

BIODEGRADABLE ALIPHATIC/AROMATIC COPOLYESTERS BASED ON TEREPHTHALIC ACID AND POLY(L-LACTIC ACID): SYNTHESIS, CHARACTERIZATION AND HYDROLYTIC DEGRADATION*

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Abstract Biodegradable aliphatic/aromatic copolyesters, poly(butylene terephthalate-co-lactate) (PBTL) were prepared *via* direct melt polycondensation of terephthalic acid (TPA), 1,4-butanediol (BDO) and poly(L-lactic acid) oligomer (OLLA). The effects of polymerization time and temperature, as well as aliphatic/aromatic moiety ratio on the physical and thermal properties were investigated. The largest molecular weight of the copolyesters was up to 64100 with molecular weight distribution index of 2.09 when the polycondensation was carried out at 230°C for 6 h. DSC, XRD, DMA and TGA analysis clearly indicated that the degree of crystallinity, glass-transition temperature, melting point, decomposition temperature, tensile strength, elongation and Young's modulus were influenced by the ratio between TPA and OLLA in the final copolyesters. Hydrolytic degradation results demonstrated that the incorporation of biodegradable lactate moieties into the aromatic polyester could efficiently improve hydrolytic degradability of the copolymer even though it still had many aromatic units in the main chains.

Keywords: Aliphatic/aromatic copolyesters; Direct melt polycondensation; Biodegradable.

INTRODUCTION

Aromatic polyesters, such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), have excellent physical and mechanical properties and are among the most important commercially available polymers with widespread application, especially in the food and beverage packaging. However, due to their strong resistance to bacterial or fungal attack they usually remain unaltered under the environment conditions, and result in a considerable waste stream. Therefore, in recent years, the synthesis of potentially biodegradable copolyesters of PET or PBT is of considerable significance and has been receiving much attention^[1, 2]. On the other hand, aliphatic polyesters could be degraded in the environment and comprise an important family of biodegradable polymers^[3]. Incorporation of biodegradable aliphatic units into the molecular chain of aromatic polyesters has been regarded as an effective strategy to obtain novel biodegradable copolyesters^[4–6]. Copolyesters of PET/PBT with aliphatic polyesters, such as PET-poly(butylene succinate)^[7], PBT-poly(butylene adipate)^[8, 9], PBT-poly(butylene succinate)^[10] and PBT-poly(succinic anhydride-ethylene oxide)^[11] have been designed and described as environmentally degradable or hydrolyzable.

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Poly(L-lactic acid) (PLLA), a typical linear aliphatic polyester, is one of the most significant and promising bio-based and biodegradable materials, which has wide application in packing materials, fibers and biomaterials. It is derived from 100% renewable resources such as cornstarch and could be eventually degraded into CO₂ and H₂O in natural compost or biodegradable and bioabsorbable in physiological environment^[12, 13]. Therefore, in the past decade great efforts have been made to design and synthesize various PLLA-based biodegradable copolymers through combining biodegradable PLLA units with nondegradable polymers, especially aromatic polyesters^[1, 14]. Chen *et al.*^[15] reported the synthesis of biodegradable aliphatic/aromatic copolyesters (M_w in a range of 16000–32900) from terephthaloyl dichloride, bisphenol-A, 1,6-hexanediol and oligolactide. Initial experiments indicated the enhanced hydrolytic degradability and good biocompatibility because of the incorporation of PLLA. Du *et al.*^[16] obtained moderate molecular weight biodegradable-cum-photoactive liquid-crystalline copolyesters (η_{inh} in a range of 0.168–0.325 dL/g) from ferulic acid, 4-hydroxybenzoic acid and D,L-lactic acid. Increasing LA content and adjusting feed ratios could improve the solubility and biodegradability of the obtained copolyesters, while still retaining the liquid crystallinity.

However, in most cases biodegradable copolyesters above are prepared based on dimethyl terephthalate or diacyl dichloride as starting reactants and aromatic components. This process would produce toxic byproducts such as methanol or hydrochloride which had adverse effects on the environment. Moreover, biodegradable behaviors of those copolyesters could not be satisfied and usually showed a slow degradation which limited the biomedical applications. For example, the maximal weight loss of copolymers prepared by Chen *et al.*^[14] was not over 7% after 100 days, and Wang *et al.*^[5] reported the synthesis of biodegradable PBT-*co*-poly (butylenes cyclohexanedicarboxylate)-*b*-PEG by using 1,4-cyclohexanedicarboxylic acid as an aliphatic moiety, which still showed a slow degradation with the maximal weight loss not exceeding 7% after 120 days.

Our intention was to develop a 'green' and economic synthetic method to obtain novel biodegradable aliphatic/aromatic copolyesters with good mechanical and thermal properties, which could be used in a wide range of applications. Based on such an aim, in this paper a direct copolymerization technique was investigated. We selected terephthalic acid (TPA) as aromatic moiety and poly(L-lactic acid) oligomer (OLLA) as aliphatic moiety. Biodegradable aliphatic/aromatic copolyesters poly(butylene terephthalate-*co*-lactate) (PBTL) were synthesized *via* direct melt polycondensation of TPA, 1,4-butanediol (BDO) and OLLA. The advantage of using such synthetic method was that the byproducts produced were nonpolluting water and one of the valuable reactants BDO. At the same time, biodegradable aliphatic segments could be efficiently introduced into aromatic main chains and destroy their regular arrangement with a random way to yield a statistical copolymer, which was preferred for hydrolytic degradability. Additionally, compared with the methodology reported in the literature, such as PET glycolysis^[1] and PBT melting^[17], direct melt polycondensation of TPA and OLLA could cut down the production cost and energy consumption and be more likely to be applied in large-scale production in the future. To the best of our knowledge, this was the first report on the synthesis of biodegradable copolyesters via direct melt polycondensation of TPA, BDO and OLLA.

EXPERIMENTAL

Materials

Terephthalic acid (TPA, AR), 1,4-butanediol (BDO, AR) and tetrabutyl titanate (Ti[OBu]₄, AR) were purchased from Shanghai Reagent Plant and used without further purification. A 90% aqueous solution of L-lactic acid was obtained from Jiangxi Musashino Bio-Chem Co. Ltd. and heated under reduced pressure to yield poly(L-lactic acid) oligomer (OLLA) ($M_n = 1024$ determined by GPC)^[1].

Analysis and Characterization

¹H- and ¹³C-NMR spectra were recorded on Bruker AC 400 instruments operating at 400 MHz. FT-IR spectra were measured by using a Nicolet Magna IR 560 spectrometer in KBr pellets. Gel permeation chromatography (GPC) was performed using a Waters 515 HPLC pump and a Waters 2410 refractive index detector. The mobile phase was chloroform (CHCl₃), and the data were recorded at a flow rate of 1.0 mL/min, and average molecular

weights of the copolyesters were determined with polystyrene as standard. Thermogravimetry analysis (TGA) was performed under nitrogen with a NETZSCH 209F₁ at a heating rate of 10 K/min. A DSC NETZSCH 200PC apparatus was used for differential scanning calorimetry (DSC) at a heating rate of 10 K/min, observing the second heating run. Wide-angle X-ray diffraction (WAXD) was performed with a Rigaku D/Max-2550pc diffractometer using Cu K α radiation ($\lambda = 0.154$ nm; 40 kV; 250 mA) in the 2θ scan range of 3° to 50° at ambient temperature. The mechanical properties were determined with a WD-5 Electronic Tensile Tester at room temperature. The dynamic mechanical data, storage modulus (E') and loss tangent ($\tan\delta$) were obtained with a NETZSCH DMA 242C apparatus with following parameters: frequency, 1 Hz; scan rate, 3 K/min.

Synthesis of Copolyesters Poly(butylene terephthalate-co-lactate) (PBTL)

In a flame dried reaction flask with mechanical stirrer 7.5 g (0.045 mol) of TPA (1), 9.0 g (0.1 mol) of BDO (2) and 0.1 wt% Ti[OBu]₄ were added under nitrogen. Under atmospheric pressure the reaction mixture was heated to 170°C for 30 min and at 200°C for another 30 min, and then up to 230°C for 2 h, followed by conducting the reaction under reduced pressure (50 kPa) until the mixture became homogeneous and transparent. Then various amounts of OLLA (4) were added into the resulting product BHBT (3) under nitrogen and heated at 230°C for several hours under reduced pressure (260 Pa) to yield poly(butylene terephthalate-co-lactate) (PBTL) (5). The copolyesters obtained were dissolved in 50 mL of chloroform, isolated by precipitation in 500 mL of ethyl ether, collected on a filter and then dried under vacuum at 40°C for 48 h. The ¹H- and ¹³C-NMR and FT-IR spectra of copolyesters 5 with different feed ratio are almost identical and differ only in relative signal intensities. For example copolyester 5c:

¹H-NMR (400 MHz, CDCl₃): $\delta = 1.40$ – 1.56 (m, CH₃ lactate); 1.71 – 1.97 (m, CH₂ BDO); 4.17 – 4.43 (m, CH₂ BDO); 5.15 – 5.38 (m, CH lactate); 8.10 – 8.14 (m, C₆H₄).

¹³C-NMR (400 MHz, CDCl₃): $\delta = 16.67$ (CH₃ lactate), 25.40, 64.36 (OCH₂CH₂ BDO), 69.47 (CH lactate), 129.51, 133.95 (C₆H₄), 165.65, 170.28 (CO).

FT-IR (KBr, cm⁻¹): $\nu = 3435$ (m, ν OH), 2961 (w, ν_{as} CH₃), 1756, 1725 (s, ν C=O), 1458, 1408, 1386 (m, ν C=C), 1272, 1196, 1119, 1104 (s, ν CO), 731 (m, ν CH₂).

The number average molecular weight of PBTL was determined by ¹H-NMR^[1]. The total number of OH end-units was proportional to $(I_7 + I_8)/2$, the total number of terephthalate (T) units to $I_1/4$ and that of lactate (L) units to $I_2 + I_3$. So the number-average molecular weight (M_n) of PBTL could be calculated according to the following equations: $M_n = 220T + 72L + 90$, $T = I_1/2(I_7 + I_8)$; $L = 2(I_2 + I_3)/(I_7 + I_8)$.

Hydrolytic Degradation Test

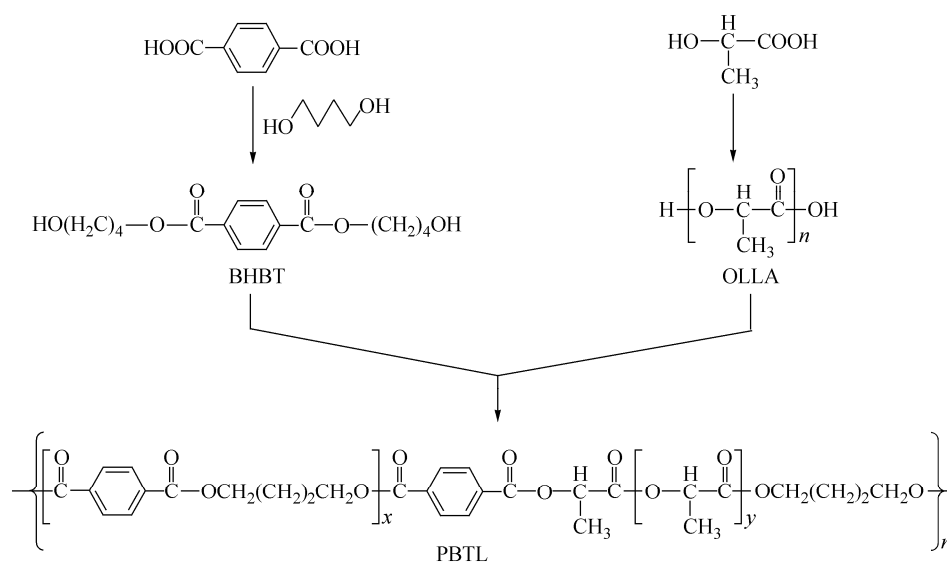
Hydrolytic degradation experiments of copolyesters were carried out in a phosphate buffer solution (PBS, pH = 7.4) at 37°C and 60°C, respectively. First, the copolymer was cast into a rectangular sample (about 10 mm \times 20 mm in size and 0.3 mm in thickness), and then was placed in a bottle with 30 mL of buffer. At predetermined degradation time intervals, the specimens were removed from the medium, rinsed with distilled water, dried under vacuum at room temperature for 48 h before analysis. Before continuing the experiment, the buffer solution was renewed. The weight loss data represent the average of at least three film samples.

RESULTS AND DISCUSSION

Synthesis of Copolyesters

A series of biodegradable aliphatic/aromatic copolyesters PBTL were synthesized *via* direct melt polycondensation of TPA, BDO and OLLA (Scheme 1). The effects of polymerization time, temperature and feed ratio of monomers on the synthesis of PBTL were investigated, and the data are summarized in Table 1. As shown in Table 1, the molecular weights of PBTL were strongly dependent on the polymerization time and temperature. With increasing polymerization time and temperature, the number-average molecular weights (M_n) were varied in the range of 10900–26700 determined by ¹H-NMR^[1] and 13100–30700 by GPC. When the polymerization time was 6 h and the temperature was 230°C, the highest molecular weight ($M_n = 30700$, $M_w = 64100$, determined by GPC) copolyester could be obtained. From Table 1, it was indicated that changes of

reaction time and temperature had little effect on getting copolymers with high molecular weight. Higher temperature or longer reaction time benefited for thermal degradation and cyclization into lactide of aliphatic PLA segment, which would result in the breakage of the main chain of copolymer, thus the molecular weights of copolyesters were difficult to increase. Low polymerization temperature of 210°C did not favor the disposal of small molecules, such as BDO, formed during the polymerization and hampered the proceeding of reaction, so



Scheme 1 Synthesis of the copolyesters PBTL *via* direct melt polycondensation

Table 1. Effect of polymerization time, temperature, and *T/L* ratio on the synthesis of PBTL

Temperature (°C)	Time (h)	BHBT/OLLA mass ratio	<i>T/L</i> feed ^a	<i>T/L</i> final ^b	M_n^c	GPC		
						M_n	M_w	PDI
230	2	75/25	31/69	45/55	11100	14600	29700	2.03
230	4	75/25	31/69	47/53	16500	19600	41200	2.10
230	6	75/25 (5c)	31/69	48/52	26700	30700	64100	2.09
230	8	75/25	31/69	48/52	24400	28200	59500	2.11
230	10	75/25	31/69	48/52	24100	27600	59300	2.15
210	6	75/25	31/69	40/60	10900	13100	27100	2.08
250	6	75/25	31/69	50/50	16400	20200	46000	2.27
230	6	55/45 (5a)	17/83	21/79	10800	14600	29700	2.03
230	6	65/35 (5b)	24/76	30/70	18700	20300	40500	1.99
230	6	85/15 (5d)	52/48	70/30	20100	20000	38200	1.91

^a Feed molar ratio of terephthalate and lactate moieties;

^b Final molar ratio of terephthalate and lactate moieties determined by ¹H-NMR;

^c Determined by ¹H-NMR spectrum

the product with lower molecular weight was obtained. Because the biodegradable, thermal and mechanical properties of copolyesters could be tailored by changing the feed ratio of TPA and OLLA, the influence of a series of different BHBT/OLLA (TPA/OLLA) feed ratios on the properties of PBTL was studied at 230°C when the reaction was carried out for 6 h (Table 1). The number-average molecular weights (M_n) were found to vary in the range of 10800–26700 determined by ¹H-NMR and 14600–30700 with PDI of 1.91–2.09 by GPC, depending on the copolymer composition. The results showed that the molecular weights decreased sharply with increasing molar ratio of lactate moiety in the copolyesters. The reason for that can also be attributed to the

instability of PLLA segments under the conditions of the system. While, when the PBT moiety was increased to 70%, the molecular weight of the copolymer decreased, too. This is because the T_m ($T_m = 230^\circ\text{C}$) of PBT was relatively high, higher temperature ($> 250^\circ\text{C}$) is more beneficial for PBT to carry out polycondensation. The reaction temperature at 230°C made the reactant system much stickier and the resultant small molecules such as water and THF were difficult to fly away from the system, so it was not favoring its chain growth, and the molecular weight decreased when the PBT moiety was high. The examination of GPC curves of 5a–5d showed a monomodal distribution (Fig. 1), which further indicated that the obtained products were copolymers and lactate moieties were randomly incorporated into the polyester backbones rather than blended. This was consistent with our expectation.

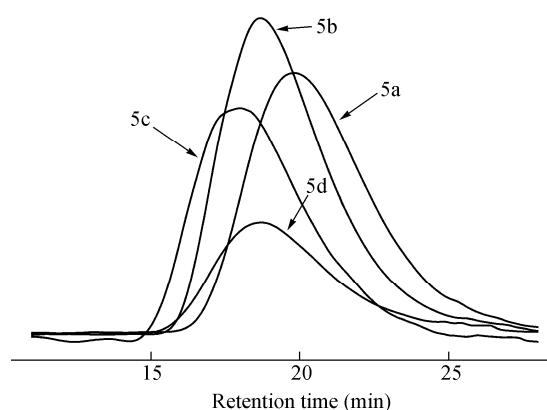


Fig. 1 GPC curves of the copolyesters 5a–5d

Structure Characterization of Copolyesters

The molecular structure of the copolyesters was investigated by ^1H - and ^{13}C -NMR spectroscopy. A typical spectrum of sample 5c together with characteristic peak assignments is shown in Fig. 2. From Fig. 2(a) the signals corresponding to CH and CH_3 in lactate moiety were observed at $\delta = 5.15\text{--}5.38$ and $1.40\text{--}1.56$, while the peaks centered at $\delta = 8.10\text{--}8.14$, $4.17\text{--}4.43$ and $1.71\text{--}1.97$ were assigned to the protons of the benzene ring, OCH_2 and adjacent CH_2 in terephthalate moiety, respectively. The ^{13}C -NMR spectrum of copolyester 5c (Fig. 2b) also showed characteristic peaks of terephthalate moieties ($\delta = 165.65$, $-\text{C}=\text{O}$; $\delta = 133.95$, 129.51 , $-\text{C}_6\text{H}_4$; $\delta = 64.36$, $-\text{OCH}_2$; $\delta = 25.40$ $-\text{OCH}_2\text{CH}_2$) and lactate moieties ($\delta = 170.28$, $-\text{C}=\text{O}$; $\delta = 69.47$, $-\text{CH}$; $\delta = 16.67$, $-\text{CH}_3$).

According to the total integrations of the peaks at $\delta = 5.15\text{--}5.38$ and $8.10\text{--}8.14$, the actual terephthalate (T) and lactate (L) moieties molar ratio of copolyesters could be easily calculated and presented in Table 1. The T/L molar ratio in final copolyesters was higher than the feed molar ratio because some OLLA could depolymerize into lactide, which would easily evaporate and cause the loss of OLLA during the reaction. From the FT-IR spectra of the copolyesters 5a–5d shown in Fig. 3, the absorption peaks at 1756 and 1725 cm^{-1} could be attributed to the $-\text{C}=\text{O}$ of lactate and terephthalate moieties, respectively. It was obvious that the intensities of the absorption band at 1756 cm^{-1} was gradually becoming weak when the final content of OLLA decreased from 79% to 30%. This phenomenon confirmed that OLLA was chemically attached to TPA and formed random copolyesters. The peaks around 1272 , 1196 , 1119 and 1104 cm^{-1} were assigned to $-\text{C}-\text{O}$. The band around 731 cm^{-1} corresponded to the $-\text{CH}_2$ group of BDO, and a broad absorption band at about 3435 cm^{-1} resulted from $-\text{OH}$ groups.

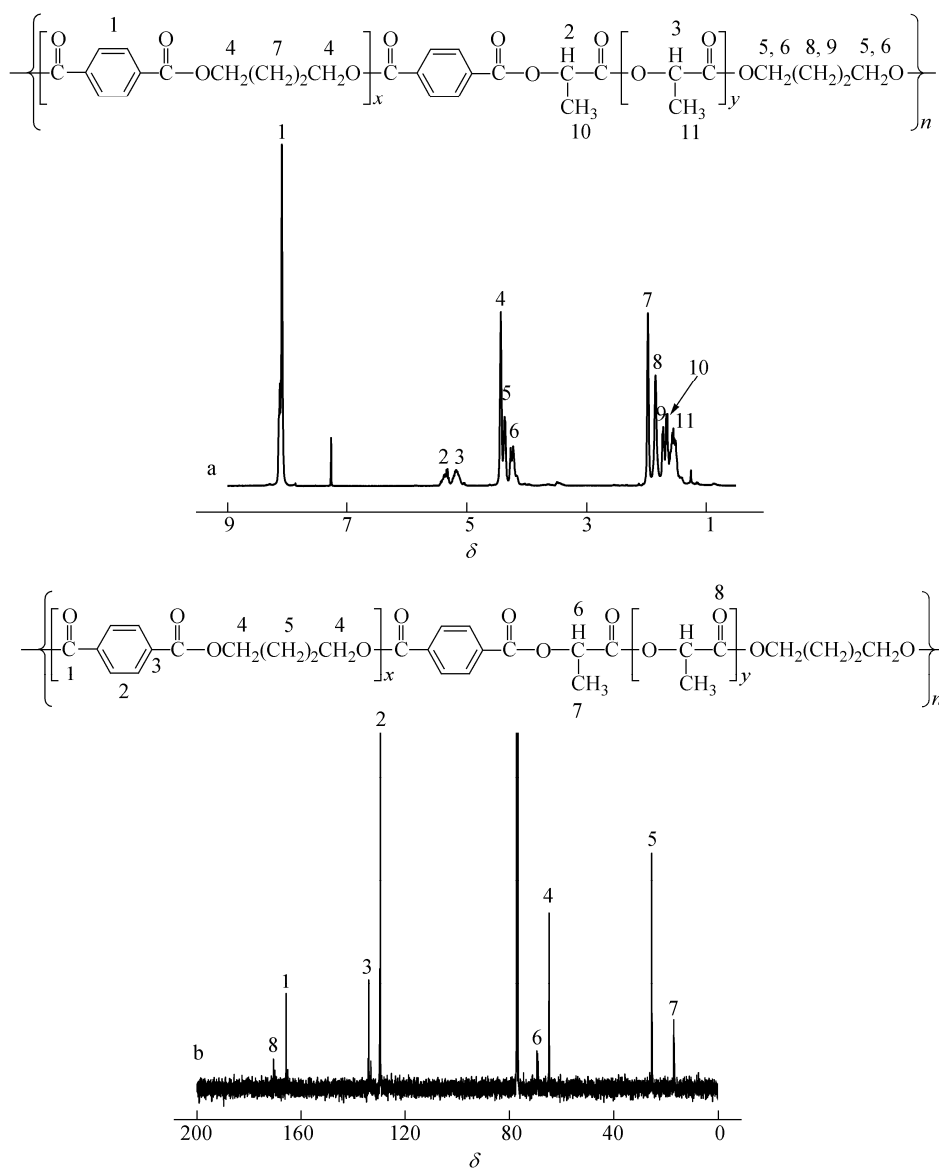


Fig. 2 The spectra of the copolyester 5c (a) $^1\text{H-NMR}$ and (b) $^{13}\text{C-NMR}$

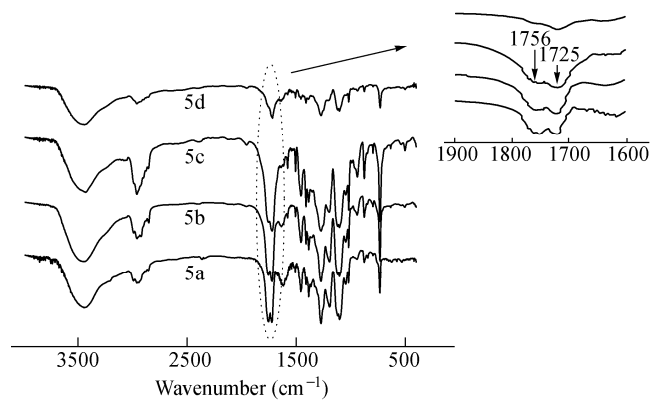


Fig. 3 FT-TR spectra of the copolyesters 5a–5d

Thermal Properties of Copolyesters

The thermal properties of PBTL were characterized by means of DSC and TGA. Figures 4 and 5 show the DSC second heating curves and TG thermograms. Seen from Fig. 4(a), the cold-crystallization exotherm and melting endotherm phenomena weakened with the reaction time. At the initial stages, the aromatic monomer and aliphatic monomer were both apt to homopolymerization, respectively. Therefore, the copolymer chains exhibited regularity to some extent and were easier to crystallize. With increasing the reaction time, the effect of transesterification on the whole chain structure was more distinct, which made the aromatic moiety and aliphatic moiety combined each other randomly and disturbed the original regularity of the main chain. Therefore the crystallization phenomena were weakened gradually. Moreover, with the reaction time increasing, the decomposition of aliphatic moiety became more serious. So the amount of aromatic moiety increased relatively, and the T_g of copolymers also became higher. The $^1\text{H-NMR}$ analysis results also showed the same trend. From Fig. 4(b), each copolyester exhibited only one glass transition temperature (T_g) in spite of the ratio of monomers, which indicated that direct melt polycondensation of TPA, BDO and OLLA resulted in random copolyesters rather than physical blends. The T_g of the copolyesters shifted to a higher temperature from 20.1°C to 31.5°C as the aliphatic lactate content decreased. The cold-crystallization exotherm and melting endotherm were observed for 5c and 5d in the heating run. Because of their higher TPA content, the PBT sequence lengths were relatively long enough to exhibit cold-crystallization and melting transitions for 5c at 95.3°C and 130.5°C, respectively. These temperatures were much lower than those of original PBT ($T_m = 230^\circ\text{C}$, $T_g = 40^\circ\text{C}$), which reflected the disruption of chain regularity caused by the incorporation of aliphatic OLLA units in PBT chains. The thermal stability of the copolyesters was characterized using thermogravimetric analysis (TGA) under nitrogen atmosphere. Compared with the previously reported copolyesters^[1, 4, 16], PBTLs have better thermal stability and the thermal decomposition temperatures (T_d) were in a range of 363.4–395.7°C (shown in Table 2). With increasing the content of lactate moiety, a gradual decrease of T_d was observed. Besides, 5a and 5b showed two-step decomposition which corresponded to long lactate sequences and PBTL random sequences contained in the copolyester (Fig. 5).

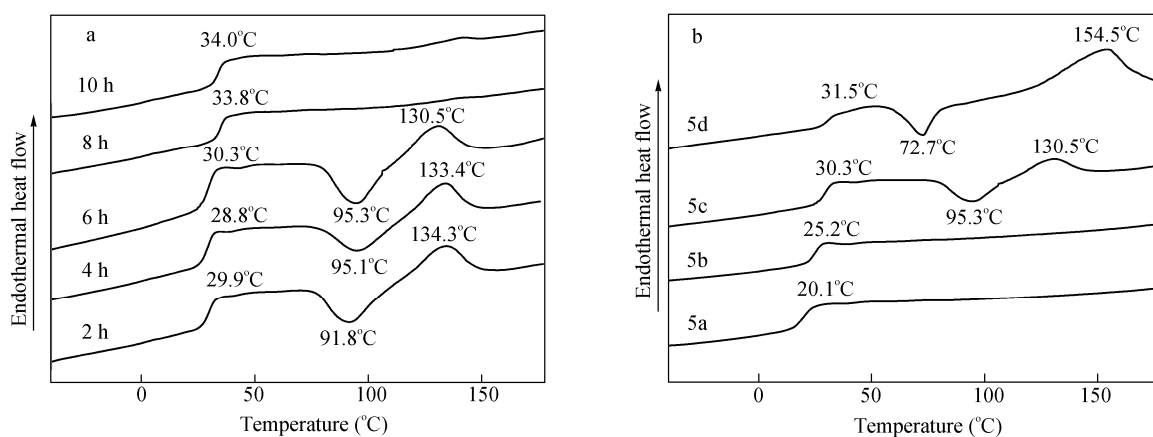


Fig. 4 DSC thermal diagrams of the copolyesters (a) with different reaction time at 230°C, (b) with different ratio at 230°C for 6 h

Table 2. Thermal properties of PBTL

BHBT/OLLA mass ratio	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C)
55/45 5a	20.1	—	—	254.5 363.4
65/35 5b	25.2	—	—	260.4 392.7
75/25 5c	30.3	95.3	130.5	395.0
85/15 5d	31.5	72.7	154.5	395.7

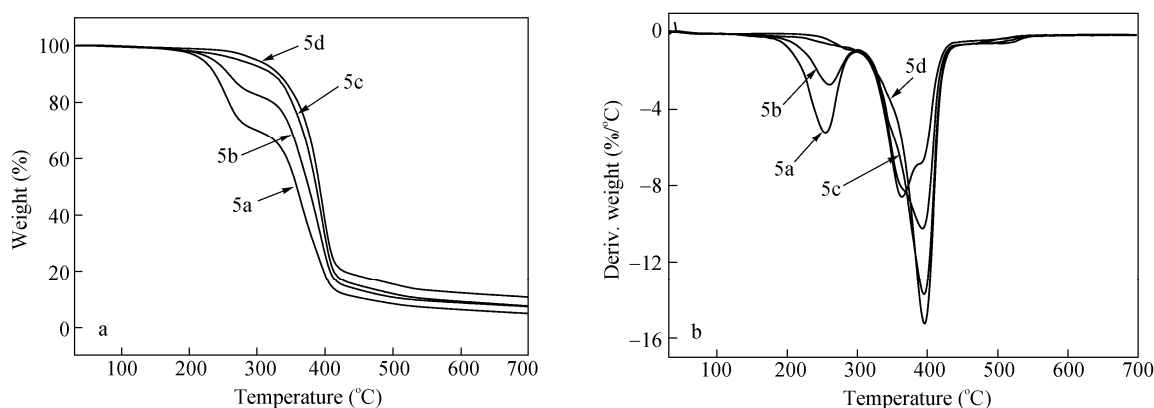


Fig. 5 TG thermal diagrams of the copolyesters 5a–5d

X-ray Diffraction Patterns of Copolyesters

The X-ray diffraction patterns of the four typical copolyesters 5a–5d are shown in Fig. 6. XRD analysis and the absence of melting endothermic and cold-crystallization peaks in DSC measurements indicated that 5a and 5b were amorphous. With the increase of lactate moieties, the crystalline structures of PBTL were gradually destroyed and the arrangement of copolyester main chains became irregular due to the spatial effect and interference of the lactate moiety. When the BHBT/OLLA feed ratio was over 75/25, sharp crystalline peaks appeared which could be ascribed to PBT chains^[18]. With the aromatic moiety increasing, aromatic chains formed were long enough and easy to crystallize. This result was also coincided with the DSC results.

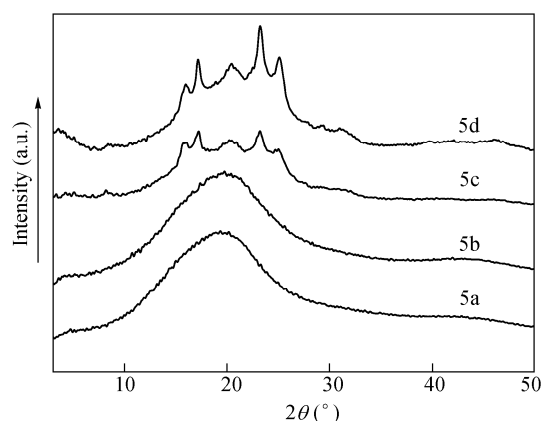


Fig. 6 Wide-angle X-ray diffraction patterns of the copolyesters 5a–5d

Mechanical Properties and Dynamic Viscoelasticity of Copolyesters

Mechanical properties of the copolyesters 5a–5c have been measured except 5d because the sample prepared from 5d was too brittle to measure its mechanical properties. Table 3 shows the tensile strength and elongation values. The sample 5c exhibited the highest Young's modulus of 9.64 MPa as compared to sample 5b (5.32 MPa) and sample 5a (4.25 MPa). The tensile strength of copolyester 5c was also the highest and up to 8.4 MPa, which was much higher than 3.6 MPa of copolyester reported by Wang *et al.*^[15]. Because of soft lactate moieties, the Young's modulus and the tensile strength of copolyesters dropped markedly with the increase of OLLA content but the elongation at break of all the samples exceeded 500% (Out of the measurement range of the tensile tester). The temperature dependence of the storage modulus (E') and the loss factor ($\tan\delta$) were evaluated by dynamic mechanical analysis (Fig. 7). At low temperatures, for example in the range of below 10°C, the storage modulus of 5c was about 1.5 times higher than that of 5a. The more OLLA contents the copolyester had, the lower the E' value was. At the temperature around each of the T_g measured by the DSC, the

E' values of samples fell drastically. All $\tan\delta$ curves just showed one peak which meant there was only one glass-transition temperature for copolymers. The T_g s in the $\tan\delta$ curve shifted to a higher temperature from 29.5°C to 39.8°C with an increase in terephthalate moieties, which were a little bit higher compared to those obtained by DSC measurements.

Table 3 Mechanical properties of PBTL

BHBT/OLLA mass ratio	T/L feed ^a	T/L final ^b	E (MPa)	σ (MPa)	ε (%)
55/45 5a	17/83	21/79	4.25 ± 0.03	3.5 ± 0.12	> 500
65/35 5b	24/76	30/70	5.32 ± 0.05	4.5 ± 0.15	> 500
75/25 5c	31/69	48/52	9.64 ± 0.04	8.4 ± 0.14	> 500

^a Feed molar ratio of terephthalate and lactate moieties;

^b Final molar ratio of terephthalate and lactate moieties determined by ¹H-NMR

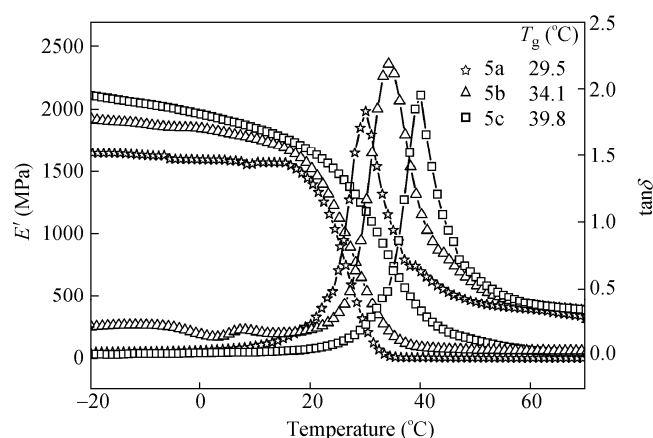


Fig. 7 Storage modulus and loss tangent of the copolyesters 5a–5c

Hydrolytic Degradation of Copolyesters

For preliminary test of hydrolytic degradability, films of the copolyesters 5a–5c were placed in PBS for several days at 37°C and 60°C, respectively. Because the sample prepared from 5d was too brittle to cast into the same sample as 5a–5c, the hydrolytic degradability of 5d can't be measured at the same level. As shown in Fig. 8, all samples underwent significant hydrolytic degradation in PBS and the rate of degradation monitored in each samples revealed temperature dependency. After 49 days in PBS at 60°C, residue weights of 35.1%, 59.8% and 76.8% were observed for the copolyesters 5a–5c, respectively, while immersed in PBS at 37°C for 60 days relatively higher residue weights were obtained (64.0%, 74.7% and 82.1% for 5a–5c, respectively). Compared with reported PLLA-based copolyesters^[14, 16], PBTLs showed a higher speed of degradation under the same conditions (in PBS at 37°C). Moreover, the results also indicated that no matter what the temperature was, the degradation rate of the copolymer always increased with increasing OLLA content. This phenomenon was attributed to the morphology of copolymers. The copolymer with high OLLA content (70 mol% or 79 mol%) was amorphous and the water easily penetrated into the bulk of the copolymer, so the degradation rate of the samples was fast, but in low OLLA content (52 mol%) sample, the water was hard to penetrate into the semi-crystalline copolymer and the degradation rate of the samples was low. Thus, the weight loss increased with an increase in OLLA content. To compare the degradation rate of PBT segment and OLLA segment, the ¹H-NMR spectra of the copolyester 5c with different degradation time are given in Fig. 9(a). The signal (Ha) at $\delta = 5.15$ –5.38 was assigned to the methine of lactate moieties, the signals Hb and Hc corresponding to the —CH₂OH end oligomers, and methyl chain units produced by degradation were located at $\delta = 3.74$ and 1.25. Based on the supposition that the integration of the peak at $\delta = 8.14$ corresponding to aromatic protons was 4, the relative integrations of Ha, Hb and Hc were calculated, and their changes after degradation are shown in Fig. 9(b). The results clearly demonstrated that with the increase of degradation time the relative integration of

lactate moieties (Ha) became weaker, while that of Hb and Hc became stronger compared to terephthalate moieties. This meant that the lactate moieties of the copolyester first easily degraded so that the main long chains were broken to form oligomers or some small molecules. Figure 10 presents the molecular weights of 5c before and after degradation in PBS at 37°C and 60°C, respectively. The obvious decrease of the molecular weight in comparison with the initial molar masses indicated that a significant chemical hydrolysis took place within the copolyester and high molecular copolyester was converted to low molecular polymers, which was coincided with our observations from Fig. 9.

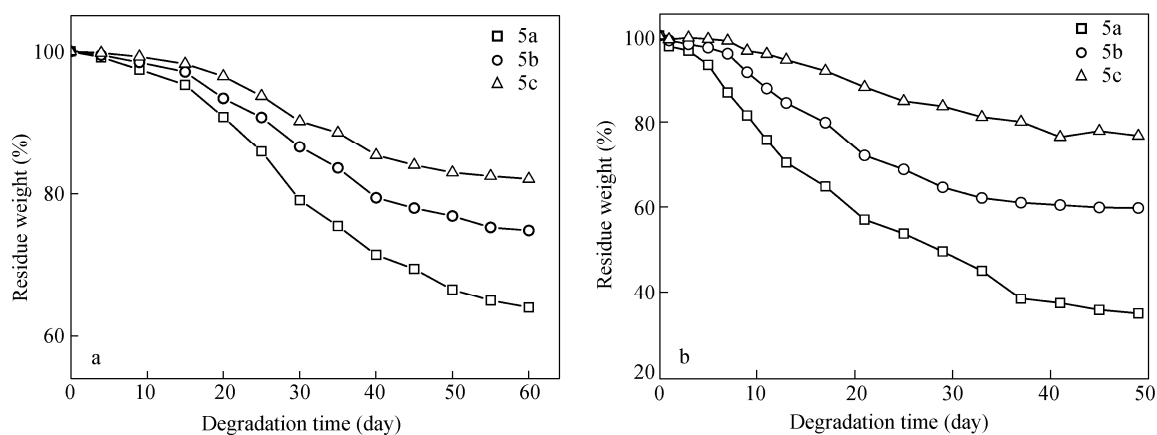


Fig. 8 Residue weight of the copolyesters 5a–5c after hydrolytic degradation in PBS (a) at 37°C and (b) at 60°C

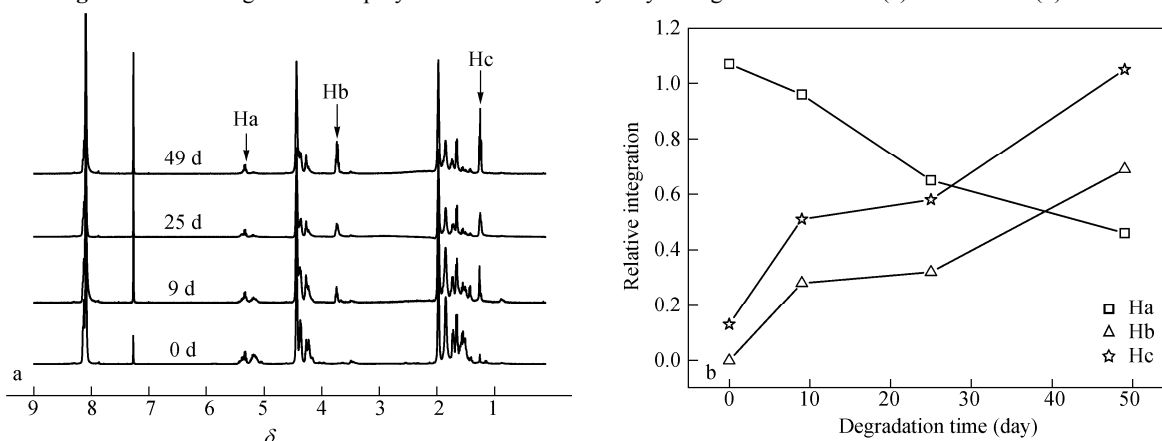


Fig. 9 (a) ¹H-NMR spectra of the copolyester 5c after hydrolytic degradation; (b) Relative integration change of the peak for Ha, Hb, Hc

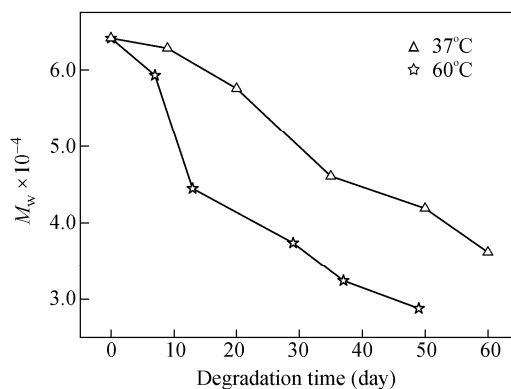


Fig. 10 The molecular weight of the copolyester 5c during hydrolytic degradation process

CONCLUSIONS

A series of biodegradable aliphatic/aromatic copolyesters PBTL were synthesized through an economical and green method of direct melt polycondensation of TPA, BDO and OLLA. Under the optimal reaction condition (230°C for 6 h), the molecular weight (M_w) of copolyester 5c could be up to 64100 with polydispersity of 2.09. GPC, ^1H - and ^{13}C -NMR, FT-IR, DSC and DMA characterization clearly indicated that aliphatic OLLA moiety had been successfully combined with the aromatic terephthalate moiety to yield a statistical copolymer rather than physical blends. With the increase of the T/L ratios in the copolyesters, T_g values gradually increased from 20.1°C to 31.5°C, and the PBTL intended to crystallize and showed the cold-crystallization exotherm and melting endotherm for 5c and 5d. Despite a high content of aliphatic lactate moieties, the mechanical properties of the copolyesters were satisfactory ($\sigma = 8.4$ MPa; $E = 9.64$ MPa for 5c). Hydrolytic degradation studies showed that incubation in PBS at two different temperatures, all samples underwent significant degradation in spite of many aromatic units in their main chains, and the residue weights of the copolyesters ranged from 64.0% to 82.1% at 37°C and 35.1% to 76.8% at 60°C depending on the content of OLLA moieties. The ^1H NMR spectra showed that the lactate moieties of the copolyester first easily degraded so that the main long chains were broken to form oligomers or some small molecules.

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