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Preparation and Characterization of Head-to-Head Polymers. III. Head-to-Head Poly(methyl Crotonate)

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ABSTRACT

Alternating copolymers of cis-butene-2 and maleic anhydride were esterfied to the methylester which corresponds to head to head (H-H) poly(methyl crotonate).
The chemical, physical, and mechanical properties and thermal degradation behavior of H-H poly(methyl crotonate) was studied and compared with the properties of head to tail (H-T) poly(methyl crotonate). This latter polymer was made by a known anionic polymerization technique and was, unlike the amorphous H-H polymer, partially crystalline. The T_g of H-H polymer was found to be higher than that of the H-T polymer. Thermal degradation behavior of H-H and H-T polymer was between the degradation behavior of H-H and H-T poly(methyl cinnamate) and poly(methyl acrylate). Poly(methyl crotonates) degraded to a substantial part to small molecules and char; methyl crotonate was found among the degradation products. H-H Poly(methyl crotonate) gave also butene-2 and a mixture of dimethyl maleate and dimethyl fumarate on pyrolysis.

INTRODUCTION

Head to head (H-H) poly(methyl crotonate) was prepared and characterized.

In earlier work we discussed the preparation and characterization of the H-H polymers poly(methyl cinnamate) and poly(methyl acrylate) [1, 2]. These polymers were examples of phenyl substituted and nonsubstituted polyacrylates. It was of interest to study the behavior, particularly the thermal degradation behavior, of substituted H-H polyacrylates but without resonance stabilizing phenyl groups. The best example was expected to be the H-H poly(methyl crotonate).

The simplest way to prepare H-H poly(methyl crotonate) was analagous to our earlier [1, 2] work by esterificiation of alternating copolymers of butene-2 and maleic anhydride. Alternating copolymers of stilbene/maleic anhydride had been earlier transformed into H-H poly(methyl cinnamate), and alternating copolymers of ethylene and maleic anhydride had been esterified quantitatively to H-H poly(methyl acrylate).

Copolymerization of cis-butene-2 and maleic anhydride had been studied [3] several years ago together with a general copolymerization study of butenes with maleic anhydride. It was found that butenes-2 could be copolymerized with maleic anhydride to low molecular weight polymers. It may be recalled that it is not possible to prepare high molecular weight homopolymers of α-olefins and particularly of internal olefins by free radical polymerization because of the radical stability and consequently nonreactivity of allylic radicals for radical addition to monomer. Copolymerization of α-olefins with olefinic monomers with electron withdrawing groups such as maleic anhydride has been readily achieved.

Earlier workers had found that cis- and trans-butene-2 reacted at about the same rate in copolymerizations with maleic anhydride and gave a polymer of the same low inherent viscosity.

H-T Poly(methyl crotonate) had been made several years ago by polymerization of trans-methyl crotonate with anionic initiators [4].

We have prepared H-T and H-H poly(methyl crotonate) of high chemical purity and studied their properties.

EXPERIMENTAL PART

Materials

The following chemicals were obtained from Eastman Kodak Chemical Co.: maleic anhydride, benzene, chloroform, and azobisisobutyronitrile (AIBN).

Maleic anhydride was dissolved in dry benzene (10% solution) and filtered by pressure filtration through a fritted filter funnel to remove insoluble material, presumably maleic acid.

Benzene from a freshly opened bottle was dried over calcium chloride and distilled from sodium metal prior to its use.

Chloroform was washed three times with water, dried over calcium chloride, and distilled from phosphorous pentoxide before it was used.

Azobisisobutyronitrile was recrystallized three times from dry methanol (10 g AIBN was dissolved in 15 ml of methanol at 35°C and then cooled to 0°, yield 7.5 g) and dried at 0.1 Torr overnight at room temperature.

cis-Butene-2 was obtained from Matheson Gas Co. and was of chemically pure grade (its composition was 99.5% cis-butene-2 and 0.5% trans-butene-2). The gas was used without further purification.

Benzoyl peroxide (BPO) containing 22% water was obtained from Polysciences, Inc., and recrystallized three times from dry ethanol (10 g BPO containing water was dissolved in 200 ml of ethanol at 40°C and cooled to 0°, yield 6.0 g). The recrystallized BPO was dried at 0.1 Torr overnight at room temperature.

N-Butylnitrosomethylurea was obtained from K and K Laboratories, Inc., and was used without purification.

trans-Methyl crotonate was obtained from Aldrich Chemical Co. and distilled from calcium hydride. The purity of this material was 99%+ according to gas chromatography.

Calcium metal was obtained from Apache Chemicals, Inc., and diethyl zinc was obtained from Texas Alkyls, Inc. Both compounds were used as obtained.

Copolymerization of cis-Butene-2 with Maleic Anhydride

cis-Butene-2 and maleic anhydride were copolymerized in a sealed polymer tube with AIBN or BPO as the initiator. A typical procedure was as follows: To a benzene or chloroform solution containing a known amount of maleic anhydride, the initiator was added at room temperature and allowed to dissolve. This solution was charged into a Pyrex polymerization tube at room temperature and the polymerization tube was connected to a vacuum line. The solution was de-gassed by cooling the mixture to Dry Ice temperature, opening the stop cock to the vacuum line until a proper vacuum was reached, then allowing the contents of the tube to warm to room temperature. This de-gassing procedure was carried out three times; cis-butene-2 was then introduced into the polymer tube. The lower part of the polymer tube was held in the Dry Ice/acetone bath and the polymer tube was sealed under 0.1 Torr.

The polymerization was carried out by inserting the sealed tube into a constant temperature bath. After the required period the tube was opened and the contents of the tube were poured into dichloromethane. The copolymer precipitated and was washed three times with dichloromethane. Finally it was vacuum filtered and dried at 0.1 Torr overnight at 50°C.

Some of the polymerizations were carried out by UV irradiation rather than by thermal decomposition of the AIBN initiator. For these polymerizations the UV light source was a photochemical reactor with a wavelength range of 3000 to 4200 Å and a maximum at 3510 Å. The UV source was purchased from Southern New England Ultra Violet Co.

The polymerizations were carried out in Pyrex glass polymerization tubes. Details of the polymerization experiments are shown in Table 1.

Esterification of Alternating cis-Butene-2/Maleic Anhydride Copolymer

Alternating cis-butene-2/maleic anhydride copolymer (4 g) was suspended in 250 ml of dry methanol which contained 50 ml of 98% sulfuric acid. The suspension was refluxed for 5 hr; after 30 minutes all the polymer had gone into solution and a clear solution was obtained. After the reaction was completed, the solution was concentrated to 50 ml at room temperature under reduced pressure and poured into a mixture of 200 ml of methanol and 300 ml of water. The polymer precipitated and was washed several times with 40% aqueous methanol until the wash liquid was neutral to litmus paper. The polymer was dried overnight at 0.1 Torr at room temperature; yield 4.5 g.

The dried polymer, which is essentially the half-ester of H-H poly(crotonic acid), was esterified further by treatment with diazomethane. The polymer was suspended in 100 ml of toluene and 60 ml of a 10% solution of diazomethane in ether [4] was added dropwise over a period of 5 hr with stirring. After about 20 ml of diazomethane solution was added, the polymer went completely into solution. The stirring was continued overnight and the polymer solution was concentrated to 50 ml under reduced pressure at room temperature. The solution was poured into 500 ml of n-hexane in order to precipitate H-H poly(methyl crotonate). The suspension was filtered and the polymer dried at 0.1 Torr overnight at room temperature; yield 3.6 g.

Polymerization of trans-Methyl Crotonate

trans-Methyl crotonate was polymerized according to an earlier method [5] by anionic polymerization with toluene as the solvent and at Dry Ice temperature (Table 2).

Measurements

The thermal degradation of all polymers was carried out in a nitrogen atmosphere using a Perkin-Elmer GTS-1 thermal balance at a programmed rate temperature increase of 5°C/min. Most results are reported as DTG (differential thermogravimetric analysis) [6]. A Perkin-Elmer DSC-1B differential scanning calorimeter was used for the measurements of polymer transitions.

TABLE 1. Copolymerization of Maleic Anhydride and cis-Butene-2[a]

Solvent		Initiator		Maleic anhydride		cis-Butene-2		Polymer yield		
Type	Amount (ml)	Type	Amount (mmole)	grams	mmoles	grams	mmoles	grams	%	η_{sp}/c[b]
C_6H_6	20	BPO	0.05	4.9	50	4.7	84	0.22	3	0.15
C_6H_6	20	AIBN	0.05	4.9	50	4.0	72	0.39	5	0.13
C_6H_6	20	BPO	0.5	4.9	50	2.8	50	1.62	21	0.15
C_6H_6	20	AIBN	0.5	4.9	50	2.8	50	1.85	24	0.15
$CHCl_3$	20	BPO	0.5	4.9	50	2.8	59	2.46	32	0.16
$CHCl_3$	20	AIBN	0.5	4.9	50	3.1	54	3.23	42	0.17
$CHCl_3$	35	AIBN	1.0	9.8	100	6.6	118	6.00[e]	39	-
$CHCl_3$	35	AIBN	1.0	9.8	100	4.9	87	4.83[e]	36	-
$CHCl_3$[c]	35	AIBN	0.1	9.8	100	6.2	110	4.47[e]	29	0.25
$C_6H_5CH_3$[d]	50	AIBN	0.1	3.9	40	3.6	60	0.54	9	0.20

[a] Polymerization temperature: 60°C. Polymerization time: 45 hr.
[b] 0.2 g/dl in dimethyl formamide at 30°C.
[c] Polymerization temperature: 35°C. Polymerization time: 24 hr. UV-induced AIBN decomposition.
[d] Polymerization temperature: -68°C. Polymerization time: 39 hr. UV-induced AIBN decomposition.
[e] No chlorine was found in the polymer.

TABLE 2. Polymerization of trans-Methyl Crotonate[a]

Methyl crotonate		Initiator amount (in mmole)[b]	Polymer yield		
milliliters	mmoles		grams	%	η_{sp}/c[c]
6	57	1.7	1.05	18.4	0.88
6	57	5.7	0.64	17.5	0.64

[a] Polymerization temperature: -78°C. Polymerization time: 24 hr. Solvent: toluene, 20 ml.

[b] Assuming an overall formula for the calcium-zinc alkyl initiator of $CaZn(C_2H_5)_4$.

[c] 0.2 g/dl in CF_3COOH at 30°C.

H-H and H-T poly(methyl crotonate) were pyrolized in a Hewlett Packard model 80 pyrolyzer. The pyrolysis was carried out in a Pt-Rh electrode. The electrodes were heated by an electric current to the appropriate temperature, which took about 10 sec for a sample size of 1 mg. The pyrolysis products were passed directly into a Varian Aerograph model 920 gas chromotograph using a 6-ft long column with a diameter of 1/4 in. containing 36% of diisooctylphthalate on Chromosorb W. The column temperature was 125°C; helium was used as the carrier gas.

RESULTS AND DISCUSSION

We confirmed the earlier work of Imoto [3] on the copolymerization of cis-butene-2/maleic anhydride; the polymer which was obtained was exclusively an alternating copolymer. One important problem in the preparation of this polymer was the limitation of the molecular weight. Imoto and co-workers had reported an inherent viscosity of 0.05 g/dl for their trans or cis-butene-2/maleic anhydride copolymer. We attempted several modificiations in order to increase the molecular weight of this alternating copolymer. It would have been convenient to have high molecular weight copolymer as starting material for the transformation to H-H poly(methyl crotonate). Such polymers would allow more extensive studies of the mechanical properties for which higher molecular weight polymers are essential. A number of experiments of copolymerizations of cis-butene-2 with maleic anhydride were carried out in benzene and chloroform with BPO and AIBN as initiators at different initiator concentrations, different reaction times, and different reaction temperatures. In all cases the molecular weight (judged by the inherent viscosity) of all copolymers was low and did not exceed 0.3 g/dl. The only influence that affected the increase of the molecular weight of our copolymers from an inherent viscosity of 0.15 to 0.25 was the decrease of the reaction temperature.

The reaction temperature was lowered by decomposing the initiator, AIBN, with UV radiation at room temperature.

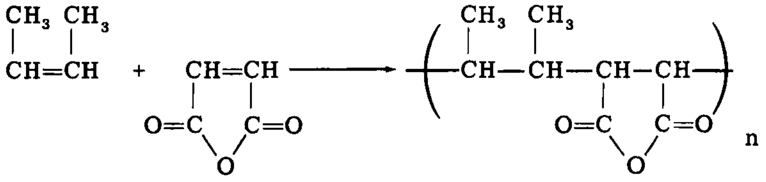
Thermal decomposition of BPO and AIBN at various concentrations gave an inherent viscosity of the polymer of 0.15 regardless of the reaction times and the initiator concentrations. As long as the reaction temperature was 60° C, there was no apparent influence of the kind and amount of solvent used for the polymerization.

At very low temperatures (-60° C), maleic anhydride was much less soluble and consequently the polymerization had to be carried out at lower monomer concentrations.

We concluded that it might be possible to increase the molecular weight of the polymer slightly with much effort by careful studies and optimization of the polymerization conditions. We also concluded that copolymers from trans-butene-2 and maleic anhydride would behave rather similarly to the cis-butene-2 as judged by the experience of Imoto and his co-workers, and we were satisfied with our experimental results.

Radical chain transfer in α-olefins or internal olefin polymerization is well known with monomers which have a hydrogen atom next to the carbon-carbon double bond which is readily abstracted. The allylic radical which is produced is very stable and does not undergo further double bond addition and consequently polymerization. This is the reason why high molecular weight homopolymers of α-olefins cannot be made by regular radical polymerization, and relatively low molecular weight polymers can only be made at extremely high pressures 7.

In copolymerization of trans-butene-2 with maleic anhydride, the highly resonance stabilized polymer radical which possesses the maleic anhydride group at the end of the growing polymer chain is probably the terminal radical most of the time during the copolymerization and is not reactive enough for radical abstraction reactions; consequently copolymers of reasonable molecular weight can be obtained without great difficulty. Nevertheless, the very reactive polymer radical with an aliphatic group at the end of the chain must also be present a fraction of the time and would be capable of abstracting a hydrogen from unreacted butene-2 to form allylic radicals which may terminate growing chains:



It is assumed in these considerations that the copolymerization of cis-butene-2 and maleic anhydride does not occur by direct "homopolymerization" of charge transfer complexes. These results also explain the fact that low molecular weight polymer has been obtained in the free radical initiated copolymerization of cis-butene-2 with maleic anhydride but not in copolymerizations of maleic anhydride with stilbene and ethylene. By optimizing reaction conditions of the cis-butene-2/maleic anhydride copolymerization, we were able to increase the inherent viscosity from the previously reported 0.05 to 0.25 g/dl. (IR spectrum, Fig. 1a.)

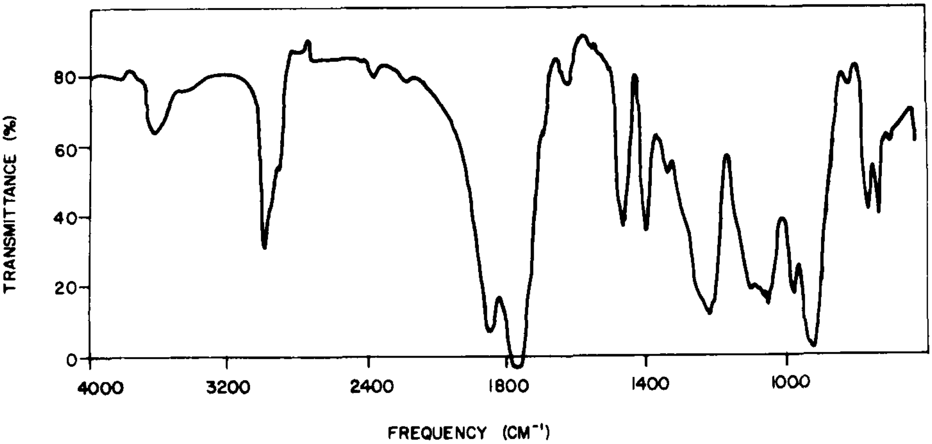
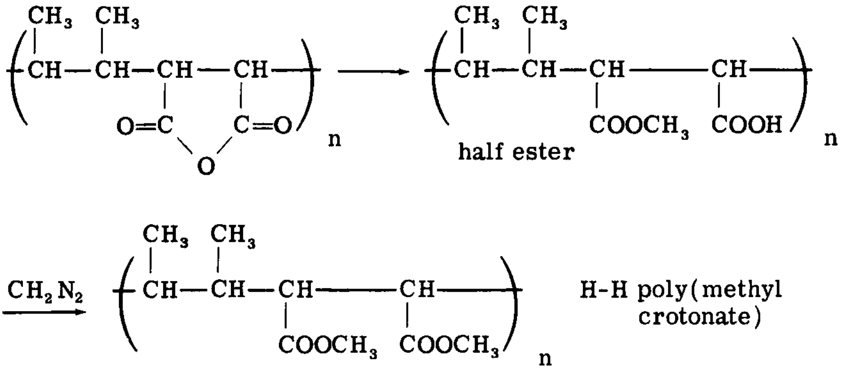


FIG. 1a. Infrared spectrum (film) of alternating cis-butene-2/maleic anhydride copolymer.

Considerations that relatively unreactive resonance-stabilized radicals are carriers of the polymerization for most of its course also explain why chloroform does not act as a chain transfer in this polymerization. We have carefully analyzed polymers obtained from copolymerizations of cis-butene-2 and maleic anhydride with chloroform as the solvent. However, within the experimental limits of the chlorine determination, no chlorine was found in the polymer.

Esterification of the cis-butene-2/maleic anhydride copolymer was accomplished in a way similar to the esterification of the ethylene/maleic anhydride copolymer reported earlier [2]. The esterification of the cis-butene-2/maleic anhydride copolymer was accomplished in two steps. The first step was the formation of the half-ester by reacting the copolymer with an excess of methanol in the presence of sulfuric acid as the catalyst:



Completion of the esterification was accomplished successfully with diazomethane in ether. The initial polymeric half-ester was not soluble in toluene, the solvent of choice. However, the suspension of the polymer went into solution as the reaction proceeded; when about 1/3 of the diazomethane solution was added, a clear polymer solution was obtained.

According to the elemental analysis (Table 3) and the IR spectrum (Fig. 1b), the polymer was completely esterfied and was in fact H-H poly(methyl crotonate). Additional evidence for the purity of the material was provided by trace analysis for free carboxyl groups. It was found by acid-base titration (which has a sensitivity of about ±0.1 mole % carboxyl groups) that our polymer contained less than 0.1 mole % of free carboxyl groups. (IR spectrum, Fig. 1b.)

TABLE 3. Analysis of H-H Poly(methyl Crotonate)

Elemental analysis, in %				Original maleic anhydride/ cis-butene-2 copolymer	
C	H	O	η_{sp}/c^{a}	Polymerization Conditions	η_{sp}/c^{b}
59.8	8.2	31.5	0.14	BPO/60°C	0.15
61.1	8.2	31.5	0.25	AIBN/35°C	0.25
60.0[c]	8.0[c]	32.0[c]			

[a] 0.2 g/dl in CF_3COOH at 30°C.
[b] 0.2 g/dl in dimethyl formamide at 30°C.
[c] Theory.

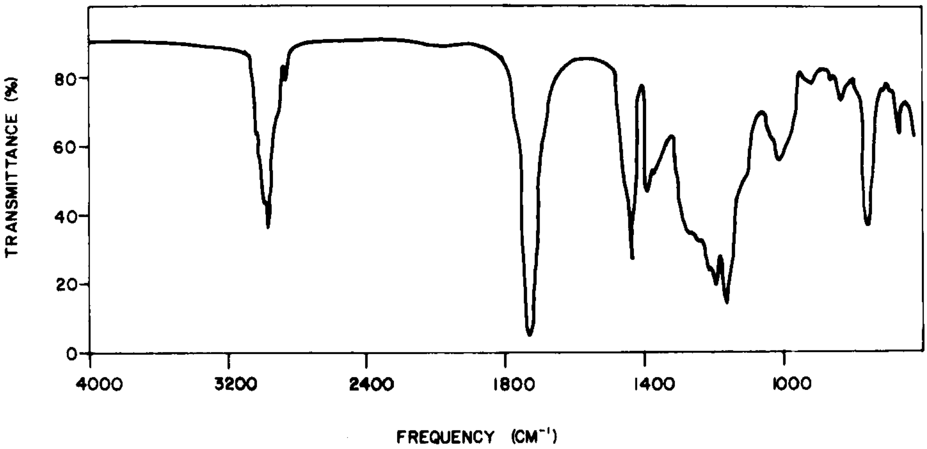


FIG. 1b. Infrared spectrum (film) of H-H poly(methyl crotonate).

H-H Poly(methyl crotonate) (with an inherent viscosity of up to 0.25 g/dl) was soluble in benzene, toluene, acetone, dimethyl formamide, trifluoroacetic acid, and dichloroacetic acid.

According to x-ray diffraction studies, H-H poly(methyl crotonate) was amorphous with a broad halo at around 4 Å. The specific viscosity of H-H poly(methyl crotonate) is low compared to poly(methyl cinnamate) and poly(methyl acrylate) which had been previously prepared. There was little change in the inherent viscosity between the cis-butene-2/maleic anhydride copolymer and the H-H poly(methyl crotonate), indicating that no molecular weight decrease occurred during the esterification reaction. However, it should be emphasized that the solvents for the solution viscosity measurements of both polymers were different.

The IR spectrum of H-H poly(methyl crotonate) (Fig. 1b) was determined as a film. It showed no evidence for residual carboxylic acid or anhydride groups and only a strong carbonyl group at 1780 to 1800 cm^{-1}. The starting material, cis-butene-2/maleic anhydride copolymer, showed strong absorption bands at 1850 and 1790 cm^{-1} and, in addition, a band at 3590 cm^{-1}, indicating that some of the anhydride groups had been hydrolyzed to free carboxylic acid groups (Fig. 1a).

H-T Poly(methyl crotonate) was prepared from trans-methyl crotonate at a polymerization temperature of -78°C in about 20% overall yield. The calcium/zinc alkyl initiator was prepared prior to the polymerization. The polymer had some crystallinity and an

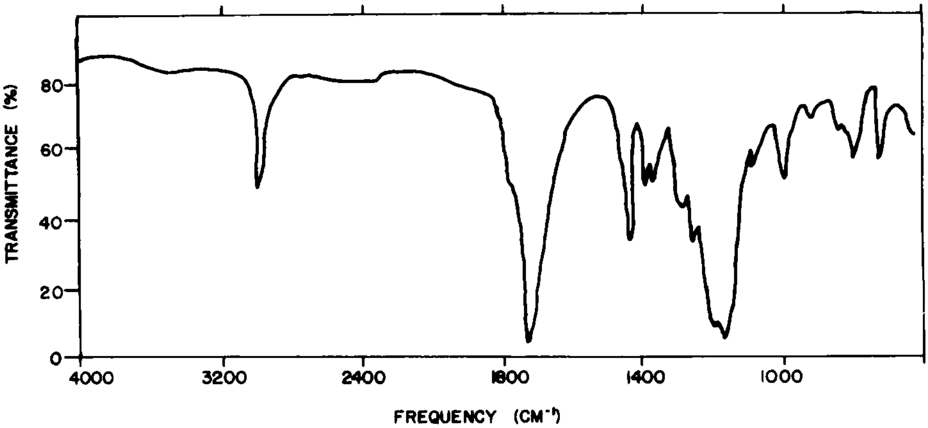


FIG. 1c. Infrared spectrum (film) of H-T poly(methyl crotonate).

inherent viscosity of about 0.9 in trifluoroacetic acid. From the anionic polymerization mechanism of polymerization, earlier investigators [5] assumed a complete H-T structure of the polymer. Our IR spectrum and particularly the NMR spectrum are consistent with that of a H-T poly(methyl crotonate) (Fig. 1c).

The NMR spectrum of H-T and H-H poly(methyl crotonate) was taken in a 3% solution of trifluoroacetic acid at 35°C. H-T Poly(methyl crotonate) has three areas of resonance; the C-methyl protons at 0.5 ppm, the methine protons at 2.1 ppm, and the methoxy protons at 3.4 ppm in a ratio of 3:2:3 as expected from the proposed structure. A 3:2:3 ratio of the protons was also observed in the case of the NMR spectrum of H-H poly(methyl crotonate). The C-methyl protons were at 0.5 ppm and the methoxy protons at 3.3 ppm. However, the chemical shift of the methine protons attached to the carbomethoxy-substituted carbon were clearly separated from those attached to the C-methyl group. The C-methine protons had a chemical shift at 1.5 ppm and the protons attached to the carbomethoxy carbon had a shift at 2.3 ppm. As in the case of previous NMR spectra [1, 2], no additional structure indicating the stereochemistry of the appropriate side groups could be evaluated on the basis of these spectra. Work is now under way on the determination of the fine structure of these polymers with the use of a 300 MHz Varian NMR Spectrometer.

The thermal behavior of H-H and H-T poly(methyl crotonate) was measured by differential scanning calorimetry (DSC). The H-H poly(methyl crotonate) showed a transition point, apparently the glass transition, at 95°C. There was no detectable glass transition

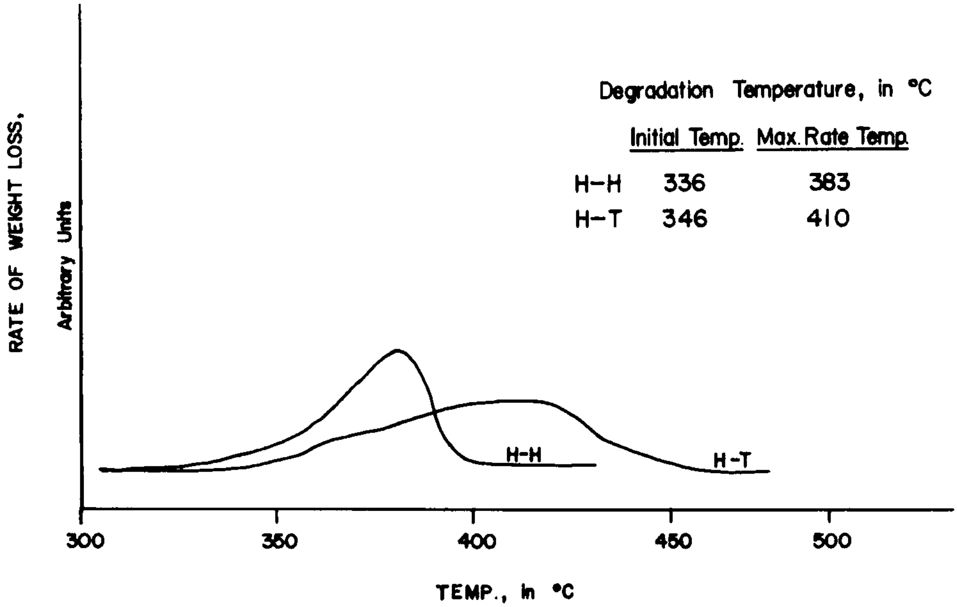


FIG. 2. Thermal degradation of H-H and H-T poly(methyl crotonate) by DTG.

in our sample of the H-T polymer until decomposition occurred around 340°C.

The thermal gravimetric analysis of H-H and H-T poly(methyl crotonate) showed that the onset of degradation and the rate of maximum degradation are substantially different from each other. The degradation of each polymer started around 340°C. The maximum rate of degradation in the case of the H-H polymer was at 380°C and for the H-T polymer at 410°C (Fig. 2). As a comparison, H-H and H-T poly(methyl cinnamate) also had different maximum rates of degradation; the H-H polymer had a maximum degradation temperature at 376°C and the H-T polymer at 410°C. Both H-H and H-T poly(methyl acrylate) had a similar maximum degradation rate temperature of 418°C.

Pyrolysis gas chromotography of H-H and H-T poly(methyl crotonate) showed that these polymers degraded primarily to small molecules, such as CO_2 and methanol; both polymers also formed a substantial amount of nonvolatile char. In the case of the H-H polymer the char was 36% of the total amount of polymer charged, and in the case of the H-T polymer, 20% char was formed upon pyrolysis (Table 4).

TABLE 4. Relative Molar Ratios of Pyrolysis Products from H-H and H-T Poly(methyl Crotonate)

	CO_2	MeOH	cis-Butene-2	Methyl crotonate	Dimethyl maleate and dimethyl fumarate	Nonvolatile char: wt% of the polymer
H-H	3.0	3.0	0.6	1	0.5	36
H-T	2.6	1.8	0	4.6	0	20

In H-H poly(methyl crotonate) pyrolysis, the primary degradation product of the C_3 to C_5 fraction was the monomer, methyl crotonate. Even in H-H poly(methyl crotonate) degradation, methyl crotonate was one of the major products of pyrolysis. However, similar to the pyrolysis of H-H poly(methyl cinnamate), fragmentation to the "original comonomers," cis-butene-2 and a mixture of dimethyl maleate and dimethyl fumurate, also occurred. These compounds were found in amounts similar to methyl crotonate on pyrolysis.

The results of the thermal gravimetric analysis and pyrolysis gas chromotography showed that poly(methyl crotonates) behave more like poly(methyl cinnamates) rather than like poly(methyl acrylate). This is not surprising since it is well known that degradation to monomer in the case of addition polymers occurs more readily when the degrading polymeric radical is resonance stabilized or highly substituted. It may be recalled that thermal degradation of poly(methyl methacrylate) gave almost exclusively methyl methacrylate monomer, but only trace amounts of monomer (methyl acrylate) was obtained when poly(methyl acrylate) was thermolyzed. A similar situation occurred when poly(α-methyl styrene) was degraded and its degradation pattern was compared with the degradation pattern of polystyrene. Poly(α-methyl styrene) degraded extensively to monomer (α-methyl styrene) while polystyrene degraded to higher molecular weight fragments and only to minor amounts of styrene monomer.

In this and previous papers, substituted poly(methyl acrylates) with different substituents on the methylene group were prepared and their properties, particularly their degradation pattern, were compared. H-H and H-T poly(methyl acrylate), poly(methyl cinnamate), and poly(methyl crotonate) degraded with different degradation patterns. Any substitution of a hydrogen atom in the backbone chain by a methyl or phenyl group lowered the degradation temperature of the substituted H-H polymers but not that of the H-T polymers. When the H-H polymers had substituents which permitted a high degree of resonance stabilization of the radicals during degradation, breakdown to monomeric units was highly favored with only small amounts of char formation.

The maximum rate of degradation was not significantly lowered if the substituent was a methyl group. Unsubstituted H-H poly(methyl acrylate) had the same thermal stability as H-T polymer. Since resonance stabilization of the degrading polymer molecules was not possible, side reactions occurred which ultimately led to char formation and the formation of very small molecules such as CO_2 and methanol.

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REFERENCES

[1] Part I, T. Tanaka and O. Vogl, Polym. J., In Press.
[2] Part II, T. Tanaka and O. Vogl, J. Macromol. Sci.—Chem., A8, 1059 (1974).
[3] T. Otsu, A. Shimizu, and M. Imoto, J. Polym. Sci., B, 2, 973 (1964).
[4] T. Tsuruta, T. Makimoto, and K. Tanabe, Makromol. Chem., 114, 182 (1968).
[5] F. Arndt, C. R. Noller, and I. Bergsteinsson, Org. Syn. Coll. Vol. II (1943).
[6] O. Vogl, V. Ivansons, H. C. Miller, and H. W. Williams, J. Macromol. Sci.—Chem., A-2, 175 (1968).
[7] B. C. Anderson, C. H. Hoover, and O. Vogl, Macromolecules, 2, 686 (1969).

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