Random Copolymerization of ε-Caprolactone and Trimethylene Carbonate with Rare Earth Catalysts

YOUQING SHEN,[1]* ZHIQUAN SHEN,[1] YIFENG ZHANG,[1] QIAOHONG HUANG,[1] LIANFANG SHEN,[2] HANZHEN YUAN[2]

[1] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

[2] State Key Laboratory of Magnetic Resonance and Atomic Molecular Physics, Wuhan Institute of Physics, Chinese Academy of Sciences, Wuhan, People's Republic of China

ABSTRACT: Random copolymerization of trimethylene carbonate (TMC) with ε-caprolactone (CL) catalyzed by rare earth chloride–epoxide or rare earth isopropoxide has been investigated for the first time. It was found that in the presence of epoxide, rare earth chlorides have high activities for the copolymerization, giving high-molecular-weight random copolymer P(CL-*co*-TMC) with a narrow molecular weight distribution. Light rare earth chloride–propylene oxide systems are more effective for the copolymerization than heavy rare earth chloride–propylene oxide systems. For the rare earth chloride–epoxide catalyst system, epoxide is the requisite component, and its amount affects the catalytic activity; while rare earth isopropoxide can catalyze the copolymerization alone. The preparative conditions of the copolymer with $NdCl_3$–5PO system were studied. The reactivity ratios of CL and TMC copolymerization with $NdCl_3$–5PO determined by Fineman–Ross method are 1.60 for r_{TMC} and 0.72 for r_{CL}, respectively. The copolymers were characterized by ^{1}H- and ^{13}C-NMR, GPC, and DSC. The mechanism study shows that the rare earth alkoxide is the active species that initiates the ring opening copolymerization of CL and TMC with acyl–oxygen bond cleavages of the monomers. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2131–2139, 1997

Key words: random copolymerization; ε-caprolactone and trimethylene carbonate; rare earth catalysts

INTRODUCTION

Poly(ε-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC) are attractive biopolymers to be used as biodegradable sutures, artificial skin, resorptable prostheses, and the design of

galenic formulations.[1–3] PCL is a semicrystalline polymer with mp of 63°C and has a useful life span approaching 1 year,[1] while PTMC is an amorphous or little crystalline polymer.[3] Its hydrolytic scission rate is slower *in vitro,* but more rapid *in vivo* than that of PCL.[3] Copolymerization is a direct access to tailor the properties of the polymer required for the different applications. For example, crystallinity and the melting point of PCL can be reduced by caprolactone (CL) random copolymerization so that the tissue irritation is minimized when it is used as implant in the body.[1] The biodegradability and controlled drug release behavior can also be adjusted by changing the composition of the copolymer.[1]

Table I   Random Copolymerization of CL and TMC by Rare Earth Catalysts

No.	LnX_3	Catalyst Type	Overall Conversion (%)	$[\eta]$ (dL/g)	M_n ($\times 10^4$)	M_w/M_n
1	$LaCl_3$	a	98	1.34	8.21	1.19
2	$PrCl_3$	a	94	1.31	8.10	1.22
3	$NdCl_3$	a	98	1.29	8.01	1.20
4	$EuCl_3$	a	81	0.77	—	—
5	$EuCl_3$	b	87	1.02	7.65	1.24
6	$GdCl_3$	a	77	0.64	—	—
7	$GdCl_3$	b	85	0.93	7.39	1.30
8	$DyCl_3$	a	62	0.60	—	—
9	$DyCl_3$	b	72	0.89	7.27	1.28
10	$ErCl_3$	a	52	0.55	—	—
11	$ErCl_3$	b	66	0.76	—	—
12	$YbCl_3$	a	29	0.19	—	—
13	$YbCl_3$	b	42	0.67	—	—
14	$La(OiPr)_3$	c	62	0.37	—	—
15	$Nd(OiPr)_3$	c	56	0.28	—	—
16	$Gd(OiPr)_3$	c	39	0.21	—	—
17	$Dy(OiPr)_3$	c	10	0.11	—	—

Polymerization conditions: TMC/CL = 50/50; (TMC + CL)/Ln = 5000 (molar ratio); 80°C; 3 h. Catalysts: (a) $LnCl_3$–5PO–γ-BL; (b) $LnCl_3$–5PO–toluene; (c) $Ln(OiPr)_3$–toluene solution.

There are few articles on the copolymerization of ϵ-caprolactone and trimethylene carbonate. Albertsson and Eklund[4] investigated the copolymerization using zinc and tin compounds as catalysts. We have recently found that rare earth halides alone are effective catalysts for the homopolymerization of TMC but not as active for the polymerization of CL and the copolymerization of CL with TMC.[5] However, in the presence of epoxide, rare earth halides show high activities for the polymerization of CL with formation of high-molecular-weight PCL.[6] Further studies showed that the rare earth halide–epoxide catalytic systems are also highly active for the copolymerization of CL with TMC, and higher-molecular-weight P(CL-

co-TMC) with a narrow molecular weight distribution can be obtained. This article reports the characteristics and mechanism of the copolymerization of CL and TMC by rare earth halide–epoxide systems and rare earth isopropoxides, with emphasis on the former.

EXPERIMENTAL SECTION

Materials

ϵ-Caprolactone (Mitsubishi) and γ-butyrolactone (γ-BL) were dried and distilled over CaH_2 twice under reduced pressure. Propylene oxide (PO),

Table II   Effect of Epoxides on the Copolymerization of CL and TMC

No.	Epoxide	Epoxide/Nd	Polymerization Time (h)	Overall Conversion (%)	$[\eta]$ (dL/g)
1	—	—	24	0	—
2	PO	3	5	97	1.70
3	PO	5	3	94	1.24
4	PO	10	2	95	0.87
5	EO	5	5	97	1.11
6	ECH	5	5	93	1.27

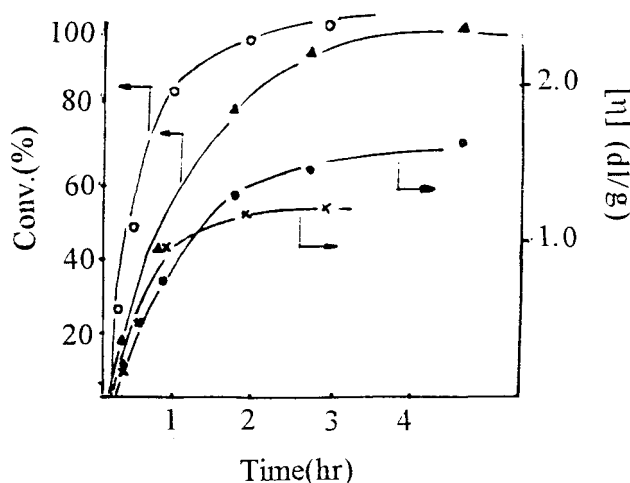Polymerization conditions: (TMC + CL)/Ln = 5000; TMC/CL = 50/50; 80°C. Catalyst: $NdCl_3$–5epoxide–γ-BL.

Figure 1 CL–TMC copolymerization catalyzed by different NdCl₃–PO systems: (○, ×) PO/Nd = 5; (△, ●) PO/Nd = 3. Polymerization conditions: (CL + TMC)/NdCl₃ = 5000; CL/TMC = 50 : 50; 80°C. Catalyst preparation is the same as in Table I.
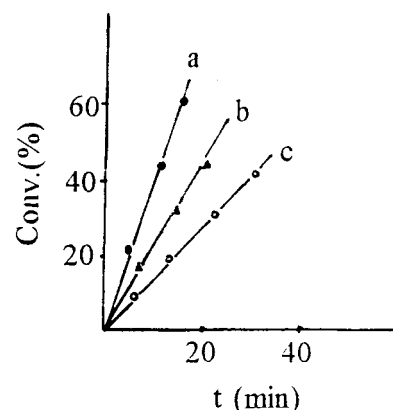
Figure 2 Effect of the comonomer composition on the initial copolymerization rate of CL–TMC. Polymerization conditions: (a) CL/TMC (molar ratio) = 75 : 25; (b) 50 : 50; (c) 25 : 75. Other conditions are the same as in Figure 1.

ethylene oxide (EO), and epichlorohydrin (ECH) were dried over CaH₂. Rare earth oxides (Ln₂O₃) with a purity of 99.99% were purchased from Shanghai Yaolong Factory.

Trimethylene carbonate was prepared by the exchange reaction of 1,3-propanediol and diethyl carbonate according to the method of Albertsson and Sjoling.[7] It was further purified by recrystallization and dried by CaH₂ before use.

Catalyst Preparation

Anhydrous rare earth chloride (LnCl₃) was prepared by heating the mixture of hydrated rare earth chloride and ammonium chloride under reduced pressure.[8] Rare earth isopropoxide was synthesized by the reaction of anhydrous rare earth chloride with sodium isopropoxide.[9] Catalyst solutions of rare earth chloride–epoxide were obtained by the reaction of rare earth chloride with epoxide in either γ-butyrolactone (γ-BL) or toluene. The concentrations of rare earth ion and chlorine in the catalyst solution were determined by titration with EDTA and HgNO₃, respectively.

Copolymerization

Copolymerization reaction (general procedure) was carried in a glass ampoule previously flamed

Table III Random Copolymerization of CL and TMC by NdCl₃–5PO–γ-BL System

No.	Temperature (°C)	TMC/CL Ratio	(CL + TMC)/Ln	Conversion (%)	[η] (dL/g)	Efficiency × 10⁻⁵ (g/molar Nd)
1	80	50 : 50	1000	100	0.81	1.1
2	80	50 : 50	2500	100	1.02	2.7
3	80	50 : 50	3000	99	1.11	3.2
4	80	50 : 50	5000	98	1.24	5.1
5	80	50 : 50	8000	34	0.62	2.9
6	80	50 : 50	8000	81*	0.97	7.0
7	80	75 : 25	5000	100	0.51	5.4
8	80	25 : 75	5000	100	1.42	5.4
9	30	50 : 50	5000	0	—	—
10	50	50 : 50	5000	67	0.57	3.6
11	60	50 : 50	5000	80	0.87	4.32
12	100	50 : 50	8000	100	1.38	8.6

Polymerization time; 3 h; asterisk indicates 10 h. Catalyst: NdCl₃–5PO–γ-BL.

Table IV   Relationship of the Compositions Between the Comonomer Feed and Copolymer

Initial Comonomer Feed x (TMC/CL)	Composition of Copolymer y (TMC/CL)	Conversion (%)
4.00	6.28	5
2.33	3.95	9
0.70	1.06	8.0
0.50	0.72	7.1
0.25	0.35	6.2

Polymerization conditions: (CL + TMC)/Nd = 5000; PO/Nd = 5; 80°C.

and purged by dry nitrogen. Monomer and catalyst were added to a glass ampule under nitrogen atmosphere, then the ampule was kept in thermostat for a desired polymerization time. The mixture was dissolved in $CHCl_3$, and the polymer was precipitated in excess methanol (containing 5% aqueous HCl), washed by methanol for several times, then dried in vacuum.

Measurements

The intrinsic viscosity of the copolymer was determined in THF at 30°C with an Ubbelohde viscosime-ter. Nuclear magnetic resonance (NMR) spectra were recorded on a Unity 200 NMR spectrometer in $CDCl_3$ at room temperature with tetramethylsilane (TMS) as the internal standard. The gel permeation chromatography (GPC) curves were recorded (Waters 150) in tetrahydrofuran (THF) at 25°C using polystyrene as standard. Thermal properties of the copolymer were measured on a Perkin-Elmer DSC-7. The sample was quenched to −100°C and maintained at this temperature for 3 min, then heated at a rate of 20°C min.

RESULTS AND DISCUSSION

Characteristics of the Copolymerization of CL and TMC

Two kinds of rare earth catalysts, rare earth halide-epoxide and rare earth isopropoxide, have been examined for the copolymerization of CL with TMC, as shown in Table I. For the light rare earth chloride–epoxide catalysts (catalyst a), γ-BL is necessary to prepare homogeneous catalyst solution because powder light rare earth chlorides, i.e., $LaCl_3$, $PrCl_3$, and $NdCl_3$, cannot react with epoxide directly.[6] Heavy rare earth chlorides
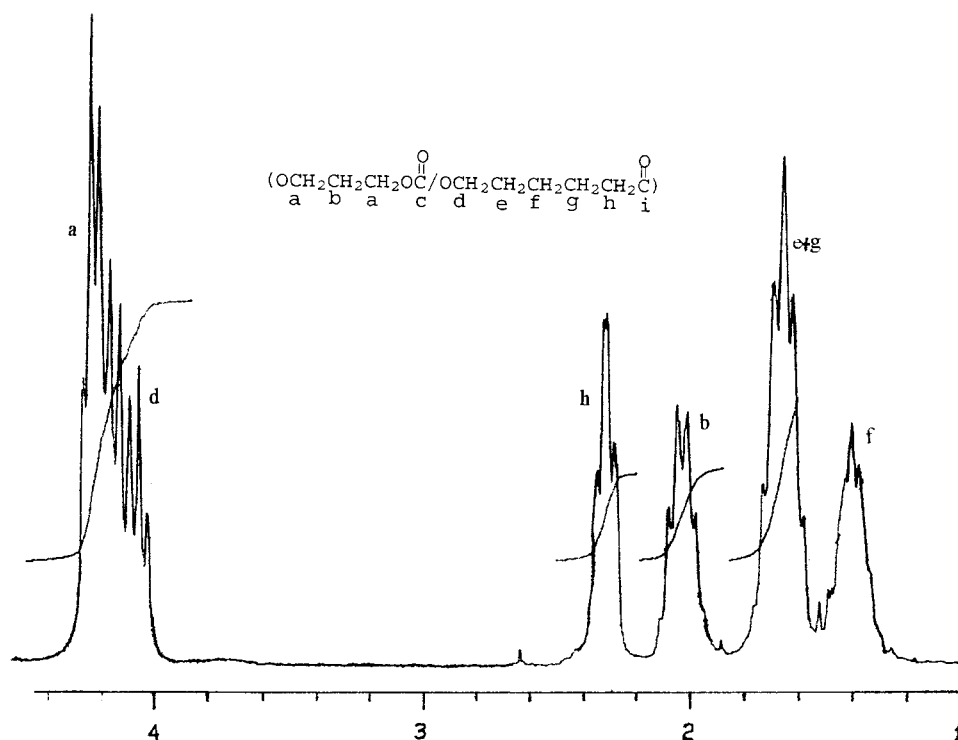

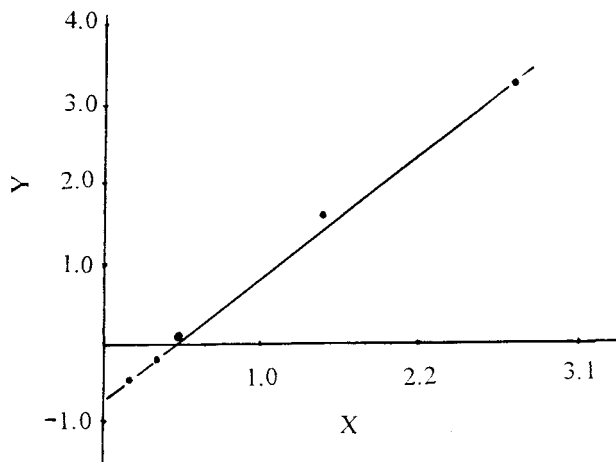**Figure 3**   Typical ^{1}H-NMR spectrum of P(TMC-*co*-CL) obtained by the NdCl$_3$–5PO system.

Figure 4 Fineman–Ross plot for the copolymerization of CL and TMC with $NdCl_3$–5PO as a catalyst. Polymerization conditions: $(CL + TMC)/NdCl_3 = 5000$; 80°C.

can react with epoxide vigorously in toluene or γ-BL and give catalyst solution (catalyst b). From the data in Table I, it can be seen that both the two kinds of rare earth catalysts are highly active for the copolymerization, even at low catalyst concentration (Monomer/Ln = 5000), and high conversion can be reached, especially for the light rare earth chloride–PO systems. The catalytic ac-

tivities of light rare earth chloride–propylene oxide systems are higher than that of heavy rare earth chloride ones. The copolymerization with $LaCl_3$–PO, $NdCl_3$–PO, and $PrCl_3$–PO systems give high-molecular-weight copolymers with intrinsic viscosities around 1.3 dL/g (M_n about 8 $\times 10^4$) with a narrow molecular weight distribution.

Table II and Figure 1 illustrate the effects of the epoxide sort and the amount of propylene oxide on the copolymerization. It can be seen that, besides PO, ethylene oxide (EO) and epichlorohydrin (ECH) also have the promotive effect on the catalytic activity of $LnCl_3$. The amount of added PO affects the copolymerization: more PO (higher PO/Nd molar ratio) added in the catalyst solution leads to a more rapid copolymerization rate and give a lower intrinsic viscosity of the copolymer. This may be due to more active species produced at a higher PO concentration.[6]

The preparative conditions of CL–TMC copolymerization with the $NdCl_3$–5PO–γ-BL system were examined (Table III and Figure 2). The comonomer composition has influenced on the initial copolymerization rate and the molecular weight of the copolymer: the higher CL content in the comonomer feed results in more rapid copolymerization and a higher molecular weight of the copolymer formed (Table IV). This trend is consis-
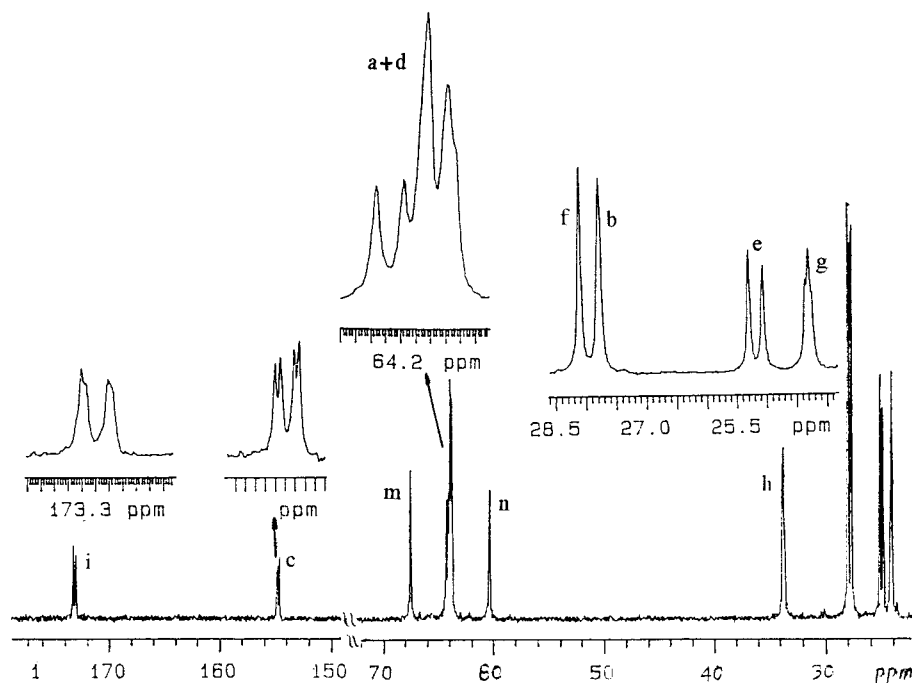
Figure 5 Typical ^{13}C-NMR curve of P(TMC-*co*-CL) prepared by the $NdCl_3$–5PO system (see Table I, no. 3).

Mw/Mn = 1.20

Mn = 80100

Elution Time (min)
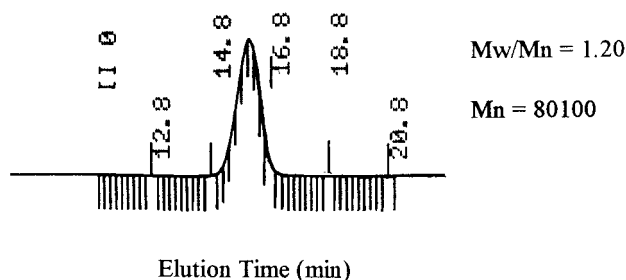
Figure 6 Typical GPC spectrum of the copolymer (Table I, no. 3).

tent with the homopolymerization characteristics of CL and TMC catalyzed by rare earth catalysts,[6] in which the polymerization of CL is more rapid and easier to give a high molecular weight of the polymer than that of TMC with the same catalyst. Another noteworthy point is that the monomer to catalyst ratio (M/Ln) in the range of 1000 to 5000 has little effect on the copolymerization. Similar to the homopolymerization of TMC, the molecular weight of the copolymer is not proportional to the M/Ln ratio. The $[\eta]$ of copolymer increases only from 0.81 to 1.24 dL/g with an increase in the M/Ln from 1000 to 5000.

Table III also shows that the optimum temperature of the copolymerization is about 80°C. At

low temperature, both the copolymerization rate and the resulting copolymer are very low. High temperature leads to a more rapid copolymerization, and the M/Ln ratio can be increased further; therefore, the catalytic efficiency is increased (Table III, no. 12).

Determination of Reactivity Ratios

In order to determine the reactivity ratios of CL and TMC, different compositions of copolymers were prepared at low conversion (<10%). Figure 3 is the ^{1}H-NMR spectrum of the copolymer. The compositions of the copolymer can be calculated from the intensity ratio of signals at 2.3 (CL unit) to 2.05 ppm (TMC unit). The Fineman–Ross method was used to calculate the reactivity ratios based on the eq. (1), as follows:

$$Y = r_t X - r_c \qquad (1)$$

where $Y = (y - 1)x/y$, $X = x^2/y$, $y = d[\text{TMC}]/d[\text{CL}]$, and $x = [\text{TMC}]/[\text{CL}]$.

The reactivity ratios r_{TMC} and r_{CL} obtained from the slope and the intercept of the line in Figure 4 are 1.60 for r_{TMC} and 0.72 for r_{CL}. This result is different from that of Albertsson and Eklund,[4] in which CL has higher reactivity than TMC when

Figure 7 DSC curves of P(TMC-*co*-CL): (a) TMC/CL (molar ratio) = 75 : 25, (b) 50 : 50, and (c) 25 : 75.

$$\underset{\text{a}}{\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OC}}\underset{\text{c}}{\overset{\text{O}}{\underset{\;}{\parallel}}}\underset{\text{d}}{(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OC}}/\underset{\text{e}}{\overset{\text{O}}{\underset{\;}{\parallel}}}\underset{\text{f}}{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}})_n\underset{\text{j}}{\overset{\text{O}}{\underset{\;}{\parallel}}}\underset{\text{k}}{\text{OCHCH}_2}(\text{OCHCH}_2)_{x_1}\text{Cl}$$
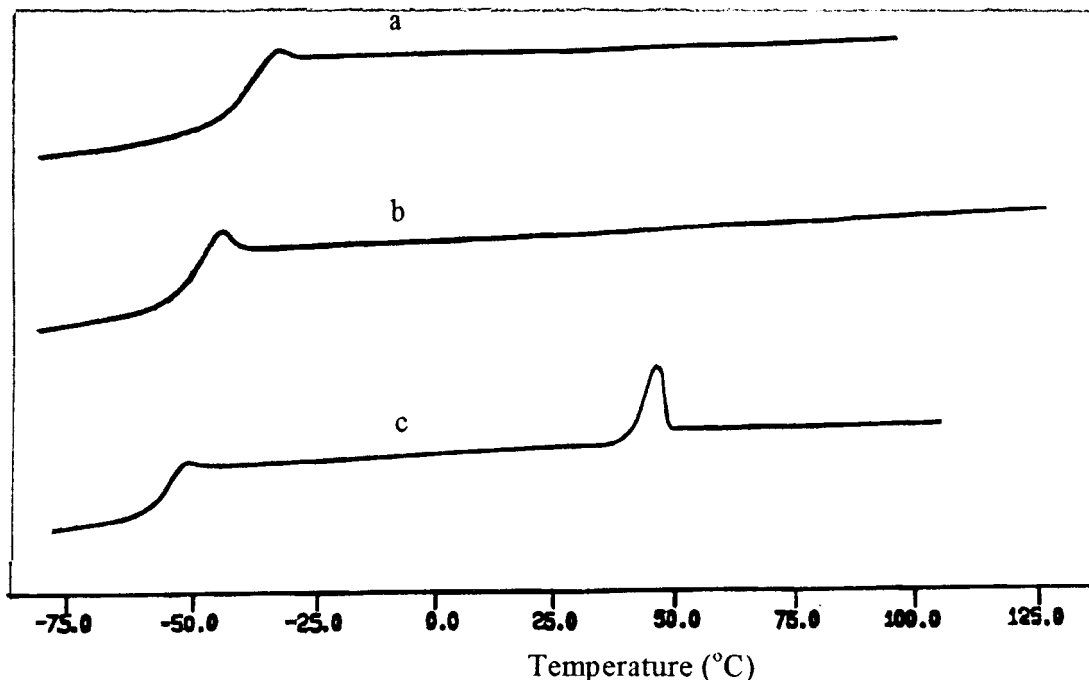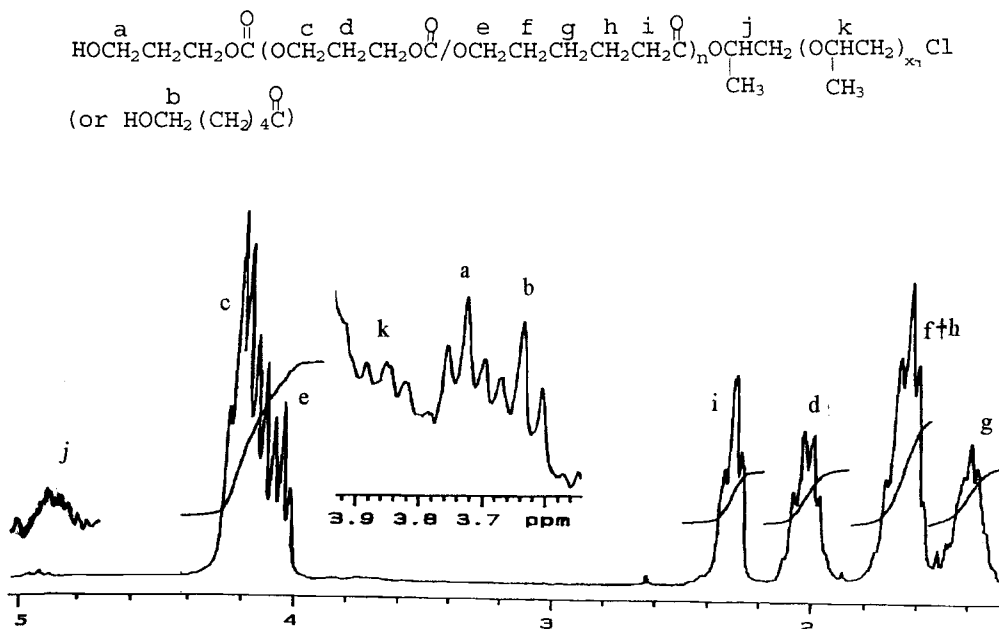
(structure)

Figure 8 ^{1}H-NMR spectrum P(TMC-*co*-CL) prepared by the NdCl$_3$–5PO system.

using Sn(Oct)$_2$ as a catalyst. This difference may arise from the different mechanisms of the copolymerizations with the two kinds of catalysts. The somewhat higher reactivity of TMC in the copolymerization with rare earth catalyst agrees with the molecular structures of TMC and CL and the coordination insertion mechanism of the copolymerization. The RO$^-$ groups in >Ln-OR catalytic species (see the Polymerization Mechanism section) can attack the higher electrophilic carbonyl carbon of TMC easier than that of CL. The value of $r_{TMC} \times r_{CL}$ for the copolymerization catalyzed by NdCl$_3$-5PO systems is close to 1.0, indicating that the copolymerization is nearly ideal.

Characterization of the Copolymer

Figure 5 shows the ^{13}C-NMR spectrum of the copolymer. The chemical shifts in the figure are assigned as follows[4]: δ = ca. 64.0 ppm (multi, Ca + Cd); δ = 27.8 ppm (Cb); δ = ca. 154.7 ppm (multi, Cc); δ = ca. 25.28 and 25.09 ppm (Ce); δ = 28.1 ppm (Cf); δ = 24.34 and 24.29 ppm (Cg); δ = 33.88, 33.84, and 33.76 ppm (Ch); δ = ca. 173 ppm (multi, Ci); δ = 67.6 ppm (Cm); and δ = 60.37 and 60.41 ppm (Cn).

It has been demonstrated that in the ^{13}C-NMR spectrum of the block copolymer of CL with TMC, there are no signals at 67.6 (Cm) and 60.4 ppm (Cn), and the signals of carbonyl carbon of CL and TMC units do not split.[10]

Therefore, the high intensities of Cm and Cn, as well as signal splitting of the carbonyl carbon units in Figure 5, indicate that the copolymer of CL and TMC catalyzed by the rare earth catalyst is not block, but rather a highly random copolymer, which is consistent with the ideal copolymerization character as illustrated by the reactivity ratios of CL and TMC, as follows:

$$\underset{\text{a}\;\;\;\text{b}\;\;\;\text{a}\;\;\;\;\;\;\text{c}\;\;\;\;\text{d}\;\;\;\text{e}\;\;\;\text{f}\;\;\;\;\text{g}\;\;\;\;\text{h}\;\;\;\text{i}}{(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OC}/\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C})}$$

$$\underset{\text{m}}{\text{OCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}}$$

$$\underset{\text{n}}{\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCO}}$$
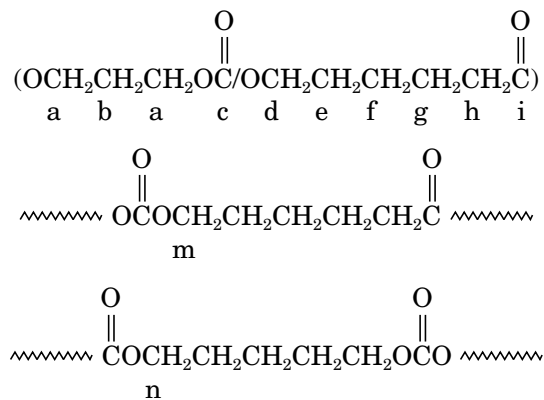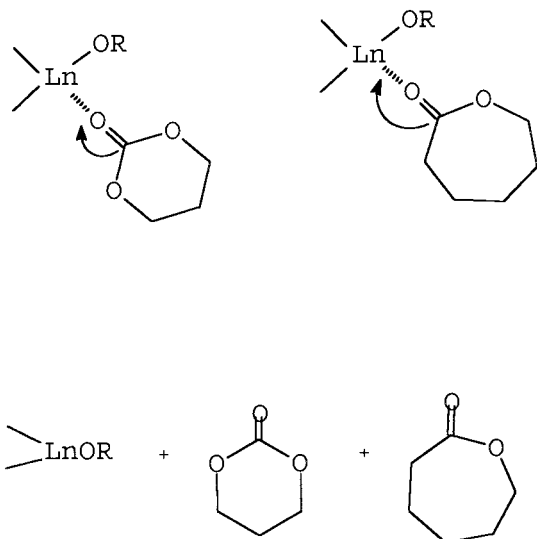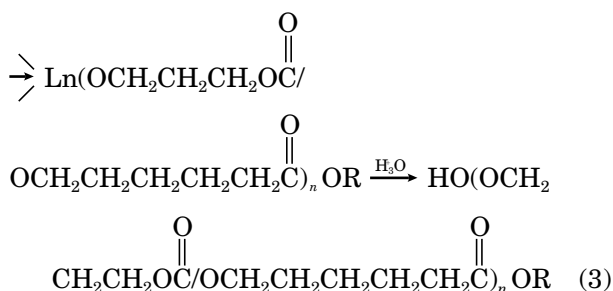
Figure 6 shows the typical GPC curves of the copolymer. By comparison with the P(CL-*co*-TMC) obtained with tin catalysts[4] and a cationic-type[5] catalyst, two apparent characters can be seen for the P(CL-*co*-TMC) prepared by these rare earth catalysts. First, the molecular weight distribution of the copolymer is very narrow, e.g.,

$$\underset{b}{\underset{(\text{or HOCH}_2(\text{CH}_2)_4\overset{\text{O}}{\overset{\|}{\text{C}}})}{}} \overset{a}{\text{HOCH}_2\text{CH}_2\text{CH}_2\text{O}}\overset{\text{O}}{\overset{\|}{\text{C}}}(\overset{c}{\text{OCH}_2}\overset{d}{\text{CH}_2\text{CH}_2\text{O}}\overset{\text{O}}{\overset{\|}{\text{C}}}/\overset{e}{\text{OCH}_2}\overset{f}{\text{CH}_2}\overset{g}{\text{CH}_2}\overset{h}{\text{CH}_2}\overset{i}{\text{CH}_2}\overset{\text{O}}{\overset{\|}{\text{C}}})_n \overset{j}{\text{OCHCH}_2}(\overset{k}{\text{OCHCH}_2})_{x}\text{Cl}$$

Figure 9 Part of the ^{13}C-NMR spectrum of P(TMC-*co*-CL) prepared by the NdCl$_3$–5PO system.

1.20, even though the copolymerization was carried out at 80°C. The narrow polydispersity character was also observed in other copolymers (Table I). This means that the initiation reaction of the copolymerization is much faster than the chain propagation reaction. Second, a high-molecular-weight copolymer can be formed with the catalyst. The number-average molecular weight can be as high as 8×10^4 (intrinsic viscosity of 1.29 dL/g).

The thermal properties of the copolymers were analyzed by differential scanning calorimetry (DSC) as shown in Figure 7. All the copolymers show a single glass transition temperature between that of poly(ϵ-caprolactone) ($-65°C$) and poly(trimethylene carbonate) (about $-28°C$), confirming the random nature of the copolymers because block copolymer has two T_gs.[10] When the content of CL unit in the copolymer is high, e.g., 75%, it appears that a melting transition results from the imperfect crystallites of the CL units.

Polymerization Mechanism

We have already demonstrated that rare earth halide can react with epoxide and give rare earth alkoxide [eq. (2)]. This kind of rare earth alkoxide and rare earth isopropoxide are high effective catalysts for the homopolymerization of CL.[6] Therefore, it may be proposed that the rare earth alkoxides produced by the reaction of rare earth halide with epoxide may also be the actual cata-

lytic species for the copolymerization, as in the following:

$$\underset{\text{O}}{\triangle}^{R} + \text{LnCl}_3 \rightarrow \overset{R}{\underset{}{\text{Ln—(OCHCH}_2)_x}}\text{Cl} \quad (2)$$

confirmed by analyzing the end groups of the polymer. Figure 8 shows the ^{1}H-NMR spectrum of the copolymer obtained by NdCl$_3$–5PO. It can be found that, besides the signals of the copolymer backbone, two triplet signals appear at 3.75 and 3.65 ppm, assigned to the CH$_2$OH end groups, which resulted from TMC and CL, respectively. Signals at about 4.9 ppm are due to the ester groups of alkoxy of the catalysts. These end groups can also be confirmed by the ^{13}C-NMR (Fig. 9). Accordingly, the structures of the copolymer can be described as follows:

$$\overset{a}{\text{HOCH}_2\text{CH}_2\text{CH}_2\text{O}}\overset{\text{O}}{\overset{\|}{\text{C}}}(\overset{c}{\text{OCH}_2}\overset{d}{\text{CH}_2\text{CH}_2\text{O}}\overset{\text{O}}{\overset{\|}{\text{C}}}/$$

$$\overset{e}{\text{OCH}_2}\overset{f}{\text{CH}_2}\overset{g}{\text{CH}_2}\overset{h}{\text{CH}_2}\overset{i}{\text{CH}_2}\overset{\text{O}}{\overset{\|}{\text{C}}})_n \overset{m}{\text{OCHCH}_2}(\overset{n}{\text{OCHCH}_2})_{x-1}\text{Cl}$$
$$\underset{\text{CH}_3}{} \quad \underset{\text{CH}_3}{}$$

$$\underset{b}{(\text{or HOCH}_2(\text{CH}_2)_4\overset{\text{O}}{\overset{\|}{\text{C}}})}$$

Scheme 1   Coordination–insertion mechanism.

or rare earth isopropoxide can be described as Scheme 1, which is called a coordination–insertion mechanism.

CONCLUSION

Rare earth chloride–epoxide is an easier prepared and highly active catalyst for the random copolymerization of ϵ-caprolactone and trimethylene carbonate. The copolymer obtained has a high molecular weight with a narrow molecular weight distribution. It is the rare earth alkoxide generated by the reaction of rare earth chloride with epoxide that catalyzes the copolymerization via a coordination–insertion mechanism.

At the same time, no signal is found at about 3.4 ppm due to the trimethylene ether units in ^{1}H-NMR, indicating that the CL and TMC copolymerization catalyzed by $LnCl_3$–PO and $Nd(OiPr)_3$ should not be a cationic process because cationic polymerization of TMC can produce ether linkage in the polymer by decarboxylation reaction.[11] These observations clearly demonstrate that rare earth alkoxide generated by the reaction of rare earth chloride and epoxide [eq. (2)] initiates the copolymerization by insertion of CL and TMC units into the Ln—OR bond with acyl–oxygen bond cleavage of CL and TMC, as follows:

$$\rightarrow Ln(OCH_2CH_2CH_2O\overset{\overset{\displaystyle O}{\|}}{C}/$$

$$OCH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C})_n OR \xrightarrow{H_2O} HO(OCH_2$$

$$CH_2CH_2O\overset{\overset{\displaystyle O}{\|}}{C}/OCH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C})_n OR \quad (3)$$

Combining the observation that TMC[5] and CL[12] coordinate with rare earth ion with their carbonyl oxygen, the mechanism of copolymerization TMC with CL catalyzed by rare earth halide–epoxide

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