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Head-to-Head Polymers

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Head-to-Head Polymers*

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ABSTRACT

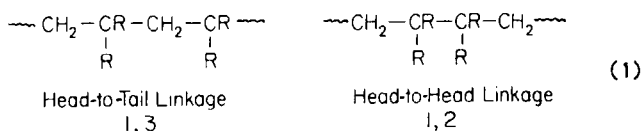
Head-to-head polymers of α -olefins, vinyl and acrylic monomers synthesized by indirect methods have shown similarities and differences in some of their behavior when compared to their counterparts of the common head to tail polymers. Head-to-head polyolefins, such as polystyrene or polypropylene, were prepared by 1,4-polymerization of the corresponding 2,3-disubstituted butadienes-1,3 followed by hydrogenation of the remaining double bonds, polyacrylates by alternating copolymerization of ethylene and maleic anhydride, followed by esterification of the polymer. Head-to-head polyacrylates were reduced to poly(allyl alcohols) which were then acrylated to the acetates and benzoates. Head-to-head poly(vinyl halides) were obtained from 1,4-polybutadiene by chlorination or bromination. The head-to-head polymers were characterized by spectroscopic analysis, some molecular weight characterization was done, and their thermal behavior was studied. The blending

*Part XXXI. Communication on Head-to Head Polymers. Part XXX: F. Xi, W. Bassett Jr., C. P. Lillya, and O. Vogl, Polym. Bull., **11**(3), 237 (1984).

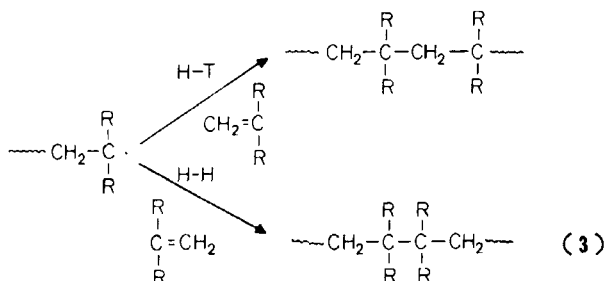
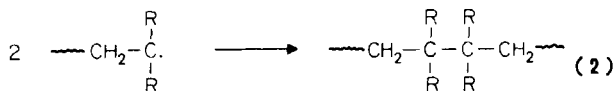
behavior with the corresponding head-to-tail polymers was studied in some cases; in others (head-to-head polystyrene), the blending with other polymers was investigated and the codegradation of the polymers was evaluated.

INTRODUCTION

Addition polymers, polymers with a polyethylene backbone chain, have the monomer units exclusively or predominantly arranged in head-to-tail (H-T) fashion, which means that the substituents are placed on alternating carbon atoms of the polymer chain [1-4]:



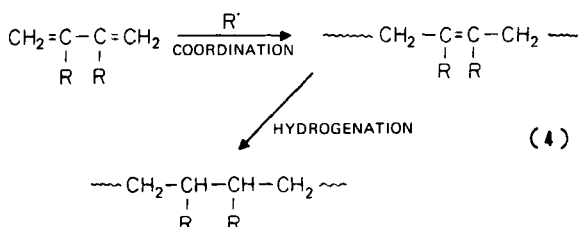
On occasions, head-to-head (H-H) and tail-to-tail (T-T) linkages are also present in these structures. These H-H linkages have been introduced by (a) recombination of polymeric radicals in radical polymerization (Eq. 2), (b) reverse addition of (halogenated) monomers in radical polymerization (important for the polymerization of fluorocarbon monomers, but also for vinyl chloride) (Eq. 3). H-H linkages have also been observed in polymers obtained by ring-opening polymerization of unsymmetric cyclic ethers; for example, propylene oxide.



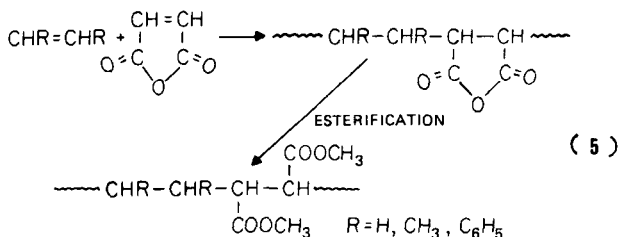
Considerable efforts have been made in the last decade to prepare pure H-H polymers of common important polymers, to characterize them, and to compare the properties with those of the corresponding H-T polymers.

H-H polymers cannot be made directly; consequently, a number of indirect approaches have been taken for their synthesis. No single method can be applied for the preparation of all the types of H-H polymers. The following methods have been developed for the synthesis of H-H polymers:

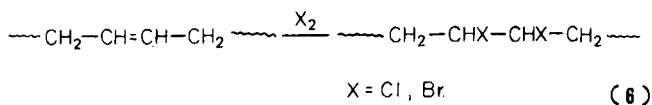
- A. For polyolefins: 1,4-polymerization of 2,3-disubstituted butadienes-1,3 followed by the hydrogenation (chemical or catalytic) of the remaining double bond of the butadiene unit of the polymer [5-20]:



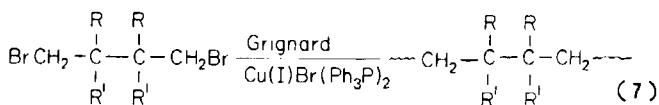
- B. For polyacrylates: Alternating copolymerization of ethylene and maleic anhydride followed by esterification [21-37]:



- C. For poly(vinyl halides): Halogenation (chlorination or bromination) of 1,4-polybutadienes-1,3 [38-56]:



- D. For disubstituted olefin polymers (polyisobutylene): Grignard polycondensation of 2,2,3,3-tetrasubstituted 1,4-dibromobutanes [57-63]:



Other methods for the synthesis of H-H polymers have been explored, but without success. One, for the possible synthesis of H-H poly(methyl methacrylate) (PMMA), is the cyclopolymerization of dimethacrylamides followed by hydrolysis and esterification; another, for H-H polymers of disubstituted olefins, is the Wurtz reaction adapted to a polymer reaction.

The selection of the individual method for the synthesis of H-H polymers depends on the type of polymer desired, the accessibility by synthesis of the intermediates or monomers, the minimum molecular weight of the H-H polymer, and the required structural purity of the polymer.

Method A was used for the synthesis of H-H polystyrene (PSt), H-H polypropylene (PP), and H-H poly(vinyl cyclohexane). Method B was used for the synthesis of H-H poly(methyl acrylate) (PMA), H-H poly(methyl crotonate), H-H poly(methyl cinnamate), H-H poly(acrylic acid), H-H poly(allyl acetate), and H-H poly(allyl benzoate); unsuccessful attempts were made for the synthesis of H-H PMMA. Method C gave H-H poly(vinyl chloride) (PVC) and H-H poly(vinyl bromide) (PVB). Polymers of disubstituted polyolefins cannot be prepared by Method A because this method requires as its last step the hydrogenation of a double bond which introduces one hydrogen atom to the already substituted carbon atom. As a consequence, methods must be devised to form either the H-H or the T-T linkage. In cyclization polymerization (to the desired 5-membered succinic acid group) these bond formations would be done simultaneously and alternately. H-H linkages would, for example, be formed by cationic polymerization of 1,4,4,4-tetrasubstituted butadienes or by oxidative coupling of styrene, α -methylstyrene, or diphenylethylene anionic radical dimers. T-T linkages could be formed by appropriate coupling reactions of 2,2,3,3-tetrasubstituted-1,4 derivatives.

In this paper we describe briefly the development of the field of H-H polymers with a critical evaluation of the contribution of the individual research group. Particular emphasis is given to the present status of our own research.

INTERPRETATION AND COMPARISON OF EXPERIMENTAL RESULTS

A considerable amount of data has been accumulated over the last decade on H-H polymers. Two research groups have been particularly active over this period, the groups of Otsu [20, 27-34] and Vogl. While Otsu concentrated primarily on H-H polymers of poly(acrylates) and

H-H polymer derived from H-H polyacrylates, Vogl took a broader view of the preparation of H-H polymers including polyacrylates. Both groups also attempted to synthesize the most important poly-(methyl methacrylate), but up to now without success.

When commenting on the synthesis of polymers, especially H-H polymers, the characterization of the materials is not always done in similar fashion. This often depends on the type of research group, availability of instrumentation, time period of research, and research tradition. In many cases the execution and interpretation of the polymer structure by spectroscopic analysis, such as infrared, ^1H and ^{13}C spectroscopy, is normally similar. Often the characterization of the polymer does not fulfill all the normal requirements. As a consequence, the actual molecular weight of these polymers is often in question. In many cases the molecular weight determination is limited to the measurement of the inherent viscosity in one solvent and probably in one concentration. In some reports, results of the gel permeation chromatography refer to the polystyrene standard.

Even more difference is encountered in the thermal analysis. The glass transition temperature is mostly determined by differential scanning calorimetry (DSC), but sometimes the onset rather than the midpoint temperature is given without mentioning this fact specifically; in some cases a softening temperature is reported. Not in all cases is the heating rate, or the sample size, or the type of instrument described. Similar problems exist with the degradation of the polymers, although the temperature at which the degradation occurs at a maximum rate has become the accepted procedure of characterization because it is not as sensitive to impurities and molecular weight as is the temperature of the onset of degradation or the temperature of 5 or 10% degradation. These temperatures have practical meaning in degradation studies of more established polymers.

Glass transition temperatures of H-H and H-T polymers are given in Table 1 and their thermal degradation behavior in Table 2.

POLYOLEFINS

Several H-H polyolefins have been made by Method A: H-H polypropylene (PP), H-H polystyrene (PSt), and H-H polycyclohexane. These syntheses required the availability of 2,3-disubstituted butadienes-1,3. 2,3-Dimethylbutadiene-1,3, necessary for the synthesis of H-H PP, is available; the others had to be synthesized. 2,3-Disubstituted butadienes-1,3 can be conceptionally synthesized by two simple laboratory procedures: from the 2,3-substituted butanediol-2,3 or 1,4. The first type is synthesized by reductive dimerization of methyl ketones; the glycols are then dehydrated with KHSO_4 . The limitation of the use of butanediols-2,3 is that these compounds must not have a hydrogen atom attached to the α -carbon atom of the substituents: the examples are phenyl- and tertiary butyl-substituents. Other 2,3-disubstituted

TABLE 1. Glass Transition Temperatures of H-H and H-T Polymers

Polymer	T_g of polymers in °C	
	H-H	H-T
Polypropylene	-39	-17
Polystyrene	97	98
Poly(vinyl cyclohexane)	88	138
Polyisobutylene	87	-61
Poly(methyl acrylate)	40	12
Poly(methyl crotonate)	107	80
Poly(methyl cinnamate)	210	190
Poly(vinyl chloride)	91	83
Poly(vinyl bromide)	76	85

TABLE 2. Thermal Degradation Behavior of H-H and H-T Polymers: Maximum Degradation Rate Temperatures

Polymer	Maximum degradation temperature in °C	
	H-H	H-T
Polypropylene	468	479
Polystyrene	397	398
Polyisobutylene	315	385
Poly(vinyl cyclohexane)	433	441
Poly(methyl acrylate)	418	419
Poly(methyl crotonate)	383	410
Poly(methyl cinnamate)	376	410

butadienes-1,3 are better made by pyrolysis of the 2,3-disubstituted butanediol-1,4 diacetates. 2,3-Disubstituted butanediols-1,4 were prepared by CuCl_2/Zn catalyzed coupling reactions of α -bromoalkanoates to the 2,3-disubstituted succinates followed by reduction of the ester group to the primary alcohol group with lithium aluminum hydride.

Polypropylene

Some polymers approaching the H-H PP compositions had been isolated from the attempted alternating copolymerization of ethylene and butene-2. Recently, deliberate efforts to make H-H PP from 2,3-dimethylbutadiene-1,3 (DMB) were simultaneously reported from three laboratories. It was important to have the polymer 1,4-structure exclusively in the polymer precursor for the synthesis of H-H PP. By anionic polymerization of DMB, a polymer of 97% 1,4- and 3% 1,2-structure was obtained. The 1,4-double bond had a 3:1 ratio of trans to cis linkages. Normal radical polymerization of DMB produced poly-DMB with a predominance of trans 1,4-structures along with almost 10% 1,2-structure of the poly-DMB. Poly-DMB was also prepared by emulsion polymerization of DMB; the polymer was found to consist of about 6% 1,2-units. Cationic polymerization of hexadiene-2,4 produced a polymer whose structure consisted of more than 10% 1,2-units.

We have prepared pure 1,4-poly-DMB by polymerizing DMB with aluminumalkyl/ TiCl_4 initiator systems. Depending on the aluminum-alkyl/ TiCl_4 ratio, 1,4-poly-DMB could be obtained that was either pure cis or pure trans polymer but had less than 2% 1,2-linkages (the limit of NMR detection technique used for this work).

Catalytic hydrogenation of ether 1,4-cis- or 1,4-trans-poly-DMB with soluble hydrogenation catalysts (particularly effective for the hydrogenation of the chain double bond in polymers) cobalt 2-ethylhexanoate and aluminumalkyl gave H-H PP. The hydrogenation is not stereospecific but is preferred cis; from cis-1,4-poly DMB erithro predominant H-H PP was obtained, and from trans-1,4-poly DMB threo predominant H-H PP was obtained. In both cases the predominant configuration was obtained in a 2:1 ratio.

The glass transition temperature of H-H PP depends not only on the molecular weight but also on the stereochemistry of the polymer; threo predominant H-H PP has a T_g of about -30°C and erithro predominant H-H PP a T_g of -40°C . Measured under the same condition by DSC, the T_g of "atactic" H-T PP had a T_g of -17 to -20°C . Blends of erithro predominant and threo predominant H-H PP are completely miscible as judged by their single T_g in the DSC. Blends of H-H PP

and H-T PP are also completely miscible over the entire range of compositions. It has been reported that the unperturbed dimensions of H-H PP in solution is smaller than that of atactic H-T PP.

The thermal degradation behavior of H-H PP and H-T PP was also studied, and it was found that the thermal stability of H-H PP and H-T PP were very similar. The temperature at which the polymers degraded at the maximum rate (MDT) (at a 20°C/min temperature increase) was 479°C for the H-T PP and 468°C for the H-H PP; these temperature values were almost within experimental error.

Polystyrene and Poly(vinyl Cyclohexane)

For the preparation of H-H PSt, 2,3-diphenylbutadiene-1,3 (DPB) was first polymerized to poly-DPB, which was accomplished with AIBN as the radical initiator. Alternative ways of polymerization of DPB, such as coordination initiation with transition metals or anionic initiators, gave either cross-linked materials or substantial 1,2-structures in the polymer. Poly-DPB initiated with AIBN had about 45% cis and 55% trans linkages in the polymer.

The hydrogenation of poly-DPB was accomplished by chemical reduction with potassium in ethanol. The structure of H-H PSt was carefully studied by NMR spectroscopy. It had erithro and threo linkages in full accordance with the trans addition of hydrogen to the double bonds in the chemical reduction. Investigating the C₁ carbon atom of the phenyl ring and the methine and methylene carbon atoms, a new long-range order interaction could be identified by NMR spectroscopy for erithro and threo linkages similar to the meso (isotactic) and racemic (syndiotactic) arrangements of pentads in the normal H-T polymers.

Complete catalytic hydrogenation of poly-DPB with Pd catalyst gave H-H poly(vinyl cyclohexane), which could also be obtained from H-H PSt.

H-H PSt has a T_g (97°C) similar to that of H-T PSt, a theta temperature of 19°C, substantially lower than that of H-T PSt (34°C). Other measurements, including melt rheology, showed H-H PSt to have a stiffer polymer chain, at least right above the T_g and in poor solvents; at the same time, H-H PSt is more soluble.

The thermal degradation behavior of H-H PSt and H-T PSt was also investigated, and it was found that the MDT of H-H PSt is 398°C, that of H-T PSt is 403°C, and that of isotactic H-T PSt is 397°C.

H-H PSt was blended with poly(2,6-dimethyl-1,4-phenylene oxide) (poly-PPO); it was found, like H-T PSt, to be miscible with poly-PPO over the entire temperature range. Codegradation of the two types of polymer blends were also studied, and it was found that two ranges of degradation temperatures were characteristic for each of the two polymer components. While poly-PPO did not influence the degrada-

tion of either H-H PSt or H-T PSt, the degrading H-H PSt slightly affected the degradation of poly-PPO, destabilizing it, and causing the degradation to occur at about 30°C lower temperatures.

H-H poly(vinyl cyclohexane) has a very bulky cyclohexane ring attached to the polyethylene chain and the T_g of the H-H polymer is 88°C, about 45°C lower than the H-T polymer of that particular stereochemistry.

Polyacrylates

H-H Poly(methyl acrylate) has been prepared by alternating copolymerization of maleic anhydride and ethylene. Esterification of the alternating copolymers of maleic anhydride and ethylene has been achieved by treating the polymeric anhydride with methanol, with sulfuric acid as the catalyst, followed by completion of the esterification with diazomethane. The corresponding copolymerization of 2,3-dimethylmaleic anhydride with ethylene as starting polymers to make H-H PMMA did not give alternating copolymers, although alternating copolymers of alkylvinyl ethers with 2,3-dimethylmaleic anhydride could be prepared. H-H poly(methyl crotonate) was synthesized from the alternating copolymer of butene-2 and maleic anhydride, H-H poly(methyl cinnamate) from the alternating copolymer of stilbene and maleic anhydride followed by esterification. Both H-H polymers were characterized and their structures established.

The T_g of the three polyacrylates were measured by DSC, thermal mechanical measurements (TMS), and by dynamic mechanical measurements. The T_g of the polyacrylates increased with increasing bulkiness of the substituents; in polyacrylates, the H-H polymers have higher T_g than the H-T polymers.

Some differences have been noted between the measurements of the T_g 's by DSC as compared to TMS.

The thermal degradation of polyacrylates was studied by DTG, pyrolysis gas chromatography, and isothermal degradation at temperatures near the MDT. The MDT of H-H and H-T poly(methyl acrylate) is the same at 418°C. Similar MDT's were found for H-T poly(methyl crotonate) and H-T poly(methyl cinnamate); the corresponding H-H polymers of the last two polymers or the substituted polyacrylates have lower MDT's.

POLY(VINYL HALIDES)

Poly(vinyl Chloride)

Chlorination of emulsion polymerized polybutadiene rubber was carried out many years ago. These polymers had a complicated struc-

ture of the butadiene units. Almost 20 years ago a more systematic study of the chlorination of *cis*- and *trans*-polybutadiene was carried out. It was found that the chlorine uptake was quantitative, and apparently no side reactions such as dehydrochlorination or cyclization were noticed. The polymers were more stereospecific as far as one could determine with the spectroscopic methods then available, and the starting polymers were normally of lower molecular weight. Some suggestions of a stereospecificity of the chlorination were noticed and a crystal structure determination was attempted.

Recently, the chlorination of high molecular weight *cis*-1,4-polybutadiene was reinvestigated on butadiene samples that had high 1,4- (99.7%) and high *cis* content (98.8%). When the chlorination was carried out at 0°C and in low concentration, the chlorination could be successfully carried out without gelation. It was found that partially chlorinated *cis*-1,4-polybutadiene is a nonmiscible polymer system; the polymer portions separate into a butadiene-rich unit and a chlorinated phase. Fully chlorinated *cis*-1,4-polybutadiene H-H PVC is a partially crystalline polymer. The T_g of H-H PVC is not unlike that of H-T PVC and has been studied; it has been the subject of some controversy. In our hands, as studied by DSC, the T_g of H-H PVC is 91°C and that of H-T PVC is 83°C.

We have also studied the blending behavior of H-H PVC with poly(ω -caprolactone) and found that H-H PVC, like H-T PVC, is completely miscible with poly(ϵ -caprolactone).

Poly(vinyl Bromide)

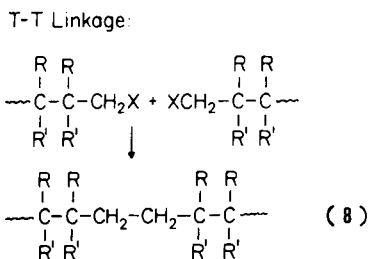
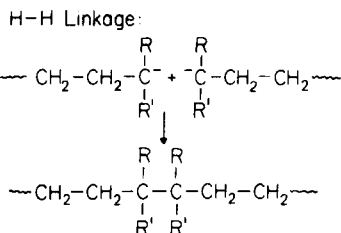
Bromination of *cis*- and *trans*-1,4-polybutadiene has been carried out in very dilute solution.

We have studied the bromination of *cis*-1,4-polybutadiene of high molecular weight and found that the bromination occurred readily in dichloromethane. Highly brominated samples of *cis*-1,4-polybutadiene are less soluble, and cosolvents such as THF or 1,2-dibromomethane had to be added to the reaction to keep the polymer in solution. As in the case of partially chlorinated *cis*-1,4-polybutadiene, partially brominated *cis*-1,4-polybutadiene segregates into a butadiene unit rich and a brominated phase. The degree of miscibility of these two phases depends on the type and amount of cosolvent; the polymer in the range of 50 to 80% bromination shows an apparently better miscibility than a polymer of the same degree of bromination made with THF as the cosolvent, suggesting that possibly in the latter case a more blocky bromination of the *cis*-1,4-polybutadiene had occurred.

The T_g of H-H PVB as compared to that of the H-T PVB is about 10°C higher.

POLYMERS FROM DISUBSTITUTED MONOMERS

H-H polymers of disubstituted monomers cannot be made by Method A, and Method B is quite unlikely to succeed. Therefore, the possible routes of polymerization are by first forming either the H-H or the T-T linkage followed by the formation of the other linkage:

Polyisobutylene

The formation of H-H linkage of polyisobutylene (PIB) by cationic polymerization of 1,1,4,4-tetramethylbutadiene-1,3 (2,5-dimethylhexadiene-2,4) proceeds in high yield to a polymer of good molecular weight. The hydrogenation of this polymer could not be accomplished by catalytic hydrogenation or by chemical reduction. Mild conditions are ineffective and forcing conditions cause depolymerization or cross-linking.

Polymerization by the formation of the T-T linkage led to the formation of H-H PIB. To accomplish this method of direct polycondensation of 1,4-disubstituted butanes, preferably the dibromides with the appropriate substitution (2,2,3,3-tetramethyl) had to be accomplished to high molecular weight polymer. In this case, the H-H linkage had to be formed first: Methyl 2-bromoisobutyrate was condensed to dimethyl 2,2,3,3-tetramethylsuccinate, this compound reduced with lithium aluminum hydride to the 1,4-glycol, which was ditosylated, and the tosyl group replaced by a nucleophilic displacement reaction with bromide.

The polycondensation was carried out by the Yamamoto method [57], which was first tested for the preparation of low molecular weight linear polyethylene. A mono-Grignard reagent was prepared from 2,2,3,3-tetramethyl-1,4-dibromobutane and condensation allowed to proceed with $\text{Cu(I)Br(Ph}_3\text{P)}_2$ as the catalyst (Eq. 7). H-H PIB was obtained which has a linear structure and a molecular weight of up to 10,000. The polymer was highly crystalline, had a T_m of 187°C , and a T_g of 87°C .

Blends of this H-H PIB with an H-T PIB (T_g of -61°C) of similar molecular weight were prepared and their miscibility studied by DSC. The polymer blends were immiscible over almost the entire composition range. This immiscibility was also seen in the codegradation of the blends. The MDT of H-H PIB is 315°C , some 70°C lower than H-T PIB. It was interesting to note that in isothermal degradation of either H-H PIB or H-T PIB isobutylene, the monomer for the H-H polymer was also the almost exclusive degradation product.

Attempts to prepare H-H PIB from 2,2,3,3-tetramethyl-1,4-dibromobutane by the chemical Wurtz reaction with sodium metal or sodium/potassium alloy led to branched polymer of relatively low molecular weight.

Attempts were made to prepare H-H poly(α -methylstyrene) (PMSt). Formation of the H-H linkage was tried by oxidation of the so-called "dimer" of the α -methylstyrene ion radical. Low molecular weight oligomers of about 800 to 1000 were obtained which had both H-H and H-T linkages in the structure. Attempted preparation of 2,3-dimethyl-2,3-diphenyl-1,4-dibromobutane has not yet been successful. A rearrangement reaction of 2,3-diethyl-2,3-diphenyl butanediol-1,4-ditosylate by bromide did not lead to the 1,4-dibromobutane but to 2,3-dimethyl-1,4-diphenyl-1,3-butadiene.

Attempts were also made to synthesize H-H PMMA: Cyclopolym-erization of methacrylic anhydride did not give polymers of pure structures, but mixtures of the desired 5-membered with 6-membered cyclized products and noncyclized structures; only 5-membered succinate structures could give H-H polymers after esterification. Copolymerization of 2,3-diethylmaleic anhydride with ethylene did not give alternating copolymers, but alkyl vinyl ethers gave alternating copolymers. Esterification of these copolymers could be accomplished to the polymeric esters, and from the observed T_g 's of these polymers an attempt was made to extrapolate for the T_g for H-H PMMA. A T_g for H-H PMMA of $160\text{-}170^\circ\text{C}$ was estimated.

ACKNOWLEDGMENTS

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