

Ring Opening Polymerization of ϵ -Caprolactone by Rare Earth Alkoxide- CCl_4 Systems

Youqing SHEN, Zhiqian SHEN,* Fuyao ZHANG, and Yifeng ZHANG

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

(Received May 23, 1994)

ABSTRACT: Rare earth alkoxides are highly active initiators for ring opening polymerization of ϵ -caprolactone in CCl_4 . The molecular weight of the polymer obtained can be as high as 1.8×10^5 (\bar{M}_v) at 60°C in an hour. The influence of solvent, rare earth element, ligand, monomer, and catalyst concentration, as well as the polymerization temperature and time was investigated. A mechanism study by IR, UV, and ^1H NMR spectra showed that the polymerization of ϵ -caprolactone catalyzed by rare earth alkoxides proceeds through a "coordination-insertion" mechanism and selective cleavage of acyl-oxygen bonds of the monomer.

KEY WORDS Ring Opening Polymerization / ϵ -Caprolactone / Rare Earth Alkoxide- CCl_4 /

In the family of polyesters, poly(ϵ -caprolactone) (PCL) is of great interest due to its biodegradability with releasing nontoxic by-products *in vitro* and *in vivo* required for synthetic polyesters used in artificial organs and drugs,^{1,2} and miscibility in many polymers.³

Therefore, various catalysts for the polymerization of ϵ -caprolactone (ϵ -CL), such as active hydrogen compounds, ionic and coordination catalysts, were investigated.⁴ Among the catalysts, coordination catalysts, bimetallic μ -oxoalkoxide,⁵ aluminium alkoxide, transition metal alkoxides,⁶ and metalloprophyrin,⁷ are the most notable, because by which a high molecular weight polymer with a narrower molecular weight distribution can be synthesized.

There are a few studies on the polymerization of ϵ -CL using rare earth compounds as catalysts.^{8,9} Recently, we found that rare earth alkoxides in carbon tetrachloride (CCl_4) are highly active catalytic systems for ϵ -CL polymerization and PCL with molecular weight

(\bar{M}_v) as high as 1.8×10^5 can be prepared with these systems.¹⁰ This paper reports a preliminary study on the characteristics and mechanism aspects of the polymerization of ϵ -CL catalyzed by rare earth isopropoxide- CCl_4 systems.

EXPERIMENTAL

Materials

ϵ -Caprolactone (Mitsubishi) was dried and distilled over CaH_2 under reduced pressure. Toluene, benzene and tetrahydrofuran (THF) were distilled over the blue benzophenone-Na complex before use. CCl_4 , CHCl_3 , CH_2Cl_2 were washed with sulfuric acid, water, aqueous NaHCO_3 successively, dried over CaCl_2 , and refluxed over CaH_2 under nitrogen atmosphere. Isopropyl alcohol was distilled over sodium isopropoxide under nitrogen atmosphere. Rare earth oxides (Ln_2O_3) with purity of 99.99% were purchased from Shanghai Yaolong factory.

* To whom correspondence should be addressed.

Catalyst Preparation

Anhydrous rare earth chlorides and rare earth alkoxides were prepared according to ref 11 and 12, respectively.

Polymerization

Polymerization was carried out in a glass ampule heated, evacuated and filled with nitrogen for several cycles before use. Solvent, monomer, and catalyst solutions were added to the ampule successively. The ampule was kept thermostated. The reaction was terminated by methanol containing 5% HCl. The polymer was reprecipitated with toluene-petroleum and dried at 30°C in vacuum.

Table I. Solvent effects on the polymerization of ϵ -CL

Solvent	ϵ -CL/Nd	Conversion		D^a	$\bar{M}_v \times 10^{-4}$
		%			
Carbon tetrachloride	2400	96	2.20	18.1	
Benzene	2400	21.0	2.28	4.2	
Toluene	2400	11.0	2.33	2.1	
Chloroform	2400	0	4.72	—	
THF	2400	0	7.35	—	
Dichloro-methane	2400	0	10.45	—	
2-Butanone	2400	0	18.51	—	

^a Dielectric constant of the solvent.

Conditions: $[\text{Nd(O-iso-Pr)}_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, 60°C, 1 hour.

Measurements

The intrinsic viscosity of polymer determined in benzene at 30°C with an Ubbelohde viscosimeter and viscosity average molecular weight (\bar{M}_v) was calculated by the following equation: $[\eta] = 9.94 \times 10^{-5} \bar{M}_v^{0.82}$.¹³ The number average molecular weight (\bar{M}_n) and molecular weight distribution (MWD) were determined by gel permeation chromatography (Waters 150) in THF at 25°C using polystyrene as standard. The corrected number average molecular weight ($\bar{M}_{n(\text{corr.})}$) was corrected by the universal calibration method. ¹H NMR spectra were obtained on a Jeol PX-90Q spectrometer in CDCl_3 at room temperature with tetramethylsilane (TMS) as the internal reference. IR and UV-VIS spectra were recorded under nitrogen atmosphere on a Shimadzu IR-570 and Beckman-50 spectrophotometer, respectively.

RESULTS AND DISCUSSION**Characteristics of the Polymerization**

Investigation of the effects of solvent on the ring opening polymerization of ϵ -CL with neodymium isopropoxide showed that ϵ -CL can be polymerized only in nonpolar solvents at catalyst concentration as low as $5.14 \times 10^{-4} \text{ mol l}^{-1}$ (Table I). The data in Table I illustrate that the neodymium isopropoxide- CCl_4 system is an extraordinary highly active catalyst system for ϵ -CL polymerization. PCL with a

Table II. Effects of various rare earth elements on the polymerization of ϵ -CL^a

Ln(O-iso-Pr)_3	Radii of Ln^{3+}	Conversion		$\bar{M}_v \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$ (Corr.)	MWD
		%				
La	106.1	100		18.5	9.18	2.04
Pr	101.3	97		18.0	9.11	1.97
Nd	99.5	96		18.1	9.10	1.92
Gd	93.8	90		14.8	8.00	1.77
Dy	90.8	84		14.5	7.67	1.37
Y	88.0	80		14.0	7.08	1.20

^a Conditions: $[\text{Ln(O-iso-Pr)}_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, ϵ -CL/Nd = 2400, 60°C; 1 hour, CCl_4 as the solvent.

Table III. Effects of the ligand on the polymerization of ϵ -CL

No.	Ln	Ligand	Conversion %
1	Nd	O-iso-Pr	96
2	Nd	O-Ph	24
3	Nd	Cl	0

^a Conditions: $[NdX_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, ϵ -CL/Nd = 2400, 60°C, 1 hour, CCl_4 as the solvent.

molecular weight as high as 1.8×10^5 (M_v) can be prepared with an activity of $2.7 \times 10^5 \text{ g PCL/molar Nd}$ at 60°C in an hour. No reactions occur between carefully purified CCl_4 or $CHCl_3$ and $Nd(O\text{-iso-Pr})_3$. The reason for the high activity of $Nd(O\text{-iso-Pr})_3$ in CCl_4 is under investigation.

Table II summarizes the results of ϵ -CL polymerization with six different rare earth isopropoxides in CCl_4 and showed that all six isopropoxides can polymerize ϵ -CL into high molecular weight PCL effectively, but isopropoxides of Gd, Dy, and Y give somewhat lower yields and molecular weights of PCL, in accordance with the smaller radii of the ions and different association of the isopropoxides.

The ligand attached to the rare earth element affects polymerization significantly, as shown in Table III. The polymerization activity of the compounds is in following order: $Nd(O\text{-iso-Pr})_3 \gg Nd(O\text{-Ph})_3 \gg NdCl_3$, which is in accordance with the nucleophilicity of the groups, O-iso-Pr > O-Ph > Cl, and contrary to the stability order of the three compounds indicated by the following reactions (1—3)¹²:

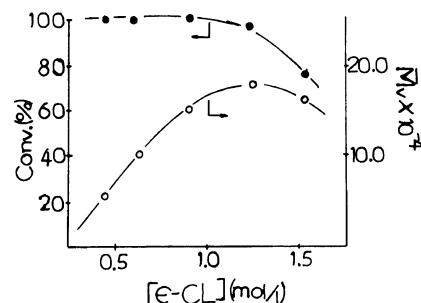
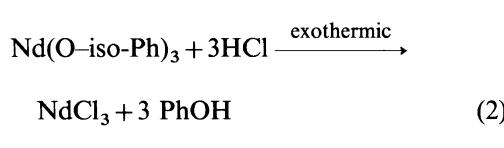
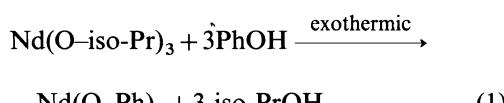


Figure 1. Effects of ϵ -CL concentration on the polymerization of ϵ -CL. Conditions: $[Nd(O\text{-iso-Pr})_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, ϵ -CL/Nd = 2400, 60°C, 1 hour, CCl_4 as the solvent.

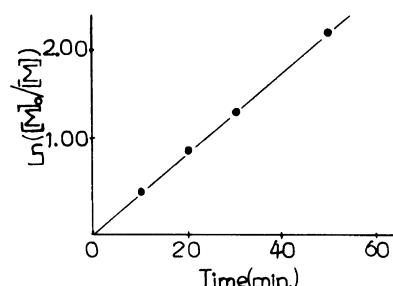
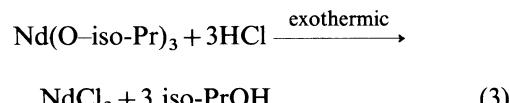


Figure 2. ϵ -CL consumption as a function of time. Conditions: $[Nd(O\text{-iso-Pr})_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, ϵ -CL/Nd = 2400, 60°C, CCl_4 as the solvent.



The effect of ϵ -CL concentration on the polymerization is shown in Figure 1. It can be seen that ϵ -CL can be polymerized completely in an hour at less than 1.2 mol l^{-1} , and the conversion of ϵ -CL drops at higher ϵ -CL concentration. The molecular weight of PCL increases with ϵ -CL after 100% conversion and reaches a maximum at 1.2 mol l^{-1} .

Figure 2 illustrates monomer consumption as a function of polymerization time, showing that ϵ -CL polymerization with $Nd(O\text{-iso-Pr})_3$ in CCl_4 is first order in the monomer. The deleterious effect of higher ϵ -CL concentrations on polymerization may be due to the high polarity of ϵ -CL molecules (dipole moment 4.45).

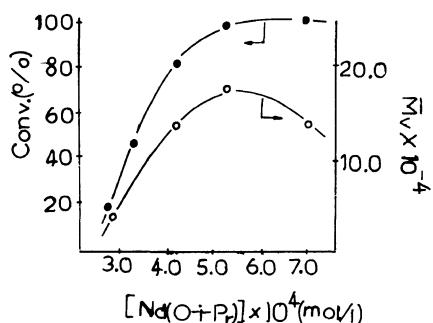


Figure 3. Effects of catalyst concentration on the polymerization of ϵ -CL. Conditions: $[\epsilon\text{-CL}] = 1.23 \text{ mol l}^{-1}$, 60°C , 1 hour, CCl_4 as the solvent.

Table IV. Influence of polymerization time and temperature on the polymerization of ϵ -CL^a

Temp. °C	Time min	Conversion		$\bar{M}_v \times 10^{-4}$
		%		
60	10	34.0		4.85
60	20	53.8		7.26
60	30	75.0		10.9
60	50	90.0		15.0
60	60	96.0		18.1
20	60	40.0		8.2
40	60	80.5		13.5
50	60	91.8		16.5
60	60	98.9		18.0
80	60	100.0		15.5

^a Conditions: $[\text{Nd(O-iso-Pr)}_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, $\epsilon\text{-CL}/\text{Nd} = 2400$, CCl_4 as the solvent.

It can be seen from Figure 3 that the conversion of ϵ -CL and molecular weight of PCL reaches 100% and 1.8×10^5 respectively at Nd(O-iso-Pr)_3 concentration of $5.14 \times 10^{-4} \text{ mol l}^{-1}$. At higher catalyst concentration, the molecular weight drops owing to increasing number of active species.

From Figures 1 and 3, it can be seen that the molecular weight of PCL gives a linear relationship with ϵ -CL concentration after 100% conversion of ϵ -CL and increases with the conversion of ϵ -CL respectively. This may mean that the polymerization has a somewhat living character.

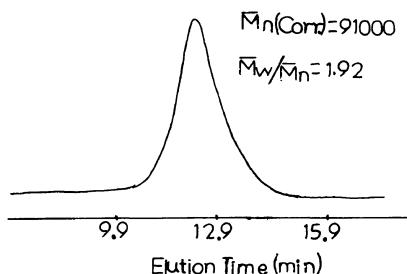


Figure 4. GPC curve of PCL. Conditions: $[\text{Nd(O-iso-Pr)}_3] = 5.14 \times 10^{-4} \text{ mol l}^{-1}$, $\epsilon\text{-CL}/\text{Nd} = 2400$, 60°C , 1 hour, CCl_4 as the solvent.

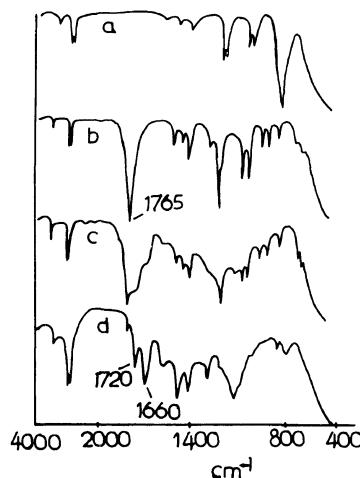


Figure 5. IR spectra of (a) $\text{Nd(O-iso-Pr)}_3\text{-CCl}_4$, (b) γ -butyrolactone, (c) $\text{Nd(O-iso-Pr)}_3\text{-}\gamma$ -butyrolactone (1 : 20), and (d) precipitate from benzene solution of Nd(O-iso-Pr)_3 and γ -butyrolactone (1 : 5) by heptane.

The effects of polymerization temperature and time are summarized in Table IV. The data show that 60°C and 1 hour are preferable for the polymerization of ϵ -CL catalyzed by Nd(O-iso-Pr)_3 in CCl_4 .

GPC measurement of PCL obtained under the above conditions shows that cyclic oligomers were not present in the polymerization, as shown in Figure 4.

MECHANISM ASPECTS

The effects of solvent and monomer concentration on the polymerization catalyzed

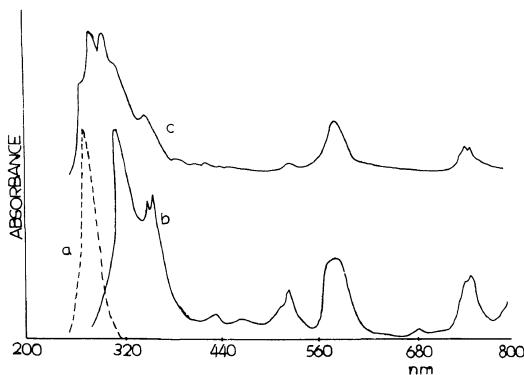


Figure 6. UV-VIS spectra of benzene solution of (a) γ -butyrolactone, (b) $\text{Nd}(\text{O-iso-Pr})_3$, and (c) $\text{Nd}(\text{O-iso-Pr})_3$ - γ -butyrolactone (1:5) benzene as a reference.

with $\text{Nd}(\text{O-iso-Pr})_3\text{-CCl}_4$ system discussed above imply that the ring opening polymerization of ϵ -CL proceeds *via* a coordination mechanism. This assumption was verified by the coordination reaction between lactone and neodymium isopropoxide identified by new absorption bands in the IR and UV-VIS spectra. A nonpolymerizable γ -butyrolactone was used instead of ϵ -CL because ϵ -CL polymerizes very quickly at a low ϵ -CL/Nd molar ratio even at -20°C . Figures 5 and 6 shows that IR absorption bands of γ -butyrolactone (1765 cm^{-1}) and UV absorption bands (280 nm) diminish and two new IR absorption bands (1720 cm^{-1} and 1660 cm^{-1})

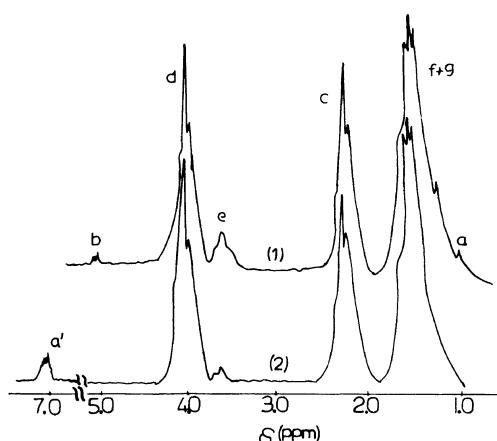
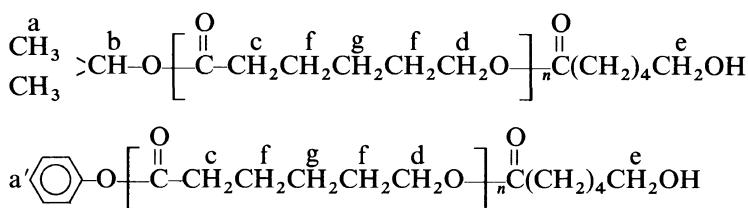


Figure 7. ^1H NMR spectra of PCL obtained with different neodymium alkoxides as the catalyst: (1) $\text{Nd}(\text{O-iso-Pr})_3$ and (2) $\text{Nd}(\text{O-Ph})_3$.

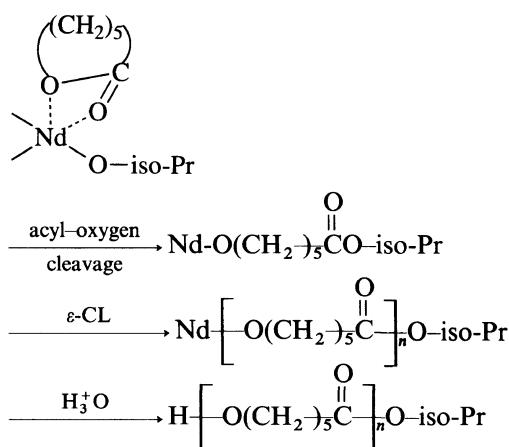
and two new UV absorption bands (290 nm and 294 nm) appear.

The ring opening model of ϵ -CL molecule can be distinguished by analysing the structure of the end groups of the polyester prepared. The ^1H NMR spectra of PCL prepared with $\text{Nd}(\text{O-iso-Pr})_3$ and $\text{Nd}(\text{O-Ph})_3$ are shown in Figure 7. Signals in the spectra were assigned as follows^{14,15}: $\delta = 1.07\text{ ppm}$ (Ha); $\delta = 5.02\text{ ppm}$ (Hb); $\delta = 2.31\text{ ppm}$ (Hc); $\delta = 4.06\text{ ppm}$ (Hd); $\delta = 1.64\text{ ppm}$ (Hf); $\delta = 1.39\text{ ppm}$ (Hg); $\delta = 3.62\text{ ppm}$ (He); $\delta = 7.20\text{ ppm}$ (Ha').



In both polymers, the same CH_2OH end group (triplet signal at 3.62 ppm) was present. Signals of isopropyl (5.02 ppm) and phenyl (about 7.2 ppm) end groups from the corresponding catalyst were also observed. The ring

opening polymerization of ϵ -caprolactone catalyzed with neodymium alkoxide proceeds *via* a coordination insertion mechanism with the cleavage of acyl-oxygen bonds of ϵ -caprolactone:



Acknowledgment. The authors gratefully acknowledge the financial support by National Natural Science Foundation of China.

REFERENCES

1. T. S. Pierre and E. Chiellini, *J. Bioactive and Compatibl Polymers*, **2**, 4 (1987).
2. C. G. Pitt, T. A. Marks, and A. Schindler, "Biodegradable Drug Delivery Systems Based on Aliphatic Polyesters: Application of Contraceptives and Narcotic Antagonists," R. Baker, Ed., Academic Press, New York, N.Y., 1980.
3. O. Olabisi, L. E. Robeson, and M. T. Shaw, "Polymer-Polymer Miscibility," Academic, New York, N.Y., 1979.
4. K. J. Ivin and T. Saegusa, "Ring Opening Polymerization," Vol. 1, Elsevier Applied Science, Amsterdam 1984.
5. A. Hamitou, T. Ouhadi, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 865 (1977).
6. H. R. Kricheldorf, M. Berl, and N. Scharnagl, *Macromolecules*, **21**, 286 (1988).
7. M. Endo, T. Aida, and S. Inoue, *Macromolecules*, **20**, 2982 (1987).
8. S. J. McLain, T. M. Ford, and N. E. Drysdale, *Am. Chem. Soc., Polym. Prepr.*, **33**, 463 (1992).
9. Z. Q. Shen, X. H. Chen, Y. Q. Shen, and Y. F. Zhang, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 597 (1994).
10. Z. Q. Shen, Y. Q. Shen, J. Q. Sun, F. Y. Zhang, and Y. F. Zhang, *Chin. Sci. Bull.*, **39**, 1005 (1994).
11. M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).
12. R. C. Mehrotra and J. M. Batwara, *Inorg. Chem.*, **9(11)**, 2505 (1970).
13. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci., Polym. Phys. Ed.*, **7**, 897 (1969).
14. C. Jacobs, Ph. Dubois, R. Jerome, and Ph. Teyssie, *Macromolecules*, **24**, 3027 (1991).
15. Ph. Dubois, R. Jerome, and Ph. Teyssie, *Polym. Bull.*, **22**, 475 (1989).