Ring-Opening Copolymerization of Ethylene Carbonate and ε-Caprolactone Catalyzed by Neodymium tris(2,6-di-*tert*-butyl-4-methylphenolate): Synthesis, Characterization, and Dynamic Mechanic Analysis

FENG CHEN, WEIPU ZHU, NING XU, ZHIQUAN SHEN

Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

ABSTRACT: The ring-opening copolymerization of ethylene carbonate (EC) with ε-caprolactone (CL) was carried out using neodymium tris(2,6-di-*tert*-butyl-4-methylphenolate) as a single-component catalyst. Copolymers containing up to 22.0% EC contents with high molecular weights (up to 23.97×10^4) and moderate molecular weight distributions (between 1.66 and 2.03) were synthesized at room temperature. Compared with homopoly(ε-caprolactone), the copolymers with EC units exhibited increased glass transition temperatures (-35.6 °C), reduced melting temperatures (44.5 °C), and greatly enhanced elongation percentage at break (2383%) based on dynamic mechanic analysis. The crystallinities of the copolymers decreased with the increasing EC molar percentage in the products. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 4050–4055, 2008

Keywords: ε-caprolactone; copolymerization; dynamic mechanic analysis; ethylene carbonate; neodymium catalyst; polyesters; ring-opening polymerization; tensile strength

INTRODUCTION

Aliphatic polyesters and aliphatic polycarbonates are important as biodegradable and biocompatible materials in the fields of medicine, pharmacy, and agriculture. Recent researches focus on the ring-opening polymerization (ROP) for their syntheses.[1–6] Although a wide variety of cyclic carbonates and esters have been successfully polymerized by ROP, those five-membered cyclic carbonates such as ethylene carbonate (EC) have proven more difficult to undergoing ROP at room temperature due to a positive enthalpy of homopolymerization.[7–9] The homopolymerization of EC only takes place at high temperature, and the product is mainly polyether instead of polycarbonate as a result of the removal of CO_2.[10–16] The copolymerization of EC with ε-caprolactone (CL) without the removal of CO_2 was first reported by Evans et al.[17] using Sm(II) compounds as initiators. Other analogous works were reported thereafter.[18,19]

Our group has developed effective lanthanide complexes for homo- and copolymerization of CL, lactides, and six-membered cyclic carbonates.[20–24] In this article, we report the neodymium tris (2,6-di-*tert*-butyl-4-methylphenolate) (Nd(DBMP)₃) as a catalyst for the synthesis of copolymers of EC with CL at room temperature. The thermal

Correspondence to: W. Zhu (E-mail: carrols@163.com) or Z. Shen (E-mail: zhiquan_shen@163.com)

and mechanic properties of the copolymers are first reported using dynamic mechanic analysis (DMA). The crystallinity and tensile strength were measured in details.

EXPERIMENTAL

Materials

CL (Acros, 99%) was distilled under reduced pressure before use. EC (Sinopec, 99%) was re-crystallized before use. Nd(DBMP)$_3$ was synthesized as described in our previous work.[22] Toluene were freshly distilled from sodium benzophenone before use.

Copolymerization

All copolymerizations were carried out in previously flamed and argon-purged 20 mL ampoules. As a typical procedure, a mixture of 0.264 g EC (3.0 mmol) and 0.798 g CL (7.0 mmol) in 8.6 mL toluene was injected into an ampoule and kept at room temperature (25 °C). Then the catalyst solution (0.02 mmol in 0.21 mL toluene) was added using a syringe. The polymerization was terminated after 6 h. The contents were dissolved in THF and precipitated from cold ethanol containing 5 wt % HCl, dried *in vacuo* at room temperature overnight, and weighed (0.847 g, 78.6% yield).

Measurements

^{1}H NMR spectra were recorded on a Bruker Avance DMX 500 MHz spectrometer in CDCl$_3$

with tetramethylsilane (TMS) as internal standard. Size exclusion chromatography (SEC) measurements were performed on a Waters 208 apparatus equipped with Waters 2410 RI detector in THF (1.5 mL/min) at 30.0 °C and calibrated to commercial polystyrene standards.

Sheets of the samples ($30 \times 12 \times 2$ mm) were used for the DMA by dynamic mechanical analyzer NETZSCH DMA 242, using single cantilever flexural geometry. A typical frequency of 6.28 rad/s (1 Hz) and a scanning rate of 3 °C/min from −150 to 100 °C were chosen. T_m was determined as onset and maximum of a tan δ curve. T_g was defined by the maximum of a E'' curve or a tan δ curve.

The crystallinity of the copolymer films ($10 \times 10 \times 0.2$ mm) was examined on a DMAX-RA X-ray diffractometer with 12 kW Cu Kα radiation ($\lambda = 1.5406$ Å).

Tensile strength tests were carried out on a universal testing machine (Reger RGT-X010, Shenzhen, China) at 25 °C with a rate of 100 mm/min, according to ASTM D638-02. Every sample was examined thrice.

RESULTS AND DISCUSSION

Random Copolymerization of CL and EC

Random copolymerization of CL and EC has been carried out by Nd(DBMP)$_3$ successfully. Table 1 summarizes the results of their copolymerizations. EC was found to be nonhomopolymeriz-

Table 1. Copolymerization of EC with CL Catalyzed by Nd(DBMP)$_3$ at Room Temperature (25 °C)[a]

Entry	EC:CL (molar ratio)	Yield (%)	$M_n{}^{b} \times 10^{-4}$	$M_w/M_n{}^{b}$	Polymer composition EC content (mol %)[c]
1	00:100	95.3	25.48	2.12	0.0
2	5:95	98.1	23.97	2.03	4.5
3	10:90	95.0	22.33	1.97	9.2
4	15:85	94.6	17.01	1.97	13.8
5	20:80	93.4	16.32	2.03	15.1
6	25:75	89.6	15.99	1.86	18.6
7	30:70	78.6	15.97	1.81	21.0
8	35:75	73.4	14.47	1.84	22.0
9	40:60	67.2	15.74	1.88	22.0
10	50:50	63.5	14.45	1.66	22.0
11	100:0	0.0	–	–	–

[a] Polymerization conditions: [CL] + [EC] = 1.0 mol/L, [Nd(DBMP)$_3$] = 2.0 × 10^{-3} mol/L in toluene, reaction 6 h.
[b] Measured by SEC.
[c] Calculated from ^{1}H NMR based on eq 1.

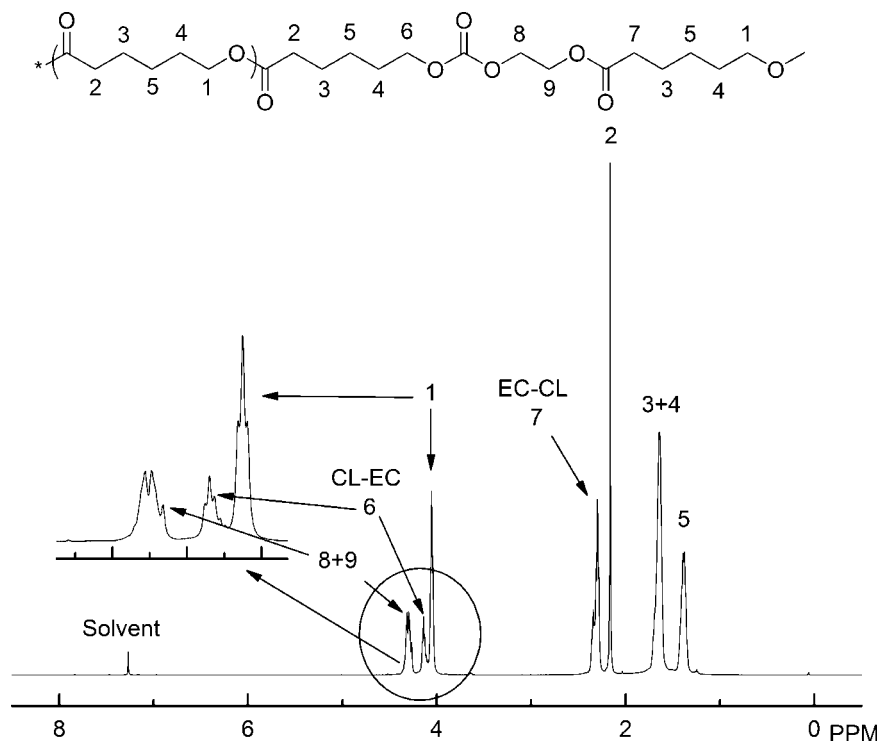**Figure 1.** ^{1}H NMR spectrum of the EC-CL random copolymer (Table 1, entry 8).

able. Nd(DBMP)$_3$ exhibits high activity of preparing copolymers with high yields and molecular weights. The data shows that the yield of copolymer could reach 90% within 6 h at the comonomers feeding molar ratio 20:80 (EC: CL) (Table 1, entry 5). The yield decreases when increasing the feeding molar ratio of EC. Figure 1 shows a typical ^{1}H NMR spectrum of random copolymer (Table 1, entry 8) and the assignments of backbone detected. The content of EC unit in the copolymer is calculated to be 22.0 mol % based on eq 1.

$$\text{EC (mol \%)} = \frac{I(\text{H}^{8+9})}{I(\text{H}^{8+9}) + I(\text{H}^{1+6}) \times 2} \times 100\%.$$

(1)

High intensity of signal H^7 provides an evidence for the directly linkage of CL and EC. The absence of signals between 3.10 and 3.30 ppm clearly indicates the absence of ether units, which are generally formed as defects by decarboxylation of EC. The results agree with the report.[19]

Rather, high molecular weight copolymers with moderate polydispersity, unimodal SEC curves, and rubbery nature was obtained (M_n = 14.45–23.97 × 10^4, M_w/M_n = 1.66–2.03). Single peak of SEC curve reveals that there was only one kind of active species during the copolymerization, and the products were copolymers rather than the blends of homopolymers.

Dynamic Mechanical Analysis

The copolymers are further verified by DMA technology. It is well known that T_m of PCL depends on the chain length ranging in 50–66 °C. Table 2 summarizes the thermal properties of PCL and the copolymers. A T_m of 44.5 °C and a T_g of −35.6 °C of the copolymer with EC content of 22.0 mol % (Table 1, entry 8) were detected, differing from those of homo-PCL (Table 1, entry 1). It is notable that there were a T_m of 62.7 °C and a T_g of −41.2 °C for the sample with low EC content (13.8 mol %). A β-relaxation at −90.0 °C was detected (Table 2, entry 3) generally ascribed to in-chain motions in the amorphous region of PCL. It is suggested that long PCL homo segments could be included in the copolymers with low EC content, reflected by the β-relaxation value and the length of PCL segment.[25]

Table 2. Thermal Properties of Various Copolymers Determined by DMA

Sample	EC content (mol %)	β-Relaxation (°C)[a]	α-Relaxation or T_g (°C)		T_m (°C)[a]
			From E''[b]	From tan δ[a]	
Entry 1, Table 1	0.0	−91.2	−51.5	−44.8	65.1
Entry 2, Table 1	4.5	−90.7	−49.2	−42.5	63.5
Entry 3, Table 1	9.2	−90.0	−47.4	−41.2	62.1
Entry 4, Table 1	13.8	−88.5	−45.1	−38.8	57.0
Entry 6, Table 1	18.6	−87.3	−46.5	−37.1	51.9
Entry 8, Table 1	22.0	−85.4	−42.1	−35.6	44.5

[a] Determined by tan δ curves.
[b] Determined by E'' curves.

The tan δ and E'' curves of DMA for pure PCL and the copolymers are presented in Figures 2 and 3, respectively. The β-relaxation and α-relaxation processes (T_g) moved to higher temperature positions while T_m to lower temperature position, when EC content in copolymer increased. Generally, T_g defined by the maximum of the E'' curve is lower than that defined by the tan δ curve. It is observed that there was only one T_g or T_m detected and no evidence for T_g or T_m of independent PCL segment.

The storage modulus (E') curves are shown in Figure 4. The copolymer with 4.5 mol % EC content has the highest storage modulus about 2.1 $\times$ 10³ MPa. But the storage modulus of the copolymer with 22.0 mol % EC content descends to a minimum about 1.1 $\times$ 10³ MPa. The moduli of copolymers range from 3.0 MPa (22.0 mol % EC content) to 20.0 MPa (4.5 mol % EC content) at 37.0 °C. PCL material has maximum modulus about 23 MPa at 37.0 °C. The property of variable modulus shows potential application in the field of medical materials. Visible rubbery plateau and gradual reduction of modulus are obviously seen.

Crystallinity Examination

XRD results of copolymers with different EC contents are shown in Figure 5. With the increasing of EC content, the intensity of each main diffraction peak of PCL decreases indicating that the copolymers have lower crystallinity than PCL.
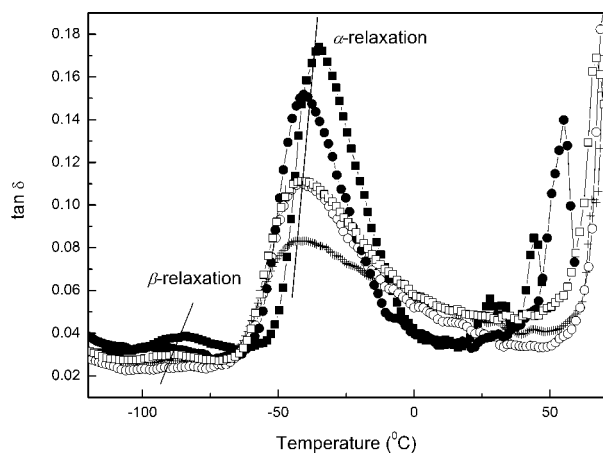

Figure 2. Tan δ of neat PCL and copolymers of different EC content: (+) neat PCL, entry 1 in Table 1; (○) copolymer with 4.5 mol % EC content, entry 2 in Table 1; (□) copolymer with 9.2 mol % EC content, entry 3 in Table 1; (●) copolymer with 15.1 mol % EC content, entry 5 in Table 1; (■) copolymer with 22.0 mol % EC content, entry 8 in Table 1.
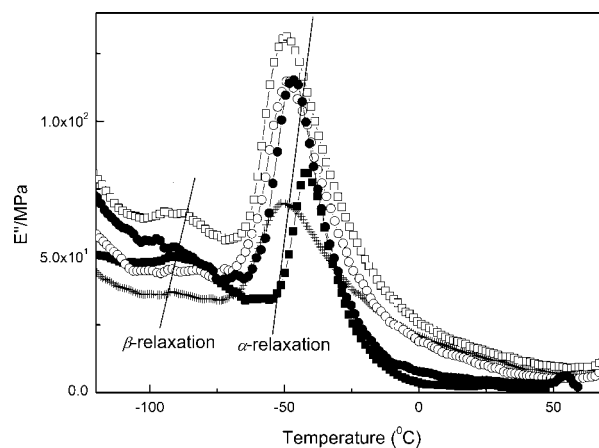

Figure 3. E'' of neat PCL and copolymers of different EC content: (+) neat PCL, entry 1 in Table 1; (○) copolymer with 4.5 mol % EC content, entry 2 in Table 1; (□) copolymer with 9.2 mol % EC content, entry 3 in Table 1; (●) copolymer with 15.1 mol % EC content, entry 5 in Table 1; (■) copolymer with 22.0 mol % EC content, entry 8 in Table 1.
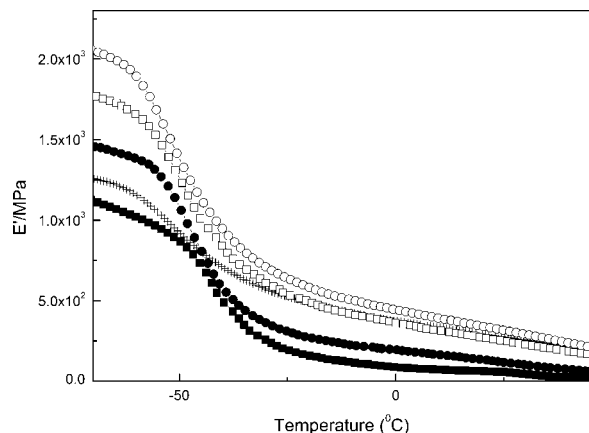
Figure 4. E' of neat PCL and copolymers of different EC content: (+) neat PCL, entry 1 in Table 1; (○) copolymer with 4.5 mol % EC content, entry 2 in Table 1; (□) copolymer with 9.2 mol % EC content, entry 3 in Table 1; (●) copolymer with 15.1 mol % EC content, entry 5 in Table 1; (■) copolymer with 22.0 mol % EC content, entry 8 in Table 1.

Tensile Strength Properties

The tensile strength properties of PCL and the copolymers were examined at 25 °C, and the results are illustrated in Table 3. PCL shows higher tensile strength and modulus. The Young's modulus of copolymers reduced from 47.0 to 3.1 MPa with the increasing EC content (4.5–22.0 mol %). However, the elongation at break was greatly enhanced from 560 to 2383%, compared with that of 165% for PCL. It suggests that the EC content in the copolymer has significant influence on the mechanical properties of the copolymer.

CONCLUSIONS

Nd(DBMP)$_3$ is an effective catalyst for CL and EC copolymerization at room temperature (25 °C). Random copolymers with high molecular weight and moderate molecular weight distributions ($M_n = 14.45 \sim 23.97 \times 10^4$, $M_w/M_n = 1.66 \sim 2.03$) could be prepared. The copolymer has the maximum EC content of 22.0 mol %. DMA provides direct examinations for defining the thermal and mechanical properties of the copolymers. The crystallinity and tensile strength of the copolymers were also examined.
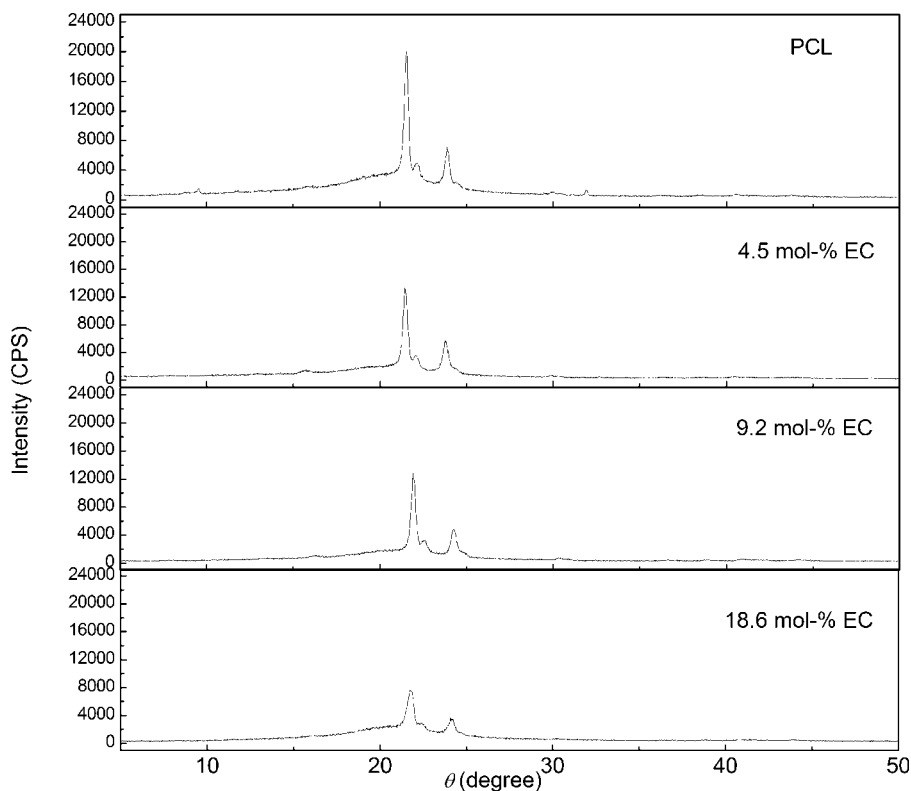

Figure 5. XRD curves of the copolymers.

Table 3. Tensile Properties of PCL and the Copolymers

Sample	EC content (mol %)	Tensile strength (MPa)	Young's modulus (MPa)	Yield strength (MPa)	Elongation at break (%)
Entry 1, Table 1	0.0	23.0 ± 0.5	57.1	23.3 ± 1.2	165
Entry 2, Table 1	4.5	20.6 ± 1.2	47.0	20.4 ± 2.2	560
Entry 3, Table 1	9.2	20.5 ± 2.1	38.7	20.6 ± 1.7	705
Entry 4, Table 1	13.8	16.2 ± 1.6	27.0	16.6 ± 0.8	944
Entry 5, Table 1	15.1	14.3 ± 1.0	22.3	12.6 ± 1.4	1140
Entry 6, Table 1	17.6	11.7 ± 2.1	18.1	11.6 ± 1.1	1552
Entry 7, Table 1	21.0	8.9 ± 2.5	11.7	8.6 ± 2.3	2197
Entry 8, Table 1	22.0	3.5 ± 1.3	3.1	3.4 ± 0.7	2383

REFERENCES AND NOTES

1. Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. Chem Rev 2007, 8, 153–180.
2. Xu, X.; Yao, Y.; Hu, M.; Shen, Q. J Polym Sci Part A: Polym Chem 2006, 44, 4409–4419.
3. Mata-Mata, J. L.; Gutiérrez, J. A.; Paz-Sandoval, M. A.; Madrigal, A. R.; Martínez-Richa A. J Polym Sci Part A: Polym Chem 2006, 44, 6926–6942.
4. Sheng, H.; Zhou, L.; Zhang, Y.; Yao, Y.; Shen, Q. J Polym Sci Part A: Polym Chem 2007, 45, 1210–1218.
5. Kostakis, K.; Mourmouris, S.; Karanikolopoulos, G.; Pitsikalis, M.; Hadjichristidis, N. J Polym Sci Part A: Polym Chem 2007, 45, 3524–3537.
6. Guillaume, S. M.; Schappacher, M.; Scott, N. M.; Kempe, R. J Polym Sci Part A: Polym Chem 2007, 45, 3611–3619.
7. Kuran, W. Prog Polym Sci 1998, 23, 919–992.
8. Rokicki, G. Prog Polym Sci 2000, 25, 259–342.
9. Ochiai, B.; Endo, T. Prog Polym Sci 2005, 30, 183–215.
10. Vogdanis, L.; Martens, B.; Uchtmann, H.; Hensel, F.; Heitz, W. Makromol Chem 1990, 191, 465–472.
11. Storey, R. F.; Hoffman, D. C. Macromolecules 1992, 25, 5369–5382.
12. Soós, L.; Deák, G. Y.; Kéki, S.; Zsuga, M. J Polym Sci Part A: Polym Chem 1999, 37, 545–550.
13. Lee, J. C. Macromolecules 2000, 33, 1618–1627.
14. Kadokawa, J.; Iwasaki, Y.; Tagaya, H. Macromol Rapid Commun 2002, 23, 757–760.
15. Poplewska, I.; Weglowska, E.; Lubczak, J. J Appl Polym Sci 2004, 91, 2750–2755.
16. Elmér, A. M.; Jannasch, P. J. Polym Sci Part A: Polym Chem 2006, 44, 2195–2205.
17. Evans, W. J.; Katsumata, H. Macromolecules 1994, 27, 4011–4013.
18. Shirahama, H.; Kanetani, A.; Yasuda, H. Polym J 2000, 32, 280–286.
19. Agarwal, S.; Naumann, N.; Xie, X. Macromolecules 2002, 35, 7713–7717.
20. Ling, J.; Shen, Z.; Huang, Q. Macromolecules 2001, 34, 7613–7616.
21. Zhu, G.; Ling, J.; Shen, Z. Polymer 2003, 44, 5827–5832.
22. Ling, J.; Shen, Z.; Zhu, W. J Polym Sci Part A: Polym Chem 2003, 41, 1390–1399.
23. Ling, J.; Zhu, W.; Shen, Z. Macromolecules 2004, 37, 758–763.
24. Zhu, W.; Ling, J.; Xu, H.; Shen, Z. Polymer 2005, 46, 8379–8385.
25. Ishida, H.; Lee, Y. J Polym Sci Part B: Polym Phys 2001, 39, 736–749.