

Copolymerization of trimethylene carbonate and 2,2-dimethyltrimethylene carbonate by rare earth calixarene complexes

Weipu Zhu, Jun Ling, Hong Xu, Zhiquan Shen*

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract

Rare earth (Nd, Y, La) *p*-tert-butylcalix[*n*]arene (*n*=4, 6, and 8) complexes alone have been developed to catalyze random and block copolymerizations of trimethylene carbonate (TMC) and 2,2-dimethyltrimethylene carbonate (DTC). The random or block structure and thermal behavior of the copolymers have been characterized by SEC, NMR, DSC, XRD and PLM. Random copolymer with M_w of 14,100 and M_w/M_n of 1.36 was prepared by neodymium *p*-tert-butylcalix[6]arene complex under the conditions: [TMC+DTC]₀/[Nd]=400, 80 °C, 8 h. The reactivity ratios of TMC and DTC are measured to be $r_{TMC}=4.68$ and $r_{DTC}=0.163$, respectively. Random copolymerization could be well designed by the feeding ratio to prepare copolymers with controlled T_m and T_g . Only 8% TMC units in the polymer chain destroyed the crystallization of PDTC showing no T_m of the copolymer in the DSC analysis.

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1. Introduction

Polymers of aliphatic cyclic carbonates are sensitive to hydrolysis due to their ester groups, which are useful materials in pharmaceutical or medical applications [1–4]. Some researches have focused on the ring-opening polymerization of six-member cyclic carbonates such as trimethylene carbonate (TMC) [5–9] and 2,2-dimethyltrimethylene carbonate (DTC) [10–14]. The copolymers of different cyclic carbonates would have wider applications in virtue of their adjustable crystallization properties, thermal behaviors, hydrolysis processes, and degradability, etc. owing to the reasonable compositions and structures of polymer chains influenced by the comonomer feeding ratio, sequence and polymerization conditions. However, few literatures have reported their copolymerization [13]. In this paper, we firstly reported the ring-opening copolymerization of TMC and DTC by using a set of novel rare earth calixarene complexes shown in Scheme 1 as catalysts.

Random and block copolymers were synthesized with monomers feeding simultaneously and sequentially, respectively. The structures of the copolymers were investigated in detail by SEC, NMR, DSC, XRD and PLM.

2. Experimental

2.1. Materials

TMC and DTC were prepared by the exchange reaction of corresponding glycol and diethyl carbonate [15], recrystallized and dried before use. Calixarenes and rare earth calixarene complexes were synthesized and purified according to the literature [14]. Other chemicals were purified with usual methods.

2.2. Polymer synthesis

Random copolymerizations were carried out in 20 mL ampoules with Schlenk technique. As a typical procedure, TMC (0.176 g, 1.72 mmol) and DTC (0.224 g, 1.72 mmol) and toluene (1.72 mL) were added into the ampoule, which was kept at 80 °C in an oil bath. Then neodymium *p*-tert-butylcalix[6]arene complex (8.60 μmol) dissolved in

* Corresponding author. Tel.: +86 571 879 51059; fax: +86 571 879 53727.

E-mail address: zhiquan_shen@163.com (Z. Shen).

1. $[\text{C4}(\text{OH})_3\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Nd}$
2. $[\text{C6}(\text{OH})_2\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Nd}_4$
3. $[\text{C8}(\text{OH})_2\text{O}_6 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Nd}_2$
4. $[\text{C6}(\text{OH})_2\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{La}_4$
5. $[\text{C6}(\text{OH})_2\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Y}_4$

Scheme 1. Structure formulas of various rare earth calixarene complexes.

toluene was introduced by a syringe to initiate the reaction. The polymerization was terminated by ethanol with 5% HCl, and the polymer precipitated from ethanol. The copolymer was treated with a KOH-saturated ethanol to remove released calixarene, washed, filtered, and dried under vacuum to constant weight.

As to block copolymerization, the solution of second monomer was introduced by a syringe into the pre-polymerized mixture. Other operations were similar to random copolymerizations.

2.3. Measurements

The intrinsic viscosity of poly(TMC-*c*-DTC) was measured with Ubbelohde viscometer in THF at 30.5 °C. Size exclusion chromatographic (SEC) measurements calibrated to commercial polystyrene standards were performed on a Waters 150-C apparatus in THF (1.0 mL/min) at 25 °C. NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Differential scanning calorimetric (DSC) curves were taken on a Perkin-Elmer Pyris 1 apparatus. To eliminate the heat history, each sample was heated fast from room temperature to +150 °C then cooled to -60 °C and heated to +150 °C for recording with a heating rate of 10 °C/min. The crystal structure of random copolymers was examined by a XD-98 X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation of wavelength $\lambda = 1.54056 \text{ \AA}$ for 2θ angles between 2 and 35°. The morphologies of copolymers were monitored with an Olympus BX51 polarized light microscope (PLM).

3. Results and discussion

3.1. Random copolymerization

Rare earth *p*-*tert*-butylcalixarene complexes have been proved as efficient single component catalysts for the homopolymerization of DTC [14]. Random copolymerizations of TMC and DTC are firstly carried out by these novel catalysts as shown in Table 1. All the five complexes exhibit high catalytic activities and prepare copolymers with high intrinsic viscosities. Table 2 shows the effect of polymerization time on the copolymerization with the monomer ratio of 50:50 in feeding catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex. The conversions, intrinsic viscosities and molecular weights increased as the duration of the copolymerization prolonged from 1 to 8 h.

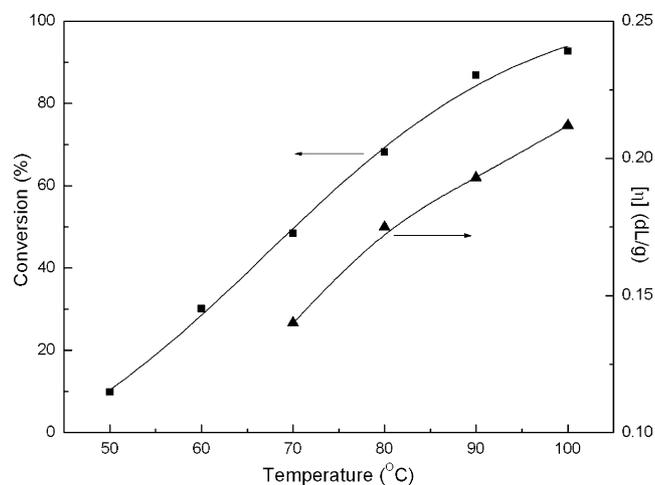


Fig. 1. Effect of polymerization temperature on TMC and DTC copolymerization catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex. Conditions: $[\text{TMC} + \text{DTC}]_0 = 2.0 \text{ mol/L}$, $[\text{TMC} + \text{DTC}]_0/[\text{Nd}] = 400$, TMC:DTC = 50:50 (feed molar ratio), 4 h, toluene.

Furthermore, the molecular weight distributions widened from 1.16 to 1.36 during this period. The molar ratio of DTC and TMC in the copolymer calculated by the intensity ratio of protons in ^1H NMR also increased with the prolonging of polymerization time indicating that TMC was more active than DTC in the reaction. When the polymerization time was prolonged to 16 h, the conversion, intrinsic viscosity and molecular weight all decreased, which attributes to the cyclization reactions.

Both the conversion and intrinsic viscosity of the copolymer increased as the polymerization temperature

Table 1
TMC and DTC copolymerization catalyzed by various rare earth *p*-*tert*-butylcalixarene complexes

No.	Complex	Conv. (%)	$[\eta]$ (dL/g)
1	$[\text{C4}(\text{OH})_3\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Nd}$	77.8	0.22
2	$[\text{C6}(\text{OH})_2\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Nd}_4$	83.2	0.24
3	$[\text{C8}(\text{OH})_2\text{O}_6 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Nd}_2$	75.9	0.15
4	$[\text{C6}(\text{OH})_2\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{La}_4$	83.9	0.16
5	$[\text{C6}(\text{OH})_2\text{O}_4 \cdot \text{CH}_3\text{C}_6\text{H}_5]_3\text{Y}_4$	77.1	0.15

Conditions: $[\text{TMC} + \text{DTC}]_0 = 2.0 \text{ mol/L}$, $[\text{TMC} + \text{DTC}]_0/[\text{Ln}] = 400$, TMC:DTC = 50:50 (feed molar ratio), 80 °C, 8 h, toluene.

Table 2
Effect of polymerization time on TMC and DTC copolymerization catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex

No.	Time (h)	Conv. (%)	TMC:DTC in polymer	$[\eta]$ (dL/g)	M_w (10^4)	M_w/M_n
1	1	21.5	75:25	–	0.59	1.16
2	3	56.7	73:27	0.17	0.95	1.20
3	4	68.2	70:30	0.18	1.03	1.22
4	8	83.2	59:41	0.24	1.41	1.36
5	16	61.5	71:29	0.17	0.74	1.18

Conditions: $[\text{TMC} + \text{DTC}]_0 = 2.0 \text{ mol/L}$, $[\text{TMC} + \text{DTC}]_0/[\text{Nd}] = 400$, TMC:DTC = 50:50 (feed molar ratio), 80 °C, toluene.

Table 3
Effect of comonomer concentration and catalyst amount on TMC and DTC copolymerization catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex

No.	[TMC + DTC] ₀ (mol/L)	[TMC + DTC] ₀ /[Nd]	Conv. (%)	[η] (dL/g)
1	0.2	400	45.0	–
2	0.4	400	50.6	0.18
3	1.0	400	62.1	0.18
4	2.0	200	93.0	0.17
5	2.0	400	68.2	0.18
6	2.0	800	63.2	0.26
7	2.0	1600	25.9	–
8	4.0	400	83.9	0.16

Conditions: TMC:DTC=50:50 (feed molar ratio), 4 h, 80 °C, toluene.

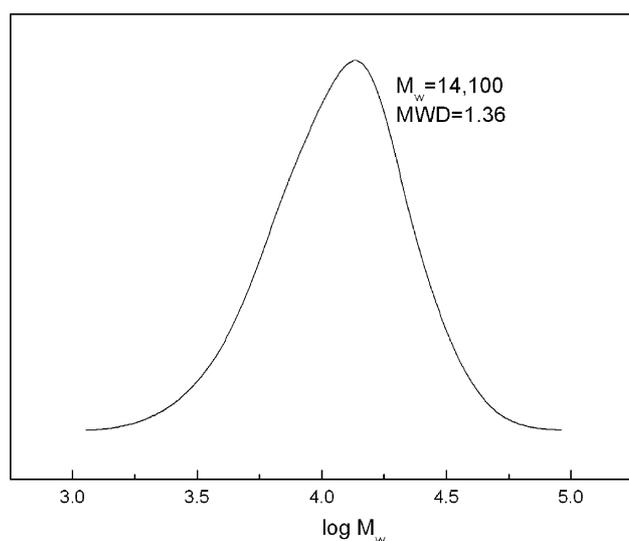


Fig. 2. SEC curve of poly(TMC-*ran*-DTC) catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex. Conditions: [TMC + DTC]₀ = 2.0 mol/L, [TMC + DTC]₀/[Nd] = 400, TMC:DTC = 50:50 (feed molar ratio), 8 h, 80 °C, toluene.

rising from 40 to 100 °C (Fig. 1). Table 3 summarizes the effect of comonomer concentration ([TMC + DTC]₀) and catalyst amount ([TMC + DTC]₀/[Nd]) on the copolymerization. Lesser catalyst amount ([TMC + DTC]₀/[Nd] = 800) prepares copolymer with higher intrinsic viscosity ([η] = 0.26, Table 3, no. 6). Higher monomer concentration gave higher conversion, but a little lower intrinsic viscosity.

Fig. 2 shows the SEC pattern of poly(TMC-*ran*-DTC) with high M_w of 14,100 and a narrow molecular weight distribution of 1.36 (Table 2, no. 4). Single peak of SEC pattern reveals that there is only one kind of active species in the copolymerization.

The components and chain structures of random copolymers are testified by ¹H and ¹³C NMR spectra shown in Figs. 3 and 4. The chain end of copolymer having either TMC (H^c, H^e) or DTC (H^f, H^h) with the structures of -CH₂CH₂OH or -C(CH₃)₂CHOH could be clearly detected

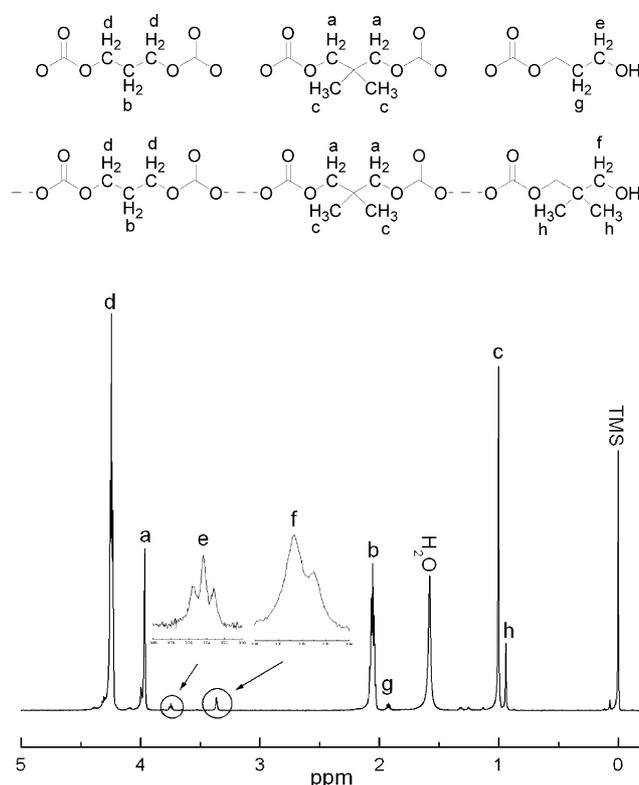


Fig. 3. ¹H NMR spectrum of poly(TMC-*c*-DTC) with the end unit of -CH₂CH₂OH and -C(CH₃)₂CHOH catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex.

(Fig. 3). In Fig. 4, three groups of peaks at 150–160 ppm indicate three kinds of carbonyl groups. C^g attributes to the carbon atoms in the TMC-DTC or DTC-TMC units, which confirms that the product is a random copolymer rather than the blend.

The thermal behaviors and crystallization properties of random copolymers are investigated by DSC, XRD and

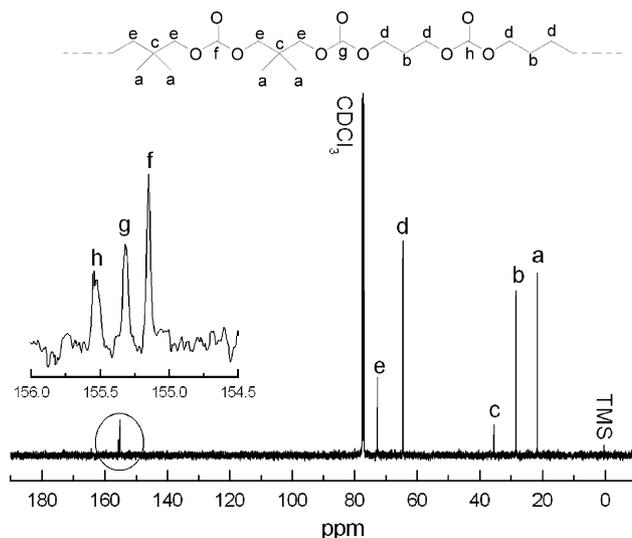


Fig. 4. ¹³C NMR spectrum of poly(TMC-*c*-DTC) catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex.

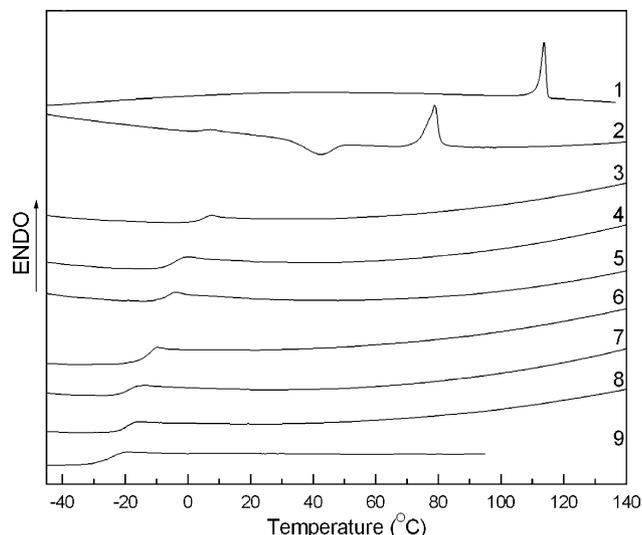


Fig. 5. DSC curves of random copolymers of TMC and DTC. Curve 1–9 represent copolymers of no. 1–9 in Table 4.

PLM. The increasing TMC contents in the copolymers will decrease the crystallinity. Fig. 5 shows the DSC curves as a function of molar ratio of TMC and DTC in copolymers (Table 4). No T_m was found in the copolymers with TMC content higher than 8%. The copolymers of DTC with TMC provide a faster degradation rate. Furthermore, the T_g s lower with higher molar ratio of TMC and DTC in copolymers. Fig. 6 displays the XRD results of Poly(TMC-*ran*-DTC) with different molar ratios of two comonomer indicating that increase in TMC unit will lower DTC crystallization with DTC content from 100 to 47% (Table 4, no. 1, 3, 5).

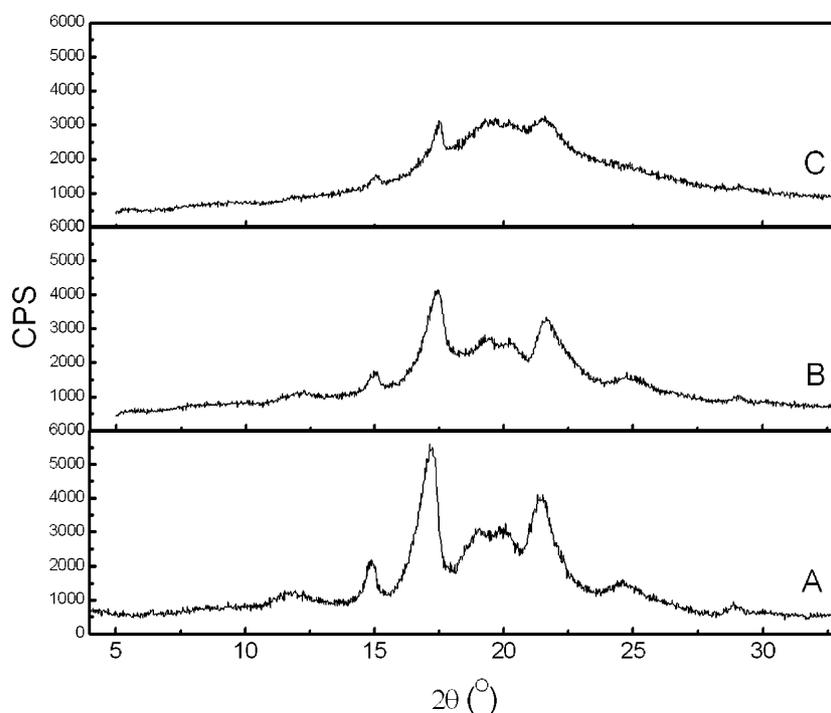


Fig. 6. XRD curves of: the samples: (A) No. 1 in Table 4; (B) no. 3 in Table 4; (C) no. 5 in Table 4.

Table 4
Thermal behaviors of copolymers with various monomer ratios catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex

No.	TMC: DTC in feeding	TMC: DTC in polymer	Conv. (%)	T_m (°C)	T_g (°C)
1	0:100	0:100	86.0	113.9	–
2	5:95	8:92	46.5	78.9	+4.79
3	10:90	14:86	61.4	–	+3.59
4	30:70	36:64	76.9	–	–0.107
5	50:50	59:41	83.2	–	–4.85
6	70:30	74:26	89.1	–	–13.8
7	90:10	91:9	86.8	–	–19.1
8	95:5	96:4	96.9	–	–19.7
9	100:0	100:0	81.2	–	–22.5

Conditions: $[TMC + DTC]_0/[Nd] = 400$, 8 h, 80 °C, toluene.

The morphologies of the copolymer recorded on PLM shown in Fig. 7 also illustrated it. The spherulite radius of DTC become smaller, and the non-crystal phase enlarges and becomes consecutive with increasing TMC units. These random copolymers with low and controlled crystallinity could be used as the environmental degradable materials [16,17] and medical materials [18,19].

In our previous work [14], it has been confirmed that in DTC ring opening polymerization catalyzed by rare earth calixarene complexes, DTC inserts into the growing chain via acyl-oxygen bond cleavage of the ring and proceeds a coordination anionic mechanism. Since, TMC has similar structure with DTC and could copolymerize with it, the mechanism of the copolymerization may be the same.

To determine the activities of TMC and DTC, their

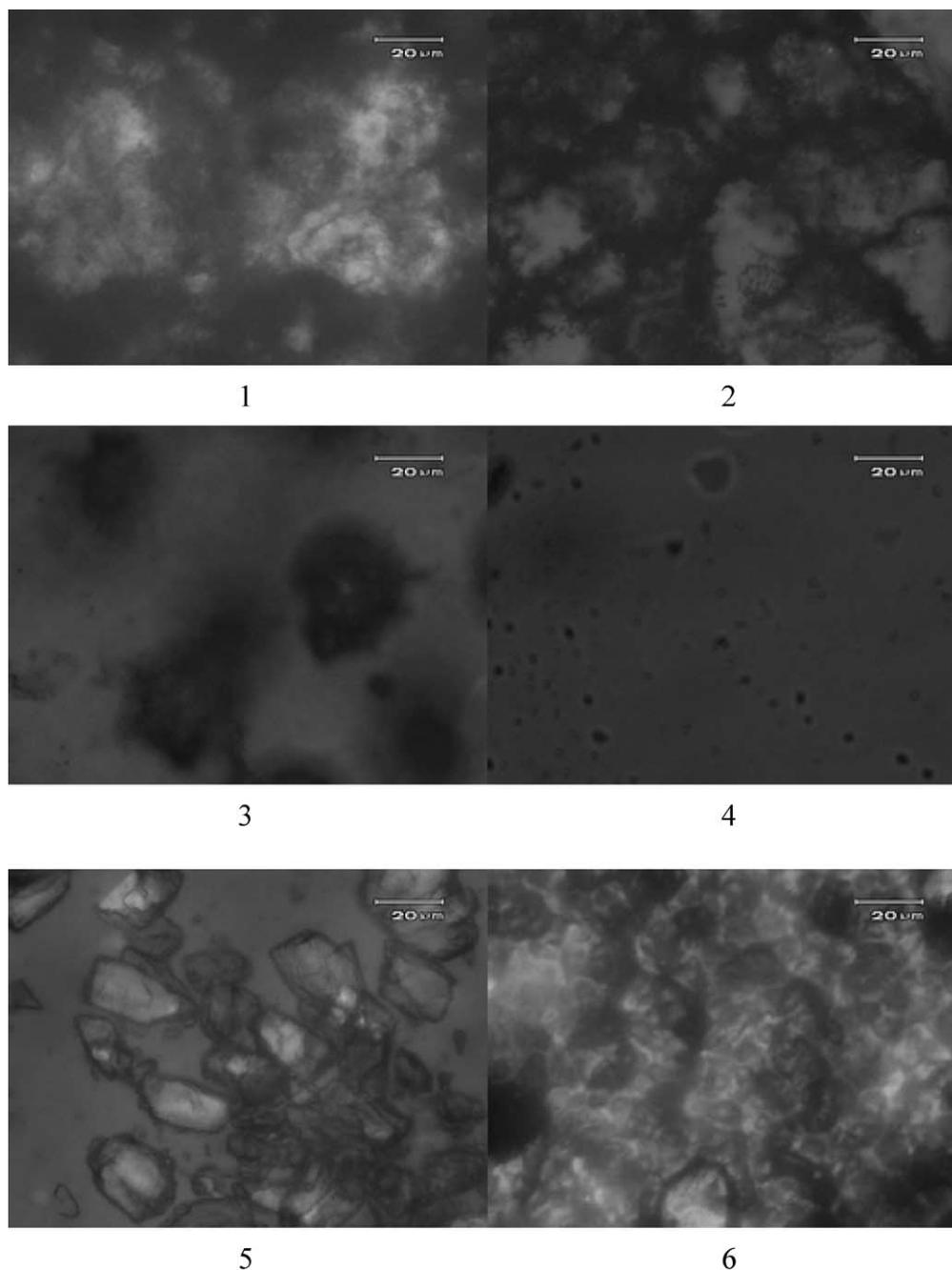


Fig. 7. Morphologies of the samples (1) no. 1 in Table 4; (2) no. 2 in Table 4; (3) no. 3 in Table 4; (4) no. 5 in Table 4; (5) poly(DTC-*b*-TMC), Fig. 9(B); (6) poly(TMC-*b*-DTC), Fig. 10(B).

reactivity ratios are measured by a set of low conversion copolymerizations at 80 °C (Fig. 8) according to the following equations [20], where ρ and R represent the comonomer ratios in feeding and polymer, respectively. As a result, $r_{\text{TMC}}=4.68$ and $r_{\text{DTC}}=0.163$ with the correlation coefficient of 0.992 are obtained.

$$\frac{\rho - 1}{R} = r_{\text{TMC}} - r_{\text{DTC}} \times \frac{\rho}{R^2} \quad (1)$$

$$\rho = \frac{[\text{TMC}]_0}{[\text{DTC}]_0} \quad (2)$$

$$R = \frac{[\text{TMC}]_p}{[\text{DTC}]_p} \quad (3)$$

3.2. Block copolymerization

Block copolymerizations were carried out by adding the monomers into the reaction system sequentially. Diblock

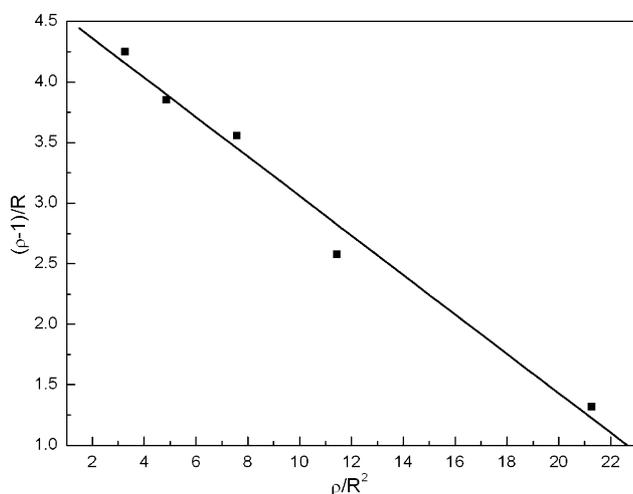


Fig. 8. Reactivity ratio calculation.

copolymers could be obtained by two feeding sequences: either DTC polymerized first or TMC first. The structure was verified by the SEC curves of poly(DTC-*b*-TMC) and PDTC before TMC was added (Fig. 9). The molecular weight increased and the molecular weight distributions still remained narrow, which indicates that TMC adds into the active chain ends of PDTC. When TMC polymerized first, similar result could be obtained (Fig. 10). Fig. 11 shows the DSC curves of the above two block copolymers with T_{ms} (46.4, 39.6 °C) due to the PDTC segments and T_g (−5.0 °C) of PTMC segments. T_{ms} are lower and T_g is higher or almost not be detected corresponding to homopolymers. The morphologies of block copolymers were taken from PLM, in which the crystals of PDTC segment could be seen clearly (Fig. 7).

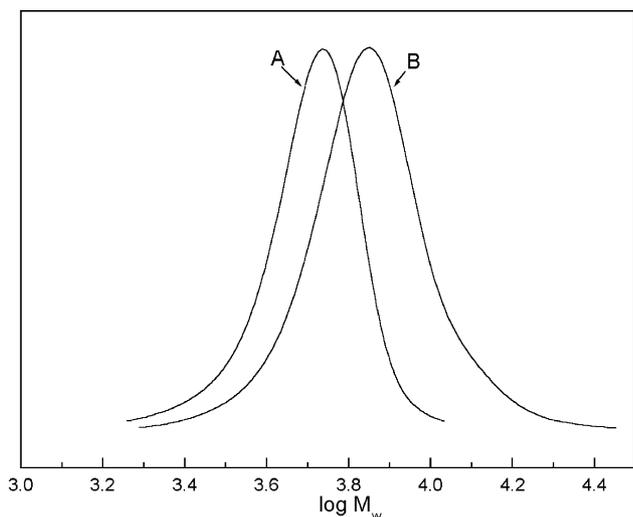


Fig. 9. SEC measurements of (A) PDTC, [DTC]₀=1.0 mol/L, [Nd]₀=5.0 × 10^{−3} mol/L, 80 °C, t_1 =3 h, toluene, conv.=86.0%, M_n =5000, M_w/M_n =1.06; (B) poly(DTC-*b*-TMC), [TMC]₀=1.0 mol/L, TMC:DTC=50:50 (feed molar ratio), t_2 =2 h, conv.=81.2%, M_n =6800, M_w/M_n =1.12 catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex.

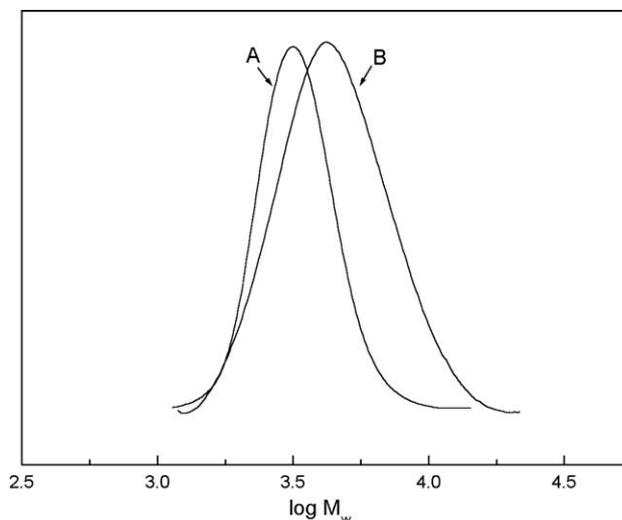


Fig. 10. SEC measurements of (A) PTMC, [TMC]₀=1.0 mol/L, [Nd]₀=2.5 × 10^{−2} mol/L, 80 °C, t_1 =2 h, toluene, conv.=88.9%, M_n =3400, M_w/M_n =1.12; (B) poly(TMC-*b*-DTC), [DTC]₀=1.0 mol/L, TMC:DTC=10:90 (feed molar ratio), t_2 =3 h, conv.=45.6%, M_n =5100, M_w/M_n =1.22 catalyzed by neodymium *p*-*tert*-butylcalix[6]arene complex.

4. Conclusion

Rare earth calixarene complexes were firstly found to be effective single component catalysts for the ring-opening copolymerization of TMC and DTC. The copolymers have been characterized with NMR, SEC, DSC, XRD and PLM having well-defined random or block structure. The reactivity ratios of TMC and DTC are r_{TMC} =4.689 and r_{DTC} =0.163. The T_{ms} of PDTC segments disappeared when more than 8% TMC unit distributes randomly in the polymer chain.

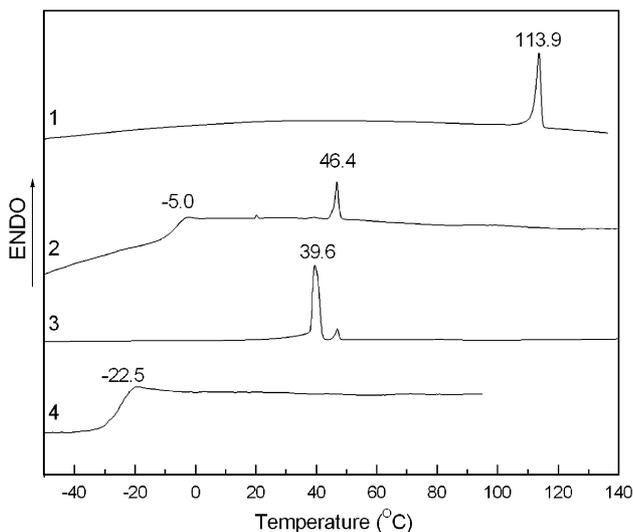


Fig. 11. DSC curves of the samples (1) no. 1 in Table 4; (2) poly(DTC-*b*-TMC), in Fig. 9(B); (3) poly(TMC-*b*-DTC), in Fig. 10(B); (4) no. 9 in Table 4.

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