Synthesis of Copolymers of a Linoleic Acid Derivative and Properties of the Copolymer Films

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ABSTRACT: Addition copolymers of maleic anhydride and a commercially available conjugated fatty acid, Pamolyn 380, were synthesized via thermal initiation. The copolymers had moderately high molecular weights and were obtained in reasonable yields. The copolymers were characterized by nuclear magnetic resonance and infrared spectroscopy and by elemental analysis. Based on this analytical data and examples from the literature, the copolymers were assigned regularly alternating chain morphology. Coatings were formulated with the copolymers, and films over a metal substrate were evaluated. The films were found to have excellent solvent resistance, high hardness, and good gloss. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 261–267, 2001

Key words: Pamolyn 380; maleic anhydride; copolymers

INTRODUCTION

In an attempt to synthesize multifunctional molecules from readily available inexpensive starting materials, we decided to investigate the Diels-Alder reaction(s) of maleic anhydride with conjugated olefins. One such conjugated olefin, Pamolyn 380, is a commercially available mixture of conjugated (primarily linoleic) fatty acids. Available literature[1,2] stated that Pamolyn 380 readily gave Diels-Alder adducts in reaction with electron-poor species. Therefore, we decided to react maleic anhydride with Pamolyn 380 under Diels-Alder conditions[3] to obtain a multi-acid functional inexpensive molecule. However, after several attempts, we were able to obtain very little Diels-Alder reaction product. Instead, moderate yields of polymer were

obtained each time. This result was initially quite puzzling. However, a search of the literature revealed a series of excellent articles by Hall et al.[4,5] concerning the reactions of electron-poor species with conjugated double bonds. The work of Hall et al. conclusively demonstrated that, in many cases, polymer was the principal or only product. The product we obtained then is the product expected, i.e., polymer. However, this particular polymer has not been reported previously so we decided to investigate the synthesis and properties of the material in more detail. [After most of this work was completed, we realized that it might be possible to obtain the desired Diels-Alder adduct by inhibiting the free radical addition reaction. Accordingly, hydroquinone (1000–1500 ppm) was added to a reaction mixture. A significant quantity of Diels-Alder adduct was obtained. However, because this adduct is now part of a proprietary product, no further details can be given at this time. This report summarizes our findings to date.
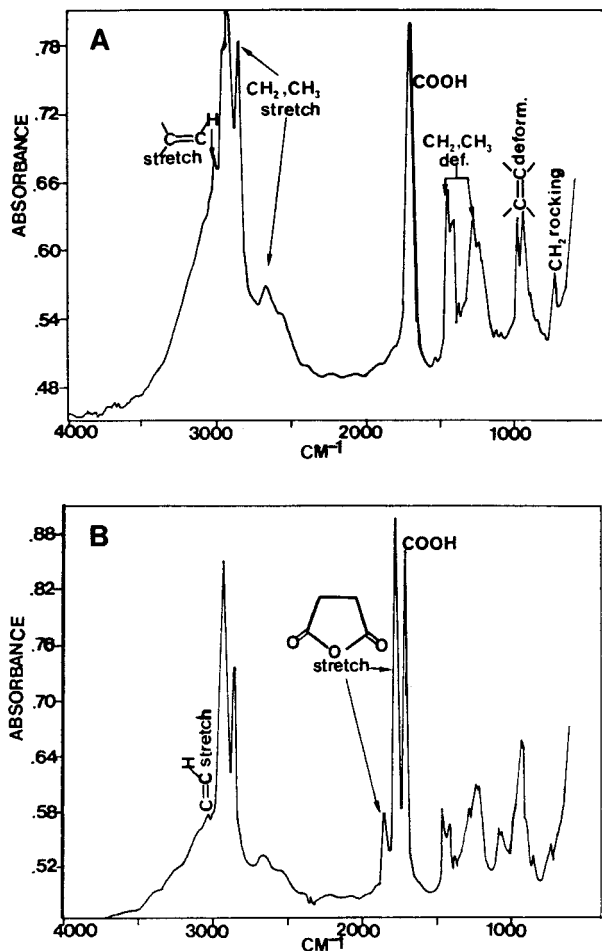
Figure 1 FTIR spectra of (A) Pamolyn 38, and (B) Pamolyn 380–maleic anhydride copolymer.

EXPERIMENTAL

General

The Pamolyn 380 used in this work was obtained form Hercules Inc. and was used as received. All other chemicals were obtained from Aldrich and were used without further purification. Molecular weights were measured with a GPC equipped with a Waters 510 pump, Waters 410 RI detector, and two Polymer Labs 30-cm linear microstyragel columns. Tetrahydrofuran was used as the eluent. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve. Nuclear magnetic resonance (NMR) spectra were obtained at ambient temperatures on CDCl$_3$ solutions of material using a Varian Gemini 300 FT NMR. Infrared spectra were recorded on films of material cast on NaCl plates using a Nicolet 5DxB FTIR.

Solvent resistance of polymer films was measured by counting the number of methyl ethyl ketone double rubs required to break through the film to the substrate below. The test was performed with an ATLAS AATCC Crockmeter. Impact resistances were measured with a Gardner Impact Tester using a 4-lb. weight. Gloss measurements were made with a BYK-Gardner Microtrigloss meter. Pencil harnesses were measured according to ASTM D3363. Galbraith Laboratories of Knoxville, Tennessee, performed elemental analysis. Glass transition temperatures were measured with a TA Instruments 2990 DSC.

Copolymer Synthesis

Pamolyn 380 (230 g) was charged to a 1-L flask equipped with a mechanical stirrer, reflux condenser, and thermometer. Freshly powdered ma-
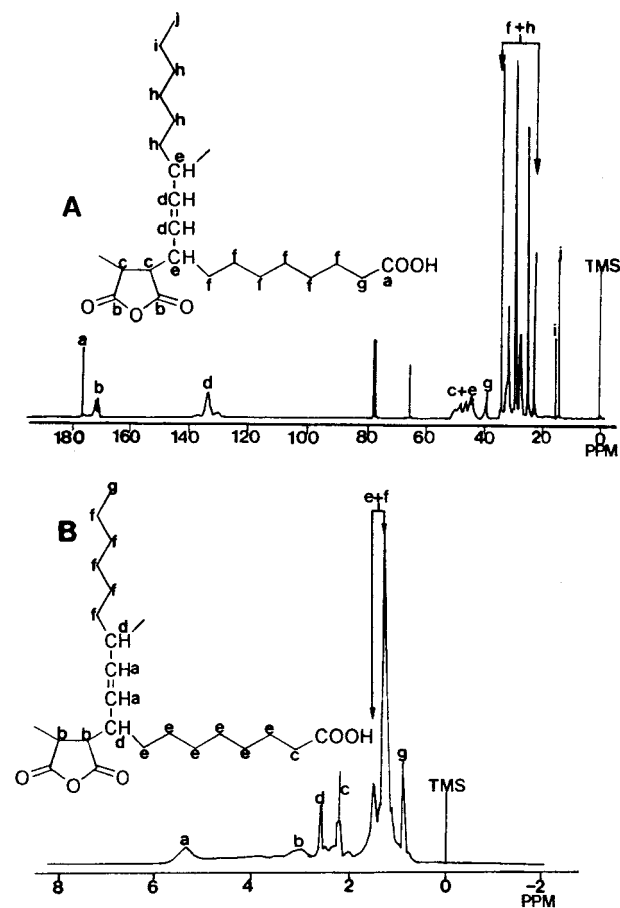

Figure 2 (A) 75.5 MHz ^{13}C-NMR spectrum of Pamolyn 380–maleic anhydride copolymer; (B) 300 MHz ^{1}H-NMR spectrum of Pamolyn 380–maleic anhydride copolymer.
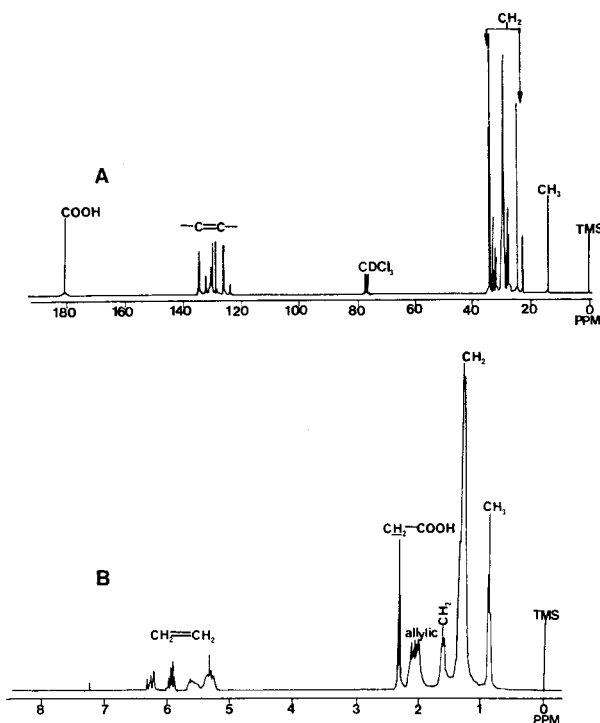
Figure 3 (A) 75.5 MHz ^{13}C-NMR spectrum of Pamolyn 380; (B) 300 MHz ^{1}H-NMR spectrum of Pamolyn 380.
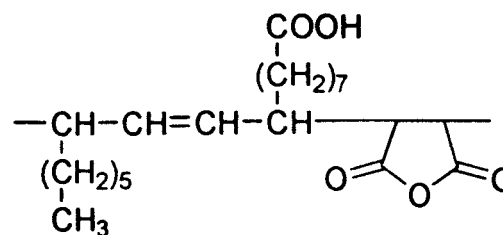

Figure 4 Copolymer structure.

tion into diethyl ether. The polymer was dried *in vacuo* at 35° until a constant weight was achieved (usually 72–100 h).

Time Conversion Experiments

Equal numbers of moles of Pamolyn 380 and maleic anhydride based on the conjugated double bond content of Pamolyn 380 (~80 mol %), were charged into clean, dry, thick-walled Pyrex glass vials. The vial contents were sparged with dry nitrogen (5 min), and the vials were then tightly sealed with Teflon lined caps. The vials were placed in a thermostated oil bath maintained at the desired temperature. The maleic anhydride is only sparingly soluble in Pamolyn 380, so it is necessary to wait until the maleic anhydride melts (20–30 s) and then vigorously shake the vial to ensure mixing of the comonomers. If this procedure is not followed, no copolymerization will occur. A vial was removed from the bath periodically, and the contents were cooled by placing the vial in an ambient temperature water bath. Chloroform was added (15 mL) and the resulting solution was then added to excess diethyl ether to precipitate the polymer. Purification was as described above.

Evaluation of Film Properties

Coating solutions were made by dissolving 50 g of copolymer in 100 g of methyl ethyl ketone and adding a stoichiometric amount (based on the maleic anhydride content) of crosslinking agent. Films were made by drawing this solution over aluminum or steel (Bonderite 1000) panels with a no. 3 Bird bar, which yielded dry film thicknesses of 1.5–2.0 mil. The panels were heated in a forced air oven at 130° for varying lengths of time. The panels were removed from the oven and allowed to cool to ambient temperature. The films were then tested for property development. As controls, copolymer films without any added crosslinker

leic anhydride (64.4 g) was then added, as rapidly as possible while the contents of the flask were vigorously stirred (no exotherm at this point). Heating of the flask contents to 150° was started. When the temperature of the reaction mixture reached 145°, an exotherm occurred that caused the temperature of the reaction mixture to suddenly increase to 170°. External heating was immediately discontinued. The exotherm subsided after ~5 min, and external heating was resumed. The reaction mixture was maintained at 150° for 5 h. After cooling the flask contents to ambient temperature, 200 mL of CHCl$_3$ was added to dissolve the reaction mixture. The copolymer was isolated by adding the CHCl$_3$ solution to an eight-fold excess of diethyl ether. Purification was effected by two reprecipitations from CHCl$_3$ solu-

Table I   Elemental Analysis Results

	% C	% H	% O
Theoretical[a]	69.84	8.99	21.16
Experimental	70.54	9.97	20.60

[a] Calculated for a pure 1:1 alternating copolymer.

Table II   Copolymer Data

Polymer	Mol Fraction of Maleic Anhydride in Feed	Polymerization Temperature (°C)	Polymerization Time (Min)	Wt % Conversion	M_n	M_w	M_w/M_n
1	0.56	150	300	35.8	13,600	56,000	4.12
2	0.50	150	300	33.0	12,400	49,000	3.95
3	0.50	150	210	42.9	15,600	60,600	3.88
4	0.50	130	20	25.5	22,000	31,600	1.44
5	0.50	130	40	32.5	26,400	46,500	1.76
6	0.50	130	65	39.4	33,000	60,400	1.83
7	0.50	130	110	41.5	31,600	58,500	1.85
8	0.50	130	170	42.5	32,800	61,000	1.86
9	0.50	140	20	38.0	32,500	32,500	2.06
10	0.50	140	40	40.4	34,000	34,000	2.15
11	0.50	140	65	41.0	29,000	29,000	2.21
12	0.50	140	110	40.5	30,000	30,000	2.13
13	0.50	140	170	42.8	30,500	30,500	2.13
14	0.50	150	22	31.4	22,000	22,000	2.25
15	0.50	150	33	33.4	21,400	21,400	2.13
16	0.50	150	50	35.0	21,000	21,000	2.31
17	0.50	150	100	34.5	21,000	21,000	2.19
18	0.50	150	160	34.0	23,400	23,400	2.14

were made and heated for the same lengths of time as the films with crosslinker.

Solvent Extraction Studies

Carefully weighed quantities of cured films (250.0–300.0 mg) were placed in clean, dry vials. Tetrahydrofuran was added (10 mL) and the vials were tightly sealed with Teflon-lined caps. The mixtures were kept at ambient temperature, with periodic agitation, for 5 days. After this time period, insoluble material was isolated by filtration and dried *in vacuo* at 25° until a constant weight was achieved.

RESULTS AND DISCUSSION

The work done by Hall et al.[4,5] showed that copolymers synthesized from maleic anhydride and conjugated olefins had regularly alternating chain morphologies. Work by Gaylord et al.[6,7] has also shown that maleic anhydride olefin copolymers have regularly alternating chain structures. In addition, Smith and Kharas[8] have reported that the tendency toward alternation increases as the polarity differences between the two monomers increases. Certainly, in the present case, the polarity difference between maleic anhydride and

Pamolyn 380 is large. The data from these workers strongly suggests then that the Pamolyn 380– maleic anhydride copolymers have regularly alternating chain structures. The direct evidence gathered in this work supports this suggestion to a point that the authors believe conclusive, i.e., Pamolyn 380–maleic anhydride polymers are regularly alternating. First, experiments in which Pamolyn 380 or maleic anhydride alone was subjected to the copolymerization conditions yielded no high molecular weight species. The Pamolyn 380 gave a low yield (~8–9%) of dimer and the maleic anhydride gave a low (4–5%) yield of oligomer. The infrared spectra (Fig. 1), show that both aliphatic and anhydride species are present (band assignments in Figure 1).[9] Likewise, the ^{13}C-NMR spectrum [Fig. 2(A)], shows that anhydride is present.[10] However, neither of these spectra is quantitative, so the relative amounts of each monomer cannot be determined. The ^{1}H-NMR spectrum is quantitative [Fig. 2(B)]. Integration of the appropriate resonance's (assignments in the Figure)[5–7,11] show a maleic anhydride content of 49–50% and that one of the double bonds of the Pamolyn 380 has been consumed. A ^{1}H-NMR spectrum and a ^{13}C-NMR spectrum of Pamolyn 380 have been included for comparison purposes [Fig. 3(A and B)]. Elemental
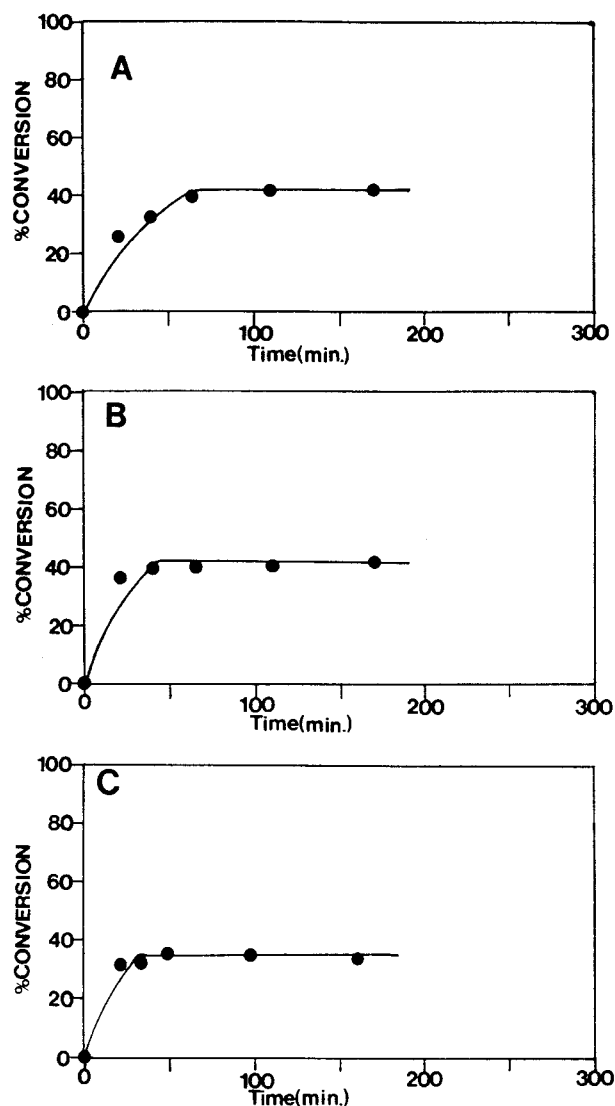
Figure 5 Time-conversion plots. (A) Polymers 4–8; (B) polymers 9–13; (C) polymers 14–18.

analysis results, presented in Table I, also support a 1:1 copolymer, as the calculated percentages of carbon, hydrogen, and oxygen are very close to those obtained experimentally.

As stated above, the results obtained in the present work as well as the results obtained by other researchers justify the assignment of the structure given in Figure 4 to the Pamolyn 380–maleic anhydride copolymer. (A more detailed analysis of the copolymer structure including cistrans ratios are currently underway and will be communicated at a later date.)

Other data obtained from the copolymerization experiments are listed in Table II. Polymerizations 4–18 summarize the data obtained in the

time-conversion experiments. This data is also shown plotted in Figure 5. The maximum conversions obtained seem to be 42–43 wt %. This conversion is reached between 2- and 3-h reaction time, although acceptable conversions can be reached in as little as 40 min (Polymer 10). The overall relatively modest conversions obtained could be attributed to chain transfer reactions, equilibrium between polymerization and depolymerization, viscosity of the medium (limits reaction rate), or some combination of these factors. Molecular weight distributions can be quite broad, again possibly because of some of the factors listed above, but the distributions are monomodal in all cases. The optimum temperature for the copolymerization seems to be 140° at this point. A reaction was attempted at 100°. Although some polymer was formed, the yield, 12.2%, was low and a long reaction time was required (8.5 h). [It is possible that higher yields of copolymers could be obtained at all temperatures by using initiators such as AIBN. This did not occur to us at the time of this investigation, but was kindly suggested by one of the referees. We will be investigating this possibility in the near future.]

Film Property Evaluation

Because of the low T_g (−41 to −45°) of these copolymers, films with good properties can only be obtained through crosslinking. Because cure of epoxies by anhydrides is well known,[12] we chose several epoxy species to investigate as crosslinking agents for the Pamolyn 380–maleic anhydride copolymers. The epoxies we chose are shown in
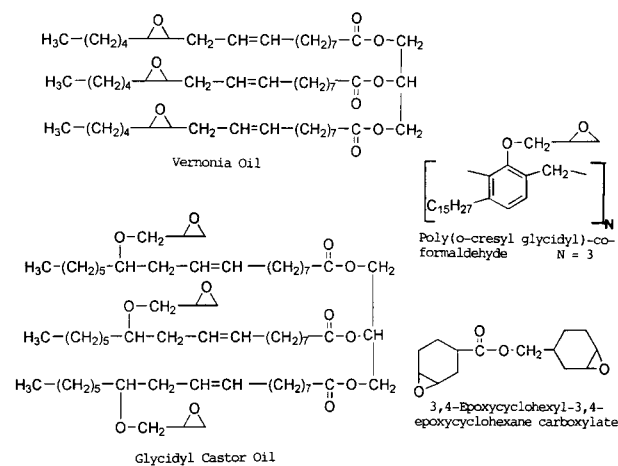

Figure 6 Crosslinker molecules.

Table III   Copolymer Data

Film	Crosslinker[a]	Substrate	Cure Time (Min)	Methyl Ethyl Ketone Double Rubs	Pencil Hardness	Forward Impact (in lbs.)	60° Gloss
1	CGE	Steel	30	40	H	60	84
2	CGE	Steel	60	50	H	40	86
3	CGE	Steel	120	70	2H	30	84
4	CGE	Steel	180	105	3H	30	87
5	CGO	Steel	30	6	B	80	89
6	CGO	Steel	60	14	B	80	91
7	CGO	Steel	90	20	F	80	87
8	CGO	Steel	120	26	F	70	87
9	CGO	Steel	180	40	H	60	88
10	CGO	Steel	1440	85	2H	40	86
11	VO	Al	15	4	2B	—	93
12	VO	Al	30	7	2B	—	94
13	VO	Al	60	8	B	—	93
14	VO	Al	90	10	B	—	95
15	VO	Al	270	16	B	—	91
16	VO	Al	300	25	H	—	94
17	VO	Al	420	35	H	—	94
18	VO	Al	1290	58	H	—	92
19	VO	Steel	1290	86	2H	50	88
20	ECEC	Steel	30	5	B	80	89
21	ECEC	Steel	60	12	B	80	91
22	ECEC	Steel	90	19	HB	80	86
23	ECEC	Steel	120	44	H	60	89
24	ECEC	Steel	180	200+	5H	20	87

[a] CGE, poly(*o*-cresyglycidyl ether)-*co*-formaldehyde; GCO, glycidyl castor oil; VO, vernonia oil; ECEC, 3,4-cyclohexyl methyl-3,4-epoxy cychlohexane carboxylate.

Figure 6. The properties of the films are summarized in Table III.

Table IV shows a list of the methyl ethyl ketone double rubs obtained for the control films. Only the results for the longest bake times are listed in the Table, because these are the most instructive. The film results show that crosslinking is indeed taking place. However, as an additional check, solvent extractions were performed. Table V lists the results of these experiments.

In all cases, there is a significant quantity of insoluble gel, showing that a crosslinking reaction is indeed occurring. The film properties imparted by the different crosslinking species are those expected, for the most part. The lowest molecular weight diepoxy, ECEC, yields films with the highest solvent resistance and the greatest gel content. This epoxy is more mobile, and can therefore reach more anhydride units before decreasing chain mobility slows the rate of crosslinking to near zero. Likewise, the larger molecules, VO and GCO, yield films with the low-

Table IV   Control Solvent Resistances

Film	Substrate	Cure Time (Min)	Methyl Ethyl Ketone Double Rubs
1	Al	1290	2
2	Steel	1440	5

Table V   Solvent Extraction Results

Sample	Crosslinker	Cure Time (Min)	Wt % Insoluables
1	CGE	180	83.4
2	GCO	1440	78.3
3	VO	1290	71.5
4	ECEC	180	97.2

est solvent resistances and gel contents, although for many applications, the solvent resistances obtained would be adequate. The CGE gives films with moderately high solvent resistances and gel content. It seems that in all cases, relatively long bake times are required to obtain films with the best properties. All the epoxies used are somewhat sterically hindered so this result is not surprising. The use of less-hindered epoxies and higher bake temperatures should yield films with good properties in shorter time intervals.

CONCLUSIONS

We have shown that it is possible to obtain a copolymer from maleic anhydride and a commercial conjugated fatty acid, Pamolyn 380, in moderate yields. The copolymers have reasonable molecular weights and monomodal if somewhat broad molecular weight distributions. Analysis of the copolymers and the results of other workers show that the copolymers have a regularly alternating chain morphology. Film studies show that the copolymers can be crosslinked with a variety of multifunctional epoxy species. The films obtained have good–excellent solvent resistances, high harnesses, and good gloss. Although long bake times at 130° are required, it is likely that higher bake temperatures and more mobile cross-

linkers will result in the production of films with good properties in shorter time intervals.

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