



Ring-opening polymerization of ϵ -caprolactone by lanthanide tris(2,4,6-tri-*tert*-butylphenolate)s: Characteristics, kinetics and mechanism

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ABSTRACT

Lanthanide tris(2,4,6-tri-*tert*-butylphenolate)s are highly active initiators for ring-opening polymerization of ϵ -caprolactone to give polycaprolactone with number average molecular weight as high as 8.3×10^4 at 20 °C in 20 min in toluene. The effects of solvent, rare earth element, monomer/initiator molar ratio, monomer concentration, as well as polymerization temperature and time have been investigated. The kinetic studies of ϵ -caprolactone polymerization have indicated that the polymerization rate is first-order with respect to both monomer and initiator concentrations. The overall activation energy amounts to 39.3 kJ/mol. Mechanistic studies show that the monomer inserts into the growing chain with the acyl-oxygen bond scission.

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1. Introduction

Biodegradable polymers have been extensively investigated for temporary therapeutic applications such as surgical sutures, bone fracture internal fixation devices, drug delivery systems, as well as tissue engineering scaffolds [1,2]. In the family of biodegradable synthetic polymers, polycaprolactone (PCL) appears most attractive because of its excellent thermal properties and permeability to drugs.

In recent years, ring-opening polymerization of ϵ -caprolactone (CL) has been widely studied using many efficient initiators based on titanium [3,4], tin [5–7], zinc [8], and aluminium [9–11] metals. In spite of the wide use of these metal initiators for ring-opening polymerization of CL, they have some disadvantages such as high toxicity. In contrast, rare earth initiators have low toxicity, high efficiency, capability of living polymerization and easy removal from products. Thus they are very attractive. Some rare earth compounds have been successfully used for the preparation of PCL [12–16]. Further study revealed that single component rare earth aryloxide could show excellent catalytic activity toward the ring-opening polymerization of CL to prepare PCL with higher molecular weight and conversion. This paper reports the characteristics, kinetics, and

mechanism of CL polymerization catalyzed by novel single component lanthanide tris(2,4,6-tri-*tert*-butylphenolate) ($\text{Ln}(\text{OTTBP})_3$) (Scheme 1).

2. Experimental

2.1. Materials

CL (Acros product, 99%) was dried over calcium hydride for 48 h and distilled under reduced pressure. Toluene and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone before use. Carbon tetrachloride (CCl_4) and dichloromethane (CH_2Cl_2) were dried by refluxing over phosphorus pentoxide (P_2O_5) and distilled. All other materials were of analytical grade and used as received.

2.2. Initiator preparation

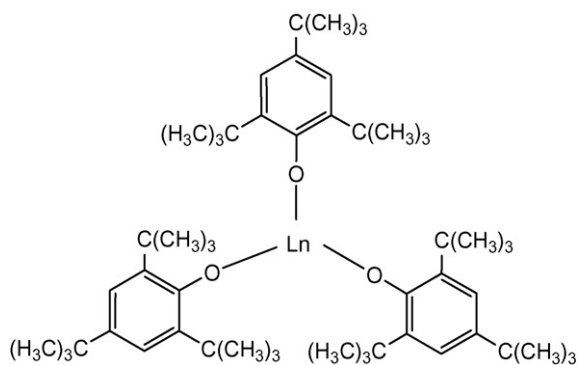
Initiators were prepared using a Schlenk tube and vacuum-line technique under purified nitrogen. Anhydrous rare earth chlorides were prepared by heating the mixture of a hydrated rare earth chloride and the corresponding ammonium chloride under reduced pressure [17]. $\text{Ln}(\text{OTTBP})_3$ complexes were synthesized by the reaction of anhydrous rare earth chloride and sodium 2,4,6-tri-*tert*-butylphenolate [18].

2.3. Measurements

^1H NMR spectra of PCL were recorded on a Bruker AV-400 MHz spectrometer in CDCl_3 at room temperature with TMS as internal

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Scheme 1. Structure of $\text{Ln}(\text{OTTBP})_3$, $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Er}, \text{and Y}$.

standard. Number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of PCL were measured in THF at 40 °C by GPC (220) with a refractive index detector and a set of columns (PL gel 10 μm Mixed-B 300 mm \times 7.5 mm and PL gel 10 μm Guard 50 mm \times 7.5 mm) and calibrated using polystyrene standards. Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C/min with a DSC 2010 instrument.

2.4. Polymerization procedure

All polymerization reactions were carried out in glass ampoules under nitrogen atmosphere. Solvent, monomer and initiator were added to the ampoule successively by syringes. Reactions were quenched by methanol containing 5% HCl. The product polymer was washed with methanol several times, and then dried under vacuum to constant weight at 40 °C.

3. Results and discussion

3.1. Characteristics of the polymerization

Table 1 lists the influence of different rare earth initiators on the polymerization. The data show that their catalytic activities decrease in the following sequence: $\text{La} > \text{Sm} > \text{Gd} > \text{Nd} > \text{Y} \approx \text{Er}$. Lanthanum tris(2,4,6-tri-*tert*-butylphenolate) ($\text{La}(\text{OTTBP})_3$) exhibited the highest activity and gave PCL with higher number average molecular weight (8.3×10^4). The difference in the activity among various rare earth initiators may be related to the radius of rare earth metal ion, discrepancy in the valence electron configuration and the ancillary ligands in the coordination sphere of the metal [19–21]. Because the light rare earth ions have larger radius than heavy ones, they easily make monomer coordinate to the ions. At

Table 1
Influence of different rare earth elements on the polymerization of CL

| $\text{Ln}(\text{OTTBP})_3$ | $[\text{CL}]/[\text{Ln}]$ | Conv (%) | $M_n \times 10^{-4}$ |
|-----------------------------|---------------------------|----------|----------------------|
| La | 1500 | 100 | 8.30 |
| | 1200 | 95.0 | 3.35 |
| Sm | 1500 | 60.7 | 2.14 |
| | 1200 | 80.9 | 2.10 |
| Gd | 1000 | 15.2 | 2.80 |
| | 800 | 39.3 | 2.67 |
| Nd | 1000 | – | – |
| | 800 | 11.4 | 2.69 |
| Er | 500 | 15.6 | 6.98 |
| Y | 500 | 7.5 | 4.35 |

Reaction conditions: $[\text{CL}] = 2 \text{ mol/l}$, 20 min, 20 °C, in toluene.

Table 2
Effect of different solvents on the polymerization of CL

| Solvent | $[\text{CL}]/[\text{La}]$ | Conv (%) | $M_n \times 10^{-4}$ |
|--------------------------|---------------------------|----------|----------------------|
| Toluene | 1500 | 100 | 8.3 |
| | 1200 | 95.0 | 3.35 |
| CCl_4 | 1500 | 95.3 | 2.56 |
| | 1200 | 92.6 | 2.41 |
| THF | 1500 | 16.7 | 1.30 |
| | 1200 | 30.2 | 1.10 |
| CH_2Cl_2 | 1500 | – | – |
| | 1200 | 20.8 | 1.06 |

Reaction conditions: $[\text{CL}] = 2 \text{ mol/l}$, 20 min, 20 °C.

Table 3
Ring-opening polymerization of CL with $\text{La}(\text{OTTBP})_3$

| $[\text{CL}] \text{ (mol/l)}$ | $[\text{CL}]/[\text{La}]$ | Conv (%) | $M_n \times 10^{-4}$ | MWD |
|-------------------------------|---------------------------|----------|----------------------|------|
| 1.0 | 1500 | 95.8 | 2.75 | 2.02 |
| 1.5 | 1500 | 98.1 | 4.20 | 2.55 |
| 2.0 | 1500 | 100 | 8.30 | 2.10 |
| 2.5 | 1500 | 95.2 | 3.51 | 2.20 |
| 3.0 | 1500 | 90.1 | 2.32 | 2.23 |
| 2.0 | 1000 | 93.2 | 1.52 | 2.08 |
| 2.0 | 1200 | 95.0 | 3.35 | 3.41 |
| 2.0 | 1800 | 96.3 | 4.50 | 2.51 |

Conditions: 20 °C, 20 min, toluene.

the same time, a rare earth compound formed by d and s orbital electrons was more effective for the CL polymerization than that formed by f-orbital electrons, for example, $\text{Gd} > \text{Nd}$, although the radius of Gd^{3+} is smaller than that of Nd^{3+} . Y and Er were similar in the activity, which may be due to similar radii of Y^{3+} and Er^{3+} . Further interpretations on activity sequence of rare earth element are still under investigation.

Polymerization reactions of CL were carried out using toluene, CCl_4 , CH_2Cl_2 , or THF as solvent. The results are summarized in Table 2. The complete conversion (100%) of the monomer and high molecular weight of PCL were obtained when toluene was used as solvent, which indicates that polar solvents are not beneficial to the CL polymerization. This result suggests that the polymerization of CL proceeds via a coordination mechanism.

The effects of the CL concentration and monomer/initiator ($[\text{CL}]/[\text{La}]$) molar ratio on the polymerization of CL are shown in Table 3. Both the CL conversion and molecular weight increased with increasing CL concentration below 2 mol/l and the CL conversion and molecular weight of PCL dropped at higher CL concentrations ($>2 \text{ mol/l}$). At higher initiator concentrations, the molecular weight dropped owing to increasing number of active species. Normally, the broader molecular weight distribution may mainly contribute to the transesterification reaction during the polymerization process.

Table 4
Effect of reaction temperature and time on the polymerization

| Temp (°C) | Time (min) | Conv (%) | $M_n \times 10^{-4}$ | MWD |
|-----------|------------|----------|----------------------|------|
| 0 | 20 | 94.5 | 4.71 | 3.53 |
| 10 | 20 | 97.0 | 6.02 | 3.10 |
| 20 | 20 | 100 | 8.30 | 2.10 |
| 30 | 20 | 98.8 | 8.20 | 2.89 |
| 40 | 20 | 97.8 | 8.10 | 3.12 |
| 20 | 5 | 65.1 | 3.51 | 2.05 |
| 20 | 10 | 80.3 | 5.22 | 3.02 |
| 20 | 15 | 90.2 | 6.71 | 2.78 |
| 20 | 25 | 100 | 8.00 | 2.20 |
| 20 | 30 | 100 | 7.04 | 2.38 |

Conditions: $[\text{CL}] = 2 \text{ mol/l}$, $[\text{CL}]/[\text{La}] = 1500$, toluene.

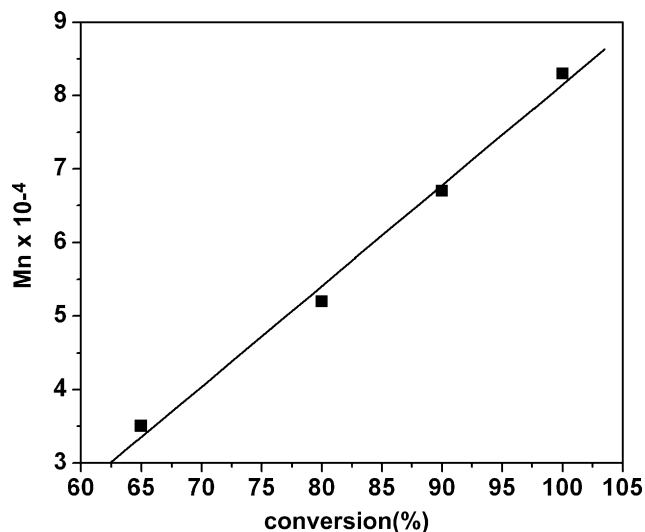


Fig. 1. Relationship between conversion and molecular weight.

The time and temperature dependence of the CL conversion and molecular weight of PCL are listed in Table 4. Our data show that 20 °C and 20 min are preferable for the polymerization of CL catalyzed by La(OTTBP)₃ in toluene. We found that the number average molecular weight of PCL increased linearly with the conversion of CL, as shown in Fig. 1. This may imply that the polymerization with La(OTTBP)₃ has some living character.

3.2. Mechanism of ϵ -caprolactone polymerization

In order to study the polymerization mechanism initiated by La(OTTBP)₃, a low molecular weight PCL sample was prepared and terminated by isopropanol. The ¹H NMR spectrum is shown in Fig. 2.

The proton signals corresponding to the end groups –COOCH(CH₃)₂ and –CH₂OH show a multiplet peak at 5.02 ppm (H^b), a doublet peak at 1.22 ppm (H^a), and a triplet peak at 3.65 ppm. Other signals in the spectrum are assigned as follows:

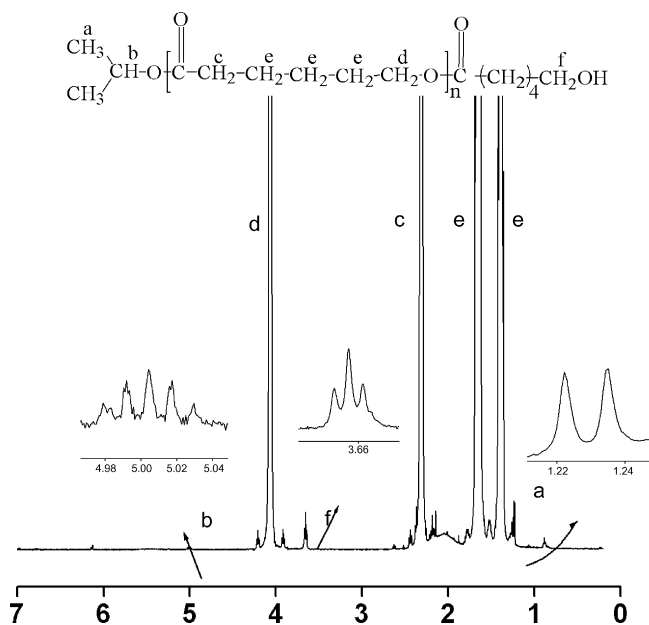
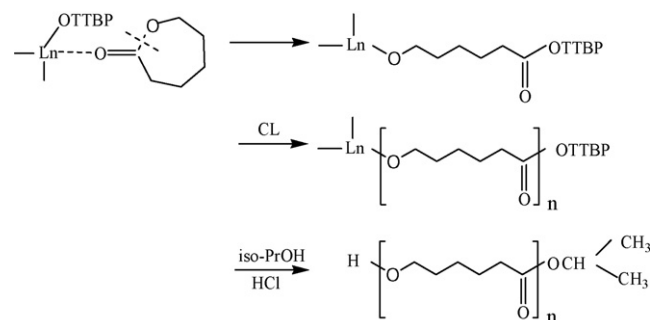


Fig. 2. ¹H NMR of PCL terminated by isopropanol.



Scheme 2. Polymerization mechanism of CL catalyzed by Ln(OTTBP)₃.

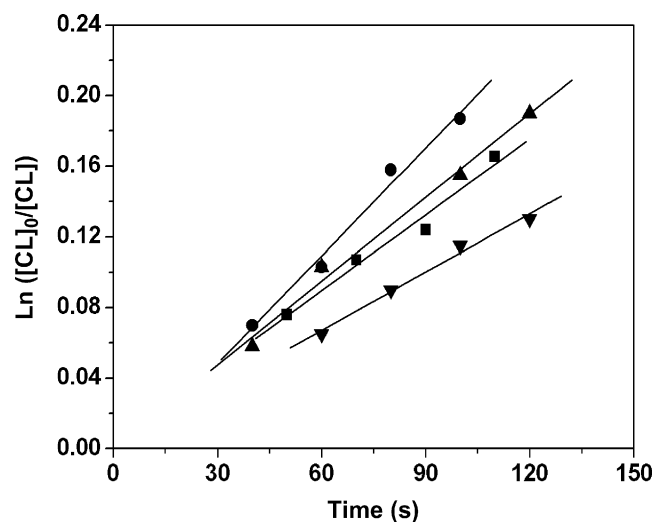


Fig. 3. $\ln([CL]_0/[CL])$ as a function of time. Conditions: $[CL] = 2 \text{ mol/l}$, 20 °C, in toluene; (●) $[La] = 1.13 \times 10^{-3} \text{ mol/l}$; (▲) $[La] = 1.99 \times 10^{-3} \text{ mol/l}$; (▼) $[La] = 1.33 \times 10^{-3} \text{ mol/l}$; (■) $[La] = 1.65 \times 10^{-3} \text{ mol/l}$.

$\delta = 4.06 \text{ ppm}$ (H^d). $\delta = 2.31 \text{ ppm}$ (H^c). $\delta = 1.39$ and 1.64 ppm (H^e) [20]. No evidence of tri(*tert*-butyl)phenyl ether end groups was observed. These observations confirm that the ring-opening polymerization of CL with La(OTTBP)₃ in toluene proceeds via a coordination-insertion mechanism. Monomer coordinated to the

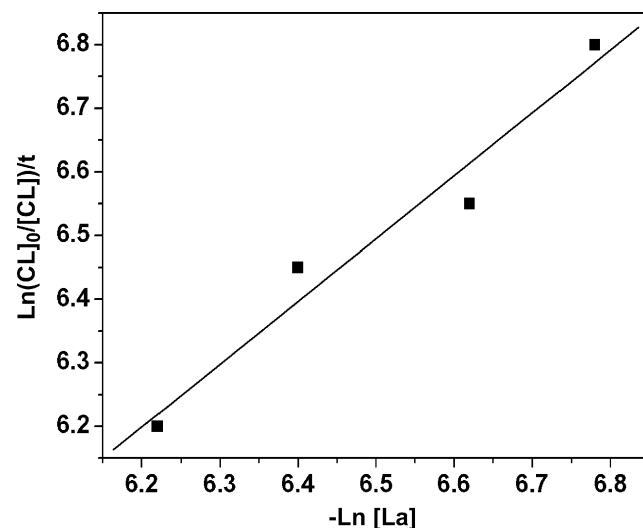


Fig. 4. Correlation of $-\ln([CL]_0/[CL])/t$ with $-\ln[La]$.

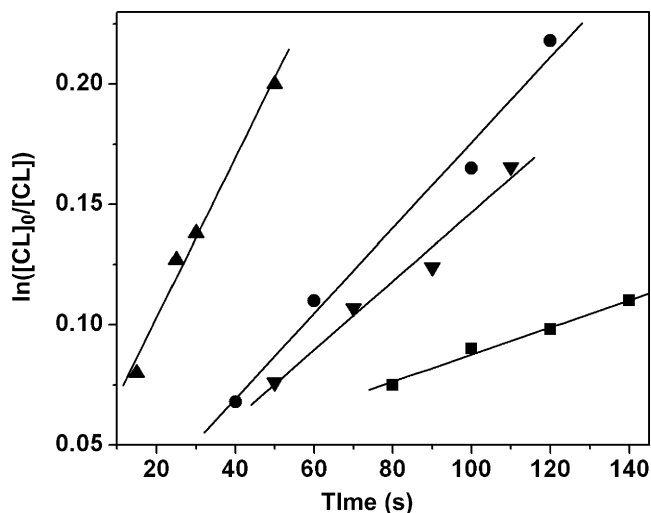


Fig. 5. $\ln([CL]_0/[CL])$ vs. time plot for different temperatures. Conditions: $[CL] = 2 \text{ mol/l}$, $[CL]/[La] = 1500$, toluene; (■) $T = 0^\circ\text{C}$; (●) $T = 10^\circ\text{C}$; (▼) $T = 20^\circ\text{C}$; (▲) $T = 30^\circ\text{C}$.

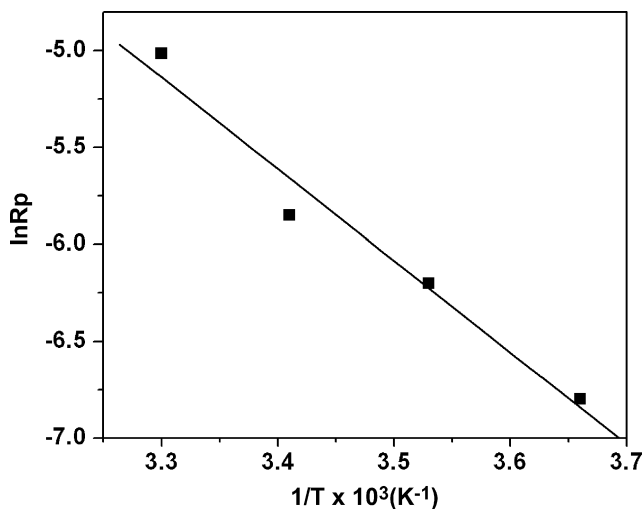


Fig. 6. Effect of polymerization temperature on polymerization rate.

rare earth metal, and opened the ring via acyl-oxygen bond cleavage forming a growing chain. The following monomer repeated these steps to insert into the La–O bond in propagation process (Scheme 2).

3.3. Kinetics of ϵ -caprolactone polymerization

The kinetics of CL polymerization with $\text{La}(\text{OTTBP})_3$ in toluene was investigated by the weight method. The polymerization reaction was terminated at a low conversion (20%). Linear plots of $\ln([CL]_0/[CL])$ versus time at four different catalyst concentrations indicate that the polymerization reaction is first-order in monomer (Fig. 3). A first-order in the initiator was also obtained from the

slopes of the plots in Fig. 4. Thus, the polymerization rate equation can be written as

$$R_p = k_p[CL][\text{La}(\text{OTTBP})_3],$$

where k_p is the polymerization rate constant. Fig. 5 presents the plots of $\ln([CL]_0/[CL])$ versus time at four different temperatures. The correlation between the $\ln R_p$ and the reciprocal of polymerization temperature ($1/T$) has been plotted in Fig. 6. According to the Arrhenius equation, the overall activation energy was calculated at 39.3 kJ/mol.

4. Conclusion

The polymerization of CL was initiated efficiently by $\text{La}(\text{OTTBP})_3$. PCL with molecular weight of about 8.3×10^4 and number average molecular weight distribution of 2.10 can be prepared with $\text{La}(\text{OTTBP})_3$ after 20 min at $[CL]/[La] = 1500$ in toluene at 20°C . The kinetics studies of the $\text{La}(\text{OTTBP})_3$ system demonstrate that the polymerization rate is of the first-order in monomer concentration and in initiator concentration, respectively, and that the overall activation energy amounts to 39.3 kJ/mol. Mechanistic studies show that monomer inserts into the growing chains with the acyl-oxygen scission rather than the cleavage of alkyl-oxygen bond.

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