Controlling Ring-Opening Copolymerization of ϵ-Caprolactone with Trimethylene Carbonate by Scandium Tris(2,6-di-*tert*-butyl-4-methylphenolate)

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ABSTRACT: Copolymers of ϵ-caprolactone (CL) and trimethylene carbonate (TMC) have been synthesized through ring-opening polymerization using a novel initiator of scandium tris(2,6-di-*tert*-butyl-4-methylphenolate). CL and TMC polymerizations proceed via the "coordination anionic mechanism" with acyl−oxygen bond cleavage. Five kinds of copolymers with different structures of X, XB, AXB, AB, and BAXB are synthesized under different polymerization conditions and characterized by ^{1}H NMR, GPC, and DSC, where X, A, and B denote as random blocks of CL and TMC, PTMC blocks, and PCL blocks, respectively.

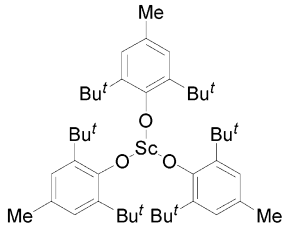
Introduction

There are only a few papers reported that scandium compound can be used as catalyst for ring-opening polymerization of lactide, lactones, and cyclic carbonates, such as scandium triflate ($Sc(OTf)_3$) in the presence of alcohol or H_2O applied in a living or controlled ring-opening polymerization of lactide and lactones.[1−3] Copolymers of lactones and cyclic carbonates are sensitive to hydrolysis due to the aliphatic ester groups, which lead to pharmaceutical or medical applications. Copolymer properties and applications are depended on their chain structures. AXB copolymers (X as a random copolymer block) of ϵ-caprolactone (CL) and 2,2-dimethyltrimethylene carbonate (DTC) were synthesized with *sec*-butyllithium or potassium dihydronaphthylide via simultaneous polymerization.[4] ABA triblock copolymers of CL and trimethylene carbonate (TMC) were prepared by means of a special cyclic initiator of 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP).[5] Random copolymers of CL and TMC were prepared by lanthanum or yttrium tripropoxide and used as nerve guide materials.[6,7] Copolymers of ethylene carbonate (EC) with CL or δ-valerolactone (VL) were produced using $(C_5Me_5)_2$-SmMe(THF) as initiator.[8] Recently, our group has reported rare earth triphenolates are effective initiators for homo- and copolymerization of CL, TMC, and DTC as well as the polymerization mechanism with them.[9,10] In this paper, a novel single-component rare earth initiator of scandium tris(2,6-di-*tert*-butyl-4-methylphenolate) ($Sc(OAr)_3$, Scheme 1) is first reported for the copolymerization of CL and TMC. Five sorts of copolymers with different chain structures as X, XB, AXB, AB, and BAXB have been synthesized by controlling polymerization conditions.

Experimental Section

Materials. CL (Acros product, 99%) was distilled under reduced pressure prior to use. TMC and $Sc(OAr)_3$ were prepared according to the methods in the literature.[11,12] Toluene and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone before use. Dichloromethane (CH_2Cl_2) was dried with calcium hydride and distilled. Nitrobenzene was dried over phosphorus pentoxide, filtered, and distilled under reduced pressure. 2-Propanol was refluxed over magnesium powder and distilled. Other chemicals were used as received.

Scheme 1. Structure of $Sc(OAr)_3$



Polymer Synthesis. Polymerizations were carried out in previously flamed and argon-purged 20 mL ampules at required temperature with Schlenk techniques. The initiator $Sc(OAr)_3$ was dissolved in toluene (0.0172 mol/L) and introduced into the reaction mixture by a syringe.

Homopolymerization. For a typical procedure, 0.440 g of CL was dissolved in 5.5 mL of toluene and warmed by an oil bath to 40 °C before 0.45 mL of initiator solution was introduced. The polymerization was terminated by ethanol with 5% HCl, and the polymers were dried in a vacuum to constant weight. The yield and analytical data depending on various polymerization times are listed in Table 1.

Copolymerization with Comonomer Feeding Simultaneously. For example, 0.124 g of TMC and 0.323 g of CL in 2.6 mL of toluene were injected in an ampule and kept at 0 °C. Then 1.18 mL of initiator solution was added by syringe. The copolymer was obtained with the same treatments mentioned above. The yield and analytical data depending on various polymerization times are listed in Table 2.

Copolymerization with Comonomer Feeding Sequentially. The AB copolymer as an example, 0.082 g of TMC was dissolved in 1.9 mL of toluene in an ampule, kept at 0 °C, and 0.78 mL of initiator solution was injected. After 1 h polymerization, 0.214 g of CL was introduced into the reaction mixture. The copolymer was terminated and precipitated after 23 h polymerization.

Measurements. ^{1}H NMR spectra were recorded on a Bruker Avance DMX 500 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Gel permeation chromatographic (GPC) measurements calibrated to commercial polystyrene standards were performed on a Waters 208 apparatus with Waters 2410 RI detector in THF (1.5 mL/min) at 30.0 °C. The three polystyrene columns used are Styragel HT 3 (molecular weight range $500-3 \times 10^4$), HT 4 ($5 \times 10^3-6 \times 10^5$), and HT 5 ($5 \times 10^4-4 \times 10^6$). The intrinsic

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Table 1. Homopolymerization of CL and TMC Initiated by Sc(OAr)$_3$[a]

monomer	solvent	temp (°C)	time (h)	yield (%)	M_v[b] × 10^{-4}	M_w[c] × 10^{-4}	M_w/M_n[c]
CL	toluene	0	2.0	10.9		3.76	1.83
CL	toluene	0	6.0	30.0	0.99		
CL	toluene	0	16.0	58.0	1.38	2.62	2.34
CL	toluene	40	2.0	87.1	2.22	11.7	1.94
CL	toluene	40	3.0	88.6	2.40		
CL	CH_2Cl_2	40	5.0	46.1	3.05		
CL	CH_2Cl_2	40	24.0	91.1	1.59		
CL	THF	40	5.0	33.6	1.42		
CL	THF	40	18.0	47.0	2.06		
CL	nitrobenzene	40	24.0	*d*			
TMC	toluene	0	0.25	34.9			
TMC	toluene	0	0.75	69.9		2.17	1.53

[a] Polymerization conditions: [CL] = [TMC] = 0.6 mol/L, [Sc(OAr)$_3$] = 1.2 × 10^{-3} mol/L. [b] Viscosity measurements. [c] Measured by GPC. [d] No polymer was obtained.

Table 2. Simultaneous Copolymerizations of CL with TMC Initiated by Sc(OAr)$_3$[a]

						content of diad (%)[c]		
run	time (h)	temp (°C)	yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	TMC−TMC	CL−CL	TMC−CL, CL−TMC
1	6.0	100	77.1	6.08	2.09	6.3	59.8	33.9
2	0.5	0	9.3			61.3	16.2	22.5
3	1.0	0	14.2	0.75	1.35			
4	2.0	0	24.7	0.93	1.46	56.3	21.8	21.9
5	3.0	0	31.4					
6	4.0	0	54.7	2.55	1.71	29.4	50.1	20.5
7	12.0	0	80.0	2.72	2.06	23.8	59.2	17.0

[a] Polymerization conditions: feeding CL:TMC = 70:30 (molar ratio), toluene as solvent, [CL + TMC] = 1.0 mol/L, [Sc(OAr)$_3$] = 5 × 10^{-3} mol/L. [b] Measured by GPC. [c] Calculated from ^{1}H NMR spectrum: $\sum I = [I(H^{i+i'}) - I(H^k)]/2 + I(H^f) + I(H^k) + I(H^a)$. TMC − TMC diad = $\{[I(H^{i+i'}) - I(H^k)]/2\}/\sum I$, CL−CL diad = $I(H^a)/\sum I$, TMC−CL, CL−TMC diad = $[I(H^f) + I(H^k)]/\sum I$.

viscosity of poly(ϵ-caprolactone) (PCL) was measured with an Ubbelohde viscometer in *N*,*N*-dimethylformamide (DMF) at 30.0 °C. The viscosity-average molecular weight of PCL was calculated according to the following equation:[13] $[\eta]$ (dL/g) = 1.94 × $10^{-4}M_v^{0.73}$. Differential scanning calorimetric (DSC) curves were taken on a NETZSCH DSC 204 calibrated with eight substances: KNO_3, indium, bismuth, tin, zinc, CsCl, mercury, and cyclohexane. All DSC data in this paper were recorded from the second heating scan: the samples were cooled to −100 °C, heated to +100 °C, cooled to −100 °C again, and then heated to +100 °C for scan. The rates were 10 °C/min for heating and −30 °C/min for cooling. T_g and T_m were determined as onset temperature and endothermic maximum temperature, respectively.

Results and Discussion

Homopolymerization of CL and TMC. Sc(OAr)$_3$ has been first applied to initiate polymerizations of CL and TMC successfully. Table 1 summarizes the features of their homopolymerizations. The polymerization rates (especially in CL case) initiated by Sc(OAr)$_3$ are slower than those by La(OAr)$_3$.[9]

The polymerization activities of CL by Sc(OAr)$_3$ in different solvents decrease in the following sequence: toluene > CH_2Cl_2 ∼ THF ≫ nitrobenzene, as shown in Table 1. The fact of weaker polar solvent promoting polymerization indicates the polymerization takes place a coordination mechanism rather than an ionic mechanism. A sample of low molecular weight PCL terminated by 2-propanol has been prepared and subjected to ^{1}H NMR analysis as shown in Figure 1. One end of the PCL chain is the esterified isopropyl group −COO-CH(CH$_3$)$_2$ according to the signals at 5.0 ppm (multiplet, H^g in Scheme 2) for the CH group and 1.21−1.23 ppm (doublet, H^h) for CH_3 groups. Furthermore, the other chain end is $-CH_2OH$ according to its methylene protons signal at 3.63−3.66 ppm (triplet, H^e). On the contrary, no signal of an isopropyl ether end group is detected in the ^{1}H NMR spectra. All the facts prove that

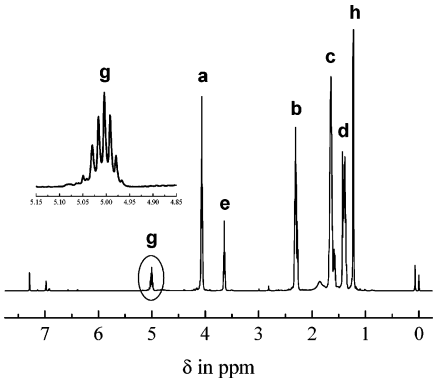


Figure 1. ^{1}H NMR spectrum of a poly(ϵ-caprolactone) sample terminated by 2-propanol.

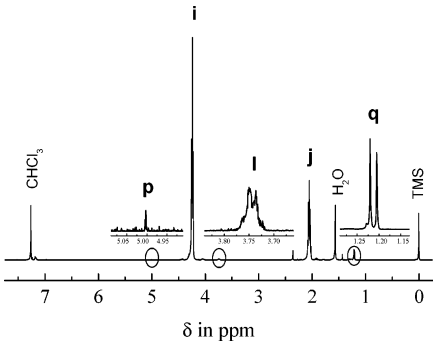
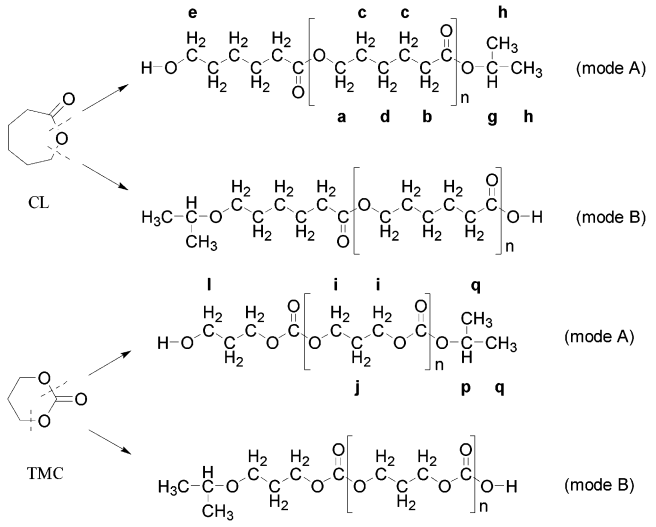


Figure 2. ^{1}H NMR spectrum of a poly(trimethylene carbonate) sample terminated by 2-propanol.

the CL monomer ring is opened via acyl−oxygen bond cleavage, as shown in Scheme 2, mode A.

The ^{1}H NMR spectrum of a similar 2-propanol-terminated poly(trimethylene carbonate) (PTMC) sample is shown in Figure 2. Multiplet peaks at 5.0 ppm for H^p, doublet at 1.20−1.22 ppm for H^q, and triplet at 3.72−3.80 ppm for H^l are detected, which also proves

Scheme 2. Ring-Opening Modes of CL and TMC: Mode A for Acyl−Oxygen Bond Cleavage and Mode B for Alkyl−Oxygen Bond Cleavage



acyl−oxygen bond cleavage of TMC (mode A in Scheme 2).

Copolymerization with Comonomer Feeding Simultaneously. Adding monomers simultaneously is a widely used method to synthesize random copolymers. A toluene solution (1.0 mol/L) of CL and TMC (50:50 molar ratio) was prepared and heated to 100 °C, in which $Sc(OAr)_3$ toluene solution (5×10^{-3} mol/L) was introduced by a syringe. After 8 h polymerization, copolymer with 80.1% yield was obtained. GPC measurement reveals that the copolymer has a number-average molecular weight (M_n) of 3.98×10^4 and monomodal distribution index of 1.98.

Figure 3 is the ^{1}H NMR spectrum of the copolymer and assignments of backbone signals detected, by which the molar ratio of CL units and TMC units in the copolymer is calculated to be 46.1:53.9. Four groups of peaks at 4.0−4.3 ppm indicate the four kinds of diad structures. High intensities of H^f and H^k provide an evidence for the direct bonding of CL with TMC. The average chain length of homo-PCL block and homo-PTMC block are calculated to be 2.4 and 2.5, respectively, by the intensities of H^a, H^f, H^k, and $H^{i+i'}$.

There are two insertion modes of TMC monomer into Sc−PCL active center as illustrated in Scheme 3. If the alkyl−oxygen bond cleavage of TMC occurred (mode B), the ether groups of $-CH_2OCH_2-$ would form in the copolymer chains. However, no signal of such group is detected in ^{1}H NMR spectra of all the copolymers synthesized. Thus, it can be concluded that $Sc(OAr)_3$ initiates an acyl−oxygen bond cleavage ring-opening polymerization of CL and TMC via the same coordination anionic mechanism as that of lanthanide compound.[10]

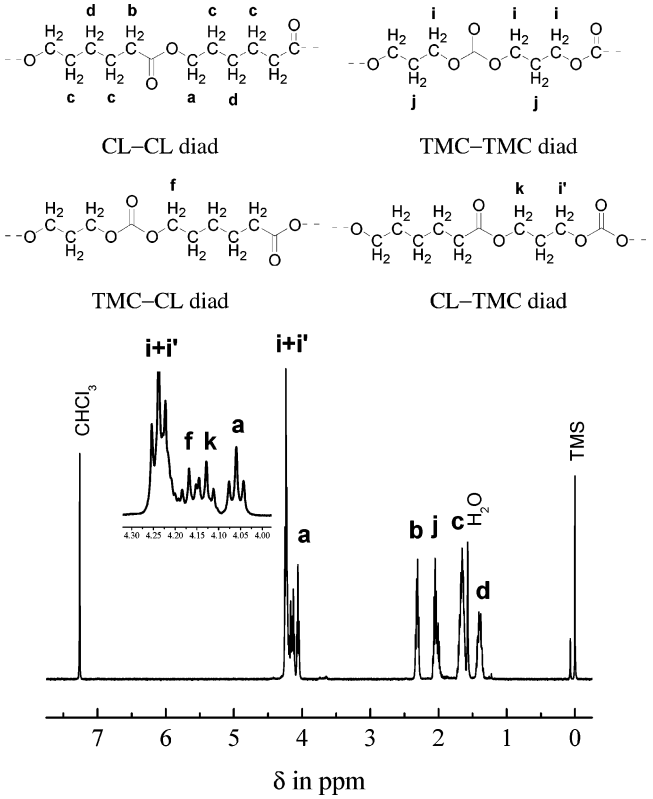
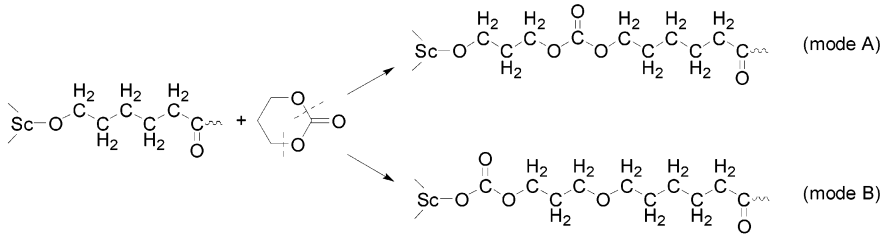


Figure 3. ^{1}H NMR spectrum of random copolymer of CL with TMC (X copolymer, run 1 in Table 3).

The copolymer structure can be further verified by DSC analysis. It is well-known that T_m of PCL depended on its molecular weight and crystallinity shifts in the range 50−66 °C. A T_m of 51.5 °C for homopolymer PCL and a T_g of −29.6 °C for homopolymer PTMC are detected, while for the copolymer no T_g or T_m is found in the scanning range. All the results imply that a highly random copolymer (denoted as X) has been prepared.

Concerning that the polymerization rate of TMC is a little faster than CL, another kind of simultaneous copolymerization has performed at 100 °C with the monomer feeding ratio of 70:30 (CL:TMC, molar ratio). TMC and CL gave random copolymer block at the first stage of polymerization. After all the TMC monomers had inserted into copolymer chains, the remained CL develops a homo-PCL block (denoted as B). Thus, an XB copolymer was obtained (yield = 77.1%, X block ≈ 50%) as shown in Table 2 run 1. Calculated from the intensities of $H^{i+i'}$, H^k, H^f, and H^a in the ^{1}H NMR spectrum (Figure 4), the percentages of diad structures of TMC−TMC, CL−CL, and TMC−CL, CL−TMC are 6.3%, 59.8%, and 33.9%, respectively. In addition, the average length of TMC in X block is 1.18, which means most of TMC units neighbor CL units. Its DSC curve

Scheme 3. Possible Active Centers in the Growing Copolymer Chains with Different TMC Ring-Opening Modes



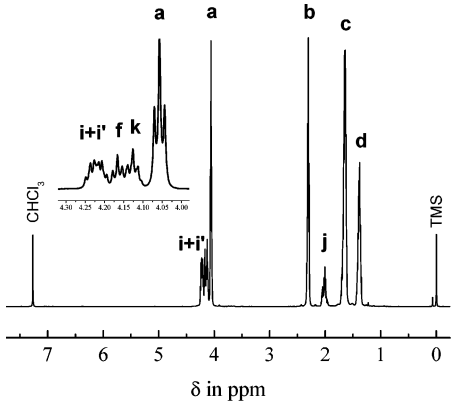


Figure 4. ^{1}H NMR spectrum of XB copolymer (run 1 in Table 3).

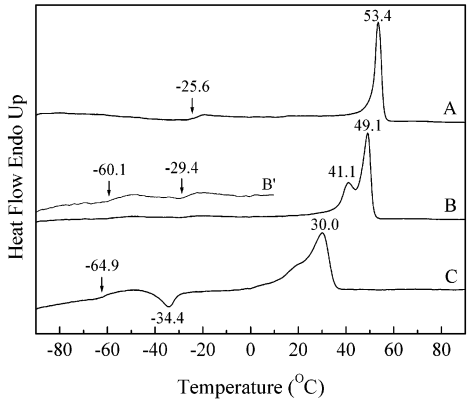


Figure 5. DSC curves of polymer blend of poly(ϵ-caprolactone) and poly(trimethylene carbonate) (curve A, PCL:PTMC = 50:50 molar ratio), AXB copolymer (curves B and B′, run 7 in Table 2), and XB copolymer (curve C, run 1 in Table 2).

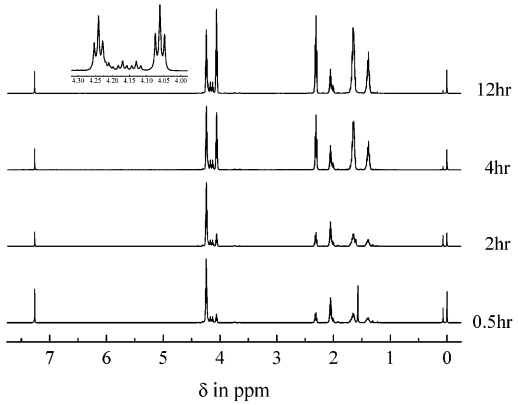


Figure 6. ^{1}H NMR spectra of AXB copolymers terminated at different polymerization times (runs 2, 4, 6, and 7 in Table 2).

in Figure 5C shows a T_g of −64.9 °C and a T_m of 30.0 °C for the existing PCL block.

Data in Table 1 indicate that TMC exhibits a much higher activity in toluene than CL at 0 °C. Therefore, TMC and CL copolymerization (CL:TMC = 70:30 molar ratio) were carried out at 0 °C with simultaneous comonomer feeding to prepare AXB copolymer. The results at various polymerization times are listed in Table 2, and their ^{1}H NMR spectra and GPC curves are shown in Figures 6 and 7, respectively. The content of CL−CL diad as well as the yields and the molecular weights of copolymers increases with prolonging polymerization time. During the reaction period, TMC polymerized first within a very short time forming a PTMC-rich block (denoted as A) into which a few CL monomers might insert. When the concentration of TMC decreased to a lower level, CL began to compete with TMC monomer inserting into the active chain and produced a random X block. At last, only CL monomer remained, and then a homo-PCL block (denoted as B) was developed. Thus, an AXB copolymer could be prepared in which X block was about 20% calculated from ^{1}H NMR. This chain structure was confirmed by the DSC results (Figure 5B): a T_g of −29.4 °C for PTMC block coexists with a T_g of −60.1 °C and both two T_ms of 41.1 and 49.1 °C for PCL block. The fact that the values of two T_ms in AXB copolymer are higher than those in XB copolymer confirms the better crystallization of PCL block due to less influence of the shorter X block.

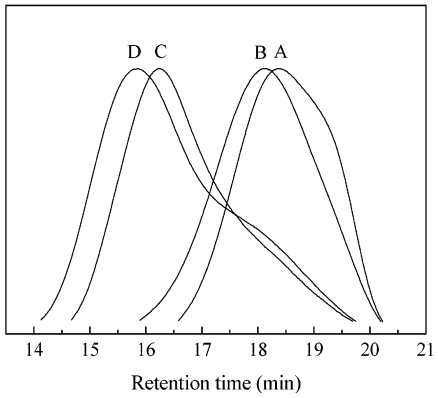


Figure 7. GPC measurements of AXB copolymers terminated at different polymerization times: 1 h (curve A, run 3 in Table 2), 2 h (curve B, run 4 in Table 2), 4 h (curve C, run 6 in Table 2), and 12 h (curve D, run 7 in Table 2).

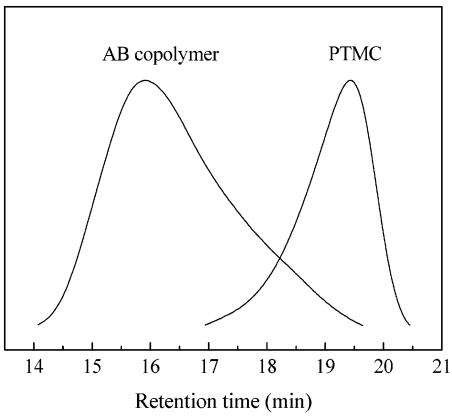


Figure 8. GPC measurements of PTMC (M_n = 0.50 × 10^4, M_w/M_n = 1.24, see Experimental Section) and poly(TMC-*b*-CL) (AB copolymer, M_n = 2.95 × 10^4, M_w/M_n = 1.87, run 4 in Table 3).

Copolymerization with Comonomer Feeding Sequentially. Sequential copolymerization of TMC with CL was carried out by adding CL monomer (CL:TMC = 70:30 molar ratio) into a prepolymerized PTMC ([TMC] = 0.3 mol/L, [Sc(OAr)$_3$] = 5 × 10^{-3} mol/L, toluene, 0 °C, 1 h) and then polymerizing 23 h. A diblock copolymer of poly(TMC-*b*-CL) (yield = 62.5%) was obtained and denoted as AB copolymer. Its structure was verified by the GPC curves of PTMC (before CL added) and AB copolymer as shown in Figure 8. The molecular weight increases, retaining a narrow monomodal distribution, which indicates that the CL monomer has grown onto the PTMC living chain. Moreover, Figure 9 illustrates the ^{1}H NMR spectrum of AB

Table 3. Thermal Properties of Various Poly(CL-*co*-TMC)s[a] (A: TMC Block; B: CL Block; X: Random Block)

run	polymer chain structure	temp (°C)	feeding ratio (CL:TMC)	feeding sequence	$T_{g,CL}$ (°C)	$T_{g,TMC}$ (°C)	T_m (°C)
1	X[b]	100	50:50	simultaneous feeding	not found	not found	not found
2	XB[c]	100	70:30	simultaneous feeding	−64.9	not found	30.0
3	AXB[d]	0	70:30	simultaneous feeding	−60.1	−29.4	41.1, 49.1
4	AB[e]	0	70:30	TMC first, then CL	not found	−27.5	53.1
5	BAXB[f]	0	70:30	CL first, then TMC	not found	−22.2	52.4, 55.6

[a] Polymerization conditions: toluene as solvent, [CL + TMC] = 1.0 mol/L, $[Sc(OAr)_3] = 5 \times 10^{-3}$ mol/L. [b] 8 h. [c] Run 1 in Table 2. [d] Run 7 in Table 2. [e] [TMC] = 0.3 mol/L, 1 h for TMC polymerization and then another 23 h polymerization after CL added. [f] [CL] = 0.7 mol/L, 6 h for CL polymerization and then another 18 h polymerization after TMC added.

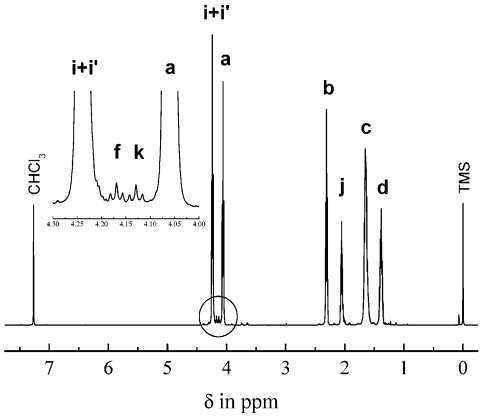


Figure 9. ^{1}H NMR spectrum of AB copolymer (run 4 in Table 3).

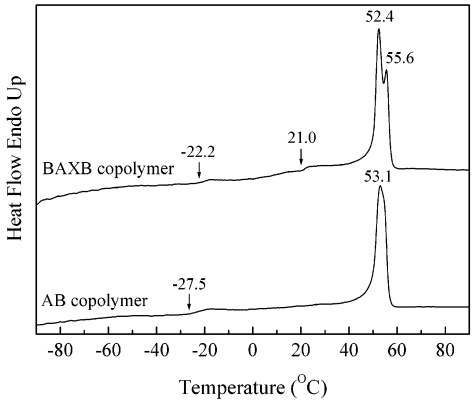


Figure 10. DSC curves of AB (run 4 in Table 3) and BAXB copolymer (run 5 in Table 3).

copolymer by which the molar ratio of CL:TMC is calculated as 62.1:37.9. Very weak signals of H^k and H^f are detected, proving the direct linkage of TMC with CL unit. The DSC curve of AB copolymer is shown in Figure 10 as another structural proof. Both TMC and CL blocks show their characteristic thermal behaviors: a T_g of −27.5 °C for TMC block and a T_m of 53.1 °C for CL block.

BAXB copolymer of CL with TMC was prepared by another monomer adding sequence. Toluene solution of CL and $Sc(OAr)_3$ ([CL] = 0.7 mol/L, $[Sc(OAr)_3] = 5 \times 10^{-3}$ mol/L) was mixed at 0 °C and polymerized for 6 h. The conversion of CL monomer was 25.6%. Then, a high concentrated toluene solution of TMC monomer (CL:TMC = 70:30, molar ratio) was added by a syringe. After another 18 h polymerization, the copolymer of CL with TMC yielded 55.2%. Figure 11 illustrates GPC curves of the products terminated and isolated at 6 h (PCL homopolymer), 7 h (1 h after TMC added), and 24 h (BAXB copolymer). As the polymerization time prolonged, the molecular weight increased. The DSC curve of BAXB copolymer (Figure 10) shows two T_m peaks at 52.4 and 55.6 °C, which may be caused by two PCL blocks with different chain lengths.

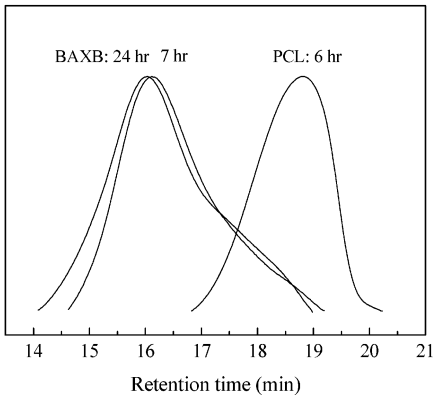


Figure 11. GPC measurements of poly(ϵ-caprolactone) ([CL] = 0.7 mol/L, $[Sc(OAr)_3] = 5 \times 10^{-3}$ mol/L, toluene, 0 °C, 6 h: $M_n = 0.74 \times 10^4$, $M_w/M_n = 1.22$) and BAXB copolymers (7 h: $M_n = 3.10 \times 10^4$, $M_w/M_n = 1.55$; 24 h: $M_n = 3.36 \times 10^4$, $M_w/M_n = 1.68$, run 5 in Table 3).

Conclusions

A novel highly effective initiator scandium tris(2,6-di-*tert*-butyl-4-methylphenolate) has been developed for the copolymerization of CL and TMC at 0 and 100 °C. The copolymers with different chain structures of X, XB, AXB, AB, and BAXB are prepared by controlling polymerization temperature, monomer feeding ratio, and feeding order. Table 3 summarizes their thermal properties and synthetic methods. This paper presents both a concept and an example to prepare certain structure copolymers by controlling polymerization conditions.

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