

Homo- and Copolymerization of ϵ -Caprolactone and 2,2-Dimethyltrimethylene Carbonate by Rare Earth Initiators[†]

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Rare earth tris(2,6-di-*tert*-butyl-4-methylphenolate) [$\text{Ln}(\text{OAr})_3$, Ln = La, Nd, Dy, Y] alone has been developed to initiate polymerization of ϵ -caprolactone (CL) and random copolymerization of CL with 2,2-dimethyltrimethylene carbonate (DTC). The structures of polymers were analyzed by GPC, IR and NMR methods. Their crystal and thermal properties were discussed in terms of DSC. The initiating efficiencies were mainly affected by the size of rare earth metal in the sequence of $\text{La}(\text{OAr})_3 > \text{Nd}(\text{OAr})_3 \sim \text{Y}(\text{OAr})_3 > \text{Dy}(\text{OAr})_3$. $\text{La}(\text{OAr})_3$ exhibited rather high activity to prepare PCL with a molecular weight of 2.15×10^5 and M_w/M_n of 2.27. The composition of random copolymer can be quantitatively controlled either by reaction time or by feed ratio of monomer.

Keywords ring-opening polymerization, random copolymerization, rare earth initiator, aliphatic polyester

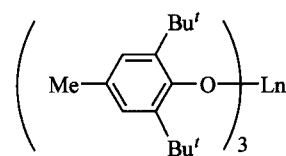
Introduction

Aliphatic polyesters and polycarbonates have attracted growing interest for their excellent properties of biodegradability, biocompatibility and low toxicity. Their expected uses include drug delivery medium, surgical sutures, body implant materials, cell culture substrate, agricultural membrane and so forth. Many of these materials can be synthesized by ring-opening polymerization (ROP) of lactones, lactides, or cyclic carbonates, for which various effective initiating systems have been developed.^{1,4} It is rather difficult to remove all initiator residues from polymerization system. Therefore, non-toxicity or low toxicity of initiators is demanded. Rare earth

metals are low toxic to human health as LD_{50} of La_2O_3 is 10000 mg/kg (rat).⁵ So far many rare earth catalyst systems have been developed for the homopolymerizations of lactides,⁶⁻⁸ lactones,⁷⁻¹¹ cyclic carbonates or their copolymerizations.¹²⁻¹⁵ Compared with the other metal catalyst systems, rare earth metal systems show unprecedented activities in ROP under mild conditions, and can control the polymerization process quite well.

Rare earth tris(2,6-di-*tert*-butyl-4-methylphenolate) [$\text{Ln}(\text{OAr})_3$, Ln = La, Nd, Dy, Y] (Scheme 1) alone has been developed as an efficient initiator for ROP of 2,2-dimethyltrimethylene carbonate (DTC), ϵ -caprolactone (CL) and trimethylene carbonate (TMC).¹⁶⁻¹⁸ The results of further studies on the effects of various rare earth metals in $\text{Ln}(\text{OAr})_3$, the structures and thermal behaviors of the polymers are described in this paper.

Scheme 1 Structure of $\text{Ln}(\text{OAr})_3$, Ln = La, Nd, Dy, Y



Experimental

DTC and $\text{Ln}(\text{OAr})_3$ were synthesized as reported.^{19,20} CL (Mitsubishi Chemical) was dried over CaH_2 , purified by distillation under reduced pressure prior to

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[†]Dedicated to Professor HUANG Yao-Zeng on the occasion of his 90th birthday.

use. All polymerizations were carried out in 20 mL ampoules pre-flamed *in vacuo* and filled with dry argon to remove moisture and oxygen. In copolymerizations, CL and DTC were mixed in toluene and kept at certain temperature before injecting the initiator by a syringe. The products were quenched by 5% HCl, precipitated from methanol, and dried under vacuum until reaching a constant weight. The monomer conversion was determined gravimetrically.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DMX500 spectrometer in CDCl₃ with TMS as internal standard. Gel permeation chromatographic (GPC) analyses were carried out on a Waters 150C apparatus in tetrahydrofuran (THF) with an eluate rate of 1.0 mL/min at 30 °C. The molecular weight was calibrated using polystyrene standards with a narrow molecular weight distribution. Differential scanning calorimetry (DSC) measurements were performed with a Perkin Elmer Pyris 1 apparatus. Each sample was heated from -60 to 150 °C (the first heating scan), cooled immediately to -60 °C and heated again to 150 °C (the second heating scan). The heating rate is 10 °C/min. Infrared (IR) spectra (KBr) were detected on a Bruker Vector 22 apparatus.

Results and discussion

Polymerization features

All the four Ln(OAr)₃ (Ln = La, Nd, Dy, Y) could initiate the ROP of CL under mild conditions to prepare high molecular weight and $M_w/M_n = 1.8\text{--}2.6$ polymers with high conversions. The polymerization results

are listed in Table 1. Using La(OAr)₃, PCL with M_w of 2.15×10^5 and M_w/M_n of 2.27 was obtained in 90 min at 30 °C in toluene with a molar ratio [CL]/[La(OAr)₃] of 3000, having an efficiency of 277.4 kg PCL/mol La (Run 2, Table 1). The activity of lanthanum (La) is higher than those of neodymium (Nd), dysprosium (Dy) and yttrium (Y). The activity sequence is as follows: La > Nd > Y > Dy. This is supposed due to the different size of these four rare earth metals [La (0.188 nm) > Nd (0.182 nm) > Y (0.181 nm) > Dy (0.177 nm)]. Larger metal was easier to be coordinated by the carbonyl group when the monomer inserted into Ln—O bond.¹⁷

The influence of temperature on conversion and molecular weight of PCL is shown in Fig. 1. Conversion increased with the elevated temperature in the range of 0–40 °C.

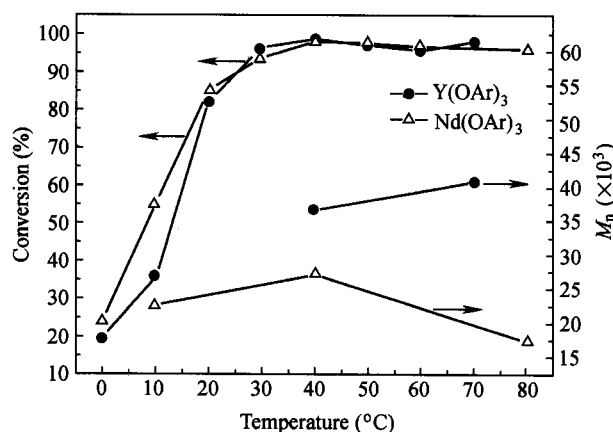


Fig. 1 Polymerization of CL with rare earth initiators at various temperatures. [CL] = 1.0 mol/L, [CL]/[Y(OAr)₃] = 750, [CL]/[Nd(OAr)₃] = 500, 15 min, in toluene.

Table 1 Homopolymerization of CL in toluene

Run	Initiator	[CL] (mol/L)	[CL]/ [Ln(OAr) ₃]	T (°C)	Time (min)	Conv. (%)	M _w (×10 ³)	M _w /M _n
1	La(OAr) ₃	0.60	1200	30	90	90.6	65	1.87
2	La(OAr) ₃	0.60	3000	30	90	81.1	215	2.27
3	La(OAr) ₃	1.0	1000	20	60	95.1	—	—
4	Nd(OAr) ₃	2.0	500	15	60	100.0	51	2.32
5	Nd(OAr) ₃	1.0	500	30	15	93.8	—	—
6	Y(OAr) ₃	1.0	750	40	15	98.6	92	2.52
7	Y(OAr) ₃	1.0	500	15	30	89.0	—	—
8	Dy(OAr) ₃	1.0	750	15	30	75.1	87	2.03
9	Dy(OAr) ₃	1.0	500	15	30	83.0	—	—

Table 2 Copolymerization of CL with DTC^a

Run	Initiator	[CL + DTC]/ [Ln(OAr) ₃]	T (°C)	Time (min)	Conv. (%)	M _w (× 10 ³)	M _w /M _n
1	La(OAr) ₃	1000	20	35	99.2	47	1.62
2	La(OAr) ₃	800	15	30	95.9	51	1.60
3	Nd(OAr) ₃	200	20	30	98.3	79	1.90
4	Y(OAr) ₃	200	20	30	68.8	—	—
5	Y(OAr) ₃	100	20	15	89.9	42	1.49
6	Dy(OAr) ₃	100	15	60	63.5	22	1.25

^a Polymerization conditions: CL:DTC = 50:50 (molar ratio in feeding), [CL + DTC] = 1.0 mol/L, toluene as solvent.

Ln(OAr)₃ could initiate random copolymerization of CL with DTC as well. The results are shown in Table 2. The efficiency of various rare earth metals in initiating copolymerization had the same sequence as that in homopolymerization of CL. GPC patterns showed a single peak for every copolymer sample. Furthermore, their molecular weight distributions were in the range of 1.2—1.9 which was narrower than that of PCL, indicating that there was only one kind of propagating center in copolymerization.

The copolymerization exhibited high reaction rate and high conversion even at low temperatures or low monomer concentrations, as shown in Table 3. DTC was more active than CL in the reactions, and copolymerization was faster than homopolymerization of CL, especially at low temperature. Therefore, the influence of temperature on conversion was not so obvious as that of homopolymerization of CL in the range of 0—40 °C.

Table 3 Copolymerization of CL with DTC initiated by Y(OAr)₃^a

Run	[CL + DTC] (mol/L)	T (°C)	Time (min)	Conv. (%)
1	1.0	0	15	90.7
2	1.0	10	15	89.4
3	1.0	20	15	89.9
4	1.0	30	15	88.7
5	1.0	40	15	88.4
6	1.0	50	15	69.8
7	1.0	60	15	85.6
8	0.14	20	30	74.3
9	0.30	20	30	87.7
10	0.50	20	30	90.4
11	0.70	20	30	89.7
12	1.0	20	30	95.0

^a Polymerization conditions: CL:DTC = 50:50 (molar ratio in feeding), [CL + DTC]/[Y(OAr)₃] = 100, toluene as solvent.

Both the copolymerization conversion and the concentration of CL in copolymers depend on the reaction time under a fixed feed ratio of CL:DTC. Fig. 2 illustrates that the conversions increase with the copolymerization time. The reactivity ratio of CL is much smaller than that of DTC ($r_{CL} = 0.20$, $r_{DTC} = 13.4$).¹⁸ Much more DTC monomers than CL inserted into growing chain at the beginning of the copolymerization. The concentration of CL in copolymer increased along with the total conversion as listed in Table 4. Therefore, conversion, molecular weight and concentration of CL units in copolymer all increased while prolonging polymerization time. The copolymerization exhibited some features of living polymerization. As an example, random copolymer of poly(CL-ran-DTC) ($M_w = 4.7 \times 10^4$, $M_w/M_n = 1.62$) was obtained

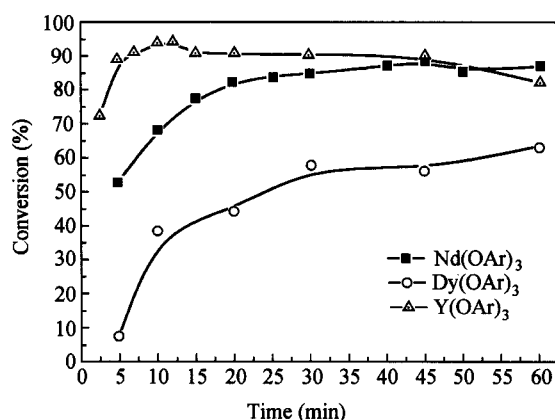


Fig. 2 Copolymerization of CL with DTC. CL:DTC = 50:50 (molar ratio in feeding), toluene as solvent. Nd(OAr)₃: [CL + DTC] = 0.50 mol/L, [CL + DTC]/[Nd(OAr)₃] = 200, 15 °C; Y(OAr)₃: [CL + DTC] = 0.50 mol/L, [CL + DTC]/[Y(OAr)₃] = 100, 20 °C; Dy(OAr)₃: [CL + DTC] = 1.0 mol/L, [CL + DTC]/[Dy(OAr)₃] = 100, 15 °C.

in 35 min, giving high conversion of 99.2% with $\text{La}(\text{OAr})_3$ as initiator and the composition ratio of copolymer approximately equals to the feed ratio. The compositions of copolymers can be quantitatively predicted either by controlling polymerization time or by feed ratio.

Table 4 Copolymerization of CL with DTC initiated by $\text{La}(\text{OAr})_3^a$

Run	Time (min)	Conv. (%)	CL:DTC ^b (molar ratio)	M_w ($\times 10^3$)	M_w/M_n
1	5	38.0	17:83	18	1.49
2	8	42.0	—	—	—
3	10	47.6	20:80	22	1.53
4	20	60.1	31:69	27	1.75
5	22	64.8	—	—	—
6	25	88.9	49:51	32	2.05
7	35	99.2	54:46	47	1.62

^a Polymerization conditions: CL:DTC = 50:50 (molar feed ratio), $[\text{CL} + \text{DTC}] = 1.0 \text{ mol/L}$, $[\text{CL} + \text{DTC}]/[\text{La}(\text{OAr})_3] = 1000$, at 20 °C in toluene. ^b Calculated by ^1H NMR.

Characterization

In Fig. 3 the IR spectrum of random copolymer poly(CL-ran-DTC) was compared with that of homopolymer. The band from 1724 cm^{-1} to 1753 cm^{-1} is due to the stretching vibration of the C-O groups. The band at 1386 cm^{-1} is the characteristic of $\text{C}(\text{CH}_3)_2$ group. The absorptions of plane vibration of $(\text{CH}_2)_5$ group were at 732.9 cm^{-1} .

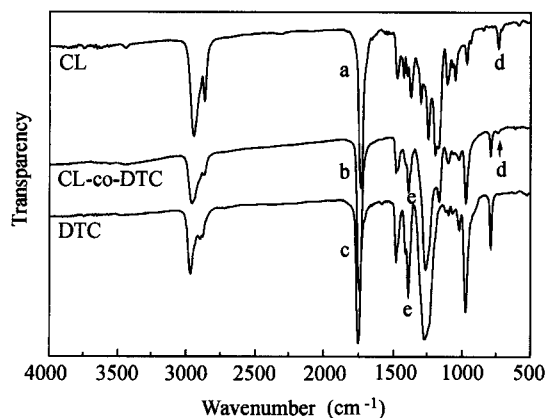


Fig. 3 IR spectra of homopolymer CL, DTC and random copolymer CL-co-DTC. ν (a): $1724\text{--}1739 \text{ cm}^{-1}$, ν (b): $1735\text{--}1750 \text{ cm}^{-1}$, ν (c): $1744\text{--}1753 \text{ cm}^{-1}$, ν (d): 732.9 cm^{-1} , ν (e): 1386 cm^{-1} .

The structure of the random copolymer was characterized by NMR. There are four peaks at δ 3.84–4.16 in ^1H NMR (Fig. 4) distinguishing the four diad units of the copolymer (Scheme 2). Fig. 5 illustrates the δ 3.84–4.16 peaks of the copolymers polymerized at various time. Peak b in ^1H NMR reflecting CL-CL diad unit strengthens with the increasing CL% and copolymerization time. Peaks a and d in ^{13}C NMR spectra (Fig. 6) at δ 68.1 and 69.1 confirm the existence of copolymer, which coincides with other reported results.²¹

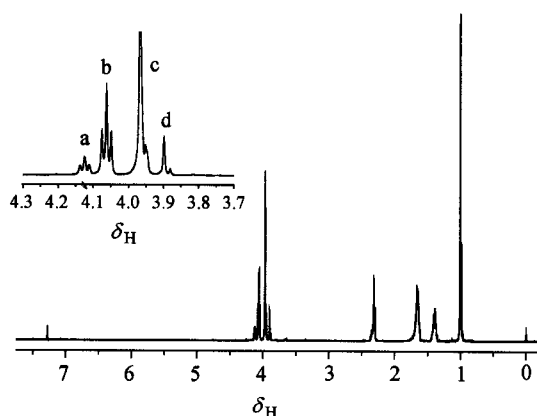
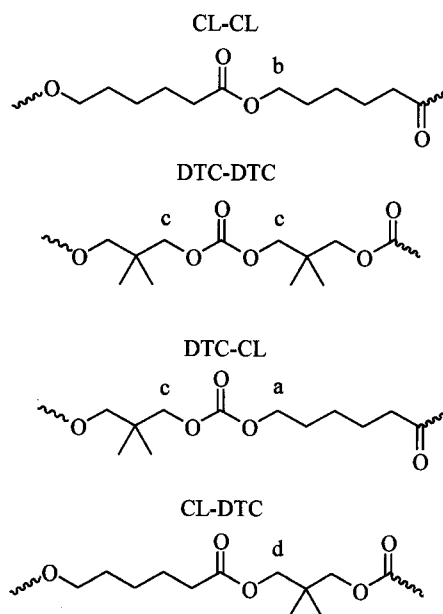


Fig. 4 ^1H NMR spectrum of copolymer CL-co-DTC.

Scheme 2 NMR contributions of copolymers



Monte Carlo method has been used to simulate the copolymerization.²² Though DTC and CL units dominate in the beginning and the ending segment of a copolymer

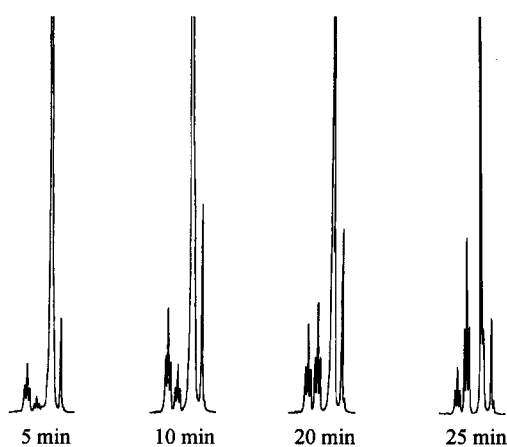


Fig. 5 ^1H NMR spectra of random copolymers at various polymerization time.

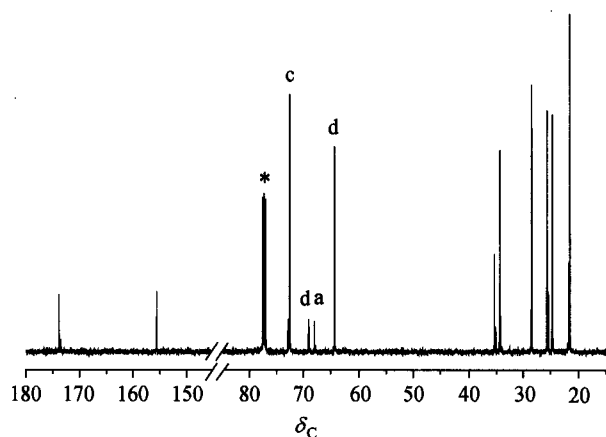


Fig. 6 ^{13}C NMR spectrum of CL-co-DTC.

chain, respectively, Monte Carlo simulation indicates that the minor units (*e. g.* CL in the beginning segment) are embedded in the major units and change the properties of copolymer chain. Figs. 7 and 8 show the DSC curves as a function of molar ratio of CL:DTC in copolymers with two heating scans (see Experimental section). The resultant thermal properties of T_g s, T_m s and ΔH_m s are summarized in Table 5. In the first heating scan, two kinds of crystallization were defined, one about 50–70 °C and the other about 80–100 °C. The former is much like the behavior of PCL and the latter is like PDTC. With the increase of the minor units embedded in copolymer chain, the melting temperature decreased as compared with that of the homopolymer of major units. For example, T_m of copolymer shifted toward a relatively lower temperature with the decrease of CL% in copolymer from PCL. 50% CL was a critical point at which two melting peaks ap-

peared. When CL% kept decreasing from 50% to 20%, T_m of copolymer increased toward that of PDTC. The crystallinity decreased with reducing CL% according to the fact that melting enthalpy (ΔH_m) is proportional to crystallinity. While CL% was less than 50%, the crystallinity increased toward that of PDTC. This could broaden the application area of PCL by adjusting its crystallinity because there is a close relationship between crystallinity and behavior of materials. In the second heating scan after a rapid cooling, both T_m and ΔH_m became less or disappeared when DTC% was higher than 50%, and T_g rose from -33.8 to -7.5 °C. The crystal was destroyed and the thermal properties of the copolymer changed from rigid to elastic at such quenching rate. Their mechanical properties might be changed, and are under further researches.

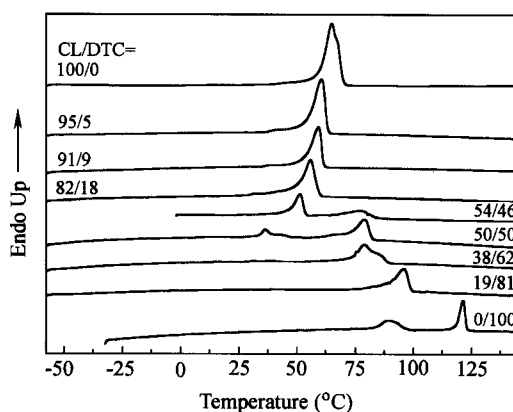


Fig. 7 DSC curves of random copolymers in the first heating scan.

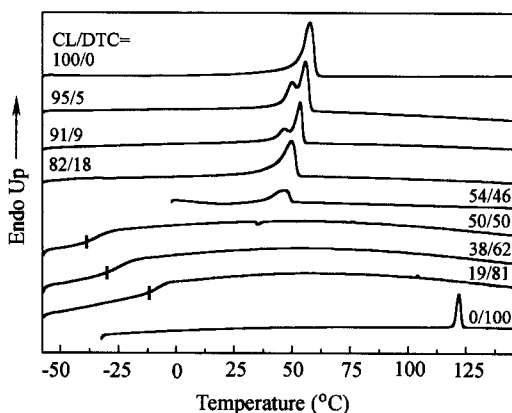


Fig. 8 DSC curves of random copolymers in the second heating scan.

Table 5 Thermal behavior of copolymers of CL with DTC

CL:DTC ^a	M_n ($\times 10^3$)	M_w/M_n	Heating Scan	T_g ($^{\circ}\text{C}$)	$T_{m,1}$ ($^{\circ}\text{C}$)	$\Delta H_{m,1}$ (J/g)	$T_{m,2}$ ($^{\circ}\text{C}$)	$\Delta H_{m,2}$ (J/g)
100:0	95		First		65.1	87.8		
			Second		57.7	58.3		
95:5	46	1.98	First	38.6	60.6	68.3		
			Second		55.7	45.7		
91:9	54	1.88	First	36.8	59.4	56.6		
			Second		53.6	39.8		
82:18	58	2.23	First	30.4	55.9	49.5		
			Second		49.7	40.1		
54:46	29	1.62	First		51.4	14.8	77.3	10.1
			Second		47.0	12.0		
50:50	40	1.65	First		36.3	5.2	79.0	18.1
			Second	-33.8				
38:62	31	1.59	First				79.0	25.1
			Second	-27.0				
19:81	22	1.56	First				96.1	36.7
			Second	-7.5				
0:100			First		89.8	17.7	121.5	21.1
			Second				122.1	23.6

^a Calculated from ¹H NMR, molar ratio.

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