Characteristics and Mechanism of ϵ-Caprolactone Polymerization with Rare Earth Halide Systems

Youqing Shen*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Zhiquan Shen, Jianliang Shen, and Yifeng Zhang

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

Kemin Yao

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

Received December 12, 1995; Revised Manuscript Received February 20, 1996[⊗]

ABSTRACT: Ring-opening polymerization of ϵ-caprolactone catalyzed by rare earth halides and rare earth halide−epoxide has been carried out for the first time. It was found that rare earth halides have low activities for the polymerization of ϵ-caprolactone, but in the presence of epoxide, rare earth halides are highly active for the bulk and solution polymerization of ϵ-caprolactone, with high molecular weight poly(ϵ-caprolactone) (PCL) formed. With the $NdCl_3$−20PO system, PCL with a molecular weight of 22.4×10^4 can be easily obtained at 30 °C, and the molecular weight of PCL can be increased to 42×10^4 at 60 °C with a catalyst efficiency of 100×10^4 g of PCL/mol of $NdCl_3$. The catalytic activities of the rare earth halides are affected by the kind of rare earth element, halogen, epoxide, amount of added epoxide, catalyst concentration, and polymerization temperature. It has been found that rare earth halides react with epoxide and produce halogen rare earth alkoxides: $(X_{3-x}Ln\{[OCH(R)CH_2]_yX\}_x$, X = Cl, Br, I). A study on the polymerization mechanism showed that the resulting rare earth alkoxide bond initiates the polymerization of ϵ-caprolactone via a "coordination−insertion" mechanism with acyl-oxygen bond cleavage of the monomer during the ϵ-caprolactone polymerization catalyzed by rare earth halide−epoxide.

Introduction

Biodegradable poly(ϵ-caprolactone) (PCL) is an attractive polymer that can be used as a synthetic biomaterial or controlled drug release matrix due to its biodegradability and biocompatibility.[1] Ring-opening polymerization of ϵ-caprolactone (CL) is a convenient route to prepare high molecular weight PCL.[2] Various catalysts containing alkali metals,[3] aluminum,[4] zinc,[5] tin,[6] and early transition metals[7] have been developed for the ring-opening polymerization of ϵ-caprolactone. Recently, rare earth alkoxide[8] catalysts and organolanthanide catalysts such as $(C_5Me_5)_2LuCH_3$[9] and $(C_5Me_5)_2Sm(THF)_x$[10] have also been used in ϵ-caprolactone polymerization. High molecular weight PCL can be prepared by coordinate catalysts,[4] while anionic catalysts lead to a living ring−chain equilibrium and produce cyclic oligomers.[3]

In our group, it has been found that rare earth coordinate catalysts[11] and one component rare earth catalysts[12,13] also exhibit high activities for ϵ-caprolactone polymerization. Further study showed that rare earth halides—the raw materials of organolanthanide—are also effective for CL polymerization, and epoxide can greatly increase the activities of rare earth halides. This paper reports the characteristics and mechanism of ϵ-caprolactone polymerization catalyzed by rare earth halides.

Experimental Section

Materials. ϵ-Caprolactone (Mitsubishi) was dried and distilled over CaH_2 twice under reduced pressure. Propylene oxide (PO), ethylene oxide (EO), epichlorohydrin (ECH), and allyl glycidyl ether (AGE) were dried over CaH_2. Metaformaldehyde (TOX) was recrystallized from dry benzene. Tetrahydrofuran (THF) and toluene were distilled over the blue benzophenone−Na complex. Rare earth oxides (Ln_2O_3) with a purity of 99.99% were purchased from the Shanghai Yaolong factory.

Catalyst Preparation. Anhydrous rare earth halides were prepared by heating the mixture of hydrated rare earth halide and the corresponding ammonium halides under reduced pressure, respectively.[14] Catalyst solutions for ϵ-caprolactone solution polymerization were obtained by the reaction of rare earth chloride with epoxide in toluene. The concentrations of rare earth ion and chlorine in the catalyst solution were determined by titration with EDTA and $HgNO_3$ respectively, and the value of Cl/Ln was thus calculated.

Polymerization (General Procedure). All the polymerization reactions were carried out under dry nitrogen. Afterward, the mixture was dissolved in toluene, and the polymer was precipitated in excess methanol (containing 5% HCl), and washed with methanol several times, and then dried under vacuum.

Measurements. The intrinsic viscosity of PCL was determined in benzene at 30 °C with an Ubbelohde viscosimeter, and the viscosity-average molecular weight (M_v) was calculated by the equation $[\eta] = 9.94 \times 10^{-5} M_v^{0.82}$.[15] NMR spectra were recorded on a JEOL 90Q or a Bruker AR 500 NMR spectrometer in $CDCl_3$ at room temperature with TMS as the internal reference. IR spectra were measured on a Shimadzu IR-570 spectrometer. The GPC curves were recorded by gel permeation chromatography (Waters 150) in THF at 25 °C with polystyrene as the standard.

Results

Anhydrous rare earth halides are easily prepared and very stable. It was found that above 100 °C, rare earth halides can catalyze the polymerization of ϵ-caprolactone. Table 1 illustrates the results of the bulk poly-

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

Table 1. Bulk Polymerization of ϵ-Caprolactone by Rare Earth Halides[a]

LnX_3	time (h)	temp (°C)	conv (%)	$M_v \times 10^{-4}$
$LaCl_3$	40	100	58.3.	2.1
$NdCl_3$	40	100	82.5	4.5
$NdCl_3$	16	100	21.1	-
$NdCl_3$	16	130	100	3.9
$NdCl_3$	32	100	53.0	2.4
$NdBr_3$	32	100	55.8	2.5
NdI_3	32	100	60.6	3.2
$SmCl_3$	40	100	85.0	4.7
$DyCl_3$	40	100	88.0	2.7
$YbCl_3$	40	100	100	3.6
YCl_3	40	100	45.3	1.2

[a] Conditions: $CL/LnX_3 = 120$.

Table 2. Bulk Polymerization of ϵ-Caprolactone with Rare Earth Halide–20 Propylene Oxide Systems[a]

LnX_3	polym time (min)	conv (%)	$M_v \times 10^{-4}$
$LaCl_3$	560	87	26.7
$PrCl_3$	280	92	23.2
$NdCl_3$	240	100	22.1
$NdBr_3$	40	100	16.5
NdI_3	30	100	16.8
$SmCl_3$	180	100	19.7
$EuCl_3$	180	100	18.3
$GdCl_3$	150	97	18.1
$DyCl_3$	100	100	17.5
$YbCl_3$	60	100	16.1

[a] Conditions: $[LnX_3] = 3.01 \times 10^{-3}$, 30 °C, PO/Ln = 20.

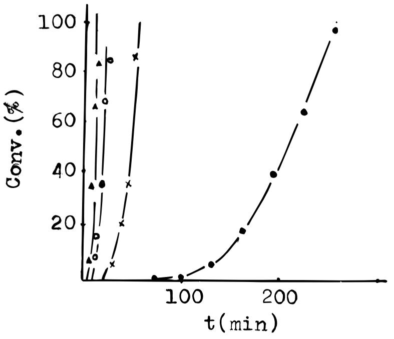


Figure 1. Time–conversion curves of ϵ-caprolactone bulk polymerization with various rare earth halide–propylene oxide systems: (▲) NdI_3–PO; (○) $NdBr_3$-PO; (●) $NdCl_3$–PO; (×) $DyCl_3$–PO. Polymerization conditions: $[LnX_3] = 3.01 \times 10^{-3}$ mol/L, 30 °C, PO/Ln = 20, bulk.

Table 3. Bulk Polymerization of ϵ-Caprolactone Catalyzed by Neodymium Chloride in the Presence of Different Kinds and Amounts of Epoxide[a]

cyclic ether	cyclic ether/Nd	$t_{100\%}$(min)[b]	$M_v \times 10^{-4}$
EO	20	150	15.9
PO	10	480	14.9
	20	240	21.8
	40	75	17.0
	100	70	16.0
ECH	10	480	17.4
	20	300	16.3
	30	260	16.1
AGE	20	300	15.4
none[c]		600[d]	
THF	20	600[d]	
TOX	20	600[d]	

[a] Conditions: $[NdCl_3] = 3.01 \times 10^{-3}$mol/L, 30 °C. [b] Time of ϵ-caprolactone reaching 100% conversion. [c] No cyclic ether added. [d] No polymer obtained after 10 h of polymerization.

merization of ϵ-caprolactone with rare earth halides. It can be seen that all the tested rare earth chlorides and neodymium bromide and iodide are effective for CL polymerization, but lanthanum and yttrium chlorides are less effective: catalysis by lanthanum chloride for 40 h gave a CL conversion of only about 58%, compared with 100% conversion with ytterbium chloride. There is no remarkable difference in catalytic activity between $NdCl_3$, $NdBr_3$, and NdI_3. The polymerization temperature affects the reaction significantly: Below 100 °C, the polymerization reaction proceeds very slowly, but it becomes more rapid at 120 °C. The molecular weight of PCL of ϵ-caprolactone polymerization singly catalyzed by rare earth halide is below 50 000 (M_v).

The catalytic activities of rare earth halides can be greatly increased by the addition of epoxide, as shown in Table 2. In the presence of propylene oxide, all the rare earth chlorides and neodymium halides are highly effective for the bulk polymerization of ϵ-caprolactone with a high polymerization rate, and high molecular weight PCL is formed even at room temperature. For example, a PCL with a molecular weight of 22.4×10^4 can be easily prepared by CL bulk polymerization with the $NdCl_3$–20PO system at 30 °C for 4 h. The data in Table 2 also show that heavy rare earth chloride–propylene oxide systems have higher catalytic activities than light rare earth chloride–propylene oxide systems: the time for CL to reach 100% conversion ($t_{100\%}$) is more than 560 min for the polymerization catalyzed by the $LaCl_3$–20PO system, while only 60 min by the $YbCl_3$–20PO system.

In contrast to the similar activities of neodymium halides in CL polymerization singly catalyzed by rare earth halide, neodymium bromide and iodide have much higher catalytic activities than neodymium chloride in the presence of propylene oxide: NdI_3–PO > $NdBr_3$–PO $\gg$ $NdCl_3$–PO, as shown in Table 2 and Figure 1.

Time–conversion curves (Figure 1) show that the CL bulk polymerization with rare earth halide–propylene oxide systems has an induction period which is needed for generating active species by the reaction of rare earth halide with epoxide (see the discussion section). The induction periods of CL bulk polymerization with various catalyst systems are different: it is only several minutes for catalysis by the NdI_3–20PO or $NdBr_3$–20PO system, and about 20 min by $DyCl_3$–20PO system, and as long as 100 min with the $NdCl_3$–20PO. Furthermore, the propagation rates of CL polymerization with the NdI_3–20PO, $NdBr_3$–20PO, and $DyCl_3$–20PO systems are also much faster than that catalyzed by $NdCl_3$–20PO. This difference in catalytic activity of rare earth halide–propylene oxide systems has been ascribed to the different reactivities of rare earth halide with propylene oxide (see discussion below).

The molecular weights of PCLs formed with more active catalysts, e.g., NdI_3–20PO, $NdBr_3$-20PO, and $DyCl_3$–20PO, are somewhat less than those with relatively less active catalysts, because heavy rare earth chlorides and neodymium bromide and iodide react with propylene oxide more easily and produce larger amounts of active species, as discussed below.

Besides propylene oxide, other three-membered cyclic ethers (epoxide) also have a promotive effect on the catalytic activities of rare earth halides (Table 3), but five-membered (THF) and six-membered (TOX) cyclic ethers do not. The catalytic activity order of $NdCl_3$ combined with different epoxides is: $NdCl_3$–20 ethylene oxide (EO) > $NdCl_3$–20 propylene oxide (PO) > $NdCl_3$–20 epichlorohydrin (ECH) $\cong$ $NdCl_3$–20 allyl glycidyl ether (AGE), which is consistent with the reactivities of the epoxide. The molecular weight of PCL formed at 100% conversion by the $NdCl_3$–20EO system is some-

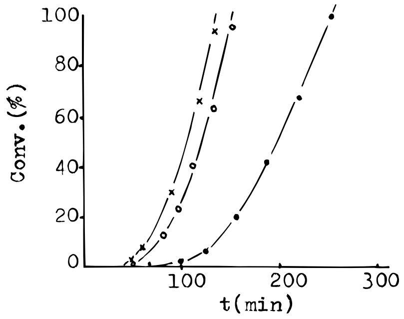


Figure 2. Time−conversion curves of ϵ-caprolactone bulk polymerization with $NdCl_3$−xPO systems: PO/Nd = 50 (×), 30 (○), and 20 (●) Polymerization conditions: $[NdCl_3] = 3.01 \times 10^{-3}$ mol/L, 30 °C, bulk.

Table 4. Bulk Polymerization of ϵ-Caprolactone with the $NdCl_3$−20PO System

no	$[NdCl_3] \times 10^3$	temp (°C)	$t_{100\%}$ (min)[a]	$M_v \times 10^{-4}$
1	9.47	30	75	6.2
2	4.74	30	120	11.4
3	3.15	30	240	22.2
4	2.37	30	350	28.9
5	1.89	30	600	34.0
6	3.15	45	45	22.8
7	3.15	60	30	21.8
8	3.15	70	17	20.2
9	3.15	90	5	18.1
10	1.67	60	80	39.4
11	1.05	60	240	42.1

[a] Time of CL reaching 100% conversion.

what lower than that by the $NdCl_3$−20PO system at 100% conversion due to the higher activity of EO.

Table 3 also shows that the more PO or ECH added to the polymerization systems, the shorter is the $t_{100\%}$ and the lower is the molecular weight of the PCL formed. The time−conversion curves at different PO/Nd ratios (Figure 2) show that the shortness of $t_{100\%}$ at higher PO/Nd ratio derives from the reductions of induction period and propagation time.

The optimum conditions of ϵ-caprolactone bulk polymerization with the $NdCl_3$−20PO system were examined, and the results are shown in Table 4. From the data in the table, three points can be drawn. First, the molecular weight of PCL can be controlled by the catalyst concentration: Decreasing neodymium chloride concentration leads to increasing molecular weight of PCL and catalyst efficiency (Table 4, nos. 1−5). At 30 °C, PCL with a molecular weight as high as 28.9×10^4 can be prepared with a catalyst activity of 44×10^4 g of PCL/mol of $NdCl_3$. Second, at higher polymerization temperature, the $NdCl_3$ concentration can be further decreased, accordingly giving a higher molecular weight of PCL and higher catalyst efficiency. For example, at 60 °C for 4 h, 1 mol of $NdCl_3$ can prepare 100×10^4 g of PCL with a molecular weight of 42×10^4. Third, increasing polymerization temperature can greatly reduce the $t_{100\%}$ of the ϵ-caprolactone polymerization. At a $NdCl_3$ concentration of 3.15×10^{-3} mol/L, the $t_{100\%}$ is 240 min at 30 °C, 30 min at 60 °C, and just 5 min at 90 °C. Figure 3 shows that at higher temperature, the reduction in $t_{100\%}$ also derives from the short induction and propagation times of ϵ-caprolactone polymerization.

In conclusion, rare earth halides combined with epoxide are highly efficient for the bulk polymerization of ϵ-caprolactone, giving a high molecular weight PCL. It was also found that heavy rare earth chlorides can react with epoxide in toluene and yield homogeneous solution, which can catalyze the solution polymerization of ϵ-caprolactone, as shown in Table 5. No apparent reaction between light rare earth chlorides ($LaCl_3$, $PrCl_3$, $NdCl_3$) and epoxide in toluene was found.

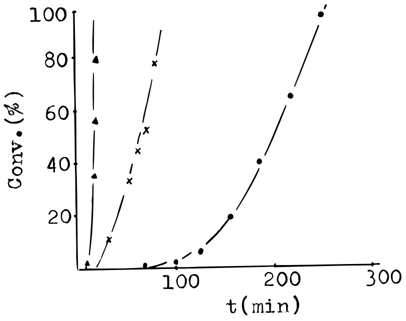


Figure 3. Effect of temperature on the bulk polymerization of CL with the $NdCl_3$−20PO system: (▲) 60 °C; (×) 45 °C; (●) 30 °C. Polymerization conditions: $[NdCl_3] = 3.01 \times 10^{-3}$ mol/L, PO/Ln = 20, bulk.

Table 5. Solution Polymerization of ϵ-Caprolactone by Heavy Rare Earth Chloride−Epoxide[a]

no	epoxide	$LnCl_3$	epoxide/Ln	conv (%)	$M_v \times 10^{-4}$
1	PO	$GdCl_3$	10	100	9.08
2	PO	$DyCl_3$	10	100	10.2
3	PO	$YbCl_3$	10	100	6.13
4	PO	$DyCl_3$	20	100	8.3
5	PO	$DyCl_3$	30	100	5.3
6	EO	$DyCl_3$	10	100	7.0
7	ECH	$DyCl_3$	10	100	8.3

[a] Polymerization conditions: $[Ln] = 3.5 \times 10^{-3}$ mol/L, [CL] = 5.0 mol/L, 60 °C, 1 h; catalyst: $LnCl_3$ + toluene + epoxide, 20 °C, aging 1 h.

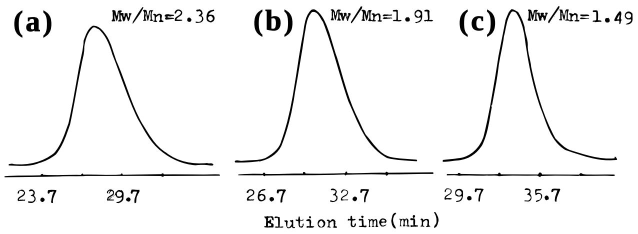


Figure 4. GPC curves of PCL obtained by under the following conditions: (a) $PO/NdCl_3 = 20$, 240 min, conversion 100%; (b) $PO/NdCl_3 = 70$, 75 min, conversion 100%, $[NdCl_3] = 3.01 \times 10^{-3}$ mol/L, 30 °C, bulk; (c) Table 5, no. 2.

From the data in Table 5, it can be found that there is no large difference in catalytic activities between different heavy rare earth chloride−epoxide systems. The ϵ-caprolactone polymerizations in toluene with different catalyst systems all can give a 100% conversion in an hour at 30 °C, but the molecular weights of PCL obtained with various catalyst systems are different due to the different amounts of active species produced.

Figure 4 shows the GPC curves of PCLs obtained with the $NdCl_3$−PO and $DyCl_3$−10PO systems. It can be found that the molecular weight distribution of the PCL derived with $NdCl_3$−70PO is narrower than the one obtained with the $NdCl_3$−20PO system. This may be attributed to the rapid initiation reaction resulting from the faster reaction of $NdCl_3$ with PO at higher PO concentration. This explanation can also be verified by the narrower molecular weight distribution of the PCL obtained by the solution polymerization of ϵ-caprolactone catalyzed by the $DyCl_3$−10PO system.

Discussion

The results stated above demonstrate that epoxide can greatly activate rare earth halides for the ϵ-capro-

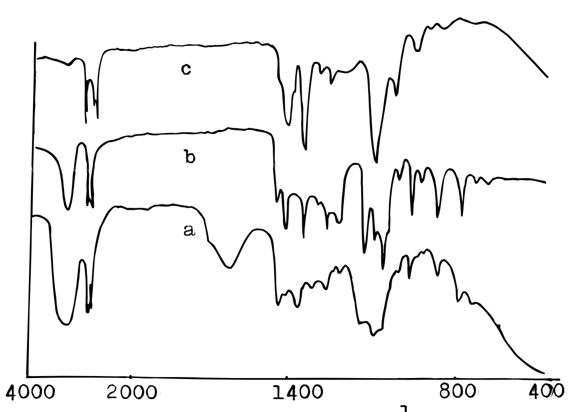


Figure 5. IR spectra of (a) compound a separated from the $DyCl_3-PO$ reaction solution, (b) 1-chloropropanol, and (c) poly(propylene oxide).

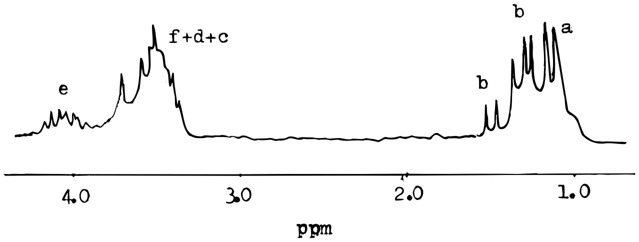


Figure 6. ^{1}H-NMR (90 MHz) spectrum of compound a separated from the $DyCl_3-PO$ reaction solution.

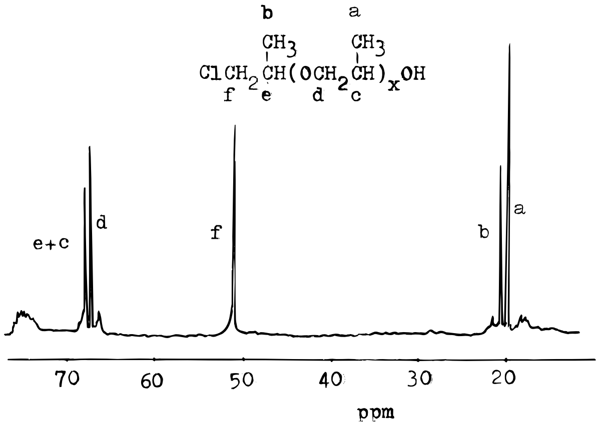
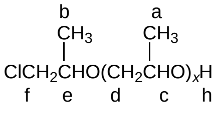


Figure 7. ^{13}C-NMR (125 MHz) spectrum of compound a separated from the $DyCl_3-PO$ reaction solution.

lactone polymerization, therefore, it can be postulated that there must be a reaction between rare earth halides and epoxide. In fact, heavy rare earth chlorides can react with epoxide exothermally, and the reaction products can easily dissolve in toluene, CCl_4, and other organic solvents. These solutions are very sensitive to moisture. When water is added, a precipitate immediately separates from the solution. Analysis shows the precipitate is $Ln(OH)_3$. From the terminated catalyst solution, a viscous organic liquid can be extracted.

Figure 5 shows the IR spectra of compound a (separated from the $DyCl_3-PO$ reaction solution), poly(proplene oxide) (PPO), and l-chloro-2-propanol. By comparing the spectra, it can be found that compound a has an ether absorption band at 1080 cm^{-1} and the typical absorption bands of 1-chloro-2-propanol at 1130 and 1050 cm^{-1}. At 3400 cm^{-1}there is also a strong absorption band due to OH. Figures 6 and 7 show the ^{1}H-NMR and ^{13}C-NMR spectra of compound a, respectively. By referencing the standard spectra of model compounds (Table 6), signals are assigned as follows. ^{1}H-NMR: $\delta = 1.13$ (doublet, H_a); $\delta = 1.25$ (doublet) and 1.45 (doublet) (H_b); $\delta =$ ca. 3.5 ppm (multiplet, $H_d + H_f + H_c$); $\delta = 4.01$ (multiplet, H_e). ^{13}C-NMR: $\delta = 20.1$ (C_a); $\delta = 20.9$ (C_b); $\delta = 68.1$ (C_{e+c}); $\delta = 67.6$ (C_d); $\delta = 51.3$ (C_f).

These facts indicate that compound a separated from the $DyCl_3-PO$ reaction solution is a mixture of propylene oxide oligomers. The x value estimated from the intensity ratio of C_a to C_b in Figure 7 is about 1.5, indicating that the compound a is mainly composed of the dimer and trimer of propylene oxide.

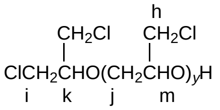


$$\underset{f}{\mathrm{ClCH_2}}\underset{e}{\overset{\overset{b}{\mathrm{CH_3}}}{\mathrm{CH}}}\mathrm{O(}\underset{d}{\mathrm{CH_2}}\underset{c}{\overset{\overset{a}{\mathrm{CH_3}}}{\mathrm{CH}}}\mathrm{O)}_x\underset{h}{\mathrm{H}}$$

compound a

Powder $NdCl_3$ cannot react with epoxide directly, but $NdCl_3$ dissolved in γ-butyrolactone (γ-BL) can react with epoxide rapidly. The ^{1}H-NMR spectrum shows that $NdCl_3$ in γ-BL also reacts with propylene oxide, and gives oligomers of propylene oxide too (Figure 8).

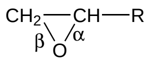
Heavy rare earth chlorides can also react with ECH in toluene exothermally, giving a yellowish homogeneous solution. Figure 9 shows the ^{13}C-NMR spectrum of compound c separated from the reacted solution of $DyCl_3-ECH$ and the corresponding signal assignments. This figure also indicates that compound c is mainly a hexamer of epichlorohydrin estimated by the intensity of C_b and C_j, which is in agreement with the strong ether band absorption at 1100 cm^{-1} in the IR spectrum of compound c (Figure 10).



$$\underset{i}{\mathrm{ClCH_2}}\underset{k}{\overset{\mathrm{CH_2Cl}}{\mathrm{CH}}}\mathrm{O(}\underset{j}{\mathrm{CH_2}}\underset{m}{\overset{\overset{h}{\mathrm{CH_2Cl}}}{\mathrm{CH}}}\mathrm{O)}_y\mathrm{H}$$

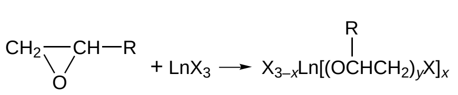
compound c

In the ^{13}C-NMR spectra of compounds a and c (Figures 7 and 9), it is noteworthy that there are no signals due to 2-chloro-1-propanol ($HOCH_2CHClCH_3$) in compound a or 2,3-dichloro-1-propanol ($HOCH_2CHClCH_2Cl$) in compound c (see the chemical shifts of model compounds in Table 6). These observations clearly corroborate that the cleavage model of PO or ECH is not via α but rather β, cleavage when they react with rare earth chloride.



Chlorine titration shows that the reaction solutions of rare earth chloride–epoxide still contain titratable chloride ions (Cl^-) (Figure 12), which means that some of the three chlorines in $LnCl_3$ are still attached to the rare earth ion ($Ln-Cl$).

From the above results, one can conclude that rare earth halides react with epoxide and yield halogen rare earth alkoxides (eq 1). This reaction is different from that of ferric chloride with propylene oxide, in which the cleavage of propylene oxide is via α cleavage.[16]



$$\mathrm{CH_2{-}CH{-}R\ (epoxide)} + \mathrm{LnX_3} \longrightarrow \mathrm{X_{3-x}Ln[(O\overset{\overset{R}{|}}{C}HCH_2)_yX]_x} \quad (1)$$

X = Cl, Br, I; R = H, CH_3, CH_2Cl, $CH_2OCH_2CH=CH_2$, etc.

Table 6. Chemical Shifts of Model Compounds (ppm)[a]

compound	^{1}H-NMR a	^{1}H-NMR b	^{1}H-NMR c	^{1}H-NMR d	^{13}C-NMR a	^{13}C-NMR b	^{13}C-NMR c
$\overset{a}{CH_3}\overset{b}{CH}(\overset{d}{OH})\overset{c}{CH_2}Cl$	1.25, 1.49 (q)	3.91	3.45, 3.60 (m)	3.71	20.3	67.7	50.8
$[(\overset{a}{CH_3})\overset{b}{CH}\overset{c}{CH_2}O]$	1.14 (d)	(b + c) ca. 3.4 (multi)			17.4	75.3	73.1
$\overset{a}{CH_3}\overset{b}{CH}(OH)\overset{c}{CH_2}OH$					19.0	68.4	67.7
$Cl\overset{a}{CH_2}\overset{b}{CH}(OH)\overset{c}{CH_2}OH$	ca. 3.66	3.88	ca. 3.66		46.4	72.3	64.0
$Cl\overset{a}{CH_2}\overset{b}{CH}(OH)\overset{a}{CH_2}Cl$					46.0	71.1	
$[O\overset{a}{CH_2}\overset{b}{CH}(\overset{c}{CH_2}Cl)]$					68.5	78.0	44.0
$Cl\overset{a}{CH_2}\overset{b}{CH}Cl\overset{c}{CH_2}OH$					44.6	63.4	61.1

[a] Data from Sadtler Standard Spectra.

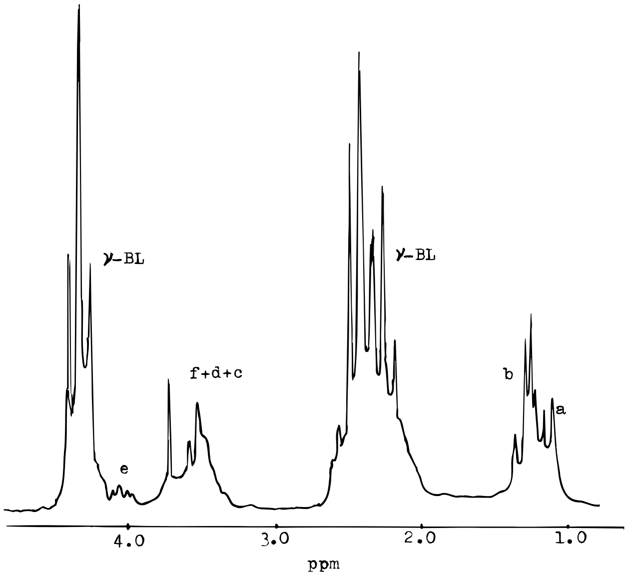


Figure 8. ^{1}H-NMR spectrum (90 MHz) of compound b separated from the $NdCl_3-\gamma$-BL−PO reaction solution.

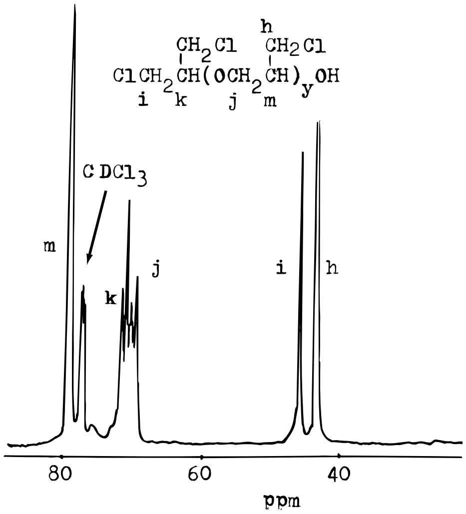


Figure 9. ^{13}C-NMR (125 MHz) spectrum of compound c separated from the $DyCl_3$−ECH reaction solution.

It has been demonstrated that rare earth alkoxides are very effective for ϵ-caprolactone polymerization;[12] therefore the resulting halogen rare earth alkoxide generated by the reaction of rare earth halide with epoxide may be the actual initiator in the ϵ-caprolactone polymerization with rare earth halide−epoxide as catalyst. This assumption can be verified by analyzing the end groups of the PCL formed. The ^{1}H-NMR spectrum of PCL obtained by the $NdCl_3$−PO system and the signal assignments are shown in Figure 11. In addition to the backbone signals of PCL, triplet signals at 3.6 ppm assigned to $C\mathit{H}_2OH$ and ca. 5.1 ppm assigned to $COOC\mathit{H}(CH_3)CH_2O$ are present. Therefore, the structure of PCL obtained with the rare earth halide−epoxide system is as follows:

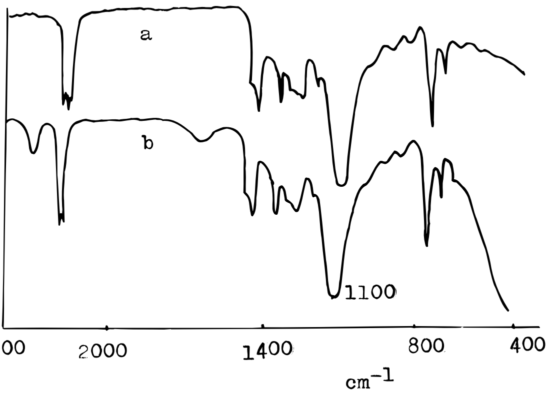


Figure 10. IR spectra of (a) compound c separated from the $DyCl_3$−ECH reaction solution and (b) poly(epichlorohydrin).

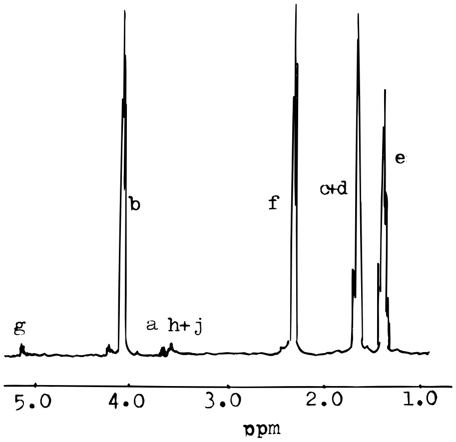
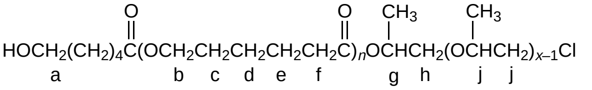


Figure 11. ^{1}H-NMR (500 MHz) spectrum of PCL obtained with the $NdCl_3$−PO system.



$$HO\underset{a}{CH_2}(CH_2)_4\overset{O}{\overset{\|}{C}}(O\underset{b}{CH_2}\underset{c}{CH_2}\underset{d}{CH_2}\underset{e}{CH_2}\underset{f}{CH_2}\overset{O}{\overset{\|}{C}})_nO\underset{g}{\overset{CH_3}{\overset{|}{CH}}}\underset{h}{CH_2}(O\underset{j}{\overset{CH_3}{\overset{|}{CH}}}\underset{j}{CH_2})_{x-1}Cl$$

Therefore, in the polymerization of ϵ-caprolactone catalyzed by rare earth halide−epoxide systems, it is

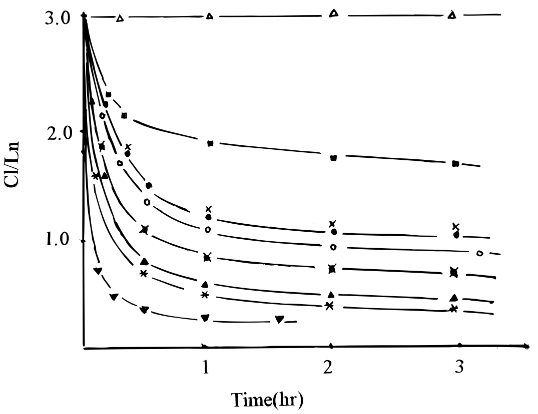
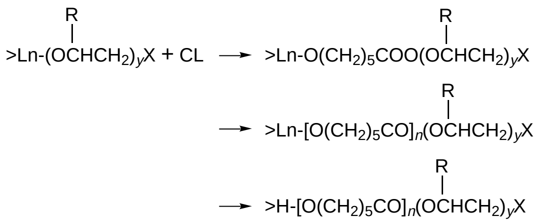


Figure 12. Changes of Cl/Ln with time in different rare earth chloride−epoxide reaction solutions: (△) $NdCl_3$−20THF or $NdCl_3$−20TOX; (▲) $NdCl_3$−20EO; (○) $NdCl_3$−20PO; (●) $NdCl_3$−20ECH; (×) $NdCl_3$−20AGE; (⊗) $NdCl_3$−50PO; (*) $DyCl_3$−20PO; (◆) $LaCl_3$−20PO; (▼) $NdCl_3$−20PO (at 60 °C). $[NdCl_3] = 0.0424$ mol/L, 25 °C, γ-butyrolactone as solvent.

proposed that rare earth alkoxide bonds produced by the reaction of the rare earth halide with the epoxide catalyze the polymerization of ϵ-caprolactone via a "coordination−insertion" mechanism with acyl-oxygen bond cleavage of CL (eq 2).



$$\begin{aligned} &\text{>Ln-(O}\overset{\text{R}}{\text{C}}\text{HCH}_2)_y\text{X} + \text{CL} \longrightarrow \text{>Ln-O(CH}_2)_5\text{COO(O}\overset{\text{R}}{\text{C}}\text{HCH}_2)_y\text{X} \\ &\longrightarrow \text{>Ln-[O(CH}_2)_5\text{CO]}_n\text{(O}\overset{\text{R}}{\text{C}}\text{HCH}_2)_y\text{X} \\ &\longrightarrow \text{>H-[O(CH}_2)_5\text{CO]}_n\text{(O}\overset{\text{R}}{\text{C}}\text{HCH}_2)_y\text{X} \qquad (2) \end{aligned}$$

Because the produced rare earth alkoxide bond (>Ln−OR) is the actual active site in the rare earth halide−epoxide catalyst, factors affecting the generation rate and the number of Ln−OR bonds would have influences on the catalytic activity of the rare earth halide−epoxide. Equation 1 shows that the number of residual halogens still attached to the rare earth ion (X/Ln) relates to the average number of rare earth alkoxide bonds per Ln^{3+} (x): $X/Ln = 3 - x$. A faster decreasing X/Ln value and lower X/Ln value indicate the a faster Ln−OR bond generation rate and more Ln−OR bonds produced, respectively. In order to examine the reaction of rare earth halide with epoxide in CL bulk polymerization catalyzed by rare earth halide−epoxide, nonpolymerizable γ-butyrolactone (γ-BL), which has a molecular structure similar to that CL, was used as a model compound to dissolve rare earth halide. Figure 12 shows changes of Cl/Ln in different rare earth chloride−epoxide reaction solutions. By comparing the different curves, the following conclusions can be drawn: (1) There is no Cl/Nd change in the $NdCl_3$−THF or $NdCl_3$−TOX system, which means there is no reaction between $NdCl_3$ and THF or TOX. (2) The generation rate and the number of Nd−OR bonds of different $NdCl_3$−epoxide systems decrease in the order $NdCl_3$−EO > $NdCl_3$−PO > $NdCl_3$−ECH ≅ $NdCl_3$−AGE. (3) $NdCl_3$ reacts with PO more rapidly and yields more Nd−OR bonds as the amount of PO or the reaction temperature increases. (4) $DyCl_3$ reacts more easily with PO than $NdCl_3$ and $LaCl_3$. In the bulk polymerization of ϵ-caprolactone catalyzed by rare earth halide−epoxide, the rapid reaction of LnX_3 with epoxide, i.e., the rapid generation of active species, decreases the induction period and the more Ln−OR bonds produced increase the propagation rate of the bulk polymerization. Accordingly, it can be found that the phenomena observed in Figure 12 are consistent with the characteristics of ϵ-caprolactone bulk polymerization with rare earth halide−epoxide, as described above.

Conclusion

Rare earth halides react with epoxide and give halogen rare earth alkoxides ($X_{3-x}Ln\{[OCH(R)CH_2]_yX\}_x$, X = Cl, Br, I), which are highly active for the ring-opening polymerization of ϵ-caprolactone. The mechanism study showed that the resulting rare earth alkoxide bonds initiate the polymerization of ϵ-caprolactone via a "coordination−insertion" mechanism.

Acknowledgment. We gratefully acknowledge the financial support of the National Nature Science Foundation of China and the National Laboratory of Polymerization Reaction Engineering of Zhejiang University. We also thank the State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics, Academia Sinica, Wuhan, for the NMR study.

References and Notes

(1) Pitt, C. G.; Marks, T. A.; Schindler, A. In *Controlled Drug Release of Bioactive Materials*; Baker, R., Ed.; Academic Press: New York, 1980; p 19.
(2) Peckham, G. T.; Filichioni, E. M. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Wiley: New York, 1967; Vol. 2, p 170.
(3) Ito, K.; Yamashita, Y. *Macromolecules* **1978**, *11* (1), 68.
(4) Ouhadi, T.; Stevens, C.; Teyssie, Ph. *Makromol. Chem. Suppl.* **1975**, *1*, 191.
(5) Barakat, I.; Dubois, Ph.; Jerome, R. *Macromolecules* **1991**, *24*, 6542.
(6) Okuda, J.; Rushkin, I. L. *Macromolecules* **1993**, *26*, 5530.
(7) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982.
(8) Mclain, S. J.; Drysadale, N. E. *Polym. Prepr.* **1992**, 174.
(9) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097.
(10) Evans, W. J.; Katasuata, H. *Macromolecules* **1994**, *27*, 2330.
(11) Shen, Z. Q.; Chen, X. H.; Shen, Y. Q.; Zhang, Y. F. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *33*, 597.
(12) Shen, Y. Q.; Shen, Z. Q.; Zhang, F. Y.; Zhang, Y. F. *Polym. J.* **1995**, *27*, 59.
(13) Shen, Z. Q.; Shen, Y. Q.; Sun, J. Q.; Zhang, F. Y.; Zhang, Y. F. *Chin. Sci. Bull.* **1994**, *39* (13), 1096.
(14) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.
(15) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 897.
(16) Colclough, R. O.; Gee, G.; Higginson, W. C. E.; Jackson, J. B.; Litt, M. *J. Polym. Sci.* **1959**, *34*, 171.

MA9518363