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New Polymer Structures

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ABSTRACT

A number of new polymers have been studied. They include polymers obtained by chain reaction polymerization of olefins and epoxides with functional groups where the polymerizable group was separated from the functional group by an inert spacer group, the preparation of head-to-head polymers, and the preparation of optically active polymers based on the macromolecular asymmetry.

FUNCTIONAL POLYMERS FROM EPOXIDES AND OLEFINS

Polymers with a polyethylene or polyoxyethylene backbone chain and functional groups directly attached to the polymer chain have been known for a long time [1-3]. Acrylates or methacrylates have a carboxylate group attached to the polymer backbone chain. In poly(vinyl alcohol), a hydroxyl group is attached to the polyethylene backbone chain. Its derivatives, particularly poly(vinyl acetate) and poly(vinyl butyral) [4], have achieved commercial importance. Polystyrene derivatives have been made by reactions on preformed polystyrene or by polymerization of derivatives of polystyrene, for example poly(styrenesulfonic acid) [5] and poly(chloromethylstyrene) [6]. Their reaction

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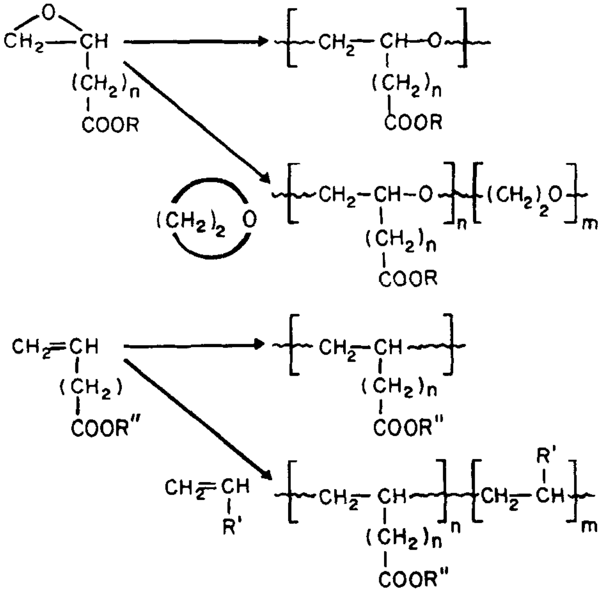
products with secondary and tertiary amines have reached importance as ion-exchange resins.

Polymers of epichlorohydrin have been important as polymers whose chlorine atoms could be replaced by nucleophilic reactions with carboxylates, amines, or other nucleophiles [7].

Particularly well studied are the polyacrylates and the polymethacrylates and their hydrolysis. It had been found early that the completeness of the hydrolysis of the esters depended very much on the conformation of the polymer chain in solution. Well known is the incompleteness of the base-catalyzed hydrolysis of poly(methyl methacrylate) to poly(methacrylic acid). The acid hydrolysis of poly(methyl methacrylate) is more easily accomplished. In all cases, stiffness of the polymer backbone chain has played an important role in the efficiency of hydrolysis.

Reactions on groups that are attached to a polyoxyethylene chain rather than to a polyethylene backbone chain have been known to proceed much more readily. Polyepichlorohydrin (PECH) is more reactive, not only because of the well-known reactivity of the chloromethyl ether group but even more importantly because in the backbone chain there are three atoms in the repeat units [8-10].

It was therefore of interest to investigate homo- and copolymerizability of carboxy-substituted oxiranes and olefins:



(1)

Polymers from Methyl ω-Epoxyalkanoates

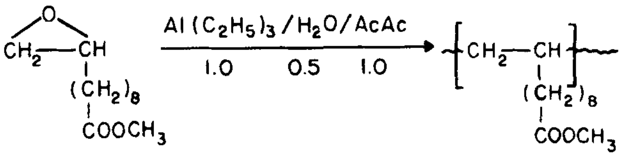
We found in our earlier work on the polymerization of ethyl glycidate (EG) that homopolymerization under cationic conditions did not proceed easily; even the copolymerization of EG with trioxane (TO) proceeded only with difficulty, and the polymers of TO and EG were obtained in only low molecular weight [11, 12]. Chain transfer during this polymerization was suspected, which would give only relatively small amounts of EG incorporated into the polymer chain; it was believed that the incorporation of EG probably occurred when much of the polymerization was completed and comonomer (EG) incorporation was close to the end of the polymer chain. By using a special gas-phase polymerization technique [13] and a flow reactor it was possible to carry out these copolymerizations under steady-state conditions, which provided copolymers with constant copolymer compositions but still with poor incorporation of EG.

Further and more intensive studies of the copolymerization of EG with oxiranes or other cyclic ethers, oxetane, and tetrahydrofuran (THF) were carried out under cationic conditions. We found that copolymerization of EG could be accomplished with propylene oxide, 1-butene oxide, and oxetane when a specially prepared and aged but traditional initiating system of triethylaluminum/water/acetylacetone (1.0/0.3/0.5) was used as the initiator [14, 15]. Again, the incorporation of the functional monomer EG was low, and it was found that at low feed ratios (up to 15 mol%) of EG, only 10% of the total amount of the EG comonomer (or 1 mol%) was incorporated into the polymer. When the amount of EG in the feed ratio was increased, not only did the amount of EG in the copolymer remain at the same level of 10% of the feed ratio, but the molecular weight of the polymers obtained in these polymerizations started to decrease very rapidly.

It was therefore concluded that the low incorporation of EG into the copolymer was probably caused by the influence of the functional group on the polymerizable oxirane ring. We proposed a simple working hypothesis: (a) to separate the polymerizable oxirane ring from the functional group by methylene spacer groups with an increasing number of methylene groups and (b) to study the polymerizability of the functional epoxide (for example, by determining the yield of polymerization at standard times or molecular weight and molecular weight distribution) as a function of the number of methylene groups between the oxirane ring and the carboxylate group. Not only was homopolymerization of individual functional oxirane monomers with an increasing number of methylene groups to be studied, but also the copolymerization of functional oxiranes with other nonfunctional oxiranes and especially with ethylene oxide.

When, in earlier work EG had been used as the comonomer with ethylene oxide, EG was not incorporated into the polymer and only homopolymer of ethylene oxide was obtained [15].

In our initial work to develop initiating systems that are suitable for the polymerization of functional epoxides, we found that a specially prepared triethylaluminum/water/acetylacetone initiating system of the composition (1.0/0.5/1.0), a member of the family of the Vandenberg initiating systems, was effective as initiator for this class of functional epoxides. This system not only polymerized very effectively and to high molecular weight oxiranes from ethylene oxide to 1-dodecene oxide, but this initiator system was also clearly a member of the coordinative anionic initiating system as are all acetylacetone-modified aluminum alkyl initiating systems [16-19]:



(2)

When methyl ω-epoxyalkanoates (MEA's) were prepared from methyl ω-alkenoates by peroxidation with m-chloroperoxybenzoic acid, it became clear that the oxidation of methyl acrylate to methyl glycidate was extremely slow. The oxidation of methyl 3-butenoate (n = 1) is somewhat faster, and n = 2 even faster. From n = 3 (methyl 5-hexenoate) the epoxidation proceeded at a reasonable rate and was completed at over 90% conversion in about 3 h. Methyl alkenoates with n > 3 were oxidized at approximately the same rate, indicating that a spacer group of three methylene groups seemed to be necessary in order to separate the functional carboxylate group from the polymerizable oxirane ring.

A similar result was obtained when the ^{13}C-NMR chemical shift values of the methine groups of the oxirane rings of the MEA's were studied. From the initial value of 48 ppm, the ^{13}C-NMR chemical shift value of subsequent homologous compounds increased and leveled off at the ^{13}C-NMR value of methyl ω-epoxypentanoate; from there on, the value remained constant (Figs. 1 and 2). Results indicating that 3 methylene groups are necessary to effectively separate the oxirane ring from the carboxylate group were obtained when the polymerization of the methyl ω-epoxyalkanoates was studied with the triethylaluminum/water/acetylacetone (1.0/0.5/1.0) initiating system using 5 mol% of the aluminum compound for the homopolymerization.

The polymer yields of homopolymerization for n = 0, 1, and 2 were very low and ranged up to 10%, but the yields in the polymerization of functional epoxides of n = 4 and higher were in excess of 50%. The polymer yield of n = 3 has not yet been accurately determined, but it is believed that the yield is lower, indicating that the influence of the functional group on the polymerization of the oxirane ring (Fig. 3) requires three methylene groups.

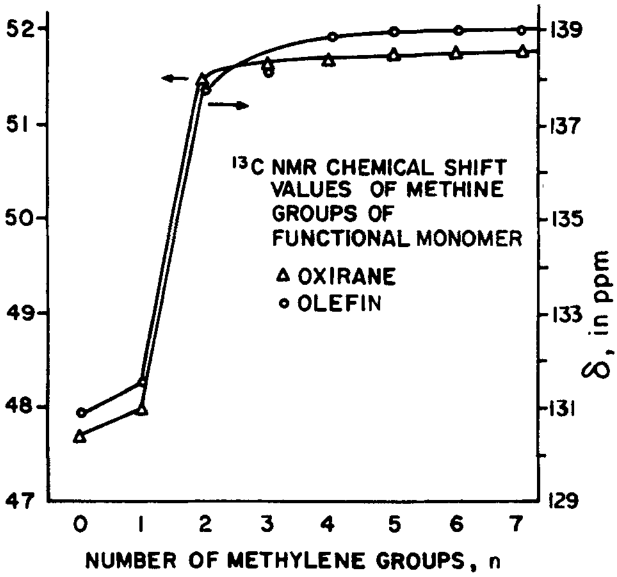


FIGURE 1.

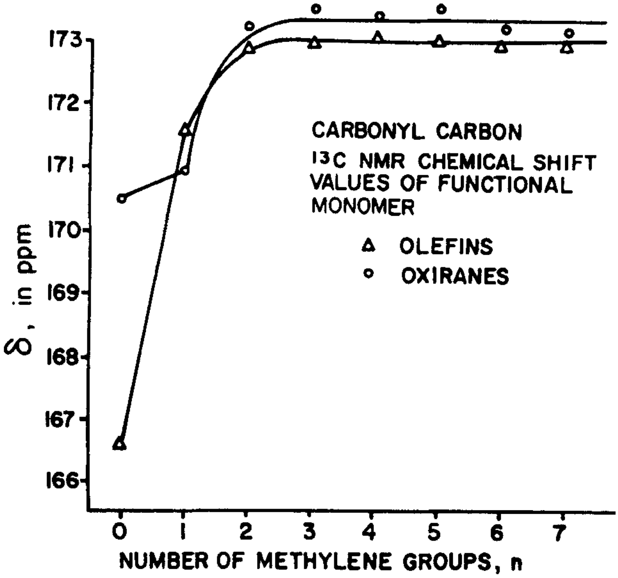


FIGURE 2.

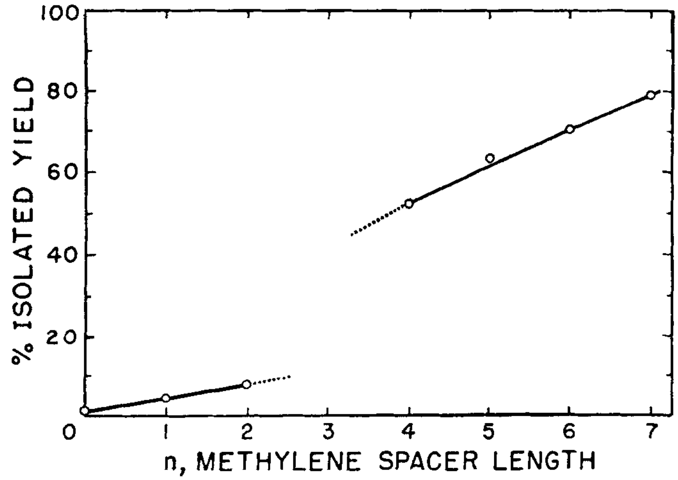


FIGURE 3.

Indications that three methylene groups are necessary to separate the influence of the carboxylate group on the polymerization of the oxirane group were also obtained when the copolymerization of methyl ω-epoxyalkonoates with oxiranes and oxetane was studied. Methyl 4,5-epoxypentanoate copolymerized with a number of oxiranes, propylene oxide, 1-butene oxide, 1-hexene oxide, and other oxiranes and gave copolymers with less methyl 4,5-epoxypentanoate incorporated than was added to the polymerization feed mixture. However, with methyl 7,8-epoxyoctanoate and methyl 10,11-epoxyundecanoate as the comonomer, the amount of comonomer incorporated into the copolymer with various oxiranes was the same as that of the comonomer mixture in the feed. When 30 mol% of the methyl 7,8-epoxyoctanoate was present in the feed, approximately 30 mol% of the comonomer units were found in the comonomer.

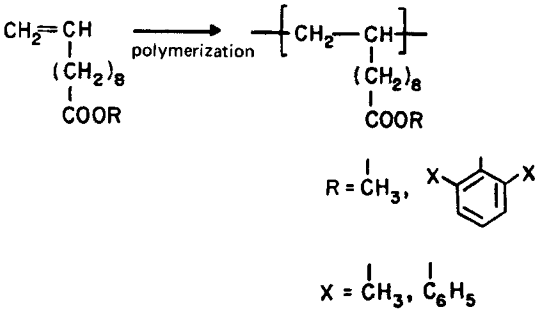
Polymers from Alkenoates

Not only is the polymerization of epoxides with a functional carbomethoxy group now accomplished, but the more difficult task of polymerizing functional olefins has also recently been achieved.

The polymerization of olefins with free radical initiators is limited to ethylene, styrene, and other olefins which do not have a hydrogen atom attached to the carbon atom alpha to the olefin double bond. When attempts were made to polymerize such olefins with free radical initiators, normally hydrogen abstraction from the monomer by the generated radical or by the growing polymer radical readily occurred. Low molecular weight compounds based on allyl radicals, for example, by allyl radical recombination, but no high molecular weight polymers, were obtained. As a consequence of this behavior, the only polymerization of choice for olefins with methylene groups in the side chains is the polymerization with coordination-type initiators, as was demonstrated by the now famous work of Natta and his group.

When functional carboxylate groups are attached at the end of such a side chain, the problem becomes more complicated because the polarity and reactivity of such groups can cause reaction with the initiating systems. Attempts to accomplish this polymerization of such functionally substituted olefins, and particularly the copolymerization of ethylene or propylene with a functional comonomer or an ethylene/propylene mixture with a functional termonomer, has been attempted in the past [20]. Some patents described the incorporation of small amounts of olefins substituted with a carbomethoxy group [20] or carboxylate salts [21]. The attempts also involve the copolymerization of ethylene with specific alkenoate esters. Norbornene polymerization has also been achieved when a carboxylate group is attached to the norbornene ring [22]. In fact, homopolymerization of norbornene with the nitrile group has been accomplished [23]. The norbornene double bond is much more reactive than the normal olefin double bond and is consequently not a very typical carbon-carbon double bond.

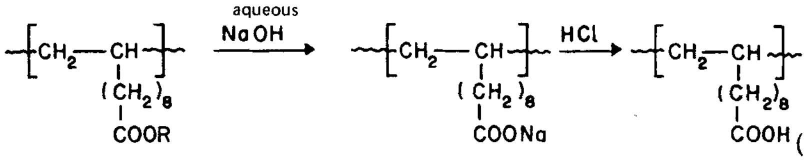
In our work on the polymerization of functional epoxides, we had to prepare the olefin-terminated carboxylates. Our first objective was to prepare esters of ω-alkenoic acids that might undergo coordination polymerization with Ziegler-Natta initiators. A number of esters were prepared including the methyl, trifluoroethyl, 2,6-dimethyl phenyl, and the 2,6-diphenyl phenyl esters of undecenoic acid [24].



(3)

Polymerization of functional olefins with ester groups having hindered phenyl ring was accomplished with $TiCl_3$:$AlCl_3$/acetylacetone-modified initiator which were reduced by Et_2AlCl. When the conventional amount of initiator mixture was used for the polymerization of the olefin ester, no polymer was obtained. Gradual increase in the amount of Et_2AlCl as a means of complexation for the ester group of the undecenoic acid showed that polymers could be obtained when the complex of Et_2AlCl with the undecenoic ester was added to the coordination initiator formed by the reaction of the modified $TiCl_3$ with the

Et_2AlCl initiating system. A maximum yield and molecular weight of homopolymer of 2,6-dimethylphenyl undecenoate (DPU) was obtained at a composition of more than 3 mols of Et_2AlCl for complexation per mol of DPU. The polymer was of high molecular weight and could be hydrolyzed with sodium hydroxide in aqueous 1,4-dioxane to the polymeric acid salt which could then be neutralized to the polymeric acid:



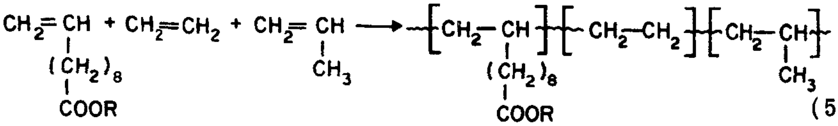
$$\sim\!\left[CH_2-\underset{\substack{|\\(CH_2)_8\\|\\COOR}}{CH}\right]\!\sim \xrightarrow[\text{NaOH}]{\text{aqueous}} \sim\!\left[CH_2-\underset{\substack{|\\(CH_2)_8\\|\\COONa}}{CH}\right]\!\sim \xrightarrow{\text{HCl}} \sim\!\left[CH_2-\underset{\substack{|\\(CH_2)_8\\|\\COOH}}{CH}\right]\!\sim \qquad (4)$$

The polymerization of esters of undecenoic acid other than the hindered substituted phenyl esters (e.g., DPU) was not easily accomplished. It was, however, found very recently that the polymerization of methyl 10-undecenoate could be accomplished, although the yield of polymer was only about 20%. No optimization of the reaction conditions has yet been attempted in order to maximize the yield of the methyl 10-undecenoate polymerization with coordination initiators.

The polymerization of 8-nonenoic acid esters ($n = 6$) could also be accomplished with the initiator system similar to that used for the DPU polymerization. We also have solid information that the polymerization of 7-octenoic acid esters ($n = 5$) can be achieved. We have, however, not accomplished the polymerization of ω-alkenoates with $n < 5$ methylene groups.

From our work we can conclude that the number of methylene groups used as spacers between the polymerizable olefin and the carbomethoxy group must be greater than in the case of the polymerization of functionally substituted oxiranes to functionally substituted poly(ethylene oxides). Only one methylene group in substituted polyethylene is between the carbon atoms which have the substituent in polyolefins, consequently providing a stiffer backbone chain. This structure requires more methylene groups as spacers to separate the carboxylate ester group from the polymerizable carbon-carbon double bonds. In polymers of functional epoxides there is a methylene and an ether oxygen separating the carbon atoms that carry the substituent.

2,6-Dimethylphenyl undecenoate (DPU) also served as a very suitable comonomer for the coordination polymerization with various α-olefins and ethylene:



$$CH_2=\underset{\substack{|\\(CH_2)_8\\|\\COOR}}{CH} + CH_2=CH_2 + CH_2=\underset{\substack{|\\CH_3}}{CH} \longrightarrow \sim\!\left[CH_2-\underset{\substack{|\\(CH_2)_8\\|\\COOR}}{CH}\right]\!\left[CH_2-CH_2\right]\!\left[CH_2-\underset{\substack{|\\CH_3}}{CH}\right]\!\sim \qquad (5)$$

The copolymerization with 1-dodecene and 1-hexene proceeded very well, as did the copolymerization of DPU with 1-butene. Copolymers with reasonable incorporation of the comonomer DPU were obtained without loss of molecular weight. In attempted copolymerization with propylene, only about 7-10 mol% DCU was incorporated into the copolymer. In ethylene copolymerizations it was difficult to incorporate more than 5 mol% of DCU into the copolymer, apparently because of the substantial difference in the reactivity of ethylene and DPU toward coordination polymerization.

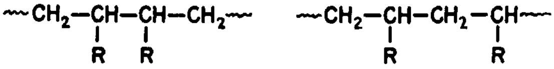
Two kinds of copolymers were synthesized when ethylene and propulene (mixed in the ratio of 1:12 by volume, reflecting approximately the reactivity ratios of the two comonomers in coordination polymerization) were used for the copolymerization with DPU. With titanium-based coordination initiators, the polymers obtained were crystalline and showed two crystalline melting points which were approximately 15° C lower than either melting point that one would expect for the melting points of linear polyethylene or isotactic polypropylene. This result suggests the presence of short blocks of ethylene and propylene in this terpolymer. With vanadium-based coordination initiators (reduced with Et_2AlCl), amorphous polymers with only the T_g of the polypropylene portion of the polymer were observed.

Selected homopolymers of the functional olefins, but also some of the copolymers, were hydrolyzed with aqueous 1,4-dioxane solutions of sodium hydroxide, and ionomers were obtained; they were characterized in a preliminary way.

HEAD-TO-HEAD POLYMERS

The synthesis of pure head-to-head (H-H) structures of common addition polymers, such as polystyrene, polypropylene, poly(vinyl chloride), and polyacrylates, have become of interest. It had become desirable to have these H-H polymers prepared, and to have their spectral, thermal, and other properties identified and characterized and the solid-state properties of these polymers studied and compared with those of normal and commercially important head-to-tail (H-T) polymers.

H-H polymers cannot be prepared as yet by direct methods; consequently, several techniques have to be used to synthesize H-H polymer structures [25, 26]:



$$\sim CH_2-\underset{R}{\underset{|}{CH}}-\underset{R}{\underset{|}{CH}}-CH_2\sim \qquad \sim CH_2-\underset{R}{\underset{|}{CH}}-CH_2-\underset{R}{\underset{|}{CH}}\sim \qquad (6)$$

For the preparation of H-H polyolefins, the reaction sequence of choice starts with the synthesis of 2,3-disubstituted butadienes-1,3, which are then polymerized by 1,4-polymerization. The remaining double bond of the polymer between the carbon atoms in 2 and 3 positions of the monomer unit is then reduced either catalytically or chemically. For the preparation of H-H polypropylene, 2,3-dimethylbutadiene-1,3 was polymerized to 1,4-trans-poly(2,3-dimethylbutadiene-1,3) or 1,4-cis-poly(2,3-dimethylbutadiene-1,3); either of these polymers could be hydrogenated with a soluble cobalt catalyst modified with aluminum alkyls. H-H polypropylene is amorphous and shows a T_g of -20°C which is about 15°C lower than that of H-T polypropylene. The T_g is somewhat dependent on the stereochemistry of the linkage between the carbon atoms which also have the methyl groups as their substituents. The erythro-predominant (about 65%) structure has a T_g about 10°C higher than that of the threo-predominant (about 65%) H-H polypropylene. The thermal stability of the substituted carbon-carbon bond as judged by the maximum degradation temperature is approximately the same for H-H and H-T polypropylene.

H-H polystyrene was prepared by a basically similar sequence of reactions. The polymerization of 2,3-diphenylbutadiene-1,3 to the 1,4 polymeric structure could be achieved by radical polymerizations with azobisisobutyronitrile as the initiator; reduction of the polymer was then done with potassium in ethanol. H-H polystyrene is quite similar in many properties to H-T polystyrene. However, there are some subtle and very significant differences, not in the degradation behavior but in the solution properties. The melt rheology behavior of H-H polystyrene is different than that of H-T polymer, but at 190°C, well above the T_g of the polymer, their behavior is identical. H-H polystyrene also blends well with poly(2,6-dimethyl-1,4-phenylene oxide), the well-known blending agent for H-T polystyrene, and the blends are compatible over the entire range of compositions.

Poly(vinyl halides) were prepared by either chlorination or bromination of 1,4-cis-polybutadiene-1,3 [27]. H-H poly(vinyl chloride) has properties fairly similar to those of H-T poly(vinyl chloride), and H-H poly(vinyl bromide) to those of H-T poly(vinyl bromide); both H-H polymers are miscible in all proportions with the corresponding H-T polymers. It was also found that H-H poly(vinyl chloride) is, like H-T poly(vinyl chloride), miscible in all proportions with poly(ϵ-caprolactone) [28].

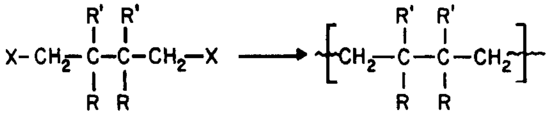
Polyacrylates or substituted polyacrylates have been synthesized from the copolymers obtained by alternating polymerization of maleic anhydride and ethylene or internal olefins followed by the complete esterification of the anhydride portion of the polymers. In this way H-H poly(methyl acrylate), H-H poly(methyl crotonate), and H-H poly(methyl cinnamate) were prepared. The T_g of these amorphous polymers is approximately 30-40°C higher for the H-H polymers than for the corresponding H-T polymers, although the reverse is true for polyolefins with very bulky groups; H-H poly(vinyl cyclohexane) has a T_g almost 50°C lower than that of the H-T polymer [25, 26].

Attempts have also been made to prepare H-H poly(methyl methacrylate). To date, these attempts have not led to the correct structure of H-H poly(methyl methacrylate). Cyclopolymerization of methacrylic anhydride gave exclusively 6-membered cyclopolymer, which upon hydrolysis and esterification with methanol gave normal H-T poly(methyl methacrylate) [29]. Polymerization of dimethacrylamide gave predominantly 5-membered imide ring structure; however, these dimethylsuccinimide structures could not be hydrolyzed by any of the methods which have been tried to date.

Another attempt for the preparation of H-H poly(methyl methacrylate) was the alternating copolymerization of ethylene and dimethylmaleic anhydride [30]. Although copolymers were obtained, they were low in incorporation of dimethylmaleic anhydride. As the amount of incorporation of dimethylmaleic anhydride by using forcing reaction conditions increased and became higher than 30 mol%, the molecular weight of the copolymers dropped drastically. All the copolymers could be esterified to the polymeric methyl esters, and efforts were made to extrapolate from the T_g's of the individual copolymers to the T_g of the methanol-esterified alternating copolymer of dimethylmaleic anhydride and ethylene, namely H-H poly(methyl methacrylate). We estimated a T_g of about 165°C for H-H poly(methyl methacrylate), knowing full well that the actual value of the T_g will very much depend upon the stereochemistry of the carbon-carbon bond of the two highly substituted carbon atoms, each of which has as the substituents a methyl group and a carbomethoxy group.

A number of techniques for the preparation of H-H polymers that are very effective for the preparation of polyolefins and poly(vinyl halides) are not suitable for the preparation of H-H polymers of disubstituted olefins. We mentioned in the last paragraph that approaches have been made by alternating copolymerization of ethylene with, in this particular case, dimethylmaleic anhydride. However, this polymerization did not lead to alternating copolymers.

In principle, H-H polymers can be constructed from two 4 carbon atom units which can be linked together by some polymer-forming reactions. One basic approach is first to make the H-H linkages and subject the "monomer" to a polyreaction, forming the tail-to-tail (T-T) linkages:



$$X{-}CH_2{-}\underset{R}{\overset{R'}{C}}{-}\underset{R}{\overset{R'}{C}}{-}CH_2{-}X \longrightarrow \left[CH_2{-}\underset{R}{\overset{R'}{C}}{-}\underset{R}{\overset{R'}{C}}{-}CH_2 \right] \qquad (7)$$

$R = R = CH_3$

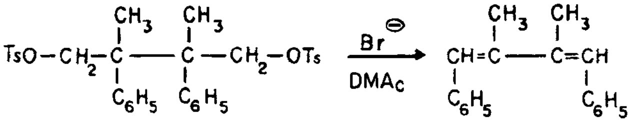
$R = CH_3,\ R' = C_6H_5$

Formation of the H-H linkage by polymer reaction was explored many years ago by Richards [31, 32], who attempted to prepare H-H polystyrene and H-H poly(α-methylstyrene) from the so-called dimers prepared from the α-methylstyrene radical anion. Richards attempted the oxidation of the dimeric radical anion with iodine, quinone, and also organic dibromides, and claimed that H-H polymers had been obtained. This elegant method was done at a time when characterization of the materials could not always unequivocally show the purity of the structural units. We have repeated some of this work and have used the more recently developed oxidation methods with copper and nickel complexes in attempts to repeat the synthesis of pure H-H poly(α-methylstyrene) [33].

We have not been able to prepare pure H-H poly(α-methylstyrene). All well-known and apparently well-described techniques for forming pure α-methylstyrene radical anion dimers, where the dimer is linked by the T-T linkage of the two methylene groups, have failed, although oligomeric materials of molecular weights of approximately 1000 (a decamer) could be obtained. From NMR structural analysis it was very clear that not only H-H but also H-T linkages were present in these oligomers, although the elemental analysis fitted very well the basic structure of $(C_9H_{10})_n$. We must therefore conclude that H-H poly(α-methylstyrene) has still not been prepared in pure form.

We also attempted to prepare H-H poly(α-methylstyrene) by first forming the H-H linkage and, in a subsequent polymer-forming reaction, forming the T-T linkage. This sequence of reactions was done by first preparing the starting material, dimethyl 2,3-dimethyl-2,3-diphenylsuccinate, which was reduced with lithium aluminum hydride to the glycol, which was then converted to the tosylate. The tosylate, a mixture of the meso and the racemic forms, mp 120 and 170°C, could be separated by crystallization.

Either pure isomeric tosylate or a mixture of the tosylates, when transformation into the dibromide with tetra-n-butylammonium bromide in dimethylacetamide was attempted, gave, instead of the desired dibromide, a bromine-free compound of the formula $C_{18}H_{18}$ which was found to be 1,4-diphenyl-2,3-dimethylbutadiene-1,3 [34, 35]:



$$\mathrm{TsO{-}CH_2{-}\underset{C_6H_5}{\overset{CH_3}{C}}{-}\underset{C_6H_5}{\overset{CH_3}{C}}{-}CH_2{-}OTs \xrightarrow[\text{DMAc}]{\text{Br}^{\ominus}} \underset{C_6H_5}{CH}{=}\overset{CH_3}{C}{-}\overset{CH_3}{C}{=}\underset{C_6H_5}{CH}} \qquad (8)$$

The compound was apparently obtained by a double phenonium rearrangement. Work on the synthesis of H-H poly(α-methylstyrene) is continuing.

As in the case of the attempted synthesis of H-H poly(α-methylstyrene) from four carbon units, H-H polyisobutylene can conceptually be prepared by first forming the T-T linkage and then in a polyreaction forming the H-H linkage.

Grignard condensation of 2,5-dimethyl-2,5-dibromohexane with various types of catalyst did not lead to any polycondensation product. Cationic polymerization of 2,5-dimethylhexadiene-2,4 at -78°C gave the polymer of 1,1,4,4-tetramethylbutadiene-1,3 in nearly quantitative yield and of reasonable molecular weight. However, in spite of considerable efforts, neither chemical nor catalytic hydrogenation to H-H polyisobutylene was successful. As much as 60-70% hydrogenation was achieved by chemical means, but crosslinking to insoluble polymer occurred under more forcing conditions.

H-H polyisobutylene with a molecular weight up to 10,000 was obtained by Grignard coupling reaction using $Cu(I)Br(PPh_3)_3$ as the catalyst [36, 37]. The polymer had a T_m of 187°C and a T_g of 87°C, and had the characteristics of an H-H polyisobutylene. All assignments of chemical shift of the ^{1}H- and ^{13}C-NMR spectra could be made. These polymers still have bromine endgroups. We believe it is possible to prepare even higher molecular weight material for the study of polymer properties which require high molecular weight. H-H polyisobutylene has a maximum degradation temperature of 315°C, about 70°C lower than that of H-T polyisobutylene [38]. H-H polyisobutylene and H-T polyisobutylene, when solution blended, gave polymer blends which showed that the polymers are essentially immiscible over the entire range of composition, indicating again that miscibility of polymers depends very much on interactions of groups with some polarity; hydrocarbon polymers of even slightly different structures are in principle immiscible [39].

When the formation of H-H polyisobutylene was attempted from 2,2,3,3-tetramethyl-1,4-dibromobutane by the Wurtz reaction, H-H polyisobutylene with a considerable amount of branching was obtained, as primary free radicals are involved in the polymer-forming reaction which caused radical abstraction. We believe that the Grignard condensation according to Yamamoto, which was finally successful, goes through copper compounds. Although condensation to polymer occurred formally by a radical mechanism, such radicals are not truly free primary and highly reactive radicals. No branching in this H-H polyisobutylene has been observed.

OPTICAL ACTIVITY BASED ON MACROMOLECULAR ASYMMETRY

The optical activity of an organic compound is associated with an asymmetric carbon atom, as in the case of sugars, amino acids, and such compounds as camphor, many alkaloids, and steroids. This type of optical activity is usually measured in solution. Another kind of optical activity is associated with the solid state of materials and is seen in materials in the crystalline state. This kind of optical activity is produced by the dissymmetry of the structure in the solid state. A number of inorganic compounds such as certain types of sodium chlorate or sodium bromate show this kind of optical activity; it disappears when the crystal is dissolved or molten. A well-known case is quartz, or polymeric silicon dioxide, where the silicon or oxygen atoms are arranged in helices. The packing of such dissymmetric helices gives very high optical rotations, up to several hundred degrees per millimeter of pathway through the material. This optical activity is, of course, also a function of the wavelength of light [40].

It has been noticed that a preferred helical arrangement can also be found in solid polymers or in a solution of polymers where chiral centers, optically active asymmetric carbon atoms, are attached directly to the main polymer chain or separated from it, perhaps by only one or two atoms. Although this observed optical activity is numerically high (100-200° specific rotation), the percentage of preferred helicity may be quite low, since the specific rotation of helical inorganic crystals may be over 10,000°. It is unknown what percentage of the overall optical activity of the polymer is due to chain helicity. It is estimated that the contributions of the helicity to the optical activity may be 5 or 10% of the actual theoretical and achievable values that could be obtained if all the polymeric helices were of only one screw sense. Well known is the optical activity that is contributed by the helicity in the tertiary structure of proteins.

Over the last 20 years we have been interested in the preparation of optically active polymers (a) whose structure is completely helical without the possibility of any configurational reversal, (b) whose helicity alone contributes to the optical activity of the polymer (no asymmetric atoms), and (c) whose barrier of rotation along bonds in the main chain is very high or infinite.

Polychloral is such a polymer and was expected to fulfill this basic and simple concept. In 1963 we made for the first time optically active polychloral with the lithium alkoxide of chloresterol as the anionic initiator, although the optical activity could not be measured at that time [41].

Chloral can be polymerized by an anionic polymerization initiator where the optical activity is either in the anion or in the cation. Polychloral samples were prepared by cryotachensic polymerization. Chloral monomer is initiated above the ceiling temperature of polymerization, injected between glass plates, and then polymerized to polychloral in film form by immersing the assembly for the film casting in ice/water. By this technique, films of about 0.1 to 0.2 mm thickness could readily be prepared. After the film was stabilized with methanolic hydrogen chloride, it was extracted to remove monomer and other impurities, and soaked in diphenyl ether to eliminate birefringence. Diphenyl ether is also the best swelling agent with the proper refractive index for the measurement of optical activity in polychloral films in the solid state.

The first successful experiment that resulted in polychloral having a measurable optical activity originating from the secondary structure (the isotactic helix) was performed by Corley [42], who used the optically active initiator tetramethylammonium (+) ketopinate. He obtained a polymer with a specific rotation of (+) 2400 ± 800° at a λ of 589 nm. In another case, the optically active counterion (+)-methyl-n-propylbenzylphenyl phosphonium was used to introduce macromolecular asymmetry, and optically active polychloral with a specific rotation of (-) 2700 ± 200° at a λ of 589 nm was obtained. The errors of this specific rotation were due to the optical activity measurements being performed in the solid state because all the birefringence had not been eliminated. Work was continued with chiral initiators belonging to the family of mandelates. 1-(-)-O-Acetylmandelic acid of (-) 153° was converted to the tetramethylammonium salt with a specific rotation of (-) 86° and d(+)-O-acetylmandelic acid [(+) 151°] was neutralized to the tetramethylammonium O-acetylmandelate [(+) 88°]. These initiators were used in 0.5 mol% concentration for the preparation for polychloral; optically active polychloral with a maximum specific rotation of (-) 1860 ± 70° when initiated with tetramethylammonium (+)-O-acetylmandelate and (+) 1180 ± 90° when initiated with tetramethylammonium (-)-O-acetylmandelate was obtained. When tetramethylammonium (+)-O-methylmandelate of (+) 52° was used as initiator, optically active polychloral of (-) 175 ± 20° was obtained, and tetramethylammonium (-)-O-methylmandelate of (-) 56° gave a polychloral sample of (+) 210 ± 20° [43].

Higher optical activity of polychloral was obtained when lithium alkoxides of chiral methyl mandelates were used to initiate polymerization. The specific rotation of methyl d(+)-mandelate was (+) 142°, and that of methyl 1(-)-mandelate was (-) 141°. Optically active polychloral obtained from the lithium salt of methyl d(+)-mandelate had a maximum value of rotation of (+) 3600 ± 110°, and that made with the lithium salt of methyl 1(-)-mandelate as the initiator had a maximum value of (-) 4670 ± 240°. The lithium alkoxide made from d(+)-2-octanol gave a maximum value of (+) 4200°, while polychloral made from 1(-)2-octanol prepared under slightly different conditions gave a value of about (-) 2000°. It is clear in this case that the maximum value had not been achieved. Lithium cholestan-3β-oxide, when used as initiator for the polymerization of chloral, gave a polychloral sample of an optical activity of about (+) 3000° and lithium cholestene-3β-oxide a value of (+) 3600° [44].

Additional information became available when the optical activity of the polychloral films was determined as a function of the holding time of the initiated mixture of initiator and chloral monomer above the polymerization temperature prior to cryotachensic polymerization to prepare polychloral films.

All the values of optical rotation that have been mentioned were taken from films when the initiated monomer was held for about 10 min at 65°C. When these values were extrapolated to zero holding time of the initiated monomer before cooling, an optical activity of the polychloral samples of about 5000° for all "strong" initiators could be estimated. These values depend very much on the type of initiator used and require strong nucleophiles, such as alkoxides.

It has been shown by NMR spectroscopy that strong nucleophiles such as alkoxides add the first chloral monomer unit essentially quantitatively above the ceiling temperature of chloral polymerization. Weaker nucleophiles such as acetate and chloride add to the first chloral monomer unit to an extent below the detection limit of NMR spectroscopy. It can be seen from our data that all values of polychloral samples with low optical activity were obtained with initiators whose anions carrying the chiral center were either weak initiators such as acylates, for example, acetates, or may in addition have the chiral center one or two atoms removed from the nucleophile. Only in the case of initiators where the optical activity was in the cation did we find high optical activity for polychloral samples initiated with weak nucleophiles. This was the case for the polymerization of chloral with an optically active tetraalkylphosphonium salt. These results show that when the optical activity is positioned in the cation, the ultimate activity is retained more effectively in optically active polymers based on macromolecular asymmetry. Ultimately, initiators with optically active cations may be the initiators of choice to introduce optical activity into helical isotactic polymers.

One of the possibilities of racemization is that the chiral centers of the initiator might be racemized under this condition of initiation and polymerization. We carried out some experiments to shed light on this problem and found that with optically active acetyl mandelate or cholesteroxide this was not the case as each initiator was found to have its optical activity unchanged after heating under initiation conditions for 1 h.

A number of alkoxide initiators were held in solution in chloral at 65 to 85°C for 1 to 3 h. The solution was then cooled to polymerize the chloral. The resultant polychloral samples were completely inactive optically.

Since the chiral initiator is not racemized under this condition, the stereochemistry of the equilibrium of the addition of the first chloral unit, and more likely the stereochemistry of the addition of the second and possibly third monomer chloral unit, are most likely essential. The polymerization of chloral to isotactic polychloral requires complete meso placement of the monomer addition. To have optically active polymer requires that all chloral units be added in meso placements. The racemization we seem to be experiencing is consequently believed to be caused by an equilibrium of meso with racemic placements of the chloral units, either in the first equilibrium, the equilibrium of the initiator and the first chloral unit, or, what appears more likely, the equilibrium of the second chloral monomer unit to the already formed alkoxide which has chloral as the terminal unit. This scenario could explain how polychloral obtained from strong nucleophiles as initiators and polymerized immediately after mixing gave the highest optical activity. On the other hand, when this mixture (with strong nucleophiles as initiator) was held for some time at higher temperature (85 to 65°C), complete racemization occurred. Since the equilibrium of the strong nucleophile with the first chloral unit is essentially all on the side of monomer addition, it is believed that under the most favorable conditions stereospecific addition of chloral to the alkoxide occurs. Stereospecific addition of the second chloral unit can also occur under favorable conditions. The chloral-terminated alkoxide so obtained is a weak nucleophile and hence perhaps can also undergo addition of a second chloral monomer in either meso or racemic placement. The equilibrium of the addition of a second chloral unit is undoubtedly on the left side of the equation (dissociation). Unfortunately, attempts to measure this equilibrium have not yet been successful as the second unit cannot yet be detected by NMR spectroscopy. This observation indicates that the addition of the second chloral monomer unit and indeed every subsequent monomer unit are unfavorable above the T_c.

There is, of course, always the possibility that the equilibrium of the addition of the chloral monomer as the third and fourth units also plays a role in the "racemization" of chloral polymerization. It is, however, believed that once the first turn (four monomer units) of the helix is formed, continued monomer addition causes the chloral to form the isotactic polymer in the helical configuration.

Another possibility is that the adduct of lithium alkoxide with one chloral unit decomposes to yield alkyl formate and trichloromethyl anion on long heating in chloral solution. The trichloromethyl anion would then itself, of course, decompose to yield chloride ion–an optically inactive initiator for chloral polymerization. This would explain the absence of optical activity in polychloral prepared with optically active alkoxides kept in warm chloral solution for long time periods before polymerization.

In conclusion, we have given examples of new developments in polymer synthesis in three areas. (a) Polymers with spacer groups of several methylene groups attached between the polymerizable oxirane or olefin group in the functional carboxylate group. These polymers and copolymers will allow access to a variety of functional polymers: polymerbound stabilizers, antioxidants, dyes, and drugs. Copolymers when hydrolyzed gave new ionomers or polyelectrolytes. (b) Head-to-head polymers provided new structures that will help our understanding of the thermal stability and of the thermal degradation behavior of common addition polymers, structure/property relationships in polymers, and a better understanding of the glass transition temperature. (c) Finally, the concept of optical activity based on macromolecular asymmetry (helicity) for isotactic polymers that may be completely free of chiral centers has been fully developed to provide polymers with optical activity based solely on the optical behavior of helices with only one screw sense.

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