

Multicarboxylic Aromatic Acid Core Initiator for the Synthesis of Star-Shaped Poly(ϵ -caprolactone) with Carboxyl End Groups

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ABSTRACT: We successfully carried out the ring-opening polymerization of ϵ -caprolactone with 1,3,5-benzenetricarboxylic acid and 1,2,4,5-benzenetetracarboxylic acid as the core initiators at 225°C in bulk, and three-armed and four-armed star poly(ϵ -caprolactone)s [poly(ϵ -CL)s] with carboxyl end groups were obtained. No transesterification, which would have led to a decrease in the molecular weight of poly(ϵ -CL), was found. The effects of the polymerization conditions on the polymerization are discussed; the poly(ϵ -

CL)s were characterized by $^1\text{H-NMR}$, gel permeation chromatography, and thermogravimetric analysis in detail. A mechanism of alkyl-oxygen bond scission by the nucleophilic attack of the carboxyl anions via hydrogen proton transfer is presented for this system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3713–3717, 2006

Key words: initiators; ring-opening polymerization; star polymers; thermogravimetric analysis (TGA)

INTRODUCTION

Aliphatic polyesters have received increasing attention because of their excellent biocompatibility, biodegradability, mechanical properties, and permeability to many drugs.^{1,2} The rapidly growing interest has also been found in the mechanism investigation and application of catalysts in the ring-opening polymerization (ROP) of lactides and lactones, such as lactides,³ β -butyrolactone,⁴ adipic anhydride,⁵ and ϵ -caprolactone (ϵ -CL).^{6–8} However, most of these studies have focused on systems in which a variety of polyol^{9,10} and hydroxyl-end macromonomers^{11–13} were used as initiators, aluminum isopropoxide [$\text{Al}(\text{O}^i\text{Pr})_3$] or stannous octoate (SnOct_2) was used as a catalyst, and the homopolymer, block/branched copolymer, and star polymer of poly(ϵ -caprolactone) [poly(ϵ -CL)] with hydroxyl end groups were synthesized.

It is well known that the function and modification of the end groups of polymers constitute a very important and difficult field. Polymers with functional end groups can be modified further to form a variety of copolymers with special architectures.^{14,15} Most studies concerning the synthesis of starlike poly(lactones) including the hydroxyl-end poly(lactones) have been described before.¹⁶ The development of a

method for the synthesis of poly(lactones) with carboxylic acid end groups in one step may be interesting and significant, and it may extend our ability to further modify poly(lactones) and greatly promote their application in industry and other fields.

Recently, Báez et al.¹⁷ found that the water can initiate the polymerization of lactones in the presence of decamolybdate anions, and the hydroxyl- ω -(carboxylic acid) poly(lactones) was obtained directly. Lee et al.¹⁸ reported the preparation of the poly(lactides) with carboxylic acid end groups after several successive reactions with the pentaerythritol as the initiator. Nevertheless, the cases in which carboxylic acids were directly used as initiators for the ROP of ϵ -CL were limited. Bixler et al.⁸ reported that poly(ϵ -CL) could be synthesized by unitary carboxylic acids such as caproic acid, 3-phenylpropanoic acid, isobutyric acid, and trimethylacetic acid, but the weight-average molecular weight (M_w) of poly(ϵ -CL)s were lower than 5500 g/mol. Zhang et al.¹⁹ adopted succinic acid as the initiator to synthesize poly(ϵ -CL) with terminal carboxylic acid groups under conditions of high vacuum and high temperature, and its number-average molecular weight (M_n) was below 3000 g/mol. More recently, Yu et al.²⁰ reported the microwave-assisted polymerization of ϵ -CL in the presence of chlorinated acetic acids and benzoic acid (BA), and its molecular weight reached 44,800 g/mol. Unfortunately, in all cases of with aliphatic acids as initiators, after chain propagation for some time, a decrease in molecular weight was observed because of the transesterification

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between excessive free small acids and ester bonds of poly(ϵ -CL). Recently, some groups discovered transesterification in the presence of aromatic acids in the preparation of copolyesters from poly(ethylene terephthalate) and PCL blends²¹ and copolyesters from poly(ethylene terephthalate) with acetoxycarboxylic acid, diacetoxycarboxylic acid, and terephthalic acid (TPA),²² but all of these reactions were performed at higher temperatures (>280°C).

This article describes a new method for the synthesis of poly(ϵ -CL) with multiarms with trimesic acid (TMA) and pyromellitic acid (PMA) as initiators in the absence of catalysts; no transesterification between the polymers and small molecular acids leading to the degradation of poly(ϵ -CL) was detected in our system.

EXPERIMENTAL

Materials

ϵ -CL (99%; Acros, Belgium) was dried over CaH₂ for 48 h and then distilled under reduced pressure before use. BA [analytical reagent (AR) grade; Shanghai Huangdu Chemical Factory, China], TPA (AR grade; Beijing Chemical Factory, China), TMA (Acros), and PMA (AR grade; Changzhou Lianbang Chemical Co., Ltd., China) were used as received without further purification. All other reagents and solvents were purified by common purification procedures.

Polymerization of ϵ -CL

All of the bulk polymerizations were carried out in glass vessels. Typically, a 100-mL ampule with a magnetic bar was charged with TMA (105 mg, 0.5 mmol; for TPA, and PMA, 83 and 127 mg, respectively, were used) and ϵ -CL (10 g, 87 mmol); the mixture was degassed in an ice-water bath for 1 min and then filled with nitrogen. After this procedure was repeated three times, the system was kept at 400 mmHg, and then, the vessel was immersed in a preheated silicon-oil bath at 225°C for 3 h. The product was dissolved in tetrahydrofuran (THF) and precipitated in cooled methanol. After three cycles of this process, the resulting white powdery polymer was dried at 30°C for 12 h.

Measurements

¹H-NMR spectroscopy was performed on a Bruker DMX-500 spectrometer (Germany) with tetramethylsilane as the internal standard and chloroform-d (CDCl₃) as the solvent. The molecular weights and molecular weight distributions of the polymers were derived with a Agilent1100 gel permeation chromatograph (USA) with a refractive-index detector, filler, two Mix-C PL-gel columns (500 Å, relative molecular

weight = 500 to 3 × 10⁶; injection volume = 20 μL), solvent, and THF as the eluent with a flow rate of 1.0 mL/min. The gel permeation chromatograph was calibrated with monodispersed polystyrene standards. Thermogravimetric analysis (TGA, USA) was conducted on a PerkinElmer Pyris 1 thermogravimetric analyzer at 10°C/min from 100 to 550°C under a nitrogen atmosphere.

RESULTS AND DISCUSSION

ROP of ϵ -CL with aromatic acids

In the polymerization of ϵ -CL with PMA, TMA, TPA, and BA as the initiators, the key points were what the difference was between the aliphatic and aromatic acids when they were used as initiators, how we could confirm that the carboxyl groups of the phenyl ring initiated the polymerization of ϵ -CL simultaneously, and how poly(ϵ -CL)s with four, three, two, and one arms were formed.

We know that when the ratio of the monomer to initiator ($[M]/[I]$; where $[M]$ is the monomer concentration and $[I]$ is the initiator concentration) and conversion were fixed, the molar ratio of the monomer to carboxyl groups ($[M]/[-COOH]$) was 1:2:3:4 for BA, TPA, TMA and PMA and that polymers with similar molecular weights should have been obtained if the carboxyl groups of the phenyl ring initiated the polymerization of ϵ -CL simultaneously. It was obvious that in these conditions the polymerization time for BA was the longest and for PMA was the shortest. However, in the polymerization, it was not easy to keep the same conversion for the different systems, but we could make the polymerization time constant. In other words, for the same polymerization time, the ratio of obtained polymer molecular weights for these initiators should have been nearly in the range of 1:2:3:4 if the carboxyl groups of the phenyl ring initiated the polymerization of ϵ -CL simultaneously. Table I shows the results for the polymerization time of 3 h and with molecular weights of poly(ϵ -CL) of 5800 for BA, 11,000 for TA, 15,400 for TMA, and 20,600 for PMA; the ratio between them was approximately 1:2:3:4, and the molecular weight distribution in all cases was rather narrow ($M_w/M_n < 1.35$). Figure 1 shows the gel permeation chromatography (GPC) traces of poly(ϵ -CL) obtained by the initiation of different aromatic acids; the same results are illustrated in Table I. In this system, as shown in Figure 1, a weak shoulder peak in the GPC traces in addition to the main peak was observed. How could we explain this phenomenon? We think that in our system, although no transesterification between the poly(ϵ -CL) chains and small molecular aromatic acids was detected during the polymerization, the carboxylic acid end groups of one polymer chain may have attacked the ester linkage of

TABLE I
Results of the Polymerization of ϵ -CL with Different Aromatic Acids in Bulk at 225°C for 3 h

Run	Aromatic acid	$[\epsilon\text{-CL}]/[\text{I}]$	$[\epsilon\text{-CL}]/[-\text{COOH}]^a$	$M_p^{b,c}$	M_n^c	M_w/M_n^c	$\epsilon\text{-CL}$ conversion (%)
1	None	—	—	—	—	—	—
2	BA	175	175	5,800	5,700	1.14	5
3	TPA	175	87.5	11,000	9,700	1.22	12
4	TMA	175	58.3	15,400	15,200	1.26	26
5	PMA	175	44	20,600	13,800	1.31	35.6
6	PMA	350	88	17,900	10,000	1.22	32

^a The value of $[\epsilon\text{-CL}]/[\text{I}]$ versus the carboxyl group number of aromatic acids.

^b The maximum molecular weight according to the peak elution volume from the GPC trace.

^c Measured by GPC in THF with a polystyrene standard and a refractive-index signal detector.

another polymer, which led to an increase in the molecular weight of one polymer chain and a decrease in another polymer chain. Thus, a weak shoulder on the GPC curves appeared. As the conversion increased, the molecular weight increased, too, but the peak became broader, and the polydispersity was larger than before. At the higher conversion (78%) for TMA, the polydispersity reached 1.49.

Thus, we concluded that in our system, all carboxyl groups in the aromatic rings initiated the polymerization of ϵ -CL simultaneously, and poly(ϵ -CL) with three and four arms with TMA and PMA as initiators was obtained, as shown in Scheme 1.

Effect of different kinds of carboxylic acids on the polymerization of ϵ -CL

As we mentioned before, in previous research on the polymerization of ϵ -CL with carboxylic acids as initiators, aliphatic acids were commonly used. In those systems, an unavoidable decrease in the molecular weight of the poly(ϵ -CL)s was found when the poly-

merization time reached about 30 to 50 min because of the transesterification of excessive free small carboxylic acids with the ester bonds of poly(ϵ -CL). However, in this study, we did not observe transesterification between the polymers and free small carboxylic acids because the molecular weight did not decrease with increasing polymerization time even when it reached 5 h. Figure 2 shows the relationship of the molecular weight with polymerization time for different types of carboxylic acids; only aromatic acids showed nice linear results during the whole polymerization process. Figure 3(a,b) shows the TGA curves of PCL initiated by excessive PMA and the mixture of PCL and PMA, in which no loss weight was found at 225°C for PCL and the mixture of PCL and PMA. The obvious degradation of PCL was only observed at temperatures higher than 257°C.

We believe that in the ϵ -CL polymerization with carboxylic acids as the initiators, the carboxylic acids

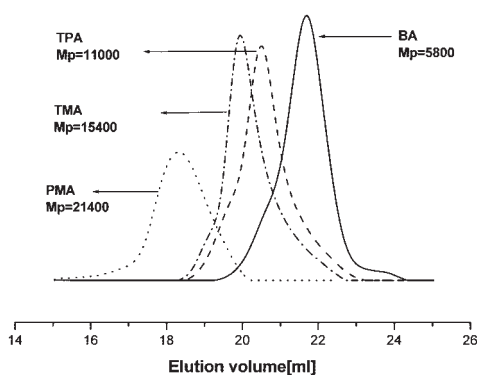
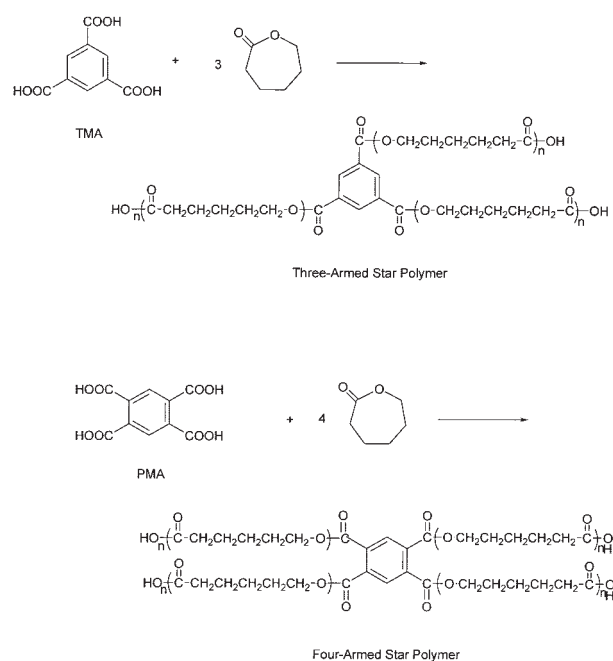


Figure 1 Stack GPC traces (refractive index detector) of homopoly(ϵ -caprolactone) obtained by the polymerization of ϵ -CL with the same amount of ϵ -CL and molar fraction of aromatic acid (BA, TPA, TMA, or PMA). The molar ratio of carboxyl group content in the mixture was 1:2:3:4. M_p = maximum molecular weight according to the peak elution volume from the GPC trace.



Scheme 1

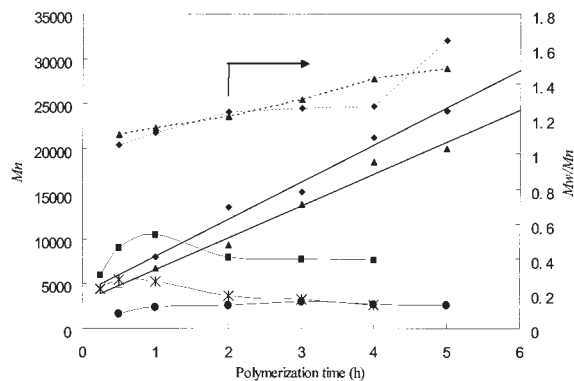


Figure 2 Dependencies of the (—) molecular weights (GPC) and (---) polydispersities (GPC) on the polymerization time of ϵ -CL with (\blacktriangle) TMA and (\blacklozenge), respectively, as initiators and with $[\epsilon\text{-CL}]/[\text{I}] = 175$ at 225°C . To compare with the aromatic acids, (\blacksquare) trimethyl acetic acid,⁸ (\bullet) succinic acid,¹⁵ and ($*$) chloroacetic acid¹⁶ were introduced as initiators.

were excessive enough to increase the initiation efficiency. In all cases, the first step is hydrogen proton transfer of carboxylic acid to the oxygen atom of the

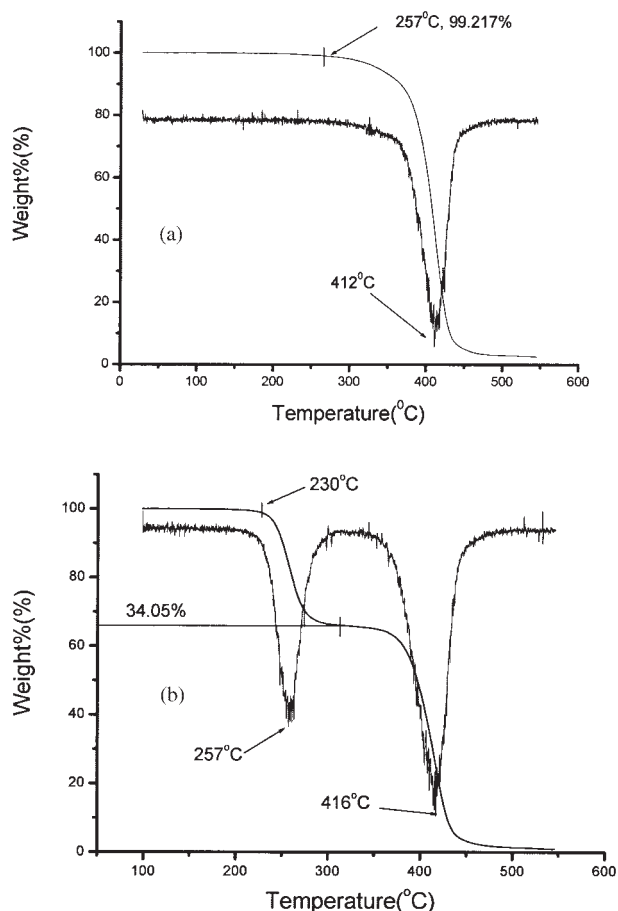
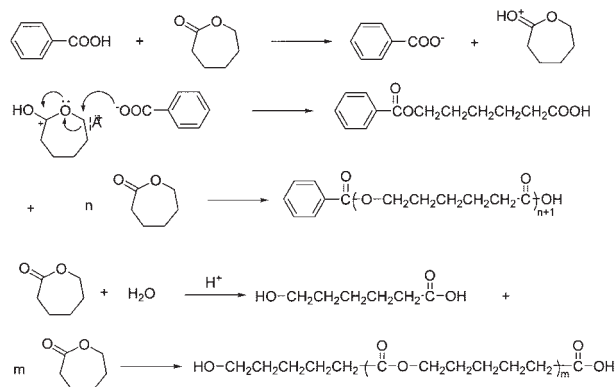


Figure 3 TGA spectra of (a) PCL and (b) a mixture of PCL and PMA (1:2 w/w).



Scheme 2

carbonyl group in ϵ -CL, as shown in Scheme 2. Then, coordination of the alkyl-oxygen scission occurs by the nucleophilic attack of the carboxyl anion on the carbon atom of the alkyl-oxygen bond with part of a positive charge. In the case of aliphatic acids, the alkyl was an electron-withdrawing group, so the transesterification was easily performed due to the strong nucleophilicity of the remaining free aliphatic carboxyl anions. However, when aromatic acids were used, the negative charge of carboxyl anions was conjugated by a phenyl ring, so the nucleophilicity of carboxyl anions was weakened, which led to difficulty in transesterification.

Effect of the variation of $[\epsilon\text{-CL}]/[\text{I}]$ on polymerization

In the bulk polymerization of ϵ -CL, the monomer was also the solvent for the polymer. With increasing polymerization time, the viscosity of the system also increased; the polymer chains were more difficult to move, so it was impossible for them to propagate simultaneously, and distribution was widened. For example, when $[\epsilon\text{-CL}]/[\text{I}]$ was 175, the polydispersities changed from 1.31 for 3 h to 1.41 for 5 h in the case of PMA. However, if $[\epsilon\text{-CL}]/[\text{I}]$ increased to 350, that is, the values of $[\epsilon\text{-CL}]/[\text{—COOH}]$ varied from 44 to 88, under the same polymerization conditions, the polydispersity became narrower. Its value changed from 1.31 to 1.22. In this case, the molecular weight and monomer conversion were nearly the same (runs 5 and 6 in Table I). This meant that at lower conversions ($<35\%$), poly(ϵ -CL)s with high molecular weights (10,000–20,000) and narrower molecular weight distributions ($M_w/M_n < 1.26$) were obtained. At the same time, the conversion and the molecular weight increased under the condition of no catalyst. If the polymerization time was prolonged to 5 h, the conversion increased to over 70%; only the polydispersity became broader due to the higher viscosity of the reaction system and the transesterification between the polymer chains.

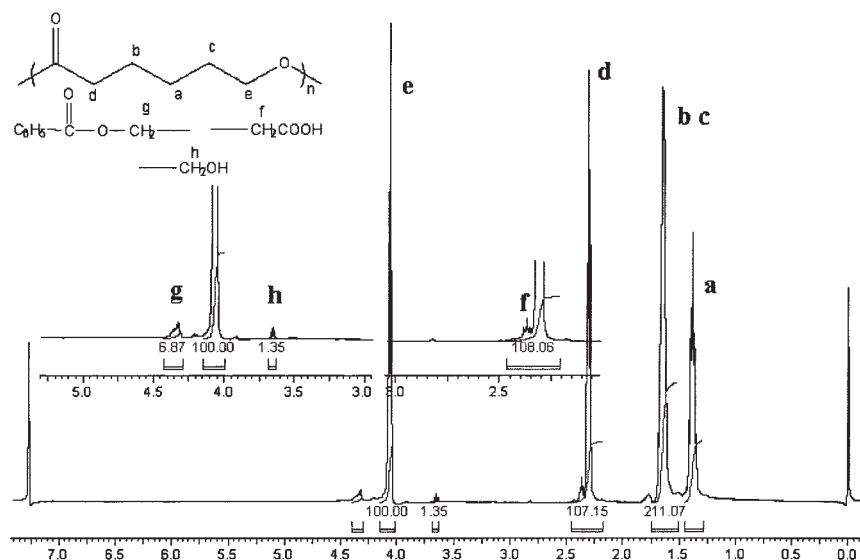


Figure 4 Typical ^1H -NMR spectrum of four-armed star-shaped poly(ϵ -CL) with carboxylic acid end groups initiated by PMA.

Characterization of poly(ϵ -CL)

Figure 4 illustrates the typical ^1H -NMR spectrum of a four-armed star-shaped poly(ϵ -CL) with carboxylic acid end groups initiated by PMA. In addition to the typical signals of the main chain of poly(ϵ -CL) at 1.38 (H^{a}), 1.65 (H^{b} , H^{c}), 2.30 (H^{d}), and 4.06 (H^{e}), there were additional signals of the end groups of poly(ϵ -CL). The small signal with triplex peaks at 2.36 ppm, which was near to proton c, were assigned to the methylene protons (f) in $-\text{CH}_2-\text{COOH}$ at the end of the polymer chains. At the same time, signal g at 4.31 was assigned to the methylene group adjacent to the PMA core. The tiny signal at 3.65 ppm was the methylene proton (h) in $-\text{CH}_2-\text{OH}$, which was caused by the polymerization of ϵ -CL initiated by the water in the presence of free small acid¹⁷ (see Scheme 2). Despite the efforts made to keep the vessels and reactants dry, a small quantity of water was still unavoidable during the experiment.

As shown in Scheme 2 and Figure 4, the intensities of the methylene protons (f) should have been equal to the sum of the intensities of the methylene protons (g and h), so the number of poly(ϵ -CL)s with hydroxyl end groups ($-\text{CH}_2-\text{OH}$) could be calculated from following equation [where $I(h)$ and $I(g)$ are the integrated squares of the methylene protons h and g, respectively]. Its value was 16%:

$$-\text{CH}_2-\text{OH}(\%) = \frac{I(h)}{I(g) + I(h)} \times 100\%$$

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