THERMAL AND CRYSTALLINE PROPERTIES OF RANDOM COPOLYMER OF CL AND DTC PREPARED BY La(OAr)$_3$

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Abstract

Thermal and crystalline properties of random copolymer of ε-caprolactone (CL) and 2,2-dimethyl trimethylene carbonate (DTC) prepared by lanthanum tris(2,6-di-*tert*-butyl-4-methyl-phenolate) (La(OAr)$_3$) have been investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and wide-angle X-ray diffraction (WAXD). Fox equation interprets the relationship between glass transition temperature (T_g) and copolymer compositions. T_g decreases from PDTC (16.7°C) to PCL (–65.1°C), reflecting the internal plasticizing effect of CL units on DTC units in the copolymers. The introduction of CL units to PDTC can effectively improve its heat resistance. Small amount of DTC (5% molar) in PCL chain improves the mechanical properties of the polymer, which had elongation of 1000, much higher than that of PCL (8.8).

Introduction

Aliphatic polyesters are of great interest for their excellent biodegradability, bio-compatibility, permeability and low toxicity, and have been widely used in medical field or as environment friendly materials. Many of them can be synthesized by ring-opening polymerization (ROP) of lactones, lactides, or cyclic carbonates, for which various effective catalyst systems have been developed [1–4] and thermal analyses reported [5–7]. Compared with other metal catalyst systems, rare earth metal compounds show unprecedented activities in ROP under mild conditions, and can control the polymerization process quite well. In our previous works, it has been reported that lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) (La(OAr)$_3$) alone effectively initiate polymerization of ε-caprolactone (CL) and random copolymerization of CL with 2,2-dimethyltrimethylene carbonate (DTC) [8, 9]. In this paper, the

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relationship between the microstructure and thermal and crystalline properties, as well as mechanical behavior of these polymers has been reported.

Experimental section

The polymerizations and characterizations (GPC and NMR) of the homo- and copolymers of CL with DTC initiated by La(OAr)$_3$ are described in [8]. Differential scanning calorimetry (DSC) measurements were performed with a Perkin Elmer Pyris 1 apparatus. Each sample was heated from –100 to 150°C (first heating scan), cooled immediately to –100°C and heated again to 150°C (second heating scan). The heating rate is 10°C min^{-1}. The samples for TG analysis were carried out with a Perkin Elmer Pyris 6 thermogravimetric analyzer in the temperature range of 50–450°C at a 10°C min^{-1} rate under a nitrogen flow. WAXD was performed at room temperature using D/max-ra diffractometer operated at 40 kV and 40 mA with graphite crystal filter, CuK$_{\alpha 1}$ radiation (λ=1.54056 Å). The specimens were fixed on the equipment, and the data were collected with every 0.02°. Tensile strength of the polymer specimens prepared from toluene solution casting was measured at room temperature with an Instron 1121 machine at a speed of 100 mm min^{-1}. Each specimen had a gauge length of 20 mm, and a gauge width of 3 mm with variable thickness (0.25–0.35 mm). The value reported is an average of three specimens. The Young's modulus was obtained from the tangent of the initial slope of stress *vs*. strain curve.

Results and discussion

The glass transition temperatures (T_g), melting temperatures (T_m) and initial decomposition temperatures (T_{di}) of the random copolymers of CL with DTC obtained by DSC and TG were summarized in Table 1. Homopolymer PCL has a T_g of –65.1°C, a T_{di} of 392.9°C and a T_m of 65.1°C, whereas PDTC has a T_g of 16.7°C, a T_{di} of 249.2°C and two T_ms of 89.8 and 121.5°C corresponding two different crystal forms [10]. The T_gs of the copolymers are lowering from PDTC to PCL, and they can be predicted by Fox equation (Eq. (1)) quite well.

$$\frac{1}{T_g} = \frac{W_{PCL}}{T_{g,PCL}} + \frac{W_{PDTC}}{T_{g,PDTC}} \tag{1}$$

where W_{PCL} and W_{PDTC} are the mass fraction of the two monomer unit in the copolymers. This phenomenon might indicate that CL units have internal plasticizing effect on PDTC. The values of T_{di} rise from 249.2°C of PDTC to 392.9°C of PCL with increasing CL content in the copolymers, showing that the introduction of CL units into PDTC can effectively improve the heat resistance of the polymer.

We have tried to use Flory equation (Eq. (2)) [11] to elucidate the relationship between T_m of copolymers with their composition.

$$\frac{1}{T_m} = \frac{1}{T_m^0} - \ln X_A \frac{R}{\Delta H_m} \tag{2}$$

Table 1 The thermal properties of random copolymers

CL:DTC[a]	$M_n \cdot 10^{-3}$	M_w/M_n	$T_g/°C$	$T_{gF}/°C$[b]	$T_{di}/°C$	$T_m/°C$	$T_{mF}/°C$[c]	$\Delta H_m/J\ g^{-1}$
100:0	35	1.87	−65.1	–	392.9	65.1	–	87.8
95:5	46	1.98	−58.6	−61.7	389.5	60.6	60.3	68.3
91:9	54	1.88	−54.0	−59.0	333.4	59.4	56.4	56.6
82:18	58	2.23	−57.1	−52.6	318.5	55.9	47.2	49.5
50:50	40	1.65	−32.8	−28.3	309.5	36.3/79	10	5.2/18.1
38:62	31	1.59	−24.2	−18.3	309.9	79.0	−7.2	25.1
19:81	22	1.56	−5.9	−1.5	269.3	96.1	−42.5	36.7
0:100	19	1.90	16.7	–	249.2	121.5/89.8	–	21.1/17.7

[a]Molar ratio in the copolymer calculated by ^{1}H NMR spectrum
[b]glass transition temperatures come from Fox equation
[c]Melting temperatures come from Flory equation.

where T_m and T_m^0 are the equilibrium melting temperatures of copolymer and homopolymer, ΔH_m is the heat of fusion of each molar repeat unit, X_A is the molar fraction of crystallizable A units, and R is the gas constant. PCL is used as crystallizable unit (X_A) to calculate the T_m values of copolymers listed in Table 1. Data shown indicated that only 5% DTC copolymer's T_m calculated from Flory equation is equal to the experimental value. The reason might be related to the crystallinity of the polymers.

Figure 1 illustrates the crystallization patterns of the copolymers by WAXD. PCL homopolymer exhibits the main Bragg peaks at 21.5 and 24°, whereas PDTC homopolymer has peaks at 17 and 21°. While DTC content is lower than 18%, the reflection patterns belong to PCL crystallization pattern. But when DTC content is higher than that of CL, crystallinity of copolymers becomes small due to the disruption of two crystallization patterns. Copolymer with less CL content (<20%) reveals PDTC crystallization patterns.
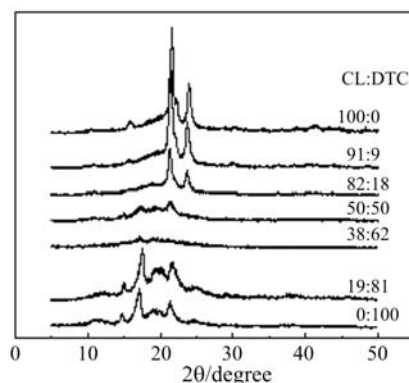

Fig. 1 WAXD of copolymers of CL and DTC with different compositions

To improve PCL's property, copolymers have been explored. Table 2 lists the mechanical properties of two copolymers with low DTC content and PCL. The data show that copolymer with 5% DTC has much higher value of elongation at maximum stress and break than PCL. But when DTC content is up to 18%, the copolymer becomes brittle.

Table 2 Mechanical properties of PCL and P(CL-ran DTC)

CL:DTC	σ/MPa	ε_{t1}/%	ε_{t2}/%	E_t/MPa
100:0	20.1	8.8	9.70	520
95:5	21.7	1.003	1037	280
91:9	8.66	250	430	161
82:18	–		brittle	

σ – Maximum tensile stress, ε_{t1} – Elongation at maximum stress, ε_{t2} – Elongation at break, E_t – Young's modulus

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