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Macromolecular Design and Architecture

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MACROMOLECULAR DESIGN AND ARCHITECTURE

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A. INTRODUCTION

Polymer science and the industries producing and utilizing polymers have made tremendous progress over the last three decades, and the use of polymeric materials is ever increasing. In this period the worldwide production and use of plastic materials has grown from a few million tons in 1960 to about 130 to 140 million tons today (Fig. 1). It is expected that the amount of 200 million tons may be reached by the year 2000 (Fig. 2) [1, 2]. Initially, the production and use of polymeric materials were concentrated in the industrialized countries: the United States, Western Europe, and Japan with about 80% of production, and the east European countries and the Soviet Union with 12%. As the amount and uses of polymers increase over the next decade, the relative proportion of polymers by weight will decrease in the industrialized countries as compared to the east European countries and the lesser developed countries. In about 30 years the amount of plastic materials used may reach

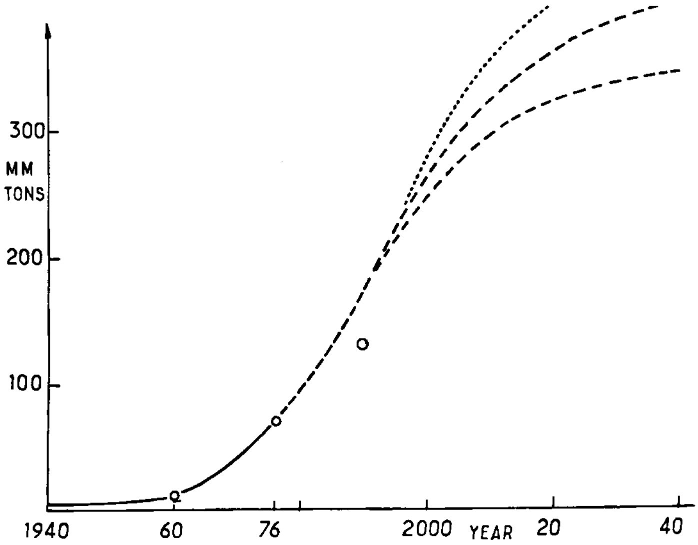


FIG. 1. Development of worldwide polymer production since 1950.

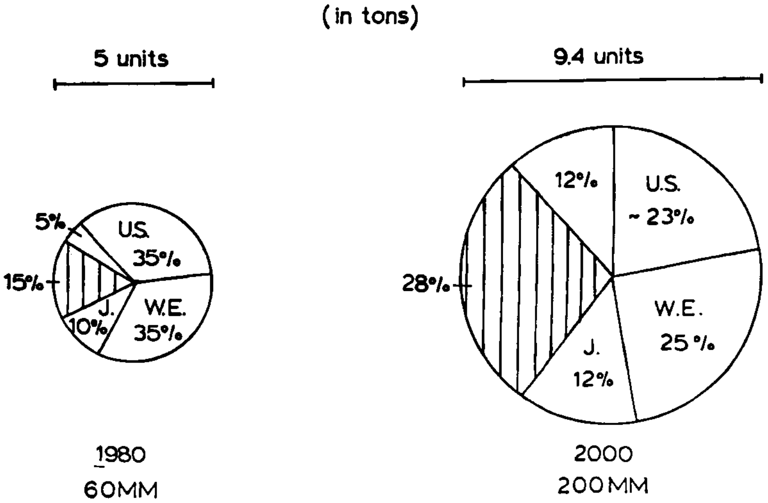


FIG. 2. Polymer production forecast for 2000. Areas with vertical lines indicate former socialist countries.

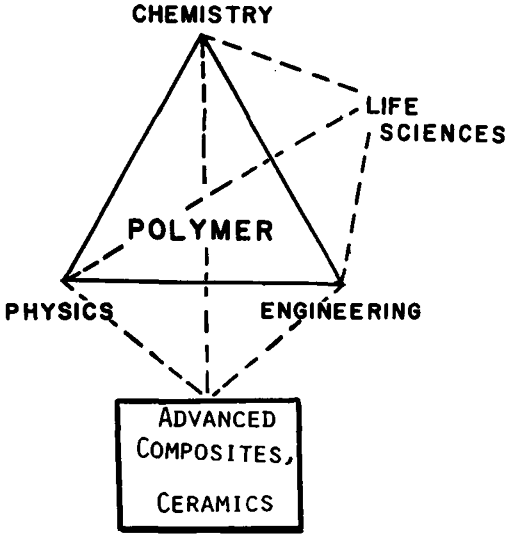


FIG. 3. Interactions the various disciplines of polymer science.

400 million tons. There are 130 million tons of plastic materials produced today; this represents a consumption of about 4% of the world's oil production [3, 4].

It should also be pointed out that in the industrialized countries about 80 to 100 kilograms per year are being used per person while in countries like China the use of plastic materials is about 8 kilograms per capita per year, up from 2.5 kilograms about 10 years ago. The situation is not substantially different for lesser developed countries. Another comparison may be made for the actual value of the production of objects made of plastic materials. In the United States alone the value is somewhere between 150 to 200 billion dollars or about 4% of the gross national product.

Polymers and polymer science have developed through a combination of chemistry, physics, and engineering (Fig. 3). It appears that every 10 years an additional dimension has been added [5]. If one were to look at the actual thrust of research development in polymer science, the 1950s witnessed great developments in polymer chemistry, the 1960s in polymer physics, the 1970s in polymer engineering, and the 1980s in functional polymers. In the 1990s we expect to have substantial thrusts forward in

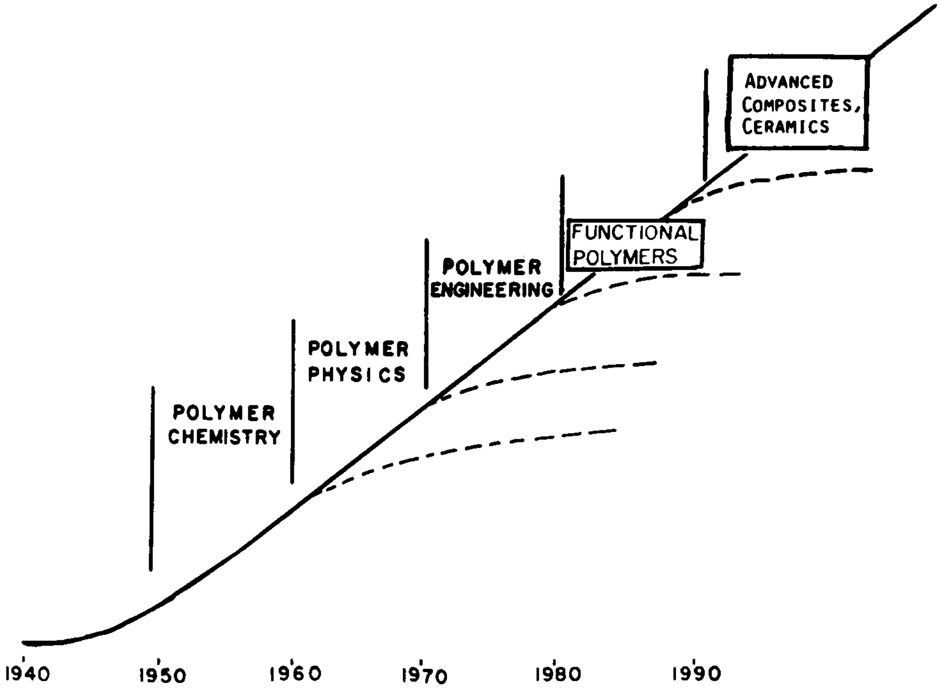


FIG. 4. Development of the emphasis of different disciplines in polymer science.

the areas of polymers in advanced materials, the life sciences, and ceramics (Fig. 4).

Polymer development can also be described in a cyclical (helical) fashion. We may start imagining the basic knowledge of polymer science and natural polymers as the basis of the polymer "tree of life"; we can see the initial development of polymer chemistry followed by polymer physics and engineering. After two decades of developments in other areas, sophisticated polymer chemistry again became the driving force for forward development, as for example in the newly developing fields of functional polymers (Fig. 5). Sophisticated polymer physics and engineering seem to be evolving in the 90s into such fields as advanced composites, novel polymeric materials, blends and alloys; they all represent sophisticated branches of polymer physics and engineering [6]. We have used this type of representation in order to recognize the fact that many polymers exist and very often crystallize in helical form.

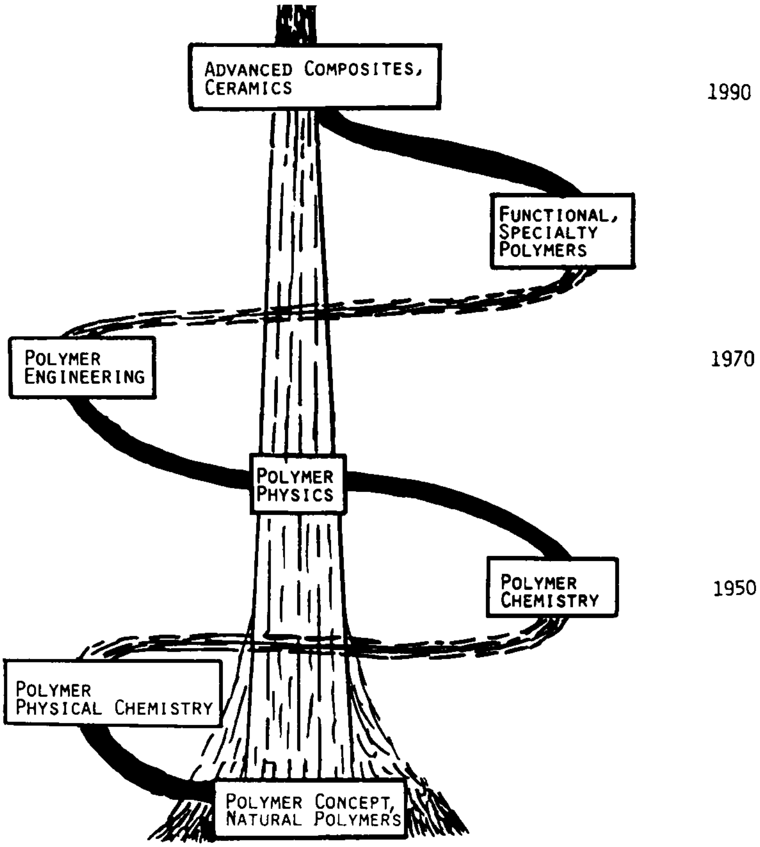


FIG. 5. Polymer science development.

The particular area of advanced materials and its developing importance can also be recognized by comparing (Fig. 6) the development and the use of steel versus synthetic polymers by volume [6, 7]. In 1974 the production and utilization of plastic materials exceeded that of nonferrous metals, and in 1979 it exceeded steel. Much of the major development in composite materials is in its use in automobile and aircraft design. Initially made for military aircraft (Fig. 7), these new designs will ultimately be used in civilian aircraft which will be more fuel efficient and which will produce transportation vehicles with lower weight but equal performance [6].

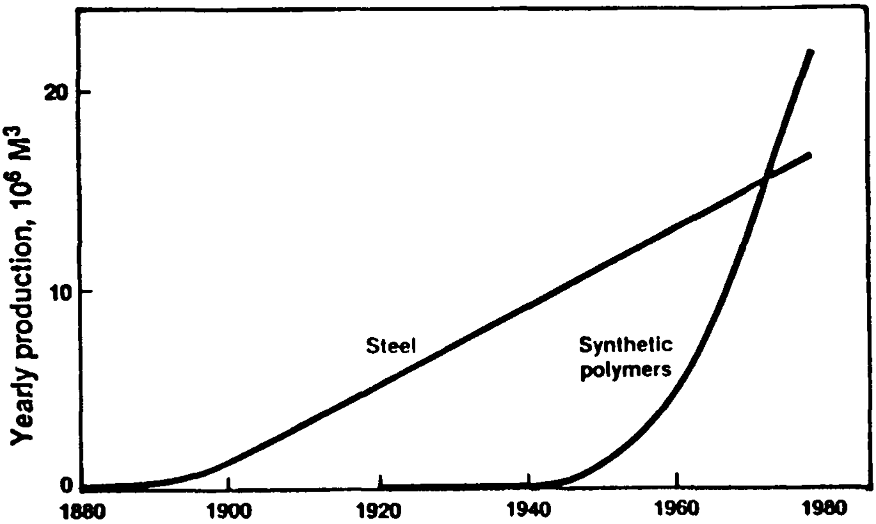


FIG. 6. Annual production of polymers vs steel on a volume basis.

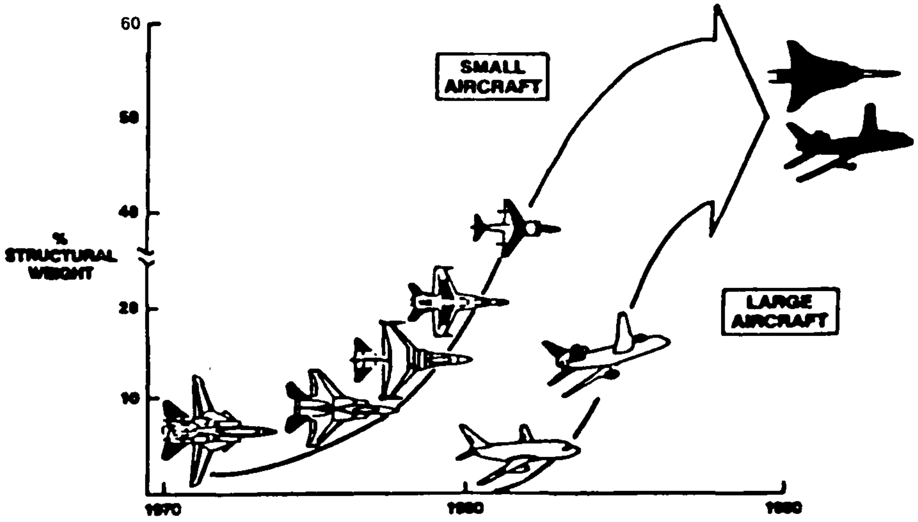


FIG. 7. Use of polymers in aircraft.

In the middle 1970s a significant change occurred in the development of polymer science and engineering [8]. While in the earlier stage of development polymerization techniques were perfected, the production of monomers brought polymer science and engineering to its most efficient state. The five major large scale plastics produced are polyethylene (both high density and low density), polypropylene, poly(vinyl chloride) and polystyrene, which are generally called commodity plastics. More sophisticated breakthroughs and needs directed the development of specialty polymers (sometimes called functional polymers because of the functionality and the functional groups involved in their performance). Particularly important developments were engineering plastics and, more recently, polymer alloys, polymer membranes, and stabilizing systems of higher sophistication for commodity plastics.

For the purpose of this discussion, we will divide macromolecular design and architecture into *(a) Macromolecular Engineering* [9] such as the anionic polymerization of styrene and methyl methacrylate, cationic polymerization of isobutylene and vinyl ether, coordination polymerization such as group transfer polymerization, the polymerization of functional olefins and epoxides, and metathesis polymerization; *(b) Direct Polymerization of Monomers into Composites* such as the synthesis and ring-opening polymerization of giant rings with 20 to 40 high performance "monomer units" in the ring [10, 11], but also more advanced polyurethane type of reactions [12]; *(c) Functional Polymers* such as polymerizable or polymeric stabilizers (antioxidants, flame retardants, and ultraviolet stabilizers), the copolymers, blends, compatibility, grafting on polyolefins surfaces, particularly by photografting, which will also be discussed [13-15]; and *(d) Design of the Perfect Polymer Helix* in which the design of initiator and monomer, type of end groups, bulk of side groups in the monomer, counterion effects and, ultimately, the synthesis of the helix of only one screw sense will also be evaluated [16, 17].

B. MACROMOLECULAR ENGINEERING

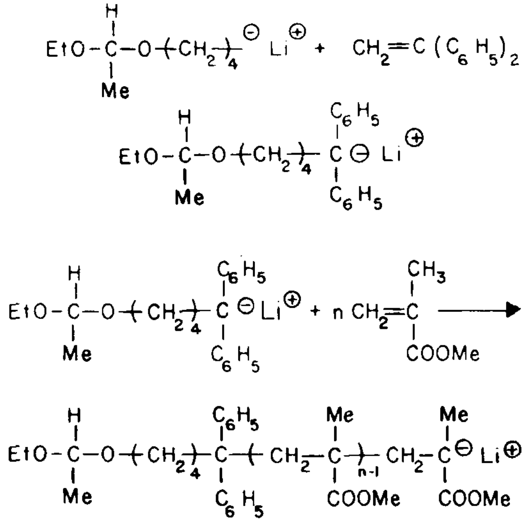
Macromolecular engineering has been developed over the last two decades by utilizing anionic, cationic, and coordinative polymerizations. In anionic polymerization, advances have been made in classical polymerization, new aspects of methyl methacrylate polymerization, coordinative anionic ring-opening polymerization, group transfer polymerization, and the coordinative anionic polymerization of functional olefins and epoxides.

While initially anionic polymerization was developed in the 1950s for styrene, the rules of living polymerizations were also developed which resulted in elegant structures such as monodispersed polystyrenes, block copolymers with exactly defined block lengths, star polymers, difunctional styrene oligomers, and low molecular weight polymers with networks of exact connector length. The ABA block polymers of styrene/butadiene (or isoprene)/styrene triblock polymers and ultimately macromonomers based on polystyrene were discovered and developed as well.

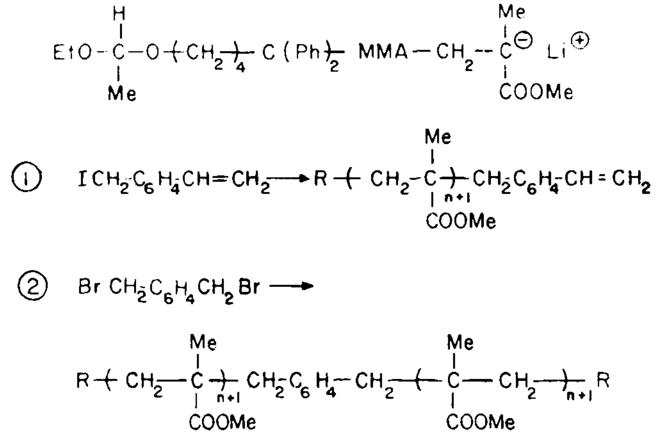
The polymers that have been prepared by the elegant method of living anionic polymerization are ultimately styrene polymers. Although these styrene polymers have limited utility, living anionic polymerization has become important in newly developing coating areas such as automotive coatings using methyl methacrylate and other acrylic polymers.

In the anionic living polymerization of methyl methacrylate, it was found that classical living polymerizations can be carried out very readily as long as the polymerization temperature is kept below −40°C; otherwise cyclo termination and ejection of methoxide ion will occur (Eq. 1) [18, 19]. In order to carry out the reaction in a practical way, an acetal lithium initiator is capped with diphenylethylene which then becomes the actual initiator. With this system at low temperature, anionic polymerization can be carried out successively. If the polymerization is terminated with a compound such as iodomethylstyrene, a styrene-type macromer is obtained. If it is terminated with dibromoxylene, dimerization occurs and, by selective hydrolysis of the acetal linkage, a bifunctional polymeric glycol of twice the molecular weight is obtained (Eq. 2). This polymerization is an excellent technique for the preparation of acrylic polymers. Its major drawback is the low temperature requirement.

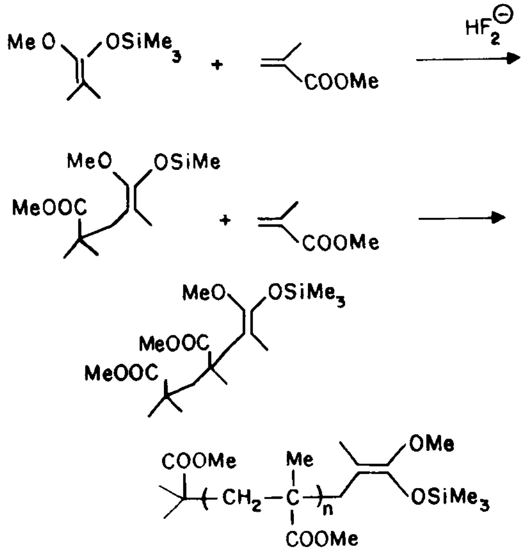
A different and to some extent better method of carrying out these reactions is by an anionic coordinative technique; this polymerization method is most commonly called group transfer polymerization [20–22]. It consists of initiation with a silicone ketene acetal, which with catalysts such as carboxylates or HF_2^- forms a reactive initiating species. At slightly elevated temperature this procedure allows the homopolymerization of all methacrylates and acrylonitrile (Eq. 3). If a bifunctional final polymer is desired, a corresponding ketene acetal of the structure shown in Eq. 4 is used as the initiator; propagation only occurs on the siloxane



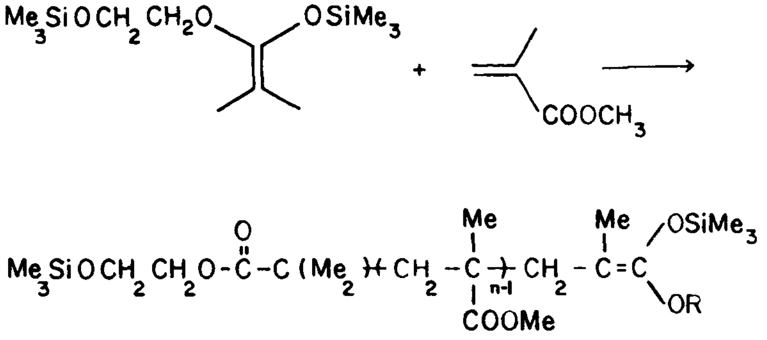
EQUATION 1. Anionic polymerization of methyl methacrylate.



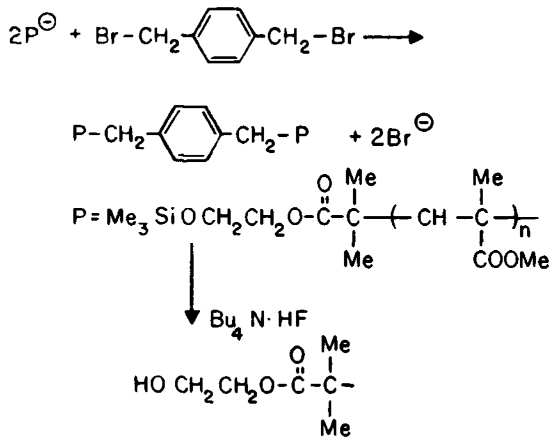
EQUATION 2. Functionalization of anionic methyl methacrylate polymers.



EQUATION 3. Group transfer polymerization of methyl methacrylate.



EQUATION 4. Telechelic polymers of methyl methacrylate by group transfer polymerization.



EQUATION 5. Bifunctional telechelic polymers of methyl methacrylate by group transfer polymerization.

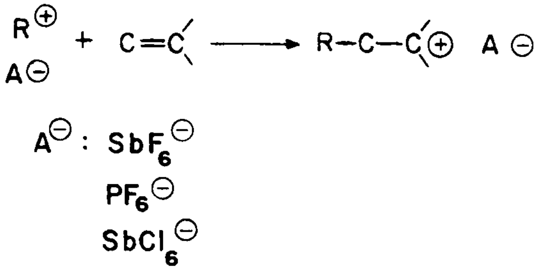
portion that is in conjugation with the double bond. This polymerization is a living polymerization and provides polymers with a polydispersity very close to 1; by reaction with a suitable bifunctional compound, end-terminated polymethacrylates with twice the molecular weight are obtained (Eq. 5).

Group transfer polymerization allows the preparation of many polymeric methacrylates. For example, it is possible to produce those with aliphatic esters such as methyl ester, butyl ester, 2-ethylhexyl and lauryl ester. In all of these reactions the OH group is protected by a trimethysilane group.

Group transfer polymerization also allows the preparation of block copolymers, block copolymers with short reactive blocks at the chain end, star-type polymers, microgels, dispersing agents based on methacrylates, and even functional methacrylate polymers [22].

It is, however, often more convenient to prepare polymethacrylates by conventional emulsion polymerization, copolymerization via solution polymerizations, especially with the new technique of this acrylic polymerization, or a radical polymerization which is essentially a coordinative radical polymerization using cobalt porphyrines as the initiator/modifier. By this method, macromonomers based on methyl methacrylate can be prepared very efficiently.

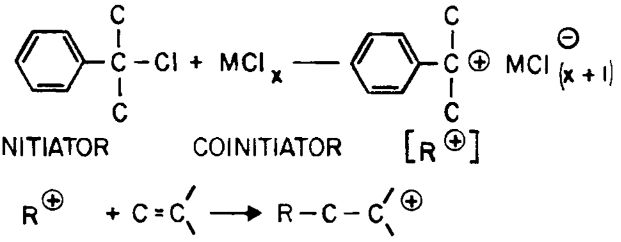
Great advances have been made in cationic polymerization in the field



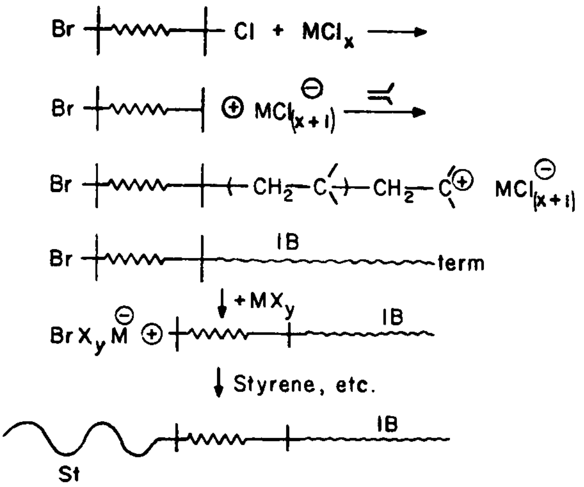
EQUATION 6. Cationic macromolecular engineering.

of macromolecular engineering by using cationic polymerization (Eq. 6). The basic principles of modern cationic polymerizations have been developed and applied by the inifer techniques: the initiating-transfer techniques using minifers, binifers, and trinifers [23] (Eq. 7). Block copolymers can now be prepared by cationic polymerization because it has been perfected to such a level that nearly monodisperse polymer systems of isobutylene, styrene, and vinyl ether are attainable [24]. Many examples of pseudo-living polymerization and quasi-living polymerization are common [25, 26].

In living cationic polymerizations the essential feature is a nonnucleophilic anion such as SbF$_6^-$, PF$_6^-$, and SbCl$_6^-$. These stable anions force propagation, even of reactive species, to proceed without decomposition by disproportionation of the complex anion. The initiator transfer polymerization was perfected with such compounds as tertiary butylchloride or dimethylbenzylchloride by using MCl$_x$ (for example, boron trichloride) as the coinitiator. For binifers, compounds with 2 tertiary butyl



EQUATION 7. Minifers, binifers, and trinifers and their use in cationic polymerization.

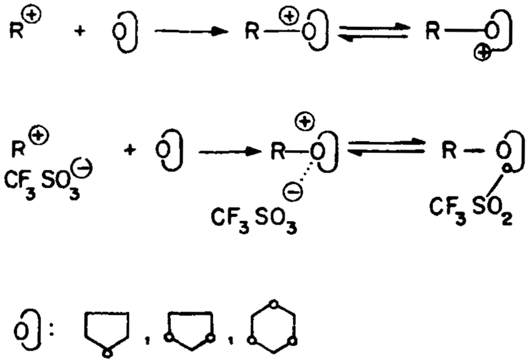


EQUATION 8. Block polymers of isobutylene by cationic polymerization.

groups at the end of a methylene chain of 6 to 8 carbon atoms with 1 chlorine and 1 bromine atom will allow selectivity of the transfer reaction, giving initially an end-capped species which in the example shown in Eq. 8 is bromine terminated. The latter must be activated with a different kind of coinitiator in order to extend the polymerization.

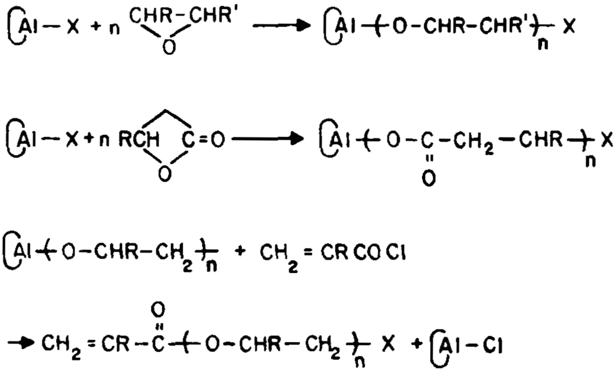
Macromolecular engineering has also made great advances in ring-opening polymerizations, including that of such cyclic ethers as tetrahydrofuran, dioxolane, and trioxane by using trifluoromethyl sulfate as the counterion (Eq. 9). Telechelic polymers are obtained by a most intriguing polymerization technique that uses activated monomers [28, 29].

Substantial advances have also been made in vinyl ether systems by using HI/I_2 as the initiating species [30, 31]. These vinyl ether polymerizations are relatively unreactive living polymers which give rise to very stable systems because the propagating cation is partially an oxonium ion, which is known to be less reactive than the classical carbocation or carbenium ion. Propagation occurs readily only when it is carried out on either a tertiary carbenium ion, on a phenyl-substituted carbenium ion (styryl carbenium ion), or when the reaction is starve-fed in the monomer, which is exemplified in the living polymerization of isobutylene.

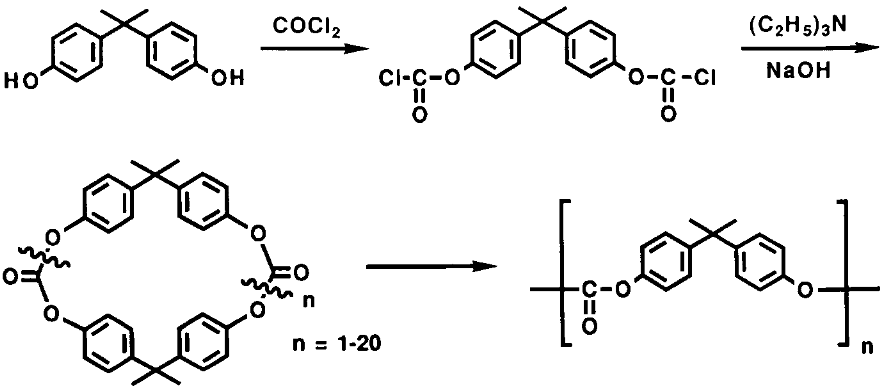


EQUATION 9. Cationic polymerization of cyclic ethers.

A most impressive example of macromolecular engineering in the polymerization of cylic ethers and lactones is polymerization with aluminum alkyls complexed with porphyrine derivatives. This system allows not only the polymerization of cyclic ethers but also that of cyclic esters and, when photochemically activated, of methacrylates; it was recently used in the so-called “immortal” polymerization (Eq. 10) [32, 33]. By capping these living cationic polymerization systems with, for example, acryloyl chloride, polymerizable macromonomers which can be polymerized or copolymerized as acrylic monomers have been obtained [34].



EQUATION 10. “Immortal” polymerization.



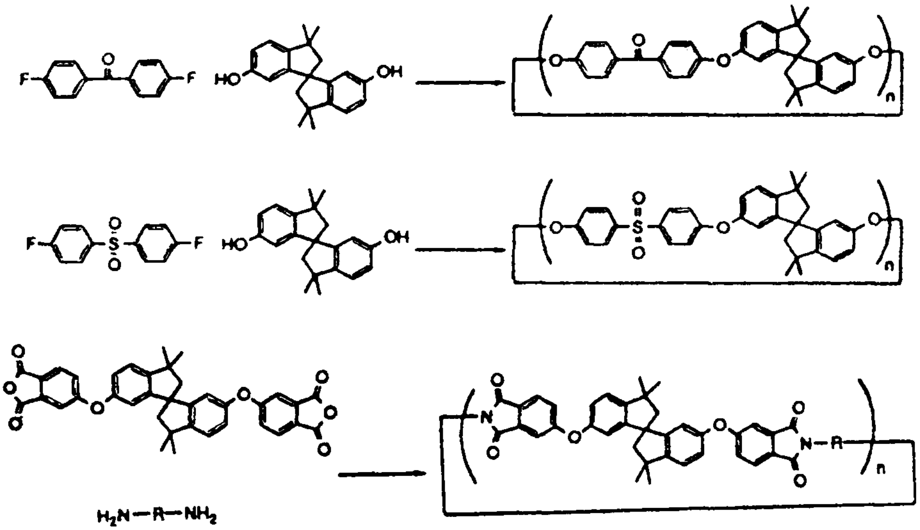
EQUATION 11. Preparation and polymerization of giant cyclics: Polycarbonates.

C. NEW MONOMERS AND NEW PRINCIPLES OF POLYMERIZATION

Group transfer polymerization of methyl methacrylate has revolutionized coordinative anionic polymerization; it is a superb example of controlled, nonstereospecific polymerization of acrylic monomers which gives polymers that are of considerable practical interest [20–22].

A new technique has very recently been developed for the preparation of giant macrocycles and their polymerization [35, 36] (Eq. 11). The first important example involved the preparation of polycarbonates [10, 11]. Polycarbonates are normally made from phosgene and Bisphenol A. The resulting polymers have molecular weights of about 50,000 to 100,000. Polycarbonates are highly desirable because of their exceptionally good Izod impact strength; they can also be used either directly or in blends with other polymers, particularly with other polyarylates.

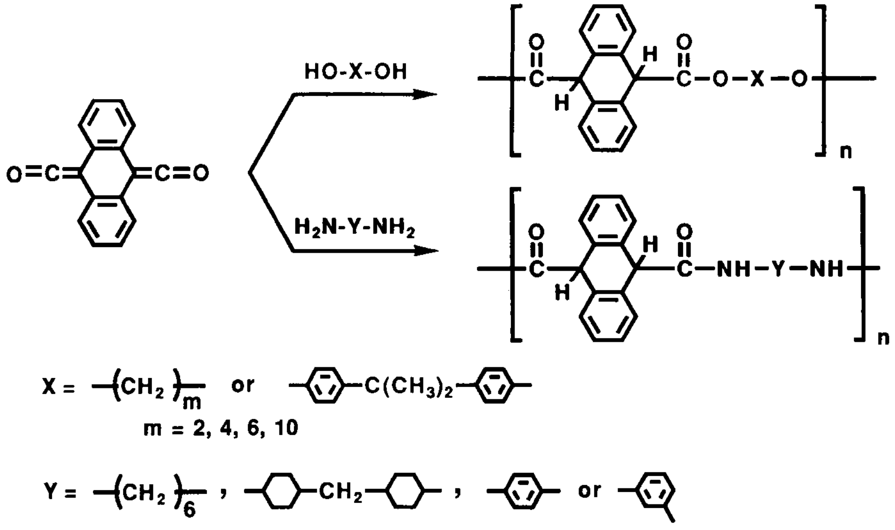
In this new technique, Bisphenol A is first reacted with excess phosgene to form the bischloroformate. The bischloroformate is isolated and carefully allowed to react with sodium hydroxide and triethylamine, which is the best-known catalyst for this reaction. If carried out properly, conditions are similar to the high dilution technique discovered some 70 years ago which gave cyclic compounds in high yield. This new technique can be carried out in solutions of 20 to 30% concentrations of the reactants; under optimal conditions it gives over 90% macrocy-



EQUATION 12. Preparation and polymerization of giant cyclics: Polyethers, polysulfones, and polyimides.

clic monomers with 20 to 40 monomer units per macrocycle. Very small amounts of linear oligomers are also formed. These must be removed because they interfere with further polymerization reaction. It is desirable to maintain the cyclic oligomers as mixtures in order to keep the melting point of the mixture below 200°C. This mixture, when melted, has a very low viscosity and allows a great deal of fluidity and penetration of the monomer into reinforcing agents. The monomer can be polymerized with basic catalysts at 200°C or above, giving linear polymers of polycarbonates of high molecular weight (in excess of one million) and often broad molecular weight distribution. This technique is excellent for the preparation of composites because of the ease of penetration of the liquid monomer. The polymerization occurs in excess of a 99.5% conversion to polymer with a low degree of shrinkage.

Similar macrocycle-forming reactions can also be carried out with diacid chlorides, such as isophthaloyl chloride, which give cyclic oligomers of arylates which can then be polymerized to polymeric arylates [36]. The formation of giant macrocycles followed by ring-opening polymerization has been extended to the preparation of polymides, polysulfones, polyesterimides, and other aromatic polymers (Eq. 12) [37].



EQUATION 13. Diketenes as polymer intermediates.

Another development of a new monomer for the preparation of useful polymers stems from the recognition that diketenes can be prepared in a stable form [38, 39]. Ketenes and diketenes are isoelectronic with isocyanates and bis-isocyanates. The most stable of the ketenes and diketenes are those that have aromatic rings attached to the ketene groups. As a consequence, anthracene-9,10-diketene was prepared and found to be stable to about 100°C in the solid state and in solution. However, long exposure at this temperature will cause dimerization, yielding polymeric structures (which are not stable above 220°C and decompose back to the ketene structure). Polymerization of anthracene-9,10-diketenes was demonstrated with glycols, such as ethylene glycol, butanediol-1,4, hexanediol-1,6, decanediol-1,10, and Bisphenol A or hydroquinone to form polyesters. Polyesters were also obtained with oligomeric etherglycols and polyesterglycol with a molecular weight of about 1500. Polyamides were obtained from hexamethylenediamines, methylene dicyclohexanediamine, *m*-phenylene diamine, and *p*-phenylene diamine (Eq. 13).

Since this symposium deals with polymer alloys and novel polymer structures, one new development should also be mentioned. It is known that polystyrene and polyvinyl ethers give completely miscible polymer blends. The degree of miscibility of these structures is, however, ex-

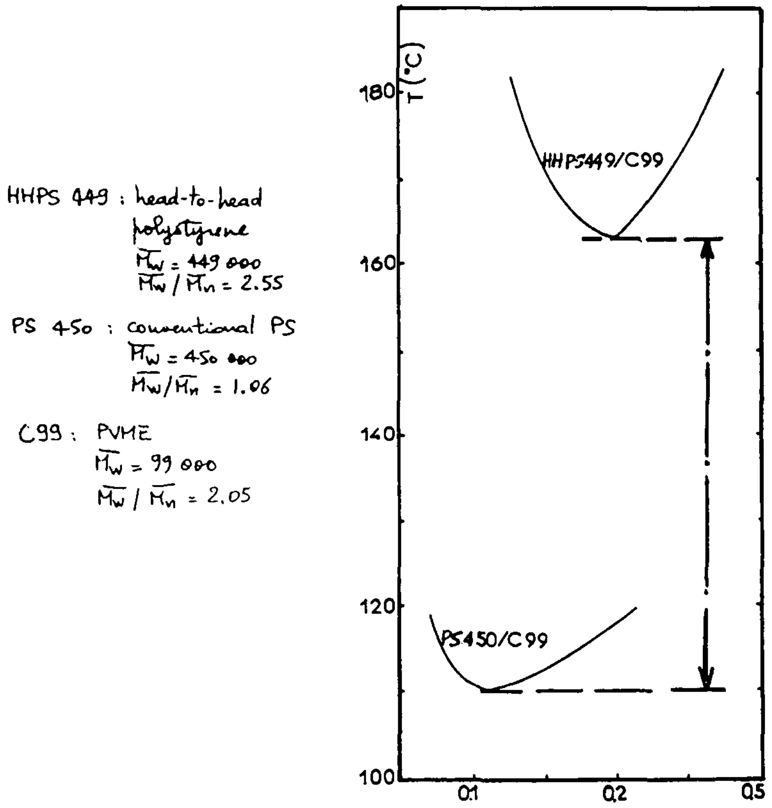


FIG. 8. Miscibility of H-T or H-H polystyrene with polymethylvinyl ether.

pressed in a more quantitative way by the lower mixing temperature. In the case of normal head-to-tail polystyrene, the critical mixing temperature is approximately 110°C with about 12 mol% of polymethylvinyl ether in the mixture. In head-to-head polystyrene mixtures with polymethylvinyl ether of comparable molecular weight, the lower mixing temperature is near 160°C at about 20 mol% of polymethylvinyl ether. The difference is greater than 50°C, indicating that polymethylvinyl ether and head-to-head polystyrene are substantially less miscible than the conventional head-to-tail polystyrene (Fig. 8) [40].

D. FUNCTIONAL POLYMERS

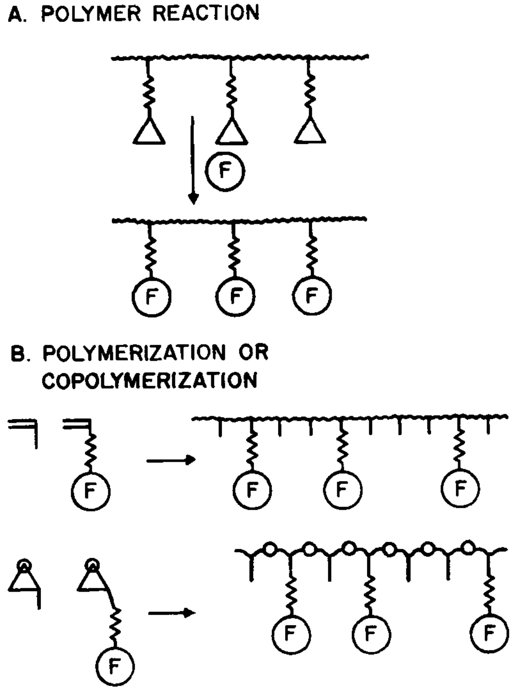
Functional polymers are those polymers whose efficiency and characteristics are based on a functional group [41]. In a second definition, they are polymers whose characteristics are based on a function of the polymer as a whole such as in polymeric membranes or polymeric drugs. In the first type, a specific and often carefully designed functional group is attached to a polymer chain, and the functionality provides the main characteristics. Typically functional groups are chemically reactive groups, biologically active groups, electro-active groups (synthetic metals), liquid crystalline (mesogenic) groups, photo-active groups (photochromic, photoreactive), and more commonly ionic, polar, or optically active groups [42].

Functional polymers may be prepared by polymerization and copolymerization or by polycondensation; or the functional groups may be incorporated into the polymer chain by polymer reactions. Functional groups may be at the end of the polymer chains or dispersed along the polymer main chain, or the functional groups may be attached to the main chain either directly or via spacer groups (Fig. 9).

Main Chain Functional Polymers

Polymers with functionalities in the main chain very often have aromatic groups which consequently cause the polymers to become infusable, intractable, and nonfabricable [43, 44]. The problem of fabricability and intractability has been overcome in the case of aromatic polyimides, but has only been solved partially for other "high temperature polymers" such as polybenzoxazoles and polybenzothiazoles. For a number of aromatic liquid crystalline, lyotropic polyamides or thermotropic polyesters, these problems have also been solved or, at least, workable solutions have been found. Electrically conducting polymers such as polyacetylenes are also known for their poor fabricability [45]. In many cases, especially for liquid crystalline polymers, it was found that a small flexible spacer group or irregularities introduced into the structure of the aromatic main chain can remedy some of the problems of intractability.

In one case, the problem of functional groups in polymers was solved in a specific way. The copolycarbonates of bithionol and glycols, where the glycol units were small, are essentially intractable. If, however, the copolycarbonate consists of poly(ethylene glycol) units with a *DP* of at least 10, copolycarbonates can be prepared that not only have useful



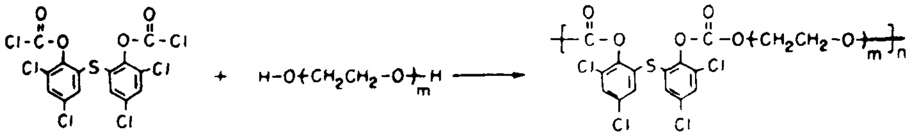
A. POLYMER REACTION

B. POLYMERIZATION OR COPOLYMERIZATION

FIG. 9. Positions of functional groups on polymer chains.

characteristics, but they are also degradable by hydrolysis and therefore provide an easy release of the bacteriacide bithionol (Eq. 14) [46, 47].

In the case mentioned above, intractability was solved by an appropriately designed spacer. In cases where the polymer backbone needs to be maintained, such as in the case of electrically conducting materials or nonlinear optical polymers [which have specific X(3) characteristics]



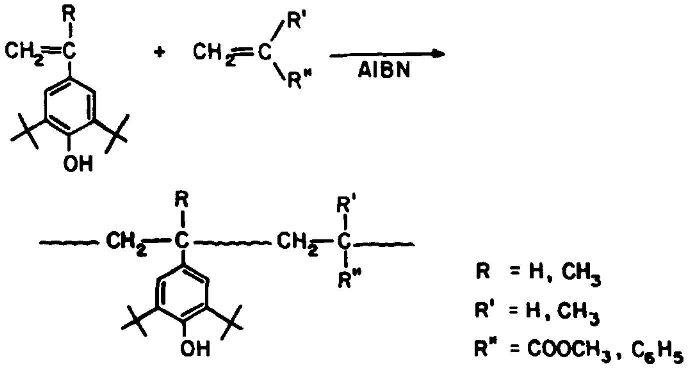
EQUATION 14. Polycarbonates of bithionol with poly(oxyethylene) glycol spacer groups.

[48], it is useful to incorporate side chains that provide a mechanism for fabricability. For example, the polymer of thiophene, although well known for its electrical properties in doped form, can be made into a fabricable form if, instead of the normal thiophene, an alkyl thiophene with a certain length of alkyl side chain is polymerized [50]. A similar development was made for polymers of diacetylenes where side chains improve the fabricability by sufficiently destroying very strong chain interactions. Of course, some properties are lost in this kind of modification of the main chain molecular structure.

Polymerizable, Polymeric, and Polymer-Bound Stabilizers

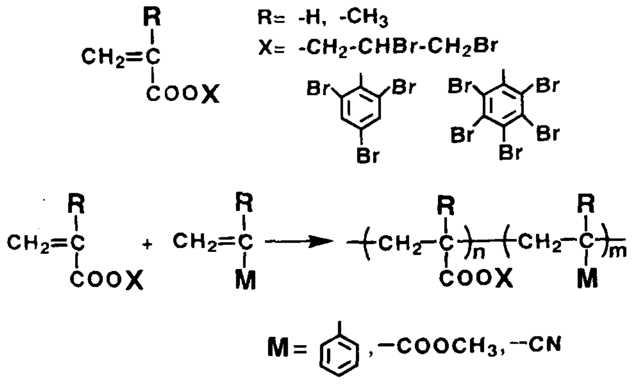
Traditionally, stabilizers for polymers such as antioxidants, ultraviolet stabilizers, and flame retardants have been low molecular weight compounds. In the last few years, several problems have arisen regarding these stabilizers which include their potential toxicity, their loss during fabrication, and their loss by evaporation or leaching. Oligomeric or even polymer-bound stabilizers of this kind have the potential to eliminate these problems [51]. In addition, the problem of compatibility at higher levels of incorporation of the stabilizer is also needed. This is difficult when the base polymers are either highly crystalline with only a small amorphous faction, or when the stabilizers that have low miscibility (solubility) are needed in higher concentrations to provide protection throughout the polymer sample. Another problem is the potential danger of toxicity. Low molecular weight chlorine, bromine, or phosphorous compounds, commonly used as flame retardants, have the potential of being toxic as do phenolic derivatives that are commonly used as antioxidants or ultraviolet stabilizers.

For several years we have been interested in polymeric antioxidants, flame retardants, and ultraviolet stabilizers. As polymeric antioxidants, we will describe the preparation and polymerization of 2,6-ditertiary butyl-4-vinyl (or 4-isopropenyl) phenol. These compounds were synthesized and found to polymerize readily with isoprene, butadiene [51], and such resonance stabilized monomers as styrene and methyl methacrylate (Eq. 15) [52]. These polymers were obtained in all copolymer composition proportions, although it was practical to have only up to about 10 to 15 mol% of the polymerizable antioxidant incorporated. These copolymers have been shown to be good antioxidants for their parent polymers, and if the butadiene or isoprene copolymers were hydrogenated, the hydrogenated polymers are good antioxidants for polyethylene and polypropylene.



EQUATION 15. Polymerizable antioxidant in styrene and methyl methacrylate polymers.

Flame retardants are often halogen-containing materials. We have shown that three types of acrylates and methacrylates can be readily polymerized and copolymerized with styrene, methyl methacrylate, and acrylonitrile. The esters contained 2,4,6-tribromophenyl, pentabromophenyl, and 2,3-dibromopropyl derivatives (Eq. 16). These copolymers were studied for their flame retardancy in polystyrene, and it was found that the limited oxygen index (LOI) can be increased by 30% by the incorporation of only about 5% of these copolymers. Normally, about 10 to 12% of flame-retardant material is used in order to protect polystyrenes and similar polymers from their being highly flammable [53, 54].



EQUATION 16. Polymerizable flame retardants and their copolymerization.

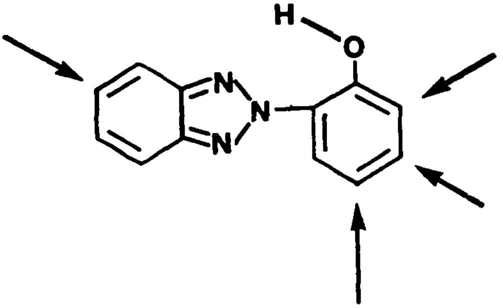
Ultraviolet stabilizers are particularly prone to evaporation from the surface of polymeric materials upon exposure to sunlight. The surface is the location where the stabilizing action is particularly needed. As a consequence, efforts have been made for over 20 years to prepare polymerizable ultraviolet stabilizers. The first attempts were made on the copolymerization of a UV stabilizer with ethylene [55] which, unfortunately, did not allow any significant incorporation. On the other hand, in such cases as the 2(2-hydroxyphenol)2*H*-benzotriazole derivatives, compounds with polymerizable groups have been claimed in patents, although their polymerization has never been described in detail [56–58].

Typical ultraviolet stabilizers are UV screens, UV absorbers, excited state quenchers, free radical scavengers, or hydroperoxide decomposers. For the protection of polyolefins, hydroperoxide decomposition is important. These compounds are very active in the photodecomposition of hydroperoxide. They include hindered amine (HALS) stabilizers and are needed for ultraviolet protection of polyolefins. Most other stabilizers belong to the category of screens (absorbers or excited state quenchers). The definition is not always clear, and the efficiency of the individual compounds is not always clearly defined. It can, however, be said that compounds that are active in these categories have a hydroxyl group attached either to a carbonyl group or to a triazole ring. In the early studies the polymerizable salicylate derivatives were investigated and found to be effective [59, 60]. Polymerizable 2-hydroxybenzophenones were also found effective, and their polymerization and copolymerization were studied [61].

With the recognition that 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives are the most effective compounds for protecting polymeric materials from ultraviolet and photodegradation, a concerted effort was started in the development of polymerizable derivatives in this category (Eq. 17) [62]. The fluorescence behavior of 2(2-hydroxyphenyl)2*H*-benzotriazoles is an indication of their effectiveness as a ultraviolet stabilizer (Fig. 10).

The work was based on the early discovery of these compounds in the 1920s [64] and the recognition that they were efficient stabilizers in the middle and late 1950s [65]. The higher price of this group of compounds, and the additional cost of a polymerizable form, has prevented the broad utilization of these derivatives. Various substitutions on the 2(2-hydroxyphenyl)2*H*-benzotriazole ring have resulted in the preparation of a number of polymerizable ultraviolet stabilizers.

Polymerizable stabilizers with one and two benzotriazole rings in the chemical structure, but also with one, two, and three hydroxyl groups in the molecule, have been synthesized [65, 66]. One category of com-



POLYMERIZABLE GROUPS

$-CR{=}CH_2$

$-OCO-CR{=}CH_2$

$-OCH_2CHOHCH_2OCOCR{=}CH_2$

$-CH_2NHCOCH{=}CH_2$

$R = H, CH_3$

EQUATION 17. Polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives.

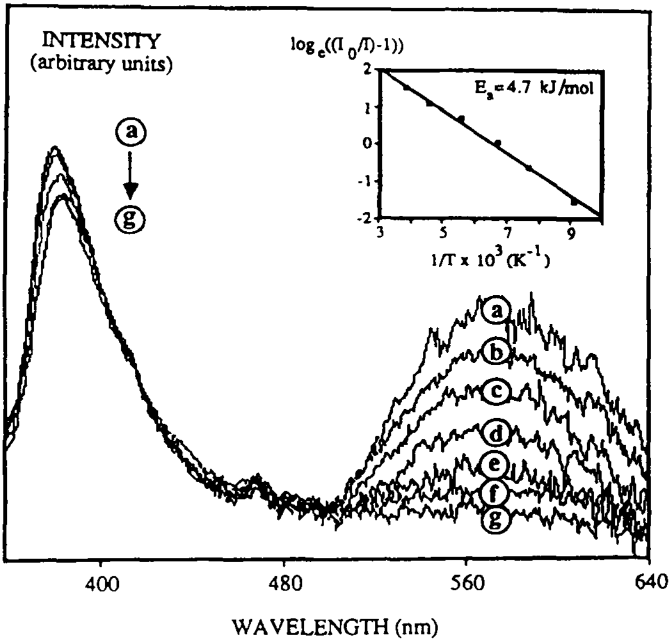
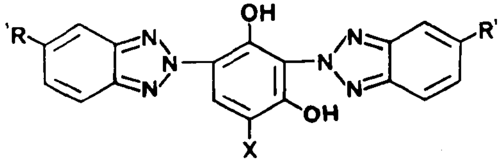


FIG. 10. Fluorescence spectrum of a typical 2(2-hydroxyphenyl)2*H*-benzotriazole.



$R' = -H, -OCH_3, -COOMe$

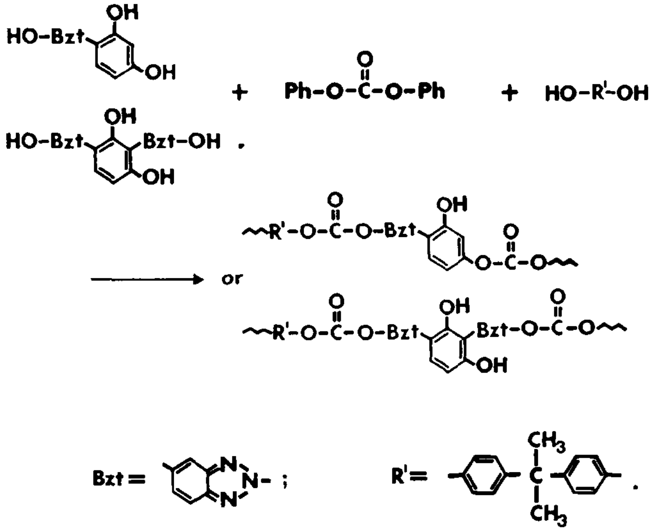
$X = -COCH_3, -COC_6H_5, -CH{=}CH_2, -C(CH_3){=}CH_2$

EQUATION 18. Polymerizable disubstituted 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives.

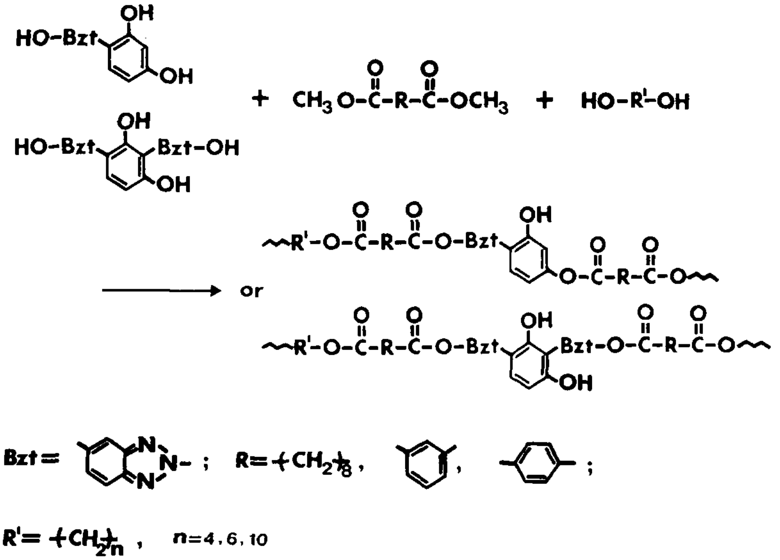
pounds included structures with two polymerizable hydroxyl groups in the mono- or di-nuclear benzotriazole units (the hydrogen-bonded hydroxyl group is not as reactive but is necessary for the photoreaction needed for energy dissipation which causes stabilization) (Eq. 18). Carboxyl groups in the R′ position and hydroxyl groups in the R′ position gave monomers that could be incorporated into polyesters, particularly polycarbonates, and also polyamides. The carboxylic acid could also be incorporated into polyamides [69]. Dihydroxy compounds with the mono-nuclear benzotriazole structure, such as 2(2,4-dihydroxyphenyl)2*H*-5-hydroxybenzotriazole (Eq. 19), can also be incorporated readily into polycarbonates and polyesters by both direct esterification using diacid esters (Eq. 20) or by transesterification (but not acid chloride reactions); the ultraviolet stabilized polycarbonates are of considerable interest (Eq. 21) [67–72].

2(2-Hydroxyphenyl)2*H*-benzotriazoles have been prepared with vinyl [65] or isopropenyl [73, 74] moiety in the 5 position with groups in the 4 position such as hydroxyl, (meth)acryloxy, and (meth)acryloxy-2,3 dipropyloxy, and hydroxy groups in the 5-position of the benzotriazole ring as well as the (meth)acrylamidomethyl groups (Eq. 17) [75].

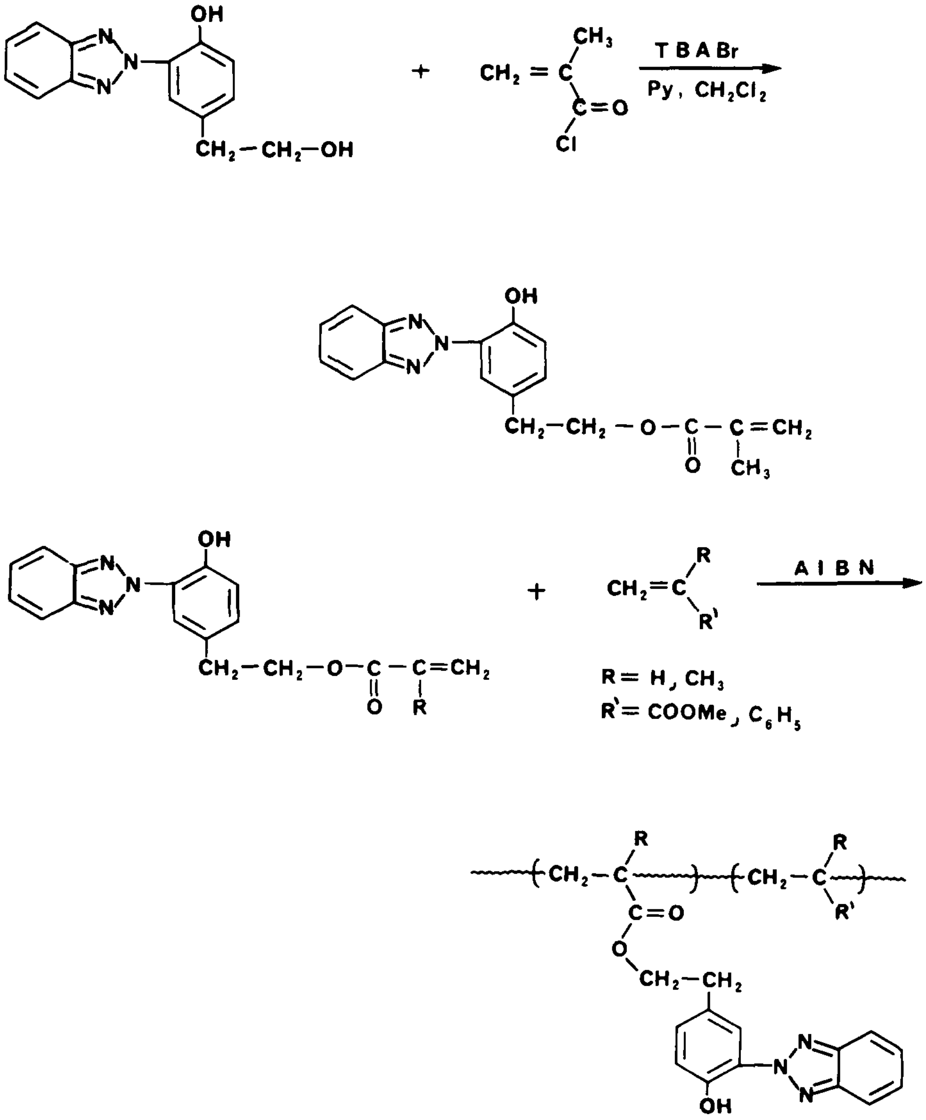
I will give only two major examples of the incorporation of 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives into polymers. The first one is the preparation of the methacryl derivative of the 2(2-hydroxy-5-hydroxyethyl-phenyl)2*H*-benzotriazole [76]. The methacrylic ester could be copolymerized with ABIN as the initiator, and copolymers of methyl methacrylate and styrene were obtained (Eq. 21). A similar incorporation of the 5(2-hydroxyethyl) derivative of 2(2-hydroxyphenyl)2*H*-benzotriazole was also achieved by a transesterification reaction on



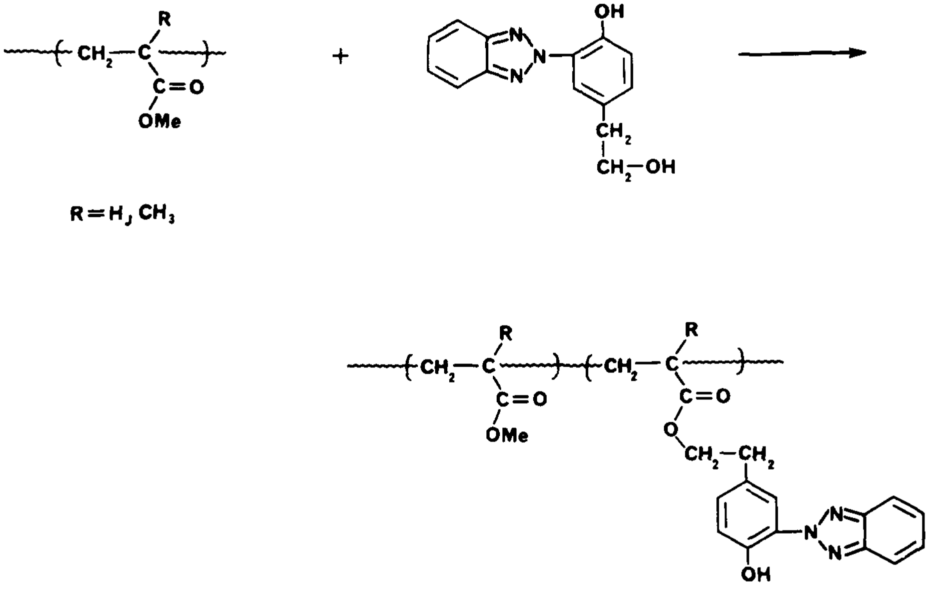
EQUATION 19. Polycarbonates stabilized with 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives.



EQUATION 20. Linear aromatic polyesters stabilized with 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives.



EQUATION 21. Incorporation of 2(2-hydroxy-[2′-hydroxyethyl]-phenyl) 2*H*-benzotriazole into poly(methyl methacrylate): By copolymerization.

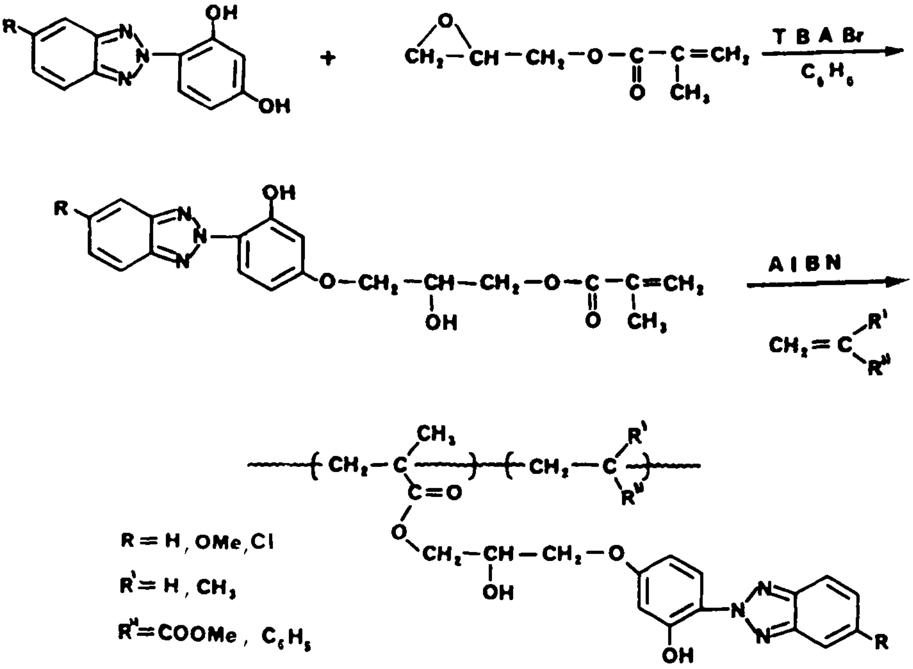


EQUATION 22. Incorporation of 2(2-hydroxy-[2′-hydroxyethyl]phenyl) 2*H*-benzotriazole into poly(methyl methacrylate): By Transesterification.

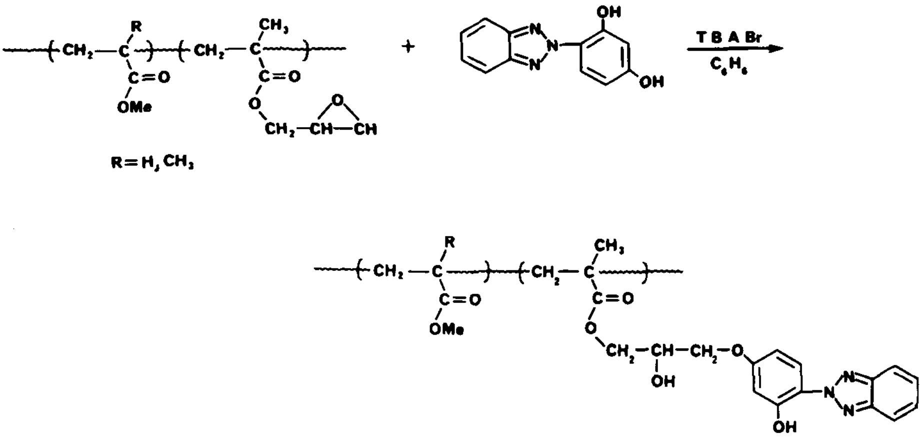
methyl methacrylate polymer (Eq. 22). Another example of an incorporation of the easiest available 2(2,4-hydroxyphenyl)2*H*-benzotriazole was achieved by a ring-opening reaction of a glycidyl group (Eq. 23) of glycidyl methacrylate followed by copolymerization with methyl methacrylate or other (meth)acrylates [76]. The reaction of 2(2,4-dihydroxyphenyl)2*H*-benzotriazole with a polymer containing the glycidyl methacrylate group has also been demonstrated (Eq. 24).

The acrylates and methacrylates of 2(2,4-hydroxyphenyl)2*H*-benzotriazole were esterified with acryloyl or methacryloyl chloride, giving a phenyl ester-type methacrylate. A convenient reaction can also be carried out by glycidyl methacrylate with (2,4-hydroxyphenyl)2*H*-benzotriazole to give the glycidyl derivative—an alkyl acrylic ester. In recent years, chloro derivatives in the benzotriazole portion of the ring have broadened the ultraviolet spectrum into the visible region. These have become interesting candidates for lens applications where the ultraviolet absorber needs to be permanently incorporated in optical lenses [76].

Up to now, we have considered the incorporation of polymerizable ultraviolet absorbers into polymer chains by copolymerization or by



EQUATION 23. Glycidyl methacrylate reaction with 2(2,4-dihydroxyphenyl)2*H*-benzotriazole and copolymerization.



EQUATION 24. Reaction of 2(2,4-dihydroxyphenyl)2*H*-benzotriazole with poly(glycidyl methacrylate) groups.

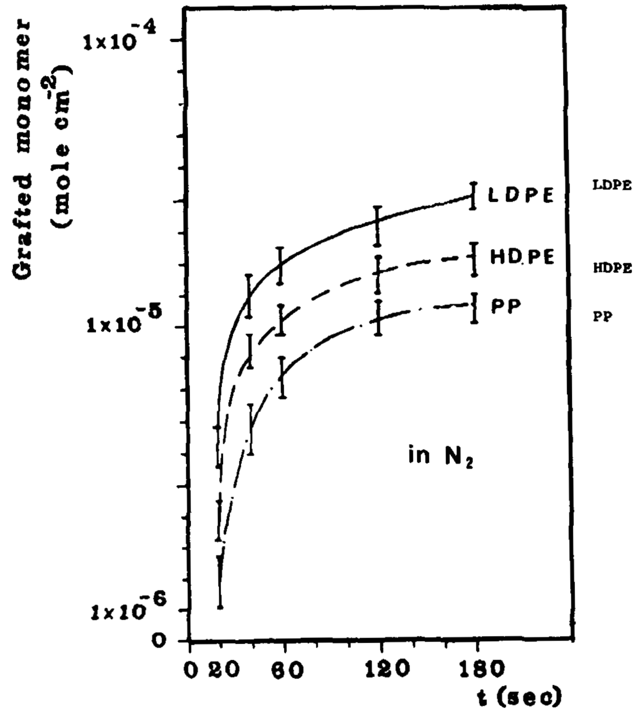


FIG. 11. Photografting of monomeric 2(2-hydroxyphenyl)2*H*-benzotriazole photostabilizers onto polyolefins.

polymer reaction on the already formed polymer. Two new aspects of incorporating an ultraviolet stabilizer in the appropriate place have been discovered recently.

The first one is the incorporation of polymerizable ultraviolet stabilizers by chemical grafting [68, 77–79] or by photografting with a photosensitizer [80]. It has been shown that 2(2-hydroxy-5 vinyl (or isopropenyl)phenyl) 2*H*-benzotriazole or 2(2-hydroxy-4(meth)acryloxy)phenyl) 2*H*-benzotriazole can be photografted onto the surface of polyethylene or polypropylene films by using benzophenone as the sensitizer for the photografting reaction. (Fig. 11) [80]. It is clear that photografting of a photostabilizer can only occur at a wavelength where the photosensitizer has an absorption maximum and the ultraviolet stabilizer has an absorption minimum (Fig. 12). The photostabilizer has its maximum at 235 nm

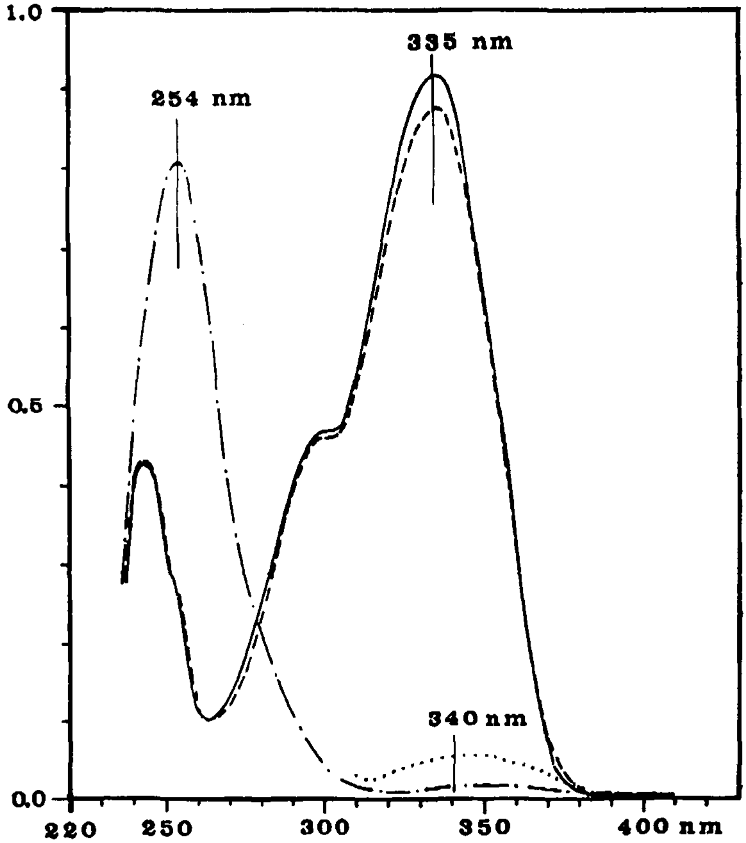
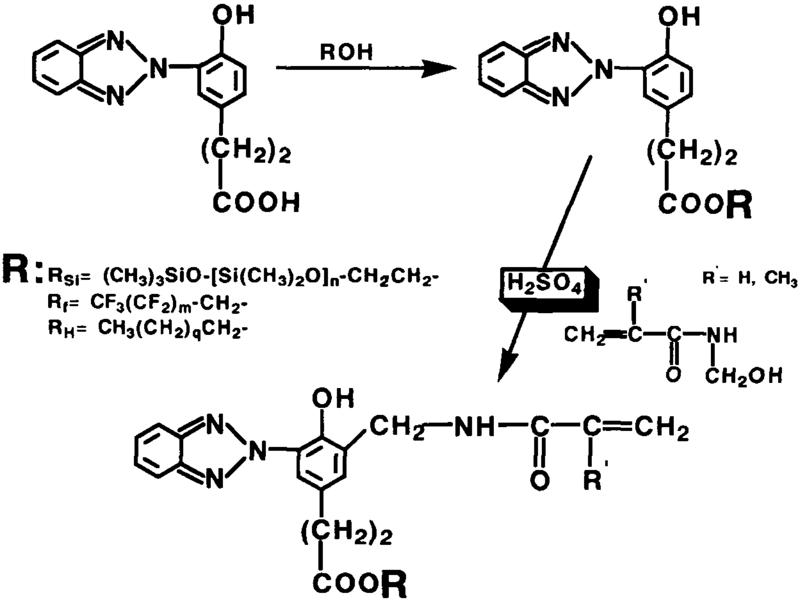


FIG. 12. Absorption spectra of monomeric photostabilizers and benzophenone.

and its minimum around 260 nm while the photosensitizer (benzophenone) absorbs at 254 nm. The success of the incorporation is demonstrated in Fig. 11 which shows excellent grafting efficiency successfully carried out in a few minutes. Comparison is made for photografting in air and in nitrogen on several polyolefin surfaces with several polymerizable photostabilizers.

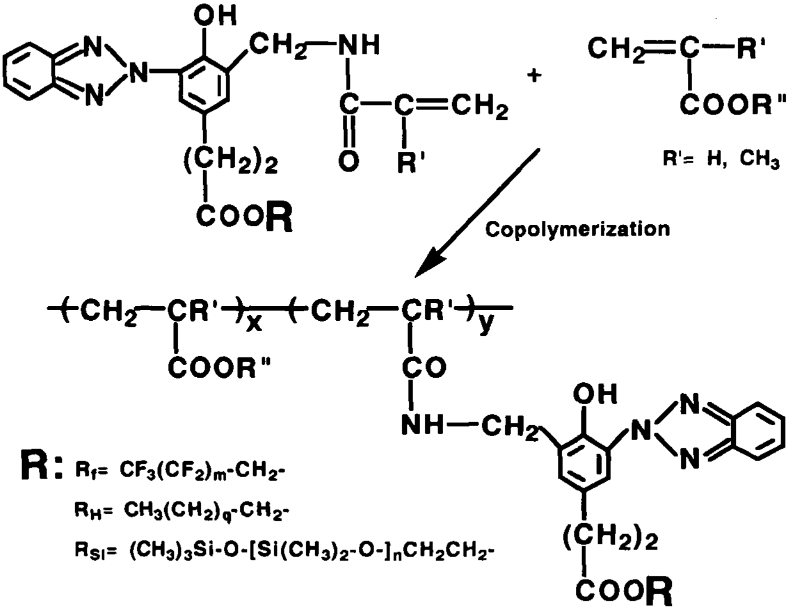
Another technique is presently in the advanced stages of development: morphology control which brings the ultraviolet stabilizer to the surface of a coating [81]. In the photografting case the polymeric film is extruded



EQUATION 25. Preparation of (meth)acrylamide 2(2-hydroxyphenyl)2*H*-benzotriazole monomers with surface-active groups.

or molded and the film is then soaked with the stabilizer and photografting is accomplished. The present case is more applicable for a coating application where the material goes from a liquid state to a solid glassy state. In this case the photostabilizers, primarily 2(2-hydroxy-5[2-carboxyethyl]phenyl)2*H*-benzotriazole, are esterified with fluorocarbon alcohols, hydrocarbon alcohols of long hydrocarbon chain length, and silicone alcohols (Eqs. 25 and 26). The compounds are then allowed to react with (meth)acrylomidomethanol [75] to give the final derivatives which are then copolymerized. On casting of these materials, the fluorocarbon group or silicone group help bring the stabilizers to the surface. ESCA measurements show that the fluorocarbon and silicone groups are substantially at the surface of the film, thus bringing the stabilizer to the surface of the film where it is needed most.

Early indications show that polymer-bound ultraviolet stabilizers of 2(2-hydroxyphenyl)2*H*-benzotriazoles are substantially more effective than the lower molecular weight UV stabilizers. It had been estimated from aging studies that these stabilizers should give weathering charac-



EQUATION 26. Polymerization of surface-active polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazoles.

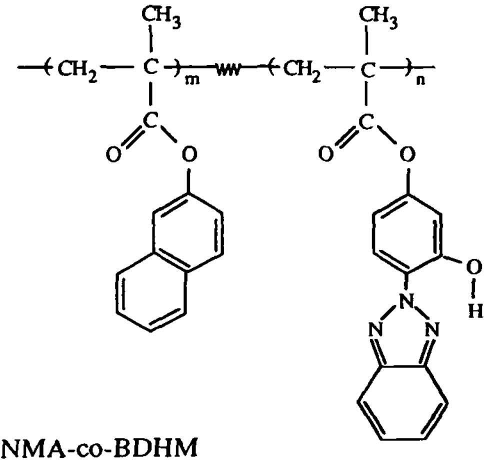
teristics which are increased by a factor of 3 or better over the low molecular weight compounds (Table 1) [83, 84].

The effects of polymer-bound ultraviolet stabilizers of the 2(2-hydroxyphenol)2*H*-benzotriazole type have been extended and simplified by the copolymerization of 2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole with 2-naphthyl methacrylate (Eq. 27). These copolymers show a substantial fluorescence emission at 560 nm. The fluorescence behavior was studied as a function of temperature. It was found that the activation energy is near zero. It was also determined that the absorption at 320 nm, which is indicative of photolytic degradation, increases linearly as a function of irradiation time. No change was found in copolymers containing 6.2 mol% 2(2-hydroxy-4-acryloxyphenyl) 2*H*benzotriazole. Relatively little influence of the photodegradation was found when 2(2-hydroxy-5-methylphenyl)2*H*-benzotriazole was added in 6.7 mol% during the radiation experiment (Fig. 13). This phenomenon has been explained by a migration of the photon energy to the acceptor where the

TABLE 1. Molecular-Weight Distribution Data on Aged and Control Samples

Aging time, h	$\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
0 (Control #1)	93,000	188,000	2.03
750	98,000	202,000	2.05
1700	75,000	273,000	3.62
2170[a]	75,000	273,000	3.62
0 (Control #2)	64,000	120,000	1.90
3700	69,000	171,000	2.49

[a] Gel formation noted. Approximate estimate of gel formation is 20% in the sample aged for 2170 h and ~30% in the sample aged for 3700 h.



2NMA-co-BDHM

EQUATION 27. Naphthyl methacrylate copolymers with 2(2-hydroxy-4-methacryoxyphenyl)2*H*-benzotriazole.

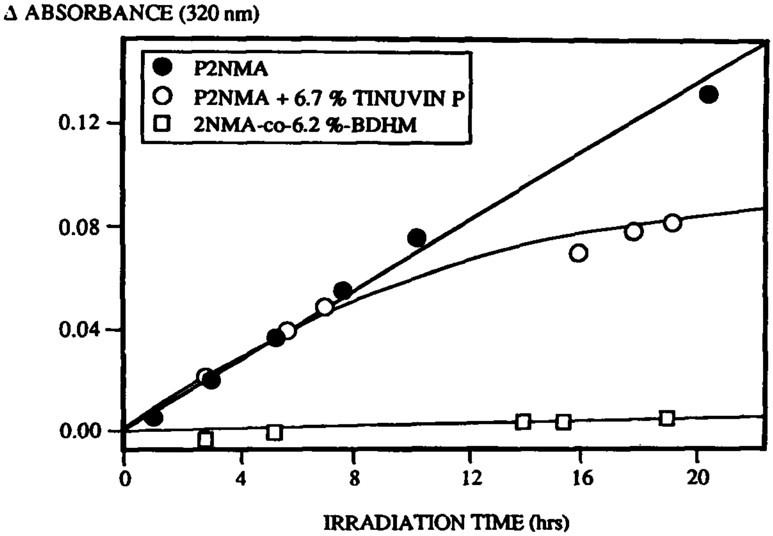


FIG. 13. Effectiveness of polymer-bound ultraviolet stabilizers.

emission is then dissipated in a nonradiative way as shown in Fig. 14 [85-87].

The proposed general photophysical behavior of 2(2-hydroxyphenyl)2*H*-benzotriazoles is shown in Eq. 28.

E. SPACER GROUPS IN FUNCTIONAL POLYMERS

Functional groups are usually attached directly to the polymer main chain, as, for example, carboxylic acid groups in polyacrylic acid and the carbomethoxy groups in poly(methyl methacrylate). Much rarer are examples where the functional group is attached via a spacer group to the polymer main chain. The linking of a functional group through various spacer groups is quite common in natural polymers. For example, in proteins, which possess amine functional groups in the cases of lysine and arginine, and the carboxylic acid group in the case of glutamic acid.

In the last few years, at least four major groups of polymers have been developed which have functional carboxylic acid groups at the end of a spacer group which is attached to the polymer main chain. These

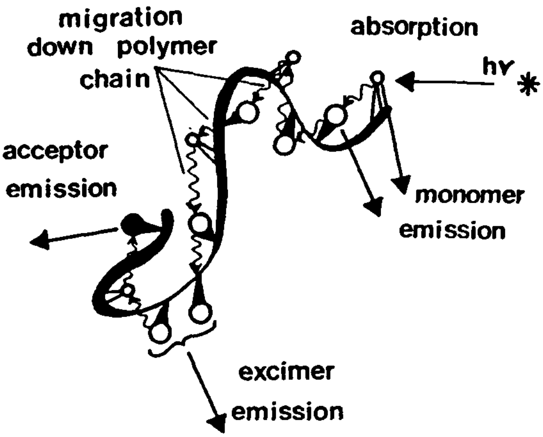
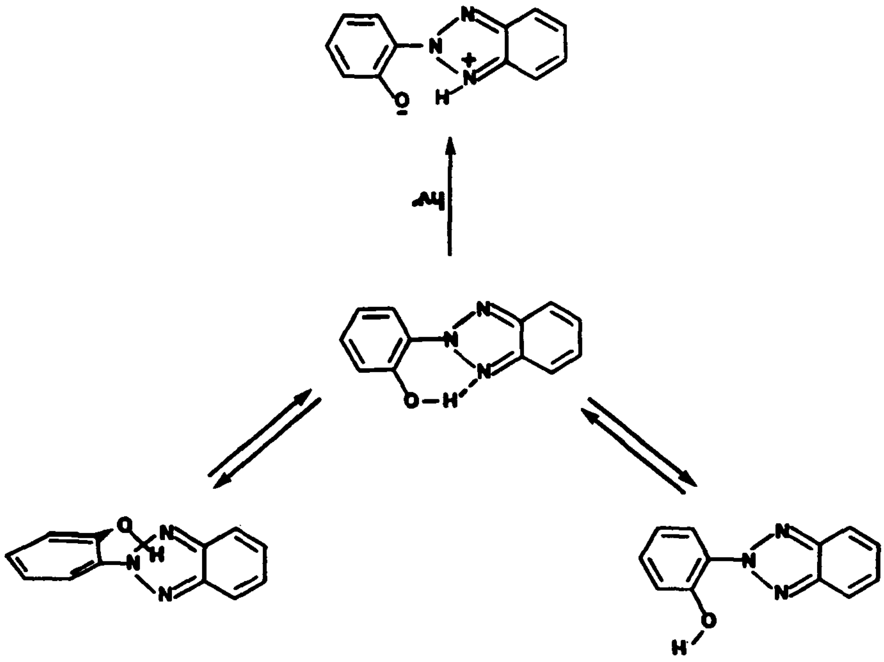


FIG. 14. Proposed mechanism of energy migration along a polymer chain.



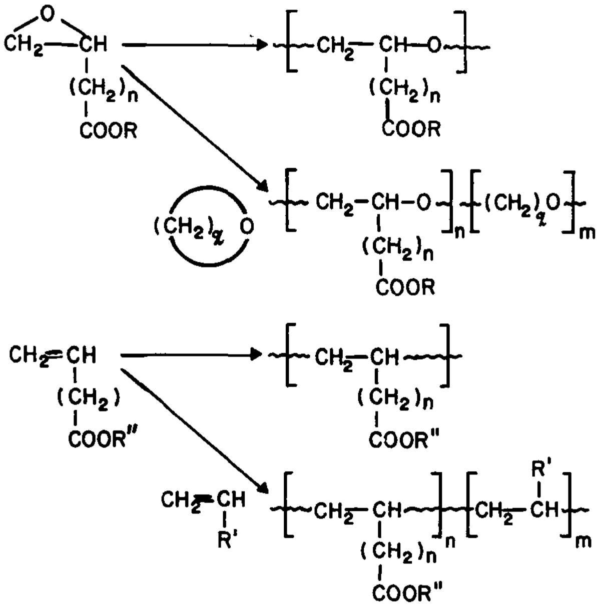
EQUATION 28. Mechanism of 2(2-hydroxyphenyl)2*H*-benzotriazole energy dissipation.

polymers include poly(oxyethylene), polyethylenes, polysiloxanes, and poly(meth)acrylates.

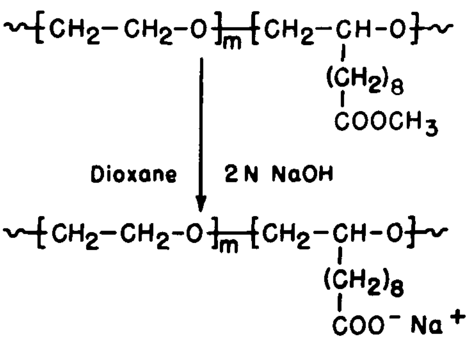
Functional groups in polysiloxanes attached via spacer groups have been prepared by polymer reactions where a functional group with an olefin terminal functionality was allowed to react with SiH [88, 89]. This palladium-catalyzed reaction is essentially quantitative; however, it does have the disadvantage of having a reaction on the main chain. These silane reactions have been used to prepare polysiloxanes with mesogenic and nonlinear optical and electroactive groups attached. These polymers also have the advantage that the base polymers have a low glass transition temperature typical for siloxanes.

Another group of methacrylate monomers and polymers which have the functional group attached via a glycol unit with various numbers of methylene groups have been studied [90]. Mesogenic and nonlinear optical groups have been attached via this chain. The basic glass transition temperature is typical of that for a methacrylate or acrylate backbone. Another important group of polymers contains a tetrafluoroethylene backbone chain with sulfonic acid and carboxylic acid pendants; they are similar in composition to the ionomers made of ethylene and acrylic or methacrylic acid (10 to 12 mol%) [91]. The flexible spacer group in these fluorocarbon polymers are units of hexafluoropropylene oxide.

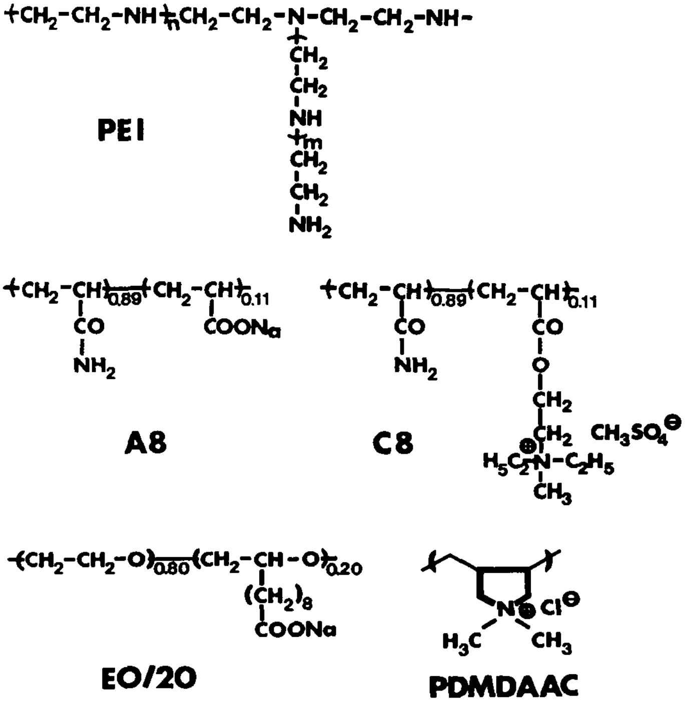
We have been interested in the effect of methylene spacer links in polyethylene- and polyoxyethylene-type polymers. We have demonstrated that in the polymerization of ω-alkenoates (especially the 2,6-dimethylphenyl esters), when the monomers were complexed with excess dialkylaluminum chloride and polymerized with modified propylene polymerization initiating systems, homopolymers and copolymers of high molecular weights can be obtained (Eq. 29) [92–96]. Polymerization and copolymerization of ω-epoxyalkenoates, both the methyl and the 2,6-dimethylphenyl ester, gave polymers of high molecular weight with aluminum alkyl/acetyl acetonate/water initiating systems [97, 98]. In those cases, both polymers and copolymers can be prepared in large quantities. Polymers and copolymers could be readily hydrolyzed with aqueous sodium hydroxide or with aqueous sodium hydroxide/organic solvents such as 1,4-dioxane. Polymerization of ethylene oxide and methyl-10,11-epoxy undecanoate gave copolymers which could be hydrolyzed to the carboxylic acid and gave ethylene-oxide-based ionomers (Eq. 30). These ionomers were studied for their behavior (Eq. 31) as simplex-forming polyanionic salts [97]. It was shown that they form uniform gels with polycationic polymers at ionic concentrations as low as 1.5%.



EQUATION 29. Polymers of 10,11-epoxyundecanoate and 10-undecenoate.



EQUATION 30. Hydrolysis of the copolymer of 10,11-epoxyundecanoate and ethylene oxide.

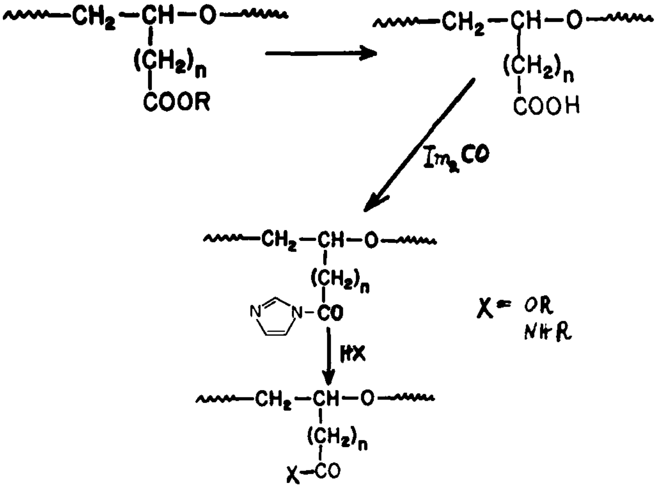


EQUATION 31. Simplex formation of poly(oxyethylene) carboxylic acids.

Normal ionomeric anionic polymers which have the ionomeric carboxylate or sulfonate group attached directly to the polymer chain, such as cellulose derivatives, require 10 to 12% carboxylate functional groups for network formation.

Polymeric carboxylic acids, such as copolymers of ethylene oxide, propylene oxide, and 2-butyene oxide, were studied for their ionomeric properties [98]. Again, only about 1.5% of carboxylate groups are needed in the copolymer to achieve maximum ionomeric properties. We are now in the process of investigating the reactions of the homopolymers and copolymers of the carboxylated acid derivatives of polyethylene- and polyoxyethylene-based polymeric carboxylic acids.

We have developed an efficient way of preparing carboxylic acid derivatives by reacting free carboxylic acids with diimidazolyl carbonyl [99, 100]. The imidozolide is formed quantitatively with the evolution of 1



EQUATION 32. Preparation of polymeric imidazolides.

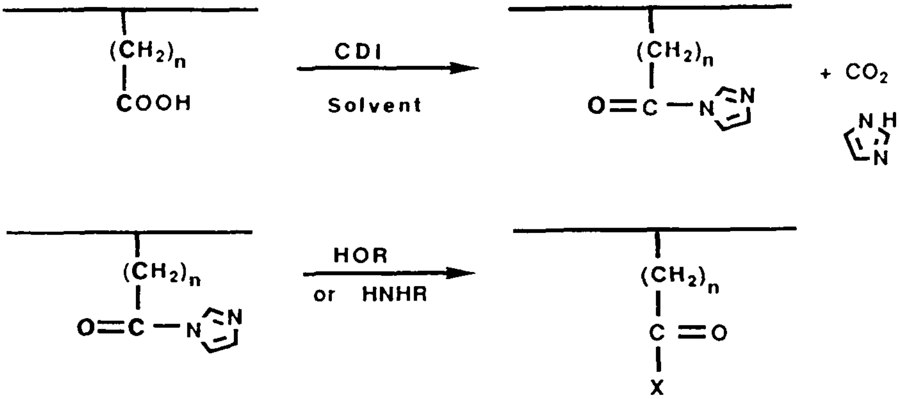
mol of carbon dioxide and the liberation of 1 mol of imidazole (Eq. 32).

Reactions with phenols, aromatic and aliphatic amines, and selected alcohols gave polymeric esters and amides in essentially quantitative reactions (Eq. 33).

F. HELICAL POLYMERS

For a number of years we have been involved in the study of helical polymers, specifically in the design and synthesis of the perfect polymer helix [101-104].

The first time it was recognized that helical structures play a significant role in polymer structures was when the structure of the alpha helix for poly(alpha-amino acids) was determined by x-ray crystallography, first published by Pauling in the early 1950s [105] (Fig. 15). The alpha helix is just one of the structures in which poly(alpha amino acids) and proteins can exist. The formation of the helical structure is assisted by the fact that each amino monomer unit (except glycine) has a chiral carbon atom and only *L*-amino acids are found in natural proteins. The effectiveness of the chiral substituent on the side chain is further enhanced by the bulkiness of the side group and rigidity, as in the case of



Examples:
1-Mesogenic groups
2-Groups with potential
NLO properties
3-Electrically active groups
4-Optically active groups

EQUATION 33. Synthesis and reaction of polymeric imidazolides.

proline which directs the conformation of the poly(alpha amino acids) into a helix. The helix and other poly(alpha amino acid) structures are held together by hydrogen bonding and by the proper placement of water molecules in the crystalline state. The alpha helix of poly(alpha amino acids) is a "weak" helix and can easily be transformed into the beta-sheet conformation at relatively low temperatures. The transitions from the alpha-helix to the beta-sheet structure occurs by "melting and reforming" of hydrogen bonds which occurs between 35 and 55°C depending upon the nature and size of the substituent attached to the chiral carbon atom [105].

A helical structure also exists for the DNA molecule; it has the structure of a double helix [106]. Again, the structure is held together by hydrogen bonding and pairing of the two types of heterocyclic bases: pyrimidines and purines. Hydrogen bonding here is somewhat stronger. Still, this particular type of hydrogen bonding is subject to dissociation at about 85°C [107]. Figure 16 shows a computer simulation of a DNA molecule. It shows that DNA is not a completely rigid molecule; one repeat unit of the macromolecule consists of 10 monomer units of a repeat unit length of 34 Å. Ten of these repeat units, or about 100

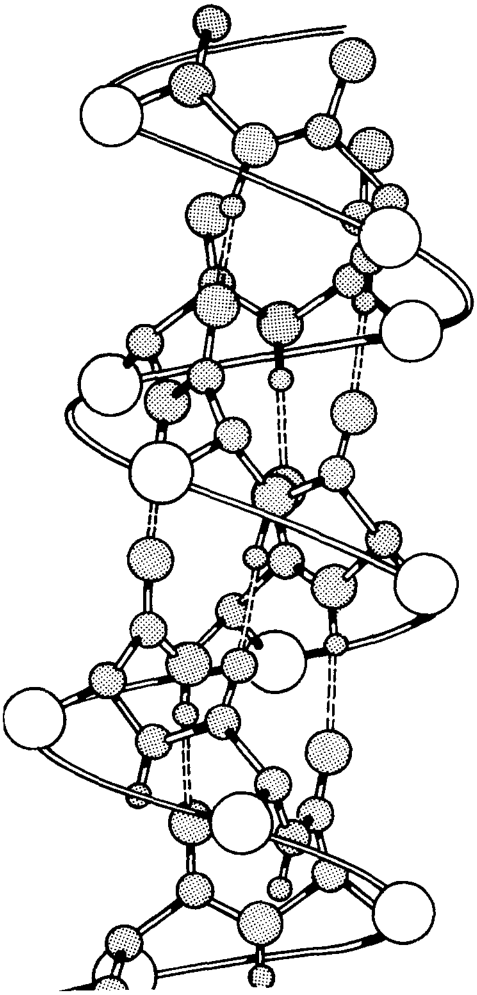


FIG. 15. The alpha-helix of amino acids.

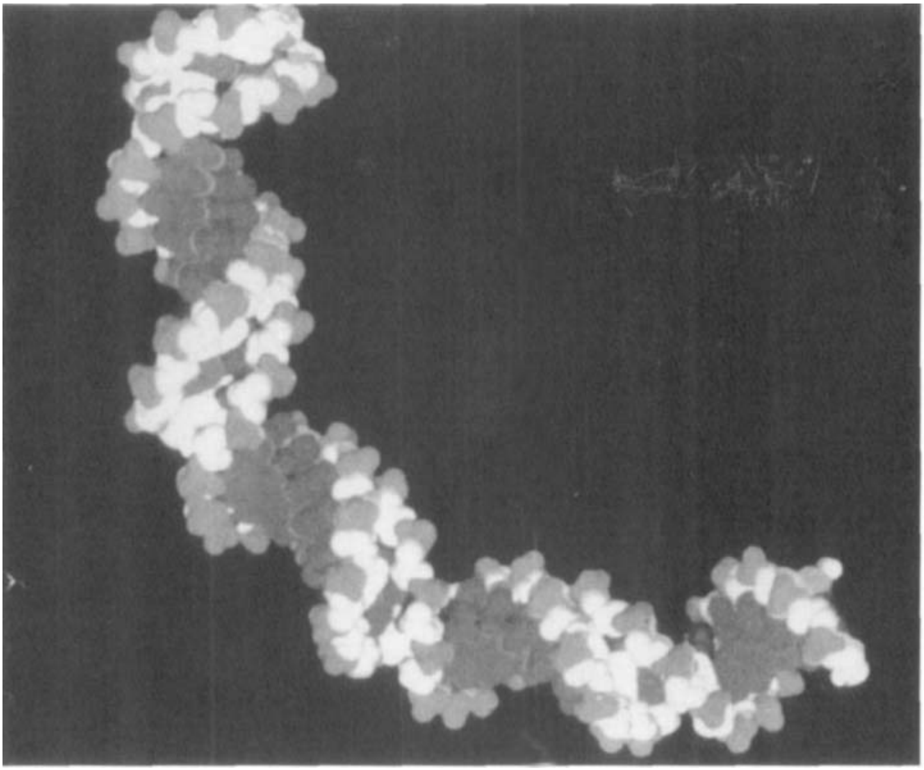


FIG. 16. The double helix of DNA.

nucleic acid residues, are “flexible enough” to allow the bending of the nucleic acid structure onto itself [108]. This behavior has been observed in some virus structures; the DNA part of the structure is actually bent over the central part of a protein structure.

Isotactic polymers such as polypropylene or polyacetaldehyde crystallize in helical structures: Polypropylene in a 3/1 helix [a 3/1 structure means that there are three monomer units in one full turn of the helix unit (Fig. 17)], [109]; polyacetaldehyde in a 4/1 helix [113]. In polypropylene the helix is accommodated in 6.5 Å [111], which means that each monomer unit in the helical polypropylene chain has a unit length of about 2.2 Å; this is 0.4 Å less than what would have been expected for a planar zigzag arrangement. To accommodate isotactic polypropylene

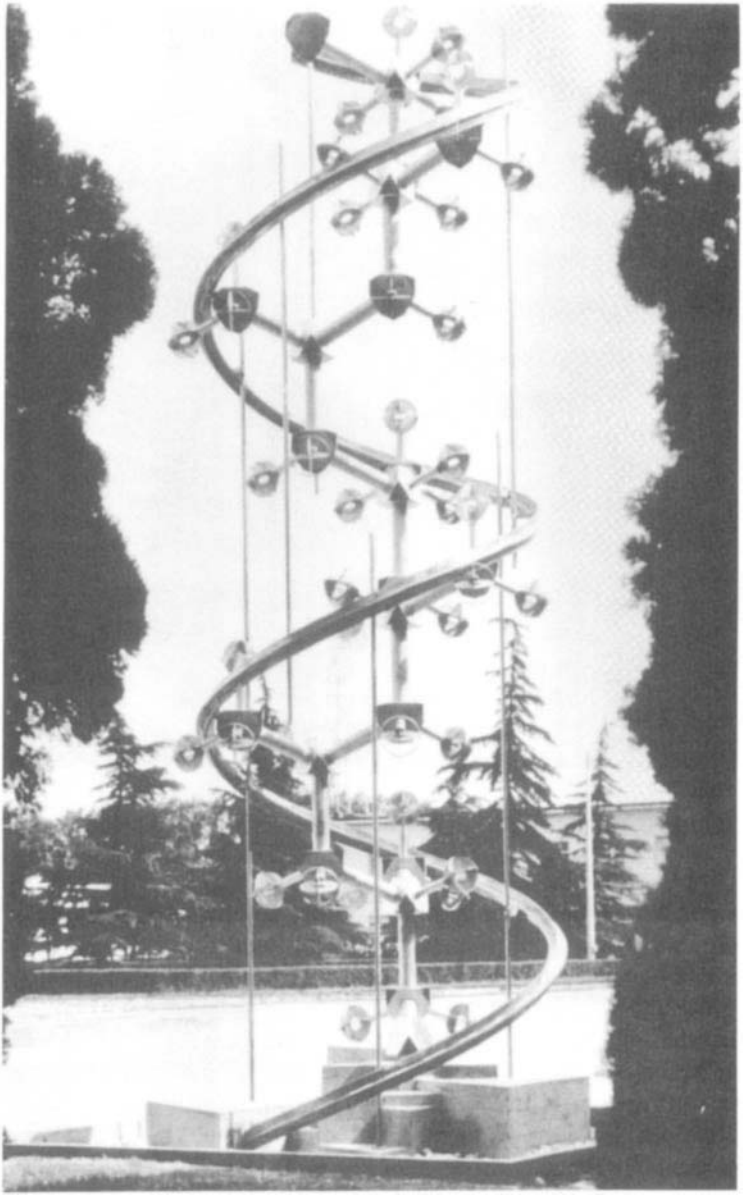


FIG. 17. Polypropylene helix as shown in the model in front of the Giulio Natta Research Center in Ferraro, Italy.

in 6.5 Å, the structure must be that of a 3/1 helix. As mentioned, many polymers crystallize in helical structures; polyacetaldehyde does so in a 4/1 helix with a repeat distance of 4.8 Å or with a monomer unit length of 1.20 Å [110]. Polyethylene is probably one of the few polymer exceptions; it crystallizes in a planar zigzag structure exclusively [112]. Polyoxymethylene crystallizes in a slightly distorted 2/1 helix [110].

We have considerable experience in stereospecific aldehyde polymerization. As a consequence, we have explored polyaldehydes as the most promising example for the synthesis of the perfect helix. Helical structures in polymers are not helices of one screw sense: each of these helical structures consists of a 50/50 mixture of left-handed and right-handed helices.

Interestingly enough, artists have used helical columns for a long time to enhance the beauty of buildings, especially the interiors of churches. In the interior of the University Church in Vienna (built in 1627) (Fig. 18) [114], the artists used two helices, one left handed and one right handed, each to focus on the display of specific paintings. A similar structure can be seen at the exterior of the church in the center of Prague, behind the St. Vitus Cathedral.

We mentioned that the common helical polymers exist as racemic 50:50 mixtures of left- and right-handed helices. The unit cell structure of many of these polymers is often more complicated; they consist of four helices, two are left handed, the two are right handed. This can be seen in the structure of poly(*n*-heptaldehyde) (Fig. 19) [115]. This type of structure has also been anticipated by artists as seen in the structure in Notre Dame Cathedral in Montreal (Fig. 20) [116]. Bernini has also anticipated these helical structures in his construction of the altar (in 1666) in St. Peters Cathedral in Rome (Fig. 21) [117].

If you have ever looked at snails you know that their shells have a twist. Most shells, such as the one from the Cuban tree snail *Liguus virgineus*, are right handed, but there are examples within a given species where left-handed versions caused by mutations appear. In the growth of snail shells, we see a growth by conical symmetry (Fig. 22) [118]; some climbing plants climb in helical fashion (Fig. 23). The crystallization of helical macromolecular structures proceeds by cylindrical symmetry.

Crystallization of certain inorganic crystals also occurs in an asymmetric fashion. Sodium chlorate and bromate are isotropic ionic crystals. Sodium iodate is ionic, quartz (silicon dioxide) is polymeric with covalent bonds, and benzil is an asymmetric molecular crystal. The latter three crystal types belong to the category of uniaxial crystals (the refractive

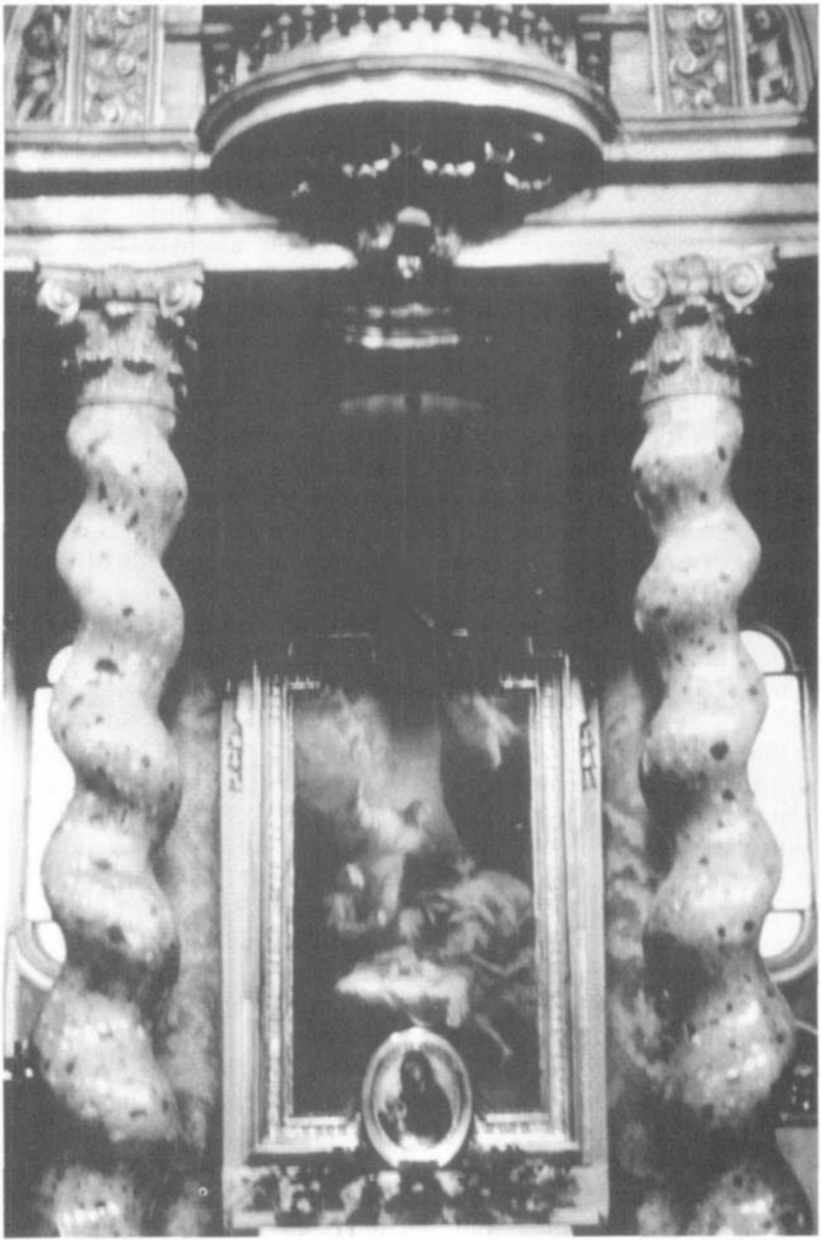


FIG. 18. Side altar in the University Church in Vienna.

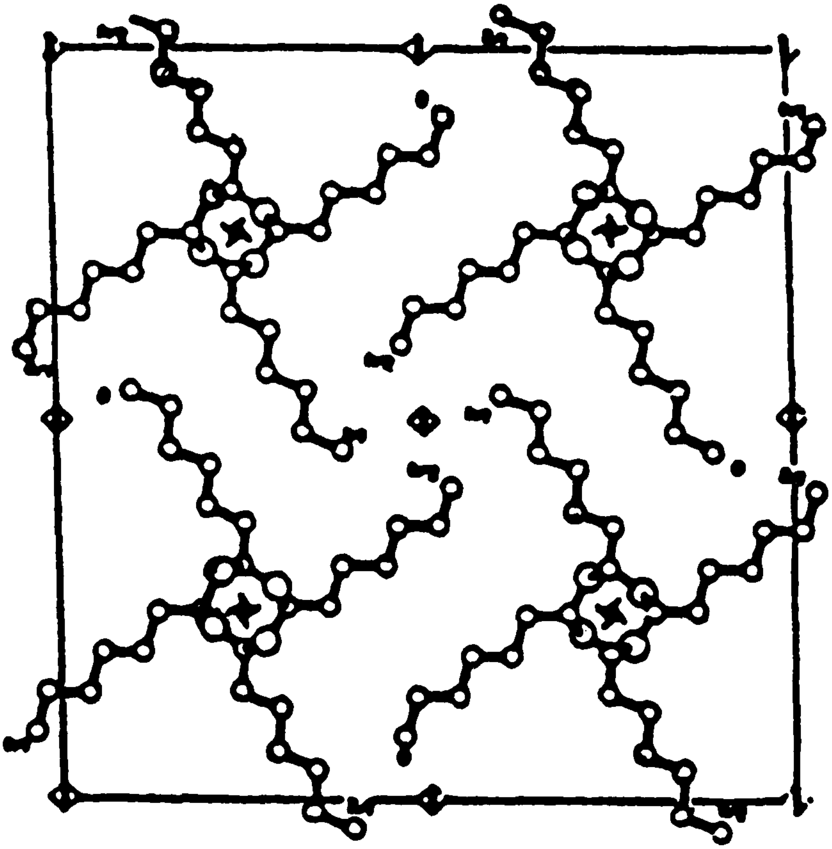


FIG. 19. Unit cell of isotactic poly(*n*-heptaldehyde).

index is different in the growth direction than in the other two crystal directions). These optical asymmetries are most likely also based on a helical structure (Fig. 24) [119, 120].

Organic chemists have known that high optical rotations are obtained when the optical activity is based on molecular or macromolecular asymmetry such as in cholesteric liquid crystals [121] and in helicenes (Fig. 25) [122]. Optical rotations in the thousands of degrees have been measured, while the optical rotation of chemical compounds with chiral carbon atoms have optical rotations in the tens to hundreds of degrees. It was therefore expected that the optical rotation of rigid macromole-

FIG. 20. Main altar of Notre Dame in Montreal.

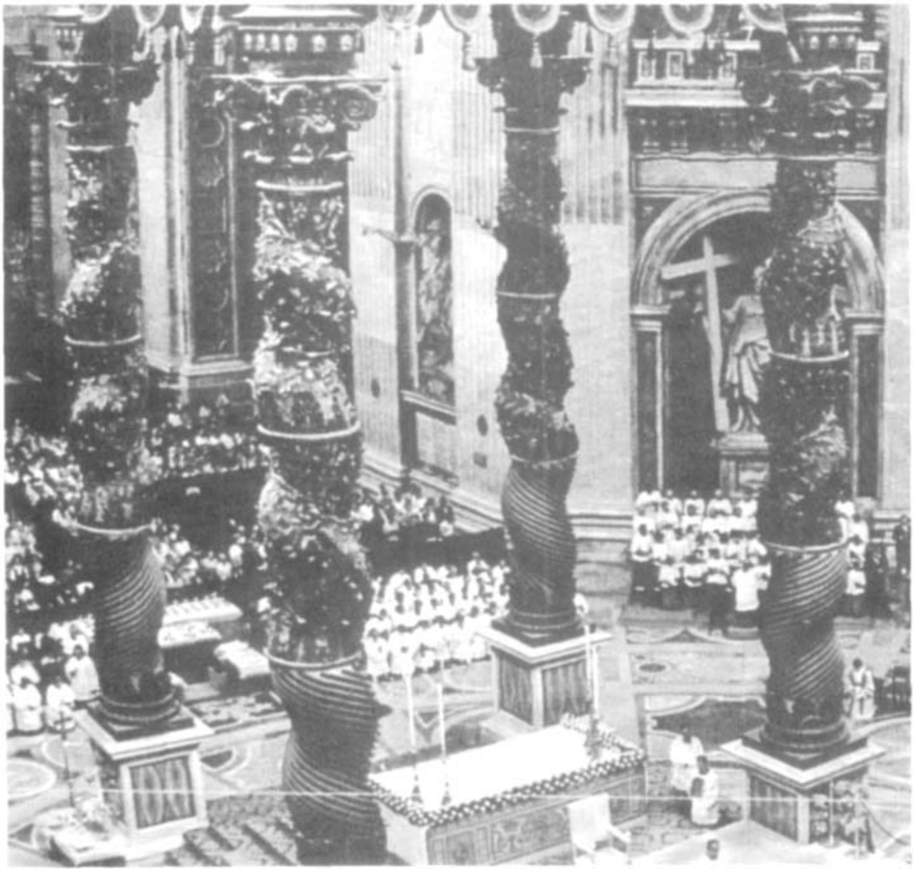
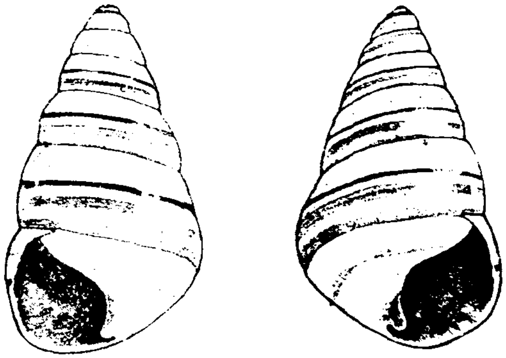


FIG. 21. Main altar of St. Peters Basilica in Rome.

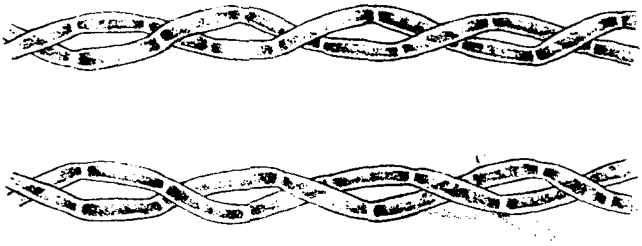
cules of one single screw direction, especially in very rigid macromolecules, might also have optical rotations in the thousands of degrees.

Our basic approach has been to study polyaldehydes because it was believed that the side group size could be tailored to the point that would allow polymer chain growth in one screw sense only. The result would be similar to the restricted, one screw sense growth of the snail shell.

We found very early that perhaloacetaldehydes are more suited for this study than regular aliphatic aldehydes [123, 124]. They polymerize more readily, and side group size can be easily regulated by substitution



LIGUUS VIRGINEUS



BACILLUS SUBTILIS

FIG. 22. Picture of *Liguus virgineus* and *Bacillus sobtilis*.

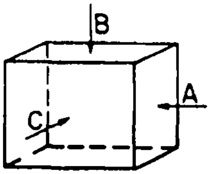
of the various halogen atoms (fluorine, chlorine, and bromine). We have known for some time that trichloroacetaldehyde (chloral) polymerizes exclusively to isotactic polymer; no stereospecific initiators are needed. It was furthermore found that perhaloacetaldehydes with at least two chlorine atoms in the trihalomethyl group also give only isotactic polymers.

Polychloral is isotactic and possesses a 4/1 helix with a repeat distance of 5.2 Å. The polyacetal helix is in the center, and only the chlorine atoms from the trichloromethyl groups of the side chain can be readily seen (Fig. 26) [125, 126].

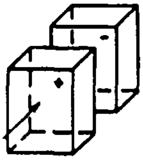
CONVOLVULUS ARVENSIS LONICERA SEMPERVIRENS

FIG. 23. Picture of *Convolvulus arvensis* and *Lonicera sempervirens*.

The requirement for optical activity based on macromolecular asymmetry is a monomer which polymerizes in a helical, normally isotactic, fashion. High conformational energy barriers are necessary to prevent helix inversion, and an optically active initiator has to be used to induce the polymerization to a helical polymer of one screw sense only. There is another way to induce helicity in polymeric chains, a principle that was used some years ago for polyolefins. It requires the use of monomers (polymerizable olefins) with an asymmetric chiral center adjacent to the polymerizable group [127].



Direction	Dimensions mm	Beam mm	$[\alpha]_D$ °
A	9.3	2	-114
B	8.5	2	-113
C	2.4	6	-121



Crystal	Thickness mm	Optical rotation °
+	2.39	-7.22
-	3.00	+9.13
Difference		
calculated	+0.61	+1.91
measured	+0.61	+1.91

Measurements of Optical Activity of Sodium Chlorate Powder in a Carbon Tetrachloride - Carbon Disulfide Mixture, n_D = 1.517 (1 ml Suspension)

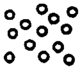
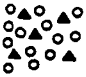
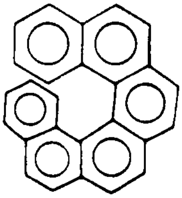
	Powder	Weight g	Optical rotation °/ml
	+	0.0050	+0.058
	-	0.0136	-0.156
	+	0.0050 (27 %)	
	-	0.0136 (73 %)	
	Mixture ▲	0.0086	-0.098

FIG. 24. Measurements of optical activity of sodium chlorate.



Hexahelicene

specific rotation, $[\alpha]_D^{25}$ = (+) or (−) 3700°

FIG. 25. Structure of helicenes.

Our objective was to use chiral initiators and achiral monomers, however, so all optical activity would be due to macromolecular asymmetry alone.

Anionic polymerization of chloral gives a polymer that is a living but dormant polymeric alkoxide. This polymer must be stabilized [128], otherwise it will depolymerize as the temperature is raised substantially above the ceiling temperature of 58°C (the threshold temperature, not the ceiling temperature, when neat chloral is polymerized).

If the polymerization of chloral is initiated with an achiral initiator such as tertiary butoxide, the first addition product is the racemate, the

FIG. 26. Molecular model of polychloral.

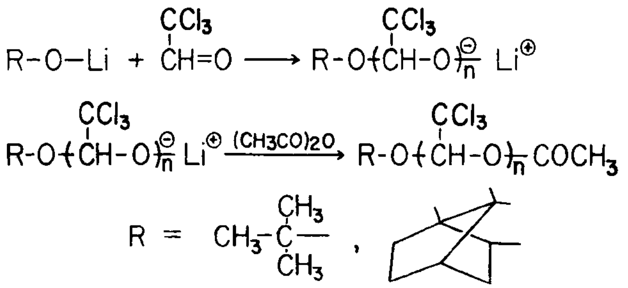
R and *S* form of the unimeric alkoxide. Further addition is in principle possible to form the racemo and meso addition product of the *R* and *S* form. Minimum energy calculations for the development and the stereochemistry of dimers and trimers have shown that the meso (48.47 kcal/mol) and racemo (48.14 kcal/mol) additions have almost exactly the same energy [129]. Subsequent additions can occur by racemo and meso addition. As further additions of the chloral monomer occur, the addition possibilities become very restricted, however. If, after the first addition of a chloral monomer unit, further addition occurs in the meso form, the polymer formed *in the helical conformation* has either a D helix or a L helix. Let us say that meso addition of the *R* form results in the formation of the D helix of polychloral. All meso additions to the *S* form of the first addition product will result in the formation of the L helix.

The polymer obtained from sequences of meso additions will be optically inactive even though it is 100% isotactic; it is a racemic (50:50) mixture of the left- and right-handed helices [130, 131]. Every time, however, that a racemo addition occurs (followed by a continued sequence of meso additions), the screw sense of the polymer helix is reversed. This reversal is possible in the developing stereochemistry of the second and third additions of chloral monomer. After this addition sequence, the selection allows only meso addition, and the sense of the screw direction of the polymer chain is fixed.

G. CONSTRUCTION OF THE HELIX

One of our goals for the last three decades has been to design and synthesize helical polymers that have polymeric structures of only one screw sense [134]. To achieve this objective, it is necessary to control the stereochemistry and conformational specificity in the polymer structure and its synthesis.

We reasoned that the best workable class of polymers would be polyacetals. We knew that aldehydes, with the simplest example being formaldehyde, polymerizes to polyoxymethylene that crystallizes in a helical structure [110]. Unlike the preferred zigzag structure of crystalline linear polyethylene, polyoxymethylene crystallizes in a 2/1 helix. Higher aliphatic polyaldehydes exist predominantly in their isotactic stereochemical form, and polyperhaloaldehydes with larger side groups, such as the polymer of trichloroacetaldehyde (chloral), exists exclusively as isotactic



EQUATION 34. Oligomerization of chloral.

4/1 helices [126]. We reasoned that we should be able to change the size of this side group easily, thereby controlling the exact size of the group that is necessary to prepare the ideal helix.

Trifluoroacetaldehyde (fluoral) can readily be polymerized with anionic initiators to form polyfluoral. With lithium tertiary butoxide as the initiator and with the right initiator/monomer ratio, followed by immediate acetate endcapping, a mixture of fluoral oligomers could be prepared [135].

We have studied this oligomer mixture (Eq. 34) by a very specific and sensitive technique of mass spectrometry, e.g., potassium ion mass spectrometry of the desorped species (K^+ IDS). This technique allows the identification of individual masses (plus K^+) of the oligomers without their decomposition [136]. The mass spectrum reveals masses up to the undecamer (Fig. 27) for tertiary butoxide-initiated species and borneoxide-initiated fluoral oligomers (Fig. 28). It is clear that all the molecular ions of the oligomers are present. However, the lower oligomers do not appear in the spectrum with the correct intensity. Due to their high volatility, a part of the lower oligomers were lost during sample preparation in the high vacuum required for mass spectral analysis.

Mass spectrometry can accurately determine the masses of molecular ions but cannot distinguish the stereochemistry of the individual compounds of the same masses. Recognition and identification of individual compounds can be done by very careful GC analysis (Fig. 29). The gas chromatogram of the oligomer mixture clearly showed one unimer and two dimers. In principle, there should be four trimers and eight tetramers. We can indeed recognize three trimers, several tetramers, and several pentamers. Almost all the stereoisomers are present in the oligomer mixture. When lithium borneoxide was used as initiator for the

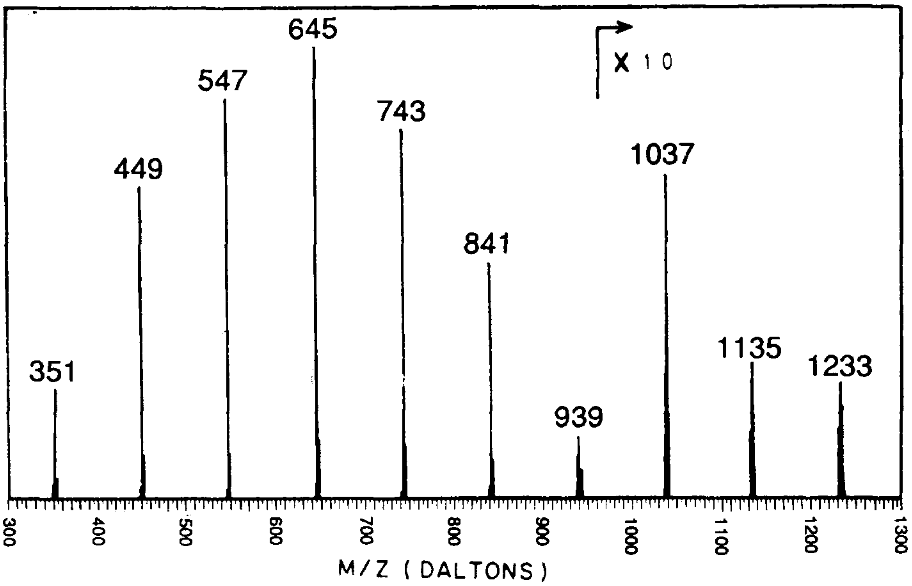


FIG. 27. K$^+$ IDS mass spectrum of tertiary butoxide-initiated acetate-capped fluoral oligomers.

fluoral oligomerization (followed by acetate endcapping), a mixture of fluoral oligomers was obtained which were analyzed by GC. Individual "mer" fractions of the oligomers were identified, up to the decamer, by their K$^+$ IDS spectrum.

Initiation of chloral with lithium tertiary butoxide followed by termination with acetic anhydride gives linear chloral oligomers [132, 134]. Depending upon the ratio of the initiator, the chloral monomer oligomeric product might be shifted to higher molecular weight. The chloral oligomers discussed above have been obtained by initiation with the achiral initiator, tertiary butoxide, and the individual compounds are consequently 50:50 mixtures of compounds of *R* and *S* configurations. The trimer is consequently a 50:50 mixture of *RRS* and *SSS* structures, the tetramer of *RRRR* and *SSSS* structures, etc. The heptamer structure also shows the continued development of a 4/1 helix for polychloral with a sight twist which produces a 11/3 helix.

Mixtures of the linear chloral oligomers were subjected directly to mass spectrometry [137, 138]. Molecular masses up to that of the hep-

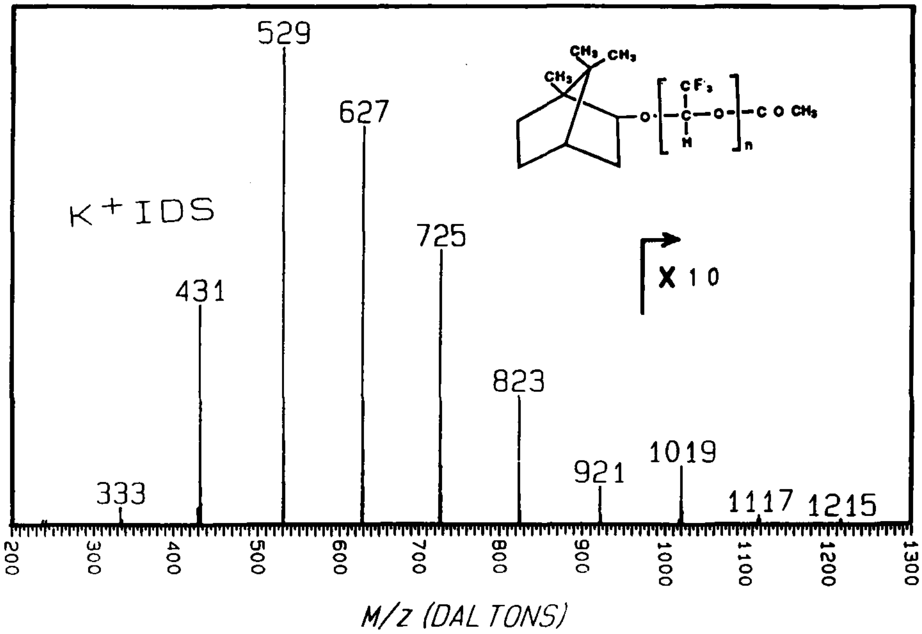


FIG. 28. K$^+$ IDS mass spectrum of borneoxide-initiated acetate-capped fluoral oligomers.

tamer at 1187 daltons could be identified (Fig. 30). Each of the oligomers was characterized by its K$^+$ IDS behavior and by the chlorine isotope distribution patterns of the individual molecular masses. Examples of the trimer, tetramer, pentamer, and hexamer are shown in Figs. 31 and 32. The entire linear oligomer mixture was fractionally distilled, and the individual fractions representing the unimer, the dimers, the trimers, and the tetramers were then subjected to mass spectrometer analyses. This allowed not only a more exact characterization of the individual linear oligomers, but also the isolation of individual compounds and individual stereoisomers.

Gas chromatography was then carried out on these fractions. The chromatogram clearly shows the isomer distribution. We can see one unimer and two dimers (Fig. 33). As more chloral monomer units are added in the oligomerization, chloral monomer addition becomes very stereospecific. The trimer fraction has essentially only one peak, the

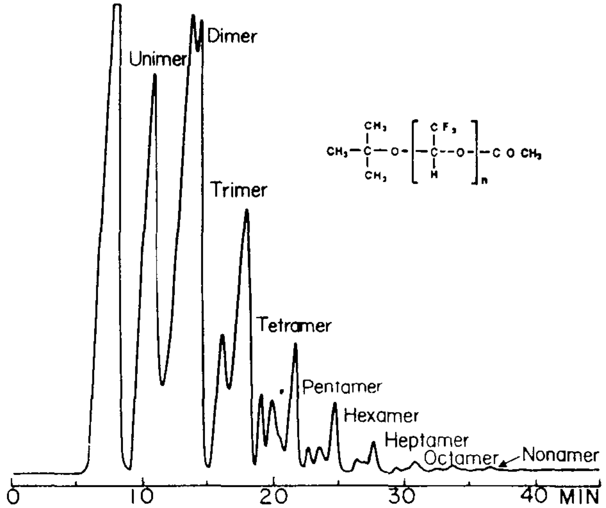


FIG. 29. Gas chromatogram of tertiary butoxide-initiated acetate-capped fluoral oligomers.

all-meso (*mm*) peak (Fig. 34). The pentamer is completely specific and consists only of *mmmm* stereochemical configuration with a specific conformation—the gauche$^+$/skew$^-$ (or gauche$^-$/skew$^+$) conformation which leads to the helical conformation. The isomers of the higher linear chloral oligomers were isolated by HPLC. We have been able to crystallize the dimer, trimer, tetramer, and pentamer. Careful 1-H and 13-C NMR studies, particularly by two-dimensional NMR spectroscopy (NOSY), of the higher oligomers allows exact determination of the structures of the individual compounds.

Confirmation was achieved by complete single crystal analysis of the individual isomers from the dimer to the hexamer (Fig. 35) [139–144]. The dimer (mp 74°C) has the structure of a meso (*m*) placement or a *SS* configuration, the trimer structure has a *mm* or *SSS*, the tetramer has a *mmm* structure or *SSSS*, and the pentamer the *SSSSS* structure (Fig. 36). The *mmm* (*SSSS*) tetramer isomer is the only compound present in the tetramer fraction. Investigation of the structure of the individual compound by single crystal x-ray analysis, combined with the assignment of the individual chemical shift values, establishes beyond any reasonable doubt the absolute configuration of the compounds. The tetramer

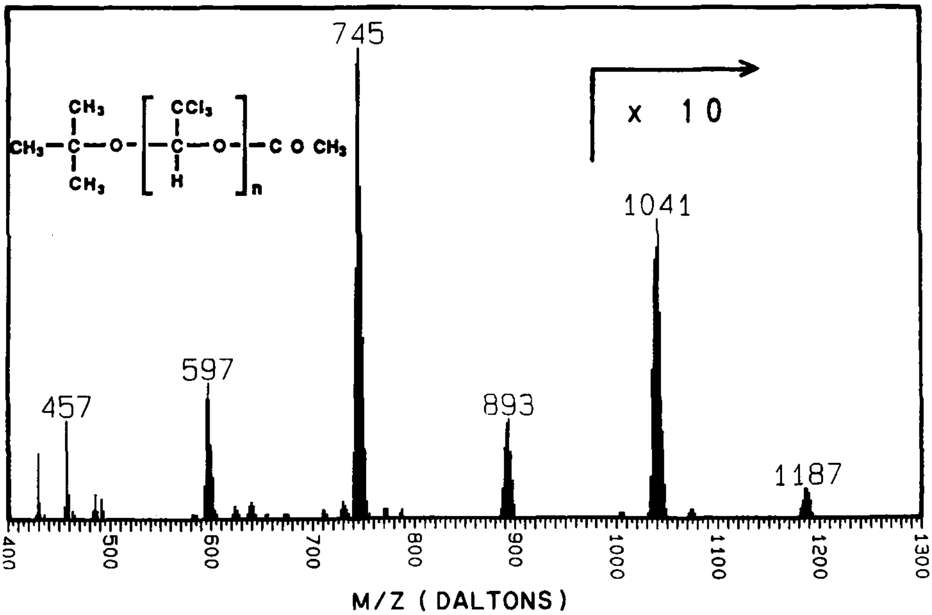


FIG. 30. K^+ IDS mass spectrum of the tertiary butoxide-initiated acetate-capped chloral oligomer mixture.

structure is the first turn of a 4/1 helix with a 4.8 Å repeat distance; the structure of the polychloral itself has been established as a 4/1 helix with a 5.2 Å repeat distance. The hexamer structure is shown in Fig. 37 (Eq. 35) [153].

Work is also underway to prepare and analyze the oligomers of triphenylmethyl methacrylate [146–152]. Poly(triphenylmethyl methacrylate) is known to have a helical structure although the exact configuration does not seem to be known. The study of the triphenylmethyl methacrylate polymers and its oligomers seems to have advantages and disadvantages as compared to our chloral polymers. The determination of the structure of the polymers and work on the oligomers are complementary.

H. MACROMOLECULAR ASYMMETRY

Oligomerization of chloral initiated with lithium tertiary butoxide gives optically inactive 50/50 mixtures of the isomers, and, for the same reason, polymerization gives optically inactive polymers (Fig. 38). In

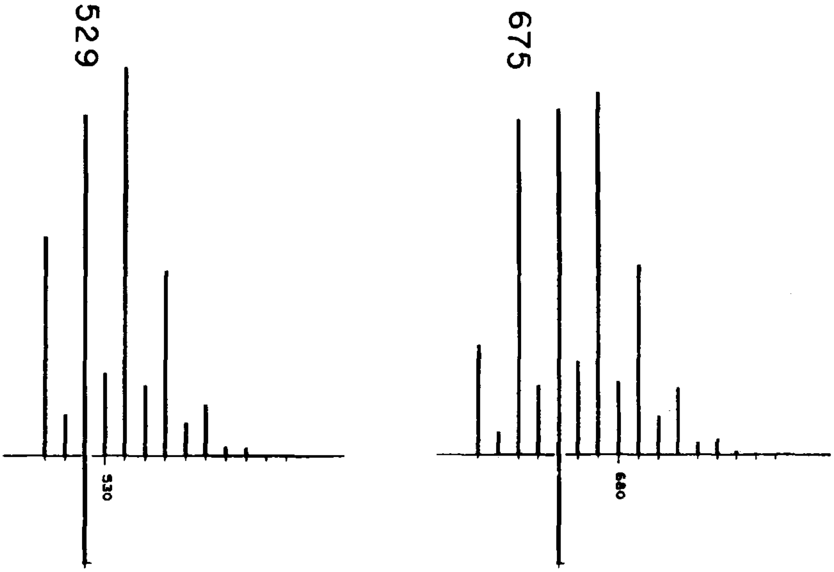


FIG. 31. Isotope pattern analysis of tertiary butoxide-initiated acetate-capped chloral trimer and tetramer.

order to prepare a polymer helix of one screw sense, it is necessary to match the side group bulk to achieve complete stereospecificity and 100% isotacticity; a particularly useful example is the trichloromethyl group of chloral.

The initiating alkoxide can be a chiral alkoxide which then becomes the initiating end of the polymer chain. The (anionic) initiator can be achiral, and the counterion could be a chiral capable of directing monomer addition stereospecifically *from the beginning*. It is then also possible to synthesize helical polymer structures of pure stereochemistry and conformational specificity. In order to accomplish this and to synthesize single helices with macromolecular asymmetry, it is necessary to design the structure of the initiating species in such a way that complete specific addition occurs from the *first addition*, i.e., from the initiation step. This means that a chiral initiating alkoxide must be synthesized that can add chloral in only one stereochemical sense, which then allows only meso addition after the first addition.

We have shown experimentally that this approach is in principle possible. Tricyclohexylmethoxide does not add chloral to form the

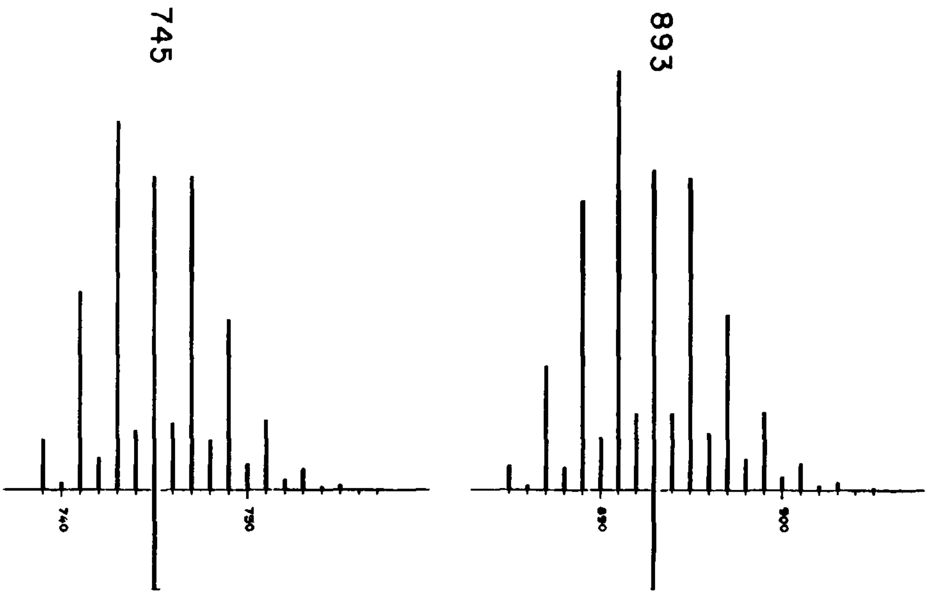


FIG. 32. Isotope pattern analysis of tertiary butoxide-initiated acetate-capped chloral pentamer and hexamer.

chloral-terminated alkoxide. Other alkoxides, such as triphenylmethoxy, diphenyltertiarybutoxy, or even dicyclohexyltertiarybutoxide, added to chloral. Some of them were even stereopreferred, but none of them were stereospecific. Only one addition product resulted [132, 133].

Using a chiral polymerization initiator that is large enough so that only one stereospecific addition of the first monomer unit to the alkoxide can occur is an essential requirement for synthesizing the perfect helix of one screw sense. This is true for the initiation process where the initiator remains at the end of the polymer chain, not when the chiral induction is in the counterion. With the chiral initiating alkoxides we have been using up to now, we cannot control the stereospecificity of the first addition of chloral to the initiator. The specificity develops after the second and third monomer additions.

Lithium borneoxide was also used for the oligomerization of chloral (followed by acetate capping) [153]. Analysis of the mixture of oligomers by mass spectrometry shows individual molecular mass peaks up to the heptamer at 1119 daltons (Fig. 39). Figure 40 shows the mass spectrum

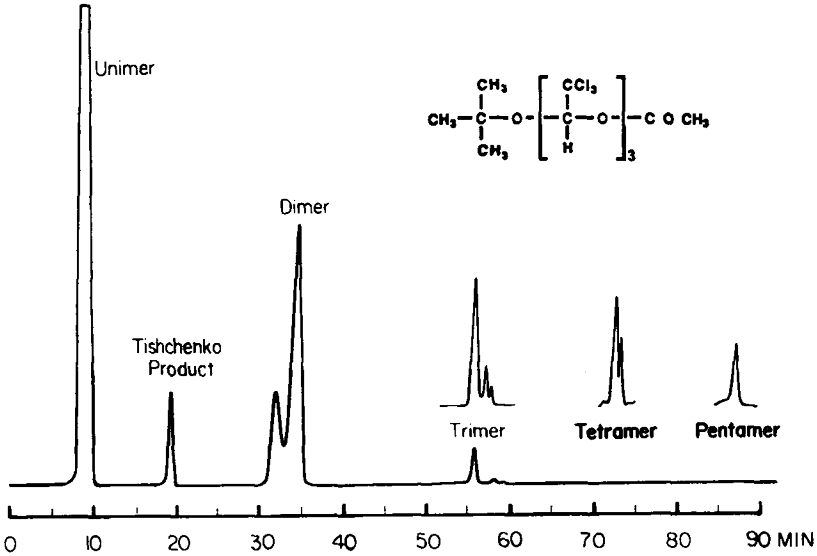


FIG. 33. Gas chromatogram of tertiery butoxide-initiated acetate-capped chloral ologomer mixture.

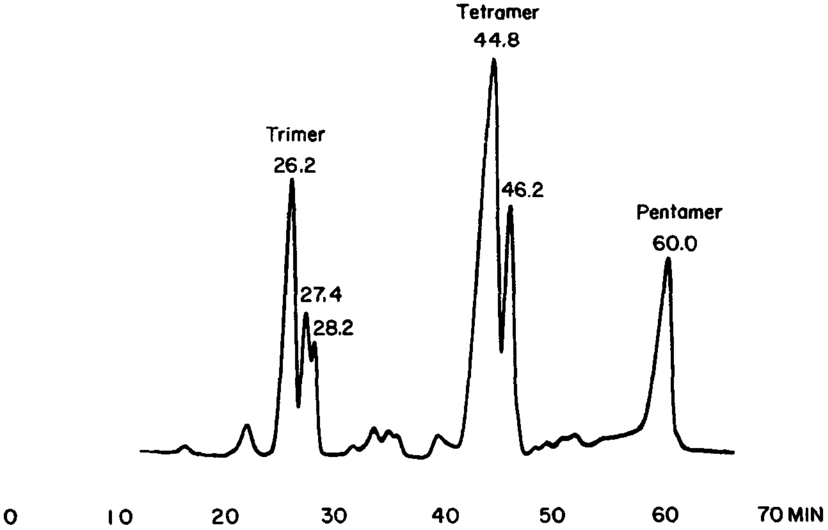


FIG. 34. Gas chromatogram of the higher fractions of tertiary butoxide-initiated chloral oligomers.

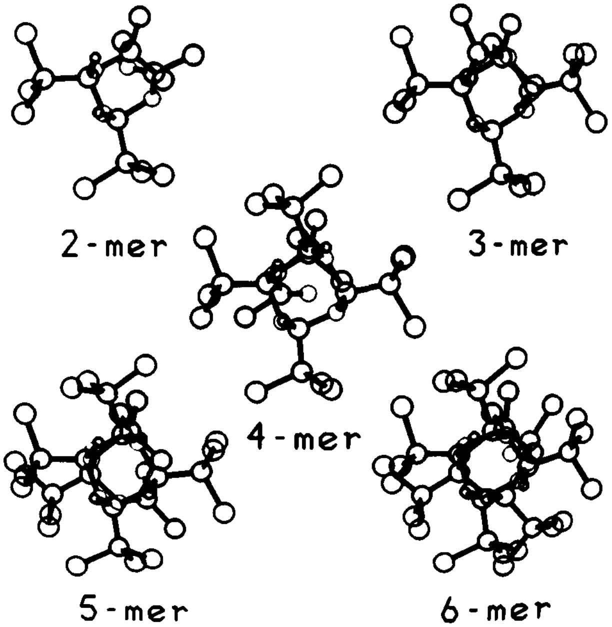


FIG. 35. Structure of tertiary butoxide-initiated acetate-capped chloral oligomers from dimer to hexamer.

of the unimer, and Fig. 41 shows the x-ray structure of the dimer. The GC trace of the unimer indicates the presence of two stereoisomers resulting from the racemo and meso addition; the unimer is a 45/55 mixture [140, 141]. However, as we go to higher oligomers, at the tetramer there is complete stereospecificity and only one isomer is observed. In this case the specificity must be associated with optical activity based on macromolecular asymmetry.

Similar oligomerization studies with bromal have also afforded the unimers. These are also now fully characterized, and several higher oligomeric products are in the process of being characterized [154, 155].

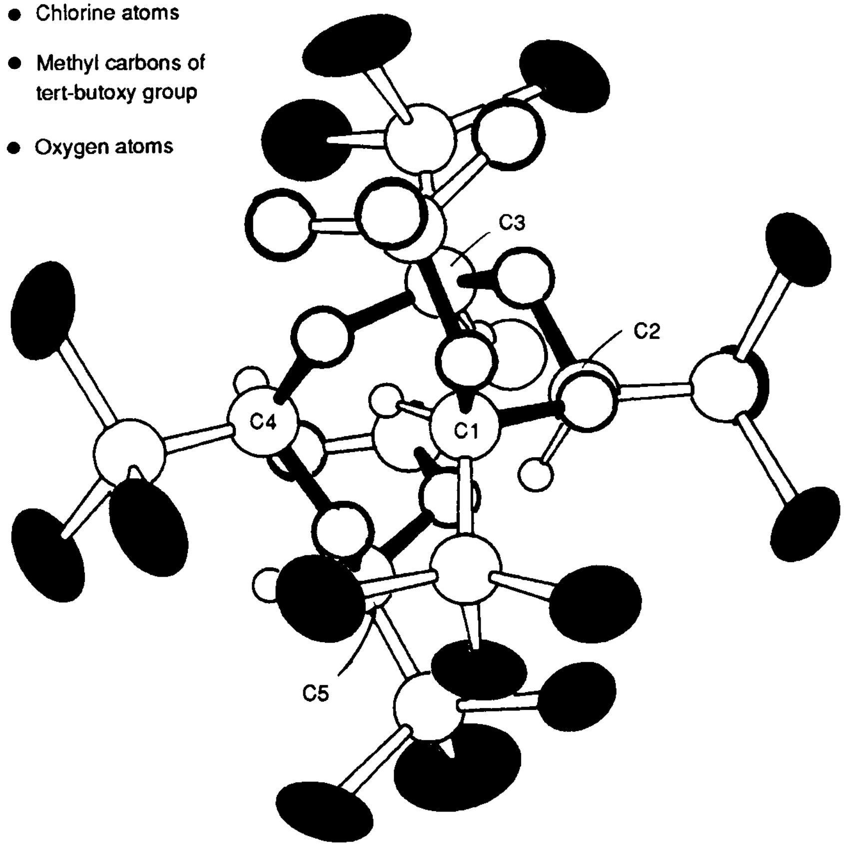


FIG. 36. X-ray crystal structure of tertiary butoxide-initiated acetate-capped chloral pentamer as viewed from the direction of the *c*-axis.

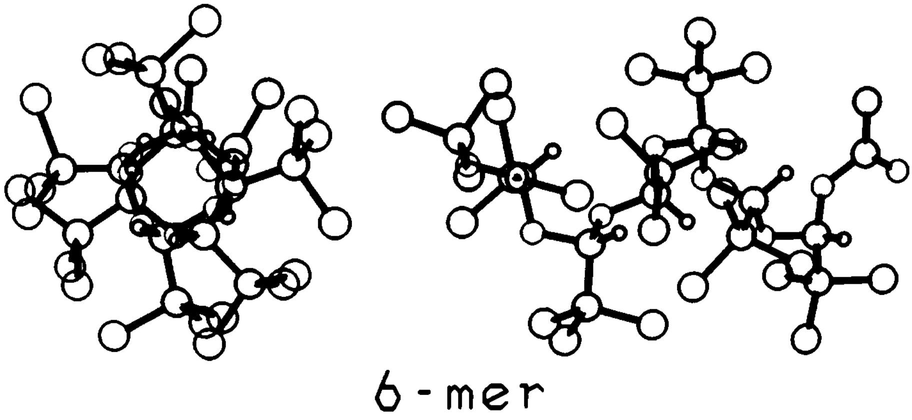
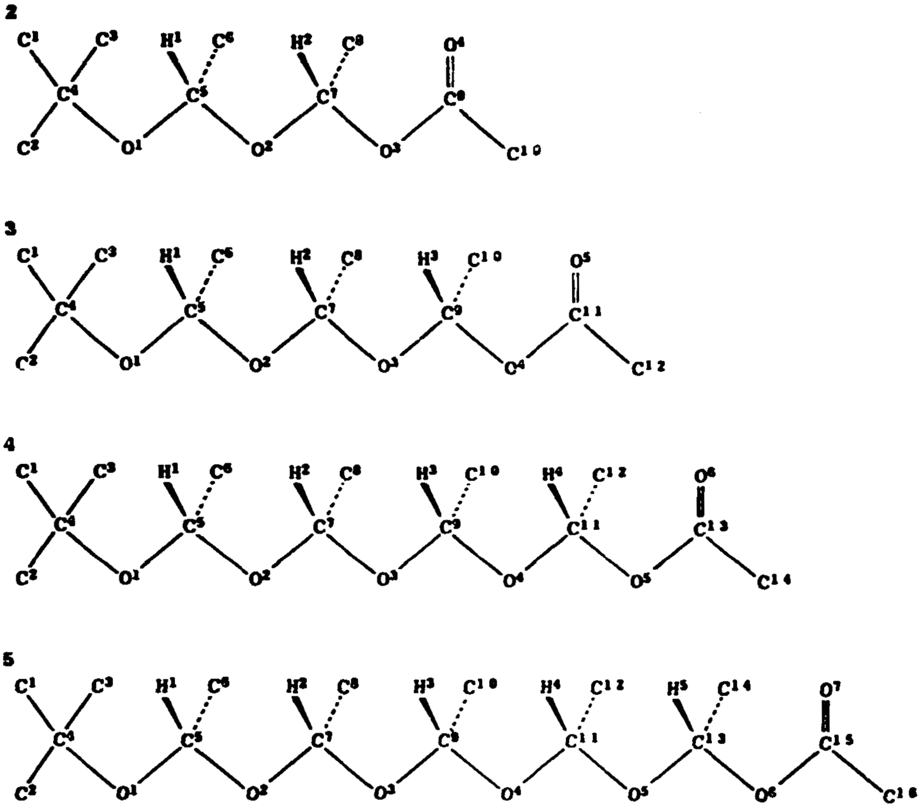


FIG. 37. X-ray crystal structure of tertiary butoxide-initiated acetate-capped chloral hexamer.



EQUATION 35. Oligomers of polychloral with numbering system of the individual atoms for x-ray analysis.

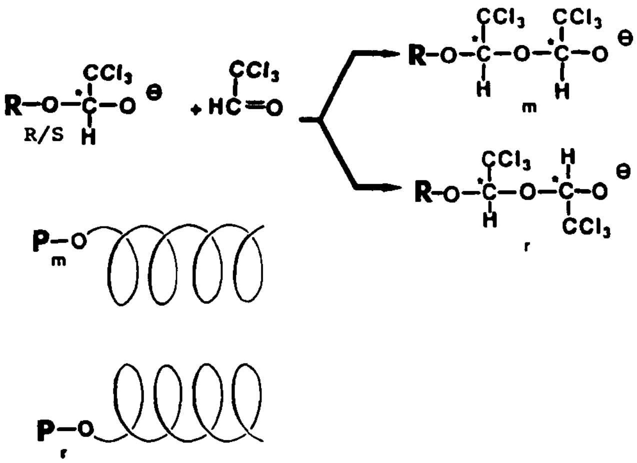


FIG. 38. Development of the polychloral helix.

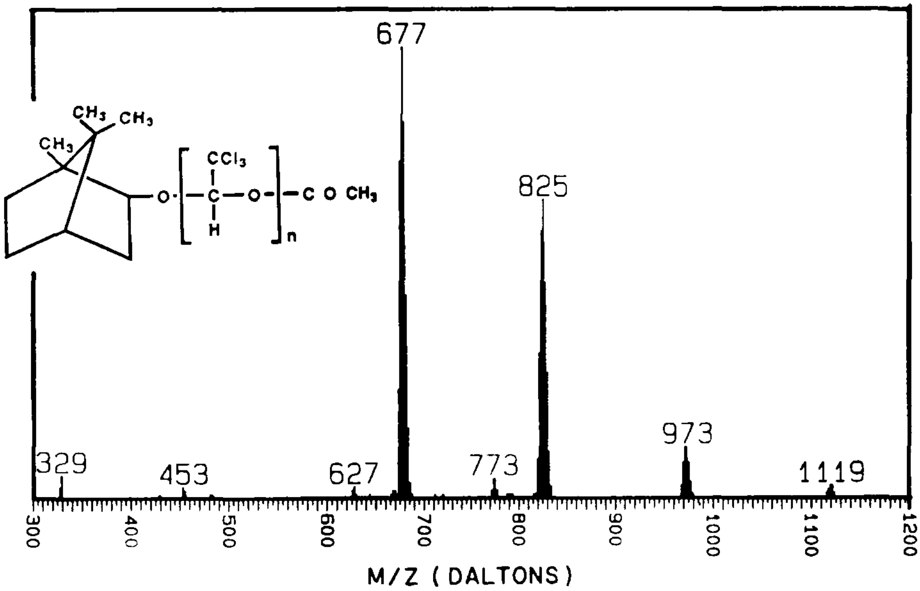


FIG. 39. K$^+$ IDS mass spectrum of borneoxide-initiated acetate-capped chloral oligomers.

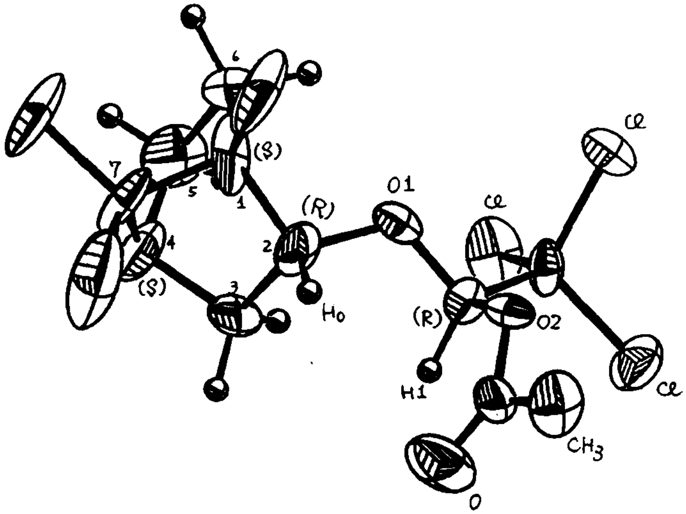


FIG. 40. X-ray structure of borneoxy-(*R*)-chloral unimer.

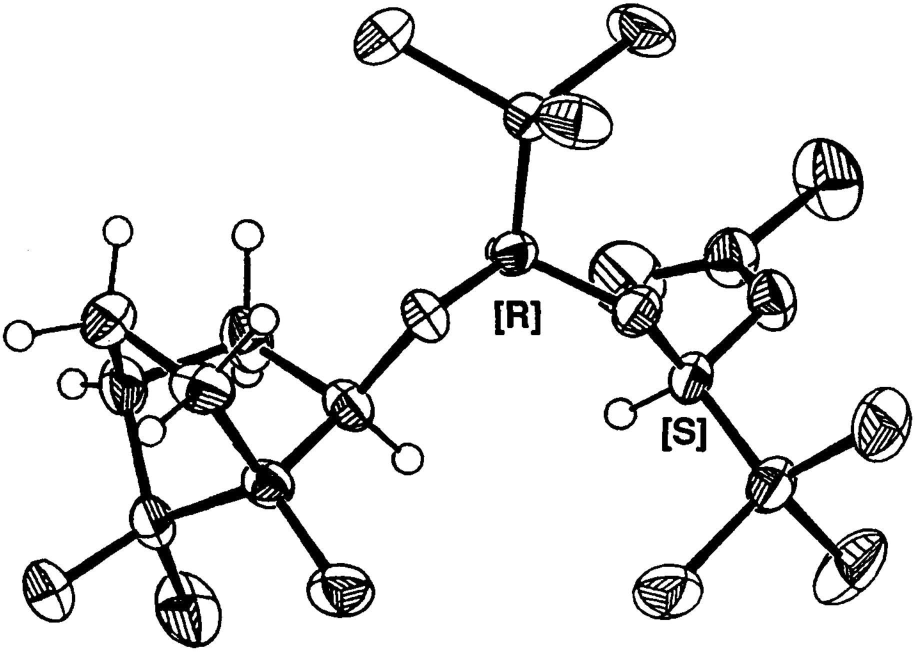


FIG. 41. X-ray structure of borneoxy-(*R,S*)-chloral dimer.

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