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Characteristics, Kinetics and Mechanism of ε - Caprolactone Polymerization by Lanthanide Tris(2.6 – dimethylphenolate)s

Lifang Zhang[1,2], Cuiping Yu[1], Zhiquan Shen(✉)[1]

[1]Institute of Polymer Science, Zhejiang University, Hangzhou, 310027, China
[2]Shanxi Normal University, Linfen, 041004, China
Tel: 86-571-87951059, Fax: 86-571-87951773, Email: zqshen@163.net

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Summary

Polycaprolactone(PCL) was synthesized via the ring–opening polymerization of ε -caprolactone(ε -CL) with lanthanide tris(2.6 – dimethylphenolate)s[Ln(ODMP)$_3$] as initiator under mild conditions for the first time. The effects of reaction conditions on the ε -CL polymerization are discussed. Kinetic studies indicate that the polymerization rate is first order with respect to both monomer concentration and catalyst concentration, respectively, and the overall reaction activation energy amounts to 62.3kJ/mol. ^{1}H NMR end group analysis on the polymer demonstrates the ring–opening polymerization of ε -CL proceeds according to coordination-insertion mechanism with acyl-oxygen bond cleavage of the monomer.

Introdution

Some rare earth compounds such as rare earth halide, rare earth alkoxide, rare earth aryloxide and organolanthanide(III) complex have been developed as initiators for the synthesis of biodegradable and biocompatible aliphatic polyesters[1-7]. Until now, the number of papers using single rare earth compound as initiator for ε -CL polymerization is limited. Some rare earth compounds have been successfully used as single component initiators for the preparation of aliphatic polyesters in our group[8-11]. We now report lanthanide tris(2.6 – dimethylphenolate)s [Ln(ODMP)$_3$] (Scheme1) as a new kind of single component initiator for the ring–opening polymerization of ε -CL firstly. The polymerization characteristics, kinetics and mechanism are presented in this paper.

Experiment

Materials

ε -CL(Mitsubishi) was dried over Calcium hydried for 48h, distilled under reduced pressure. Toluene and tetrahydrofuran(THF) were purified by distillation over the blue benzophenone-Na complex just before use. CH_2Cl_2 and CCl_4 were dried and refluxed over P_2O_5 under nitrogen atmosphere. Rare earth oxides (Ln_2O_3) with purity of 99.99% were purchased from Shanghai Yuelong factory.

Initiator Preparation

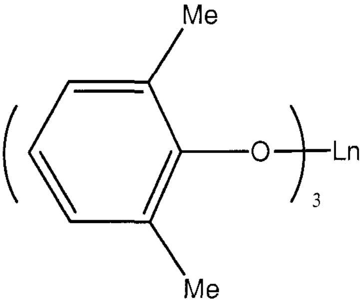
Anhydrous rare earth chlorides and $Ln(ODMP)_3$ were prepared according to ref[12,13].

Polymerization

All polymerizations were carried out in glass ampules under dry nitrogen atmosphere. Solvent and monomer were added into ampule successively. Initiator dissolved in toluene was introduced into monomer solution by syringe. The polymerization was terminated by methanol containing 5%HCl. The polymer was washed with methanol several times, and then dried under vacuum at 40℃.

Measurements

Intrinsic viscosity of polymer was determined in dimethylformamide at 30℃ with an Ubbelohde viscosimeter. The viscosity average molecular weight(Mv) was calculated according to the following equation [14]: $[\eta] = 1.91 \times 10^{-4} Mv^{0.73}$. The number average molecular weight (Mn) and molecular weight distribution(MWD) were measured by gel permeation chromatograph (Waters 150) at 25℃, using THF as eluent and calibrated with polystyrene standards. ^1H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in $CDCl_3$ at room temperature with tetramethylsilane(TMS) as internal standard.



$Ln(ODMP)_3$: Ln = La, Nd, Sm, Gd, Er ,Y

Scheme 1. Structure of $Ln(ODMP)_3$

Results and Discussion

Characteristics of the polymerization

Table 1 shows the results of ring-opening polymerization of ε -CL in toluene using various rare earth initiators. The data indicate that all initiators can induce the ε -CL polymerization, but the catalytic activity of light rare earth compounds is higher than that of heavy rare earth ones. The polymerization activity sequence is : La > Nd ≈ Sm ≈Gd > Er ≈Y. La(ODMP)$_3$ has the highest activity and can prepare PCL with viscosity average molecular weight about 6.5×10^4 under mild conditions. The reason of the activity difference between various rare earth initiators may result from their different electronic and coordination abilities.

Tablel. Influence of different rare earth elements on the polymerization of CL

Ln(ODMP)$_3$	[CL]/[Ln]	Conv (%)	$M_v \times 10^{-4}$ (g·mol^{-1})
La	1000	100	6.46
	800	100	5.60
Nd	1000	50.5	5.25
	800	94.8	3.54
Sm	1000	50.7	4.56
	800	94.8	2.75
Gd	1000	48.7	.3.57
	800	92.2	2.55
Er	1000	7.44	1.87
	800	14.1	1.23
Y	1000	---	---
	800	14.4	2.13

Reaction conditions: [CL] = 2.5mol/L, 1h, 60℃ in toluene

Table 2 gives the results of the ring-opening polymerization of ε -CL with La(ODMP)$_3$ in various organic solvents. It can be seen that the monomer conversion of 100% and higher molecular weight PCL are obtained in nonpolar solvents under the conditions used, and toluene is preferable for the ε -CL polymerization.

Table 2. Effect of solvents on the polymerization of CL

Solvent	[CL]/[La]	Conv (%)	$M_v \times 10^{-4}$(g·mol^{-1})
Toluene	1000	100	6.46
	800	100	5.60
CCl_4	1000	100	3.03
	800	100	2.95
CH_2Cl_2	1000	17.3	2.39
	800	47.9	0.93
THF	1000	16.8	0.73
	800	15.3	0.66

Reaction conditions: [CL] = 2.5mol/L, 1h, 60℃

The influences of ε-CL concentration, monomer/initiator(CL/La) molar ratio, reaction temperature and time were examined with La(ODMP)$_3$. The results are summarized in Table 3 and 4. As seen in Table 3, both the monomer conversion and molecular weight increase with increasing of ε-CL concentration until 2.5mol L^{-1}, then the molecular weight of polymer decreases somewhat over 2.5mol/L. It is also found from Table 3 that CL/La molar ratio is relatively critical in obtaining a high conversion and molecular weight polymer. Although the conversion of ε-CL reaches 100% within CL/La molar ratio from 600 to 1000, the polymer molecular weight has the higher value at the molar ratio of 1000.

Table 3. The ring-opening polymerization of CL by La(ODMP)$_3$

No.	[M] (mol/L)	[CL]/ [La] (molar ratio)	Temp (℃)	Conv (%)	M_v x 10^{-4} ($g\,mol^{-1}$)	$M_n \times 10^{-4}$ ($g\,mol^{-1}$)	MWD
1	1.0	1000	60	27.4	2.80	2.61	1.44
2	2.0	1000	60	74.1	4.32	3.97	1.60
3	2.5	1000	60	100	6.46	6.28	1.66
4	3.0	1000	60	97.5	6.04	5.74	1.69
5	4.0	1000	60	91.3	4.34	4.21	1.77
6	2.5	600	60	100	3.78	3.54	1.95
7	2.5	800	60	100	5.60	5.42	1.86
8	2.5	1200	60	66.8	4.99	4.63	1.57

Reaction conditions: 1h, in toluene

Polymerization temperature and time have greater effect on the monomer conversion and molecular weight of the resulting polymers, as shown in Table 4. It can be seen that 60℃ and 1hour are the most suitable reaction conditions for the ring-opening polymerization of ε-CL initiated by La(ODMP)$_3$ in toluene. Figure1 illustrates the number average molecular weight as a function of monomer conversion in the range of 20 to 60min, indicating that there is a linear relationship. This may imply that the ε-CL polymerization with La(ODMP)$_3$ has somewhat living character.

Table 4. Effect of reaction temperature and time on the polymerization

No.	Temp (℃)	Time (min)	Conv (%)	$M_v \times 10^{-4}$ ($g\,mol^{-1}$)	$M_n \times 10^{-4}$ ($g\,mol^{-1}$)	MWD
1	40	60	13.9	3.69	3.64	1.54
2	50	60	76.2	5.58	5.30	1.62
3	60	60	100	6.46	6.28	1.66
4	70	60	100	6.06	5.93	1.73
5	60	20	27.4	2.36	2.12	1.23
6	60	30	48.8	3.58	3.39	1.34
7	60	40	70.1	4.83	4.72	1.47
8	60	50	92.0	5.80	5.79	1.58
9	60	70	100	6.20	6.19	1.71

Reaction conditions: [CL] = 2.5mol/L, [CL]/[La] = 1000, in toluene

Kinetics and mechanism of the polymerization

The monomer consumption vs. reaction time dependence of ε -CL polymerization by La(ODMP)$_3$ in toluene at 60℃ is shown in Figure 2, which suggests that ε -CL polymerization is first order with respect to monomer concentration. The linear relationship of monomer conversion (c) and catalyst concentration in Figure 3 also shows the polymerization rate is first order with respect to catalyst concentration. Thus, the polymerization rate equation can be written as:

$$Rp = k_p [CL] [Ln(ODMP)_3] \qquad (1)$$

Where k_p is the polymerization rate constant. Figure 4 shows the effect of reaction temperature on the polymerization rate. According to the Arrhenius equation, the apparent activation energy of the polymerization is 62.3kJ/mol.

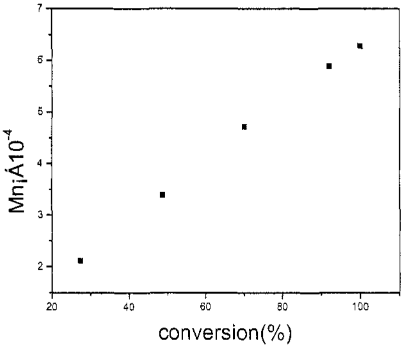


Figure 1. Relationship between molecular weight of PCL and the monomer conversion. Conditions are the same as Table 4

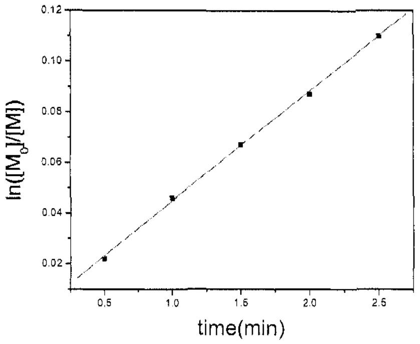


Figure 2. ln([M$_0$]/[M]) as a function of reaction time. Conditions: [CL] = 2.5mol/L, [La] = 3 × 10^{-3}mol/L, 60℃, toluene

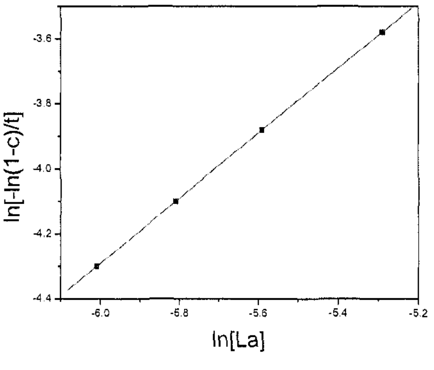


Figure 3. Correlation of ln[-ln(1-c)/t] with ln[La]. Conditions: [CL] = 2.5mol/L, 60℃, toluene

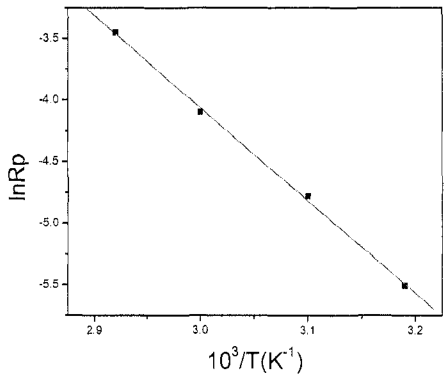


Figure 4. Effect of reaction temperature on polymerization rate. Conditions are the same as Fig.3

The mechanism of the ring-opening polymerization of ε -CL with La(ODMP)$_3$ in toluene has been investigated. The ^1H NMR spectrum of a low molecular weight PCL terminated by isopropanol is shown in Figure 5. The doublet and multiplet peaks at 1.25 and 5.02ppm are assigned to methyl(H^a) and methenyl(H^b) proton of isopropyl group, respectively. The other chemical shifts of protons are assigned as follows: δ = 2.31ppm(H^c), δ = 4.06ppm(H^d), δ = 1.39 and 1.66ppm(H^e), δ = 3.65ppm(H^f)[15]. The results indicate that the isopropyl is introduced into the living chain at the termination stage. Thus, it is presumed that the ring-opening polymerization of ε -CL with La(ODMP)$_3$ proceeds via a coordination insertion mechanism with acyl-oxygen bond cleavage of ε -CL.

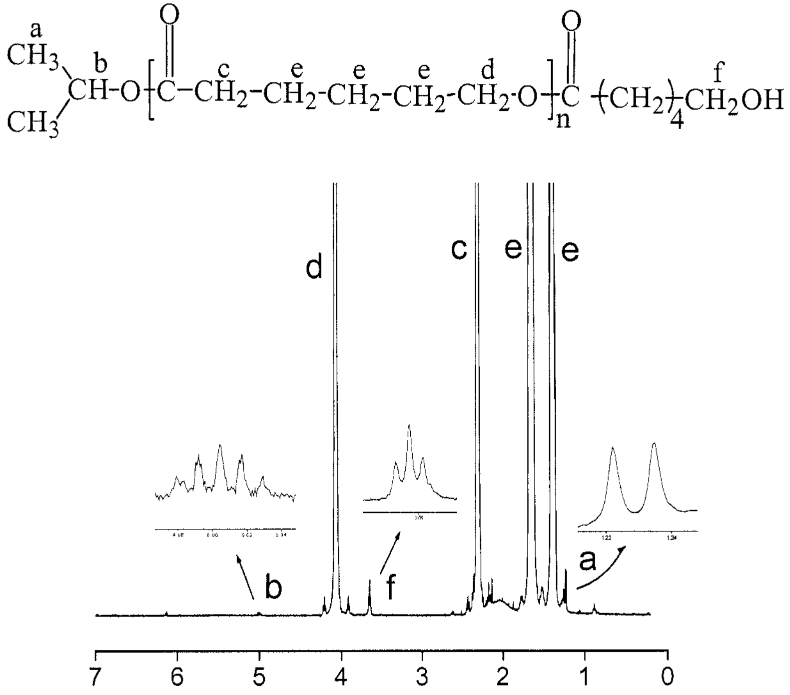


Figure 5. ^1H NMR of PCL terminated by isopropanol

In conclusion, lanthanide tris(2.6 – dimethylphenolate)s [Ln(ODMP)$_3$], especially La(ODMP)$_3$ are effective single initiator for the ring-opening polymerization of ε -CL. PCL with molecular weight of about 6.5 × 10^4 and MWD of 1.66 can be prepared with La(ODMP)$_3$ after 1h at [CL]/[initiator] = 1000, in toluene, at 60℃.

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