

Polymerization of ϵ -Caprolactone With Maleic Anhydride: Synthesis and Characterization

RAMASWAMY MANI, JUDE CURRIER, MRINAL BHATTACHARYA

Department of Biosystems and Agricultural Engineering, University of Minnesota, St. Paul, MN 55108

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ABSTRACT: High-molecular-weight polymers of ϵ -caprolactone (CL) and maleic anhydride (MA) with anhydride group content of about 1% wt have been synthesized and studied. The polymerization reaction was carried out in bulk under nitrogen atmosphere. Stannous octoate ($\text{Sn}(\text{oct})_2$), and 2,2'-azobisisobutyronitrile (AIBN) were used as a catalyst and an initiator, respectively. A two-level design of experiments was used to study the effect of various conditions on the characteristics of the copolymer. Reaction time, temperature, and concentration ratio of various reactants (two monomers, monomer to catalyst, and monomer to initiator) were the independent variables used, and the dependent variables included the molecular weight and the anhydride content in the polymer. Nuclear magnetic resonance (NMR) studies indicate that the succinic anhydride units were incorporated individually either to the polymer chain end or backbone. Anhydride content in the polymer and gel permeation chromatograph (GPC) studies indicate that the maleic anhydride acts as the true initiating species rather than as a comonomer in the system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3189–3194, 2000

Key words: bulk polymerization; ϵ -caprolactone; maleic anhydride; functional polyester

INTRODUCTION

Blends form a major part of the plastic industry. To obtain materials with satisfactory overall properties it is necessary to reduce interfacial tension to generate a small phase size and increase interfacial adhesion to transmit applied force effectively between the component phases.¹ The process of stabilizing polymer blends is commonly called *compatibilization*. A compatibilization strategy that is most frequently used includes the addition of a premade block/graft or functional copolymer composed of blocks that are each miscible with one of the homopolymers.² The choice of a block or graft copolymer is based on the

miscibility of its segments with the blend components and such a copolymer tends to concentrate at the interface as an emulsifier. However, it appears that all commercial blends made from highly immiscible polymers are compatibilized reactively.^{3–5} That is, coupling of reactive groups on each of the immiscible polymers forms a block or graft copolymer. Research conducted in our laboratories^{6–11} indicates that blends of anhydride functional polymer and starch could lead to products with useful end properties.

Copolymerization of ethene,^{12,13} propene,¹³ dienes,¹⁴ and styrene^{15–17} with maleic anhydride has been studied extensively. The cationic ring-opening polymerization of 4-methylene-1,3-dioxolane has also been studied.^{18,19} The copolymerization of 4-methylene-1,3-dioxolane with electron-accepting monomers, such as methyl methacrylate and maleic anhydride, gave alternating copolymer

Correspondence to: M. Bhattacharya.

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via a charge transfer complex (CT complex).^{20,21} Nakamura and Wang²² reported the synthesis of polyesters with reactive groups in the main chain or side chain using organic two-phase interfacial polycondensation.

The present work was undertaken to study the polymerization of ϵ -caprolactone with maleic anhydride in bulk, resulting in a fully biodegradable functionalized polymer. Polymerization of ϵ -caprolactone with maleic anhydride using stannous octoate as the catalyst and 2,2'-azobisisobutyronitrile (AIBN) as the initiator were carried out in bulk under nitrogen atmosphere. A statistical experimental design having two levels (low and high) have been used for efficient experimental runs. The molecular weight, molecular weight distribution, and the anhydride content in the polymer have been determined.

EXPERIMENTAL

Materials

Maleic anhydride (MA, 99%), AIBN (98%), and stannous 2-ethylhexanoate (stannous octoate) (Sigma) were obtained from Aldrich Chemical Company. ϵ -Caprolactone was obtained from Union Carbide and used without further purification. All solvents used in this study were analytical grade and obtained from Aldrich Chemical Company.

Polymerization Procedure

All polymerizations were carried out in bulk under nitrogen atmosphere using stannous octoate as the catalyst and AIBN as the initiator. The bulk polymerization reactions were performed in a three-neck reaction flask equipped with a mechanical stirrer and nitrogen gas inlet. The ϵ -caprolactone, stannous octoate, and AIBN were charged into the reaction flasks to obtain the various copolymer compositions and polymerized at 150°C and 190°C in a silicone oil bath for 2 and 5 h. Maleic anhydride was added to the reaction flask 20 min after the polymerization reaction started to minimize the chain termination reactions and molecular weight distribution. The product obtained was dissolved in toluene and precipitated into cold methanol. The polymer was isolated by filtration and dried in vacuo at room temperature for 24 h. For the analysis, the polymer was refluxed with xylene for 4–5 h and the

hot solution was filtered into methanol. The precipitated polymer was further washed with fresh methanol in order to remove any unreacted monomer and initiator and then dried in a vacuum oven for 24 h at room temperature.

Determination of Anhydride Group Content

The weight percentage of the maleic anhydride group in the polycaprolactone was determined by direct titration. The anhydride content in the polycaprolactone was determined by titration of the acid groups derived from anhydride functional groups by using the procedure outlined in the literature.²³ One gram of extracted polymer was refluxed with 200 mL water-saturated xylene for 1 h. Then, the hot solution was titrated against 0.05 N ethanolic KOH using thymol blue in dimethyl formamide (1%) as an indicator. A 1.0 mL excess of KOH was added and the deep-blue color was back-titrated to a yellow end point by the addition of 0.05 N isopropanolic hydrochloric acid in hot condition. A blank titration was also carried out in the same way for comparison.

Intrinsic Viscosity

The intrinsic viscosity $[\eta]$ measurements were carried out in a constant temperature bath (Cannon CT-1000, Cannon Instruments, State College, PA) using a Ubbelohde viscometer at 30°C. The polymer samples were dissolved in toluene and then diluted to required concentrations.

Gel Permeation Chromatography

The number average $[M_n]$ and weight average $[M_w]$ molecular weight and molecular weight distribution (MWD) of the samples were determined using a Waters 150-C ALC/GC with a refractive index detector. A phenogel (Phenomex, Torrance, CA) having three columns (300 \times 7.8 mm) with 5, 10, and 100 μ m particle size was used for separation. The refractive index versus the elution volume was obtained for each sample and correlated to the elution volume versus molecular weight for the polystyrene standard.

Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance (NMR) spectra of the samples were recorded using a Varian VXR300 instrument with a 12.2- μ s (90°) pulse and an acquisition time of 2.0 s using TMS as a reference. The samples were dissolved in deuter-

Table I Results of the Polymerization of ϵ -Caprolactone with Maleic Anhydride and AIBN in Bulk, Catalyzed by Stannous Octoate

Expt. #	Time (h)	Temp. (°C)	[CL]/[Sn(oct) ₂]	[MA]/[CL]	[MA]/[AIBN]	Conversion (%)	Anhydride content (wt. %)	M _n ^b	M _w ^b	MWD ^b
1	6	110	600	1	—	no reaction	no reaction	no reaction	no reaction	no reaction
2	6	140	1500	—	—	85	—	143076	373453	2.61
3	6	140	600	0.1	—	78	1.6	52942	220188	4.16
4 ^a	6	140	600	0.1	—	44	2.05	29383	60028	2.04
5	8	140	1000	0.1	—	25	2.13	26239	48346	1.84
6	8	140	—	—	600	no reaction	no reaction	no reaction	no reaction	no reaction
7	6	140	600	0.1	600	77	2.09	52828	148533	2.81
8	6	140	600	0.05	1	52	2.24	34126	55023	2.16

^a MA added 15 min after the polymerization has started.

^b Molecular weights obtained from GPC measurements.

ated chloroform and the spectra recorded at room temperature.

RESULTS AND DISCUSSION

A statistical design of experiments (DOE) was used to study the effect of various process conditions and reaction concentrations on the various properties of the copolymer. The independent variables (factor) chosen for the design were polymerization time, reaction temperature, monomer (ϵ -caprolactone) to catalyst (stannous octoate) ratio, monomer to maleic anhydride (MA) ratio, and maleic anhydride to initiator (AIBN) ratio; the dependent variables were $[\eta]$, M_n and M_w, and anhydride content in the polymer. The polymerization reactions were carried out at two levels (low and high) for each factor.

A preliminary study was conducted to determine the level of each factor that produced acceptable copolymer. The results from these experiments are summarized in Table I. Polymerization of ϵ -caprolactone (CL) with MA using stannous octoate (Sn(oct)₂) as the catalyst and AIBN as an

initiator were carried out in bulk under nitrogen atmosphere. No polymerization reactions were observed at temperatures at or below 110°C (Expt. #1) and in the presence of only an initiator (AIBN) without a catalyst (Expt. #6). At a temperature of 140°C, the polymerization of ϵ -caprolactone with MA showed about 2 wt % of anhydride group content in the polymer with a broad molecular weight distribution. The two different levels (low and high) of each factor (time, temperature, MA/ ϵ -caprolactone ratio, ϵ -caprolactone/stannous octoate ratio and MA/AIBN ratio) were chosen based on the preliminary studies (Table I) of the polymerization of ϵ -caprolactone with MA and are shown in Table II. The maximum polymerization temperature was at 190°C because maleic anhydride tended to vaporize at 760 mm of Hg at 200°C. The [MA]/[CL] ratio was chosen 0.05 and 0.1 as there was no polymerization reaction at higher concentration of MA (Expt. #1). This could be due to the faster chain termination reaction rate at the higher concentration of MA.

The fractional factorial experimental design and the results are summarized in Table III. The anhydride content of copolymers having lower

Table II Two Different Levels (Low and High) of Each Factor

	Factor				
	A	B	C	D	E
	Time (h)	Temperature (°C)	[MA]/[CL]	[CL]/[Sn(oct) ₂]	[MA]/[AIBN]
Low level (L)	2	150	0.05	500	2
High level (H)	5	190	0.1	1000	100

Table III Polymerization Conditions and Results of Polymerization of ϵ -Caprolactone with Maleic Anhydride

Run #	Factor Combination ^a (ABCDE)	Anhydride Content (wt %)	Conversion (%)	$[\eta]$ (dL/g)	M_n^b	M_w^b	MWD ^b
1	LLLLL	0.95	38	0.631	21658	37269	1.721
2	HLLLL	1.44	29	0.487	16264	26064	1.603
3	LHLLL	1.05	59	0.853	33385	48463	2.072
4	HHLLL	2.26	29	0.484	16251	31560	1.942
5	LLHLL	2.20	27	0.461	15260	22535	1.477
6	HLHLL	ND	ND	ND	ND	ND	ND
7	LHHLL	2.97	23	0.372	12888	19915	1.545
8	LLLHL	1.57	15	0.397	15301	22602	1.477
9	HLLHL	1.43	24	0.722	26829	40135	1.629
10	LHLHL	0.92	26	0.809	29888	42917	1.436
11	LLHHL	2.21	13	0.399	14486	17689	1.859
12	LLLLH	0.75	62	0.867	35126	59326	1.689
13	HLLLH	0.66	46	0.714	26433	48142	1.821
14	LHLLH	0.46	59	0.861	33592	58019	1.727
15	LLHLH	1.30	28	0.408	15864	24175	1.524
16	LLLHH	1.23	13	0.349	14317	21565	1.506

^a The presence of L and H indicates that corresponding factor is at low and high level, respectively.

^b Molecular weights obtained from GPC measurements.

ND, not determined.

molecular weight, and $[\eta]$ indicated that higher termination reactions occurred with maleic anhydride. In addition, the longer reaction time yielded a lower molecular weight copolymer with a higher anhydride group content (Run #2 and 4). This could be due to the chain scission/chain transfer reactions in the longer reaction time. Albertsson and Gruevegard²⁴ reported that the transesterification reactions occurred after the first 2 h reaction time in the copolymerization of ϵ -caprolactone with 1,5-dioxepan-2-one, which increased the polydispersity.

The reaction temperature had significant effect on the molecular weight obtained (Run #3, 10, and 14). However, no significant difference in the molecular weight at longer reaction time (Run #4) and higher level of [MA]/[CL] ratio (Run #10) were observed. This could probably be due to the chain scission at the longer reaction time in the presence of AIBN and the faster termination reaction rate, respectively. It was observed that at a higher level of [MA]/[CL] ratio, (Run #5, 11, and 15) the faster chain termination reaction rate resulted in a polymer with lower molecular weight and higher anhydride content. These results indicate that the anhydride groups act as a true initiating species rather than as a monomer. In addition, the monomer/catalyst ratio [CL]/

[Sn(oct)₂] had a significant effect on the molecular weight obtained with a longer reaction time (Run #9) and higher reaction temperature (Run #10). However, there was no difference in molecular weight when the other factors were at a low level (Run #8) or even at higher levels of [MA]/[CL] ratio (Run #11) and [MA]/[AIBN] ratio (Run #16). Furthermore, the [MA]/[AIBN] ratio had a significant effect on the molecular weight obtained with all factors at a lower level (Run #12), longer reaction time (Run #13), and higher reaction temperature (Run #14). This result indicates that the higher the maleic anhydride concentration, the greater the probability of increased chain termination reactions.

Lin et al.¹⁵ reported the formation of alternating copolymers of styrene-maleic anhydride copolymerization through polar transition states in polar solvents. At temperatures above 120°C, random copolymers were obtained in decalin (nonpolar solvent) due to the absence of charge-transfer complexes.¹⁵ Copolymers of styrene and MA, when prepared at moderate temperatures, have a strong tendency towards alternation, which results in an equimolar ratio of comonomeric units in the final polymer.¹⁷ Pan et al.²⁵ reported the copolymerization of 4-methylene-2-styryl-1,3-dioxolane with MA in the presence or absence of

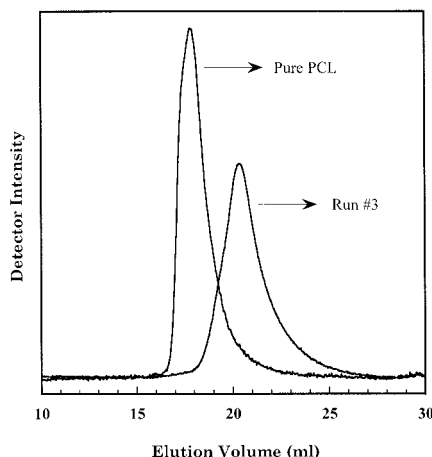


Figure 1 Gel permeation chromatograms for pure polycaprolactone (control) and Run #3. Gel permeation chromatograms for pure polycaprolactone (control) and Run #3.

AIBN yielded only the homopolymer of former with no anhydride group detected in the polymer. However, during the copolymerization of 4-methylene-2-methyl-2-styryl-1,3-dioxolane with MA yields an adduct of the both monomers. In the present system, we observed the anhydride content in the polymer varies from 0.66 to 2.97 wt % could be due to the chain termination reactions. Because the presence of low anhydride content in the polymer, it is difficult to propose a reaction mechanism.

Gel permeation chromatograms (GPC) for pure polycaprolactone (control) and the polymerization of ϵ -caprolactone with MA (Run #3) are shown in Figure 1. The molecular weights are given in Table III. Results from GPC measurements on the polymers showed no peaks (Fig. 1) for poly(maleic anhydride) and the distribution of degrees of polymerization was broad (MWD = 1.5 – 2.0). The broad distribution of the polymer is attributed to the increased chain termination reactions, because the maleic anhydride acts as the true initiating species rather than as a monomer.

The $^1\text{H-NMR}$ spectrum of pure polycaprolactone (control) and the polymer obtained from polymerization of ϵ -caprolactone with MA (Run #4) is depicted in Figure 2. In this figure, only the spectrum from 3.0 to 4.0 ppm is shown and no change in the spectrum was observed, except in this region, for both the pure and grafted polymers. The resonance at 3.69 to 3.76 ppm in spectra (Fig. 2b) could be assigned to single succinic anhydride units. A similar resonance had been

observed in this region for dodecylsuccinic anhydride and eicosane-*g*-maleic anhydride products, although there is some difference in the present case.^{26,27} The second resonance, from 3.91 to 3.95 ppm, probably arose from side-chains containing two or more anhydride units. The sample may also contain some poly(maleic anhydride) that would contribute to resonances in this region of the spectrum.²⁸ However, the spectrum of poly(maleic anhydride) showed the broad group of resonances (4–5 ppm) centered at 4.5 ppm, and a weak signal was detected below 3.5 ppm.^{29,30} On the other hand, the spectrum of the grafted material shows resonances only in the 2.5 to 3.7 ppm region and this is typical of a substituted succinic anhydride.^{29,30} This supports the evidence that succinic anhydride rings are individually attached to the polymer chains either at the chain end or polymer backbone. On the other hand, the grafted polymer containing more than one succinic anhydride unit must be absent or if present is in negligible amount. This is in agreement with GPC measurements.

CONCLUSIONS

Polymerizations of ϵ -caprolactone with maleic anhydride in bulk under nitrogen atmosphere were carried out using stannous octoate as a catalyst and AIBN as an initiator. A statistical design of experiments at two levels (low and high) was used for efficient experimental runs. The independent variables were molecular weight and the anhydride group content in the polymer. The higher

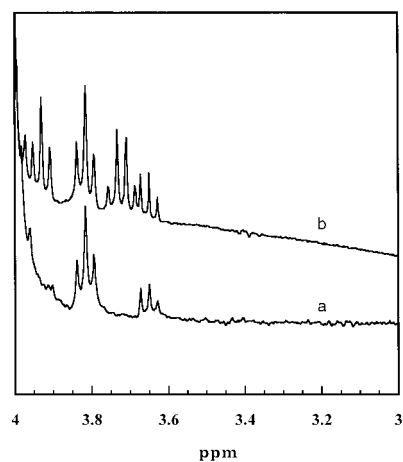


Figure 2 $^1\text{H-NMR}$ spectrum of (a) pure polycaprolactone (control) and (b) Run #4.

anhydride group content in the polymer resulted in a lower molecular weight copolymer, which indicated that increased termination reactions occurred with maleic anhydride. Higher molecular weight polymers with anhydride group content of about 1% wt were obtained at the higher level of reaction temperature, monomer/catalyst ratio, and lower amount of [AIBN] in the polymerization reactions. GPC studies confirm that the absence of poly(maleic anhydride) and broad distribution due to more chain termination reactions is observed. NMR spectrum confirmed that succinic anhydride groups are individually attached to the polymer chains either at the chain end or polymer backbone. These studies indicated that the maleic anhydride acts as the true initiating species rather than as a comonomer in the present system. The anhydride functional polycaprolactone could be an efficient compatibilizer for polymer blends.

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