# A Novel Aromatic–Aliphatic Copolyester Consisting of Poly(1,4-dioxan-2one) and Poly(ethylene-*co*-1,6-hexene terephthalate): Preparation, Thermal, and Mechanical Properties

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ABSTRACT: A novel multiblock aromatic–aliphatic copolyester poly(ethylene-*co*-1,6-hexene terephthalate)-copoly(1,4-dioxan-2one) (PEHT-PPDO) was successfully synthesized via the chainextension reaction of dihydroxyl teminated poly(ethylene-*co*hexane terephthalate) (PEHT-OH) with dihydroxyl teminated poly(1,4-dioxan-2-one) (PPDO-OH) prepolymers, using toluene-2,4-diisocyanate as a chain extender. To produce PEHT-OH prepolymer with an appropriate melting point which can match the reaction temperature of PEHT-OH prepolymer with PPDO-OH prepolymer, 1,6-hexanediol was used to disturb the regularity of poly(ethylene terephthalate) segments. The chemical structures and molecular weights of PEHT-PPDO copolymers were characterized by <sup>1</sup>H NMR, FTIR, and GPC. The DSC data showed that PPDO-OH segments were miscible well with PEHT-OH segments in amorphous state and that the crystallization of copolyester was predominantly contributed by PPDO segments. The TGA results indicated that the thermal stability of PEHT-PPDO was improved comparing with PPDO homopolymer. The novel aromatic–aliphatic copolyesters have good mechanical properties and could find applications in the field of biodegradable polymer materials. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2828–2837, 2010

**KEYWORDS**: copolyester; copolymerization; synthesis

**INTRODUCTION** Aromatic polyesters, particularly poly(ethylene terephthalate) (PET), has found more and more application in food packing and textile industry because of its excellent thermal stability and high mechanical strength.<sup>1-3</sup> Unfortunately, this polymer has resistance to microbial and fungal attack and usually remains unaltered in the environment. On the contrary, most of the synthetic biodegradable polymers are aliphatic polyesters, such as poly(lactic acid) (PLA),<sup>4,5</sup> poly(butylene succinate) (PBS),<sup>6,7</sup> and poly(*p*-dioxanone) (PPDO).<sup>8,9</sup> PPDO is an aliphatic polyether ester that has attracted more and more attentions in the recent years owning to its excellent biodegradability, biocompatibility, and good mechanical properties.<sup>10,11</sup> It is considered as a prospective candidate not only for medical application but also for universal application such as coatings, films, and molded products.9,12

In recent years, considerable interest has been attracted by the preparation and application of aliphatic–aromatic copolymers, some of which even have been proved to have good biodegradability when the aliphatic composition was switched to a certain ratio. Aliphatic–aromatic random copolymers such as poly(ethylene succinate-*co*-terephthalate),<sup>13</sup> poly(butylene adipate-*co*-terephthalate) (PBAT),<sup>14</sup> and poly(butylene succinate-*co*-terephthalate)<sup>15</sup> were synthesized successfully in which PBAT with 44 mol % adipate component was already commercialized by BASF company and with the trademark as Ecoflex<sup>®</sup>. Besides, PET-*co*-aliphatic polyester type multiblock copolyesters also have been synthesized, such as poly(ethylene terephthalate-*co*-butylene succinate),<sup>16</sup> poly(ethylene terephthalate-*co*-acropolactone),<sup>17</sup> and poly(ethylene terephthalate*co*-lactic acid) (PET-PLA).<sup>18–21</sup> Compared with the other aliphatic polyester, PPDO not only has ester bond but also has ether bond in their chemical structure which made it have excellent flexibility. Combining PPDO with PET can impart the copolymers with good biodegradability and flexibility.

It is known that the onset decomposition temperature of PPDO is much lower than that of PET, so PPDO would be subjected to immediate thermal degradation if it were reacted with the molten PET. The same problem also appeared in the synthesis of PET-PLA copolyester. To avoid this, some researchers had to polymerize the PET monomers with PLA oligomers<sup>22,23</sup> at a relatively low reaction temperature, which would restrict the reactivity of PET monomers, or introduce aliphatic diol/acid component into the backbone of PET to get appropriate low melting point.<sup>18</sup> However, the molecular weight of the resulting copolyesters

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synthesized via the above method was not very high. As we know, the lower molecular weight would encumber the application of the copolyester. An effective way to obtain high-molecular-weight copolymer was the chain-extension reaction, which has been widely used in the polyurethane and polyester industry to link two or more macromolecules to achieve high molecular weight.<sup>24,25</sup> At present, there have been few reports on the synthesis of the aliphatic–aromatic copolyesters using chain-extension reaction. Du et al.'s work<sup>26–28</sup> revealed that the aliphatic–aromatic copolyester with urethane bonds in the backbones still had good biodegradability. Therefore, we used toluene-2,4-diisocyanate (TDI) as a chain extender to connect PET and PPDO units into one polymer chain.

In this study, dihydroxyl terminated poly(ethylene-*co*-1,6hexene terephthalate) (PEHT-OH) prepolymer with suitable melting point was synthesized by polymerization of ethylene glycol, 1,6-hexanediol, and dimethyl terephthalate. Dihydroxyl terminated PPDO prepolymers were synthesized via ring-opening polymerization of *p*-dioxanone monomer initiated by 1,4-butanediol with stannous octoate as a catalyst. Then, TDI was used as a chain extender to synthesize the PEHT-PPDO copolyesters. The chemical structure, the thermal stability, the thermal transition behaviors, and the mechanical properties of the copolymer were well investigated. As far as we know, this is the first report on the synthesis of PET-PPDO copolymer using this method.

#### **EXPERIMENTAL**

#### Materials

*p*-Dioxanone (PDO) was provided by the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China). The monomer was distilled under reduced pressure until the purity was greater than 99.8% before use. Stannous octoate  $(Sn(Oct)_2)$  was purchased from Sigma (USA) and used as received. Ethylene glycol (EG, AR grade) and 1,4butanediol (BD, AR grade) were received from Kelong Chemical Corp. (Chengdu, China) and were used without futher purification. Dimethyl terephthalate (DMT) was obtained from Guoyao Chemical Plant (Chengdu, China). Toluene-2,4diisocyanate (TDI) (AR grade) obtained from Bodi Chemical Plant (Tianjin, China) was used without further purification. All the other chemicals with AR grades were used as received.

# Synthesis of Dihydroxyl Terminated Poly(1,4-dioxan-2one) (PPDO-OH) Prepolymers

Ring-opening polymerization of PDO was carried out in a flame-dried glass reactor with the magnetic stirring. The reactor was dried and purged with nitrogen three times before addition of PDO whose purity was more than 99.9%. 1,4-Butanediol was injected by a syringe and the reactor was heated in a oil bath at 80 °C with stirring for 10 min. Then, the catalyst SnOct<sub>2</sub>/toluene solution was introduced into the flask with the molar ratio of 500:1 (PDO:SnOct<sub>2</sub>), and the mixture was stirred for 48 h in nitrogen atmosphere. After the reaction, the reactor was fast cooled down to the room

temperature, and the resulting PPDO-OH prepolymer was reduced to small particles in a grinder. The obtained product was dried in vacuum oven at 60 °C for 48 h. The PPDO homopolymer was prepared by chain extension reaction of PPDO prepolymer, the synthetic method was followed by our previous work.<sup>8</sup>

# Synthesis of Dihydroxyl Terminated Poly(ethylene-*co*-1,6-hexene terephthalate) (PEHT-OH) Prepolymers

Dihydroxyl teminated HO-PEHT-OH prepolymer was synthesized via a two-step reaction, transesterification and polycondensation. At first, a predetermined molar ratio (DMT/EG = 1/2.2) of DMT and EG monomers with a catalyst, zinc acetate (0.05 wt % amount of dimethyl terephthalate) were added into a 250-mL single-necked round-bottomed flask equipped with the mechanical stirrer. The mixture was stirred at 175 °C for 4 h under nitrogen, and the product of transesterification reaction, bishyroxyethyl terephthalate, was obtained. The water separator was used to collect the methanol which was produced in the reaction so as to calculate the yield. Then, bishyroxyhex terephthalate was also prepared via the same transesterification procedure, and the feed ratio of monomers and the mount of catalyst were the same as in the preparetion of bishyroxyethyl terephthalate.

Second, PEHT-OH prepolymer was prepared by the condensation polymerization of predetermined molar ratio of bishyroxyethyl terephthalate and bishyroxyhex terephthalate. Bishyroxyethyl terephthalate and bishyroxyhex terephthalate were mixed in a 500-mL three-necked round-bottomed flask, and antimony trioxide (0.8 wt % amount of dimethyl terephthalate) was added as a catalyst. Initially, the temperature of the reaction mixture was gradually increased to 210 °C and kept for 1 h. Then, the system was heated to 250 °C and maintained for another 1 h. Furthermore, the vacuum was gradually reduced to 60 Pa in 0.5 h, and the temperature was increased to 280 °C. About 1 h later, a viscous liquid was produced, and then cooled down to the room temperature under nitrogen. The resulting product was purified by dissolving in chloroform and then precipitating in excessive methanol. The white powder product was dried to constant weight in vacuum oven at 60 °C for the further investigation.

# Synthesis of PEHT-PPDO Copolyesters by Chain-Extension Reaction

The chain-extension reaction was accomplished using a glass reactor under nitrogen atmosphere. PPDO-OH and PEHT-OH prepolymers were put into the reactor which was evacuated and purged with nitrogen for three times, and then the reactor was immersed in a silicone oil bath at 150 °C. When the prepolymers were molten completely, a predetermined amount of TDI was injected into the reactor. The chain-extension reaction proceeded for 1 h with a mechanical stirrer under nitrogen protection. After reaction, the reactor was cooled down to the room temperature rapidly. The resulting copolymers were also purified by dissolving in chloroform and then precipitating in excessive methanol and then the white powder was dried to constant weight in vacuum oven at 60 °C for further investigation.



**SCHEME 1** The synthetic processes of PPDO-OH (A) prepolymer, PEHT (B) prepolymer and PEHT-PPDO copolyester (C).

#### **Intrinsic Viscosity**

The intrinsic viscosities of PPDO-OH, PEHT-OH, and PEHT-PPDO were measured with an Ubbelohde viscometer at 30  $^{\circ}$ C using phenol/1,1,2,2-tetrachloroethane (1/1, v/v) as solvent.

### Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Fourier transform infrared spectrometer in a range of wave numbers from 4000 to 300 cm<sup>-1</sup>. The specimens were milled into powders and then mixed and laminated with KBr. The resolution and scanning time were 4 cm<sup>-1</sup> and 32 times, respectively.

### Nuclear Magnetic Resonance Spectroscopy

The chemical structures and compositions of the obtained polymers were characterized by a Varian Inova 400 NMR spectrometer at ambient temperature, using  $CDCl_3$  as the corresponding solvent and tetramethylsilane as the internal chemical shift standard.

#### **Gel Permeation Chromatography**

The molecular weights and polydispersity of the polymers were determined by gel permeation chromatography at 35 °C with Waters instrument equipped with a 2414 refractive index detector, a model 1515 pump, and a Waters model 717 autosampler. Chloroform was used as the eluant at a flowing rate of 1.0 mL/min, and the sample concentration was 2.5 mg/mL.

# **Differential Scanning Calorimetry**

Differential scanning calorimetry analysis was carried out on a TA Instrument DSC-Q100. Samples were quickly heated to 160 °C and kept for 5 min to remove thermal history, then were cooled to -20 °C at a rate of 10 °C/min, and finally were reheated to 160 °C at the same rate.

#### **Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) was used to determine the thermal stabilities of PPDO-OH, PEHT-OH, and PEHT-PPDO. The thermograms were recorded from room temperature to 500 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere on a TA Instruments TGA-Q500. The isothermal



stability of PEHT-PPDO was carried out to monitor the variation of intrinsic viscosity with time above its melting temperature from which the degradation of PEHT-PPDO in processing conditions could be simulated. The samples were put into an isothermal oven at 120  $^{\circ}$ C and taken out for intrinsic viscosity testing for a given interval time.

#### **Mechanical Properties**

Tensile strength and elongation at break of PEHT-PPDOs were tested on an Instron Universal Testing Machine (Model 4302, Instron Engineering Corp., Canton, MA) at crosshead speed of 50 mm/min at room temperature. The samples were prepared via hot pressing and cutting with a dumbbell-shaped cutter. The thickness and width of samples were 0.5 mm and 4 mm, respectively. The length of the sample between two pneumatic grips of testing machine was 20 mm. Each sample was tested for seven times, and the results were averaged to gain a mean value.

#### **RESULTS AND DISCUSSION**

# Characterization of the Synthesized PPDO-OH and PEHT-OH

PPDO-OH was synthesized by ring-opening polymerization of PDO with 1,4-butanediol (BD) as an initiator, using SnOct<sub>2</sub> as a catalyst [Scheme 1(A)]. The chemical structure and number-average molecular weights of PPDO-OH were characterized by <sup>1</sup>H NMR spectra (shown in Fig. 1). We can see that resonances located at 4.36 ppm ( $\delta$ H<sup>e</sup>), 4.21 ppm ( $\delta$ H<sup>c</sup>), and

3.81 ppm ( $\delta H^d$ ) were assigned to the three methylene of PPDO, respectively. The signals occurring at 4.11 ppm ( $\delta H^b$ ) and 1.74 ppm ( $\delta H^a$ ) were assigned to the methylene protons of BD. Futhermore, the signals of 3.77 ppm ( $\delta H^{d'}$ ) and 3.75 ppm ( $\delta H^{e'}$ ) were assigned to the terminal methylene group of PPDO-OH. The integral area ratio of  $\delta H^b$  to  $\delta H^a$  was about 1:1, demonstrated that BD was incorporated into the polymer chain and PPDO had two terminal hydroxyl groups. The number-average molecular weight ( $M_n$ ) of PPDO-OH prepolymers could be determined according to the following equation:

$$M_{\rm nPPDO-OH} = 2 \times \left[ (I_{3.81} + I_{3.77}) / I_{3.75} \right] \times 102 + 90$$
 (1)

where  $I_{3.81}$  and  $I_{3.77}$  were the intensity of the internal, and terminal methylene groups of the PPDO-OH, respectively.  $I_{3.75}$  was the intensity of the methylene groups which were close to the terminal hydroxyl groups. The values 102 represented the molecular weight of the repeating units of PPDO, and 90 was the molecular weight of BD.

PEHT prepolymers were synthesized by ethylene glycol, 1,6hexanediol, and dimethyl terephthalate by two-step reactions: transesterification and polycondensation [Scheme 1(B)]. The chemical structures and number-average molecular weights of PEHT prepolymers were characterized by <sup>1</sup>H NMR and shown in Figure 2. It can be seen in Figure 2 that the component ratio of the 1,6-hexanediol segments in PEHT prepolymers was higher than the feed ratio. The reason for this was that the boiling point of EG (196–198 °C) was



FIGURE 2 <sup>1</sup>H NMR spectra of PEHT-OH.

much lower than that of HD (253–260  $^{\circ}$ C), thus the former was easier to be evaporated from the reaction system than the latter during the condensation polymerization.

<sup>1</sup>H NMR spectrum (Fig. 2) revealed the chemical structure and number-average molecular weights of PEHT-OH. The peak occurring at 4.70 ppm ( $\delta H^{f}$ ) could be assigned to methylene protons of the repeating -OCH<sub>2</sub>CH<sub>2</sub>O- units, and the terminal methylene protons of -OCH<sub>2</sub>CH<sub>2</sub>O- units could be observed at 3.98 ppm ( $\delta H^k$ ) and 4.50 ppm ( $\delta H^j$ ), respectively. The signals at 8.08–8.11 ppm ( $\delta H^s$ ,  $\delta H^t$ ) could be reasonably attributed to methine proton of the phenyl groups, and these two peaks could not be obviously distinguished as their chemical shifts were very close to each other. It was found that the three different methylene protons of the repeating  $-0(CH_2)_60$  units were observed at 4.35 ppm  $(\delta H^g)$ , 1.82 ppm  $(\delta H^h)$ , and 1.59 ppm  $(\delta H^i)$ . Moreover, the peaks at 4.35 ppm ( $\delta H^p$ ), 3.66 ppm ( $\delta H^r$ ), and 1.47 ppm  $(\delta H^{q})$ , belonging to the terminal methylene protons of  $-O(CH_2)_6O$  units based on the distance to the phenyl groups, respectively. Therefore, the number average molecular weight of resulting PEHT prepolymer was deduced according to the following two equations:

$$D_{\rm P} = \frac{I_{\rm s} + I_{\rm t}}{(I_{\rm i} + I_{\rm r})/2}$$
(2)

$$M_{\rm n.PEHT} = D_{\rm P} \times \left(\frac{I_{\rm f}}{I_{\rm f} + I_{\rm h}} \times 62 + \frac{I_{\rm h}}{I_{\rm f} + I_{\rm h}} \times 118 + 166 - 18\right)$$
(3)

where  $D_p$  was the polymerization degree of PEHT prepolymer,  $I_t$  and  $I_s$  designated the peak intensities of methane protons of phenyl groups.  $I_j$  and  $I_r$  represented the peak intensities of the terminal methylene protons of  $-OCH_2CH_2O-$  and  $-O(CH_2)_6O-$  units, respectively.  $I_f$  and  $I_h$  were the intensities of methylene protons of the repeating  $-OCH_2CH_2O-$  and  $-O(CH_2)_6O-$  units; the proportion of which could provide the molar ratio of ethylene glycol units to 1,6-hexanediol units in PEHT prepolymers. The molecular weights of ethylene glycol, 1,6-hexanediol, terephthalic acid, and  $H_2O$  were 62, 118, 166, and 18, respectively.



FIGURE 3 <sup>1</sup>H NMR spectra of PEHT-PPDO copolyester.

# Synthesis and Characterization of PEHT-PPDO Copolyesters

PEHT-PPDO copolyesters were prepared through chainextension of PPDO-OH and PEHT-OH prepolymers in the presence of TDI at 150 °C for 1 h. The reaction process was shown in Scheme 1(C). Based on our previous work,<sup>21</sup> the molar ratio of —NCO/—OH should be 1:1 to obtain the products with high molecular weight and the high efficiency of the chain extension. Therefore, in this study, the molar ratio of —NCO/—OH was fixed at 1:1.

The chemical structures of PEHT-PPDO were characterized by FTIR and <sup>1</sup>H NMR. The <sup>1</sup>H NMR spectrum of the copolyesters was shown in Figure 3. It was found that all the characteristic signals ascribed to both repeated segments of PPDO-OH ( $\delta$ H<sup>c</sup>,  $\delta$ H<sup>d</sup>) and PEHT-OH ( $\delta$ H<sup>f</sup>,  $\delta$ H<sup>g</sup>,  $\delta$ H<sup>h</sup>,  $\delta$ H<sup>i</sup>) prepolymers were presented in the spectrum of PEHT-PPDO. Furthermore, the signals which belonged to PPDO-OH ( $\delta$ H<sup>e'</sup>,  $\delta$ H<sup>d'</sup>) and PEHT-OH ( $\delta$ H<sup>j</sup>,  $\delta$ H<sup>k</sup>,  $\delta$ H<sup>q</sup>,  $\delta$ H<sup>r</sup>) disappeared respectively, indicating that all the terminal hydroxyl groups of prepolymers had thoroughly reacted. The peaks occurring at 2.19 ( $\delta H^w$ ) could be attributed to methyl protons of TDI, and the phenyl protons of TDI units located at about 7.08 ( $\delta H^z$ ), 7.06 ( $\delta H^u$ ) and 6.72 ( $\delta H^v$ ). The composition of the copolyesters was determined by <sup>1</sup>H NMR, which could be calculated according to the following equation:

$$PEHT/PPDO(mol/mol) = [(I_{s} + I_{t})/4]/(I_{d}/2)$$
(4)

where  $I_t$  and  $I_s$  designated the peak intensities of methane protons of phenyl groups belonged to PEHT component,  $I_d$  was the intensity of the internal methylene groups of the PPDO component.

The FTIR spectra of PEHT-OH, PPDO-OH prepolymers, and PEHT-PPDO copolyester were illustrated in Figure 4. It can be seen clearly that the characteristic absorptions of PPDO-OH prepolymer such as  $1736 \text{ cm}^{-1}$ ,  $1533 \text{ cm}^{-1}$ , and  $1431 \text{ cm}^{-1}$ , which belonged to the absorption of carbonyl group, methylene and C—O—C stretching, respectively, were found. O—H vibration at about  $3500 \text{ cm}^{-1}$  assigning to both prepolymers disappeared in PEHT-PPDO spectrum, which



FIGURE 4 FT-IR spectra of PEHT-OH, PPDO-OH, and PEHT-PPDO copolymer.

demonstrated that the hydroxyl groups of the prepolymers were consumed completely. The new peak at around 3350 cm<sup>-1</sup> attributed to *N*—H stretching vibration can be found, meanwhile the —NCO— stretching at 2200 cm<sup>-1</sup> disappeared, all of which evidenced that TDI was thoroughly reacted and the isocyanate groups had been changed to ure-thane groups. It illustrated that the chain extension proceeded just as we expected and the ratio of —NCO/—OH we chose was effective for the reaction.

To investigate the effect of the chemical strucuture on the properties of the copolyesters, PEHT-PPDOs with different compositions had been synthesized, which was named as PEHT-PPDO1–PEHT-PPDO5. The compostions of the obtained copolymers were listed in Table 1. It can be seen from Table 1 that the intrinsic viscosity of PHET-PPDO copolymers increased with the increasing feed weight ratio of PEHT-OH and reached the maximum when the feed ratio of PEHT-OH to PPDO-OH was 75:25 (PEHT-PPDO3). After that, the intrinsic viscosity of PEHT-PPDO decreased gradually when the feed ratio r



FIGURE 5 GPC diagrams of PEHT-OH, PPDO-OH, and PEHT-PPDO copolyesters.

tio of prepolymers kept growing. As we know, the reactivity of hydroxyl groups of these prepolymers was different, when the feed ratio of PEHT-OH to PPDO-OH was 75:25, the hydroxyl groups in reaction system had the highest reactivity, which made the chain-extension efficiency achieve the maximum.

The molecular weights of PEHT-OH, PPDO-OH prepolymers, and PEHT-PPDO copolyester were determined by GPC (shown in Fig. 5), and the detailed results were also listed in Table 1. The GPC traces of PEHT-PPDO1 to PEHT-PPDO5 showed a single peak, demonstrated that a complete reaction took place without unreacted prepolymers remaining.<sup>29</sup> The GPC results can prove that using NMR to calculate the amount of chain extender TDI was a useful method in chain-extension reaction. From Table 1, we can see that all copolyesters had higher molecular weights, indicated that the chain-extension reaction was successfully achieved. Mean-while, it could be found that the molecular weights of PEHT-OH and PPDO-OH prepolymers calculated by NMR spectra

TABLE 1 TH	ne Composition	and the Molecular	Weights of Pl	EHT-PLLA Copolyesters
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	Feed Rat	tio (wt %)	Composi (wi	Composition Ratio (wt %)					
Sample <sup>a</sup>	PEHT-OH	PPDO-OH	PEHT-OH	PPDO-OH	<i>M<sub>n,NMR</sub></i> (g/mol)	M <sub>n,GPC</sub> ×10 + (g/mol)	M <sub>w,GPC</sub> ×10 + (g/mol)	$PD^{b}$	[η] (dL/g)
PPDO-OH	100	-	-	-	6,353	0.78	1.45	1.86	0.33
PEHT-OH	-	100	-	-	8,181	0.82	1.91	2.33	0.38
PEHT-PPDO1	56.3	43.7	58.7	41.3	_c	4.96	14.28	2.88	0.81
PEHT-PPDO2	65.9	34.1	60.9	39.1	_c	5.75	15.87	2.76	0.90
PEHT-PPDO3	75.0	25.0	70.8	29.2	_c	7.87	31.01	3.94	1.10
PEHT-PPDO4	86.5	13.5	83.4	16.6	_c	6.94	23.94	3.45	0.80
PEHT-PPDO5	93.5	6.5	98.0	2.0	_c	5.96	14.42	2.42	0.70

<sup>a</sup> All samples are synthesized at 150 °C for 1 h.

<sup>b</sup> Polydispersity.

<sup>c</sup> The molecular weight can not be calculated by <sup>1</sup>H NMR.



FIGURE 6 TG curves of PEHT-OH, PPDO, and PEHT-PPDO copolyesters.

were lower than those determined by GPC; this phenomenon could be explained by the different characteristics of two testing methods.<sup>30</sup> The molecular weight distribution of PEHT-PPDO copolyesters were a little broader than that of prepolymers, which could ascribed to the fast reaction rate and the difficult controllability of the chain extension. It could be observed that the polydispersity of PEHT-PPDO3 was the broadest of five PEHT-PPDO samples, which can be ascribed reasonably to its high molecular weight.

# **Themal Stability of PEHT-PPDO Copolyesters**

The thermal stabilities of PEHT-PPDO were studied by TGA. The TG curves of PEHT-OH prepolymer, PPDO homopolymer, and PEHT-PPDO were shown in Figure 6, and the relevant thermal decomposition temperatures were summarized in Table 2. There was no residue left for PEHT-OH prepolymer and only 0.2wt % residue for PPDO homopolymer at 500 °C. At the same time, the residue of PEHT-PPDO1 to PEHT-PPDO5 copolyesters ranged from 2.18 to 3.93%. It can be found that the PEHT-PPDO curves included two thermal degradation stages. The first stage with a maximum decomposition temperature from 230 to 270 °C belonged to the decomposition of PPDO segments, and the second stage with a maximum decomposition temperature of aroud 400 °C was due to the PEHT segments. From Table 1, we can find that all PEHT-PPDO samples had a higher initial decomposition temperature  $(T_{5\%})$  and maximum decomposition temperature  $(T_{\text{max1}})$  than those of PPDO homopolymer, even though PPDO homopolymer had much higher intrinsic viscosity  $([\eta]$ = 2.0 dL/g, demonstrated that all PEHT-PPDO copolyesters have better thermal stability than PPDO homopolymer. It was also be found from Table 1 that the values of  $T_{5\%}$  were increased with the increase of PEHT content in the copolyesters, but  $T_{max2}$  that was ascribed to the decompositon of PEHT almost invaried with the composition. This demonstrated that the presence of aromatic groups, which derived from PEHT, can obviously reduce the unzipping depolymerization of PPDO segments and eliminated to generate PDO monomers.31

# Thermal and Crystallization Behaviors of PEHT-PPDO Copolyesters

The DSC cooling and heating scans of PEHT-OH, PPDO-OH, and PEHT-PPDO with different weight ratios were shown in Figures 7 and 8, respectively. The relevant data determined from Figure 7 and Figure 8 were summarized in Table 2. No crystallization peak could be detected in the cooling scans for all the samples due to their slow crystallization rate, and only glass transition temperatures could be observed from their cooling scans. However, in the heating scans, all the samples showed the obvious melting point, indicated that the copolyesters were semicrystallization polymer.

When PEHT content was low, such as PEHT-PPDO1 $\sim$  3, the cold crystallization exothermal peaks could be detected, and it became wider and weaker with the increase of PEHT content. For PEHT-PPDO4 and PEHT-PPDO5, we can not find the cold crystallization exothermal peaks. As we know, the crystallizability of PPDO segment was better than that of PEHT due to its chain regularity. So, the decrease of PPDO content would decrease the crystallizability and the crystallization rate of the copolyesters. Beside this, the introduction of TDI

Sample					T <sub>m</sub>	(°C)		<i>T</i> <sub>d</sub> (°C)		
	<i>T</i> <sub>g1</sub> (°C)	<i>T</i> <sub>g2</sub> (°C)	$T_{c}$ (°C)	$\Delta H_{\rm c} ~({\rm J/g})$	T <sub>m1</sub>	T <sub>m2</sub>	$\Delta H_{\rm m}{}^{\rm a}$ (J/g)	$T_{5\%}^{b}$	T <sub>max1</sub> c	T <sub>max2</sub> d
PEHT-OH	-	15.7	72.6	33.2	105.9	117.1	21.8	364.1	-	399.1
PPDO	-9.3	_	44.0	54.8	101.4	_	64.2	194	234.3	-
PEHT-PPDO1	-7.9	19.7	54.6	32.0	99.6	117.6	37.3	224.1	245.3	400.1
PEHT-PPDO2	-6.6	22.0	66.3	3.0	99.3	117.7	12.0	233.7	250.0	400.2
PEHT-PPDO3	-6.4	24.6	67.7	14.4	99.4	119.2	24.6	258.4	275.5	400.5
PEHT-PPDO4	-5.7	24.5	-	_	99.5	117.1	8.2	260.2	269.2	400.2
PEHT-PPDO5	-	29.8	-	-	-	117.2	7.3	272.8	272.1	400.2

TABLE 2 The Thermal Degradability and Thermal Transition Data of PEHT-OH, PPDO, and PEHT-PPDO Copolyesters

<sup>a</sup>  $\Delta H_{\rm m}$  concluded the progress of  $T_{\rm m1}$  and  $T_{\rm m2}$ .

<sup>b</sup> Decomposition temperature of polymers at weight loss of 5%.

<sup>c</sup> The maximum-decomposition-rate temperature in the first stage (PPDO segment).

<sup>d</sup> The maximum-decomposition-temperature in the second stage (PEHT segment).



FIGURE 7 DSC cooling scans of PEHT-OH, PPDO-OH, and PEHT-PPDO copolyesters.

further disturbed the regularity and flexibility of copolyester chains. The above reasons made the crystalline enthalpy  $(\Delta H_c)$  and the melting enthalpy  $(\Delta H_m)$  decreased gradually with the increase of PEHT content.

From Table 2, it can be seen that there were two glass transition temperatues and melting points for PEHT-PPD01 $\sim 3$ . For example, PEHT-PPD01 presented an obvious glass transition temperature (-7.9 °C) which was close to the  $T_{\rm g}$  of PPD0 (-9.3 °C) and an inconspicuous  $T_{\rm g}$  at 19.7 °C which was approached  $T_{\rm g}$  of PEHT. With the increase of PEHT content, PEHT made main contribution to the  $T_{\rm g}$ s and  $T_{\rm m}$ s of the copolyesters, and finally it made PEHT-PPD04 and PEHT-PPD05 have only one  $T_{\rm g}$  and  $T_{\rm m}$  close to those of PEHT. From Table 2, it can be found that PEHT-PPD03 had the highest  $T_{\rm m2}$  of the five copolymer samples, which may be due to its the highest molecular weight.



FIGURE 8 DSC second heating scans of PEHT-OH, PPDO-OH, and PEHT-PPDO copolyesters.

# TABLE 3 The Mechanical Properties of PEHT-PPDO Copolyesters

Sample	Tensile Strength (MPa)	Elongation at Break (%)
PEHT-PPDO 1	31.4 ± 1.2	417.1 ± 34
PEHT-PPDO 2	$36.0\pm0.6$	$302.4\pm23$
PEHT-PPDO 3	$36.9\pm2.4$	$364.3\pm16$
PEHT-PPDO 4	$38.0\pm0.8$	$\textbf{318.9} \pm \textbf{9}$
PEHT-PPDO 5	40.2 ± 1.7	$332.6\pm28$

### **Mechanical Properties**

Mechanical properties of polymers are extremely important for potential applications. In this study, the tensile properties of the copolyesters have been investigated and the results were listed in Table 3. It was found that the tensile strength of the copolymers increased with the increase of PEHT component, which should be ascribed to the gradual increase of aromatic segment content. For PEHT-PPD01, the content of aliphatic and aromatic segments was approximately the same, which resulted in the minimal tensile strength and maximal elongation at break. When the PEHT content further increased, however, the elongation at break decreased, but its decrease extent had no direct relationship with their PEHT content. PEHT-PPD03, which had the maximal molecular weight, had a higher elongation at break than the other samples, but it was still lower than that of PEHT-PPD01.

# CONCLUSIONS

A series of PEHT-PPDO copolyesters with different compositons have been successfully synthesized by chain-extension reaction, using TDI as the chain extender, which were confirmed by FTIR and the molecular weights determined from <sup>1</sup>H NMR or GPC. When the weight ratio of PEHT-OH to PPDO-OH was suitable, the copolyester with the maximal molecular weight could be obtained. The TG results indicated that the thermal stability of PEHT-PPDO was improved compared with PPDO homopolymer. The crystallization rate was lowed due to their chain irregularity. The crystallization behaviors of PEHT-PPDO were predominantly contributed by PPDO segments. All the copolyester showed the good elongation at break and tensile strength which had great relationships with their PEHT content. A study on the biodegradability of the copolyesters is underway.

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