development of newer, better controlled polymerization techniques and demanded a more fundamental understanding of how localized structures along a polymer chain can impact both the macromolecular and supramolecular ordering found within a bulk polymer sample. During the past quarter century, tremendous progress toward the tailored design of well-defined polymeric materials has been made as a number of the papers presented in this volume indicate.

INTRODUCTION

The word *polymer*, a molecule consisting of *many* (*poly*)units, came into use toward the end of the last century; the word *macromolecule*, implying a large molecule, has also been in use for a long time. Not until 1920 was it recognized that polymers are indeed giant macromolecules which are held together with regular sigma bonds and are not "associates" or "agglomerates" of relatively small molecules based on principles of association that were known from colloids.

Today, the expressions *polymer* or *macromolecule* are frequently used—but not correctly—interchangeably, and it is difficult to imagine these terms being absent from the modern scientific language.

Two other expressions should also be mentioned here: *materials* and *plastics*. Again, the expression *materials* is used in various ways, but generally, it is used for the combined categories of ceramics, metals, alloys, and polymers. The expression *plastics* generally applies to *materials* that are synthetic polymers but also applies to modified natural polymers.

One definition says that plastics has several meanings, such as easily shaped or formed, capable of being molded, and false or synthetic [3]. The latter meaning probably gave rise to the association of the word with synthetic polymers. The expression plastics seems to associate "plastics" with synthetic polymers as it is documented by the German word *Kunststoffe* (*artificial materials*). Polymers are not really "plastic" in the same sense as metals, but they can also be shaped and molded. The word plastics is often used interchangeable with polymeric materials.

In this article we will use the expression polymers and macromolecules quite interchangeably, but use the expression plastics for the commercial aspect and polymeric materials in a more indefinite way and for composites, where the matrix material is a polymer or a mixtures of polymers.

Polymers have become the center of what many people call today the "*plastic age*."

HISTORY

Materials

When we look back to the early part of human history, the first period, the stone age, was named after the first dominating material, *stone*. Not only stone, a ceramic material, but also some natural polymers and even composite materials were used by the people then living. We must remember that grass, wood, bamboo, and even the human body consist of hierarchical composites, most ingeniously combined by nature for the most efficient combination of materials properties.

In the following millennia, metals, such as *bronze* and *iron*, played an increasingly dominant role in the use of materials, also giving these periods their names. Figure 1 is drawn in a logarithmic scale where the last century, especially the last few decades, is exaggerated. We see that metals and metal alloys, in spite of their rapidly increasing sophistication, are decreasing in importance compared to plastic materials and ceramics. To a great extent this is due to the light weight and ease of fabrication of plastics materials [4].

When we are talking about polymers it is usually implied the polymers are organic macromolecules, composed primarily of carbon chains and sometimes with oxygen or nitrogen atoms in the macromolecules. Much of this earth consists of inorganic macromolecules, in their more sophisticated forms referred to as ceramics. Ceramic materials are crosslinked inorganic macromolecules, oxides of various metals, and also of silicon. Ceramics are also of relatively low density, usually twice that of plastic materials, but only half of that of metals. They are not as easily fabricated as most plastics but have use-temperatures of 500°C to over 1000°C. Only very few plastic materials, so-called high temperature polymers, are useful up to 400–500°C, and that only for very short periods of time.

One of the weaknesses of ceramics is their brittleness. Impressive advances have been made in the development of toughened and fiber-reinforced ceramics. Experiments are under way to design ceramic car engines. Even more impressive in advanced ceramic structures are the advances in high temperature (125 K) superconductors, mixed oxides of transition metals, such as copper, and of barium or calcium — also ceramic materials.

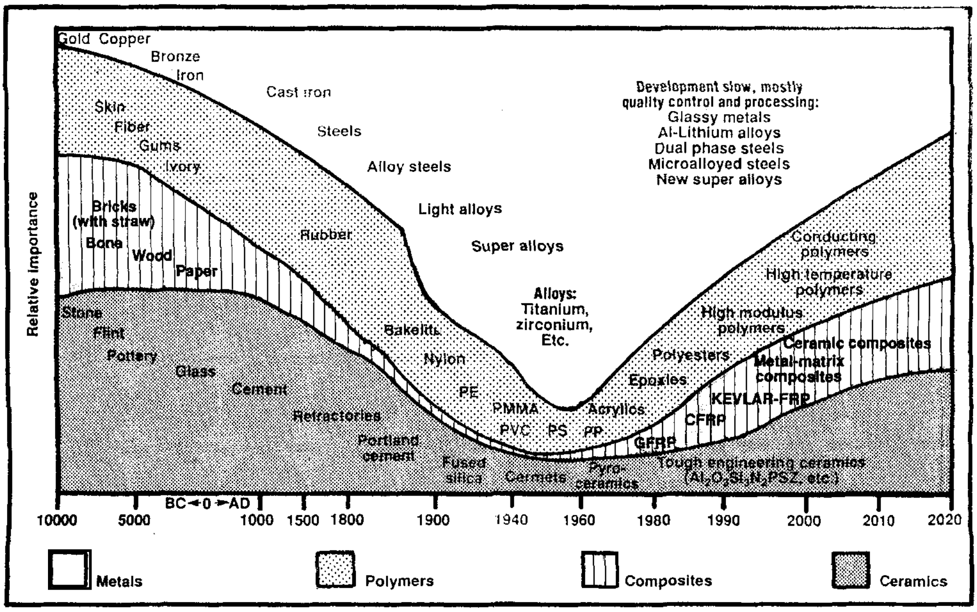


FIG. 1. Evolution of engineering materials [4].

Macromolecular Science

Polymer Characteristics

Polymer materials may be categorized into several groups. The most commonly known plastics are the *commodity plastics*. They include polyethylene, polypropylene, polystyrene, and poly(vinyl chloride). Commodity plastics have adequate properties for the reasonable price of $1.00 to $2.00 per kilogram. Higher performance polymers or *engineering plastics* include polyamides, polyesters, and polycarbonates, and to some extent also specially designed polypropylenes.

When we think of plastic materials we often think of different but very significant properties. The *clarity* of poly(methyl methacrylate), the *toughness* (high impact strength) of polycarbonates and glass-reinforced polyesters, the *high tensile strength* of superdrawn fibers, and the very *low gas permeability* of polyisobutylene, fluorinated polymers, and acrylonitrile polymers.

In the last decade we have seen the development of *functional* polymers, polymers that have special functional groups in the macromolecule. Such polymers are not so much sought for their materials properties, but rather, for the special functions that these polymers perform. Examples are polymer membranes for a variety of gas and solute separations.

If it is demanded that functional polymers are intended for special uses, they are called *specialty* polymers. For even more advanced materials and polymers of even higher sophistication, recently coined expressions are *smart* or *intelligent* polymers.

A combination of properties and price of materials – including fabrication – is known to dictate the volume that any material can command. This is also true for plastic materials. Over 80% of all plastic materials used today belong to the category of commodity plastics.

Worldwide Polymer Use

The world uses about 150 million tons of polymers annually [5]. The production of these polymers has steadily progressed over the years. Its growth [2], as shown in Fig. 2 [6], depended on the continued invention and discovery of new polymers and the commercial introduction of the products to fill a desired need. Most polymers are based on oil as the raw material. The world production of oil is somewhat in excess of 3 billion tons, and the plastics industry uses about 4% of the oil produced. We are still burning more than 90% of the oil that we harvest.

As a further comparison, it is estimated that the annual growth of wood materials (useful trees) is over twice the annual world oil production, and the annual amount of carbon dioxide utilized in photosynthesis to produce plant materials (biomass) is about 40 billion tons, or more than 12 times annual oil production.

Two important facts may be mentioned at this point. In the industrialized nations in excess of 100 kg of plastic materials per person per year is being produced. China, with nearly one-quarter of the world's population, on the other hand, uses about 10 kg per capita per year. Should the entire world population reach the living standard of people in industrialized countries with all the necessities and conveniences that are provided by the use of plastic materials, we could expect plastic production and the use of plastic materials to increase ultimately by a factor of three to four times today's production.

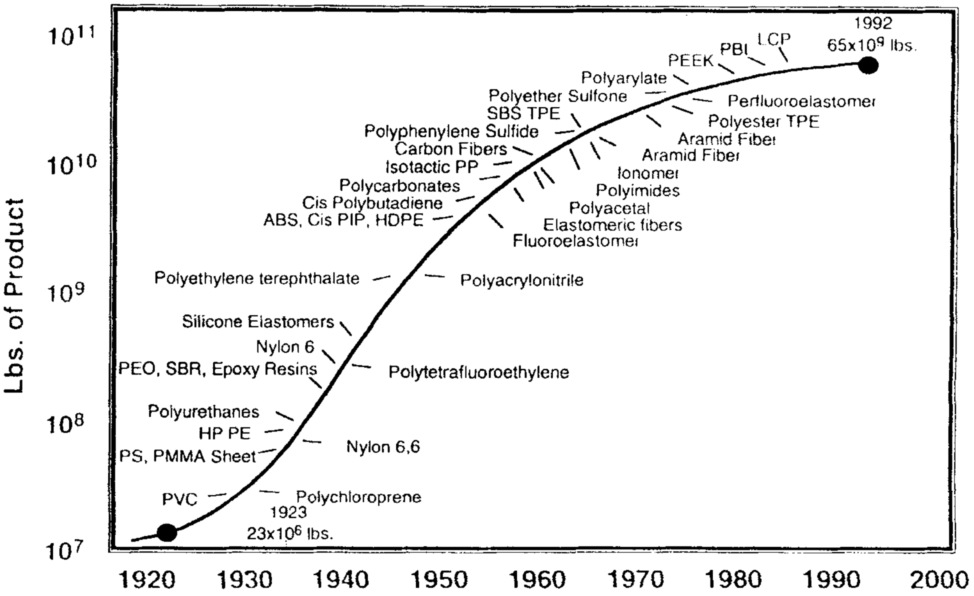


FIG. 2. United States production of synthetic polymers [6].

Sometime in the future it will be necessary to start thinking more seriously about the use of renewable materials—plant matter—or coal as the raw materials for plastics production.

COMMODITY PLASTICS

As pointed out earlier, *commodity plastics* play a very significant role in everyday life. They are of low cost, easily fabricated, and serve a wide variety of purposes. They consist primarily of the "big four": polyethylene, polypropylene, poly(vinyl chloride), and polystyrene, and they are produced in excess of 100 million tons per year each. Sometimes we divide the polyethylenes into high density (linear) and low density (branched) polyethylene. Together with the acrylics and other vinyl polymers, they dominate the plastics market in terms of volume and have dominated the volume of plastic production for the last 30-40 years. There has not been a large-scale polymer developed in the last 20 years, and we probably cannot expect the introduction into the marketplace of a new large-scale polymer in the foreseeable future.

In addition to the traditional commodity plastics that have been known since the 50s, in the 60s and early 70s a new category of polymers was introduced that could compete directly in many key properties with metals but can be synthesized and fabricated by faster and more convenient fabrication techniques—the *engineering plastics.*

Engineering plastics have a combination of properties of higher value, higher use temperatures (above 150°C), and higher modulus, to mention only a few. These engineering plastics included polyacetals, some nylons, some aromatic polyesters, polycarbonates, and in the higher range of properties (and price) the polysulfones, polyetherketones, and polyetherimides. Matching of the major desired properties—at a tolerable price level—in the category of engineering plastics determines which material is used for the required application.

As property demands are sometimes relaxed for some applications, and properties can be sufficiently improved by reinforcing with reinforcing agents such as glass and carbon fibers, or by blending with other plastic materials, the price requirements for the use of such polymeric materials becomes the dominant factor.

Polypropylene is the classic example. Production of polypropylene has been growing rapidly over the last 20 years. It is now produced at a level of about 25 million tons per year and is still growing at about 10% per year (Fig. 3) [6]. Polypropylene has properties that are sufficient for the basic requirements for engineering plastics and also is cost efficient. For many years propylene could not be polymerized at all to high molecular polymers. It was then found that it could be polymerized with transition metal coordination catalysts to a stereoregular so-called isotactic polymer, a polymer that crystallizes in a helical structure. Initially propylene had to be polymerized in solution. About 10,000 parts of polymer were produced per one part of catalyst, and the stereoregularity of the polymer was not very high; only about 3% of the catalysts had active centers.

Now we have learned to make the polymer in the monomer propylene itself or in a gas phase. We have learned how to produce polypropylene as highly (nearly 100% specific) stereospecific or, if necessary, stereospecific polypropylene of controlled (lower) stereospecificity. We have learned to produce polypropylene with nearly 100 times the catalyst efficiency and can now leave the catalyst in the plastic product. The effort worldwide to optimize catalyst efficiency (grams of polymer produced per gram of catalyst) has achieved phenomenal proportions as has the

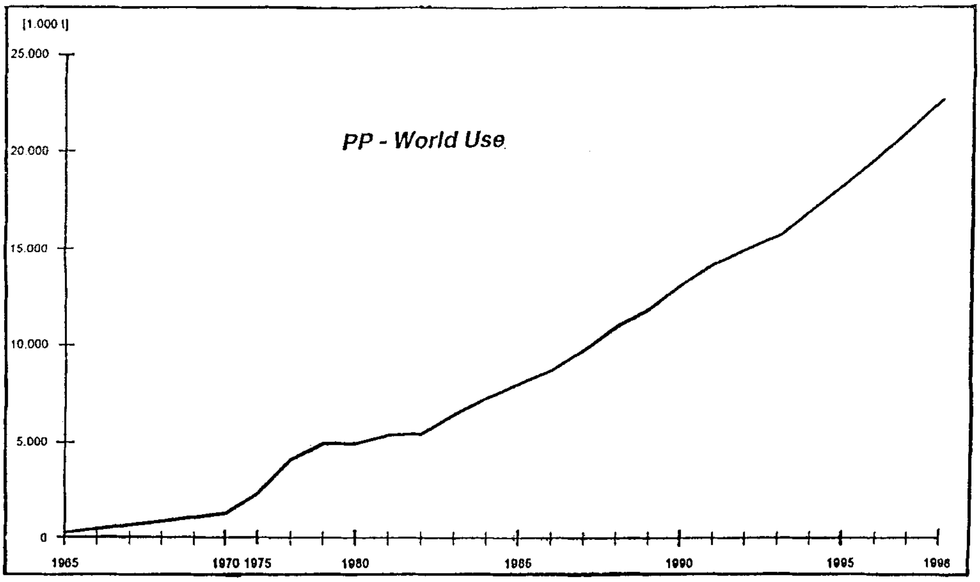


FIG. 3. Polypropylene production.

control of molecular weight and molecular weight distribution, tacticity, and tacticity distribution.

We can now make polypropylene of controlled degree of stereoregularity—and stereoregularity with regard to the distribution of the irregularity! We have learned to make syndiotactic polypropylene. This polymer has a considerably different combination of properties from the isotactic polymers (the repeat unit of syndiotactic polypropylene is a 4_1 helix as compared to a 3_1 helix for isotactic polypropylene).

We have learned how to make isotactic polypropylene (with the third generation catalysts) directly in the bulk density that is desired and in the shape that is required to feed the polymer particles directly into the extruder for extrusion or injection molding. We have learned to make copolymers and polymer alloys by these highly specific catalysts directly, and we have learned to influence and control the molecular weight distribution.

CATALYTIC PROCESSES AND POLYMERIZATION

We see further development of monomer syntheses based on catalytic processes without side products, with a minimum amount of separation and isolation, and by very direct routes. We know that olefins are made from crude oil by specific cracking techniques. Higher unsaturates, such as dienes, are washed out and separated. Early attempts for selective polymerizations of the individual components from these mixtures, although intriguing, have not been successful. More attention and efforts should be placed on this problem. Catalysts with a greater specificity for the polymerization of individual monomers are better understood and are becoming available, especially solid-state catalysts with high efficiencies, and could help solve these problems.

Another example is connected with catalytic monomer synthesis. Methyl methacrylate is synthesized technically from acetone and hydrogen cyanide. The last step consists of methanolysis of the cyanhydrin with sulfuric acid. This process, although a high yield process, produces one mole of ammonium sulfate per mole of methyl methacrylate soiled with an objectionable amount of cyanide in the product. Every time a scale-up of the process is anticipated and scheduled, the disposal problem becomes more serious. A process seems to be on the horizon that uses methylacetylene, a catalyst, carbon monoxide, and methanol. Nearly quantitative yields of methyl methacrylate have been reported.

Great progress has been made in the development of new polyolefin processes, especially processes for polypropylene. The thrust for the development of novel catalyst systems has provided solid catalysts and is now extremely sophisticated; in fact, we are now speaking about a third and even a fourth generation "Ziegler-Natta" catalyst for polypropylene production. Not only are we able to synthesize polypropylene in high yield with high stereospecificity, or even more importantly with controlled stereospecificity isotacticity (sometimes 100% isotacticity is not the most desired stereoregularity in polypropylene but rather 94%), but also in a high yield of polymer to active catalyst ratio. This means that only very low amounts of the active catalyst need to be used at the level of 2 ppm of catalyst for a high rate of polymerization to produce the proper isotacticity of the polymer. This amount of catalyst does not impart any detrimental effects to the polymer and can thus be left in the polymer. This combination allows the polymerization to be carried out in the vapor phase or in liquid propylene. In addition, not only can we now make the polymer polypropylene, but we can make it in the desired particle size and bulk density, which produces polypropylene particles that can be used directly for extrusion or for injection molding. Lastly, and in an ultimate advance, we can now make copolymers and blends or alloys of polyolefins just by using different monomers (such as ethylene and propylene or propylene and butene) in sequence.

MOLECULAR WEIGHT

Molecular Weight Distribution

One new development that has recently become very interesting is the improvement in the definition of molecular weight and molecular weight distribution. As we have known for many years, the most probable distribution of polymer moleculars weights is $\overline{M}_w/\overline{M}_n = 2$ [7]. Living polymerization can provide us with polymers of molecular weight distributions approaching $\overline{M}_w/\overline{M}_n = 1$ [8]. With new techniques of isolation and separation of essential individual species of molecular weights, it has now become possible to obtain single uniform macromolecules [9]. Up to 100 mer from both isotactic and single isotactic poly(methyl methacrylate) has been isolated. It can be seen in Fig. 4 that the initial distribution of the molecular weight species of "nearly" living polymers is $M_w/M_n = 1.06$.

Most probable molecular weigh distribution: Carothers

$$\overline{M}_w/\overline{M}_n = 2$$

Living polymers: Szwarc

$$\overline{M}_w/\overline{M}_n \approx 1$$

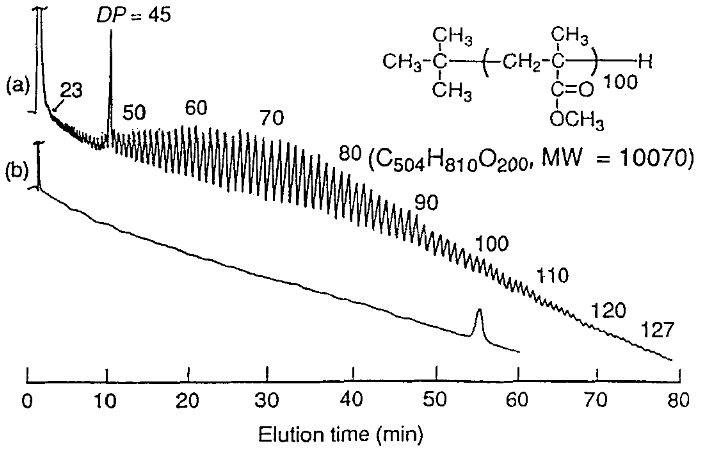
Uniform polymers: Hatada

$$\overline{M}_w/\overline{M}_n = 1.000000$$

Polymers that are uniform, in other words, single macromolecular species of high molecular weight that are of uniform molecular weight, can be compared which macromolecules commonly produced by nature. Those natural uniform polymers are proteins, nucleic acids, and some polysaccharides. Some of the most active compounds in nature are uniform proteins with molecular weights as low as 5,000 and up to 10,000 (Fig. 5) [9], well within the range of the recently isolated poly(methyl methacrylates) which are now available in 100 milligram quantities.

End Groups

A linear polymer consists of two end groups. For "addition polymers" the macromolecules have one end group from the initiating species (or when there is chain transfer, from one part of the chain transfer agent). The other end comes from the termination reaction. In condensation polymers the end group comes from one part of the reactive functional groups that are the basis of the polymerization of



SFC traces of isotactic PMMA ($\overline{DP} = 66.5$, $\bar{M}_w/\bar{M}_n = 1.07$, *mm* : *mr* : *rr* = 97.7 : 2.3 : 0.0) containing an authentic sample of the 45mer (a) and of the isolated 100mer (b).

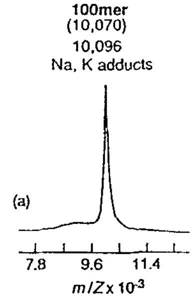


FIG. 4. Uniform poly(methyl methacrylate) [9].

an A—A with a B—B monomer or the polymerization of A—B monomers and the other end from the other "monomer."

End groups are often the weak point of a polymer [10]. It is not the length and the inherent thermal stability of the polymer main chain that leads to degradation (primarily thermal degradation during fabrication) but the relative instability of the end groups. This is true in the case of the melt instability of polyamides with free amino end groups; excessive free carboxyl groups in polyesters; vinyl groups in polyethylene, polypropylene, polyisobutylene, and other polyolefins; vinyl groups in poly(methyl methacrylate); allyl chloride ends in poly(vinyl chloride); and hemiacetalic hydroxyl groups in polyoxymethylene.

Reactions on end groups are often successfully carried out to introduce purposely specific functional groups. These reactions are either performed by "end-capping" [11] or by chain transfer or by using a functionalized initiator. For technical purposes, the acetate end-capping of hydroxyl-terminated polyoxymethylene with acetic anhydride [12] is essential for the fabrication and use of polyoxymethylene. Hydroxy- and carboxy-terminated polybutadiene is prepared by polymerization and chain transfer with the appropriate (excess) initiator, either a peroxide or

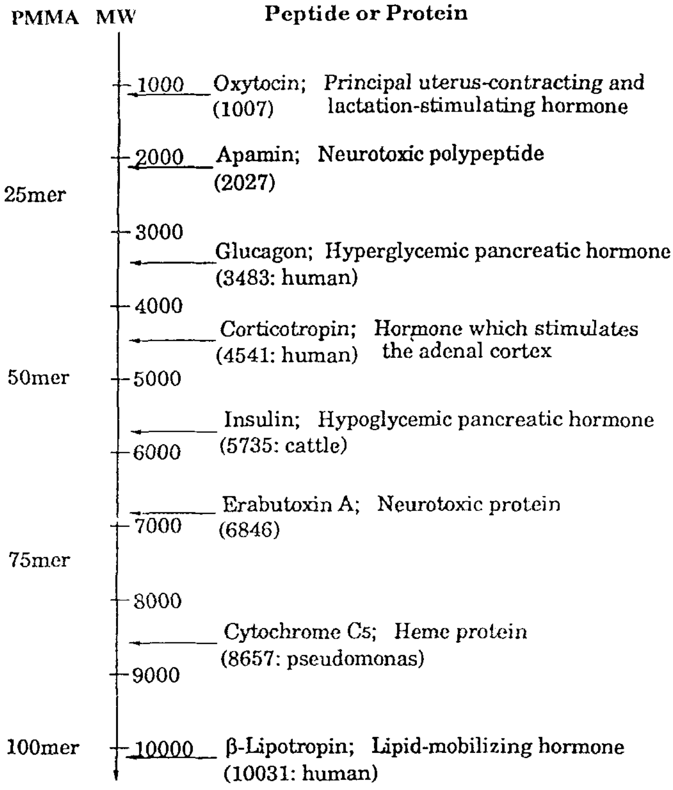


FIG. 5. Uniform natural polymers [9].

an appropriate azo initiator [13]. Ultraviolet stabilizing groups were introduced by a radical initiator containing a stabilizing group.

PRECISION POLYMERS AND MACROMOLECULAR ENGINEERING

Living Polymerization

The molecular weight distribution of 1 was achieved by living polymerization. Initially this was demonstrated by anionic polymerization [14]. Styrene polymerizations were the first examples where this technique was studied. It led to the synthesis of ABA block copolymers [15], star polymers [16], macromonomers [17] and network polymers [18] of controlled link length. It was this type of polymerization where macromolecular engineering was first used effectively. Living polymerization was soon discovered for other anionic polymerizations [19], most notably for methyl methacrylates and other methacrylates, or for the commercially used technique of so-called group transfer polymerization [20].

Cationic living polymerization, although mentioned in the early 60s [21], was really not clearly demonstrated until the "livingness" of tetrahydrofurane was shown to occur with aluminum alkyl-water systems as the initiating systems [22]. In subsequent years, living polymerization in ring-opening polymerization was perfected, and many examples of cationic living polymerization were demonstrated. Finally, the highly elusive living polymerization of olefins was demonstrated [23]. It is easier to see the living polymerization of vinyl ethers and styrene. These two types of monomers have the capability of functioning in their resonance form and give growing polymer cations that are less reactive than the growing cations from isobutylene and do not have the tremendous tendency to terminate by the loss of a proton. By judicious manipulation (starve feeding of the monomer) of the cationic isobutylene polymerization [24] or by appropriate selection of the initiating system [25], it was possible to achieve this most desirable goal. By these controlled initiation processes and the use of inifers, binifers, trinifers [26], and the preparation of bifunctional monomers, macromonomers, functional monomers, and telechelic polymers based on isobutylene, styrene, and vinyl ethers have been prepared [27].

At about the same time, radical polymerizations that allow the preparation of polymers with narrow molecular weight distribution have been reported [28].

It is now recognized that living polymerization depends on two main characteristics; instantaneous and complete initiation, that are complete additions of the initiator to the first monomer unit, and prevention of termination. It should be pointed out that living polymerization is a nonequilibrium process that produces a molecular weight distribution of 1; the polymerization can be restarted upon addition of more monomer or it can be continued with another monomer to produce block copolymers. On allowing the system to equilibrate by allowing a "living system" to stand for a considerable amount of time, the molecular weight distribution will approach 2, the most probable molecular weight distribution.

The living character of the polymerization, ionic or radical, is guaranteed or made most likely under one or the other or both conditions. The monomer is of relatively low reactivity such as in the case of resonance-stabilized monomers, and consequently resonance-stabilized growing polymer chains or the active species is present in the reaction mixtures in very low concentration. This can be achieved by the proper initiating system or by adjusting (lowering) the temperature (the latter may not always be feasible!). In ionic polymerization systems this can be achieved by coordinating either the cation in cationic polymerization or by addition of a complexing agent such as a thioether in carbocationic polymerization to mimic the vinyl ether type polymerization which apparently provides only a small amount of truly free or ion paired carbocation. Even in anionic polymerizations, a certain degree of complexation is desired, such as the sylyl system in group transfer polymerization [29], where this group prevents the termination by cyclization and allows the reaction to proceed even at 80°C. In normal anionic methyl methacrylate polymerization, temperatures of less than −40°C are needed to prevent this termination [19].

Other examples are the coordinative polymerization of epoxides with aluminum alkyl/water/acetylacetone systems [30] and the polymerization and copolymerization of epoxides and lactones with aluminum alkyl/porphyrine systems [31].

Of primary importance in living cationic systems for cyclic ethers is the use of trifluorosulfonic or trifluoroacetic acid as initiators. Perchlorate esters were the obvious source of the stabilization of the growing polystyrene cation, the formerly called "pseudocationic" polymerization of styrene [32].

Radical polymerization that has living character [33] has also been demonstrated for styrene and methyl methacrylate polymerization. In this case, the radical is complexed with a radical source that has for a long time been used as a radical trap for ESR measurements of radicals—organic nitroxides of the proper structure [34].

Living polymerization has provided an important impetus for the development of macromolecular engineering because it makes possible the preparation of polymers of the proper molecular weight at narrow molecular weight distribution. It allows the design, tailor-made preparation of block copolymers of known molecular weight, of exact length of the blocks. Similarly, polymerizable end groups can be attached to living polymers to make macromonomers [38]. When the living polymer chains are connected to a reactive core of the proper size (molecular weight), star polymers of known arm size have been prepared [35]. The living polymer can also be a block copolymer. Similarly, living polymers have been used to synthesize polymer networks of known linking spacer groups [36] and even groups of drastically different properties, such as hydrophilic and hydrophobic portions of the network [37]. Other uses for these block copolymers are as compatibilizers [38].

Coordination Polymerization

On addition of each monomer unit of substituted α-olefins, α-perfluoroolefins, and higher aldehydes, a new asymmetric center is formed that may be placed either in *meso*- or in *racemo*-placement. If the entire polymer chain consists of *m*-additions, we call this *isotactic*, all *r*-addition products *syndiotactic*, and alternating *m*- and *r*-placement *heterotactic*; when there is substantially *random* placement of the stereochemistry in each unit, we call this an *atactic* structure [39]. If the stereochemistry of the polymerization is uniform, we call the polymerization *stereospecific polymerization* and the polymer obtained is a *stereoregular polymer*.

In the late 40s the polymerization of methylvinyl ether led to a polymer that was partially crystalline; it was then speculated that the polymer might have a preferred stereochemistry [40]. A few years later, propylene was polymerized to a stereoregular polymer; the structure of the polymer has an isotactic structure [41]. Subsequently, many other α-olefins were found to be subject to similar stereospecific polymerization reactions.

Shortly afterward the polymerization of propylene oxide [42] and higher aldehydes [43] was also established. Butadienes 1,3 were polymerized to purely *cis*- or *trans*-1,4-polybutadienes [44].

Much less was known about syndiotactic polymers. It was generally assumed that the *racemo*-placement in the addition of the monomer was an error of the highly coordinated *m*-addition and highly syndiotactic polymers which were just the consequence of a "wide-open" polymerization, in terms of the "closeness" of the ion pairs. In the last decade the all *r*-addition that led to syndiotactic polymers has come into its own. Conditions and initiator systems have been found to synthesize and characterize highly syndiotactic poly(methyl methacrylate) [45], polystyrene [46], and even polypropylene [47].

Enormous progress has been made in the preparation, selection, and utilization of initiator systems involving transition metal "catalysts." We can now prepare highly or less highly isotactic polypropylene, polypropylene with specific particle size and bulk density, copolymers of α-olefins among themselves, or intimate mixtures of two homopolymers of poly(α-olefins) on a molecular scale, so-called polymer alloys [48]. We can now not only control the stereospecificity of polymerizations but also particle size and shape and even bulk density. Using this principle, many new categories and types of polymer combinations have been investigated or at least explored.

As long as we have *known* structurally synthetic and natural polymers, they have been known to be either linear or crosslinked polymers. The challenge and interest to synthesize polymers that are giant cycles and consequently would have no end groups have been discussed for a long time, and efforts to prepare such polymers have been made. *Metathesis polymerization* of cyclic olefins was for a long time believed to proceed through ring opening of the cyclic olefins. It is now known [49] that the polymerization occurs with a transition metal-carbene bond as the chain-growing center. With this new knowledge [50], considerable progress has been made and "catalyst systems" have been found to polymerize not only simple olefins or, what has recently been found, unconjugated dienes [51], but also cyclolefins with functional groups, such as ether and even ester groups if the double bond is located in a strained ring [50].

Stereoregular Polymers

The polymerization of prochiral monomers such as α-olefins, methacrylates, or higher aldehydes via chain reaction polymerization mechanisms introduces a series of pseudoasymmetric centers into the newly formed polymer backbone [52]. When the addition of monomer occurs in a stereorandom fashion, successive pseudochiral centers located along the polymer chain randomly occupy *R* and *S* configurations, leading to atactic structures. As a rule, atactic polymers tend to adopt random coil conformations and are generally devoid of order in the condensed state. Not surprisingly, considerable effort has been expended to devise polymerization techniques which give rise to stereoregular polymers with better defined molecular architectures. Notable in this regard is the preparation of isotactic, helical polypropylene and other poly(α-olefins) with Ziegler–Natta transition metal catalysts [53–55]. The stereospecific polymerization of polar monomers like the methacrylates [56] and the vinyl ethers [57] with anionic or cationic initiators, respectively, also leads to polymers with isotactic configurations. More recently, initiators and polymerization conditions have been developed for the preparation of syndiotactic polystyrene, syndiotactic polypropylene [58], and highly syndiotactic poly(methyl methacrylate) [55, 59, 60]. The preparation of isotactic polyaldehydes via ionic chain reaction polymerization has been studied extensively [61]. The stereospecific polymerization of 1,3-butadiene, isoprene, and other diene monomers to furnish stereoregular polymers has also been reported. Here, initiating conditions can be selected to give 1,2-polymers with isotactic or syndiotactic arrangements or 1,4-polymers with *cis* or *trans* geometries [62].

A number of ring-opening polymerizations can also be carried out to give stereoregular polymers [63]. Notable among these is the stereoselective polymerization of propylene oxide and higher 1,2-epoxides to give isotactic polymers, and the polymerization of lactones, cyclic acetals, and *N*-carboxy-α-amino acid anhydrides to yield stereoregular structures [64].

Copolymer Structure and Microstructure

Control over the primary sequence of monomer units along a copolymer chain constitutes another important parameter for the design of structure controlled materials. In this regard, the structural inhomogeneity and complexity of native macromolecules far exceed those found in man-made copolymers and terpolymer systems. Unique sequential arrangements in natural polymers, nucleic acid, proteins, and polysaccharides are provided by nature in a relatively complicated and slow process. Unless mechanistic considerations dictate otherwise, the growth of copolymers, terpolymers, and more complex species tend to occur in random fashion, often giving rise to polymer samples with varying degrees of heterogeneity [65].

Macromolecules with an alternating sequence of two monomer units do arise via chain reaction processes when a propagating chain end reacts exclusively with the "other" monomer because of steric or electronic repulsion. The radical copolymerization of 1,2-diphenylethylene and maleic anhydride is the classic example for such a behavior.

Step reaction polymerization of A—A and B—B monomers also provides for a strictly alternating sequence along the polymer backbone.

Particularly significant are living polymerization technique which now afford access to block copolymers having well-defined sequences and block lengths [66, 67]. However, the number of monomers which are well behaved under living polymerization conditions remains limited.

New polymerization techniques that would provide for the exact control of primary sequences and microstructure along a copolymer chain remain fertile ground for further research and development. Important advances have been made for anionic coordination polymerization by the now commercially used group transfer polymerization for methacrylates and the exact computer-controlled multistream (for each monomer initiator and solvent) technique of radical co- and terpolymerization of acrylic and other monomers.

Spacer Groups in Polymer Structures

For many years, natural polymers, especially proteins, have been known to have unusual specificities based on the arrangements of their 20 natural amino acid units, their conformation, and tertiary structure. One other characteristic in some of the amino acid units is that some functional groups, such as amino groups in lysine, the guanidino groups in arginine, and the carboxylate groups in glutamic or aspartic acid, are separated from the main polyamide chain by two or three flexible methylene *spacer groups*. Even the hydroxyl group of threonine and the mercapto group of methionine are separated from the main poly(α-amino acid) chain and the phenolic hydroxyl group of *p*-hydroxyphenyl alanine is separated by a rigid benzene ring from the main chain. In aqueous medium where the proteins are active, the hydrophobic aliphatic side groups of leucine and isoleucine provide hydrophobic interactions [68]. All these groups have specific functions, and the type of spacer and its length are essential for the tertiary structure of the protein and the high specificity of its action, which is clearly demonstrated in hormonal and enzymatic activity. One methylene group more or less in the spacer group, and the activity is diminished. The classic example is the structure of hemine, where the complexing of the iron atom with the appropriate ligand structure (provided by the lysine unit)

[69] provides the reversibility to attach molecular oxygen. The central iron atom allows the completely reversible addition of the oxygen molecule for long periods of time, which allows us to breathe and to live.

Not much attention had been paid to spacer groups in synthetic polymers, even though many very useful polymers have functional groups directly attached to the main polymer chain. Examples are the carboxylic acid functions in acrylics, the chlorine in poly(vinyl chloride), and the hydroxyl function in poly(vinyl alcohol).

It has now been recognized that spacer groups also play an important role in the chemistry of synthetic polymers [70]. Coordination polymerization of ω-carboxy alkenoates or ω-epoxyalkanoates can only be achieved effectively if a spacer group of at least 3 methylene groups is inserted between the carboxylate function and the polymerizable group [71]. Optimal properties based on the functional group were recognized in such polymers when the ionomeric properties of the sodium salts of the free acids were investigated. A substitution of only 1.5% ionic groups was found to be necessary in these cases [72]. An optimum concentration of methacrylate units (sodium salts) in ethylene-methacrylic acid "ionomer" copolymers was about 10–12% ionic salts groups.

Spacer groups were also found to be essential to tailor-make liquid crystalline polymers, especially thermotropic aromatic polyesters. Aromatic polyesters made from rigid linear units, such as the polyesters from hydroquinone and terephthalic acid, or the homopolymer of *p*-hydroxybenzoic acid, are high melting "brick dust" polymers whose melting points are above the thermal decomposition temperature of the polyesters; these polymers can therefore not be fabricated by melt (or solution) techniques. Flexible methylene groups judiciously introduced into the polymer structure in relatively small amounts bring the melting point and, even more importantly, the transition point from the crystalline to the mesogenic phase to lower temperatures which, in turn, opens a wide temperature region of the mesogenic phase.

Two examples where flexible side chains are of great importance are the fluorocarbon polymers NAFION or FLUON [73]. They have a flexible fluorocarbon side chain separating the fluorocarbon backbone chain from the ionic sulfonate of the carboxylate group.

Another case where a spacer group is introduced into a condensation polymer (a polyester of polycarbonate) was accomplished by either copolymerization with a "flexible" glycol or diacid, or by using a glycol or a diacid that already has a flexibilizing group in the monomer. The result is a specifically designed polymeric drug suitable for biological degradation [74].

NONLINEAR POLYMER STRUCTURES

Branched, Highly Branched Polymers and Dendrimers

Linear polymers, especially when the molecular weight is sufficiently high, have as a "polymer characteristic" chain entanglements which are responsible for a number of polymer properties including their solution or their melt viscosity.

Recent fabrication technologies for coatings and other applications utilize relatively low molecular weight polymers with functional groups that can easily be crosslinked.

Another conceptional approach that provides polymers of sufficient molecular weight without entanglement of the macromolecules are *highly branched polymers*

[75]. These polymers are prepared by two approaches. The first one starts with a multifunctional molecule which provides the basis of polymerizing monomers which have three functional and reactive groups in the molecule; two of them are the same [75, 76]. The macromolecular structure which is formed provides a branching mechanism at the addition of each monomer unit and is substantially spherical. A linear polymer structure is obtained under traditional polymerization conditions of monomers with a functionality of 2. Many of the highly branched polymers that were prepared initially were of relatively ill-defined character but of sufficient interest to introduce this new type of polymer and its concept. They are now also called dendrimers or "starburst" polymers.

The other approach to synthesize highly branched polymers starts with the synthesis of "wedges" and links the central functional units to synthesize the center of the macromolecule [77]. This approach allows a stepwise synthesis of well-defined "oligomer" structures and also permits the preparation of "half globes" or even segments of spheres. Both synthesis strategies result in globular polymers or polymer that resemble spheric structures, polymers that have a minimum amount of entanglements, but have all their functionalities on the surface of the polymer. These polymers are consequently an extension of the principle of star polymers. Star polymers are consequently dendrimers with long inert spacer groups.

The success of this type of polymer synthesis depends very much on the reactive groups, but almost more importantly, on the type and length of the spacer group and on the flexibility of the spacer groups that separate the reactive groups.

It was pointed out above that in highly branched polymers the surface of the macromolecule consists essentially of functional groups. Highly branched polymers and dendrimers, instead of having a "degree" of polymerization which describes the number of monomer units in a linear polymer chain, have "generations" of monomers arranged in the macromolecule like the shells of an onion, whose "surfaces" consists of end groups.

Cyclic Polymers and Oligomers

Truly cyclic polymers have only been made by cycloaddition of unconjugated diacetylenes with terminal triple bonds followed by hydrogenation. Saturated cycles with over 250 carbon ring members have been reported [78].

Cyclic oligomers are of potential technical value, and the lower members have become important [79]. The best examples are cyclic oligomers of carbonates of bisphenols, for example, Bisphenol A. Mixtures of cyclic oligomers with 20–30 ring members have been synthesized and subsequently polymerized to polycarbonates of exceptionally high molecular weight (in excess of 10^6). This polymerization technique has great promise for the preparation of composites of maximum properties that could not be prepared by conventional techniques for composite fabrication because of their high viscosity. Not only cyclo-oligocarbonates and their polymers, but also cyclic oligoesters, oligoamides, and oligoimides and their polymers have been investigated [80].

Highly Ordered Structures

For many well-defined polymers, hydrogen bonding, the stacking of aromatic rings, ionic attractions, and other intermolecular forces localized between polymer chains play a subtle role in determining the extent and type of order found in the condensed state. Important materials properties like glass transition temperature, melting temperature, solvent resistance, and mechanical strength are intimately tied to the capability of polymer chains to aggregate and to self-organize. Notable in this regard are polyamides like nylon 66 which adopts extended chain conformations that are linked through an array of hydrogen bonds to form compact ordered structures [81, 82].

RIGID POLYMER STRUCTURES

Liquid Crystalline Polymers

One type of polymer has received a great deal of attention since the early 1970s, the liquid crystalline polymers [83]. The first important polymer that played the front-runner for liquid crystallinity in polymers is poly(*p*-phenylene terephthalamide), often called by its trade name Kevlar [84]. It is wet spun from a dope of the polymer in 100% sulfuric acid in concentrations which are at the maximum of the lyophilic liquid crystalline (mesogenic) range of the solutions. The discovery and evaluation of thermotropic (liquid crystallinity in the melt) mesogenic polyester followed soon [83]. We now know the rules of how to make tailor-make mesogenic polymers and how to design the structure of the liquid crystalline polymer with the right mesogenic range, the temperature range between the crystalline/liquid crystalline and the liquid crystalline/isotropic transition which can be accomplished by rather small changes in the polymer structure. We can now also distinguish the nematic and the smectic phases of polymer melts and solutions by appropriate measurements.

Even more interestingly, we can induce cholesteric character into polymer structures by either introducing a chiral center into the monomer unit or by "seeding" the structures with a chiral cholestric monomeric substance.

Interesing are also the attempts to prepare large *cholesteric phases of helical structures* from macromolecules that have a mesogenic basic structure but have a chiral flexible side chain, with a polar group such as a cyano group located centrally in the flexible side chain [85].

All these approaches are very much directed to a controlled "self-assembly" not only of polymeric structures but also of smaller molecular structures into larger associates, loosely or fairly strongly "held-together" structures similar to biological membranes which are represented as double layers and vesicles [86].

Macromolecular assemblies have also been accomplished by "laying down" macromolecules which are assembled like soap micelles on a water surface. This technique, also called the Langmuir-Blodgett technique, allows the assembly of alternating polymeric anions and polymeric cations, layer by layer, each layer about *10-20* Å thick. This technique has been used to prepare thin sections of transparent electrically conducting polymers or of polymer thin films with nonlinear optical properties.

For over three decades attempts have been made to synthesize and tailor-make *high temperature polymers* with increasingly more attractive thermal stability. The limitations of organic polymers are well known, but the gap to close the use range between organic polymer that are relatively easily processed and those of ceramic materials which are more thermally and oxidatively desirable was highly attractive. The early commercially used *polyimides* [87] were found to have exceptional and very attractive properties, but did not quite fulfill all the optimistic industrial expectations.

Many polymer structures other than polyimides were synthesized, such as polybenzimidazoles, polybenzoxazoles, polybenzothiazoles, and polyquinoxalines, to achieve maximal properties as high temperature polymers. None of these structures has ever been a serious competitor for the polyimides. Much more beneficial than synthesizing more and more structures for the progress in high temperature polymers turned out to be the optimization of polyimide structures.

Substantial product improvement was achieved by placing a hexafluoropropyl group between the two phenyl rings of either the dianhydride or the bisphenol. These newer structures allowed the introduction of polyimides into applications that had not been previously anticipated.

Stereoregular and Conformationally Regular Polymers

The solid-state properties of isotactic and other tactic polymers of polyolefins like polypropylene, the isotactic polyaldehydes, and poly(alkylene oxides) have received considerable attention during the past four decades. With a succession of *meso* placements along their polymer backbones [88], these configurationally well-defined polymers are capable of adopting helical geometries in the solid (crystalline) state with alternating *trans*-gauche or *trans*-skew conformations. Helical structures are incorporated into regular crystalline lattices [89, 90] and, not surprisingly, most isotactic polymers possess semicrystalline morphologies with good physical and mechanical properties. Isotactic polymers with 3_1, 4_1, and nonintegral 7_2 helical motifs have been identified by x-ray diffraction studies. Helix geometry in the condensed state is strongly influenced by the size, polarity, and chirality of the pendant groups which generally reside along the polymer backbone. Larger side groups demand that a greater number of monomer units occupy one full turn in the helical screw [90] while chiral side groups can impart a preferred helical screw direction in these polymers [91–93]. By employing newly developed helix-sense selective polymerization techniques, isotactic polymers having a predominant or exclusive screw sense have been successfully prepared from monomers lacking chirality [93–95]. These materials exhibit interesting chiroptical properties in the solid state and in solution which stem from the presence of macromolecular asymmetry. Their physical and mechanical properties remain to be fully evaluated. Recently, the genesis of isotactic, helical structures along a growing polychiral chain was effectively "mapped," providing a detailed look at how the configurational arrangement of covalent bonds along a polymer backbone and the conformational geometry ultimately adopted by a macromolecule are intimately linked [96].

Helical Polymers and Optically Active Polymers

Many advances have been made in understanding the structural element that contribute to the formation of helical structures [96], the relationship between the flexibility of the backbone chain and the side groups that force the development not only of a stereospecific addition of monomer units regardless of the mechanism of the polymer formation, but also the development of the conformational specificity of helical polymer structures. Chloral and a few other monomers are examples that *stereospecific and conformationally specific polymerizations* can be achieved. Progress has also been made in identifying the structure and/or size of initiating anions or countercations in anionic polymerizations [94]. By using the proper chiral initiators, it is now possible to design them in their chiral version to synthesize the single polymer helix which implies the polymers are optically-active-based on the macromolecular asymmetry.

Optical activity of solids including polymers can now be determined since it is possible to measure both optical rotation and circular dichroism in the solid state in suspension.

What has led to the understanding of the formation of helical polymer structures was the study of selected examples of the *genesis* of this polymer formation [96] by investigating the *embryonic state*. This work was initially done by investigating the oligomerization of chloral, including the determination of the absolute configuration of each oligomer up to the octamer by single crystal x-ray analysis [97]. This work was followed by oligomerization studies of the stereospecific oligomerization of methyl methacrylate [98], and the oligomerization of propylene [99] and other monomers.

Stimuli Responsive Polymer Structures

Macromolecules endowed with stimuli-responsive functional groups are capable of reversible structural perturbation and, as such, constitute a unique class of ordered polymeric materials. Most extensively studied have been azobenzene derivatives which undergo large changes in geometry and polarity owing to the *trans* ↔ *cis* isomerization about their rotoresistent N=N double bond [100, 101]. Interconversion between *trans* and higher energy *cis* isomeric states can be effected both photochemically (*trans* ↔ *cis*) and thermally (*cis* ↔ *trans*). For polymers comprised of main-chain azobenzene linkages, "local isomerization reactions have a profound impact on the global conformation assumed by the macromolecule. Such effects have been noted in polyamides and other condensation polymers but also in azobenzene modified natural polypeptides which can undergo photoinduced α-helix-to random coil and β-structure-to random coil transitions" [102].

Other stimuli-responsive functional groups have also been exploited to induce well-defined transitions in polymer architecture via *cis* ↔ *trans* isomerization, zwitter-ion generation, ring formation, and cleavage and ionic dissociation mechanisms.

REACTIONS ON POLYMERS

Functional groups are groups that give the polymer structure special character, substantially different from the inherent properties of the basic polymer chain [103, 104]. Examples are the phenyl group in polystyrene, the cyano group in acrylonitrile, the chlorine group in poly(vinyl chloride), the hydroxyl group in poly(vinyl alcohol), and the carboxyl acid group in poly(acrylic acid) which are attached directly to the polyethylene main chain. Polystyrene has a T_g of about 100°C, poly(vinyl chloride) has a high melt viscosity, and poly(acrylic acid) is water soluble.

There are numerous functional group that have been introduced into polymer structures. They include functionalities with electrical, optical, and biological characters.

Many polymer modifications have been made by so-called *postreactions on polymers*. These types of reactions have been known for a long time. They include the acetate end capping of the terminal hemiacetal group in polyoxymethylenes [105], the reaction of poly(vinyl alcohol) with *n*-butyraldehyde to "butacite," and the chlorination and sulfochlorination of polyethylene. Originally most of these reactions were carried out in solution, but more recently some of these reactions are performed in the melt, directly in the extruder, or in the solid state. The demand for commercial success of a polymer reaction depends on the most efficient way to accomplish the final result to provide a new product in the most economic way.

As some polymerization are now successfully accomplished in liquid monomer (propylene or vinyl chloride), postreactions have also been directed from the liquid state (in solution and in the melt) to reactions in the solid state. Reactions in homogeneous medium, in solution, or in the melt give different products as compared to those in the solid state. Solid-state reactions on polymers allow grafting on polymers that have been borderline in their engineering plastic properties so that the grafted polymers are brought into the engineering plastics range without significantly increasing the price of the initial polymer.

Interesting and useful examples of grafting are photografting of acrylic acid on polyolefins, especially on surfaces [106], and photografting of ultraviolet stabilizers on polyolefin surfaces [107] to place the functionality where it is most needed—on the surface!

Reactions on polymers have been a most successful and fertile ground of polymer modification. Biologically active groups have been attached to polymer chains to act either directly or to have the biologically active groups released as "polymeric drug" by chemical hydrolysis or by enzymatic action [108]. Other active groups that have been attached are polymeric stabilizers, polymeric antioxidants, and other specifically active groups. For improved UV stability, new polymerizable UV stabilizers have been developed that can either be copolymerized or grafted onto the polymers [109, 110].

POLYMER BLENDS

For a long time it was known that two polymers (or copolymers) could be mixed to the advantage and optimization of properties [111]. It might be that rubber toughening of polystyrene was the first important example of polymer blends where two polymers provided a melange that resulted in a product of optimal properties; another important example is "rubber toughened nylon". A number of polymer systems of two or more polymers which were "nonmiscible" were mixed and found to have synergistic properties superior to those of the individual polymers. Polystyrene and poly(2,6-dimethylphenylene oxide) produced a miscible polymer and a most successful commercial product [112]. This product was the first example of a successful "completely miscible" polymer blend. Today, the terms miscibility, immiscibility, and compatibility are well defined although somewhat different from the original definitions.

In the last few years the area of polymer blends and alloys has exploded in terms of examples and understanding. There are examples where nonmiscibility is absolutely essential in order to achieve the desirable ultimate properties. In other cases miscibility is desired. It is now clear that this can be achieved by interaction of specific groups in the two types of polymers that are the components of miscible polymer blends.

Interactions such as hydrogen bonding or other specific polymer interactions not only require the proper matching of the type and number of the two requisite groups in the individual polymers, but also the matching of molecular weight and perhaps of molecular weight distribution. Polar group interactions in polymer blends are important driving forces for the stability of miscible blends. Examples are polystyrene and poly(vinyl methyl ether), poly(vinyl chloride) and polycaprolactone, and other polymer blends involving polymers with polar groups.

COMPOSITES

Polymer science and technology has replaced and continues to replace metals, including aluminum and magnesium, in lightweight materials which allow weight reduction and ease of fabrication.

The importance of filled compositions and composites has been known for a long time in rubber technology (carbon-filled rubber), in phenol-formaldehyde resins (cellulose and wood powder fillers), in glass fiber reinforcements of unsaturated polyesters, and in epoxy resins. But it was not until carbon and Kevlar fiber came onto the market that a new and advanced technology of composites was born.

These advanced composites based on carbon fibers may still be using advanced epoxies as matrix materials, but more likely such composites use polyimides either based on polyamic acid as the intermediate or, more likely, based on maleimide-type polyimide resins. These advanced composites in their full development not only provide the desired reduction in weight but also have the additional promise that they are not subject to the same type of fatigue that is quite common after 10–20 years of strenuous use for metals.

POLYMER CRYSTALLINITY AND MORPHOLOGY

Polymer Crystallization

Macromolecules are synthesized by chemical means, but they are used for their physical and mechanical properties or because of their biological activity. In dilute solutions the macromolecular properties approach those of single macromolecules in the solvent. As the concentration increases, the interaction of macromolecules becomes more important for the overall properties. Also important for the development of polymer properties is the flexibility or stiffness of the macromolecules, and the interaction possibilities of portions of the macromolecules.

Many properties of macromolecules have been identified. The basic ones are the unorganized, amorphous state which is the glassy state at low temperature and the rubber state at higher temperature, and the crystalline and liquid crystalline states. We know that order in the structure of a macromolecule and specific ordered interactions will favor the crystalline state, and macromolecular design is directed toward achieving regular structures if crystallinity is desired. Examples are stereospecific polymers like isotactic polypropylene, isotactic polystyrene, and syndiotactic polystyrene. Crystallinity is observed because of ordering and interactions of polymer chains with each other such as in the nylons and aromatic polyesters. Bulky substituents in the main chain or phenyl side groups of the regular atactic polystyrene tend to increase the rigidity of the polymer chain and consequently the glass transition temperature.

Polyethylene is often considered the simplest macromolecule [113]. Normal linear polyethylene crystallizes readily, but the whole polymer chain, which is 10,000 units long, cannot crystallize as a whole chain but in units of about 100 [114, 115]. The structures are called lamellae. It requires the technique of "gel spinning," crystallization under high pressure, preferably of "ultra-high molecular weight" polyethylene (with a length of 100,000 ethylene units), to produce polyethylene structures with the structure of an extended polymer chain [116].

Polyethylene lamellae (and not always perfect lamellae) are held together by tie molecules. The crystalline structure is not perfect, and crystalline regions usually consist only of about two-third of the total material. The crystalline lamellae are then arranged in so-called spherulites, higher-ordered structures that are the result of the ordered aggregation of the crystallites. Most of the macromolecules in the melt are in the form of random coils that intertwine with each other. During the crystallization process the polymer chains slide by each other in attempts to align in the regular fashion.

Crystallization can be suppressed by introducing into the polymer chain side groups known as short chain or long chain branching. Crystallization can also be suppressed by the introduction of ionic groups as in the case of ionomers. Crystallization can be induced or somewhat controlled by assisting the formation of the first nuclei by the addition of nucleating agents. The design of the polymer structure and the selection of efficient nucleating agents is of considerable help in providing a smooth crystallization without "post-crystallization."

Many polymers crystallize in helical polymer conformations [81]. We have examples of 2, 3, and 4 polymer units, or slight variations of them, in the unit cell; these numbers describe the shallowness or width of the helix. Polypropylene must be a stereoregular isotactic polymer in order to be able to crystallize as the 3_1 helix; polyoxymethylene and polytetrafluoroethylene crystallize in nearly 2_1 helices [90].

Crystalline polymers often exist in more than one crystal form. For polypropylene we are talking of the α, β, and even the γ-form [117]. Selection of the proper nucleating agent can produce any of the forms or a combinations of forms, each with different mechanical properties. Crystallization can also be helped by annealing to assist the formation of more perfect crystals.

Attempts have been made to design mechanical properties by copolymerization, graft copolymerization, and especially by the design and synthesis of block copolymers of varying degrees of block length and molecular weight distribution of the lengths of the block.

Other Solid-State Properties of Polymers

Important solid-state properties that have attracted the imagination of macromolecular designers and architects include electrical properties. *Conducting polymers* such as polyacetylenes, polypyrrols, polythiophenes, and poly(phenyl vinylenes) have been extensively studied, as have polymers with *nonlinear optical properties*. Polymers with *piezoelectric* behavior—an important solid-state property—have also found considerable interest.

Polymers with novel optical properties have an unusual refractive index behavior in the solid state. They are liquid crystalline polymers that are amorphous but possess different refractive indices in the three directions [118]. Polymers have been designed that have optical activity based on macromolecular asymmetry or macromolecules that are a priori not stereoregular but where a helical conformation (in solution) of one helical sense can be induced by adding a small amount of molecules with chiral structures to the solution [119].

We can and have learned a great deal from the way nature has arranged the smooth functioning of life in living creatures. For example, the arrangements of membranes to transport many molecules through predetermined pathways which are then utilized, stored, and discarded.

One important role in the interface of polymer science and biology and medicine is the delivery of drugs [108]. Polymer science has contributed a great deal toward the design and synthesis of vehicles for the delivery of drugs so that they can be introduced into the patient continuously at the amounts necessary without the necessity of temporarily using an "overdose" of the drug.

Optimization and maximization of polymer properties have been done by using many techniques which are familiar to the *conoscenti* of polymer science. This includes optimization of molecular weight, molecular weight distribution, stereospecificity in polymer structures, copolymer composition, comonomer distribution, block and graft type, and distribution.

Morphology Engineering

Of substantial importance is the control of morphology, which might be called "morphology engineering," to synthesize chemical structures that fulfill several functions, one of which is to provide the desired morphology.

A recently discussed example is the incorporation of a specifically synthesized polymerizable UV stabilizer [2] which is an excellent example of the design of *surface-active polymer structures*. In this case the UV stabilizing portion of the molecule is equipped with a polymerizable group, in our case a methacrylamidomethyl group, to which a surface-active group, such as a fluorocarbon or a silicon group of the optimum length, is attached. After copolymerization with the appropriate comonomer (methyl methacrylate), the coating is applied and a film is formed that has a fluorocarbon surface and the stabilizer near the surface of the film surface [2].

PLASTICS DISPOSAL

As mentioned in the beginning, about 150 million tons of plastic materials are produced today, and we must all be concerned with the disposal of these plastic materials. The municipal waste in New York City is comprised of about 8% polymeric materials, together with 15% metals, about 10% glass, and nearly 40% paper [120]. Certain polymers, when properly separated, can be recycled. Recycling of plastics materials will ultimately amount to not more than 15% of the total amount of polymers produced and used; polyester bottles are one of the easiest objects to be recycled [120].

We should be reminded that some metals, especially those obtainable from scrapped cars and the aluminum from beverage cans, are now being collected and reintroduced in controlled amounts into the production of iron and aluminum. Only a relatively small percentage of the "used material" can be added to newly processed iron or aluminum, perhaps 10-20%.

We cannot do this kind of recycling as readily with plastic materials. When plastics materials are ready for recycling, for many types of plastic materials, like polyolefins, too much of the chemical structure has irreversibly deteriorated—autooxidized—and it is not feasible to reuse this "aged" material. Adding it to "new" polymeric materials and reprocessing the mixture would give materials with substantially lower and inacceptable properties of the reprocessed polymer.

Selected items of commerce that do not utilize properties of the material and are more or less "throw away" items, such as plastic flower pots, can use such mixtures of reprocessed plastic products with inferior properties at a low price, but how many flower pots do we need?

In the United States we now primarily use *recycling* and *landfill* to dispose of much of our refuse, including plastic materials. *Composting* is also being debated, especially in Europe, as a reasonable possibility for disposing of refuse (including plastics materials). In countries like Japan, where land is expensive and not available for landfilling, *combustion* (in air) to carbon dioxide and water and reuse of the energy produced seems to be the only real choice.

The city of Vienna, Austria, a city of 1.5 million inhabitants, has increasingly used combustion for the disposal of garbage. The percentage of combustion has increased from less than 40% in 1988 to over 60% in 1993 (Fig. 6) [121].

Recently, attempts have been made to carry out thermal degradation of polymers in the presence of reducing media in an attempt to produce oil-type products that are similar to the cracking products from oil refining. Ultimately, economic factors will determine the choice of disposal methods for each location. In other words, the questions will have to be answered: Who is willing to pay how much for the problems of disposing of what we are producing, what we are using, and what is left over.

FUTURE TRENDS AND CONCEPTS

As pointed out earlier, the development in polymer science and technology consists of *commodity plastics* and *polymeric materials for special uses.* No new large-scale polymer has been introduced in the last two decades. It is still polyethylene, polypropylene, polystyrene, and poly(vinyl chloride) with their variations. On a smaller scale, there are the polyesters, polyamides, phenol-, urea- and melamine-formaldehyde resins, and epoxies. No new large-scale resins are expected to be introduced in the near future.

Research on commodity plastics will be on a small scale. The common commodities will grow according to the demand of the growing population and needs in the Third World. For that reason we can expect that polymer production and use will grow to 400-600 million tons in the next 25 to 30 years to be 3 to 4 times more than today's use. Much of the production can be done next to the refineries that are

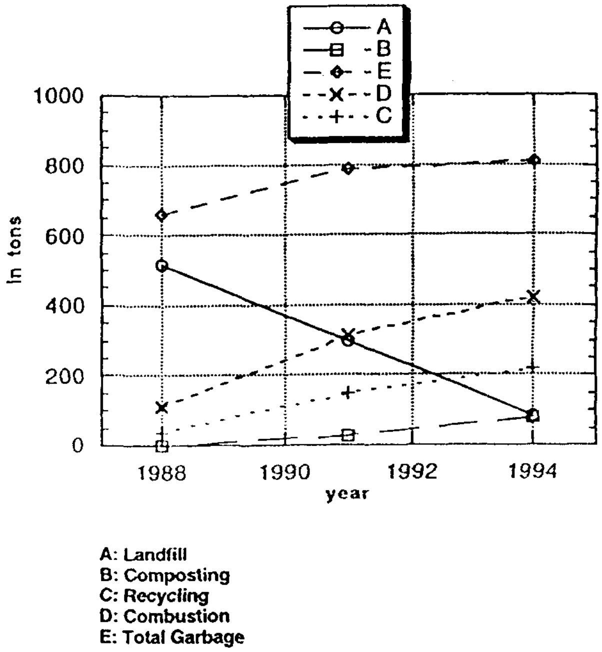


FIG. 6. Garbage treatment in Vienna, Austria [121].

the source of the monomers, especially polyolefins. Sophisticated upgrading of commodities requires some tailor-making and, consequently, research. The upgrading of polyolefins will demand reactions, such as grafting, in the extruder and in the solid phase. This adds to the cost and demands for higher performance of the final product. The volume will consequently be smaller. Much is expected from novel catalyst systems that produce simpler, faster, and a wider variety of products.

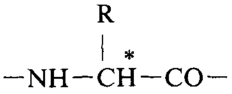
Not only will the market demand these kinds of products, but it will also demand products that can be produced in a more efficient way with higher flow during processing, faster crystallization, higher mechanical properties, and polymers with a more suitable balance of properties. This will not only be required from polymeric materials but also from blends and filled and reinforced compositions.

Polymers for special uses will have a small volume but they will occupy almost the entire research efforts. We have heard of macromolecular architecture and design, macromolecular engineering, morphology engineering, the interphase between synthetic polymers and natural polymers, gene controlled engineering of polymer properties [for poly(α-amino acids], self-assembly of macromolecules in the nanometer range, tailor-making of electrically conducting polymers, and polymers with nonlinear optical properties.

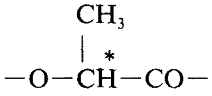
We have also learned the rules for the development of stereospecific and conformationally specific polymers, the rigid single polymer helix, and optical activity based on macromolecular asymmetry. We have found under which conditions helical one-handedness can be achieved (see Table 1) [122], and that chiral nucleation might give entirely new structures of helical polymers. Since most polymers that crystallize in helical structures give, for statistical reasons, mixtures of 50:50

TABLE 1. Reasons for One-Handedness of the Polymer Helix

1. Chiral center is in the main chain. Examples: Poly(α-amino acids), polylactides

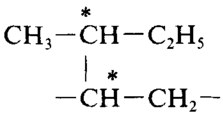


$$-NH-\overset{R}{\overset{|}{C}}{}^{*}H-CO-$$

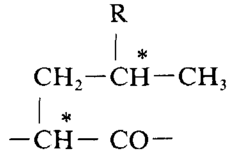


$$-O-\overset{CH_3}{\overset{|}{C}}{}^{*}H-CO-$$

2. Chiral center in α-position to polymerizable group. Examples: Nucleic acids, Poly(3-methylpentene), Poly(citronellal)

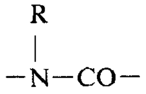


$$\begin{array}{l} CH_3-\overset{*}{C}H-C_2H_5 \\ \quad | \, * \\ -CH-CH_2- \end{array}$$



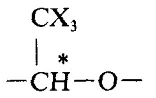
$$\begin{array}{l} \qquad\quad R \\ \qquad\quad | \, * \\ CH_2-CH-CH_3 \\ \ | \, * \\ -CH-CO- \end{array}$$

3. No true chiral center in the monomer unit but handedness of polymer helix introduced by chiral additive. Example: Polyisocyanates

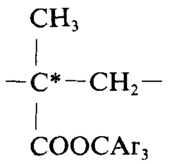


$$-\overset{R}{\overset{|}{N}}-CO-$$

4. Rigid helix: Configurationally and conformationally specific. Examples: Polychloral, some poly(triarylmethyl methacrylates). Chiral initiators: Chiral anions or chiral cations



$$-\overset{CX_3}{\overset{|}{C}}{}^{*}H-O-$$



$$-\underset{COOCAr_3}{\underset{|}{\overset{CH_3}{\overset{|}{C^*}}}}-CH_2-$$

5. Chiral separation of rigid helix polymers; e.g., on a chiral column. Example: Polyisocyanides

$$-\overset{R}{\overset{|}{\overset{N}{\overset{\|}{C}}}}-$$

6. Chiral nucleation of crystallization of helical polymers

left- and right-handed helices such as in polypropylene (Fig. 7), it should be possible to crystallize such polymers to polymeric single helix structures by chiral nucleation. This principle should not be limited to helical isotactic structures but also to other helical structures such as polyoxymethylene, polytetrafluoroethylene, and poly(1,1,2,2-tetramethylethylene oxide). A good example has been shown in the chiral nucleation of the crystallization of the inorganic salts sodium chlorate and bromate [123].

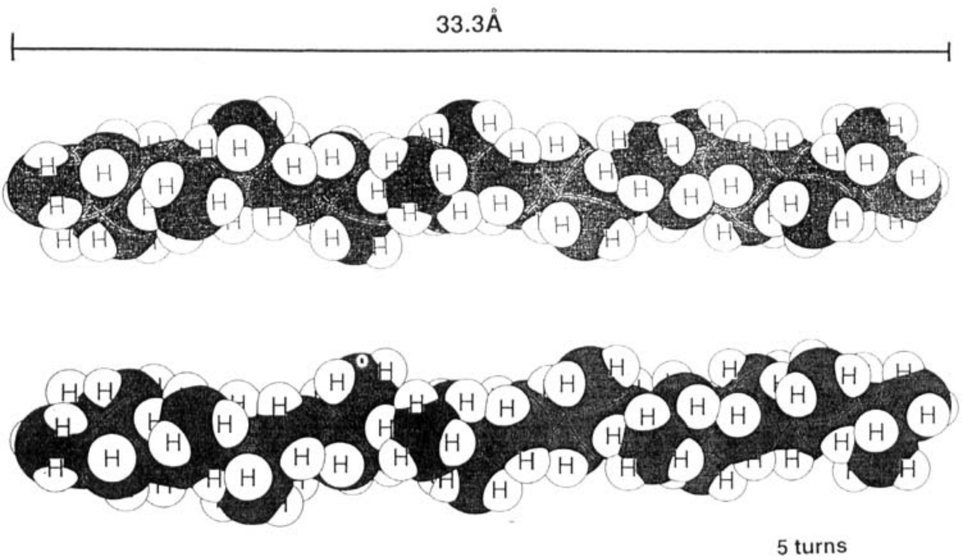


FIG. 7. Polypropylene structure.

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REFERENCES

[1] J. D. Jaycox, O. Vogl, and K. Hatada, in *Macromolecular Architecture and Design* (K. Hatada, T. Kitayama, and O. Vogl, Eds.), Dekker, New York, In Press.
[2] O. Vogl, G. D. Jaycox, and K. Hatada, *J. Macromol. Sci.—Chem., A27*(13 & 14), 1781 (1990).
[3] R. J. Farris, *Trends Polym. Sci., 1*(2), 38 (1993).
[4] A. MacLachlan, *Prog. Polym. Sci., 19*(6), 1049 (1994).
[5] O. Vogl, Lecture, The Royal Swedish Academy of Sciences, February 12, 1993.
[6] J. Miller, Lecture, "Polymer 94" Symposium, Vadodara, India, February 1994.
[7] W. H. Carothers, *Trans Faraday Soc., 32*, 39 (1936).
[8] M. Szwarc, *Nature, 178*, 1168 (1956).
[9] K. Hatada, K. Ute, and N. Miyake, *Prog. Polym. Sci., 19*(6), 1067 (1994).
[10] O. Vogl, V. Ivansons, H. C. Miller, and H. W. Williams, *J. Macromol. Sci.—Chem., A2*, 175 (1968).
[11] T. A. Koch and P. Lindvig, *J. Appl. Polym. Sci., 1*, 166 (1959).

[12] H. Staudinger, *Die Hochmolekularen Verbindungen, Kautschuk und Cellulose*, Springer Verlag, 1932.

[13] S. F. Reed Jr., *J. Polym. Sci., Part A, 9*, 2029 (1971); Ibid., p. 2147.

[14] M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc., 78*, 2656 (1956).

[15] S. Schlick and M. Levy, *J. Phys. Chem., 64*, 883 (1960).

[16] C. Strazielle and J. Herz, *Eur. Polym. J., 14*, 5 (1977).

[17] P. Rempp and J. E. Herz, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Wiley, New York, 1989, Suppl. p. 793.

[18] R. Milkovich and M. T. Chiang, US Patent 3,786,116 (1974).

[19] B. C. Anderson, G. D. Andrews, P. Arthur Jr., H. N. Jacobson, L. R. Melby, A. J. Playtis, and W. H. Sharkey, *Macromolecules, 14*, 1599 (1981).

[20] O. W. Webster, US Patent 4,407,034 (1983).

[21] C. E. H. Bawn and A. Ledwith, *Q. Rev., 16*, 361 (1962).

[22] T. Saegusa and S. Matsumoto, *Macromolecules, 1*(5), 442 (1968).

[23] J. P. Kennedy, *J. Macromol. Sci.—Chem., A18*, 1 (1982). M. Miyamoto, M. Sawamoto, and T. Higashimura, *Macromolecules, 17*, 265 (1984).

[24] J. P. Kennedy, *J. Macromol. Sci.—Chem., A18*, 1185 (1982/83). R. Faust and J. P. Kennedy, *Polym. Bull., 15*, 317 (1986).

[25] M. Sawamoto, S. Aoshima, and T. Higashimura, *Makromol. Chem., Macromol. Symp., 13/14*, 513 (1988).

[26] J. P. Kennedy, L. R. Ross, and O. Nuyken, *Polym. Bull., 5*, 5 (1981).

[27] J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed., 18*, 1523 (1980).

[28] G. F. Mejs and E. Rizzardo, *J. Macromol. Sci., Rev. Chem. Phys., C30*(3&4), 359 (1990).

[29] O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, and P. V. RajanBabu, *J. Am. Chem. Soc., 105*, 5706 (1983).

[30] J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Epoxides*, Interscience, New York, 1963.

[31] T. Aida and S. Inoue, *Macromolecules, 14*, 1162, 1166 (1981).

[32] P. H. Plesch, *The Chemistry of Cationic Polymerization*, Macmillan, New York, 1963.

[33] J. Barton and E. Borsig, in *Complexes in Free-Radical Polymerization* Polymer Science Library 6; (A. D. Jenkins, Ed.), Elsevier, 1988.

[34] A. H. Janovicz, US Patent 4,694,054 (1986).

[35] J. A. Simms and H. J. Spinelli, *J. Coatings Technol., 59*, 125 (1987).

[36] P. Rempp and E. W. Merrill, *Polymer Synthesis*, 2nd ed., Huthig and Wepf, Basel, Switzerland, 1991.

[37] J. P. Kennedy, Lecture, *Polymer Science for the 21st Century*, New York, November 1992.

[38] M. Jiang and H. Xie, *Prog. Polym. Sci., 16*, 977 (1991).

[39] M. Farina, M. Peraldo, and G. Natta, *Angew. Chem., Int. Ed., 4*, 107 (1965).

[40] C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert, and A. O. Zoss, *Ind. Eng. Chem., 40*, 2104 (1948).

[41] G. Natta, P. Pino, G. Mazzanti, P. Corradini, and U. Giannini, *Rend. Accad. Naz. Lincei*, [VIII], *19*, 397 (1955).

[42] M. E. Pruitt and J. M. Baggett, US Patent 2,706,181 (1955).

[43] O. Vogl, Belgian Patent 580,553 (1959).

[44] G. Natta, L. Porri, P. Corradini, and D. Morero, *Chim. Ind. Milan, 41,* 398 (1962).
[45] T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull., 20,* 505 (1988).
[46] N. Ishihara, T. Semiya, M. Kuramoto, and M. Uoi, *Macromolecules, 19,* 159 (1986).
[47] J. A. Ewen, L. R. Jones, A. Ravasi, and J. D. Ferrara, *J. Am. Chem. Soc., 110,* 6256 (1985).
[48] P. Galli and J. C. Haylock, *Prog. Polym. Sci., 16,* 443 (1991).
[49] R. R. Schrock, *Acc. Chem. Res., 23,* 158 (1990).
[50] R. H. Grubbs and W. Tumas, *Science, 243,* 907 (1989).
[51] K. B. Wagener, J. M. Boncella, and J. G. Nel, *Macromolecules, 24,* 2649 (1991).
[52] M. Farina, "The Stereochemistry of Living Macromolecules," *Top. Stereochem., 17,* 1-111 (1987).
[53] G. Natta, P. Pino, F. Corradini, E. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc., 77,* 1708 (1955).
[54] K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem., 67,* 426 (1955).
[55] I. Pasquon, L. Porri, and U. Giannini, "Stereoregular Polymers," in *Encyclopedia of Polymer Science and Engineering,* Vol. 15, 2nd ed. (H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, eds.), Wiley-Interscience, New York, 1989.
[56] T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell, and J. D. Stoups, *J. Am. Chem. Soc., 80,* 1768 (1958).
[57] G. Natta, G. Dall'Asta, G. Mazzanti, U. Giannini, and S. Cesca, *Angew. Chem., 71,* 205 (1959).
[58] E. A. Youngman and J. Boor Jr., "Syndiotactic Polypropylene," *Macromol. Rev., 2,* 33 (1967).
[59] B. C. Anderson, G. D. Andrews, P. Arthur Jr., H. W. Jacobson, L. R. Melby. A. J. Playtis, and W. H. Sharkey, *Macromolecules, 14,* 1599 (1982).
[60] T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull., 20,* 505 (1988).
[61] O. Vogl, "Aldehyde Polymers," in *Encyclopedia of Polymer Science and Engineering,* Vol. 1, 2nd ed. (H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, eds.), Wiley-Interscience, New York, 1985, and references cited therein.
[62] G. Natta, L. Porri, P. Corradini, and D. Morero, *Chem. Ind., 40,* 362 (1958).
[63] S. Kambara and A. Takahashi, *Makromol. Chem., 63,* 89 (1963).
[64] H. R. Kricheldorf and T. Mang, *Ibid., 182,* 3077 (1981).
[65] G. Odian, *Principles of Polymerization,* 3rd ed., Wiley-Interscience, New York, 1991, pp. 453-467.
[66] T. Aida, *Prog. Polym. Sci., 19,* 469 (1994).
[67] O. W. Webster, *Science, 251,* 887 (1991).
[68] R. A. Simpson and W. Kauzman, *J. Am. Chem. Soc., 75,* 139 (1953).
[69] R. E. Dickerson and I. Geis, *Hemoglobin: Structure, Function, Evolution and Pathology,* Benjamin/Cummings Publishing Co., Menlo Park, California, 1983.

[70] O. Vogl, J. Muggee, and D. Bansleben, *Polym. J., 12*, 677 (1980).

[71] J. Muggee and O. Vogl, *J. Polym. Sci., Polym. Chem. Ed., 22*, 2501 (1984).

[72] J. Koetz, K. J. Linow, B. Phillipp, L. P. Hu, and O. Vogl, *Acta Polym., 38*, 667 (1987).

[73] H. Ukihashi, M. Yamabe, and H. Miyake, *Prog. Polym. Sci., 12*, 229 (1986).

[74] W. Deits, O. Vogl, and E. Westhead, *J. Macromol. Sci.—Chem., A16*, 691 (1981).

[75] Y. H. Kim and O. W. Webster, *Polym. Prepr., ACS Div. Polym. Chem., 29*(2), 310 (1988).

[76] D. A. Tomalia, M. Hall, and D. M. Hedstrand, *J. Am. Chem. Soc., 109*, 1601 (1987).

[77] C. J. Hawker and J. M. J. Frechet, *Ibid., 112*, 7638 (1990).

[78] H. Hoecker, "Organic Cyclic Oligomers and Polymers," in *Cyclic Polymers* (J. A. Semlyan, Ed.), Elsevier Applied Science, London, 1986, pp. 197–223.

[79] D. J. Brunelle and T. G. Shannon, *Macromolecules, 24*, 3035 (1991).

[80] D. J. Brunelle, T. L. Evans, T. G. Shannon, E. P. Boden, K. R. Steward, L. P. Fontana, and D. K. Bonauto, *Polym. Prepr., ACS Div. Polym. Chem., 30*(2), 569 (1989).

[81] C. W. Bunn and E. V. Garner, *Proc. R. Soc., A189*, 39 (1947).

[82] H. Tadokoro, *Structure of Crystalline Polymers*, Wiley, New York, 1979.

[83] J. Preston, "Synthesis and Properties of Rodlike Condensation Polymers," in *Liquid Crystalline Order in Polymers* (A. Blumstein, Ed.), Academic Press, New York, 1978, pp. 141–166.

[84] P. W. Morgan, *Macromolecules, 10*, 1381 (1977).

[85] S. I. Stupp, S. Son, H. C. Lin, and L. S. Li, *Science, 259*, 59 (1993).

[86] G. M. Whitesides, J. P. Mathias, and C. T. Seto, *Ibid., 254*, 1312 (1991).

[87] C. O. Sroog, *Prog. Polym. Sci., 16*, 561 (1991).

[88] G. Natta and P. Corradini, *Makromol. Chem., 16*, 77 (1955).

[89] D. Poland and Scheraga, *Theory of Helix-Coil Transitions in Biopolymers*, Academic Press, New York, 1970.

[90] O. Vogl and G. D. Jaycox, *Polymer, 28*, 2179 (1986).

[91] P. Pino, "Optically Active Addition Polymers," *Fortschr. Hochpolym-Forsch., 4*, 393 (1965).

[92] A. Abe and M. Goodman, *J. Polym. Sci., Part A-1, 1*, 2193 (1963).

[93] L. S. Corley, G. D. Jaycox, and O. Vogl, *J. Macromol. Sci.—Chem., A25*, 519 (1988).

[94] L. S. Corley and O. Vogl, *Polym. Bull., 3*, 211 (1980).

[95] H. Yuki, K. Hatda, T. Niinomi, and Y. Kikuchi, *Polym. J., 1*, 130 (1970).

[96] O. Vogl, G. D. Jaycox, C. Kratky, W. J. Simonsick Jr., and K. Hatada, *Acc. Chem., 25*(9), 408 (1992).

[97] O. Vogl, F. Xi, F. Vass, K. Ute, T. Nishimura, and K. Hatada, *Macromolecules, 22*, 4658 (1989).

[98] K. Hatada, K. Ute, K. Tanaka, M. Imanari, and N. Fujii, *Polym. J., 19*, 425 (1987).

[99] P. Pino and R. Muelhaupt, *Angew. Chem. Int. Ed., 19*, 857 (1980).

[100] G. S. Kumar and D. C. Neckers, *Chem. Rev., 89*, 1915 (1989).

[101] J. L. Houben, A. Fissi, D. Baccila, N. Rusato, O. Pieroni, and F. Ciardelli, *Int. J. Biol. Macromol., 5*, 94 (1983).

[102] M. Irie, *Adv. Polym. Sci., 94*, 27 (1990).

[103] O. Vogl, in *Functional Polymers* (D. E. Bergbreiter and C. R. Martin, Eds.), Plenum Press, New York, 1989, p. 141.

[104] D. Bailey, D. Tirrell, and O. Vogl, *J. Macromol. Sci.—Chem., A12*, 661 (1978).

[105] C. E. Schweitzer, R. N. MacDonald, and J. D. Punderson, *J. Appl. Polym. Sci., 1*, 158 (1959).

[106] K. Allmer, A. Hult, and B. Ranby, *J. Polym. Sci., Polym. Chem. Ed., 26*, 2099 (1988).

[107] J. Lucki, J. F. Rabek, B. Ranby, B. J. Qu, A. Sustic, and O. Vogl, *Polymer, 31*, 1772 (1990).

[108] L. G. Donaruma and O. Vogl, *Polymeric Drugs*, Academic Press, New York, 1978.

[109] O. Vogl, G. D. Jaycox, and K. Hatada, *J. Macromol. Sci.—Chem., A27*, 1781 (1990).

[110] A. Suctic, Ph.D. Dissertation, Polytechnic University, Brooklyn, New York, 1989.

[111] D. R. Paul and S. Newman (Eds.), *Polymer Blends*, Academic Press, New York, 1978.

[112] A. S. Hay, *Polym. Eng. Sci., 16*, 1 (1976).

[113] C. W. Bunn, *Trans. Faraday Soc., 35*, 482 (1939).

[114] P. H. Geil, *Polymer Single Crystals*, Interscience Publishers, New York. 1963.

[115] P. H. Geil, F. R. Anderson, B. Wunderlich, and T. Arakawa, *J. Polym. Sci., A2*, 3707 (1964).

[116] A. J. Pennings, J. M. A. Van der Mark, and H. C. Booij, *Kolloid-Z. Z. Polym., 236*, 99 (1970).

[117] B. Lotz, Lecture, 35th Anniversary of *Polymer*, Oxford, UK, September 1995.

[118] R. A. Gaudiana, R. A. Minns, R. Sinta, N. Weeks, and H. G. Rogers, *Prog. Polym. Sci., 14*, 47 (1989).

[119] M. M. Green, C. Khatri, and N. C. Peterson, *J. Am. Chem. Soc., 115*, 4941 (1993).

[120] *New York Times*, New York, USA, 1992.

[121] *Die Presse*, Vienna, Austria, 1994.

[122] M. F. Qin, J. Bartus, and O. Vogl, *Makromol. Chem., Macromol. Symp., 98*, 387 (1995).

[123] O. Vogl, M. F. Qin, J. Bartus, and G. D. Jaycox, *Monatsh. Chem., 126*, 47 (1995).