

# Synthesis, Characterization, and Properties of Degradable Poly(l-lactic acid)/Poly(butylene terephthalate) Copolyesters Containing 1,4-Cyclohexanedimethanol

Bingtao Wang,<sup>1,2</sup> Yan Zhang,<sup>1</sup> Pingan Song,<sup>1,2</sup> Zhenghong Guo,<sup>1</sup> Jie Cheng,<sup>1</sup> Zhengping Fang<sup>1,2</sup>

<sup>1</sup>Laboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China

<sup>2</sup>Ministry of Education Key Laboratory of Macromolecular Synthesis and Functionalization, Institute of Polymer Composites, Zhejiang University, Hangzhou 310027, China

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**ABSTRACT:** High-molecular-weight copolyesters based on poly(butylene terephthalate) as rigid aromatic segments and poly(l-lactic acid) (PLLA) as degradable aliphatic segments were synthesized via the polycondensation of terephthalic acid, 1,4-butanediol (BDO), 1,4-cyclohexanedimethanol (CHDM), and PLLA oligomer. By tailoring the molar ratio of diols (BDO and CHDM), we investigated in detail the effects of the CHDM rigid hexacyclic ring on the synthesis, mechanical properties, thermal stabilities, and degradation behaviors of the copolyesters. With increasing CHDM content, the initial decomposition temperature increased

from 282.5 to 322.2°C, and the tensile strength improved by nearly four times, from 5.4 to 19 MPa. When the molar ratio of BDO/CHDM was 95/5, the weight-average molecular weight of the copolyester was 89,400 g/mol with a polydispersity of 1.96. In addition, hydrolytic degradation results in phosphate buffer solution indicate that the degradation rate of the copolyesters displayed a strong dependency on the temperature and CHDM composition. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2985–2995, 2011

**Key words:** copolymerization; degradation; polyesters

## INTRODUCTION

In the past decades, degradable polymers have attracted much more research attention because of growing concerns over the persistence of plastics, especially short-lived packaging wastes, accumulating in the environment.<sup>1</sup> Aromatic polyesters, such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), are one of the most important commercially available engineering plastics and have been used in many fields because of their excellent mechanical and thermal properties. However, their strong resistance to hydrolysis and bacterial/fungal attack results in poor degradability under environmental conditions, and consequently, they cause serious environmental problems. Therefore, great efforts have been made to design and synthesize copolyesters of PET or PBT that could

be degraded or disposed of by composting.<sup>2–6</sup> The incorporation of aliphatic polyesters, one important kind of biodegradable polymer, into the main chain of aromatic polyesters has been regarded as the most promising approach; with it, one could obtain novel aliphatic/aromatic copolyesters with high physical properties and good biodegradability.<sup>1,7–11</sup> Copolyesters of PET or PBT with aliphatic polyesters, such as PET–poly(butylene succinate),<sup>12</sup> PBT–poly(butylene adipate),<sup>13,14</sup> PBT–poly(butylene succinate),<sup>2</sup> and PBT–poly(succinic anhydride–ethylene oxide),<sup>7</sup> have been designed and are considered to be environmentally degradable or hydrolyzable.

As one of the most prominent biodegradable aliphatic polyesters, poly(l-lactic acid) (PLLA), is derived from 100% renewable resources (e.g., corn, potato, and beet sugar) and could be eventually degraded into CO<sub>2</sub> and H<sub>2</sub>O under natural conditions.<sup>15,16</sup> So PLLA has widespread applications in agriculture (as mulch films), packing materials, biomedical implants, and absorbable surgery sutures.<sup>17,18</sup> Nowadays, extensive attention has been paid to the preparation of various PLLA-based biodegradable copolymers through the combination of biodegradable PLLA units with nondegradable polymers, especially aromatic polyesters.<sup>19,20</sup> Chen et al.<sup>21</sup> reported

Correspondence to: Y. Zhang (hnpdszy@163.com).

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TABLE I  
Compositions, Molecular Weights, and Average Sequence Lengths of the PBCTLs

Sample	TPA/OLLA/BDO/CHDM <sup>a</sup>	TPA/OLLA/BDO/CHDM <sup>b</sup>	$M_n$ ( $\times 10^{-4}$ )	$M_w$ ( $\times 10^{-4}$ )	PDI	$L_T^c$	$L_L^c$
PBCTL-0	30/70/100/0	52/48/100/0	2.61	5.25	2.01	2.17	1.88
PBCTL-1	30/70/97.5/2.5	51/49/97.7/2.3	3.03	5.87	1.94	2.05	1.93
PBCTL-2	30/70/95.0/5.0	45/55/95.3/4.7	4.56	8.94	1.96	1.77	2.04
PBCTL-3	30/70/92.5/7.5	48/52/92.8/7.2	3.15	6.25	1.98	1.85	1.91
PBCTL-4	30/70/90/10	49/51/90.5/9.5	2.50	4.86	1.94	1.99	1.88

<sup>a</sup> Molar ratio in the initial feed.

<sup>b</sup> Final molar ratio determined from the <sup>1</sup>H-NMR spectra.

<sup>c</sup> As calculated from the <sup>1</sup>H-NMR spectra.

the synthesis of aliphatic/aromatic copolyesters from terephthaloyl dichloride, bisphenol A, 1,6-hexanediol, and oligolactide. The initial experiments demonstrated enhanced hydrolytic degradability and good biocompatibility with the incorporation of PLLA. Du et al.<sup>22</sup> obtained moderate-molecular-weight biodegradable-cum-photoactive liquid-crystalline copolyesters from ferulic acid, 4-hydroxybenzoic acid, and d,l-lactic acid. An increase in the lactic acid content and adjustment of the feed ratios improved the solubility and biodegradability and retained the liquid crystallinity of the obtained copolyesters. Recently, we also designed and synthesized a series of biodegradable aliphatic/aromatic copolyesters via the direct melt polycondensation of poly(l-lactic acid) oligomer (OLLA) with aromatic terephthalic acid (TPA) and 1,4-butanediol (BDO).<sup>23</sup> The results indicate that incorporation of lactate moieties into the aromatic polyester effectively improved the degradability of the copolymers, and the degradation rate could be easily tailored by adjustment of the ratio of TPA to OLLA. However, the performances of those reported biodegradable aliphatic/aromatic copolyesters were still not very satisfying and did not fulfill commercial use requirements, especially their mechanical properties and thermal stabilities. Additionally, the relatively low molecular weight also limited the copolyesters' applications in a variety of fields.

It is well known that diol components play an important role in the design and synthesis of specific polyesters. Through copolymerization with the second or third diol comonomer, copolyesters exhibit remarkably improved properties and/or some unique performances.<sup>8,9,11,24</sup> 1,4-Cyclohexanedimethanol (CHDM), with a bulky rigid cyclic chemical structure, can be readily incorporated into polyesters by high-temperature polycondensation and has proven to be an extremely valuable diol for commercial polyesters. Low-level CHDM (<5 mol %) can effectively enhance the molding characteristics of PET and make it exhibit an array of interesting properties, such as clarity, low color, toughness, and chemical resistance over a wide range of ethylene glycol (EG)/CHDM values.<sup>25</sup> Because of the unique performances, those copolyesters containing CHDM units currently enjoy considerable commercial

success in the marketplace and are widely applied in commercial and industrial fields.<sup>26,27</sup>

To improve the practical performances of biodegradable aliphatic/aromatic copolyesters, to develop novel copolyesters with perfect physical and thermal properties and good biodegradability, and to further extend our research on the preparation of biodegradable aliphatic/aromatic copolyesters,<sup>23</sup> in this study, we selected CHDM as the second diol monomer to replace part of BDO to synthesize a novel kind of copolyester, poly(butylene cyclohexanedimethylene terephthalate-co-lactate) (PBCTL). Through the adjustment of the ratio of diol components, the effects of the CHDM composition on the synthesis, mechanical properties, thermal stabilities, and hydrolytic degradation behaviors were investigated in detail.

## EXPERIMENTAL

### Materials

TPA, BDO, and tetrabutyl titanate catalyst (Ti[OBu]<sub>4</sub>) were supplied by Shanghai Reagent Plant (Shanghai, China) and were used without further purification. CHDM, which was an equilibrium mixture of 1,4-trans and 1,4-cis (70/30), was purchased from Aldrich Chemicals (Shanghai, China). A 90% aqueous solution of l-lactic acid was obtained from Jiangxi Musashino Bio-Chem Co., Ltd. (Nanchang, China), and was heated under reduced pressure to yield OLLA [number-average molecular weight ( $M_n$ ) = 1495 g/mol, weight-average molecular weight ( $M_w$ ) = 3568 g/mol] according to the previous literature.<sup>20</sup>

### Synthesis

In this study, all of the copolyesters were synthesized with a two-step polymerization (esterification and polycondensation) in the presence of Ti[OBu]<sub>4</sub> as a catalyst (0.1 wt %). The details of the synthesis were described in our previous article.<sup>23</sup> First, for the esterification, mixtures of BDO and CHDM with different molar ratios and TPA were added to a flame-dried reaction flask equipped with a mechanical stirrer

under nitrogen. The monomer mixture was heated to 200°C for 30 min and then to 230°C for 2 h; then, we conducted the reaction under reduced pressure (50 kPa) until the mixture became homogeneous and transparent. Second, for the polycondensation, OLLA was added to the resulting product under nitrogen, and a vacuum (260 Pa) was applied slowly over a period of about 30 min to minimize oligomer sublimation. The reaction was carried out at 230°C for 7 h. The feed molar ratio of TPA to OLLA was kept at 30/70 according to our previous research.<sup>23</sup>

### Characterization

<sup>1</sup>H-NMR spectra were recorded on Bruker ARX-400 instrument (Switzerland) operating at 400 MHz; CDCl<sub>3</sub> was used as the solvent, and tetramethylsilane (TMS) was used as the internal standard. Fourier transform infrared (FTIR) spectra were measured with a Nicolet Magna IR 560 spectrometer (Waltham, MA, USA) in KBr pellets. Gel permeation chromatography (GPC) was performed with a Waters 515 HPLC pump (Milford, MA, USA) and a Waters 2410 refractive-index detector. The mobile phase was chloroform (CHCl<sub>3</sub>), and the data were recorded at a flow rate of 1.0 mL/min. Thermogravimetry (TG) was performed with a Netzsch 209F<sub>1</sub> (Bavarian town of Selb, Germany) at a heating rate of 20°C/min in an atmosphere of nitrogen. A Netzsch DSC 200PC apparatus was used for differential scanning calorimetry (DSC) at a heating rate of 10°C/min; we observed the second heating run. Wide-angle X-ray diffraction (WAXD) was performed with a Rigaku D/Max-2550pc diffractometer (Tokyo, Japan) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm, 40 kV, 250 mA) in the  $2\theta$  scan range of 3–50° at ambient temperature. For mechanical testing, dumbbell specimens were prepared by compression molding (dimensions of 30 × 3.8 × 1 mm<sup>3</sup>), and tensile tests were conducted at room temperature with a cross-head speed of 50 mm/min on a WD-5 electronic tensile tester (Jinan, China). At least five specimens were tested for each value given. The dynamic mechanical measurement was performed on samples 1.5 × 35 × 12 mm<sup>3</sup> in size, with a Netzsch DMA 242C in single-cantilever mode with the following parameters: frequency = 1 Hz and scan rate = 3°C/min. The contact angle of the copolyester surface with water was measured with a Rame-Hart contact angle goniometer (Netcong, NJ, USA).

### Hydrolytic degradation

Hydrolytic degradation experiments of the copolyesters were carried out in phosphate buffer solution (PBS; pH = 7.41 at 25°C) at 37 and 60°C. At predetermined degradation time intervals, the speci-

mens (dimensions of 25 × 5 × 1 mm<sup>3</sup>) were removed from the medium, rinsed with distilled water, and dried *in vacuo* at room temperature for 48 h before analysis. Before continuing the experiment, we renewed the buffer solution. The average value of three specimens for each copolyester sample was used. The weight residue percentages of the copolyesters were calculated according to the following relationship:

$$\text{Residue weight (\%)} = W_r \times 100/W_0$$

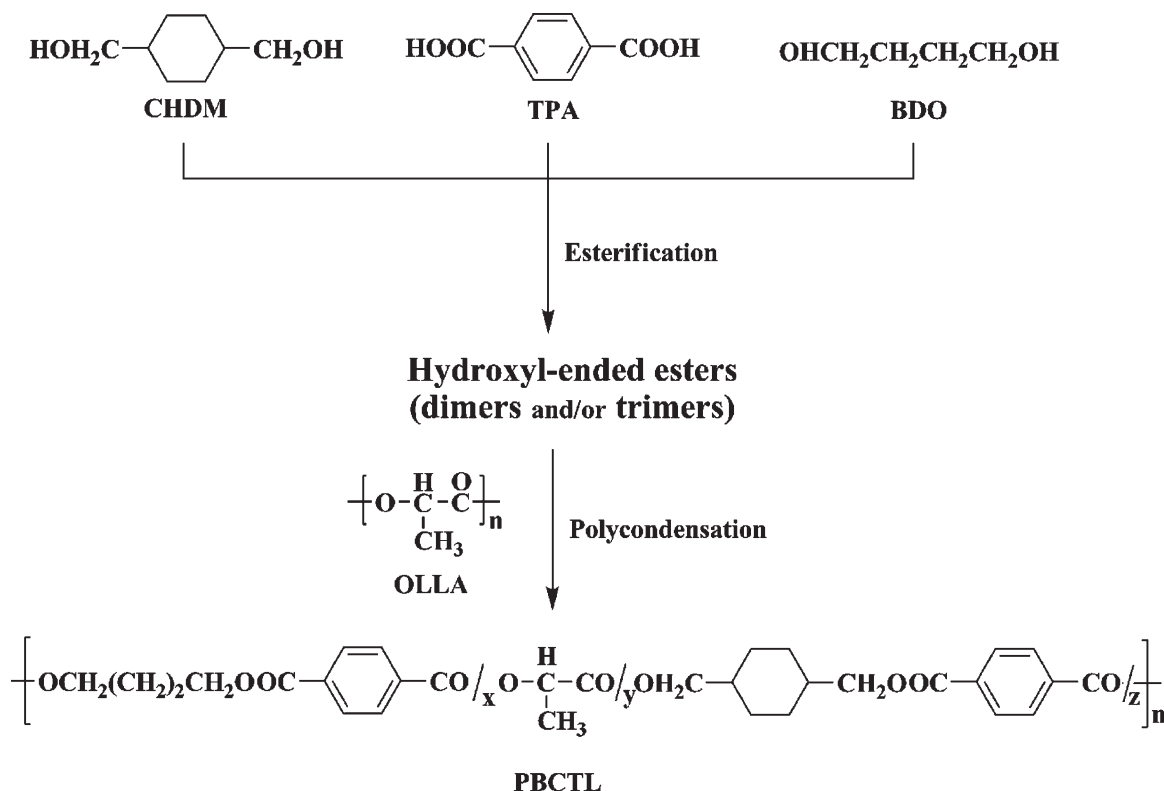
where  $W_r$  is the dry weight of the specimen after degradation and  $W_0$  is the initial weight of the specimen.

## RESULTS AND DISCUSSION

### Synthesis

As presented in Scheme 1, two-step direct melt polycondensation was used in this study to prepare the copolyesters. In the first stage, TPA and the mixtures of BDO and CHDM were esterified to form low-molecular-weight hydroxyl-ended esters. In fact, dimers and/or trimers were also expected to be formed. This process occurred at 200–230°C with the generation of water, which was continuously removed from the system to drive the reaction into the esters direction. The polycondensation of those hydroxyl-capped esters and OLLA took place in the second step at 230°C *in vacuo*. Because they had two different functional groups, lactate units could be built into the polyester chain during the reaction by transesterification, and the polycondensation between the terephthalate and lactate segments proceeded successfully. According to our previous study,<sup>23</sup> the optimal feed molar ratio of TPA to OLLA was 30/70; with this ratio we could obtain copolymers with good biodegradability and high mechanical properties. As listed in Table I,  $M_n$  and  $M_w$  were found to vary in the range of 25,000–45,600 and 48,600–89,400 g/mol, respectively, depending on the copolyester composition. With the increase in CHDM content, the molecular weights gradually became higher, and the highest  $M_w$  was 89,400 g/mol when the BDO/CHDM molar ratio was 95/5. This result implied that the reactivity of CHDM might have been higher than that of BDO. However, as more CHDM was added, a lower molecular weight was observed; this was attributed to the bulky cyclic structure of CHDM. With the rigid hexacyclic ring of CHDM in the backbones increasing, the molecular chain motion was hindered, and the reaction system became much more viscous; this prohibited small molecules, such as water or alcohols, from being extracted from the reaction. Thus, further polymerization was

T1



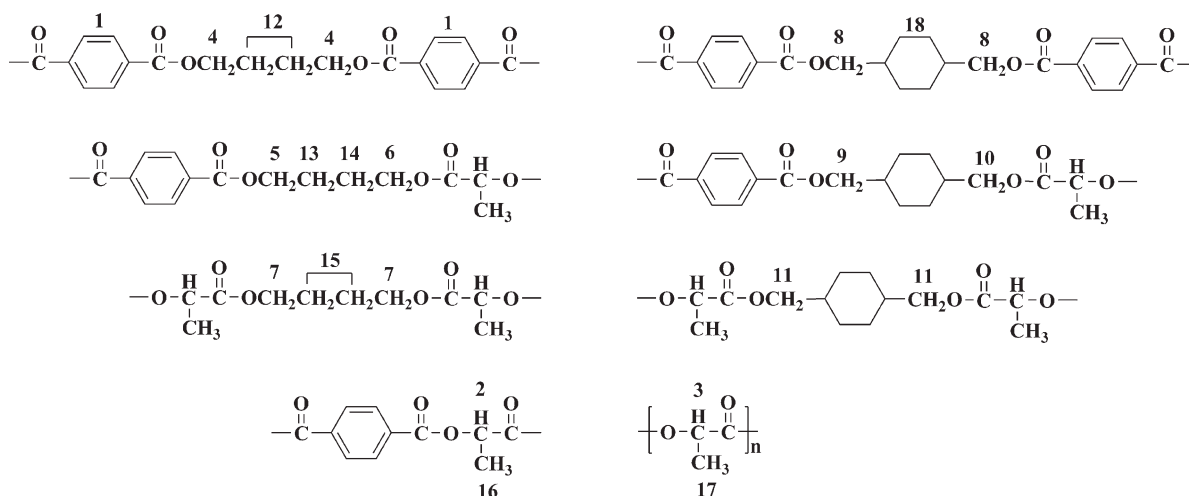
**Scheme 1** Synthetic route for the preparation of the degradable PBCTL copolyesters.

suppressed during the given polycondensation time. Such similar phenomena were also observed in a previously reported study.<sup>8</sup>

### Structural characterization

To verify the molecular structures and to determine the chemical compositions, all of the copolyesters were characterized by <sup>1</sup>H-NMR and FTIR spectroscopy. According to previous studies,<sup>8,20,21,26,28,29</sup> several probable existent segment units in the main

chains of PBCTLs are shown in Figure 1, and their corresponding characteristic peaks were assigned as shown in Figure 2, which presents a typical <sup>1</sup>H-NMR spectrum of the PBCTL-2 copolyester. The peaks centered at 8.10, 4.43, and 1.97 ppm were assigned to the protons (H<sup>1</sup>) of the benzene ring, OCH<sub>2</sub> (H<sup>4</sup>), and adjacent CH<sub>2</sub> (H<sup>12</sup>) of butylene terephthalate moiety, respectively, whereas the signals at 4.36–4.22 ppm corresponded to OCH<sub>2</sub> (H<sup>5,6,7</sup>) of butylenedioxy covalently linked to terephthalate and/or lactate. Lactate units had two characteristic peaks at 5.18 and 1.54



**Figure 1** Probable existent segment units in the main chains of the PBCTL copolyesters.

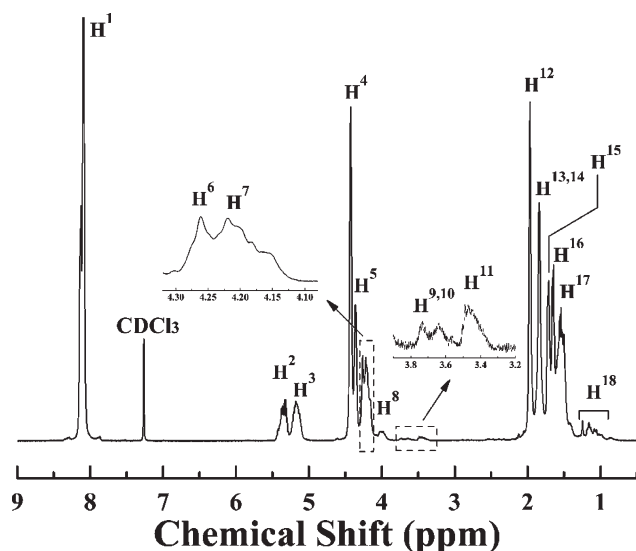


Figure 2  $^1\text{H-NMR}$  spectrum of the PBCTL-2 copolyester.

ppm, which were attributed to  $\text{CH}$  ( $\text{H}^3$ ) and  $\text{CH}_3$  ( $\text{H}^{17}$ ), respectively. Because of the conjugative effect of the benzene ring, the terephthalate ester group had a stronger electronegativity than the lactate ester group, so the multiplets around 5.34 and 1.65 ppm were attributed to  $\text{CH}$  ( $\text{H}^2$ ) and  $\text{CH}_3$  ( $\text{H}^{16}$ ) of lactate next to a terephthaloyl group. Moreover, the resonances at 4.01–3.48 ppm corresponded to  $\text{OCH}_2$  ( $\text{H}^{8-11}$ ) of cyclohexanedimethylenedioxy linked to terephthalate and/or lactate and the 1.25–0.99 ppm zone was assigned to the protons ( $\text{H}^{18}$ ) of the cyclohexyl ring. These clear differences in the chemical shifts were used to determine the chemical composition, calculate the average sequence length, and estimate the microstructure of the copolyesters. According to the integration of the characteristic peak areas of TPA ( $\text{H}^1$ ), OLLA ( $\text{H}^{2,3}$ ), BDO ( $\text{H}^{4-7}$ ), and CHDM ( $\text{H}^{8-11}$ ), we found that the composition of diol in the resulting copolyester was almost the same as that of the feed, whereas the final molar ratio of TPA to OLLA became higher because of the depolymerization of OLLA into lactide, which easily evaporated during the reaction (shown in Table I). The average sequence lengths of the aromatic butylene/cyclohexanedimethylene terephthalate ( $L_T$ ) unit and the aliphatic lactate ( $L_L$ ) unit were calculated according to the following equations:

$$L_T = \left( \frac{I_4 + I_8 + I_{5,6} + I_{9,10}}{I_{5,6} + I_{9,10}} + \frac{I_1}{I_{16/3}} \right) / 2 \quad (1)$$

$$L_L = \left( \frac{I_3 + (I_{5,6} + I_{9,10})/4}{(I_{5,6} + I_{9,10})/4} + \frac{I_2 + I_3}{I_{16/3}} \right) / 2 \quad (2)$$

where  $I_n$  represents the integrated intensities of the  $\text{H}^n$  resonances. The results, listed in Table I, indi-

cate that the copolymerization yielded statistical and random copolyesters.

The FTIR spectra of the PBCTLs were almost identical and differed only in relative signal intensities. As shown in Figure 3 for PBCTL-2, the strong and sharp absorption bands at 1752 and 1722  $\text{cm}^{-1}$  were attributed to the  $\text{C=O}$  stretching vibrations of aliphatic lactate and aromatic terephthalate moieties, respectively. The signals arising from the  $\text{C-O-C}$  stretching vibration of aromatic terephthalate ester appeared at 1270 and 1113  $\text{cm}^{-1}$ , and the peaks around 1200  $\text{cm}^{-1}$  belonged to  $\text{C-O-C}$  of the aliphatic lactate ester. Moreover, the characteristic bending vibration of  $\text{-CH}_2$  from the hexacyclic ring of the CHDM unit was located at 1456  $\text{cm}^{-1}$ , and the absorptions at 2931, 2858, and 728  $\text{cm}^{-1}$  were assigned to the asymmetric stretching vibration, symmetric stretching vibration, and bending vibration of  $\text{-CH}_2$ , respectively. The broad absorption band at about 3436  $\text{cm}^{-1}$  resulted from the end  $\text{-OH}$  group of the copolyesters. These analyses further affirmed that the copolycondensation of TPA, BDO, CHDM, and OLLA was successfully conducted to obtain random aliphatic/aromatic copolyesters in one aspect.

### Thermal properties

The thermal behaviors of the PBCTLs were characterized by means of DSC and TG, and the data are summarized in Table II. Figure 4 presents the DSC second heating curves of the PBCTLs at a rate of 10°C/min. The DSC results indicate that PBCTL copolyesters with less than 5 mol % CHDM were crystallizable, whereas those with 5 mol % or greater CHDM were amorphous. This phenomenon clearly demonstrated that the introduction of the bulky cyclic structure of CHDM into the polymer chains caused severe disruption in the crystalline regions

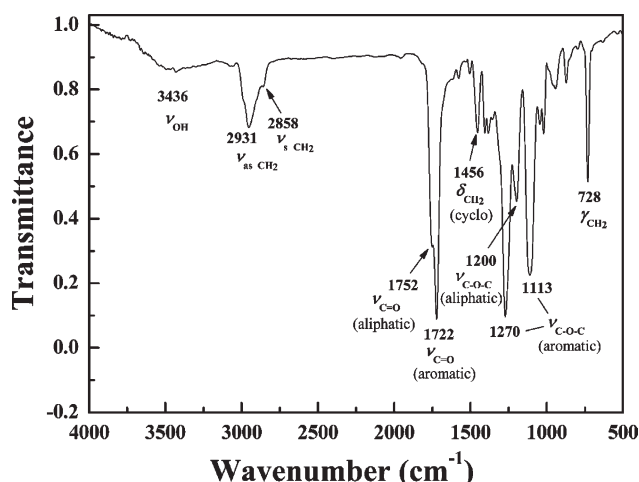


Figure 3 FTIR spectrum of the PBCTL-2 copolyester.

TABLE II  
Thermal Properties of the PBCTLs

Sample	DSC			TG		
	$T_g$ (°C)	Cold crystallization temperature (°C)	Melting temperature (°C)	$T_{\text{onset}}$ (°C) <sup>a</sup>	$T^{\text{max}}$ (°C) <sup>b</sup>	
					Stage 1	Stage 2
PBCTL-0	26.9	98.9	131.4	282.5	280.4	403.3
PBCTL-1	32.4	88.5	129.8	294.1	279.3	404.2
PBCTL-2	36.2	—	—	309.7	306.5	405.5
PBCTL-3	34.2	—	—	306.6	292.2	406.1
PBCTL-4	33.4	—	—	322.2	291.7	405.2

<sup>a</sup>  $T_{\text{onset}}$  denotes the temperature where the 5% weight loss occurred.

<sup>b</sup>  $T_{\text{max}}$  is the temperature where the maximal weight loss rate occurred.

and substantially influenced the melting temperature and crystallinity of the copolyesters. The introduction of the noncrystallizable comonomer units into the crystal structure produced some defects, which increased the crystal surface energy and reduced the melting point of the crystal.<sup>8,28</sup> DSC analysis also revealed that each copolyester exhibited only one glass-transition temperature ( $T_g$ ), which implied that the direct melt polycondensation of TPA, BDO, CHDM, and OLLA resulted in statistical copolyesters rather than physical blends. The data listed in Table II indicate that  $T_g$  increased steadily along the series with the content of CHDM units. The incorporation of CHDM units influenced the  $T_g$  values of the copolyesters, from 26.9°C for PBCTL-0 to 36.2°C for PBCTL-2. These results were consistent with those in the literature;<sup>8,29</sup> this further confirmed that the introduction of CHDM into the polyester restricted the mobility and increased the stiffness of the polymer chains. However, when the CHDM content exceeded 5 mol %, the  $T_g$  values decreased

slightly from 36.2°C for PBCTL-2 to 33.4°C for PBCTL-4. Such changes could be reasonably explained by the sharp drop in  $M_w$  from 89,400 g/mol for PBCTL-2 to 48,600 g/mol for PBCTL-4.

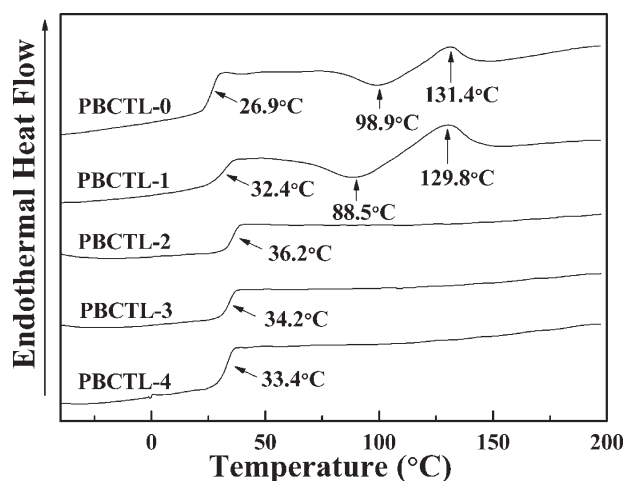


Figure 4 DSC second heating thermal diagrams of the PBCTL copolyesters.

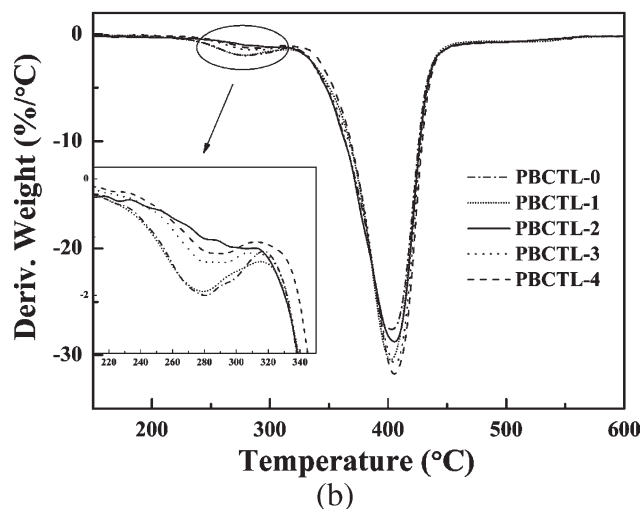
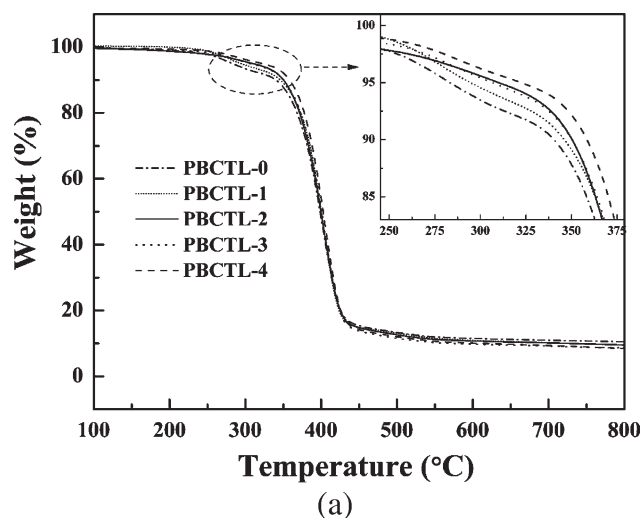


Figure 5 (a) TG and (b) differential TG curves for the PBCTL copolyesters in nitrogen.

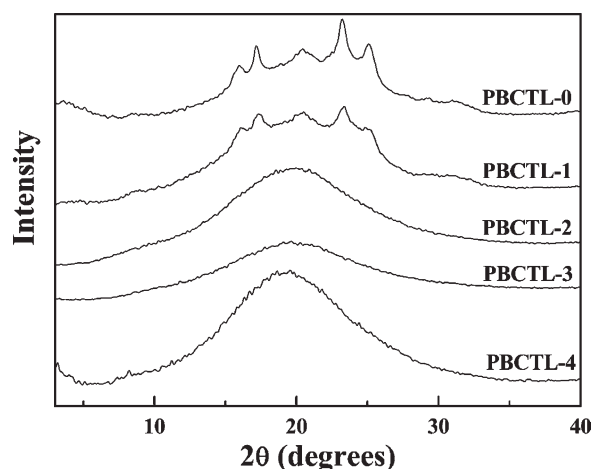


Figure 6 WAXD patterns of the PBCTL copolyesters.

Because of the incorporation of the thermally stable CHDM unit into the polyester chain, it was worth it to study the thermal stability of the synthesized copolyesters and to investigate the effect of the CHDM unit on the thermal properties of the PBCTLs. Figure 5 presents the TG and differential TG curves of the PBCTLs under a nitrogen atmosphere, and the results are collected in Table II. The onset decomposition temperatures ( $T_{\text{onset}}$ 's) of the copolyesters increased obviously from 294.1 to 322.2°C when the CHDM content increased from 2.5 to 10 mol % and were all higher than that of the copolyester without CHDM (282.5°C for PBCTL-0). So, we concluded that the addition of the thermally stable cyclic CHDM unit substantially improved the thermal stability of the copolyesters. Moreover, all of the samples exhibited two distinct thermal degradation steps. For PBCTL-2, the first weight loss step occurred at 306.5°C and was associated with the loss of relatively long lactate sequences in the copolyester, and the second step started at 405.5°C and was primarily due to the degradation of the copolyester chain. Such similar observations were also made in some previous studies.<sup>21,23</sup>

### X-ray diffraction patterns

Figure 6 shows the WAXD patterns of the PBCTLs. From WAXD analysis, PBCTL-0 and PBCTL-1 both showed sharp crystalline peaks, which occurred at  $2\theta$  values of 16.1, 17.3, 20.5, 23.2, and 25.1° and coincided with the characteristic peaks of PBT.<sup>30</sup> However, with increasing CHDM content, the crystalline structures of the PBCTLs were destroyed, and the arrangement of copolyester main chains became irregular because of the spatial effect and interference of the cyclic bulky CHDM unit; thus, the sharp peaks disappeared for the other samples. WAXD analysis and the absence of melting endothermic and cold-crystallization peaks in DSC both clearly indicated that the PBCTLs, except for PBCTL-0 and PBCTL-1, were essentially amorphous.

### Mechanical properties and dynamic viscoelasticity

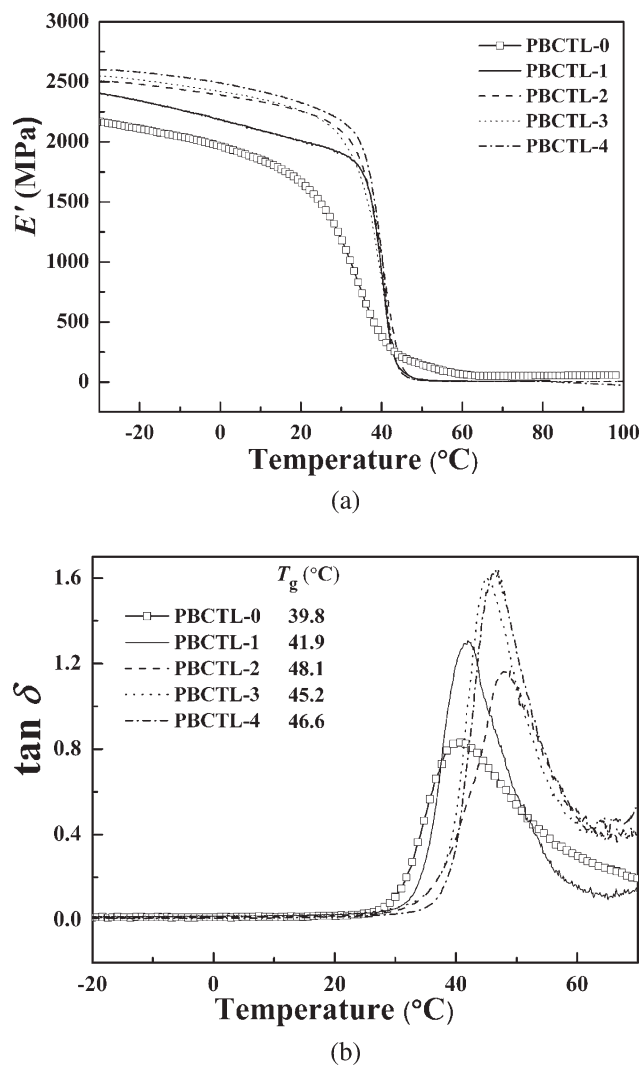
The effects of the rigid cyclic CHDM unit on the mechanical properties of PBCTLs were evaluated, and the data are summarized in Table III. There were many factors that could have affected the physical behaviors of the polymers, such as molecular weight, chemical composition, and crystallinity. PBCTL-0 and PBCTL-1 were both crystalline copolyesters and had similar molecular weights, so the chemical composition was the major factor influencing their mechanical properties. Because of the incorporation of the CHDM unit into the copolyester chain, a trend of increases in both the Young's modulus ( $E$ ) and tensile strength ( $\sigma$ ) was observed from 5.4 and 5.6 MPa for PBCTL-0 up to 54.6 and 11 MPa for PBCTL-1. This was because the cyclic bulky structure of CHDM was more rigid and stiffer than that of BDO; therefore, the replacement of part of BDO by CHDM made the molecular main chain become less flexible; this greatly improved  $\sigma$  and  $E$  of the copolyesters. As the CHDM units increased,  $E$  of the PBCTLs gradually increased to 480 MPa for PBCTL-4, which was nearly 90 times higher than that of PBCTL-0. Moreover,  $\sigma$  of PBCTLs exhibited an interesting tendency, first increasing to 19 MPa

TABLE III  
Dynamic Mechanical and Tensile Properties of the PBCTLs

Sample	$E'$ (MPa)			$T_g$ (°C) <sup>a</sup>	$E$ (MPa)	$\sigma$ (MPa)	$\epsilon$ (%)
	-30°C	0°C	30°C				
PBCTL-0	2168	1962	1179	39.8	5.6 ± 0.2	5.4 ± 0.1	180
PBCTL-1	2405	2183	1904	41.9	54.6 ± 5.1	11 ± 1.7	146
PBCTL-2	2505	2393	2090	48.1	350 ± 12.3	19 ± 1.6	120
PBCTL-3	2549	2421	2032	45.2	400 ± 15.8	18 ± 1.8	97
PBCTL-4	2601	2492	2177	46.6	480 ± 15.3	16 ± 2.1	90

<sup>a</sup> Measured at the maximal  $\tan \delta$ .

$\epsilon$  = elongation at break.



**Figure 7** Plots of (a)  $E'$  and (b)  $\tan \delta$  as a function of temperature for the PBCTL copolyesters.

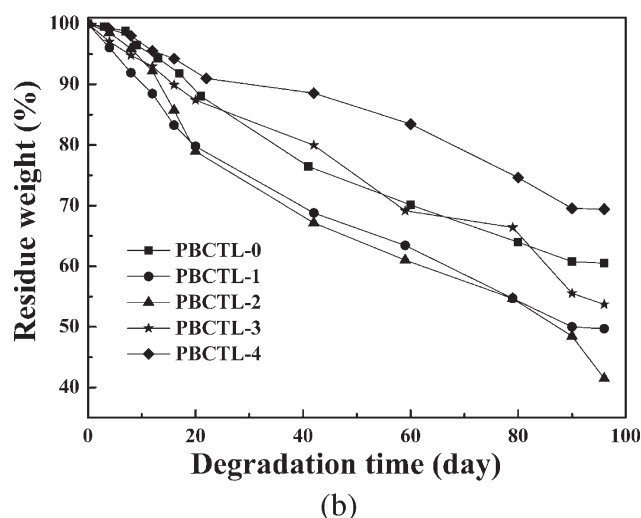
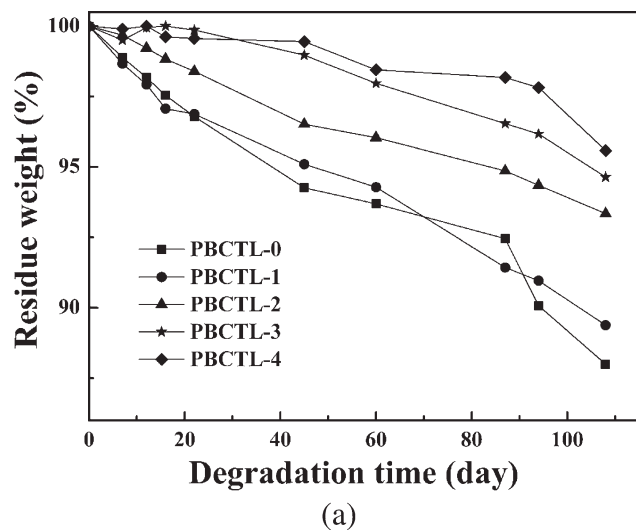
for PBCTL-2 and then declining to 16 MPa for PBCTL-4 with increasing CHDM content. The main reason was ascribed to the higher molecular weight of PBCTL-2 compared to the other samples. Therefore, the mechanical properties of the copolyesters were affected not only by the CHDM composition but also by the molecular weight.

Figure 7 presents the dynamic mechanical spectra [dynamic storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ )] as a function of temperature for the PBCTLs, and the data are shown in Table III. The results reveal that  $E'$  of the PBCTLs steadily increased with increasing CHDM content below  $T_g$ ; this indicated that the stiffness of the copolyesters was substantially improved with the incorporation of the rigid cyclic CHDM unit into the copolyester chains. For example,  $E'$  of PBCTL-4 was about 1.3 times higher than that of PBCTL-0 in the range below 0°C. With increasing temperature, the movement of polymer chain segments became easier, and at the temperature around

each of the  $T_g$ 's measured by DSC, the  $E'$  values fell drastically. All of the  $\tan \delta$  curves just showed one peak; this meant that there was only one  $T_g$  for the copolymers [Fig. 7(b)]. The  $T_g$  values in the  $\tan \delta$  curve shifted in the range from 39.8 to 48.1°C with increasing CHDM content; these were a little bit higher compared to those obtained by DSC measurement. Moreover, the maximal  $\tan \delta$  showed the degree of viscosity of the copolymer. With the rise of CHDM to 7.5 mol %, the  $\tan \delta$  at the maximum greatly increased, and a further increase in CHDM did not result in marked change of the  $\tan \delta$ .

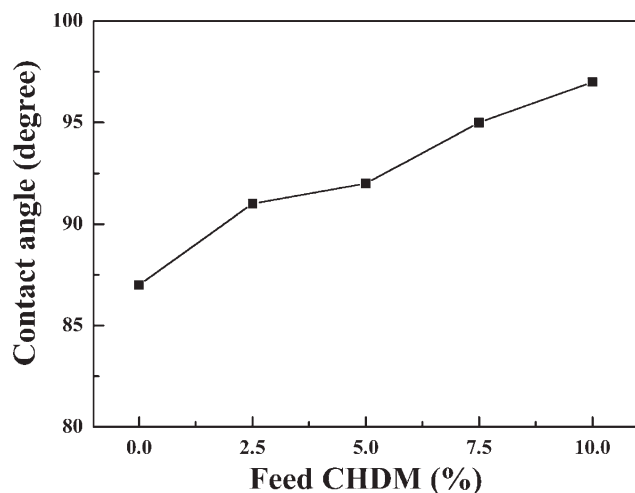
### Hydrolytic degradation of the copolyesters

The hydrolytic degradation behaviors of the PBCTLs were traced in PBS at two different temperatures (37 and 60°C), and the molecular weight of the residue



**Figure 8** Residue weight of the PBCTL copolyesters in PBS at (a) 37 and (b) 60°C as a function of the degradation time.

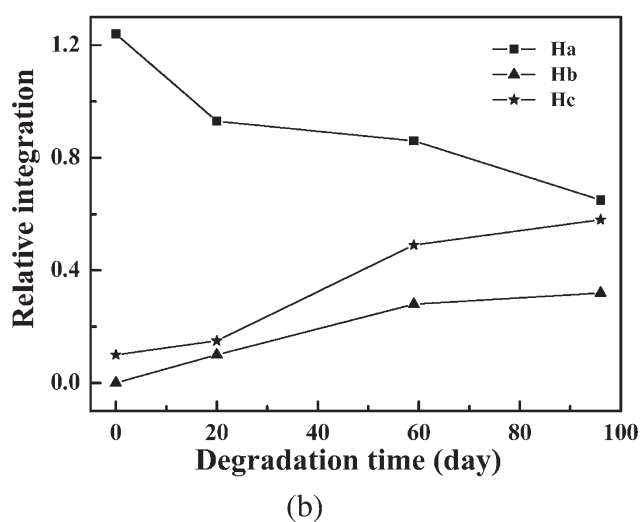
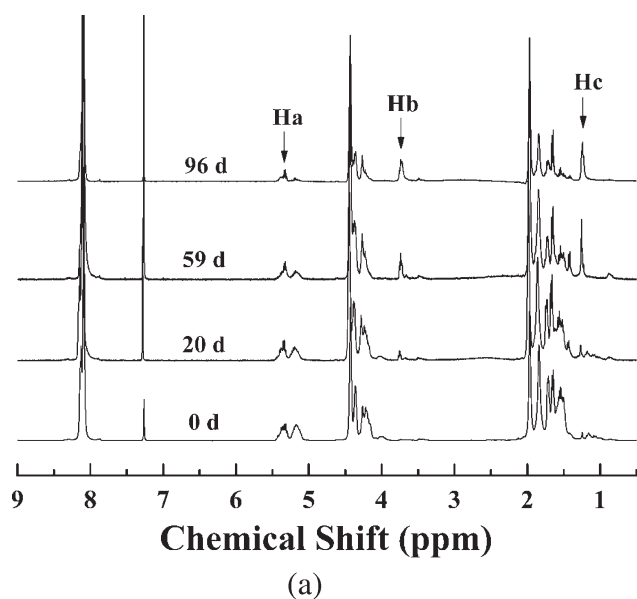




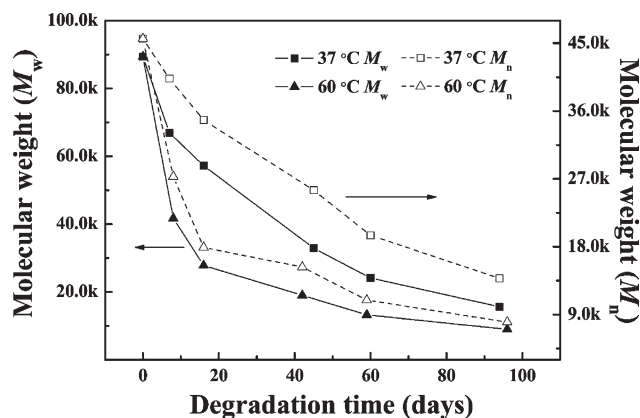
**Figure 9** Water contact angle of the PBCTL copolyesters as a function of the feed CHDM.

during the degradations was analyzed by GPC. Degradation was caused by the scission of hydrophilic ester linkages, followed by the subsequent reduction of molecular weight, to result in water-soluble oligomeric and/or monomeric products, which eventually caused weight loss in the samples.<sup>5,14,23</sup> As shown in Figure 8, all of the PBCTL samples underwent obvious degradation, although they had many aromatic units in their main chains. The degradability at 60°C was more remarkable than that at 37°C because the higher temperature favored the mobility of the amorphous phase and facilitated the hydrolysis of ester bonds. After 96 days in PBS at 60°C, residue weights of 60.5, 49.7, 41.5, 53.7, and 69.4% were observed for the PBCTLs. However, when these samples were immersed in PBS at 37°C for 108 days, relatively higher residue weights were obtained (88.0, 89.4, 93.3, 94.6, and 95.7%, respectively). The surface hydrophilicity of the polymers was an important factor affecting the degradation rate. Figure 9 shows the contact angle of water on the surface of each copolyester. With increasing CHDM content, the contact angle of water became appreciably higher; this indicated that CHDM units made the copolymer surface less hydrophilic. What is more, the degradation results also revealed a CHDM composition dependency (Fig. 8). With increasing CHDM composition, the degradation rate of the PBCTLs gradually slowed. This was because the incorporation of the rigid cyclic structure of CHDM into the macromolecular chain promoted the hydrophobic nature of these copolyesters; this negatively influenced the hydrolytic susceptibility by steric hindrance and made it difficult for the water to penetrate into the bulk of the copolymer so that hydrolysis was retarded to some extent.<sup>8</sup> Moreover, at low temperature (37°C), the degradation rate of PBCTL-0 was faster than that of PBCTL-2, whereas

at high temperature (60°C), the tendency was reverse: it became easier for PBCTL-2 to degrade, although CHDM units were contained in the macromolecular chains. The degradation performance of the polymers was affected by many factors, including the chemical structure, crystallinity, degradation environment, and so on. The cyclic structure of the CHDM unit in the copolyester chain was rigid and not easily degraded, but the introduction of these structures rendered the copolyester more amorphous and less resistant to hydrolytic attack. At 37°C, the effect of low crystallinity on the increasing hydrolytic degradation did not compensate for the effect of the bulky rigid cyclic structure of CHDM on the decrease in degradation. In contrast, at 60°C, the effect of the lower crystallinity overwhelmed the



**Figure 10** (a)  $^1\text{H-NMR}$  spectra of the PBCTL-2 copolyester after hydrolytic degradation. (b) Relative integration as a function of the degradation time for  $H_a$ ,  $H_b$ , and  $H_c$ .



**Figure 11** Molecular weight of the PBCTL-2 copolyester as a function of the degradation time in PBS.

other factors and dominated the hydrolysis rate of the copolyesters. Additionally, the lower  $T_g$  of PBCTL-2 (36.2°C) compared to the experimental temperature (60°C) also rendered the chain mobile and accelerated the degradation.<sup>5,8</sup>

To preliminarily analyze the degradation mechanisms of the synthesized copolyesters, the  $^1\text{H-NMR}$  spectra of PBCTL-2 with different degradation time are given in Figure 10(a). The signal ( $H_a$ ) at 5.18–5.34 ppm was assigned to the methine of lactate moieties, and the signals ( $H_b$  and  $H_c$ ) corresponding to the  $-\text{CH}_2\text{OH}$  end groups and methyl chain units produced by degradation were located at 3.74 and 1.25 ppm, respectively. On the basis of the supposition that the integration of the peak at 8.10 ppm corresponding to aromatic protons was 4, the relative integrations of  $H_a$ ,  $H_b$ , and  $H_c$  were calculated, and their values during the degradation are shown in Figure 10(b). The results clearly demonstrate that with increasing degradation time, the relative integration of lactate moieties ( $H_a$ ) became weaker, whereas that of  $H_b$  and  $H_c$  became stronger compared to the terephthalate moieties. This meant that the lactate moieties of the copolyester degraded first so that the main long chains were broken to form oligomers or some small molecules. Such similar observations were also found in some previous studies.<sup>5,14,31</sup> The molecular weight of PBCTL-2 as the representative sample after degradation was determined by means of GPC (presented in Fig. 11). During the hydrolytic degradation, a drastic drop in the molecular weight, up to 75% of the initial value, was observed both at 37 and 60°C in PBS. This remarkable decrease in  $M_w$  ( $M_n$ ) and the large weight loss during the degradation, as discussed, suggested that the high-molecular-weight copolyester was converted to low-molecular-weight polymers and underwent significant bulk degradation because of the cleavage of ester linkages in the main chains. In conclusion, our synthesized copolyesters

could be degraded and used as potential environmentally friendly materials in the future.

## CONCLUSIONS

High-molecular-weight PBT-based degradable aliphatic/aromatic copolyesters containing PLLA segments and various amounts of CHDM units were successfully synthesized via direct melt polycondensation. When the CHDM composition was 5 mol %, the  $M_w$  of the copolyester was highest, up to 89,400 g/mol. The  $^1\text{H-NMR}$  results indicate that the copolyesters had a random chain structure, which would be favored for hydrolytic degradation. DSC analysis revealed that the  $T_g$  values varied in the range 26.9–36.2°C, and the copolyesters were amorphous when the CHDM composition was 5 mol % or greater. Moreover, with increasing CHDM content, the thermal stabilities and mechanical properties of the copolyesters were drastically enhanced. The  $T_{\text{onset}}$ ,  $E'$ , and  $\sigma$  values of the PBCTLs substantially improved from 282.5°C, 5.6 MPa, and 5.4 MPa to 322.2°C, 480 MPa, and 19 MPa, respectively. The hydrolytic degradation results in PBS clearly demonstrate that all of the copolyesters underwent obvious degradation and the degradation rate primarily depended on the CHDM content and hydrolytic degradation temperature.

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