

Ring-opening polymerization of 2,2-dimethyltrimethylene carbonate using rare earth tris(4-tert-butylphenolate)s as a single component initiator

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Abstract

Ring-opening polymerization of 2,2-dimethyltrimethylene carbonate (DTC) has been carried out by using single component rare earth tris(4-tert-butylphenolate)s ($\text{Ln}(\text{OTBP})_3$) initiators for the first time. The influences of rare earth element, solvent, temperature, monomer and initiator concentration as well as reaction time on the polymerization were investigated. The kinetics indicates that the polymerization rate is first order with respect to monomer concentration and initiator concentration, respectively. The overall activation energy of the ring-opening polymerization amounts to 78.7 kJ/mol. Some living character of the reaction was confirmed by adding another portion of DTC monomer into an almost completely polymerized system. PDTC was characterized by ^1H NMR, GPC, IR and DSC. PDTC obtained has no ether unit which resulted from CO_2 elimination. DSC data identified two crystalline modifications and showed some influences of molecular weight on the melting point and melting enthalpy. Mechanism studies showed that monomer inserted into the growing chains with the acyl-oxygen bond scission rather than the break of alkyl-oxygen bond.

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1. Introduction

Polymers obtained by ring-opening polymerization of lactones and cyclic carbonates attract much attention during the past decades due to their potential applications in the biological and medical engineering fields [1–3]. Various effective catalysts or initiators, including cationic, anionic, coordination and enzymatic, have been developed for the ring-opening polymerization of lactones and cyclic carbonates [4–6]. In all of these catalysts or initiators, metal alkoxides and metal aryloxides are effective initiators for the synthesis of biodegradable polymers [7–11]. Recently, our group has developed new rare earth alkoxides and rare earth aryloxides for the ring-opening polymerization of lactones and cyclic carbonates. We have found that these rare earth coordination catalysts [12,13] and one component rare earth catalysts [14–16] exhibit high activities for ϵ -caprolactone

and cyclic carbonates polymerizations. Further studies showed that another new rare earth aryloxide initiator, i.e. rare earth tris(4-tert-butylphenolate)s, can also effectively initiate the ring-opening polymerization of ϵ -caprolactone [17] and DTC. This paper reports the characteristics, kinetics and mechanism of DTC polymerization initiated by rare earth tris(4-tert-butylphenolate)s ($\text{Ln}(\text{OTBP})_3$) for the first time.

2. Experimental

2.1. Materials

2,2-Dimethyltrimethylene carbonate was synthesized according to the reported method [18] and dried over P_2O_5 . Toluene and tetrahydrofuran were distilled over the blue benzophenone-Na complex. CH_2Cl_2 and CCl_4 were dried and refluxed over P_2O_5 under nitrogen atmosphere. Rare earth oxides (Ln_2O_3) with a purity of 99.99% were purchased from Shanghai Yaolong factory.

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2.2. Initiator preparation

Initiators were prepared using Schlenk tube and vacuum-line technique under purified nitrogen. Anhydrous rare earth chlorides were prepared by heating the mixture of hydrated rare earth chloride and ammonium chloride under reduced pressure [19]. Ln(OTBP)₃ were synthesized according to [20].

2.3. Polymerization

Polymerizations were carried out in glass ampoules heated, evacuated and filled with nitrogen for several cycles before use. Monomer solution and initiator solution were added into ampoule successively. The ampoules were kept in thermostat. The reaction was terminated by methanol containing 5% HCl. The resulting polymer was washed for several times and dried at 40 °C in vacuum.

2.4. Measurements

¹H NMR spectra were obtained on a Bruker Avance DMX500 spectrometer in CDCl₃ at room temperature with tetramethylsilane (TMS) as the internal reference. Differential scanning calorimetric (DSC) curves were taken on Pyris Series-DSC 7 in the temperature range from 30 to 200 °C with a heating rate of 10 °C/min and a cooling rate of 100 °C/min, the maximum of the endothermic peak was taken as the melting temperature. IR spectra were measured with a Bruker Vector 22 FT-IR spectrometer using KBr pellets. Gel permeation chromatographic (GPC) measurements were performed on a Waters 208 apparatus with THF as eluent at a flow rate of 1.5 ml/min. Polystyrene standards were used for calibration. The intrinsic viscosity of PDTC was determined in THF at 23.0 ± 0.1 °C with an Ubbelohde viscosimeter, the average light scattering molecular weight (M_{LS}) of PDTC derived from the light scattering measurements correlated with the intrinsic viscosity according to the equation [21]: $[\eta] = 8.32 \times 10^{-3} M_{LS}^{0.79}$ ml/g.

Polymerization kinetics was conducted by the weight-measuring method. For kinetic studies, the polymerization reaction was stopped below 40% conversion.

3. Results and discussion

3.1. Characteristics of the polymerization

Rare earth tris(4-tert-butylphenolate)s, [Ln(OTBP)₃], could be easily prepared from cheap reagents: anhydrous rare earth chloride and *p*-tert-butylphenol, and are easily purified and thermally stable. They are found to be effective initiators for the ring-opening polymerization of DTC for the first time. Table 1 lists the influence of different rare earth initiators on the polymerization. The data show that La, Gd or Nd compound is an effective initiator for

Table 1

Influence of different rare earth initiators on the polymerization of DTC

Ln(OTBP) ₃	[DTC]/[Ln] (molar ratio)	Conversion (%)	$M_{LS} \times 10^{-4}$
La	1000	97.6	14.9
	500	54.1	3.42
Gd	1000	97.5	8.47
	500	43.6	3.83
Nd	500	95.5	7.91
	250	7.21	–
Y	500	21.6	2.10
	250	–	–
Er	500	–	–
	250	–	–

Conditions: [DTC] = 1.0 mol/l, 60 °C, 40 min, toluene.

the ring-opening polymerization of DTC. La(OTBP)₃ has the highest activity and can prepare PDTC with M_{LS} about 15.0×10^4 over 90% yield under following quite mild conditions: [DTC] = 1.0 mol/l, molar ratio of [DTC]/[La] = 1000, 60 °C in toluene.

The effect of different solvents of La(OTBP)₃ system is shown in Table 2. It can be seen that the molecular weight of PDTC and the conversion of DTC achieved in toluene and CCl₄ are higher than those in CH₂Cl₂ and THF, Toluene is a better solvent for DTC polymerization. The results of Table 2 indicate that the ring-opening polymerization of DTC does not proceed via an ionic mechanism, but via a coordination mechanism.

The effects of reaction conditions on the DTC polymerization have been investigated in detail and the results are summarized in Table 3. It can be seen that the conversion of DTC and the molecular weight of PDTC increase with increasing [DTC]/[La] molar ratio, reaction time, monomer concentration and temperature in the range tested. The optimum conditions for the DTC polymerization in toluene are [DTC] = 1.0 mol/l, [DTC]/[La] = 1000, 60 °C, 40 min.

Although the number-average molecular weight of PDTC obtained by La(OTBP)₃ are high compared to the calculated one, proportional relationship between M_n and [DTC]/[La] was observed (Fig. 1). Fig. 2 also illustrates that the molecular weight of PDTC has a linear relationship with the conversion, and the molecular weight distribution of PDTC is around 1.1–1.5. Moreover, when another portion of DTC was introduced into the almost completely polymerized system, the fresh monomer can also 100% polymerize into polymer having a higher molecular weight as shown in Fig. 3.

Table 2

Effect of different solvents on the polymerization of DTC

Solvents	Time (min)	Conversion (%)	$M_{LS} \times 10^{-4}$
Toluene	40	100	15.2
CCl ₄	40	99.8	8.81
CH ₂ Cl ₂	120	70.8	4.35
THF	120	60.1	2.37

Conditions: [DTC] = 1.0 mol/l, [DTC]/[La] = 1000, 60 °C.

Table 3
Ring-opening polymerization of DTC by La(OTBP)₃ system

No.	[DTC] (mol/l)	[DTC]/[La] (molar ratio)	Temp. (°C)	Time (min)	Conv. (%)	$M_{LS} \times 10^{-4}$	$M_n^a \times 10^{-4}$	MWD
1	1.0	1000	60	2.5	17.6	2.60	2.55	1.09
2	1.0	1000	60	7	54.2	8.89	7.56	1.16
3	1.0	1000	60	13	81.3	12.7	10.9	1.27
4	1.0	1000	60	25	90.7	13.8	12.6	1.32
5	1.0	1000	60	40	98.6	15.7	13.7	1.45
6	1.0	800	60	40	99.5	12.3	11.4	1.46
7	1.0	500	60	40	97.6	10.8	8.46	1.49
8	1.0	250	60	40	97.1	9.23	5.64	1.52
9	1.0	125	60	40	93.5	6.80	3.87	1.55
10	0.75	1000	60	40	96.2	11.9	–	–
11	0.5	1000	60	40	93.4	9.45	–	–
12	0.25	1000	60	40	78.5	6.18	–	–
13	0.125	1000	60	40	54.1	3.55	–	–
14	1.0	1000	30	40	18.6	2.08	–	–
15	1.0	1000	40	40	54.0	5.75	–	–
16	1.0	1000	50	40	93.0	11.1	–	–
17	1.0	1000	70	40	94.6	13.9	–	–

Conditions: toluene.

^a Measured by GPC.

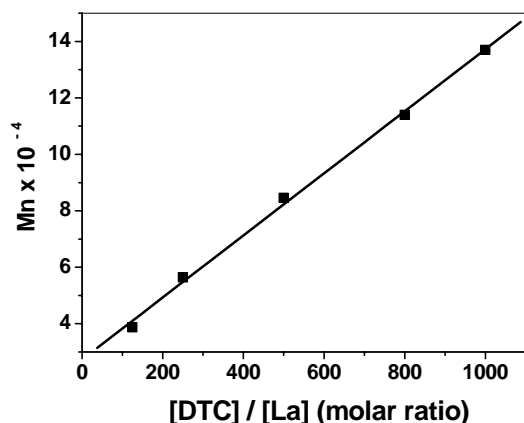


Fig. 1. Relationship between molecular weight and the [DTC]/[La] molar ratio.

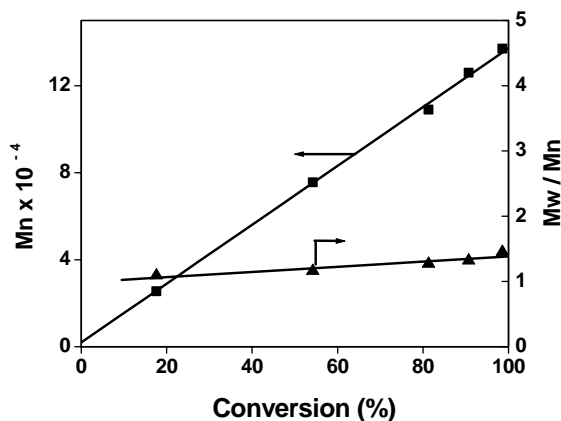


Fig. 2. Relationship between molecular weight and the conversion of DTC.

In the GPC pattern, a bimodal molecular weight distribution was observed which may result from prepolymer having not reinitiated the second stage polymerization. These results show that the reaction under the conditions used has some living character.

The ¹H NMR spectrum of PDTC (Fig. 4) shows only two single peaks at 3.97 ppm (CH₂) and 1.00 ppm (CH₃) with expected intensity ratio of 2:3 and no signals of ether are present. The IR spectrum also proves the carbonate structure by a strong band at 1747.0 cm⁻¹ and a broad band around 1267.6 cm⁻¹ due to the O–C–O stretching vibration.

The thermal behavior of the PDTC was studied by means of DSC. Fig. 5 identified two different crystalline modifications of PDTC. Modification I has a transition temperature at 90.3 °C and modification II shows a melting point of 121.2 °C. Upon cooling and reheating, modification I completely disappeared and a melting point of 121.9 °C was observed. Table 4 shows the thermal behavior of PDTC

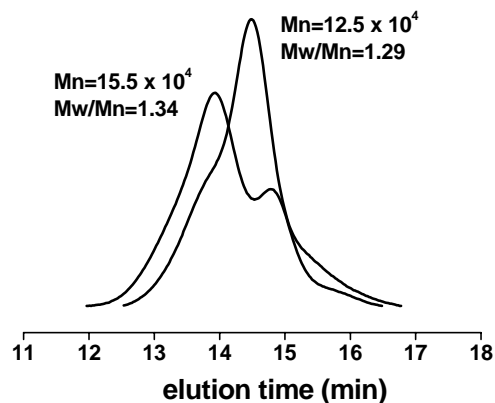


Fig. 3. GPC curves of PDTC obtained by the polymerization with La(OTBP)₃ in toluene at 60 °C.

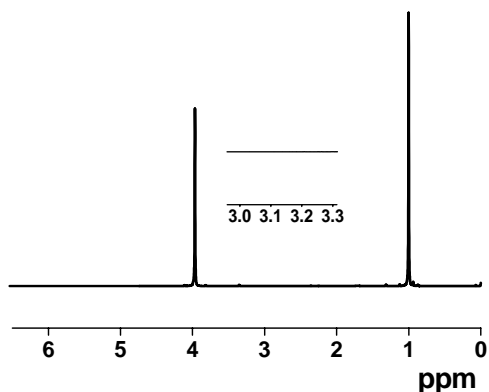
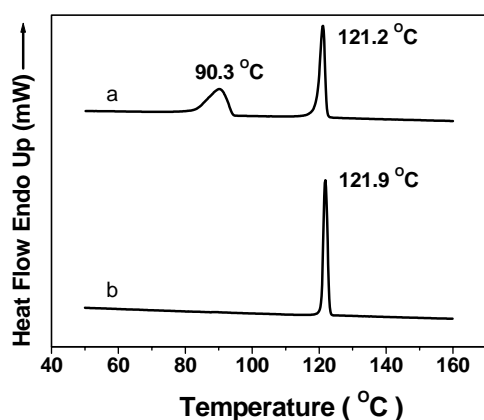
Fig. 4. ^1H NMR spectrum of PDTC.

Fig. 5. DSC curves of PDTC.

samples with different molecular weights, the melting points of both modifications I and II increase with molecular weight below 5.0×10^{-4} , the melting enthalpy of modification I somewhat decreases, while the melting enthalpy of modification II has a slight increase, which coincides with other studies [22].

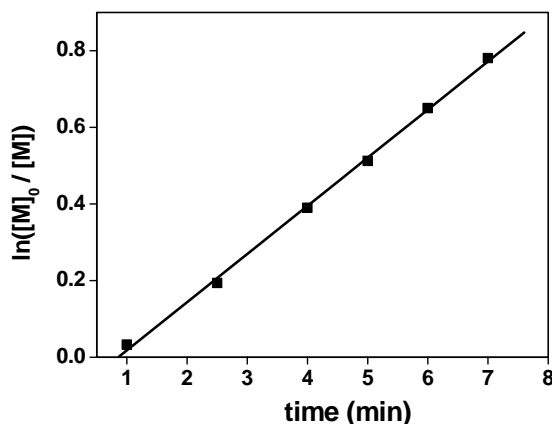
3.2. Kinetics and mechanism of the polymerization

To get more insight into the DTC polymerization by rare earth tris(4-tert-butylphenolate)s system, the kinetics of DTC polymerization in toluene has been studied. Fig. 6 showed the typical monomer consumption-time dependence of polymerization reaction in semi-logarithmic coordinates

Table 4
Thermal behavior of PDTC samples with different molecular weights

Sample	M_n^a	First heating				Second heating	
		T_f1 (°C)	ΔH_f1 (J/g)	T_f2 (°C)	ΔH_f2 (J/g)	T_f2 (°C)	ΔH_f2 (J/g)
1	8600	84.0	40.0	115.0	18.4	115.1	19.5
2	46700	88.5	24.7	121.2	24.3	121.4	25.0
3	109000	90.3	21.4	121.2	24.8	121.9	25.9
4	137000	90.7	22.5	121.2	24.04	122.4	25.8

^a Measured by GPC.

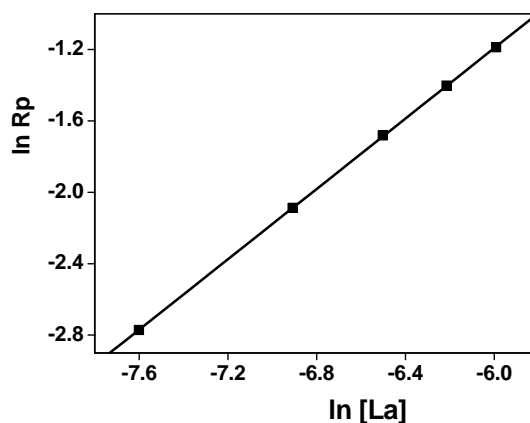
Fig. 6. $\ln([M]_0/[M])$ as a function of time.

at $[\text{La}] = 1 \times 10^{-3}$ M. Fig. 7 illustrates the correlation of polymerization rate versus concentration of $\text{La}(\text{OTBP})_3$ ($\ln R_p$ versus $\ln[\text{La}]$). These data disclose that the polymerization rate is first order with respect to the initiator concentration and monomer concentration, respectively. Therefore, the polymerization of DTC initiated by $\text{La}(\text{OTBP})_3$ under the conditions studied can be written as follows:

$$R_p = k_p[\text{DTC}][\text{La}(\text{OTBP})_3]$$

where k_p is the polymerization rate constant. At 60°C , when the monomer concentration is 1.0 mol/l, the k_p is 123.3 l/(mol min). The relationship between the $\ln R_p$ and the reciprocal of polymerization temperature ($1/T$) has been plotted (Fig. 8). According to the Arrhenius equation, the apparent activation energy is 78.7 kJ/mol.

In order to study polymerization mechanism, a PDTC sample with low molecular weight terminated by isopropanol has been prepared, and its ^1H NMR spectrum is shown in Fig. 9. Signals in the spectrum were assigned as follows: $\delta = 1.30$ ppm (d, H^a), $\delta = 4.87$ ppm (m, H^b), $\delta = 3.97$ ppm (s, H^c), $\delta = 1.00$ ppm (s, H^d), $\delta = 3.35$ ppm (s, H^e). In the polymer, the CH_2OH end group (singlet signals at 3.35 ppm) was present, signals of isopropyl (the doublet peak of H^a and the multiplet peak of H^b , intensity ratio of

Fig. 7. The plot of $\ln R_p$ vs. $\ln[\text{La}]$.

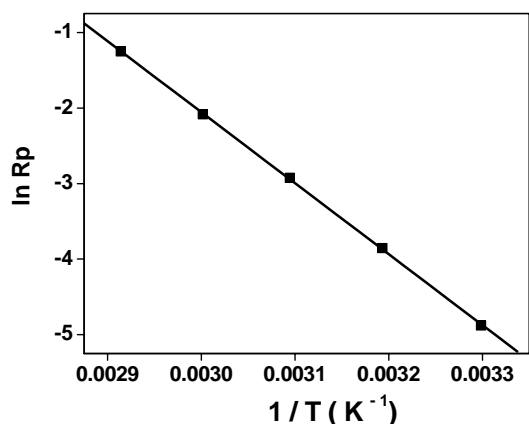


Fig. 8. Effect of reaction temperature on the rate of propagation.

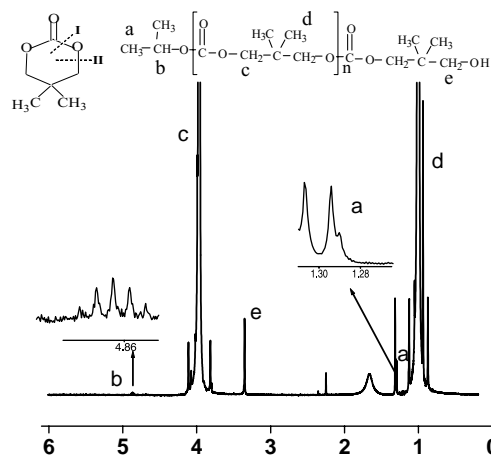


Fig. 9. ^1H NMR of PDTC terminated by isopropanol.

$\text{H}^{\text{a}}/\text{H}^{\text{b}}$ = 6:1) were also observed. It is clear that the isopropyl group is introduced into the living chain at the termination stage. Results of ^1H NMR indicate that the monomer inserts into the growing chains with the acyl-oxygen bond scission (I) rather than the break of alkyl-oxygen bond (II).

4. Conclusion

Single component rare earth tris(4-tert-butylphenolate)s are effective initiators for the ring-opening polymerization of 2,2-dimethyltrimethylene carbonate. $\text{La}(\text{OTBP})_3$ has higher activity and gives higher molecular weight PDTC. The kinetics of $\text{La}(\text{OTBP})_3$ system demonstrates that the polymerization rate has the first-order in monomer concentration and initiator concentration and the overall activation energy

amounts to 78.7 kJ/mol. The growing polymer chains were found to be active for polymerization of second monomer. PDTC obtained has no ether unit. DSC data identified two crystalline modifications and showed a little influence of molecular weight below 5.0×10^{-4} on the melting point and melting enthalpy. Mechanism studies showed that monomer inserted into the growing chains with the acyl-oxygen bond scission rather than the break of alkyl-oxygen bond.

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