Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Molecular Architecture of Polymers

Otto Vogl[a]; Jan Bartus[a]; Meifang Qin[a]; Peter Zarras[a]
[a] Polytechnic University Brooklyn, New York, USA

To cite this Article Vogl, Otto , Bartus, Jan , Qin, Meifang and Zarras, Peter(1994) 'Molecular Architecture of Polymers', Journal of Macromolecular Science, Part A, 31: 10, 1329 — 1353

To link to this Article: DOI: 10.1080/10601329409350096

URL: http://dx.doi.org/10.1080/10601329409350096

J.M.S.—PURE APPL. CHEM., A31(10), pp. 1329–1353 (1994)

MOLECULAR ARCHITECTURE OF POLYMERS

OTTO VOGL, JAN BARTUS, MEIFANG QIN, and PETER ZARRAS

Polytechnic University
Brooklyn, New York 11201, USA

ABSTRACT

The molecular architecture of polymers has been analyzed and identified. Early development of polymer science and technology has been vastly expanded and has mushroomed into a business that constitutes nearly 5% of the gross national product of the highly industrialized countries. New polymer structures have been invented, and technologies have been developed to make these inventions the businesses of tomorrow. In this paper we gave a subjective account of the most recent developments in the chemistry, physics, and technology of polymer science.

INTRODUCTION

Polymer science and technology has made great progress in the last few decades [1]. Our quality of life has become dependent on polymers and on plastic products, and the 20th century is often called the "plastics age."

Today, the world production of polymers and use is about 150 MM tons. About 80% of the monomers for polymer production are based on oil as the raw material. The world's oil production at present is about 3 MMM tons, which means that about 4% of the oil produced is used for the production of polymers. On the other hand, over 90% of our oil is being burned to produce energy.

In the United States the total value of plastic materials produced and utilized is nearly \$200 MMM or about 4% of our gross national product of about \$6 MMMM. On a per capita basis, worldwide plastic production and plastic use is about 25 kg/person/year. This is the total amount of 150 MM tons of plastic materials produced worldwide divided by the total world population. In the industrialized world this number is approaching 100 kg/person/year. These numbers are probably accurate to ±10 to 20%.

One of the most important products derived from the combustion of oil, coal, or other carbonaceous materials, including the production and incineration of plastic materials, is carbon dioxide. We frequently hear that carbon dioxide (and by implication the use of plastics) is very detrimental for the environment because it is believed that carbon dioxide causes the so-called "green house effect," a temperature increase in the earth's environment.

We know, however, that 40 MM tons of the earth's carbon dioxide is photosynthesized to grow trees and plants and to produce "biomass." We also know that about 9 MMM tons of useful wood is grown, harvested, and used per year from the 40 MM tons of carbon dioxide used for photosynthesis. Incidentally, 1 MMM tons of chitin, an aminosaccharide, is "grown" annually by shellfish in the oceans and by insects.

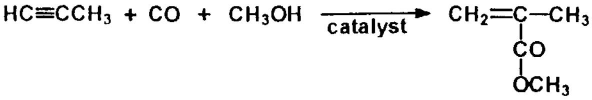
We do not have any reliable data as to the amount of carbon dioxide dissolved by the earth's oceans which cover 2/3 of the earth's surface. Even the low solubility of carbon dioxide in aqueous solutions must contribute a substantial amount of carbon dioxide that we normally do not know about and which does not seem to be considered significant in the earth's carbon dioxide cycle.

In general, discussions of carbon dioxide production and presence on earth do not include the carbon dioxide which comprises a considerable part of the gases which are introduced into the total carbon dioxide cycle from gas evolutions from the ocean floors, by volcanoes, and last, but not least, by the breathing of animals and people. It also does not include the carbon dioxide produced from carbonaceous materials that are biodegraded by bacteria and is liberated into the atmosphere from the "biomass."

CATALYTIC SYNTHESIS OF MONOMERS AND POLYMERS

One of the driving forces for the production of plastic products is the production of monomers and polymers, hopefully in quantitative yields without byproducts that have to be disposed of and without solvents that have to be recycled or disposed of.

One example for a monomer synthesis is a potentially important catalytic synthesis of methyl methacrylate from methylacetylene (Eq. 1).



$$\mathrm{HC{\equiv}CCH_3 + CO + CH_3OH \xrightarrow[catalyst]{} CH_2{=}\underset{\substack{|\\ CO\\ |\\ OCH_3}}{C}{-}CH_3}$$

EQUATION 1. Example of a catalytic, high yield monomer synthesis.

With carbon monoxide and methanol, methylacetylene with a palladium coordination catalyst gives methyl methacrylate (MMA) in reportedly high yields [2]. Over

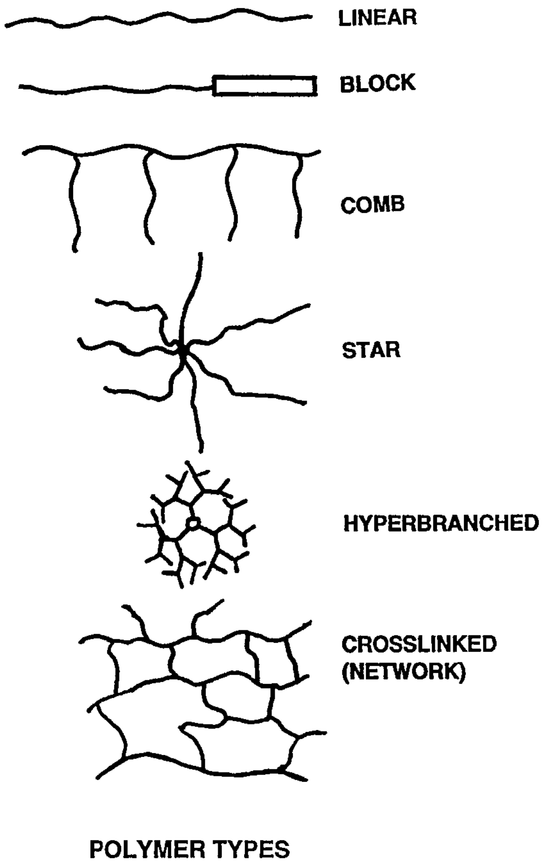


FIG. 1. Polymer types.

the years, MMA synthesis has had and has serious problems. As the demand for MMA increased over the years, the problem of the disposal of the by-products of MMA production, whose last step is the methanolysis of acetonecyanohydrin, has become serious. For each mole of MMA produced, half a mole of ammonium sulfate is produced, tainted with a small but significant amount of cyanide [3].

We also use catalytic processes for the production of some polyolefins, particularly of polypropylene. These initiating systems, also called coordination catalysts, over the years have developed from so-called first to second and then third generation "coordination" catalysts with increasing efficiency and decreasing amounts of transition metal "catalyst" needed. We have been speaking of first, second, and third generation catalytic systems and are now even speaking of fourth generation catalysts [4]. These modern systems allow us to control isotacticity, to produce polymers directly in the gas phase or in liquid monomer at almost 1,000,000 g of polymer per gram equivalent of transition metal initiator, and allow us to leave the catalyst in the polymer (it amounts to about 2 ppm). The polymer has the right bulk density, and the best initiating systems allow us to control copolymerizations of α-olefins [5]. Some of these catalyst systems and the technology of their application also allow us to produce a wide variety of polyolefins of the right bulk density and particle size and shape. It makes polymers based on polypropylene excellent and inexpensive engineering plastics with tailor-made properties.

POLYMER TYPES

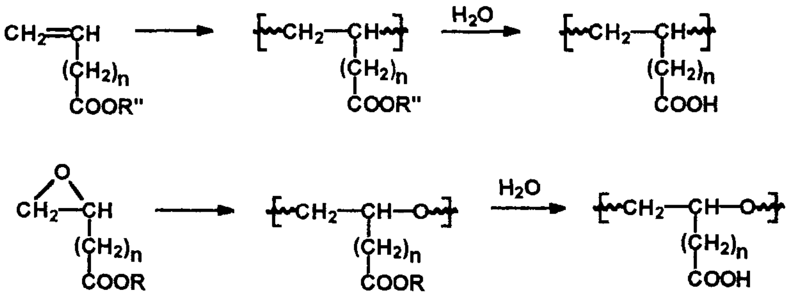
Polymer types that can now be made have increased substantially as we reached a better understanding of polymerization processes. About 40 years ago we could make linear polymers, crosslinked polymers, some copolymers, and some branched polymers. We have learned, especially through living polymerization techniques, to prepare copolymers of well-defined block length; we can make comb polymers and star polymers. These two latter categories have become important as emphasis has developed to produce polymers with different melt flow characteristics (Fig. 1). One of the most recently developed types of polymer are the hyperbranched polymers [6].

SPACER GROUPS IN FUNCTIONAL POLYMER STRUCTURES

For many years we have been interested in the development of techniques to prepare macromolecular structures that were characterized for their well-defined spacer groups as the central focus of their polymer structure. We have always known that when a functional group is attached to the polymer chain, such as the carbomethoxy group in poly(methyl methacrylate), the group behaves differently from the same group if it is not attached to a polymer chain; a good example is the low rate and incompleteness of the hydrolysis of poly(methyl methacrylate) [7]. The polymer chain was correctly blamed for this unusual behavior.

We started to study systematically the behavior of spacer lengths in polymer structures, and we investigated polymeric carboxylates and carboxylic acids based on either a polyethylene or a polyoxyethylene backbone chain [8, 9]. The carboxylic acid derivatives were to be separated from the polymer main chain by flexible spacer groups.

Instead of using the normal course of polymer reaction, we started with the synthesis of appropriate monomers which were then allowed to react with another functional group to form the monomer for polymerization. First, the polymerizability of these monomers was studied as a function of the spacer length, and then the polymers were converted in a postreaction to the final polymer with the desired functional groups. A typical example is the polymerization of epoxy or vinyl esters followed by hydrolysis of polymeric esters to polymeric acids and subsequent postreaction of the final polymeric esters and amides with special properties. Examples are functionalities with mesogenic, nonlinear, electric, and optical properties. This reaction sequence cannot only be done with homopolymers but also with copolymers (Eq. 2).



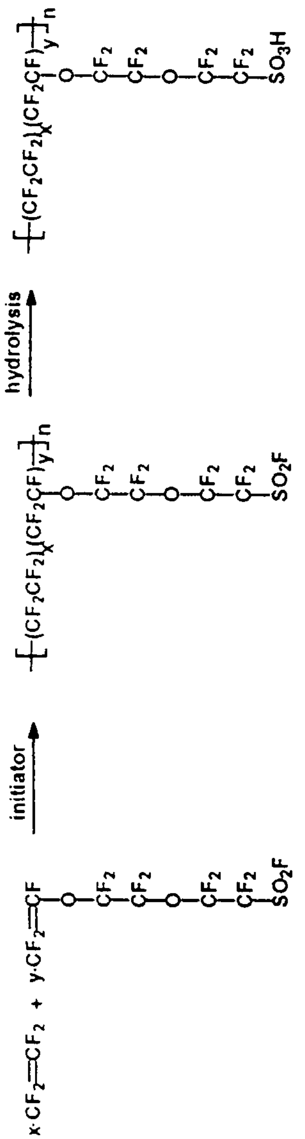
EQUATION 2. Importance of spacer length in the polymerization of functional olefins and oxiranes.

The first important example in which polymer properties are significantly influenced by a spacer group has been known for some years; this fluorocarbon copolymer had a substantial impact in membrane technology. Copolymers of tetrafluoroethylene and a sulfonylfluoride or a carbomethoxy monomer derived from hexafluoropropylene oxide were prepared and hydrolyzed to sulfonic acid (Eq. 3, see page 1334) or to a carboxylic acid functional fluorocarbon resin [10]. These polymers are known as Nafion or Flemion resins and, because of their chemical inertness, are uniquely suited as membranes for chlorine/alkali electrolysis cells.

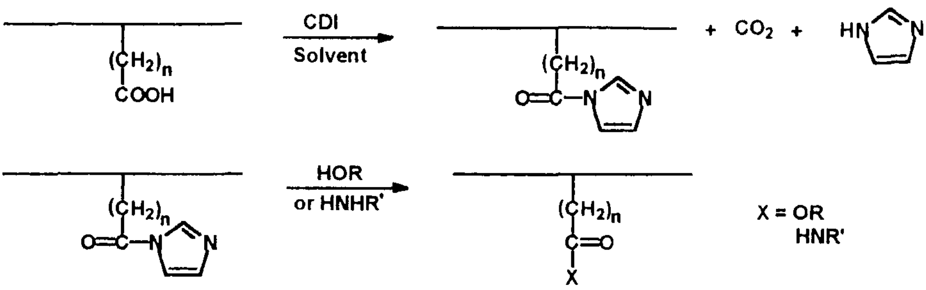
In our own laboratories we were interested in the preparation and polymerization of epoxy esters and olefin esters where the polymerizable group was separated from the functional group by flexible spacer groups [11] (Eq. 2). Methyl ω-epoxyalkanoates could be polymerized directly with aluminum alkyl/water/acetylacetonate systems, modified Furukawa catalysts [12]. The ω-alkenoates could be polymerized with transition metal coordination polymerization systems commonly used for the polymerization of propylene with the proviso that the functional carboxylate group, the 2,6-phenylester, was first complexed on a one-to-one basis with diethylaluminum chloride [13]. Not only could homopolymers be synthesized, but copolymers were also prepared. Once the polymeric esters were made, they could be readily hydrolyzed to the corresponding polymeric acids.

POLYMER REACTIONS

In the last few years we have undertaken an extensive study of the modification of polymeric acids with polyethylene and poly(oxyethylene) backbones and the characterization of the resulting polymers. Instead of the acid chloride method that is often used to transform acids to esters or amides, we have used the imidazolide technique. Carbonyl diimidazole (CDI) was allowed to react at room temperature with polymeric carboxylic acids in tetrahydrofuran (Eq. 4) [14].



EQUATION 3. Synthesis of Nafion.



EQUATION 4. Reaction of polymeric carboxylic acids with carbonyldiimidazole and subsequent reaction of the polymeric imidazolide with phenols and amines.

The imidazolide does not have to be isolated and can be used for subsequent reactions. The carboxylic acid imidazolide, once formed, is very reactive, and can undergo quantitative displacement reactions with phenols and amines to form aromatic esters or amides. With aliphatic alcohols, the reaction is frequently not quantitative, but when the alcohol is transformed into the lithium salt (for example, by reaction with *n*-butyl lithium), the reaction of the alkoxide with the imidazolide is quantitative, or nearly quantitative. We have used these esterifications and amidations to introduce groups with potential mesogenic and nonlinear optical properties, and with optically active groups.

The displacement reaction on polymeric carboxylic acid imidazolide is a facile reaction and does not produce any harmful detrimental by-products, only imidazole. This sequence of reactions allowed us to prepare functional polymers whose glass transition temperature (T_g) is based on the polymer matrix. Polymers with a polyethylene backbone have a T_g of -5°C of the matrix; the T_g of polymers with a poly(oxyethylene) matrix is about -30°C. Polymers with silicone backbones have a T_g of -120°C, and polymers with a methacrylate backbone have a basic T_g of 100°C. Our work on spacer effects in functional polymers was inspired by earlier work on side-chain crystallization of "atactic" polymethacrylates [15] and poly(2,3-dialkylbutylene terephthalate) [16], where 12 methylene units were required, and by the side-chain crystallization of isotactic polyaldehydes [17], where six methylene groups are required to begin to see the onset of side-chain crystallization.

We have introduced a number of mesogenic groups into our poly(10-undecenoates), poly(5-hexenoates), and poly(10,11-epoxyundecanoates) based on phenols and aromatic amines. The imidazolide reactions gave substitution yields of more than 98% in some cases (Eq. 4) [14]. In other cases the degree of substitution was between 70 and 80%. Some fine tuning of the reaction conditions will be needed in the future to achieve 100% substitution.

One interest in the reactivity of functional polymers whose functionality is located at the end of the flexible side chains was the salt formation of carboxylic acid or amino functions on the end of the side chain of a polymer. Copolymers of poly(10,11-epoxyundecanoic acids) were neutralized with sodium hydroxide to an ionomer.

In conventional polyethylene ionomers, about 10–12% carboxylic acid groups are commonly attached to the polymer chain. Such polymers are commercially prepared by radical copolymerization of ethylene and methacrylic or acrylic acid.

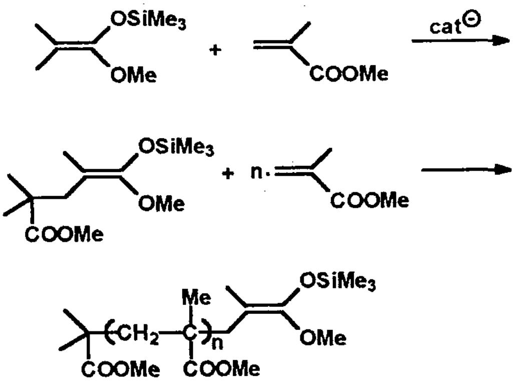
These copolymers are then partially neutralized to the ionomers. This combination gives an optimum effect of ionomer properties through ionic cluster formation which is responsible for these "ionically crosslinked" ionomers [18]. In order to form these clusters, a portion of the polymer backbone chain must be moved.

In polymers with flexible side chains which are terminated with a carboxylic acid group, such as our poly(10-alkenoic acid) or poly(10,11-epoxyalkanoic acid), only 1.5% carboxylic acid groups are needed to see the full effect of polymeric salt formation [19] because only the flexible side chains need to be moved. This can readily be seen in the salt formation of these polymers with polymeric cations, which gives another example where the spacer group separating the functional groups, in this case the carboxylate group, plays an important role.

NEW POLYMERIZATION REACTIONS

Group Transfer Polymerization of Methacrylates

A few years ago a coordinative polymerization technique was developed specifically for methyl methacrylate and other methacrylates. This technique is now known as group transfer polymerization [20] (Eq. 5).



EQUATION 5. Group transfer polymerization.

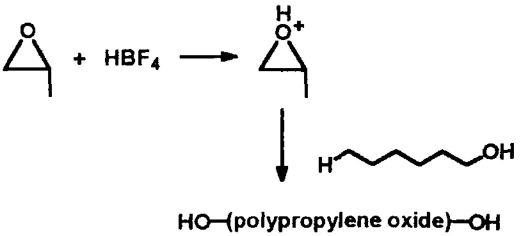
It is a living polymerization which allows the preparation of block copolymers of exact block length and also of methacrylate-based telechelic polymers with end terminal functional groups. With a properly designed initiator molecule such as an ethylene-glycol-modified silyl-protected ketene acetal, and the termination of this polymerization by recombination using xylyldibromide as the bifunctional compound, a dihydroxy-terminated telechelic polymer can be prepared. Commercialization of group transfer polymerization has allowed this methacrylate polymerization technology to be applied to several areas where acrylic polymers are used and opened opportunities for new applications.

Group transfer polymerization can also be used for the polymerization of such reactive methacrylates as glycidyl methacrylates, and, since it is a living polymerization, also allows the synthesis of block copolymers of controlled block length. By the proper handling of the polymer termination reaction using bifunctional monomers such as ethylene dimethacrylate, star polymers have been prepared [22]. Polymers can also be prepared that are of the size of microgels. Highly branched and star polymers influence significantly the rheological properties of polymer systems. Even though the molecular weights of the systems are maintained, the entanglement possibilities of the polymers are greatly decreased, leading to a significantly lower melt or solution viscosity of the polymers.

New developments in radical polymerization of methyl methacrylate using cobalt porphyrins [21] as chain length controlling radical chain transfer agents has allowed the preparation of new macromonomers based on methyl methacrylate. Using the macromonomers as comonomers provided a new dimension for the design and the tailor-making of numerous combinations of acrylic comb copolymers with new and unique properties.

Activated Monomers

Another new aspect of ring-opening polymerization has led to the synthesis of new macromonomers. Polymerization of epoxides such as propylene oxide or epichlorohydrin in the presence of glycols leads to hydroxy-terminated polyethers (Eq. 6).



EQUATION 6. Polymerization of oxiranes by “activated monomer” mechanism.

This technique utilizes the presence of *activated species*, protonated epoxides, as the actual monomers [23]. By proper termination, macromonomers can by synthesized directly.

Hyperbranched Polymers

Since the beginning of polymer science it has been known that, in condensation polymerization, high molecular linear polymers can be made by using bifunctional monomers with a functionality of exactly 2. When small amounts of compounds with a functionality of 1 were added, the molecular weight decreased by chain termination, and when materials with a higher functionality than 3 were added, crosslinking occurred.

About 10 years ago it was recognized that for a trifunctional monomer where two of the functional groups were of the same functionality and the third group was of a different functionality but capable of reacting with the first group in a polymer-forming reaction, branching would occur at every monomer addition [24]. This interesting concept of new polymer design is now known as hyperbranched polymers (Fig. 2). Examples of such trifunctional structures used to form hyperbranched polyamides are monomers with two amino groups and one carboxylic acid function.

In polymerizations that lead to hyperbranched polymers, branching occurs in each step [25, 26]. The ultimate result of such polymerizations is a spherical structure that ideally looks like an onion and may have as many as 7 or 8 layers or generations of monomer additions. At this point, steric hindrance becomes overwhelming and no further reaction can occur. If some flexible groups are introduced into the structure of the monomer between the reactive groups, the number of generations may be increased. Using this technique, it has become possible to synthesize spherical macromolecules with a surface of amino groups or with a surface of carboxylic acid groups, depending on the structure of the original monomer molecule.

Scientists have also found ways not only to prepare spheric macromolecules but also to synthesize half spheres or sectors [26]. The shapes of the molecules can be designed and their synthesis controlled by the appropriate initiation mechanisms and the groups that are used to initiate the formation of these hyperbranched networks. The synthesis strategy for the half spheres is different and starts from the outside.

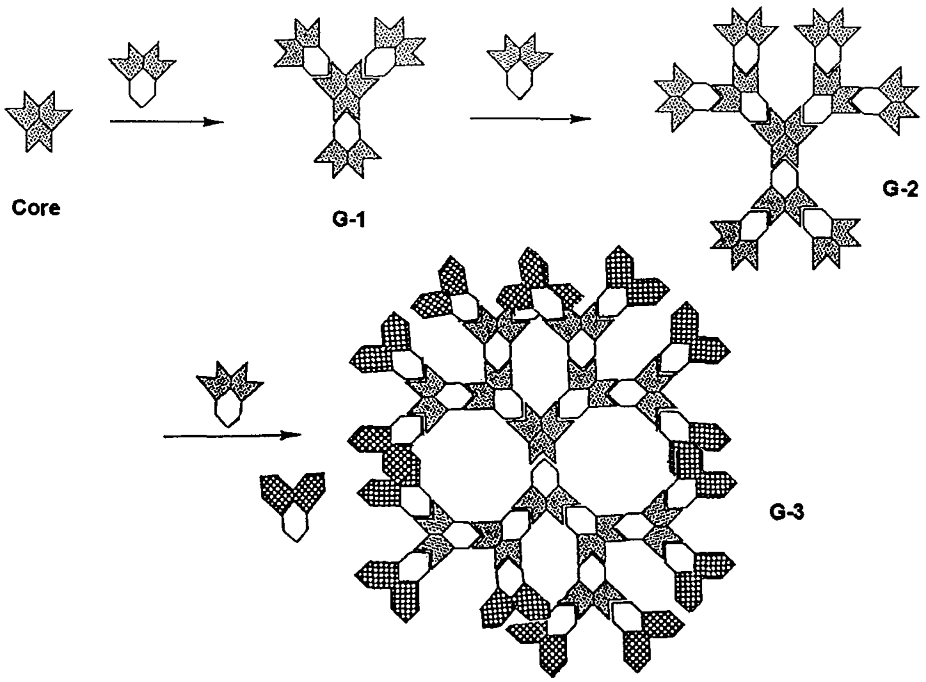


FIG. 2. Hyperbranched polymers.

The ultimate in hyperbranched networks are structures that have a high surface area and have very rigid structures [27]. Starting with the dilithium compounds of benzene or biphenyl and allowing them to react with a multiphenol, networks have been synthesized that have highly branched rigid rod substructures. Polymers have been made that have structures like zeolite with large internal surface areas approaching 1000 m^2/g. Such surface areas are in the order of the most active inorganic catalysts. The materials are very rigid because they are substantially if not completely aromatic [28].

ADVANCED COMPOSITES

End-reactive Oligomers

Composites are called advanced composites when the technology of high modulus fibers, such as carbon fibers and Kevlar, are used in combination with high performance matrix materials of "end reactive" low molecular weight oligomers. The end-reactive oligomers are ultimately cured to the advanced composites [29] (Fig. 3). The most commonly used end groups for the formation of these composites are maleimide, benzocyclobutene [30], and acetylene groups.

Low oligomers used with these end groups are polyether ketones, polyether sulfones, polyimides, and polyether imides (Fig. 3). Sometimes it is advantageous to use linear oligomers that have different end groups, but end groups that can readily react with each other. Higher polymers of the above-mentioned structures, even at relatively low molecular weights, are quite viscous and do not wet properly the fiber surfaces and crevasses. When composites are made with higher molecular weight polymers, the maximal properties of the composites are not always reached because it is difficult to obtain completely void-free pieces.

What we are seeing in advanced composites technology is really an extension of epoxy technology to higher use temperature polymers. Epoxy resins with all

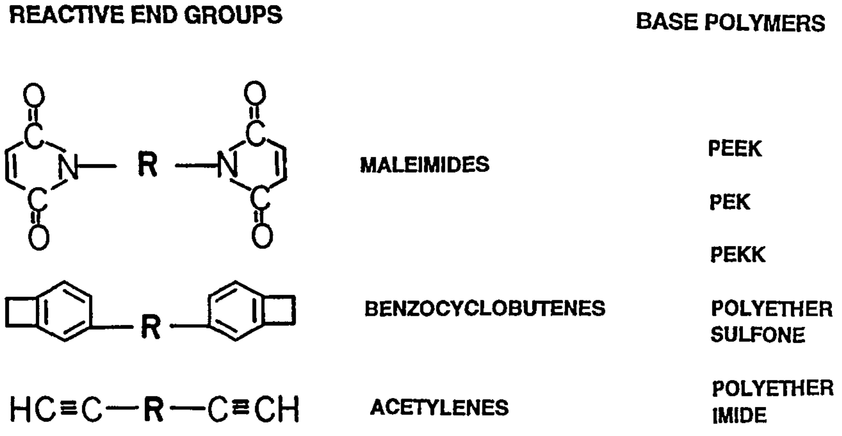


FIG. 3. End reactive oligomers for high temperature applications.

their improvements and optimization can be used up to about 300°C. Above this temperature, limitations of thermal stability and flame resistance require the use of completely aromatic systems. Water absorption is another limiting characteristic of epoxy resins. The high cost of these polymers is a negative point for the use of advanced composites. The market at this time is not too large for these composites; it is about 2000 tons worldwide for maleimides, a small but important market.

Giant Rings as Monomers

Another way of synthesizing high molecular and high performance polymers from low viscosity materials is by ring-opening polymerization of giant rings. Technology has recently been developed for the synthesis, purification, and subsequent ring-opening polymerization of such large rings [31] (Fig. 4). The application of this technique for advanced composites would in principle be the same as the technique for the application of end-group reactive oligomers. Instead of the curing of the end-terminated oligomers, the composites from giant rings are formed by ring-opening polymerization. As in the previous case, the giant ring compounds have to be prepared, the fibers for the reinforcement impregnated, and then the ring-opening polymerization must be carried in the final step to form the desired product. The optimum temperature range for the ring-opening polymerization of giant rings is between 180 and 200°C. The formation of polycarbonate from the giant ring carbonate, for example, Bisphenol A, is the best studied example. At this temperature the viscosity of the melts of the cyclic monomers is about 10^3 poises lower than the corresponding melt viscosity of the desired high molecular polymer.

Substantial work has been done and continues to be done on polycarbonates and polycarbonate copolymers, but the field of aromatic polyesters is also of inter-

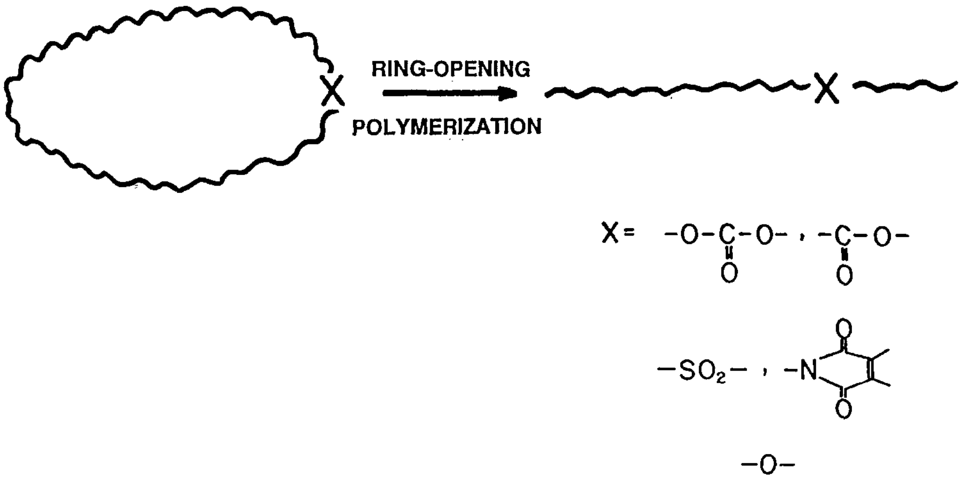


FIG. 4. Megacycles and their polymerization.

est. Frequently it is desired to utilize giant ring systems that do not produce linear structures but have kinks, such as in isophthalic (rather than terephthalic) acid and Bisphenol A. Mixtures of giant rings of various ring sizes were also found desirable to keep the melting temperatures of these monomer mixtures low enough and in a manageable range. For giant rings of isophthalic acid and Bisphenol A the ring size range is usually from 2 to 10, but for the cyclic carbonates made from Bisphenol A bischloroformates or similar bischloroformates it is more like 20 to 30.

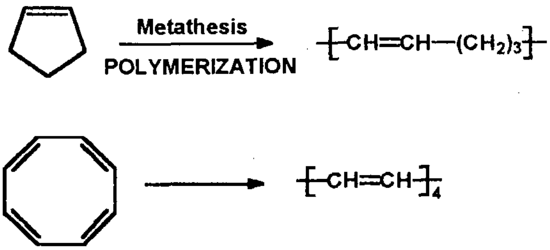
Metathesis Polymerization

Novel and interesting aspects of metathesis polymerization have developed over the last 3 or 4 years. Since it was found that the metathesis reaction, the ring-opening polymerization of cyclic olefins, actually proceeds through a carbene propagation mechanism and even the initiation is based on carbenes as intermediates, it became possible to design effective carbene-transition metal compounds as initiators. The work on metathesis has resulted in at least one commercial product, the metathesis polymer of dicyclopentadiene [32]. Some of these newer catalyst systems for metathesis reactions are relatively insensitive to polar substituents in the monomer, and even norbornene dicarboxylate can be polymerized.

EXOTIC MONOMERS AND POLYMERS

Polyacetylenes by Metathesis Polymerization

Metathesis polymerization can also be carried out with cyclooctatetraene. The demonstration of this polymerization is very dramatic (Eq. 7).



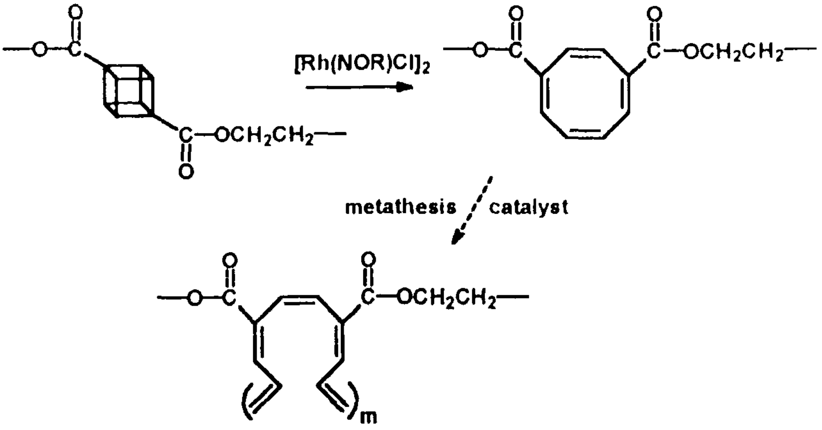
EQUATION 7. Metathesis polymerization of cyclopentene and cycloocatetraene.

When the polymerization is carried out between glass plates, the color of the liquid is first pale orange, the color of cyclooctatetraene; the liquid soon solidifies and changes color to solid *cis*-polyacetylene and finally changes to the bluish-metallic color of *trans*-polyacetylene. Normally polyacetylene is easily synthesized from acetylene and tetrabutyl titanate, but the fabrication of polyacetylene to the proper shape is very complicated. Metathesis polymerization of cyclooctatetraene seems to provide a direct polymerization technique to polyacetylene in its desired form.

We have taken the synthesis of polyacetylene from cyclooctatetraene [33] as one example for the synthesis of a most desirable polymer in fabricated form from a properly designed monomer with a simple polymerization technique. There is another potential way to make polyacetylenes by synthesizing in situ various cyclooctatetraene derivatives.

Cubanes

Cubane, C_8H_8, is a symmetrical and a highly strained organic compound that was first synthesized in the 1960s. For the synthesis of cubane itself the last step is the decarboxylation of cubane dicarboxylic acid. It has now been found that cubane dicarboxylic acid can be transformed into a polyester or into a polyamide (Eq. 8).



EQUATION 8. Cubane derivatives as polymer intermediates.

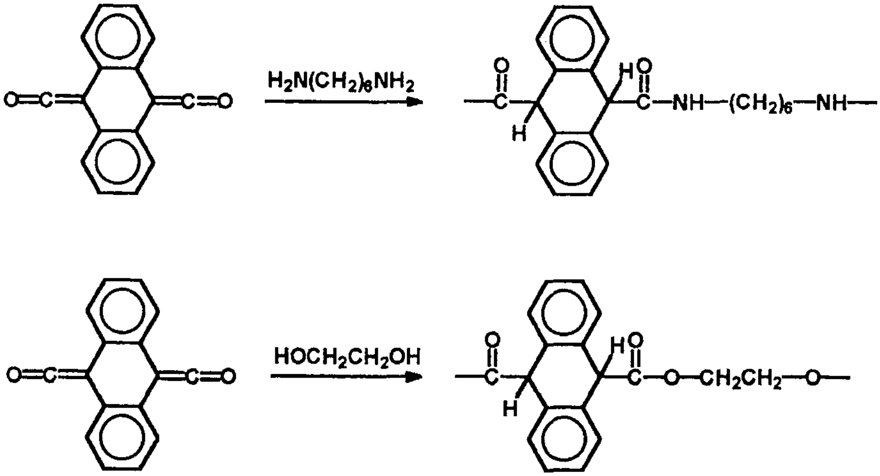
Cubane dicarboxylic acid can also be transformed into cubane diisocyanate which, in turn, can be used to form polyurethanes [34]. When cubane-containing polymers are treated with the appropriate rhodium catalyst, the cubane structure rearranges quite readily into a cyclooctatetraene structure. A metathesis catalyst could now polymerize, as indicated earlier, the cyclooctatetraene structures into polyacetylene structures within the polymer matrix.

These examples demonstrate that it seems possible to transform polymers with highly energetic structural units within the polymer into highly desirable final products that are not readily fabricated. We should also mention that a similar principle was used for multicyclic compounds that were polymerized with an expansion of volume.

Diketenes

Another example of novel polymerization reactions which was of direct interest to us was the family of diketenes as polymer intermediates. They could be considered as desirable substitutes for diisocyanates for the synthesis of polyesters rather than polyurethanes [35]. One of the problems of polyurethanes is that they have limited thermal stability. Even below 200°C they revert back to the diisocyanate and glycol components. For this reason polyurethanes have a limited application range at higher temperatures.

We have investigated the use of diketenes as polymer intermediates, and we selected for our study anthracene diketene [35] (Eq. 9).



EQUATION 9. Diketenes as polymer intermediates.

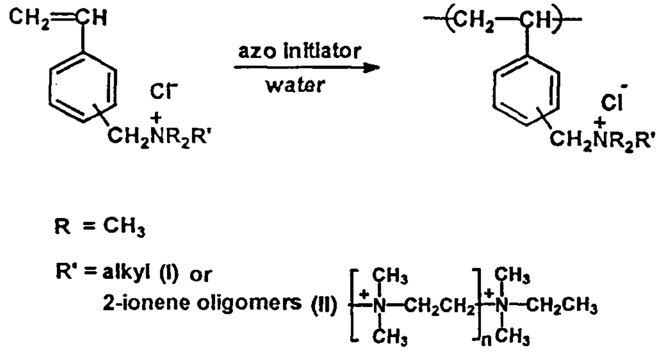
This compound, a ketene doubly substituted with aromatic rings, is thermally stable up to 100°C, at which temperature it forms a polymer obtained by a "polymeric dimerization" reaction of the ketene groups. Even in its polymeric form the structure could still be utilized because at temperatures in excess of 220°C the dimer is reversible to the monomer.

Anthracene diketene was polymerized with glycols to polyesters and with diamines to polyamides. With glycols that are normally used for the preparation of polyurethanes (polyester or polyether glycols), anthracene diketene gave polyesters with properties similar to those of polyurethanes, but as polyesters they have thermal stabilities in excess of 300°C. Polymer chain extension techniques for hydroxy-terminated polyesters, as well as other applications known for polyurethane technology, could, in principle, also be performed with our anthracene diketene.

POLYELECTROLYTES

Cationic polyelectrolytes have been known for a long time and have been described extensively. Many cationic polyelectrolytes are based on styrene derivatives and on crosslinked styrene resins. Rather than synthesizing the cationic monomers and then polymerizing them, it has become the tradition to perform a chloromethylation on crosslinked polystyrene resins and then to allow the resins to react with secondary or tertiary amines.

We were interested in the synthesis and utilization of highly hydrophilic cationic polymers with a highly available charge concentration, and we have synthesized a number of trialkylmethylstyrylammonium salts (I) made from chloromethylstyrene and trialkylamines with various lengths of the alkyl side chain [36]. We polymerized these monomers in 20–30% water solutions for monomers with short alkyl groups or in methanol for monomers with longer alkyl groups. We have also synthesized copolymers and lightly crosslinked polymers. We also synthesized short tertiary-amine-terminated 2-ionene oligomers (II), attached them to the end of the methylstyryl group, and polymerized them to polystyrenes terminated with oligomeric 2-ionene units (Eq. 10).

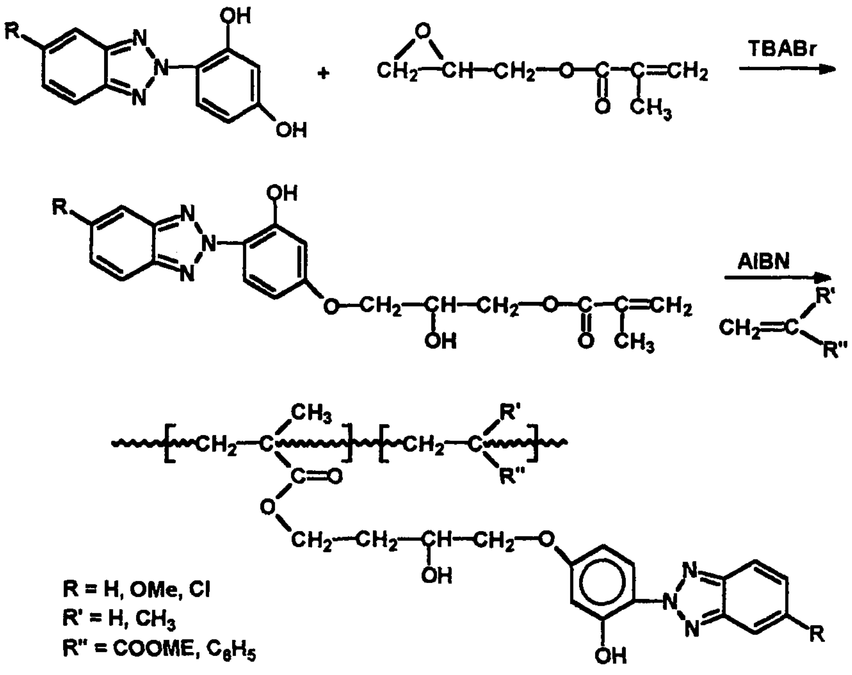


EQUATION 10. Polymeric cations based on styrene derivatives.

POLYMER-BOUND STABILIZERS AND NOVEL ULTRAVIOLET STABILIZERS

For many years we have been interested in the synthesis, characterization, and utilization of polymerizable and polymer-bound ultraviolet stabilizers. We have concentrated for the last 10 years on derivatives of 2(2-hydroxyphenyl)2*H*-benzotriazoles, and we have placed both polymerizable substituents and also substituents which could influence the UV characteristics of the basic structure all around the 2(2-hydroxyphenyl)2*H*-benzotriazole moiety [37] (Fig. 5). The characteristic main absorption of these structures is the 340 nm band, the hydrogen-bonded band which is the determining factor of the capability of these compounds to act as effective UV stabilizers.

A number of polymerizable UV stabilizers have been synthesized. One of the most important examples is 2(2,4-dihydroxyphenyl)2*H*-benzotriazole and its family of compounds. The 4-hydroxy group can easily be esterified with (meth)acrylic acid derivatives [38] or, better, allowed to react with glycidyl methacrylate [39]. The latter reaction product gives a more hydrolytically stable aliphatic acrylic ester (Eq. 11).



EQUATION 11. 2(2-Hydroxyphenyl)2*H*-benzotriazole glycidyl methacrylates and their polymerization.

These new monomers can then be polymerized with monomers such as styrene or acrylic monomers to introduce permanently the UV absorbing group into the polymer chain. The use of glycidyl-methacrylate-type monomers has been used for polymerizable UV absorbers for interocular and soft lense applications [15, 40, 41]. In this case the specific UV characteristic was that of the 4′-chloro-substituted 2(2-hydroxyphenyl)2*H*-benzotriazole moiety, 2[2-hydroxy-4-(2′-hydroxypropylethermethacryloxy)]2*H*-4′-chlorobenzotriazole. It has an absorptivity of about 80% at 400 nm and does not significantly decrease the water absorption of typical soft lenses [41] even at higher concentrations of incorporation.

One polymerizable group that is readily introduced into 2(2-hydroxyphenyl)2*H*-benzotriazoles is (meth)acrylamidomethyl [40]. *N*-Methylol(meth)acrylamide reacts with 2(2-hydroxyphenyl)2*H*-benzotriazole that has an open (unsubstituted) alpha position in an essentially quantitative fashion to form (meth)acrylamidomethyl derivatives. We have carried out this reaction successfully with 2(2-hydroxy-5-methyl-phenyl)2*H*-benzotriazole and with 2[2-hydroxy-5-(3′-carboxypropionato)-phenyl]2*H* -benzotriazole and have obtained the corresponding polymerizable UV stabilizer monomers.

(Meth)acrylamido is one family of polymerizable groups that has been successfully introduced into UV stabilizers. Another group has recently been introduced, the polymerizable maleimido group [42]. *N*-Methylolmaleimide, different from *N*-methylol(meth)acrylamide normally available in aqueous solutions, is a crystalline

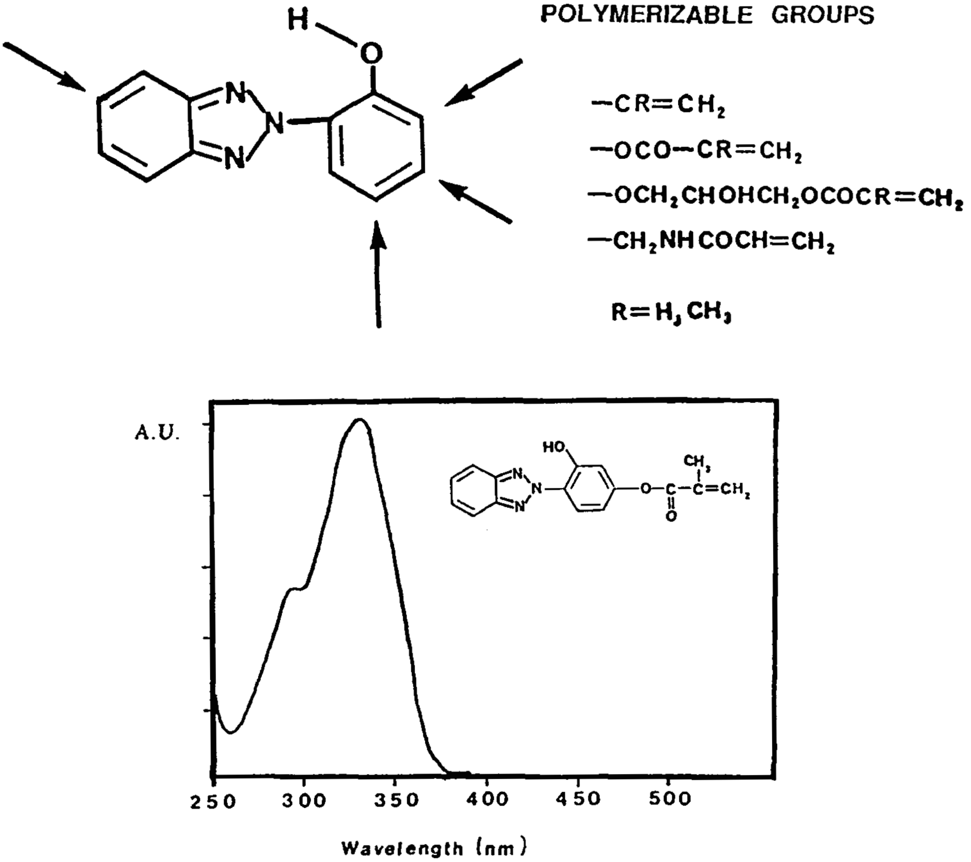
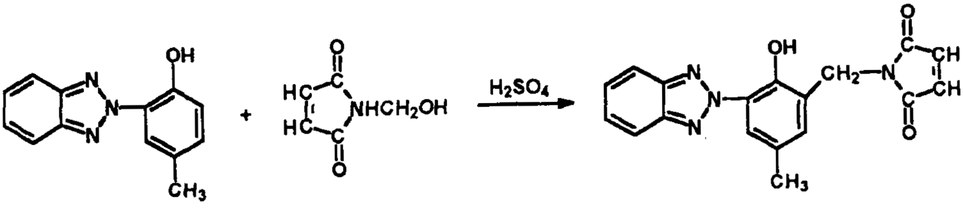


FIG. 5. Effective ultraviolet stabilizers: 2-(2-Hydroxyphenyl)2*H*-benzotriazole derivatives.

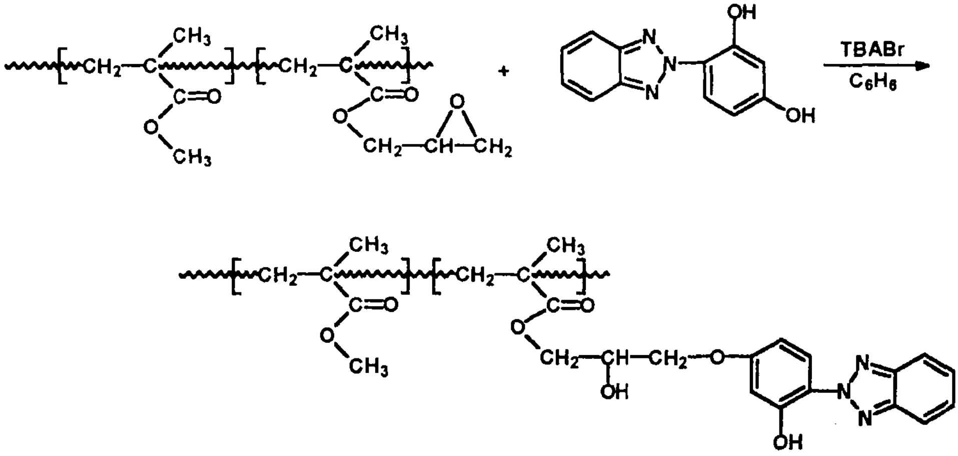
compound that can readily be isolated; mp 103°C. It reacts with compounds such as 2(2-hydroxy-5-methyl-phenyl)2*H*-benzotriazole quantitatively and gives the corresponding maleimidomethyl compound in essentially quantitative yield and of high purity (Eq. 12).



EQUATION 12. 2(2-Hydroxyphenyl)2*H*-benzotriazole methyl maleimides.

The compound is easily copolymerized with common monomers like styrene and methyl methacrylate. It is also readily incorporated into polymerization systems that produce ABS resins. In spite of free but hydrogen-bonded hydroxy groups, it is incorporated readily in these polymers. As a consequence, we were able to prepare for the first time a UV stable ABS resin.

Another technique of introducing UV stabilizing groups is by transesterification of a 2(2-hydroxyphenyl)2*H*-benzotriazole derivative with an alcoholic hydroxy group with an already prepared acrylic polymer. By reacting such molecules as 2[2-hydroxy-5-(2′-hydroxyethyl{or 3′-hydroxypropyl})phenyl]2*H*-benzotriazole with the 2-hydroxyethyl or 3-hydroxypropyl group of 2(2,4-dihydroxyphenyl)2*H*-benzotriazole with the nonhydrogen-bonded 4-hydroxy group, the UV stabilizer can be incorporated into methyl methacrylate polymers. Substitution reactions could also be carried out by reacting the hydroxy groups with the glycidyl groups of glycidyl methacrylate/acrylate copolymers [43] (Eq. 13).



EQUATION 13. Reaction of 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives with copolymers of glycidyl methacrylate.

Up to now we have discussed the incorporation of UV stabilizers into polymers by blending low molecular UV stabilizers (with all its ramifications), compatibilizing groups for specific polymer structures, increasing the molecular weight to reduce volatility, and finally incorporating polymerizable UV stabilizers by copolymerization, grafting, or attaching reactive low molecular UV stabilizers by polymer reactions or even by blending polymeric UV stabilizer "concentrates" into the polymer systems.

Surface Grafting of UV Stabilizers

In principle, UV stabilizers are most needed on the polymer surface. One possibility is surface grafting; another is the design of systems where the surface morphology can be controlled (Fig. 6).

We have accomplished photo-surface grafting of polymerizable UV stabilizers, such as 2[2-hydroxy-5-vinyl(or 5-isopropenyl)phenyl]2*H*-benzotriazole, onto the surface of polyethylene or polypropylene films [44] (Fig. 7). This work was

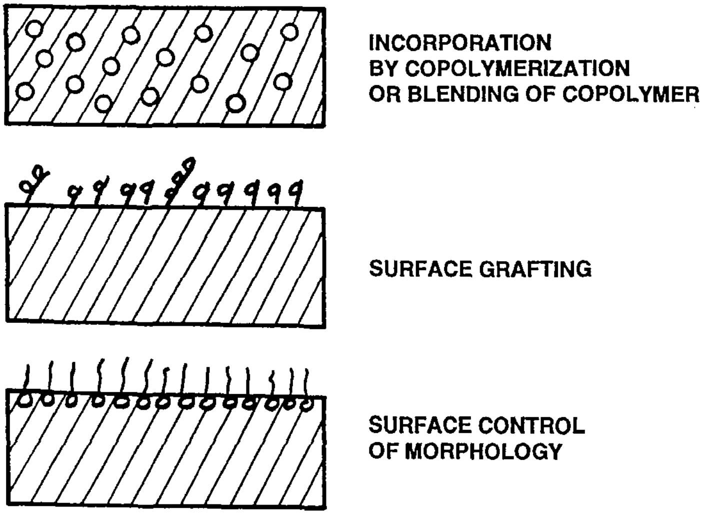


FIG. 6. Incorporation of stabilizers into polymer matrices.

achieved by using polymerizable UV stabilizers and attaching them by photografting onto the surface of the polymers. The photografting could be accomplished in 1-2 minutes. The photosensitizer necessary to graft the photostabilizer has to have its absorption maximum at the wavelength where the polymerizable UV stabilizer has its minimum. After photografting, the surface of the polymer film is covered with grafted photostabilizer. We do not know whether only one molecule of the polymerizable UV stabilizer or short chains of the UV stabilizer homopolymer are grafted onto the surface. The UV stabilizer can readily be observed by the UV spectrum or by ESCA measurements.

Surface Stratification for Most Efficient UV Stabilization

Another technique for placing a UV stabilizer on the surface of a polymer is by what we call "surface-active morphology." First, a polymerizable UV stabilizer is designed that has in its structure not only a UV stabilizing group but also a polymer-

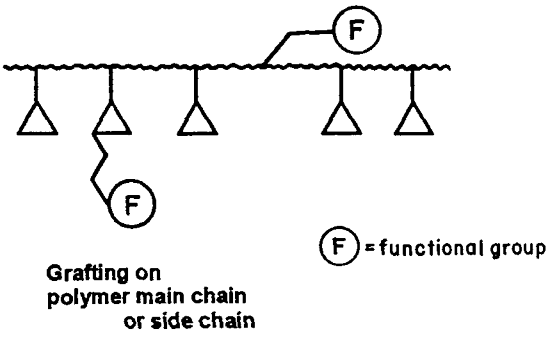


FIG. 7. Grafting on polymers.

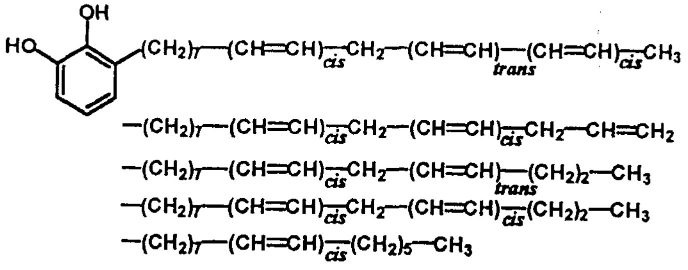
izable group as well as a group that can carry this structural arrangement to the polymer surface [45] (Fig. 6). Our specific approach was as follows: 2[2-hydroxy-5-(3′-carboxyethyl)-phenyl]2*H*-benzotriazole was esterified with an alcohol which has a fluorocarbon chain of about 12 carbon atoms, or which has a silicon group attached. We have also synthesized an ester with a C_{18} hydrocarbon chain (Eq. 14, see page 1350). These compounds were then treated with *N*-methylol(meth)-acrylamide or *N*-methylolmaleimide which introduces the (meth)acrylamidomethyl or the maleimidomethyl group into the 3-position of the phenyl ring, or in the position alpha to the phenolic hydroxy group.

The monomers were then copolymerized with methyl methacrylate, which results in the incorporation of the monomers into the polymer chain. The copolymer with the fluorocarbon monomer and the polymer was deposited from a solvent, as it would be for normal coatings application. The monomer units with the fluorocarbon side group agglomerated on the surface and provided a "monomolecular" fluorocarbon layer on the surface. The fluorocarbon surface layer could be detected by ESCA and wetting angle measurements. By necessity, the UV stabilizing moiety of the molecule would then be placed below the surface fluorocarbon layer.

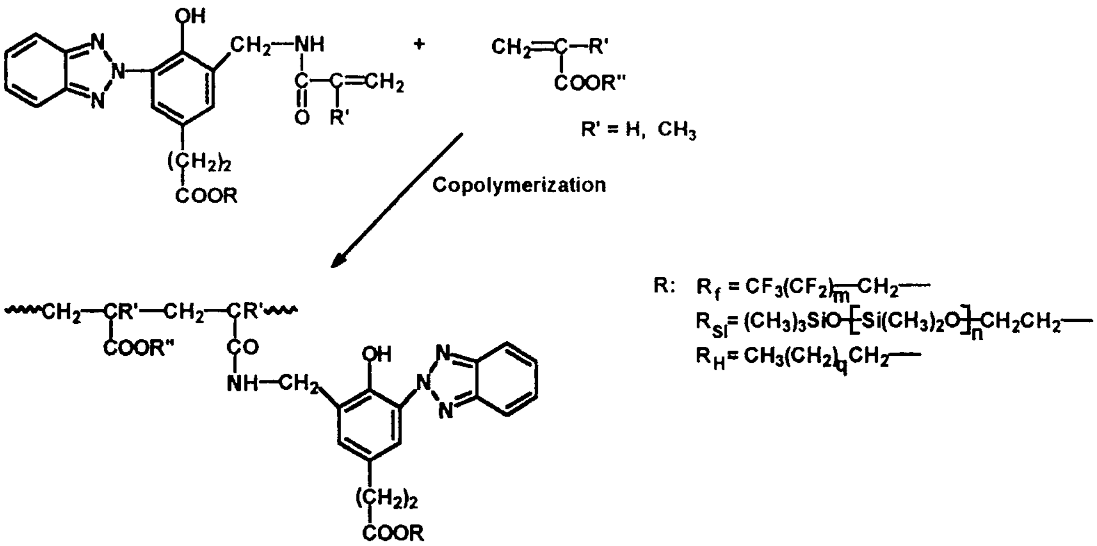
We believe we have fulfilled in principle the requirement for the stratification of the various functions of the polymer structure. We do not as yet have polymerizable UV stabilizers with surface-active groups that have a flexible spacer group between the polymerizable group and the phenyl group of the stabilizer monomer. We believe that a stabilizer molecule of this structure would fulfill the individual functions of the tailor-made stabilizer molecule and perform at the optimum level.

ORIENTAL LACQUERS

The "varnish tree" *Toxicodendron vernicifluum*, also called *Rhus verniciflua*, is the common source for Japanese lacquer. The sap of lacquer trees is collected like the sap of the rubber tree; it is a water/oil emulsion whose "oily" portion consists of about 60–65% urushiol and of about 20–25% water. The remaining 10% is water-soluble plant gums, mono-, oligo-, and polysaccharides, and small amounts of enzymes. Urushiol is a mixture of catechol derivatives substituted in the 3-position with unsaturated and saturated hydrocarbon chains (Scheme 1). The qual-



SCHEME 1. Composition of the urushi fraction of the sap of *Rhus verniciflua* (oriental lacquer).



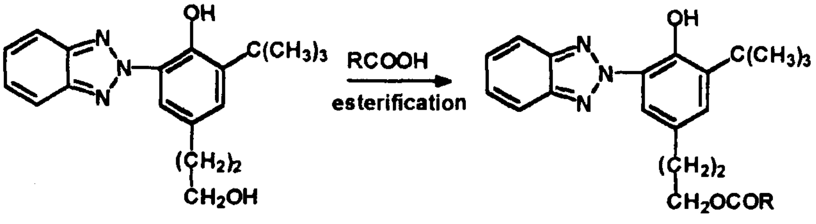
EQUATION 14. Surface-active 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives.

ity of a given raw urushi depends mainly on the amount of the urushi triene component and on the amount and activity of the oxidation enzyme laccase.

We have investigated a number of samples of the urushi fraction of Japanese lacquers, obtained from the Tsutsumi Asakishi Urushi Co., Kyoto, Japan, by a combination of modern analytical techniques, and we have identified and clearly characterized most components (Scheme 1) [46, 47].

UV Stabilization of Oriental Lacquers

Oriental lacquers are notorious for their relatively poor photooxidative stability, which limits their outdoor use. We attempted to make ultraviolet stabilizers for oriental lacquers and have synthesized stearic, oleic, linoleic, and linolenic acid esters of 2[2-hydroxy-3-*tert*-butyl-5(3′-hydroxypropyl)phenyl]2*H*-benzotriazole (Eq. 15) [48].



$R = (CH_2)_{16}—CH_3$
$(CH_2)_7CH{=}CH(CH_2)_7CH_3$
$(CH_2)_7CH{=}CH—CH_2—CH{=}CH(CH_2)_4CH_3$
$(CH_2)_7(CH{=}CH—CH_2)_3CH_3$

EQUATION 15. Ultraviolet stabilizers for oriental lacquers.

The unsaturated esters, especially the linolenic ester, could be readily incorporated into urushiol or drying oil compositions and "co-cured" into UV-stabilized oriental lacquer films or prepared co-cured films from drying oils.

ACKNOWLEDGMENTS

The work reported in this paper was supported by the Mark Chair of the Polytechnic University. We are grateful to A. Sustic and L. Kiliman for their contributions to this work.

REFERENCES

[1] H. Inoue and O. Vogl, *Kagaku To Kogyo*, *55*(2), 40 (1981).
[2] E. Drent, European Patent Appl. 271,144 (1988); *Chem. Abstr.*, *110*, 232 239c (1989).
[3] B. J. Kine and R. W. Nowak, in *Concise Encyclopedia of Polymer Science and Engineering* (J. I. Kroschwitz, Ed.), Wiley, New York, 1990, p. 16.

[4] P. C. Barbe, G. Cecchin, and G. L. Noristi, *Adv. Polym. Sci.*, *81*, 1 (1987).

[5] P. Galli and J. C. Haylock, *Prog. Polym. Sci.*, *16*, 443 (1991).

[6] D. A. Tomalia, A. M. Naylor, and W. A. Goddard, *Angew. Chem.*, *Int. Ed. Engl.*, *29*, 138 (1990).

[7] G. Smets and A. M. Hesbian, *J. Polym. Sci.*, *40*, 217 (1959).

[8] A. R. Padwa, *Prog. Polym. Sci.*, *14*, 811 (1989).

[9] J. Muggee, Ph.D. Dissertation, University of Massachusetts, Amherst, Massachusetts, 1982.

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

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

[12] D. A. Bansleben, M. Herman, and O. Vogl, *J. Polym. Sci.*, *Polym. Chem. Ed.*, *22*, 2489 (1984).

[13] M. D. Purgett and O. Vogl, *Ibid.*, *26*, 677 (1988).

[14] L. Kiliman, Ph.D. Dissertation, Polytechnic University, Brooklyn, New York, 1993.

[15] N. A. Plate and V. P. Shibaev, *J. Polym. Sci.*, *Macromol. Rev.*, *8*, 117 (1974).

[16] Z. Florianczyk, B. Deopura, R. S. Stein, and O. Vogl, *J. Polym. Sci.*, *Polym. Chem. Ed.*, *20*, 1051 (1982).

[17] I. Negulescu and O. Vogl, *Ibid.*, *14*, 2995 (1976).

[18] C. W. Lantman, W. J. MacKnight, and R. D. Lundberg, in *Comprehensive Polymer Science*, Vol. 2, (G. Allen and J. C. Bevington, Eds.), Pergamon Press, Oxford, 1989, p. 755.

[19] J. Koetz, K. J. Linow, B. Philipp, L. P. Hu, and O. Vogl, *Polymer*, *27*, 1574 (1986).

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

[21] G. F. Meijs and E. Rizzardo, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.*, *C30*(3&4), 359 (1990); A. H. Janowicz, US Patent 4,694,054 (1986).

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

[23] K. Brzezinska, R. Szymanski, P. Kubisa, and S. Penczek, *Makromol. Chem.*, *Rapid Commun.*, *7*, 1 (1986).

[24] D. A. Tomalia, D. H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, and P. Smith, *Polym. J.*, *17*, 117 (1985).

[25] Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, *112*, 4592 (1990).

[26] Y. H. Kim, *Ibid.*, *114*, 4947 (1992).

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

[28] Y. H. Kim and O. W. Webster, *Macromolecules*, *25*, 5563 (1992).

[29] C. E. Sroog, *Prog. Polym. Sci.*, *16*, 680 (1991).

[30] R. A. Kirchhoff and K. J. Bruza, *Ibid.*, *18*, 85 (1993).

[31] D. J. Brunelle, E. P. Boden, and T. G. Shannon, *J. Am. Chem. Soc.*, *112*, 2399 (1990).

[32] R. P. Geer and R. D. Stoutland, *Plastics 85, Proceedings of the SPE 43rd Annual Technical Conference, ANTEC '85*, 1985, p. 1232.

[33] F. L. Klavetter and R. H. Grubbs, *Polym. Prepr., ACS Div. Polym. Chem.*, *28*(2), 425 (1987).

[34] P. Eaton, *Pac. Polym. Prepr.*, *1*, 419 (1989).

[35] P. Zarras and O. Vogl, *Prog. Polym. Sci.*, *16*, 173 (1991).

[36] P. Zarras and P. Vogl, *Polym. Prepr., ACS Div. Polym. Chem.*, *34*(2), 424 (1993).

[37] S. K. Fu, A. Gupta, A. C. Albertsson, and O. Vogl, in *New Trends in the Photochemistry of Polymers* (N. S. Allen and J. F. Rabek, Eds.), Elsevier Applied Science, London, 1985, p. 247.

[38] S. J. Li, A. Gupta, A. C. Albertsson, and O. Vogl, *Monatsh. Chem.*, *115*, 853 (1984).

[39] A. Sustic, C. J. Zhang, and O. Vogl, *J. Macromol. Sci.—Pure Appl. Chem.*, *A30*, 741 (1993).

[40] A. Sustic. Ph.D. Dissertation, Polytechnic University, Brooklyn, New York, 1990.

[41] J. J. Falcetta, J. Park, and C. G. Smith, European Patent Appl. EP 343,996 (1991).

[42] J. Bartus and O. Vogl, Unpublished Results.

[43] A. Sustic, C. L. Zhang, and O. Vogl, *Polym. Prepr., ACS Div. Polym. Chem.*, *28*, 226 (1987).

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

[45] O. Vogl, G. D. Jaycox, and K. Hatada, *J. Macromol. Sci.—Chem.*, *A27*, 1812 (1990).

[46] O. Vogl and J. Bartus, *Polym. Prepr., ACS Div. Polym. Chem.*, *14*(1), 582 (1993).

[47] J. Bartus, W. J. Simonsick Jr., C. Garner, T. Nishiura, T. Kitayama, K. Hatada, and O. Vogl, *Polym. J.*, *26*(1), 67 (1994).

[48] O. Vogl and J. Bartus, *Polym. Prepr., ASC Div. Polym. Chem.*, *14*(1), 584 (1993).