

Composition, Thermal Properties, and Biodegradability of a New Biodegradable Aliphatic/Aromatic Copolyester

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Received 17 November 2008; accepted 25 January 2009

DOI 10.1002/app.30127

Published online 2 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of new aliphatic/aromatic copolyesters [poly(hexylene terephthalate-co-hexylene adipate) (PHTA)] were synthesized on the bases of 1,6-hexanediol, adipic acid, and dimethyl terephthalate and characterized by gel permeation chromatography, ¹H-NMR, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and compost testing. ¹H-NMR results show that the compositions of the copolyesters were in accordance with the feed molar ratios. The WAXD patterns indicated that the crystal structures of the PHTA copolyesters were determined by the dominant crystal units, and the copolyesters became less crystallizable, even amorphous, with increasing comonomer content. The DSC curves showed that the glass-transition temperatures (T_g 's) of the PHTA copolyesters decreased linearly, and both the melting temperature (T_m) and heat of fusion decreased first

and then increased with increasing hexylene adipate unit content. Under compost conditions, PHTA copolyesters with less than 60 mol % aromatic units were biodegradable. Particularly, compared with the copolyester poly(butylene terephthalate-co-butylene adipate), the PHTA copolyester with the same aliphatic/aromatic composition possessed a lower T_g and T_m and better biodegradability. Additionally, the biodegradability of the copolyesters could be predicted by the number-average sequence length of aromatic units, T_g , and the temperature difference between T_m and the temperature at which biodegradation took place. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1298–1306, 2009

Key words: biodegradable; crystal structures; thermal properties

INTRODUCTION

Nowadays, there is increasing interest in the study of biodegradable polymeric materials because conventional plastics cause serious environmental pollution. Some fully biodegradable polymers, such as poly(ϵ -caprolactone), poly(hydroxyl butyrate), poly(L-lactic acid), and poly(1,4-butanediol succinate), have been developed for commercial use and partially solve the problem of plastic waste accumulation.¹ However, the commercial applications of these aliphatic biodegradable polyesters are limited because of their high cost and relatively poor physical properties. Therefore, modifications of aliphatic polyesters have recently attracted attention. Witt et al.⁸ reported that the aliphatic/aromatic poly(butylene terephthalate-co-butylene adipate) (PBTA) copolyester was biodegradable, even though the content of aromatic units was up to 60 mol %. Consequently, aliphatic polyesters were copolymerized with aromatic polyesters to improve their properties because aromatic polyesters [e.g., poly(butylene ter-

ephthalate) (PBT) and poly(ethylene terephthalate) (PET)] have excellent mechanical properties and can be produced at low cost but are resistant to microbial attack. Park and Cho³ prepared a type of biodegradable copolyester, poly[(butylene succinate-co-butylene terephthalate)-*b*-poly(tetramethylene glycol)], which improved the elongation properties and the elasticity of aliphatic polyesters. Witt et al.⁴ also prepared a biodegradable copolyester composed of 1,3-propane diol and adipate acid or sebacic acid and terephthalic acid as a comonomer. Deng et al.⁵ prepared a biodegradable copolyester, poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate), with much better thermal properties than the aliphatic copolyester poly(butylene succinate-co-ethylene succinate). Kang and Park⁶ prepared a biodegradable copolyester, poly(butylene adipate-co-succinate)/PBT, and studied its thermal and mechanical properties, crystallization behavior, and biodegradability. The international organization BASF has already commercialized a biodegradable copolyester, PBTA, named *Ecoflex*. This copolyester overcomes some disadvantages of many aliphatic polyesters and is fully biodegradable.⁷ Eastman Chemicals Co. has developed a series of copolyester products (named *Eastar Bio*) based on PET,

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cyclohexanedimethanol, and *i*-phthalic acid. Biomax of Dupont, a copolyester based on PET and aliphatic monomers, has also been commercialized.² However, biodegradable aliphatic/aromatic copolyesters with better biodegradabilities are still anticipated.

In this study, a new type of biodegradable aliphatic/aromatic copolyesters, poly(hexylene terephthalate-*co*-hexylene adipate) (PHTA), based on 1,6-hexanediol (HDO), adipic acid (ADP), and dimethyl terephthalate (DMT) was synthesized with different compositions. The nature of the copolyesters with different compositions was studied by ¹H-NMR, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and compost testing. Compared with poly(butylene terephthalate-*co*-butylene adipate) (PBTA) synthesized with 1,4-butanediol (BDO), ADP, and DMT, the new PHTA copolyester had a lower glass-transition temperature (T_g) and melting temperature (T_m) and better biodegradability.

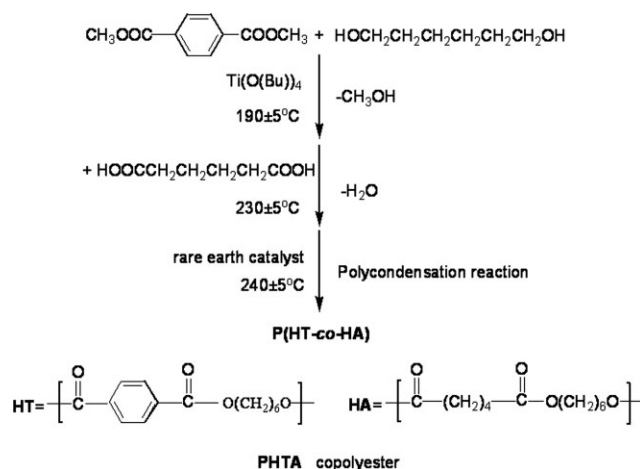
EXPERIMENTAL

Materials

DMT [chemical pure (CP) grade] was purchased from Beijing Xingjin Works (Beijing, China). ADP [analytical reagent (AR) grade] was supplied from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). HDO (AR grade) was provided by J&K Chemical Co., Ltd. (Beijing, China). BDO (AR grade) was purchased from Beijing Yili Fine Chemical Co., Ltd. (Beijing, China). Tetrabutyl orthotitanate [Ti(OBu)₄; CP grade] was obtained from Beijing Chemical Reagents Corp. (Beijing, China). All chemicals (AR grade or CP grade) were used without further purification.

Synthesis of the aliphatic/aromatic copolyesters

The poly(hexylene terephthalate) (PHT) and poly(hexylene adipate) (PHA) homopolyesters and PHTA copolyesters were prepared by the melting polycondensation of HDO with DMT and/or ADP. The PBTA copolyesters were prepared with BDO, DMT, and ADP. Ti(OBu)₄ and lanthanide acetylacetonate were used as catalysts (the preparation of lanthanide acetylacetonate was reported previously⁹). In all cases, the molar ratio of the diesters mixture and diol was fixed at 1 : 1.2. A typical polycondensation procedure was as follows: a suitable amount of DMT, HDO (or BDO), and Ti(OBu)₄ were charged into a 500-mL, three-necked flask under a nitrogen atmosphere, heated, and stirred; this was followed by a reaction at 190 ± 5°C for several hours, which ensured that more than 90% of the theoretical amount of methanol was removed. ADP was added to the reaction mixture, and the temperature was



Scheme 1 Synthetic route of the PHTA copolyesters.

raised to 230 ± 5°C under a constant nitrogen flow until more than 90% of the theoretical water was distilled off. Another catalyst, lanthanide acetylacetonate, was added to the reaction system at this time. A vacuum was then slowly applied, and the reaction temperature was raised to 240 ± 5°C. Excess HDO (or BDO) was distilled off in this period. High vacuum (< 90 Pa) was applied afterward until the end of the reaction. The synthetic route of the PHTA copolyesters is displayed in Scheme 1.

Measurements

Gel permeation chromatography (GPC)

The molecular weight of the copolyesters was measured on a Waters 208 gel permeation chromatograph. Tetrahydrofuran (THF) (Milford, MA) was used as an eluent at a flow rate of 1.5 mL/min at 30°C. Polystyrene standards were used to make a universal calibration curve.

¹H-NMR

The structure of the copolyesters was determined by ¹H-NMR (Karlsruhe, Germany) (500 MHz, CDCl₃, δ, ppm) with a Bruker Avance DMX500 instrument with tetramethylsilane (Me₄Si) as an inner standard.

WAXD

WAXD (Eindhoven, Netherlands) was obtained with a Philips X'Pert-MPD diffractometer (Cu Kα, λ = 1.54056 Å, graphite crystal filter, 40 kV, 40 mA).

DSC

The T_g , T_m , and heat of fusion (ΔH_m) values were analyzed with a Perkin-Elmer (Waltham, MA) differential scanning calorimeter. The samples were heated

TABLE I
Molecular Weights and Polydispersities of the PHTA and PBTA Copolyesters

DMT/ADP feed molar ratio	Sample	$M_w \times 10^4$	M_w/M_n	Sample	$M_w \times 10^4$	M_w/M_n
100/0	PHT	N/A	N/A	PBT	N/A	N/A
90/10	PHTA10	N/A	N/A	PBTA10	N/A	N/A
80/20	PHTA20	4.4	1.9	PBTA20	N/A	N/A
70/30	PHTA30	6.1	2.2	PBTA30	N/A	N/A
60/40	PHTA40	7.0	2.8	PBTA40	4.0	1.9
50/50	PHTA50	5.0	2.7	PBTA50	7.4	1.9
40/60	PHTA60	5.3	2.3	PBTA60	9.0	2.1
30/70	PHTA70	5.6	2.3	PBTA70	5.0	2.0
20/80	PHTA80	4.4	2.0	PBTA80	6.8	2.0
10/90	PHTA90	5.2	2.2	PBTA90	6.4	2.0
0/100	PHA	4.7	2.8	PBA	5.9	1.9

M_n = number-average molecular weight; N/A = not available by GPC because the samples could not be dissolved in the THF solvent.

from -150 to 200°C at a scanning rate of $20^\circ\text{C}/\text{min}$. T_g , T_m , and ΔH_m were gained from endothermic curves.

Biodegradability under compost conditions

A biodegradability test through composting was carried out. Samples were pressed into films with 0.2 ± 0.02 mm thickness and then were cut to a size of 20×20 mm². Specimens were incubated by composting in a $55 \pm 2^\circ\text{C}$ chamber, and the humidity was kept $60 \pm 5\%$. The samples were removed at various times, rinsed with ethanol, dried, and weighed. The biodegradation rate was determined by the weight loss (wt %).¹⁰

RESULTS AND DISCUSSION

Molecular structures and compositions of the PHTA copolyesters and comparison with PBTA

The molecular weights and polydispersities of the PHTA and PBTA copolyesters are listed in Table I. The weight-average molecular weights (M_w 's) and polydispersities of the PHTA copolyesters ranged from 4.4×10^4 to 7.0×10^4 and 1.9–2.8, respectively, whereas, those of the PBTA copolyesters were 4.0×10^4 to 9.0×10^4 and 1.9–2.1, respectively. Both copolyesters had a similar range of molecular weights. The lower molecular weight contributed to the biodegradability of the polymers. For example, polyethylene, which is resistant to microbial attack, becomes biodegradable at a molecular weight below 500. When its molecular weight exceeds a critical value (ca. 4.0×10^4), its influence becomes small.^{11,12} Thus, the influence of molecular weight on the biodegradability was not considered to be the main factor for the PBTA and PHTA copolyesters because of their high molecular weights.

The ¹H-NMR spectra of PHTA50 (where the number refers to the percentage of ADP in the sample), PHT, and PHA are shown in Figure 1, and the corresponding resonance peaks of different protons are pointed out in Scheme 2, which exhibits three

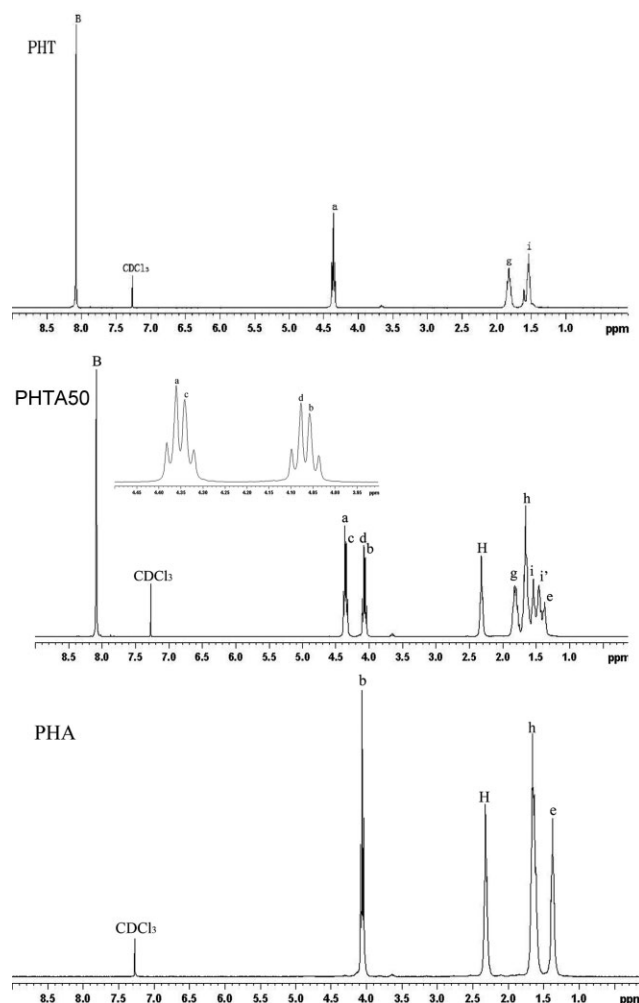
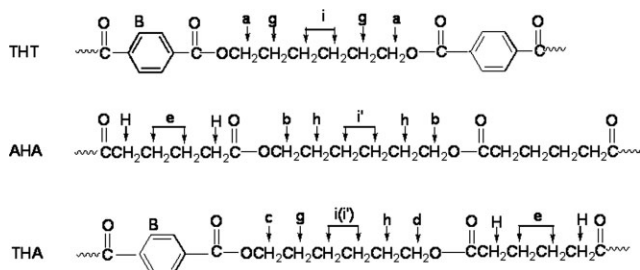


Figure 1 ¹H-NMR spectra of PHT, PHTA50, and PHA.



Scheme 2 Three possible sequences of the PHTA copolyesters. THT, aromatic segment of PHTA copolyester; AHA, aliphatic segment of PHTA copolyester; THA, aliphatic/aromatic segment of PHTA copolyester.

possible sequences of the PHTA copolyesters.¹³ As expected, the polycondensation of the three monomers generated some new chemical bonds, which were completely different from their parent homopolyesters PHA and PHT. For example, methylene protons (c: $\delta = 4.34$ ppm and d: $\delta = 4.08$ ppm) only appeared in the PHTA copolyesters but not in the PHT and PHA homopolyesters. These additional characteristic peaks confirmed that the copolymerization occurred precisely as predicted.^{14,15} Furthermore, the protons of $-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-$ in the aliphatic segments (H; the integrated intensity of the aliphatic segments is abbreviated as I_H) and of $-\text{C}_6\text{H}_4-$ in the aromatic segments (B; the integrated intensity of the aromatic segments is abbreviated as I_B) were at 2.32 and 8.09 ppm, respectively. The molar fractions of the hexylene terephthalate (HT) and hexylene adipate (HA) units of the PHTA copolyesters could be calculated by eq. (1). The splitting of the resonance peaks at 4.32–4.38 ppm (a and c) and 4.03–4.10 ppm (d and b) originated from the methylene protons in HDO attached

to the HT and HA moieties, respectively. Their corresponding integrated intensities are abbreviated as I_a , I_c , I_d , and I_b . According to the integrated intensities of different characteristic peaks, the number-average sequence lengths of the HA units (L_{HA}), HT units (L_{HT}), butylene adipate units (L_{BA}), and butylene terephthalate units (L_{BT}) in the PBTA copolyesters could be obtained by eq. (2). The degree of randomness (R) was determined by eq. (3).¹⁶ All data are listed in Table II.

$$x_{\text{HT}} = \frac{I_B}{I_B + I_H} \quad x_{\text{HA}} = \frac{I_H}{I_B + I_H} \quad (1)$$

$$L_{\text{HT}} = \frac{I_a + I_c}{I_c} \quad L_{\text{HA}} = \frac{I_d + I_b}{I_d} \quad (2)$$

$$R = \frac{1}{L_{\text{HT}}} + \frac{1}{L_{\text{HA}}} \quad (3)$$

As shown in Table II, the compositions of all of the PHTA copolyesters were almost consistent with the feed molar ratios, except for a small deviation of HA content due to the volatilization of HDO, which indicated that the composition of the copolyester could be simply controlled by an adjustment of the feed molar ratio. This also allows for the preparation the copolyesters with different properties that are closely related to the compositions.

The distribution of aromatic and aliphatic segments in the main chain could be denoted by L_{HT} and L_{HA} . With increasing aromatic unit (HT) content, L_{HT} of the PHTA copolyesters increased, whereas L_{HA} decreased. When the HT unit content was greater than 60 mol %, L_{HT} was larger than 3. Generally, copolyesters are biodegradable when

TABLE II
Composition, Number-Average Sequence Length, and R Values of the PHTA and PBTA Copolyesters

Sample	Composition (mol %)		L_{HT}	L_{HA}	R	Sample	Composition (mol %)		L_{BT}	L_{BA}	R
	x_{HT}	x_{HA}					x_{BT}	x_{BA}			
PHA	0	100	—	—	—	PBA	0	100	—	—	—
PHTA90	10.7	89.3	1.13	7.62	1.02	PBTA90	10.1	89.9	1.13	7.40	1.02
PHTA80	22.2	77.8	1.30	4.15	1.01	PBTA80	22.2	77.8	1.55	6.68	1.05
PHTA70	33.6	66.4	1.37	3.37	1.03	PBTA70	30.0	70.0	1.83	5.31	1.02
PHTA60	42.2	57.8	1.63	2.41	1.03	PBTA60	40.9	59.1	2.41	3.62	1.02
PHTA50	56.2	43.8	2.07	1.86	1.02	PBTA50	51.2	48.8	3.13	2.73	1.02
PHTA40	66.5	33.5	2.58	1.58	1.02	PBTA40	61.0	39.0	3.87	2.20	1.04
PHTA30	73.5	26.5	5.07	1.23	1.01	PBTA30	71.0	29.0	5.30	1.79	1.03
PHTA20	82.3	17.7	6.10	1.27	1.03	PBTA20	—	—	—	—	—
PHTA10	91.3	8.7	7.25	1.14	1.02	PBTA10	—	—	—	—	—
PHT	100	0	—	—	—	PBT	100	0	—	—	—

An em dash indicates that the data were not available by $^1\text{H-NMR}$ because the samples could not be dissolved in the CDCl_3 solvent.

x_{HT} , the molar fraction of hexylene terephthalate units of the PHTA copolyester; x_{HA} , the molar fraction of hexylene adipate units of the PHTA copolyester; x_{BT} , the molar fraction of butylene terephthalate units of the PBTA copolyester; x_{BA} , the molar fraction of butylene adipate units of the PBTA copolyester.

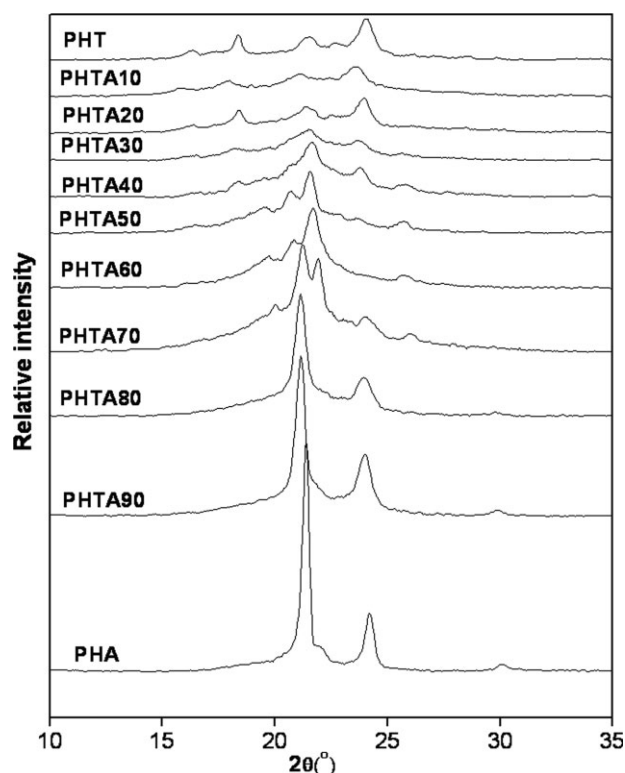


Figure 2 WAXD patterns of PHTA copolyesters with different compositions.

either their number-average sequence length of aromatic units is less than three or their number-average sequence length of aromatic units is more than three but their aromatic unit content is below 9 mol %.^{7,17} That is, biodegradation could not occur in PHTA30, PHTA20, PHTA10, and PHT because of their longer aromatic sequence lengths. In terms of the PBTA copolyesters, L_{BT} of PBTA was larger than three when the butylene terephthalate unit content was more than 40 mol %. It is clear that the PHTA with the same composition as PBTA had a shorter aromatic sequence length, which led to better biodegradability. This also means that, with similar biodegradability to PBTA, PHTA may contain more aromatic units, which potentially reduces the cost.

R can also reflect the distribution of segments in the main chain of copolyesters. For a fully random copolymer, R is equal to 1. For an alternative copolymer, R is equal to 2, whereas, a block copolymer has an R score close to 0.¹⁸ Table II shows that the R scores of the PHTA and PBTA copolyesters were close to 1; this indicates that their sequence distribution was nearly random, which was beneficial to biodegradation because of a lower crystallinity.¹

Solid-state structure and thermal properties

Figure 2 depicts the WAXD patterns of the PHTA copolyesters and the PHT and PHA homopolyesters.

It is clear that the PHA homopolyester had two sharp diffraction peaks, whereas PHT had several small sharp diffraction peaks. This was possible because of the flexibility of the main chain of PHA (i.e., it was easy to arrange orderly to form the crystalline). In addition, PHTA90 and PHTA80 had identical diffraction peaks as PHA, which demonstrated that their crystal structure came from the PHA homopolyester. However, the intensity of diffraction peaks decreased and the breadth became broader with increasing HT unit content, which indicated a decrease in the relative proportion of the crystal phase to the amorphous phase. This was due not only to the decrease in the length of crystallizable homopolymer sequence to decrease the crystallinity of the copolyesters but also to the fact that the incorporated comonomer units were seen as impurities that disturbed the crystallinity.^{2,15} PHTA20 and PHTA10 also showed the same diffraction peaks as PHT. With the enhancement in HA unit content, however, the intensity of these peaks declined and the breadth became broader. It is clear that the copolymer diffraction patterns were determined by the dominant crystal units, but the copolyesters became less crystallizable, even amorphous, with increasing comonomer content. Moreover, the diffraction peaks of PHTA70, PHTA60, PHTA50, and PHTA40 showed a transitional state from PHA to PHT, and a new diffraction peak at 21.90° (2θ) appeared, which indicated the generation of some new orders. However, PHTA30 almost showed an amorphous state.

The DSC curves of the PHTA copolyesters are shown in Figure 3, from which the T_m values and ΔH_m can be obtained. Compared with homopolyesters, the melting peaks of the PHTA copolyesters became broader, and the intensity decreased with

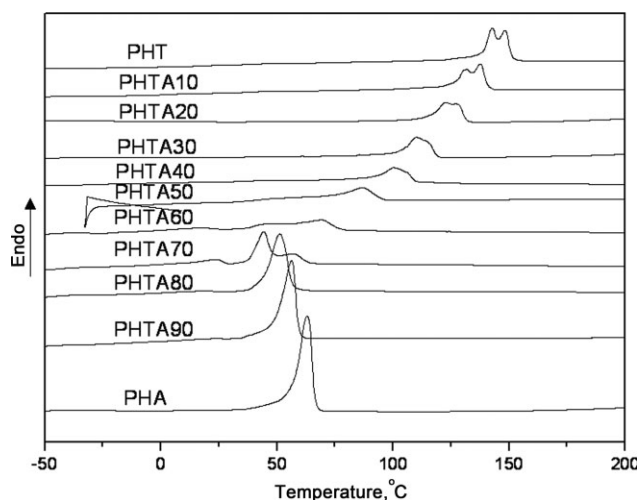


Figure 3 DSC curves of PHTA copolyesters with different compositions.

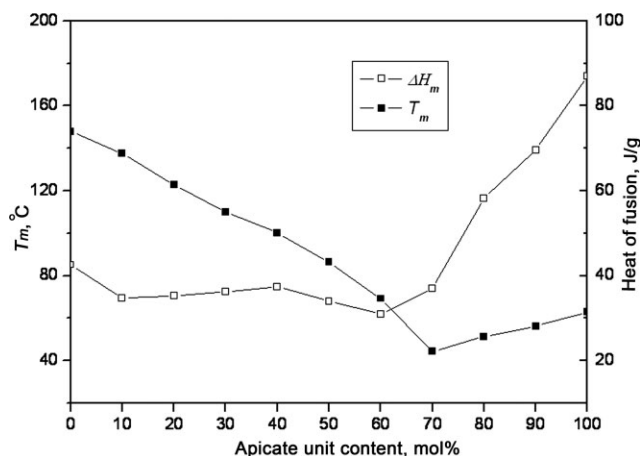


Figure 4 Variation of T_m and ΔH_m with HA molar percentage in the PHTA copolyesters.

increasing comonomer content. This was attributed to the fact that incorporating comonomer units into the main chain led to the formation of imperfect crystals, which made the melting range gradually become broader. The variation of the T_m and ΔH_m values with different HA unit contents in the PHTA copolyesters is displayed in Figure 4. T_m declined greatly with increasing HA unit content from the PHT homopolymer (147.9°C) up to a T_m of 44.4°C (PHTA70), followed by a further enhancement to the PHA homopolymer (63.0°C). The variation of T_m with composition could be predicted by eq. (4):

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{(\Delta H_m)_u} \times x_B \quad (4)$$

where T_m is the melting temperature of the copolyesters, T_m^0 is the corresponding homopolymer equilibrium melting temperature (PHT or PHA here), R is the universal gas constant, x_B is the molar fraction

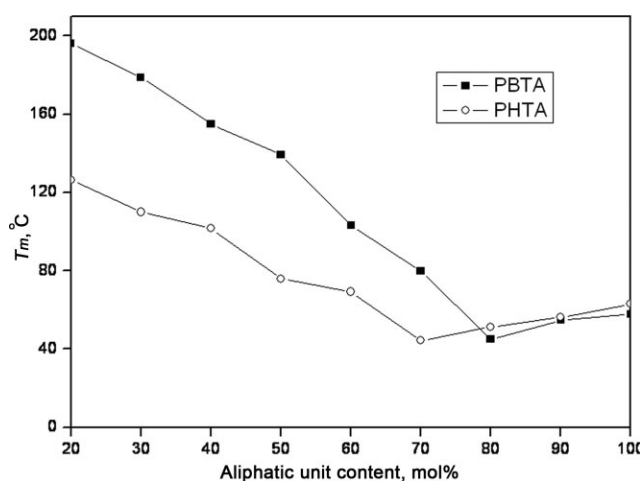


Figure 5 Comparison of the T_m values between the PHTA and PBTA copolyesters.

of the major comonomer B unit in the copolymer, and $(\Delta H_m)_u$ is the fusing heat of the homopolymer per molar repeat units.^{5,19} Furthermore, the variation in the ΔH_m values of the PHTA copolyesters with composition showed a similar tendency to that of T_m , which demonstrated that the incorporated comonomer units into the main chain weakened the crystallinity of the copolyesters.

As shown in Figure 5, the T_m values of the PBTA copolyesters were higher than those of PHTA with less than 70 mol % aliphatic unit content; however, the T_m values of the PBTA copolyesters became a little lower than those of PHTA when the aliphatic unit content exceeded 70 mol %. It is clear that a longer aliphatic unit segment in the main chain contributed greatly to the decrease of T_m when the aromatic unit content was dominant in the copolyesters. However, when aliphatic unit content was more than 70 mol %, the influence of the aliphatic unit length on T_m was negligible.

Also, the difference (ΔT_{mt}) between T_m and the temperature at which the degradation occurred (T_t) could be used to predict the biodegradability of copolyester [eq. (5)]. This was because T_m is a characteristic of polymer chains to temporarily leave their stringent order in the polymer crystals and T_t is associated with the ability of polymer chains to penetrate temporarily into microorganisms to biodegrade:²⁰

$$\Delta T_{mt} = |T_m - T_t| \quad (5)$$

where ΔT_{mt} is a measure of chain mobility of the copolyesters. The smaller the ΔT_{mt} is, the better the biodegradability is. Figure 6 describes the relationship between the biodegradability of the two copolyesters and ΔT_{mt} . The biodegradability of the

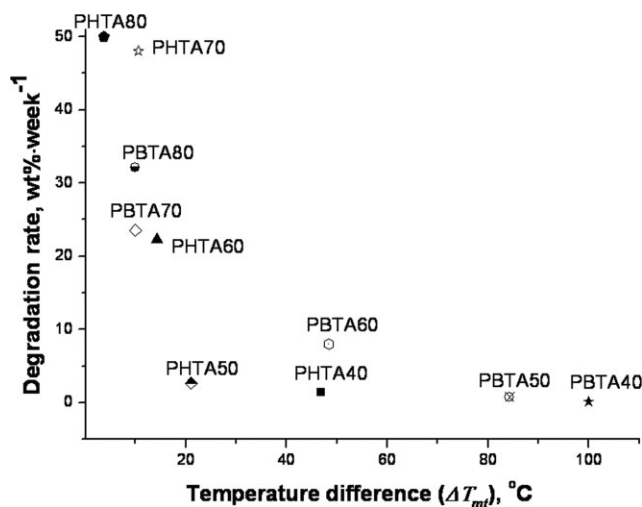


Figure 6 Relationship between the biodegradabilities of the PHTA and PBTA copolyesters and ΔT_{mt} .

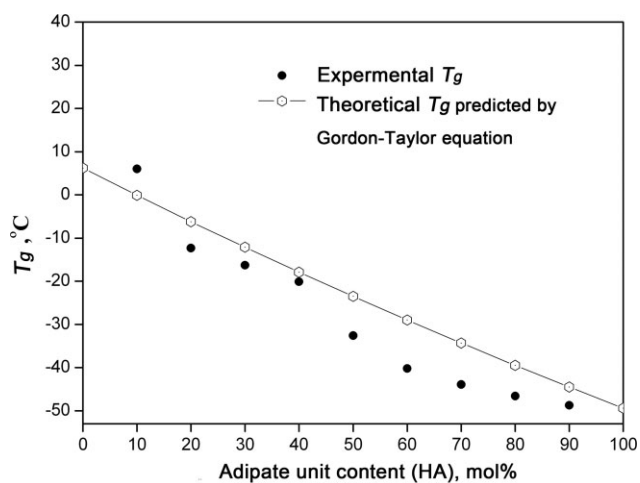


Figure 7 Variation of the T_g values of the PHTA copolyesters with HA molar percentage and the theoretical T_g values predicted by the Gordon–Taylor equation.

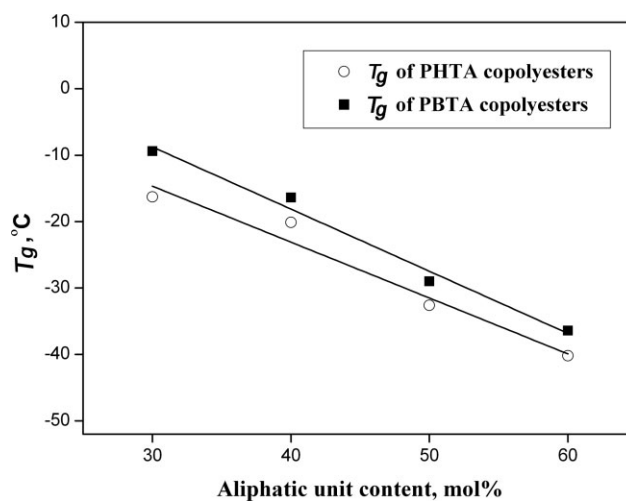


Figure 8 Comparison of the T_g values between the PHTA and PBTA copolyesters.

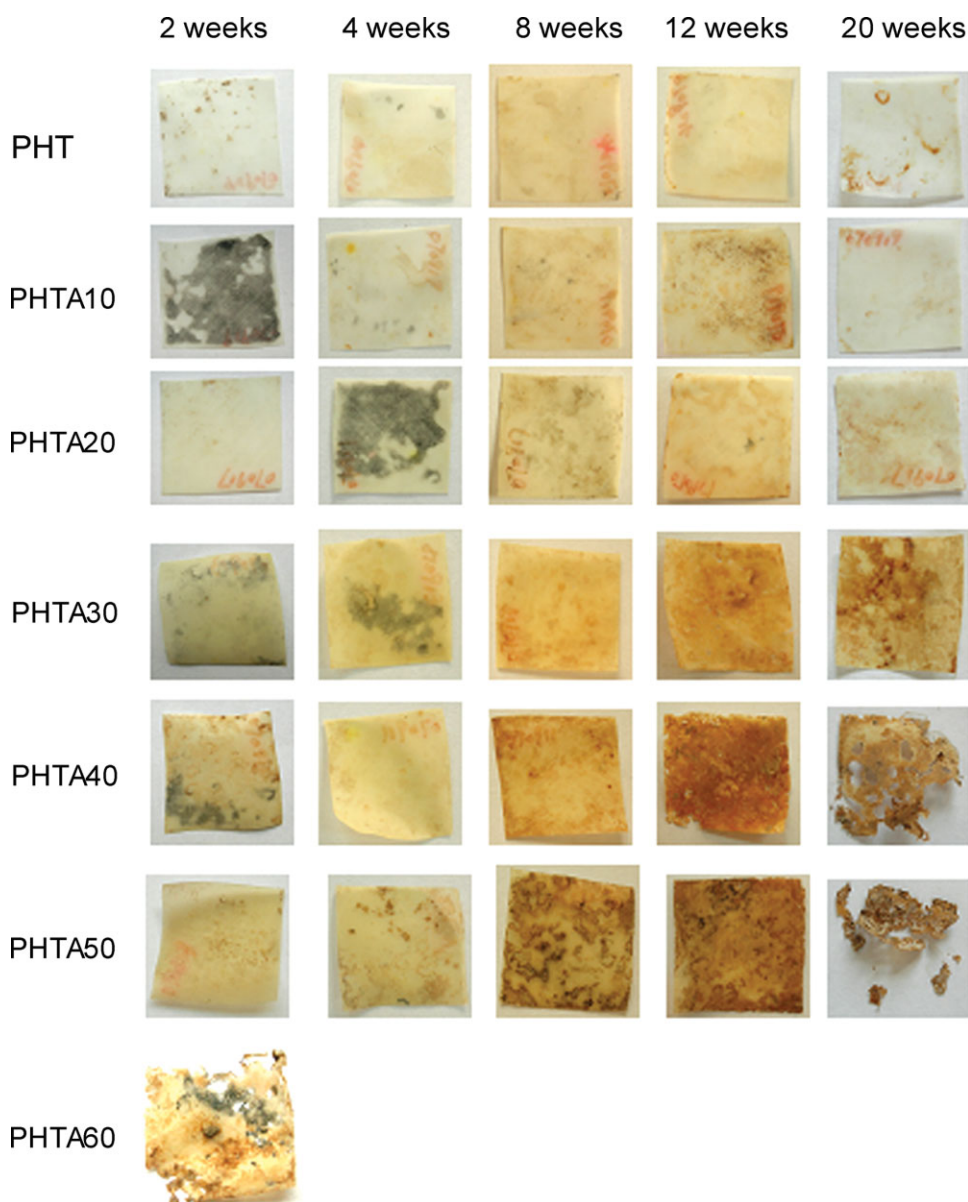


Figure 9 Biodegradation photographs of the PHTA copolyesters over time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolyesters followed the rule described previously. ΔT_{mt} could also explain why the biodegradability of the PHTA copolyesters was higher than that of the PBTA copolyesters with the same compositions.

The T_g values of the PHTA copolyesters decreased linearly with increasing HA unit content (Fig. 7). The reason was that the incorporated aliphatic units into the rigid aromatic molecular chain enhanced the mobility of the main chain. T_g could be predicted by the Gordon–Taylor equation [eq. (6)]:

$$\frac{1}{T_g} = \frac{w_{HA}}{T_{g,PHA}} + \frac{w_{HT}}{T_{g,PHT}} \quad (6)$$

where w_{HA} and w_{HT} are the mass fractions of the HT and HA units in the PHTA copolyesters, $T_{g,PHA}$ and $T_{g,PHT}$ are the glass-transition temperatures of the corresponding homopolymers, and T_g is the glass-transition temperature of the copolymer. The experimental T_g had a slight deviation from the theoretical T_g .

The T_g values of the PBTA copolyesters were 4–5°C higher than those of the PHTA copolyesters with the same compositions, but the variation tendency is similar (Fig. 8). This was possibly because of the more flexible aliphatic units in the PHTA copolyesters, which acted as soft segments to decrease T_g . That is, the PHTA copolyesters had a better performance under low temperatures than the PBTA copolyesters. Furthermore, Mueller²⁰ reported that a polymer was biodegradable when T_g was low enough to guarantee sufficient chain mobility in the amorphous phase. This was also consistent with our results with regard to the higher biodegradability of the PHTA copolyesters than that of the PBTA copolyesters.

Biodegradability of the PHTA copolyesters and the comparison with PBTA

Similar to the PBTA copolyesters, the PHTA copolyesters were biodegradable because of the existence of hydrolysable ester linkages that could be attacked by microorganisms under compost conditions. As shown in Figure 9, the surface of the films became rough and irregular at the beginning of biodegradation, and as the composting time went by, cracks occurred and the extent increased. Additionally, the interior was eroded gradually by microorganisms where cracks, tears, and holes could be observed. Meanwhile, some mildew stains appeared on the surface of film, which indicated that microorganisms actually contributed to biodegradation.

Under compost conditions, PHA, PHTA90, PHTA80, and PHTA70 were completely biodegradable within 2 weeks, and PHTA60 needed 4 weeks. The biodegradabilities of PHTA60, PHTA50,

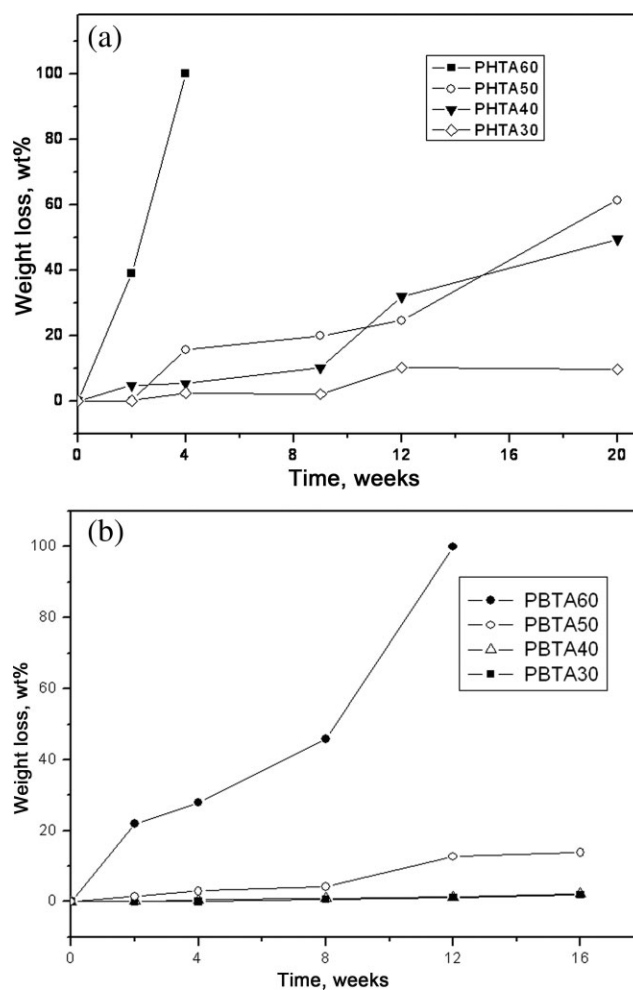


Figure 10 Weight losses of the (a) PHTA and (b) PBTA copolyesters with different compositions over time.

PHTA40, and PHTA30 are shown in Figure 10(a). Clearly, the biodegradability decreased gradually with increasing aromatic unit content. The weight loss of PHTA30 was less than 10% in 20 weeks, and biodegradation did not occur for PHTA20, PHTA10, and PHT, which demonstrated that the HT units played a negative role in biodegradation. Mueller²⁰ reported that the major factor controlling the biodegradability of aliphatic/aromatic copolyesters was the amount of aromatic units but not the chemical structure around the ester bond itself. Copolyesters are biodegradable as long as the aromatic units maintain an amorphous state. Consequently, PHTA20, PHTA10, and PHT were not biodegradable because the aromatic moiety maintained a crystal state, which was also proven by WAXD patterns (Fig. 2).

On the other hand, PBA, PBTA90 (where the number refers to the percentage of ADP in the sample), and PBTA80 were completely biodegraded after they were composted for 2 weeks, whereas PBTA70 needed 4 weeks. The biodegradabilities of PBTA60,

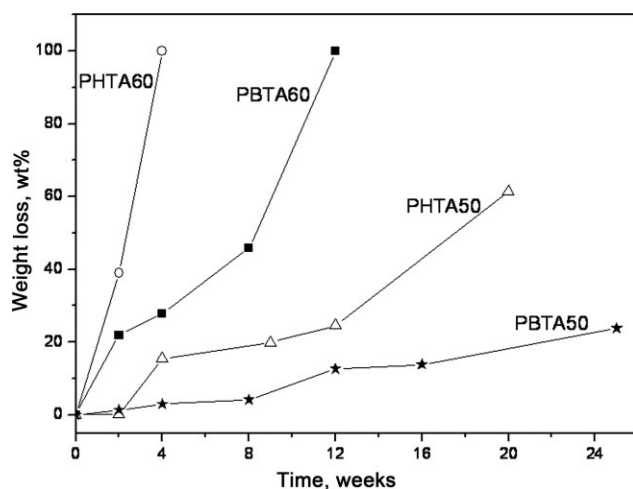


Figure 11 Weight losses of the PHTA50, PBTA50, PHTA60, and PBTA60 copolyesters over time.

PBTA50, PBTA40, and PBTA30 are also shown in Figure 10(b). The biodegradation rate became very slow when the aromatic unit content exceeded 50 mol %. PHTA had a higher biodegradability than PBTA, as shown by the comparison between the biodegradability of PHTA and that of PBTA in Figure 11. Hence, the PHTA copolyesters contained a higher aromatic unit content than PBTA with a similar biodegradability. This was possible because PBTA contained a higher aromatic unit content per molar copolyester than PHTA with the same composition because of its shorter repeating unit.

CONCLUSIONS

A series of new biodegradable PHTA copolyesters were synthesized and characterized by GPC, $^1\text{H-NMR}$, WAXD, DSC, and compost testing. We showed that the compositions of the PHTA copolyesters, which were closely related to their properties and biodegradability, were in accordance with the feed molar ratios. The crystal structures of the PHTA copolyesters were determined by the dominant crystal units and copolyesters became less crystallizable, even amorphous, with increasing comonomer unit content. The T_g values decreased linearly, and both T_m and ΔH_m decreased first and then increased with increasing HA unit content. The PHTA copolyesters were biodegradable with less than 60 mol % aromatic units. In particular, com-

pared with PBTA, the PHTA copolyesters possessed a lower T_g and T_m and better biodegradability. In addition, the biodegradability of the copolyesters could be predicted by the number-average sequence lengths of aromatic units, T_g , and ΔT_{mt} . Generally, biodegradation could only occur when the number-average sequence length of aromatic units was less than three. T_g was low enough to guarantee sufficient chain mobility in the amorphous phase, which also contributed to biodegradability. The smaller ΔT_{mt} was, the better the biodegradability of the copolyester was.

The authors thank Jinliang Qiao of Sinopec Beijing Research Institute of Chemical Industry and Yafei Lv of Beijing University of Chemical Technology for fruitful discussions. The authors are also grateful to Jinlong Gong and Mike Bastin for their helpful revisions.

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