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Head-to-Head Polymers. XXII. Toward the Synthesis of Pure Head-to-Head Poly(methyl Methacrylate): Copolymerization of 2,3-Dimethylmaleic Anhydride and Ethylene

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Head-to-Head Polymers. XXII. Toward the Synthesis of Pure Head-to-Head Poly(methyl Methacrylate):* Copolymerization of 2,3-Dimethylmaleic Anhydride and Ethylene

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ABSTRACT

Copolymerization of 2,3-dimethylmaleic anhydride and ethylene has been accomplished under ethylene pressure (up to 1000 psi) with AIBN as the initiator. The copolymers were obtained at relatively low yield and only of moderate molecular weight. The incorporation of 2,3-dimethylmaleic anhydride units into the copolymer is about 20 mol% at 1000 psi and is 33 mol% at 500 psi of ethylene pressure. Unlike maleic anhydride-ethylene copolymers, alternating 2,3-dimethylmaleic anhydride-ethylene copolymers of reasonable molecular weight have not yet been prepared. 2,3-Dimethylmaleic anhydride-ethylene copolymers could be hydrolyzed to the polymeric acids and quantitatively esterified to the polymeric methyl esters. Both anhydride and ester copolymers have been characterized spectroscopically and by their thermal behavior.

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*Part XXI: F. Xi, W. Bassett, Jr., and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 21(3), 891 (1983).

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INTRODUCTION

Alternating copolymers of maleic anhydride (MA) and ethylene (Et) have been known for a long time; they can readily be prepared by solution polymerization of MA under moderate pressure of about 400 psi Et [1-3]. These polymers have been the starting materials for the preparation of head-to-head (H-H) polyacrylates [4-8].

Copolymers of 2,3-dimethylmaleic anhydride (DMMA) were not known until recently [9-11] although earlier but incorrect reports of such copolymers were claimed in the literature [12]. The copolymerization of DMMA had initially been accomplished only with alkyl vinyl ethers (AVE); early copolymerization attempts of DMMA with styrene had only given the homopolymer of styrene [12]. The copolymers of DMMA with MVEs could be hydrolyzed and esterified to the corresponding methyl esters [9-11].

For the preparation of H-H poly(methyl methacrylate) (PMMA), one approach was considered to be the alternating copolymerization of DMMA with Et followed by hydrolysis and esterification.

It was the objective of this work to study the copolymerization of DMMA and Et and, if successful, to attempt to prepare alternating copolymers of DMMA and Et of high molecular weight. The hydrolysis and esterification of alternating DMMA-Et copolymers of reasonable molecular weight to H-H PMMA and the characterization of these polymers was the ultimate objective.

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EXPERIMENTAL PART

Materials

2,3-Dimethylmaleic anhydride (DMMA) (Aldrich Chemical Co.) was purified by three sublimations at 0.1 mm and 65°C.

Ethylene (Et) (research grade, purity 99.98%) was obtained from Matheson Gas Products and used without further purification.

Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was purified by recrystallization three times from dry methanol and was dried overnight at room temperature and at 0.5 mm.

Benzene (MCB Manufacturing Chemists, Inc., reagent grade) was heated to reflux over sodium and distilled under nitrogen.

Dimethyl sulfate (Mallinckrodt Chemical Works) was distilled before use.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 Spectrophotometer. The infrared spectra of the polymer samples were measured as films cast directly from acetone solution onto a single sodium chloride plate.

The ^{1}H-NMR spectra were recorded on a 60 MHz-24 Hitachi Perkin-Elmer Spectrometer using 10 to 15% polymer solutions in $CDCl_3$ at room temperature with TMS as the internal standard. ^{13}C-NMR spectra were obtained on a Varian CFT-20 spectrometer under complete proton decoupling.

A Perkin-Elmer DSC-2 Differential Scanning Calorimeter was used for the determination of the glass transition temperature (T_g) at a programmed temperature increase of 20°/min.

The thermal degradation was carried out in a nitrogen atmosphere using a Perkin-Elmer TGS-2 Thermogravimetric Analyzer at a programmed rate temperature of 5°C/min.

The high pressure polymerizations were carried out in a Parr stirred autoclave (Parr Instrument Company, 160 mL size) with an automatic temperature measurement and control equipment.

The molecular weight was measured on a Waters Model 201 Gel Permeation Chromatograph and calculated based on polystyrene standard samples.

Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

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Preparations

Copolymerization of 2,3-Dimethylmaleic Anhydride with Ethylene

DMMA (10.1 g, 80 mmol) and AIBN (330 mg, 2.5 mol% based on DMMA) were dissolved in benzene (80 mmol) at room temperature. The solution was transferred to the autoclave (160 mL size, Parr Instrument Co.) and the autoclave was closed.

This system was then flushed with high purity Et by alternately raising the pressure to 100 psi and then releasing (five times). The autoclave was then pressurized to approximately 300 psi; agitation was started and the charge was heated to 60°C which raised the pressure to about 400 psi. The pressure of Et increased to 900 psi and was maintained throughout the reaction by adding Et to replace the Et that was consumed during the polymerization. Total polymerization time was 5 d.

At the end of the reaction period the autoclave was allowed to cool and the pressure was released. The autoclave was opened, the solution was concentrated to about 30 mL on a rotary evaporator, and the concentrated solution was added dropwise with stirring to methanol (300 mL). A white powder precipitated which was filtered, washed 5 times with methanol, dried, and dissolved in acetone (20 mL). The solution was filtered to remove some insolubles, and poured into methanol; a fine white powder precipitated which was collected by filtration and dried overnight at 0.1 mm and 65°C. Yield: 2.3 g (14% based on DMMA), η_{inh} = 0.08 dL/g in DMF at 30°C. The molecular

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TABLE 1. Copolymerization of 2,3-Dimethylmaleic Anhydride (DMMA) with Ethylene (Et)[a]

DMMA (g)	Ethylene pressure (psig)	AIBN (mg)	Yield,[b] g (%)	η_{inh}[c]	GPC (MW)	Elemental analyses (%)		Calculated composition of copolymers
						Found	Calcd	
5.05	1,100	66	0.61 (6)	0.09	7,400	C, 70.46; H, 9.11	C, 70.56; H, 9.30	$-(C_2H_4)_{0.80}(C_6H_6O_3)_{0.20}$
5.05	1,000	66	0.74 (8)	0.10	7,800	C, 69.86; H, 9.30; N, 0.33	C,69.71; H, 9.03	$-(C_2H_4)_{0.78}(C_6H_6O_3)_{0.22}$
10.1	900	330	2.30 (14)	0.08	4,600	C, 68.31; H, 8.55	C, 68.19; H, 8.51	$-(C_2H_4)_{0.74}(C_6H_6O_3)_{0.26}$
10.1	700	330	1.56 (10)	0.09	5,300	C, 67.65; H, 8.65	C, 67.51; H, 8.28	$-(C_2H_4)_{0.72}(C_6H_6O_3)_{0.28}$
10.1	500	330	0.98 (7)	0.08	4,800	C, 66.02; H, 8.26; N, 0.97	C, 66.00; H, 7.77	$-(C_2H_4)_{0.67}(C_6H_6O_3)_{0.33}$
10.1	350	330	0.50 (4)	-	4,400	C, 63.86; H, 7.91; N, 1.22; MW, 1150 or 2300	C, 63.85; H, 7.03	$-(C_2H_4)_{0.56}(C_6H_6O_3)_{4.44}$
10.1	200	330	30 mg	-	4,100	C, 64.10; H, 7.58; N, 1.60; MW, 870 or 1700	C, 63.98; H, 7.06	$-(C_2H_4)_{0.56}(C_6H_6O_3)_{0.44}$
10.1	100	330	20 mg	-	4,200	C, 64.19; H, 7.79; N, 1.62; MW, 870 or 1700	C, 64.17; H, 7.13	$-(C_2H_4)_{0.57}(C_6H_6O_3)_{0.43}$
10.1	60	330	10 mg	-	-	-	-	-

[a] Polymerization temperature, 60°C; time 5, d; solvent: Benzene, 80 mL.

[b] Based on DMMA.

[c] 0.5 g/dL in DMF, 30°C.

weight was determined by GPC to be 4600. Elemental analysis: Found: C, 68.31%; H, 8.55%. The composition of copolymer was calculated according to the carbon/hydrogen elemental analysis data and showed about 26% of structure units of the copolymer came from DMMA. The infrared spectrum showed characteristic peaks of the succinic anhydride unit at 1785 and 1850 cm^{-1}. The copolymerizations were carried out under varied conditions of Et pressure; details of these polymerization experiments are shown in Table 1.

Esterification of Poly(2,3-dimethylmaleic Anhydride-co-Ethylene)

Poly(DMMA-co-Et) (0.5 g) was suspended in a solution of 13 g of sodium hydroxide in 110 mL of methanol. The solution was heated to reflux for several days; the polymer was repeatedly analyzed by IR during this period to estimate the progress of the hydrolysis; after 5 d less than a half of the dimethyl succinate anhydride rings in the copolymer had been opened. Distilled water (150 mL) was added to the methanol solution and a clear solution was obtained. The methanol was removed by distillation and the now aqueous sodium hydroxide copolymer solution was allowed to reflux for another 5 d. The solution was then allowed to cool to room temperature and diluted to about 300 mL by adding distilled water. Dimethyl sulfate (120 mL) was added to the solution with vigorous stirring which was maintained for 2 h. The dimethyl sulfate layer which contained the esterified copolymer was separated and the polymer was precipitated by pouring the solution into a water-methanol (4:1) mixture. The polymer was dissolved in acetone (10 mL) and the solution was poured into water which precipitated the polymer. The copolymer was collected and dried overnight at 0.05 mm and room temperature. Yield: 0.20 g. Elemental analysis: C, 64.6%; H, 9.13%. The IR spectrum showed the characteristic absorption band of ester carbonyl at 1733 cm^{-1}.

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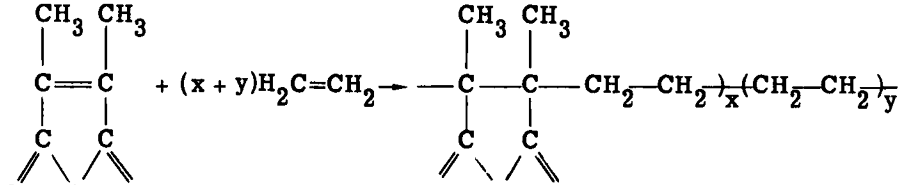
RESULTS AND DISCUSSION

Copolymerization of DMMA with Et has been achieved (Eq. 1); at higher Et pressure the copolymers are of relatively low DMMA content. At very low pressure of Et the copolymerization yielded polymers which approach alternating character but are of low molecular weight. The yield is also very low.

Copolymerization of DMMA with Et was accomplished at 1100 psi Et pressure; under these conditions the copolymer was obtained in 6% yield in 5 d reaction time and 60°C with AIBN as the initiator; the molecular weight was 7400 (GPC molecular weight) and the analysis of the copolymer showed that 20 mol% of DMMA had been incorporated into the copolymer. It should be pointed out that the low concentration of DMMA (15%) in benzene was necessary in order to keep the DMMA in solution during the reaction. At 1000 psi an 8% yield of copolymer



(1)

was obtained with an inherent viscosity of 0.10 dL/g and a 22% incorporation of DMMA units. As we go to a reaction pressure of Et of 500 psi, we obtained a copolymer in 7% yield with an inherent viscosity of 0.08 dL/g and a molecular weight of 4800; 33 mol% of the MMA units were incorporated into the copolymer (Table 1).

Decreasing the pressure from 350 to 100 psi gave, in three separate runs and in very low yield, polymers in the neighborhood of a molecular weight of about 4000 as judged by GPC (styrene standard) with 44% DMMA mol% units incorporated in the copolymer. The molecular weight, judged from nitrogen analysis of the initiator fragment in the polymer, is about 1000 when it is assumed that termination of the polymerization was by disproportion which would give a DP of 6-10. Should recombination be the exclusive termination reaction, the molecular weight of the copolymer would be twice that amount (about 2000) or a DP of about 12-20. This value of the molecular weight is particularly important when we later discuss the T_g of the corresponding esterified polymers.

All samples of poly(DMMA-co-Et) were hydrolyzed by first suspending the polymer into methanolic sodium hydroxide. The solution was heated to reflux for several days while water was added; during this procedure the progress of hydrolysis of the polymer was repeatedly analyzed by measuring the infrared spectrum of the polymer after isolation. The hydrolysis was continued for about 10 d and the polymeric sodium salt methylated with dimethyl sulfate.

The typical infrared spectrum for the initial anhydride polymer showed the double peak of the anhydride at 1785 and 1850 cm^{-1} (Fig. 1). The polymer selected for this characterization was a polymer that contained about 33% of DMMA units. After esterification only one peak of the ester band of the methyl 2,3-dimethylmaleate (fumarate) unit was left at 1733 cm^{-1}.

The ^1H-NMR spectra are shown in Fig. 2. They show the typical spectra expected from a DMMA/Et copolymer with the ^1H-NMR resonance of the methyl groups and the methylene groups in the 1.0-1.2 ppm region. After the polymer had been esterified, the ^1H-NMR resonance at 3.7 ppm for the protons of the O-methyl group of the methyl ester was observed.

In Table 2 and Figure 3 we see ^{13}C-NMR chemical shift data and the spectra of poly(DMMA-co-Et) of three copolymer compositions. The typical values for the ^{13}C chemical shifts (Fig. 3) can be identified for the carbonyl carbon atom at 175 ppm, the quartenary carbon atom

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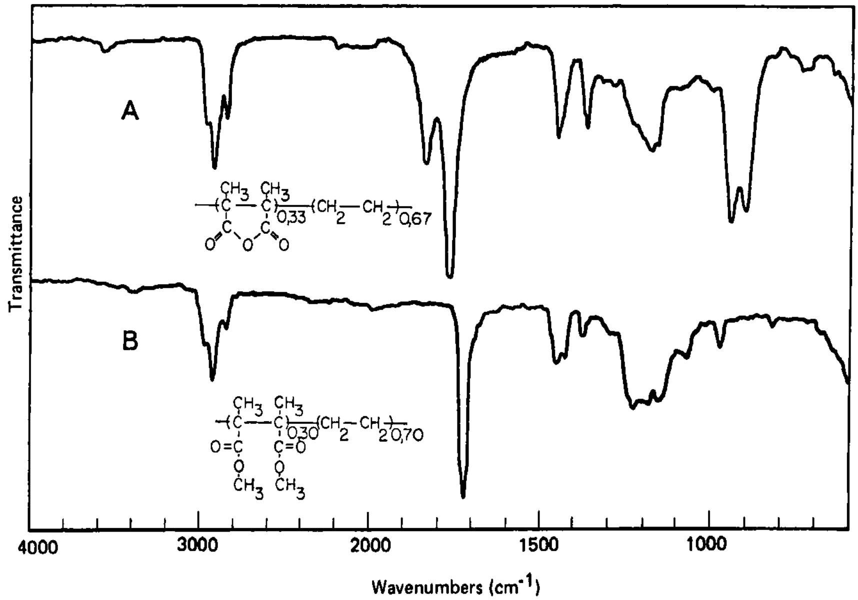

FIG. 1. Infrared spectra of (A) poly(2,3-dimethylmaleic anhydride-co-ethylene) (33% of DMMA units), (B) poly(methyl 2,3-dimethylmaleate (fumarate-co-ethylene) (30% of methyl 2,3-dimethylmaleate (fumarate) units).

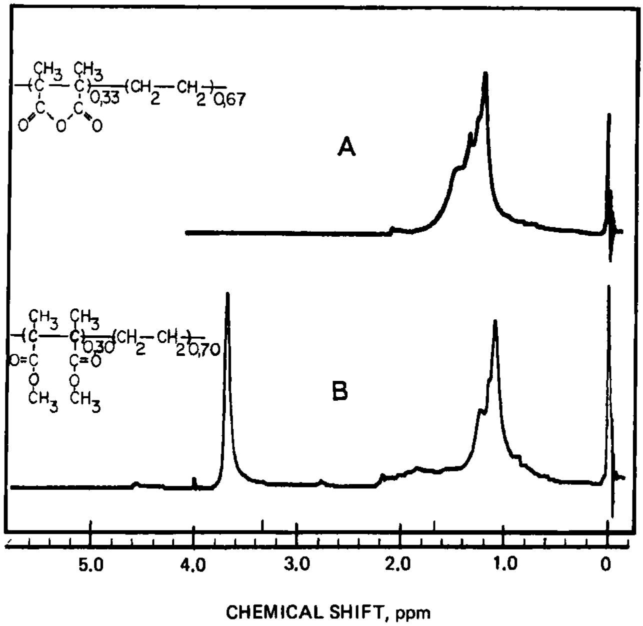

FIG. 2. ^{1}H-NMR spectra of (A) poly(2,3-dimethylmaleic anhydride-co-ethylene) (33% of DMMA units), (B) poly(methyl 2,3-dimethylmaleate (fumarate-co-ethylene) (30% of dimethyl 2,3-dimethylmaleate (fumarate) units).

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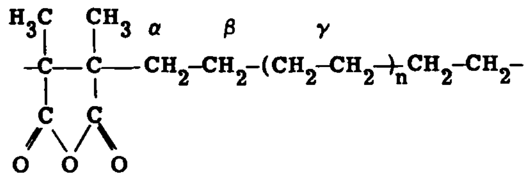
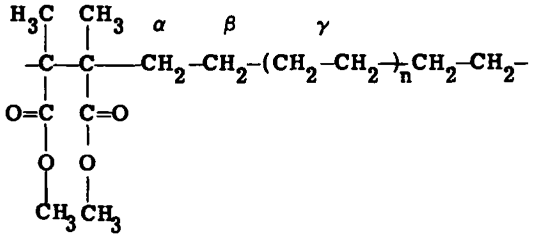
TABLE 2. ^{13}C-NMR Chemical Shift Values of Poly(2,3-dimethylmaleic Anhydride-co-Ethylene) and Its Methyl Ester

	Chemical shift (δ_{TMS})[a]						
					–CH_2–		
Polymers	–CH_3	–OCH_3	$-\overset{\mid}{\underset{\mid}{C}}-$	>C=O	α	β	γ
Poly(2,3-dimethylmaleic anhydride-co-ethylene)							
	14.5	-	52.0, 52.4	175.0, 175.2	37.3	24.5, 24.7, 24.9	29.4
Poly(methyl 2,3-dimethylmaleate (fumarate)-co-ethylene)							
	18.0	51.5	52.1	175.5	33.5	25.6, 26.4	29.5, 30.2

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[a] Solvent, $CDCl_3$, about 10%.

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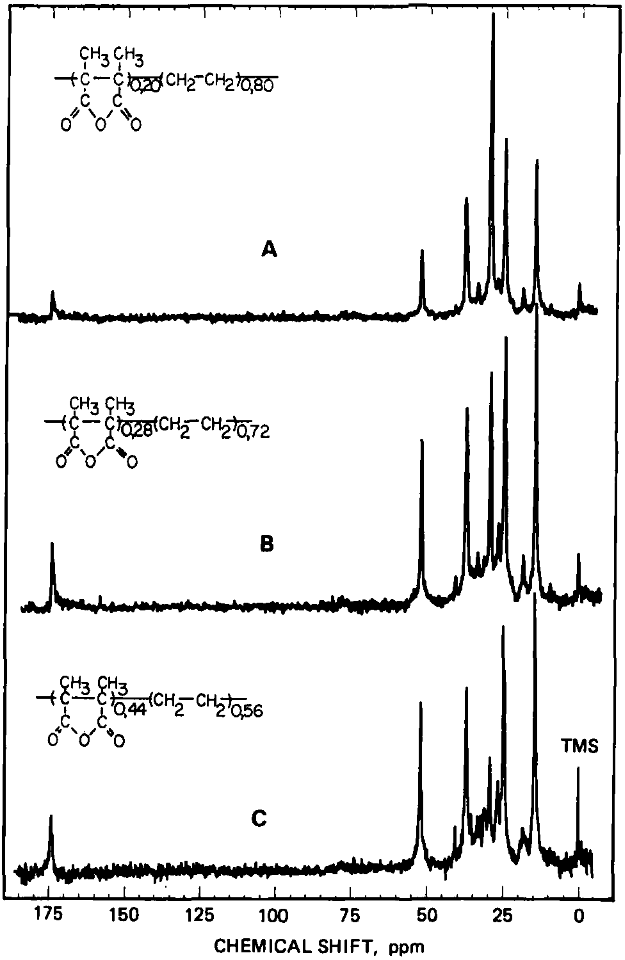

FIG. 3. ^{13}C-NMR spectra of poly(2,3-dimethylmaleic anhydride-co-ethylene): (A) 20% DMMA units, (B) 28% DMMA units, (C) 44% DMMA units.

of the tetrasubstituted succinate unit at 52 ppm, and the carbon atom of the methyl groups of the succinate unit at 14 ppm. A number of ^{13}C methylene chemical shifts can be identified for the methylene groups of the ethylene portion of the polymers ranging from 24 to 37 ppm.

When the spectrum of the copolymer of higher DMMA content was studied, we could see a change in the intensity of the peak at 15 ppm and also an intensity shift of the peak in the 25 and 26 ppm region.

These data seem to indicate that the run number of methylene groups is now different; the methylene groups directly attached to the succinate unit can be identified clearly from the methylene unit adjacent to another methylene unit. In fact, methylene units two carbon atoms removed from the methylene unit attached to the succinic anhydride unit can be identified separately. The peak at 30 ppm diminishes as we go to the spectrum (Fig. 3C) with only 56% methylene units, and only a small amount of the "free methylene" units is left. The spectrum of the polymer in Fig. 3(C) (44% DMMA units) is generally of a more complicated structure and endgroups seem to be noticeable.

It has been suggested earlier [13, 14] that when copolymerizations involving MA or its derivatives are carried out over long periods of time and with relatively large amounts of radical initiator, even if the initiator is a resonance stabilized radical such as that derived from AIBN (dimethylcyanomethyl radical), decarboxylation of succinic anhydride units in the polymer could occur, ultimately leading to branched structures. Unfortunately, the molecular weight of the polymers that are approaching alternating polymer structure are too low and the endgroups can be seen clearly which did not allow us to settle definitely the problem of decarboxylation. While we believe that we have not seen any indication of chain branching based on our analysis, low yields, low molecular weights, and a number of extraneous peaks in the ^{13}C spectrum do not exclude the possibility of some branching in the polymer.

When one observes, however, the carbonyl frequency which is very clearly separated in the spectrum, one would expect (if carboxylation had occurred) that carbonyl groups, in addition to the carbonyl carbon of the anhydride group, would show up in the carbonyl region which is relatively free of other peaks. However, because of the NOE giving low intensity of the carbonyl carbon of the anhydride group, this observation and the subsequent judgment could not be made with any certainty although only one carbonyl peak was identifiable.

One of the important objectives of this work was the determination, or at least an estimation, of the T_g of H-H PMMA by extrapolation of the copolymer's T_g to that of alternating poly(2,3-dimethylmaleate (fumarate)-co-Et) which is H-H PMMA. We have measured the T_g's of our DMMA/Et copolymers (Fig. 5) but since the copolymers had only relatively low molecular weight, the extrapolation to the T_g of the alternating DMMA/Et copolymer is uncertain. The molecular weight of DMMA/Et up to a DMMA content of 33% would probably be sufficient for an attempt to extrapolate to the T_g of the alternating copolymer (Fig. 6).

It is clear that the molecular weight of the polymer with 44 mol% DMMA units is too low and the T_g values cannot be used for the extrapolation. If one extrapolates the few values for the T_g of the

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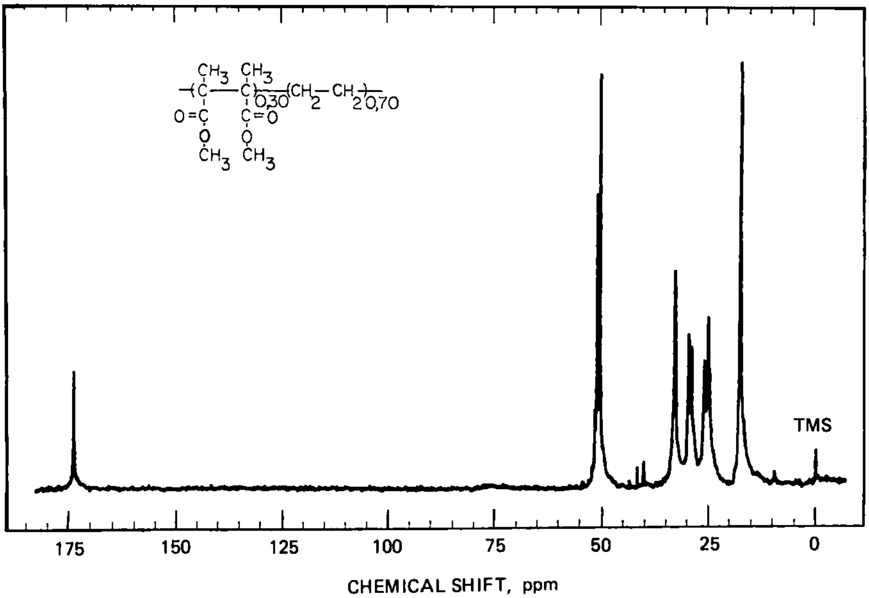

FIG. 4. ^{13}C-NMR spectrum of poly(methyl 2,3-dimethylmaleate (fumarate-co-ethylene) (30% of dimethyl 2,3-dimethylmaleate (fumarate) units).

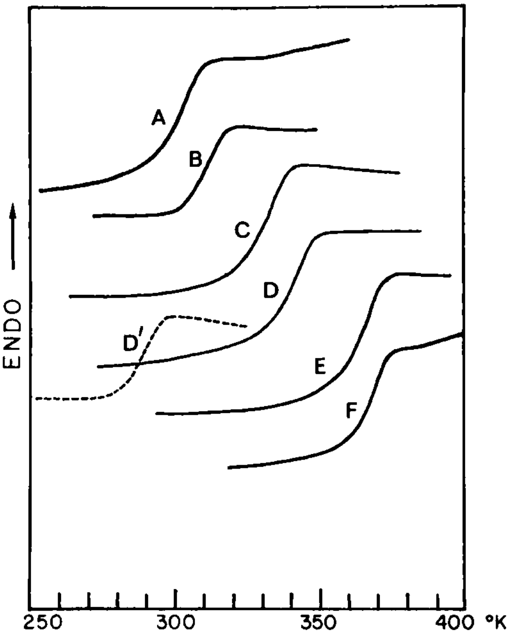

FIG. 5. DSC scan of poly(2,3-dimethylmaleic anhydride-co-ethylene) and its methyl ester. DMMA units incorporated: (A) 20%, (B) 22%, (C) 26%, (D) 28%, and its methyl ester (D'), (E) 33%, (F) 44%.

TABLE 3. Glass Transition Temperature as a Function of DMMA units in Poly(DMMA-co-Et)

DMMA units, % incorporated	T_g (°C)
20	20
22	29
26	47
28	59
33	82
44	89, 95

DMMA/Et composition from 20 to 33 mol% to the alternating copolymer composition, one finds an extrapolated T_g of 164°C.

The DMMA/Et copolymer was esterified to the 2,3-dimethylmaleate (fumarate) units containing copolymer (Fig. 4). For example, the T_g of this 28% copolymer was 8°C, 51°C lower than the T_g of the same sample (59°C) before esterification (Table 3).

Degradation studies on the DMMA/Et copolymers and their esterified materials have shown that the maximum rate of degradation is very similar to that of the esterified DMMA/MVE copolymers (Fig. 7).

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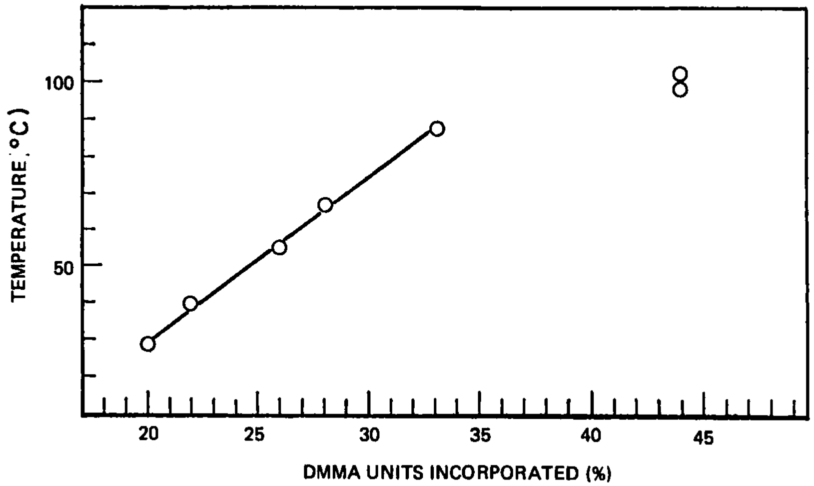

FIG. 6. Relationship between glass transition temperature (T_g) and composition of copolymers of 2,3-dimethylmaleic anhydride and ethylene of varying copolymer compositions.

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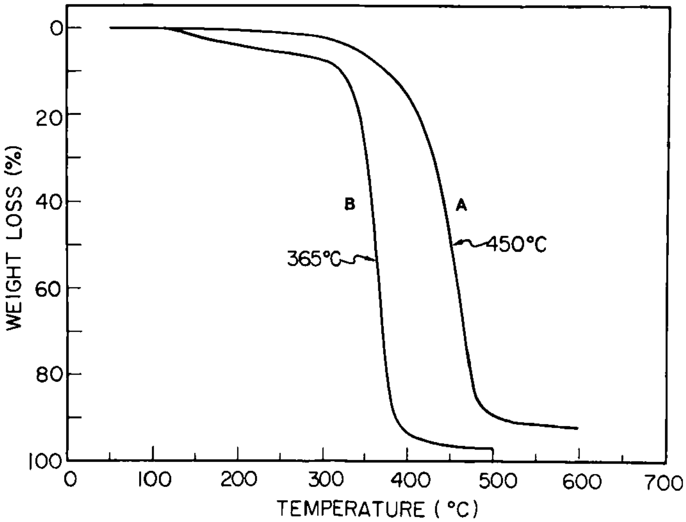

FIG. 7. Weight loss and rate of weight loss of poly(2,3-dimethylmaleic anhydride-co-ethylene) (A) and its methyl ester (B).

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