

# Catalyzed Chain Extension of Poly(butylene adipate) and Poly(butylene succinate) with 2,2'-(1,4-Phenylene)-bis(2-oxazoline)

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**ABSTRACT:** Low-molecular-weight HOOC-terminated poly(butylene adipate) prepolymer (PrePBA) and poly(butylene succinate) prepolymer (PrePBS) were synthesized through melt-condensation polymerization from adipic acid or succinic acid with butanediol. The catalyzed chain extension of these prepolymers was carried out at 180–220°C with 2,2'-(1,4-phenylene)-bis(2-oxazoline) as a chain extender and *p*-toluenesulfonic acid (*p*-TSA) as a catalyst. Higher molecular weight polyesters were obtained from the catalyzed chain extension than from the noncatalyzed one. However, an improperly high amount of *p*-TSA and a high temperature caused branching or a crosslinking reaction. Under optimal conditions, chain-extended poly(butylene adipate) (PBA) with a number-average molecular weight up to 29,600 and poly(butylene succinate) (PBS) with an intrinsic viscosity of 0.82 dL/g were synthesized. The chain-extended polyesters were characterized

by IR spectroscopy, <sup>1</sup>H-NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis, wide-angle X-ray scattering, and tensile testing. DSC, wide-angle X-ray scattering, and thermogravimetric analysis characterization showed that the chain-extended PBA and PBS had lower melting temperatures and crystallinities and slower crystallization rates and were less thermally stable than PrePBA and PrePBS. This deterioration of their properties was not harmful enough to impair their thermal processing properties and should not prevent them from being used as biodegradable thermoplastics. The tensile strength of the chain-extended PBS was about 31.05 MPa. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1555–1565, 2010

**Key words:** biodegradable; polycondensation; polyesters; synthesis; thermal properties

## INTRODUCTION

Aliphatic polyesters are one kind of important biodegradable material. They are mainly synthesized by melt polycondensation or modified methods. As common melt polycondensation often requires high-vacuum systems and longer reaction times, chain extension is one important method for enhancing the molecular weight. Chain extension is commonly swift and efficient. For some kinds of chain extenders, chain extension can be completed in several minutes.<sup>1–3</sup> In the chain extension of polyesters, different chain extenders have been used with polyesters with different terminal groups. Chain extenders

such as bisoxazolines,<sup>4</sup> bisaziridines, and diepoxides<sup>5</sup> have usually been used in the chain extension of HOOC-terminated polyesters; others such as diisocyanate,<sup>6</sup> tetracarboxylic dianhydride,<sup>7</sup> carbonyl biscaprolactam,<sup>8</sup> 1,3-isophthaloyl biscaprolactamate,<sup>9</sup> and terephthaloyl biscaprolactamate<sup>10–12</sup> and octamethylcyclotetrasilazane or hexaphenylcyclotrisilazane<sup>13</sup> have been used in the chain extension of HO-terminated polyesters.

Among them, bisoxazolines are one kind of important chain extender. They have often been used to enhance the molecular weight of poly(ethylene terephthalate) (PET) and polyamides during melt polycondensation.<sup>1,14–16</sup> Tuominen and Seppala<sup>17</sup> studied the chain extension of poly(lactic acid) with bis(2-oxazoline). Serious racemization during the melt polycondensation and chain extension resulted in an amorphous poly(lactic acid), although L-lactic acid was used as a starting material. Néry et al.<sup>14</sup> studied the chain extension of poly(butylene adipate) (PBA) with 2,2'-(1,4-phenylene)-bis(2-oxazoline) (PBOX) without a catalyst. However, PBA is just a low-melting-point aliphatic polyester; its thermal resistance is low for normal usage as a biodegradable plastic.

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In our previous study, we examined the chain extension of PBA with  $\text{—COOH}$  terminal groups by PBOX.<sup>18</sup> However, the chain-extending efficiency of this noncatalyzed chain extension was not good. The reproducibility of the noncatalyzed chain extension was poor, and high-molecular-weight polyesters were seldom obtained. After further study, we found an effective way to synthesize aliphatic polyesters with high molecular weights. It was the catalyzed chain extension of HOOC-terminated prepolymers with *p*-toluenesulfonic acid (*p*-TSA) as a catalyst. This article is about the catalyzed chain extension of HOOC-terminated prepolymers with *p*-TSA.

Poly(butylene succinate) (PBS) has a melting point of about 115°C and is a promising biodegradable plastic. In this study, we examined the chain extension of PBS with PBOX as a chain extender under the catalysis of *p*-TSA. As PBS is insoluble in tetrahydrofuran (THF) and cannot be characterized by gel permeation chromatography (GPC) with THF as an eluent, for convenience, we used HOOC-terminated poly(butylene adipate) prepolymers (PrePBAs) as starting materials to study the influencing factors of the chain extension. The chain-extension efficiency between the *p*-TSA-catalyzed chain extension and the noncatalyzed one was compared, and the obvious differences between them are shown. The chain-extended polyesters obtained were characterized by IR spectroscopy, <sup>1</sup>H-NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray scattering (WAXS), and tensile testing.

## EXPERIMENTAL

### Materials

Adipic acid (AA) and 1,4-butanediol (BD) were purchased from Beijing Chemical Factory (Beijing, China). Succinic acid (SA) was purchased from Tianjin Fuchen Chemical Reagent Plant (Tianjin, China). AA and SA were purified by crystallization with deionized water before use. BD was redistilled under reduced pressure. Dibutyltin oxide ( $\text{Bu}_2\text{SnO}$ ; 99%) was purchased from Acros Co. (Geel, Belgium). *p*-TSA was purchased from Beijing Xizhong Chemical Plant (Beijing, China).  $\text{HCCl}_3$ , methanol, and THF were all purchased from Beijing Century Red Star Chemical Co., Ltd. (Beijing, China). These reagents were all used directly as received. The chain extender PBOX was prepared according to the procedure described by N ry et al.<sup>15</sup> Its melting point was 249°C.

### Synthesis of the HOOC-terminated PrePBA and HOOC-terminated poly(butylene succinate) prepolymer (PrePBS)

To prepare PrePBA, 50.0 g (0.342 mol) of AA, 29.6 mL (0.335 mol) BD, and 0.24 g of  $\text{Bu}_2\text{SnO}$  were added

to a 250-mL, four-necked flask. The mixture was mechanically stirred and heated under an  $\text{N}_2$  atmosphere to 150–160°C until 10 mL of water formed was collected. The temperature was gradually raised to 200°C. At 200°C, the pressure in the flask was reduced in stages to 2 mmHg over a period of 4 h and kept there for 4 h. The acid value of the polyester obtained was 47.8 mg of KOH/g, which was determined by titration with 0.05N NaOH. The hydroxyl number was 0.0.

The HOOC-terminated PrePBSs was prepared by a similar method.

### Chain extension of the HOOC-terminated PrePBA and PrePBS

In a 100-mL, three-necked, round-bottom flask, 5.0 g of HOOC-terminated PrePBA or PrePBS and PBOX at different molar ratios were stirred and heated under nitrogen to 180–220°C until the mixture was melted and mixed homogeneously. *p*-TSA (0–0.15 wt %) was added. The reaction was maintained for different times until no further change in the viscosity was observed. The chain-extended polyesters obtained were purified two times through dissolution–precipitation cycles with 20 mL of  $\text{HCCl}_3$  as a solvent and 200 mL of methanol as a nonsolvent. Meanwhile, the residue of the catalyst was removed this way.

### Characterization

The acid value and the hydroxyl number were detected by a similar method to that described in the literature.<sup>19</sup> As the prepolymers were mainly terminated with HOOC— groups, their hydroxyl numbers were calculated as follows:

$$Q_v = \frac{56.1c(V_0 - V_s)}{m} + A_v$$

where  $Q_v$  and  $A_v$  (mg of KOH/g) represent the hydroxyl number and acid value,  $V_0$  and  $V_s$  (mL) represent the NaOH solution volume consumed in the titration of the blank assay and the sample respectively,  $c$  (mol/L) is the concentration of the NaOH solution,  $m$  (g) is the weight of the sample, and 56.1 is the molecular weight of KOH in g/mol.

The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and molecular weight distribution of the HOOC-terminated PrePBA and the chain-extended poly(butylene adipate) (ExtPBA) were determined by a Waters (Milford, MA) GPC515-2410 system equipped with three Styragel columns (HT3, HT5, and HT6E) and a refractive-index detector at 25°C. THF was used as an eluent with a flow rate of 1 mL/min, and polystyrene

TABLE I  
Properties of the HOOC-Terminated Prepolyesters

Prepolymer	BD/diacid (molar ratio)	$A_v$ (mg of KOH/g)	$Q_v$ (mg of KOH/g)	$[\eta]$ (dL/g)	GPC		
					$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$
PrePBA-1	0.92	48.6	0.0	0.16	3,400	7,300	2.17
PrePBA-2	0.92	47.8	0.0	0.21	3,600	11,100	3.07
PrePBA-3	0.92	46.4	0.0	0.22	4,100	9,200	2.01
PrePBA-4	0.99	21.8	0.0	0.29	9,000	18,700	2.07
PrePBA-5 <sup>b</sup>	0.98	23.7	3.9	0.26	6,900	14,500	2.09
PrePBS-1	0.98	17.3	0.0	0.38	—	—	—
PrePBS-2 <sup>b</sup>	0.99	12.6	9.8	0.38	—	—	—
PrePBS-3	0.88	25.6	0.0	0.21	—	—	—
PrePBS-4	0.88	23.0	0.0	0.26	—	—	—

The reaction conditions for PrePBA-1 to PrePBA-4 and PrePBS-1, PrePBS-3, and PrePBS-4 were as follows: 150–200°C (gradually raised), 760 mmHg, and 4 h; 200°C, 30 mmHg (gradually reduced), and 4 h; and 200°C, 2 mmHg, and 4 h. The reaction conditions for PrePBA-5 and PrePBS-2 were as follows: 150–200°C (gradually raised), 760 mmHg, and 4 h and 200°C, 30 mmHg (gradually reduced), and 4 h.

was used as a standard. The intrinsic viscosities ( $[\eta]$ ) of the HOOC-terminated PrePBA and PrePBS and ExtPBA or chain-extended poly(butylene succinate) (ExtPBS) were determined at 30°C by an Ubbelohde viscometer (Beijing Glassware Plant, Beijing, China) with chloroform as a solvent.

The <sup>1</sup>H-NMR spectra were recorded on Bruker (Zurich, Switzerland) AC-600 spectrometer with DCCl<sub>3</sub> as the solvent of the polyester and tetramethylsilane as the labeling compound. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet (Madison, WI) 60SXB FTIR spectrometer. TGA was performed with a PerkinElmer (Waltham, MA) TGA 7 analyzer from 20 to 500°C at a heating rate of 10°C/min under a nitrogen atmosphere.

The nonisothermal and isothermal crystallization properties and the glass-transition temperature of the polymers were measured with a Netzsch (Selb, Germany) DSC204F1 analyzer under a nitrogen atmosphere. In the nonisothermal crystallization, the PrePBA and ExtPBA samples were heated from 20 to 100°C at 10°C/min; the PrePBS and ExtPBS samples were heated from 20 to 160°C at the same heating rate. To determine the glass-transition temperature, the PrePBA and ExtPBA samples were first melted at 100°C for 5 min and cooled to –140°C at a rate of 40°C/min and then heated from –140 to 100°C at 10°C/min; the PrePBS and ExtPBS samples were first melted at 160°C for 5 min and cooled to –140°C at a rate of 40°C/min and then heated from –140 to 160°C at 10°C/min. In the cooling crystallization, the PrePBS and ExtPBS samples were first melted at 160°C for 5 min and then cooled to 0°C at a rate of 5°C/min. In the isothermal melt crystallization, the PBS samples were melted at 160°C for 5 min and then cooled at 20°C/min to different crystallization temperatures for crystallization in 20 min.

The WAXS measurements of the polyester samples were detected with a Rigaku (Tokyo, Japan)

D/Max 2500 VB2+/PC diffractometer with Cu K $\alpha$  radiation. The samples were continuously scanned over a 2 $\theta$  range from 5 to 50°. The degree of crystallinity was calculated with a basic method for the differentiation between crystalline and amorphous scattering in the X-ray diffraction scans.

The PBS bars (50 × 12 × 1 mm<sup>3</sup>) were hot-pressed with a 70911-24B powder press machine (Tianjin New Technical Instrument Co., Tianjin, China). The polyester samples were heated at 160°C for 5 min under 15 MPa and cooled to room temperature under the same pressure. The tensile tests were conducted on a Lloyd LR30K tensile testing machine (Fareham Hants, United Kingdom) with a crosshead speed of 50 mm/min. The measurements were performed on five parallel bars.

## RESULTS AND DISCUSSION

### Synthesis of the HOOC-terminated PrePBA and PrePBS

The HOOC-terminated PrePBA and PrePBS were synthesized by the condensation polymerization of BD and AA or SA with Bu<sub>2</sub>SnO as the catalyst. Table I shows the properties of the synthesized PrePBAs and PrePBSs. Their acid values were in the range 12.6–48.6 mg of KOH/g, and the hydroxyl number was 0.0, except for PrePBA-5 and PrePBS-2. The designations 1, 2, 3, and so on used for the prepolymers were related to different samples with different acid values and hydroxyl numbers. Different molar ratios of BD to AA or SA and different reaction conditions resulted in different acid values and hydroxyl numbers of the prepolymers. Although the molar ratios of BD to diacid were the same, the fluctuation of the reaction conditions during the synthesis process resulted in a small difference in the acid value between PrePBA-1 and PrePBA-3 and

TABLE II  
Chain Extension of PrePBA with PBOX with or without *p*-TSA as a Catalyst

PrePBA	Oxazoline/—COOH (molar ratio)	<i>p</i> -TSA (wt %)	Reaction temperature (°C)	Reaction time (h)	$A_v$ (mg of KOH/g) <sup>a</sup>	GPC		
						$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$
PrePBA-1	1.2	0.05	200	3.0	—	24,300	103,900	4.27
PrePBA-2	1.1	0.05	180	3.0	5.2	20,300	62,200	3.06
	1.2	0.05	180	3.0	4.4	19,900	62,300	3.13
	1.2	0.00	200	1.5	6.1	12,300	31,100	2.53
	1.2	0.05	200	1.5	4.1	23,200	71,000	3.06
	1.2	0.05	200	3.0	4.1	19,200	68,000	3.54
	1.2	0.10	200	0.5	—	Crosslinked		
	1.2	0.05	220	0.5	—	Crosslinked		
PrePBA-3	1.2	0.00	180	3.0	—	7,400	19,400	2.62
	1.2	0.05	180	3.0	—	21,400	67,900	3.17
	1.2	0.05	200	3.0	—	19,100	71,900	3.77
	1.2	0.05	220	0.5	—	Crosslinked		
PrePBA-4	1.1	0.05	180	3.0	6.8	27,500	80,100	2.91
	1.2	0.05	180	3.0	6.9	26,300	73,200	2.78
	1.3	0.05	180	3.0	6.3	24,200	73,300	3.02
PrePBA-5	1.2	0.05	180	3.0	5.4	29,600	62,600	2.12
	1.2	0.10	180	3.0	5.7	21,000	67,000	3.20
	1.2	0.15	180	3.0	—	Crosslinked		

<sup>a</sup> Acid value of the chain-extended PBA.

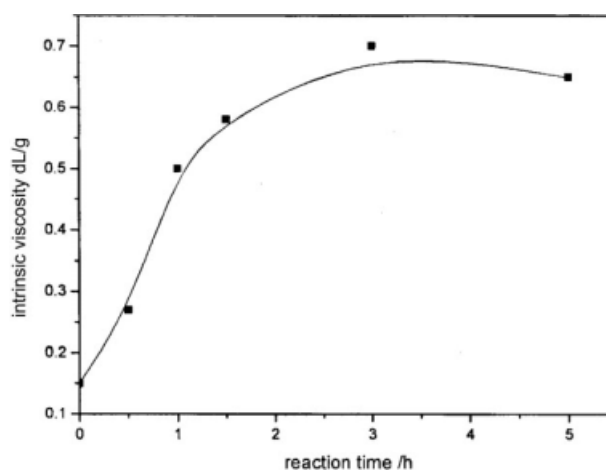
PrePBS-3 and PrePBS-4. The molar ratios of BD to diacid for PrePBA-4 and PrePBA-5 and for PrePBS-1 and PrePBS-2 were almost the same, but a lack of the 2-mmHg vacuum reaction period led to a higher number of remaining terminal hydroxyl groups. The hydroxyl numbers of PrePBA-5 and PrePBS-2 were 3.9 and 9.8 mg of KOH/g, respectively. The  $[\eta]$  values of the PrePBAs and PrePBSs and the  $M_n$ ,  $M_w$ , and  $M_w/M_n$  values of the PrePBAs detected by the GPC method are also compiled in Table I for convenient comparison to those of the chain-extended polyesters. As the PrePBSs were insoluble in THF, their molecular weight was just characterized by the viscometric method, and  $[\eta]$  was in the range 0.21–0.38 dL/g.

#### Chain extension of the HOOC-terminated PrePBA and PrePBS

Chain extension of PrePBA and PrePBS was carried out in the bulk state with PBOX as a chain extender with or without *p*-TSA as a catalyst. Table II shows the chain extension of PrePBA with PBOX. As shown in Table II, the  $M_n$  and  $M_w$  values of ExtPBA obtained from PrePBA-2 at 200°C or from PrePBA-3 at 180°C in the *p*-TSA-catalyzed reaction were much higher than those obtained in the noncatalyzed chain extension. The addition of 0.05–0.10 wt % *p*-TSA increased the chain-extending efficiency obviously, and 0.05 wt % *p*-TSA was the optimal amount. Table II also shows the influence of the reaction temperature on the catalyzed chain extension. The chain-extending efficiency was high at reaction tempera-

tures between 180 and 200°C. A large amount of catalyst and a high reaction temperature often caused a crosslinking reaction during the chain extension. PrePBA-5, having some terminal hydroxyl groups, did not lower the chain-extending efficiency. Chain-extended PBA with an  $M_n$  of 29,600 and an  $M_w$  of 62,600 was obtained when PrePBA-5 was used as a starting material and 0.05 wt % *p*-TSA was present.

Figure 1 shows the influence of the reaction time on the catalyzed chain extension. As the reaction time increased from 0 to 3 h,  $[\eta]$  of the chain-extended PBA increased gradually. At 3 h, its  $[\eta]$



**Figure 1** Influence of the reaction time on the catalyzed chain extension [PrePBA-1: oxazoline/—COOH = 1.2 (molar ratio); reaction temperature = 200°C; *p*-TSA concentration = 0.05 wt %].



increased to 0.68 dL/g, and  $M_n$  and  $M_w$  were 24,300 and 103,900, respectively. Afterward,  $[\eta]$  decreased, probably because of the thermal degradation during the long reaction period.

In the chain extension of HOOC-terminated polyesters or polyamides with bisoxazolines as chain extenders, a stoichiometric quantity of the chain extender was often not sufficient because of its loss from the system during the chain extension.<sup>14,16</sup> Sublimation of the chain extender at a high reaction temperature resulted in a loss during the chain-extension process. In this study, a little excess PBOX was also used to increase the chain-extending efficiency. Table II also shows the influence of the molar ratios between the oxazoline groups in PBOX and the carboxylic groups in PrePBA on the catalyzed chain extension. In the range of oxazoline/—COOH molar ratios from 1.1 to 1.3, a chain-extended PBA with an  $M_n$  over 19,100 and an  $M_w$  over 62,200 was obtained. As the molar ratios of oxazoline to —COOH increased from 1.1 to 1.3, the molecular weight of the chain-extended PBA decreased, maybe because of some blocking reaction of the end groups with the excessive PBOX. Chain extension showed the best results when the oxazoline/—COOH molar ratio was 1.1. When prePBA-4 with a higher molecular weight than that of prePBA-2 was used as a starting material, the molecular weight of the chain-extended PBA was much higher, and chain-extended PBA with an  $M_n$  of 27,500 and an  $M_w$  of 80,100 was obtained. Unstable structures might have been introduced to a lesser extent during the chain extension when PrePBA-4 with a higher molecular weight was used as a starting material, so a chain-extended PBA with a higher molecular weight was obtained. As shown in Table II, after the chain extension, the acid value of the chain-extended PBA decreased. Although the acid values of PrePBA-2, PrePBA-4, and PrePBA-5 were from 21.8 to 47.8 mg of KOH/g, after the chain extension, the acid values were in the range 4.1–6.9 mg of KOH/g. This decrease was also evidence of the chain-extending reaction that occurred between the oxazoline groups in the PBOX and the terminal —COOH groups in PrePBA.

Table III shows the chain extension of HOOC-terminated PrePBS with PBOX as a chain extender in the presence of *p*-TSA. The  $[\eta]$  values of the starting material PrePBS were in the range 0.21–0.38 dL/g. After the chain extension,  $[\eta]$  of PBS increased remarkably, and chain-extended PBS with a  $[\eta]$  of 0.62–0.82 dL/g was obtained at a reaction temperature of 180–200°C and *p*-TSA at 0.05–0.10 wt %. Although PrePBS-2 had a relatively high number of terminal hydroxyl groups, the terminal hydroxyl groups did not obviously lower the chain-extending efficiency, and chain-extended PBS with a  $[\eta]$  value of 0.67 dL/g was obtained.

**TABLE III**  
Catalyzed Chain Extension of PBS with PBOX

PrePBS	Temperature (°C)	Oxazoline/—COOH (molar ratio)	<i>p</i> -TSA (wt %)	$[\eta]$ (dL/g)
PrePBS-1	180	1.1	0.10	0.82
	180	1.2	0.10	0.78
	200	1.2	0.05	0.62
	200	1.2	0.10	Crosslinked
PrePBS-2	180	1.1	0.10	0.67
PrePBS-3	180	1.1	0.10	0.75
PrePBS-4	180	1.1	0.10	0.77

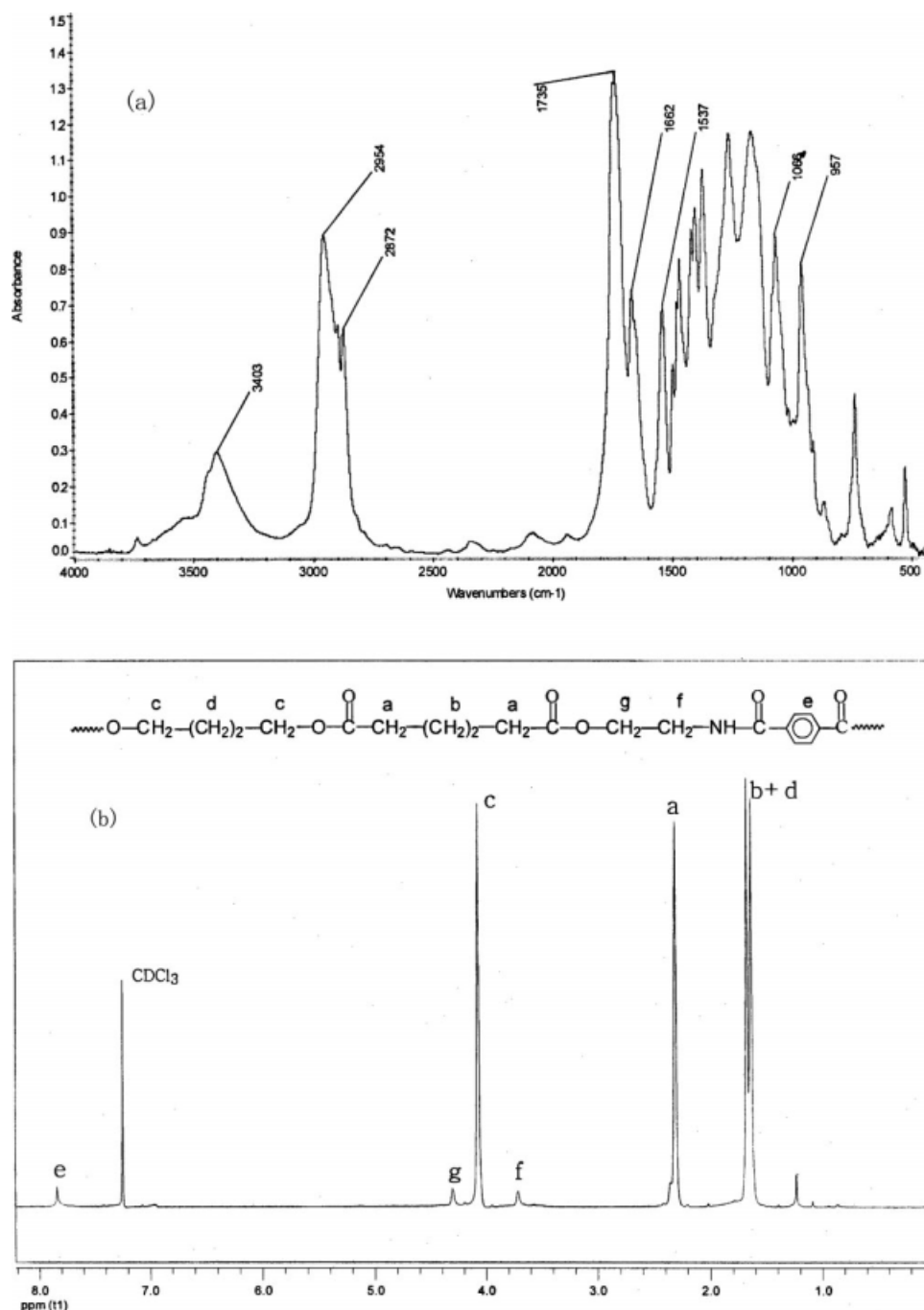
The reaction time was 2 h.

### FTIR and NMR characterization of the chain-extended PBA

Néry et al.<sup>14–16</sup> studied the chain extension of HOOC-terminated polyesters and polyamides with bisoxazolines and found that no side reaction took place. Also, Bohme et al.<sup>20</sup> studied the reaction of bisoxazolines with poly(ethylene terephthalate-*co*-oxybenzoate) with terminal carboxylic groups and found that a crosslinking reaction occurred when PBOX or 2,2'-bis-(2-oxazoline) was used as a chain extender. They assumed that the crosslinking reaction was caused by the reaction of the terminal oxazoline groups with the amide groups in the —COO—CH<sub>2</sub>—CH<sub>2</sub>—NH—CO— structures, which were formed during the chain extension. Furthermore, Sano et al.<sup>21</sup> synthesized crosslinked poly(ester amide)s from the reaction of dicarboxylic acids with excessive bisoxazolines using phosphorous acid esters as catalysts and proposed a similar crosslinking reaction process. The same crosslinked poly(ester amide)s were also synthesized with strong acids and their esters as catalysts.<sup>22</sup>

To probe the chain-extension method of PrePBA and PrePBS with PBOX with *p*-TSA as a catalyst, we characterized the chain-extended PBA obtained from the catalyzed chain extension with <sup>1</sup>H-NMR and IR spectra (Fig. 2). In Figure 2(a), the wide peak at 3403 cm<sup>−1</sup> was assigned to the stretching vibration of N—H in the amide group formed by the chain extension from PBOX. The peaks at 2954 and 2872 cm<sup>−1</sup> corresponded to the stretching vibration of C—H bonds in the —CH<sub>2</sub>— groups. The characteristic peak at 1735 cm<sup>−1</sup> was assigned to the stretching vibration of the C=O groups in the ester linkages. The peaks at 1662 and 1537 cm<sup>−1</sup> corresponded to the C=O stretching vibration of the amide groups formed by the chain extension from PBOX.

In Figure 2(b), the peaks at 2.30 and 1.63 ppm corresponded to the a-CH<sub>2</sub>— and b-CH<sub>2</sub>— hydrogens in the adipoyl structure; the peaks at 4.07 and 1.67 ppm corresponded to the c-CH<sub>2</sub>— and d-CH<sub>2</sub>— hydrogens in the butylene units. This part of the <sup>1</sup>H-NMR spectrum was almost the same as that of PBA

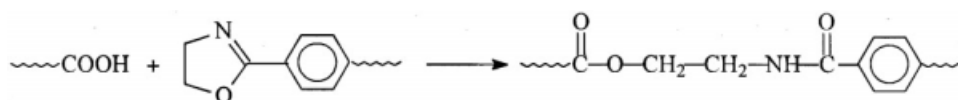


**Figure 2** (a) IR and (b) <sup>1</sup>H-NMR spectra of ExtPBA-3 [ $M_n = 21,400$ ;  $M_w = 67,900$ ;  $p$ -TSA concentration = 0.05 wt %; oxazoline/ $-\text{COOH} = 1.2$  (molar ratio); temperature = 180°C; reaction time = 3 h].

in the literature.<sup>19,23</sup> Meanwhile, the peaks at 3.70 and 4.29 ppm corresponded to the f-CH<sub>2</sub>— and g-CH<sub>2</sub>— hydrogens in the units formed in the chain extension from oxazoline groups in the chain extender, and the area ratio was almost 1 : 1. The peak at 7.83 ppm corresponded to the e-C<sub>6</sub>H<sub>4</sub>— hydrogens. No obvious crosslinking reaction was detected.

On the basis of the <sup>1</sup>H-NMR and IR studies, the increase in the molecular weight, and the decrease

in the acid value during the chain extension, we assumed that the catalyzed chain extension mainly took place as shown in Scheme 1. During the chain-extending reaction,  $p$ -TSA activated the oxazoline groups (I), and the active intermediate (II) formed. It had a much higher reactivity than the nonactivated oxazoline group. So the  $p$ -TSA-catalyzed chain extension became much easier, and chain-extended PBA and PBS with higher molecular weights were obtained. As monomers having oxazoline groups



**Scheme 1** Chain extension of HOOC-terminated PrePBA and PrePBS with PBOx.

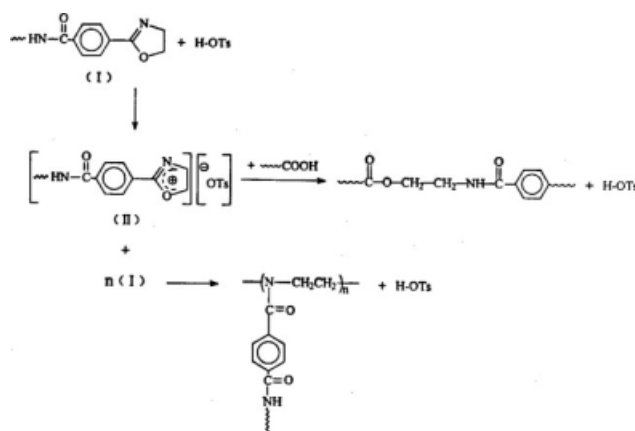
can be initiated by cationic initiators and polymerize through a cationic mechanism,<sup>24</sup> the intermediate (II) may also have initiated the cationic ring-opening polymerization of the oxazoline end groups during the chain extension. So when the reaction temperature of the catalyzed chain extension was high or the amount of *p*-TSA was high, the crosslinking reaction occurred. The catalysis of the chain extension and the crosslinking reaction with *p*-TSA is described as follows (Scheme 2).

Although the reaction temperature and the amount of the *p*-TSA were selected properly, some branching reaction may have still occurred, which resulted in a wide molecular weight distribution, as shown in Table II. As shown in Tables II and III, chain extension of PrePBA-5 and PrePBS-2 with some hydroxyl terminal groups was also successful, and chain-extended PBA and PBS with high molecular weights were obtained. In this case, the branching reaction during the chain extension might have favored the increase in the molecular weight of the chain-extended polyesters.

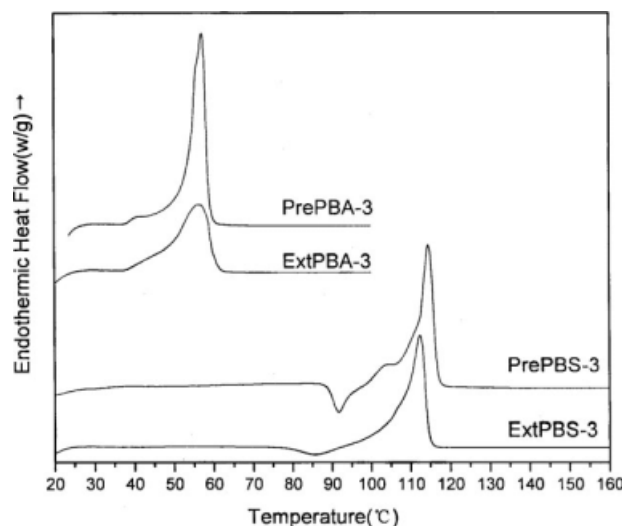
#### DSC study of PrePBA, ExtPBA, PrePBS, and ExtPBS

The nonisothermal and isothermal crystallization properties of the HOOC-terminated PBA and PBS and the chain-extended PBA and PBS were characterized by DSC spectra. Figure 3 shows the heating scan of PrePBA and ExtPBA and that of PrePBS and ExtPBS. Because the melting point of PBA was about 57°C, the PrePBA and ExtPBA samples were scanned from 20 to 100°C. PBS had melting point of 115°C, so the PrePBS and ExtPBS samples were

scanned from 20 to 160°C. The crystallization temperature, melting temperature, and enthalpy of melting of PrePBA, ExtPBA, PrePBS, and ExtPBS are compiled in Table IV (the heating run). As the theoretical enthalpy of melting values for perfectly (100%) crystallized PBA and PBS were 135.0 and 110.3 J/g, respectively, the crystallinities of PrePBA, ExtPBA, PrePBS, and ExtPBS were calculated by the division of the observed heat of fusion (i.e., the enthalpy of melting) by the theoretical value for the perfectly crystallized polymer.<sup>25,26</sup> As shown in Figure 3 and Table IV, the melting temperature of PrePBA-3 was 57.1°C. After the chain-extension reaction with PBOx, the melting temperature of ExtPBA ( $M_n = 21,400$ ,  $M_w = 67,900$ ) was 56.8°C, which was 0.3°C lower than that of the original PrePBA-3. Similarly, the melting temperature of PrePBS-3 was 114.5°C; after the chain extension, the melting temperature of ExtPBS-3 was 112.4°C, which was 2.1°C lower than that of the original PrePBS-3. Meanwhile, the enthalpy of melting and the crystallinity of the polyesters deceased obviously after the chain-extending reaction. The crystallinities of the chain-extended PBA and PBS were 27.9 and 12.3% lower than that of PrePBA and PrePBS, respectively. As shown in Figure 3, the heating curve of PrePBS-3 also showed a crystallization peak at about 91.6°C, but after the chain extension, this peak became very flat and shifted toward a low temperature (85.6°C). It also revealed some difficulties of the crystallization of the chain-extended PBS. The reason was that the diester



**Scheme 2** Catalysis of the chain extension and crosslinking reaction with *p*-TSA.



**Figure 3** Heating DSC scan of PrePBA-3, ExtPBA-3, PrePBS-3, and ExtPBS-3 (heating rate = 10°C/min).

**TABLE IV**  
**Thermal Properties of PrePBA, ExtPBA, PrePBS, and ExtPBS**  
**in the Nonisothermal DSC Scans**

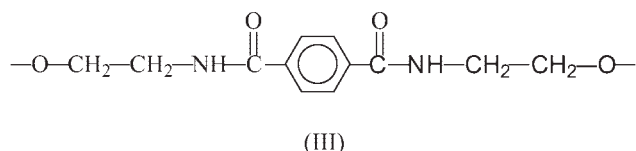
Polymer	Heating run						Cooling run	
	$T_g$ (°C)	$T_{c1}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	Crystallinity (%)		$T_{c2}$ (°C)	$\Delta H_c$ (J/g)
					DSC	WAXS		
PrePBA-3	−80.9	—	57.1	100.6	74.5	64.7	—	—
ExtPBA-3 <sup>a</sup>	−73.1	—	56.8	72.5	53.7	56.4	—	—
PrePBS-3	—	91.6	114.5	88.1	79.9	59.0	78.6	88.2
ExtPBS-3 <sup>b</sup>	—	85.6	112.4	77.3	70.1	43.7	71.8	44.9

$\Delta H_c$  = enthalpy of crystallization;  $\Delta H_m$  = enthalpy of melting;  $T_{c1}$  = crystallization temperature;  $T_{c2}$  = cooling crystallization temperature;  $T_g$  = glass-transition temperature;  $T_m$  = melting temperature.

<sup>a</sup>  $M_n$  = 21,400;  $M_w$  = 67,900; *p*-TSA concentration = 0.05 wt %; oxazoline/—COOH = 1.2 (molar ratio); temperature = 180°C; reaction time = 3 h.

<sup>b</sup>  $[\eta]$  = 0.75 dL/g; *p*-TSA concentration = 0.10 wt %; oxazoline/—COOH = 1.1 (molar ratio); temperature = 180°C; reaction time = 2 h.

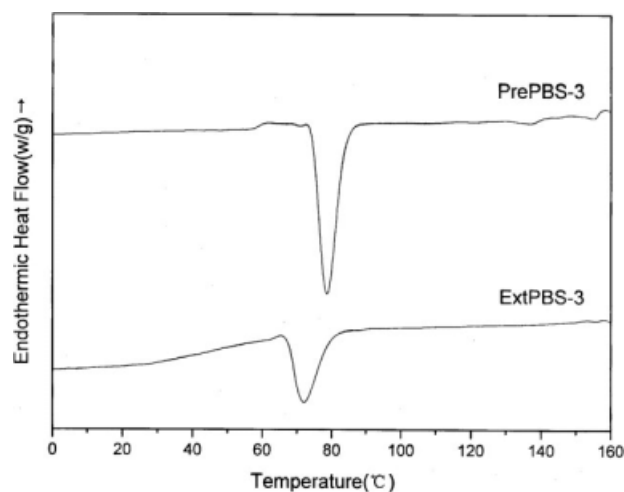
amide structural units (III) introduced by PBOX were different from the main-chain structural units of the prepolymers, which resulted in a decrease in the regularity of the chain-extended PBA and PBS. So the melting temperatures of the chain-extended PBA and PBS obtained with PBOX as a chain extender were lower than those of PrePBA and PrePBS, respectively. As for PBS, a 2.1°C decrease in the melting temperature and a 12.3% decrease in the crystallinity after chain extension might not have influenced its thermal resistance obviously because PBS had a relatively high melting temperature at about 114.5°C:



As PBS was much easier to crystallize than PBA, we also characterized the cooling crystallization behavior of PBS with DSC. Figure 4 shows the cooling scan of PrePBS-3 and ExtPBS-3, and Table IV lists the cooling crystallization temperature and the enthalpy of crystallization. The cooling crystallization temperature of PrePBS-3 was 78.6°C; after the chain extension, the cooling crystallization temperature was 71.8°C, which was 6.8°C lower than that of PrePBS-3. Meanwhile, the enthalpy of crystallization of ExtPBS-3 was just 50.9% that of PrePBS-3. The cooling crystallization of the chain-extended PBS became difficult, and the crystallinity decreased compared with that of PrePBS. As the diester amide structural units (III) introduced by PBOX were different from the major structural units of the PBS polyester and were stiffer and more easily formed hydrogen bonds, these factors increased the difficulties of the chain-extended PBS to crystallize and caused a lower enthalpy of fusion and a lower crystallization temperature than those of PrePBS. As

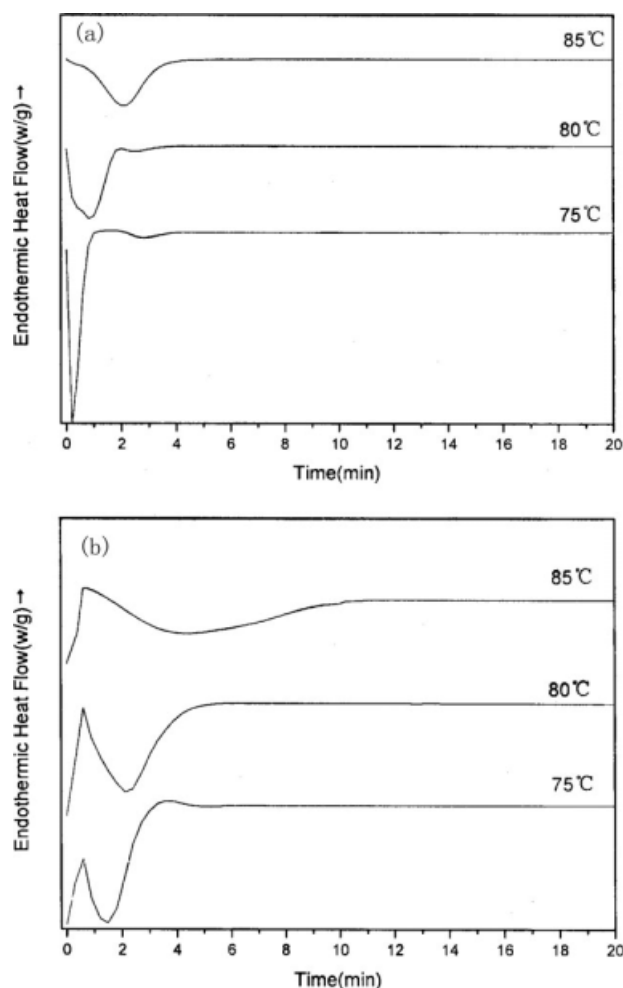
shown in Table IV, PrePBA had a glass-transition temperature of -80.9°C, which was lower than that reported in the literature<sup>26</sup> maybe because of its low molecular weight. After the chain extension, the glass-transition temperature of ExtPBA increased compared with that of PrePBA because of the introduction of the stiff diester amide structural units (III) into PBA during the chain extension. A similar phenomenon was also reported by other researchers.<sup>27</sup> As PrePBS and ExtPBS were crystallized very easily, their glass-transition temperature was not successfully determined.

Papageorgiou et al.<sup>28</sup> reported that PBS crystallized rapidly, with a crystallization temperature from 75 to 85°C, and the half-time of crystallization was less than 5 min. To compare the difference in the crystallization behavior between PrePBS and ExtPBS further, we characterized their isothermal crystallization properties. As the melt equilibrium of



**Figure 4** Cooling DSC scan of PrePBS-3 and ExtPBS-3 (temperature = 160°C; time = 5 min; cooling rate = 5°C/min).





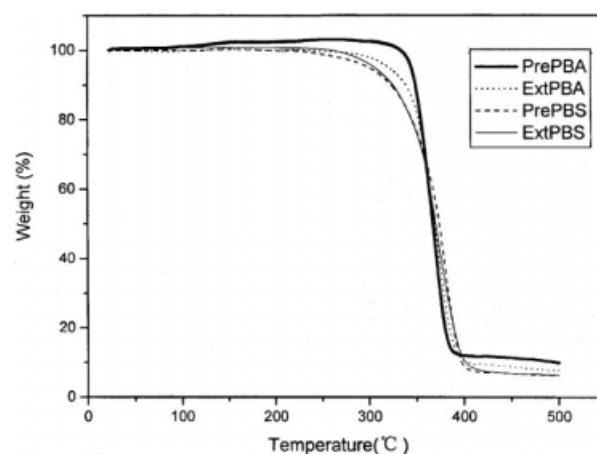
**Figure 5** Isothermal crystallization DSC curves of (a) PrePBS-3 and (b) ExtPBS-3 at different temperatures.

PBS was estimated at 140 or 132°C,<sup>29–31</sup> the samples were melted at 160°C for 5 min to remove any possible crystal nuclei remaining. Figure 5 shows the isothermal crystallization DSC curves of PrePBS-3 and ExtPBS-3 at different temperatures. The scale of the heat flow rate of every crystallization isotherm was normalized so that their peak heights could be com-

**TABLE V**  
Half-Time of Crystallization ( $t_{1/2}$ ) and Enthalpy of Crystallization ( $\Delta H$ ) of PrePBS-3 and ExtPBS-3 in the Isothermal Crystallization Process

Polymer	Temperature (°C)	$t_{1/2}$ (min)	$\Delta H$ (J/g)
PrePBS-3	75	0.3	79.4
	80	1.0	78.8
	85	2.0	75.5
ExtPBS-3 <sup>a</sup>	75	1.8	67.1
	80	2.1	66.9
	85	4.7	60.5

<sup>a</sup>  $[\eta] = 0.75$  dL/g; *p*-TSA concentration = 0.10 wt %; oxazoline/—COOH = 1.1 (molar ratio); temperature = 180°C; reaction time = 2 h.



**Figure 6** TGA curves of PrePBA-3, ExtPBA-3, PrePBS-3, and ExtPBS-3 (heating rate = 10°C/min, N<sub>2</sub>).

pared. The half-time of crystallization was directly determined as the time elapsed from the onset of the crystallization peak to the point where the crystallization was half completed. Table V shows the half-time of crystallization and the enthalpy of crystallization values of PrePBS-3 and ExtPBS-3 detected in the isothermal crystallization process. As shown in Figure 5(a,b) and Table V, at the same crystallization temperature, ExtPBS-3 had a longer half-time of crystallization and a lower enthalpy of crystallization and crystallinity than PrePBS-3. The crystallization of ExtPBS was slower than that of PrePBS. The stiff and different diester amide structural units (III) introduced by PBOX made ExtPBS difficult to crystallize. However, the half-time of crystallization of ExtPBS-3 with crystallization temperatures from 75 to 85°C was still less than 5 min; it was also easy to crystallize and suitable for processing with normal thermal processing methods.

#### TGA of PrePBA, ExtPBA, PrePBS, and ExtPBS

The thermal stability values of the prepolymers (PrePBA and PrePBS) and the chain-extended polyesters (ExtPBA and ExtPBS) were studied with TGA and are shown in Figure 6. The initial decomposition temperature, 50% mass decomposition temperature, end decomposition temperature, and end mass loss are summarized in Table VI. Table VI shows that ExtPBA and ExtPBS had lower initial decomposition temperatures, 50% mass decomposition temperatures, and end decomposition temperatures than PrePBA and PrePBS, respectively. The end mass losses of ExtPBA and ExtPBS were higher than those of PrePBA and PrePBS. The thermal stabilities of ExtPBA-3 and ExtPBS-3 were slightly lower than those of PrePBA and PrePBS. Harashina et al.<sup>32</sup> studied the thermal decomposition of ethanolamine-modified PET and [poly(ester amide)] and found

TABLE VI  
TGA Data of the Prepolyesters and the  
Chain-Extended Polyesters

Polymer	$T_i$ (°C)	$T_{50\%}$ (°C)	$T_{\text{end}}$ (°C)	End mass loss (%)
PrePBA-3	347.0	367.4	387.8	88.17
ExtPBA-3 <sup>a</sup>	346.9	364.4	381.9	90.07
PrePBS-3	352.4	373.3	394.3	88.65
ExtPBS-3 <sup>b</sup>	341.9	368.1	394.3	90.43

The heating rate was 10°C/min, and the atmosphere was N<sub>2</sub>.  $T_{50\%}$  = temperature at 50% decomposition;  $T_{\text{end}}$  = temperature at the end of the steep decomposition change;  $T_i$  = initial decomposition temperature.

<sup>a</sup>  $M_n$  = 21,400;  $M_w$  = 67,900; *p*-TSA concentration = 0.05 wt %; oxazoline/—COOH = 1.2 (molar ratio); temperature = 180°C; reaction time = 3 h.

<sup>b</sup>  $[\eta]$  = 0.75 dL/g; *p*-TSA concentration = 0.10 wt %; oxazoline/—COOH = 1.1 (molar ratio); temperature = 180°C; reaction time = 2 h.

that the modified poly(ester amide) was less stable than PET. They proposed a decomposition method to demonstrate this phenomenon. The primary thermal decomposition proceeded via a  $\beta$ -CH hydrogen-transfer reaction accompanied by carbon–oxygen bond scission in the ester amide structural units via a six-membered ring transition state to form carboxyl and *N*-vinyl amide end groups. In this study, a similar decomposition pathway might have taken place at the diester amide structural units (III), which resulted in the lower stability in ExtPBA and ExtPBS than in PrePBA and PrePBS.

### X-ray analysis and tensile testing

The crystalline structure and the degree of the crystallinity of the prepolymers and chain-extended polyesters were also determined by WAXS measure-

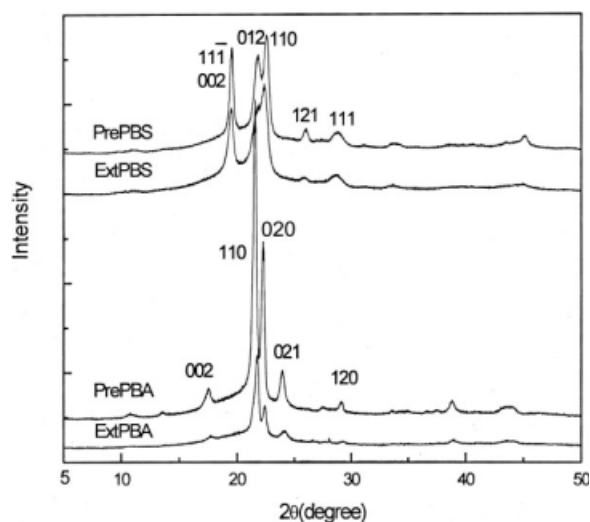


Figure 7 X-ray diffraction diagrams of PrePBA-3, ExtPBA-3, PrePBS-3, and ExtPBS-3.

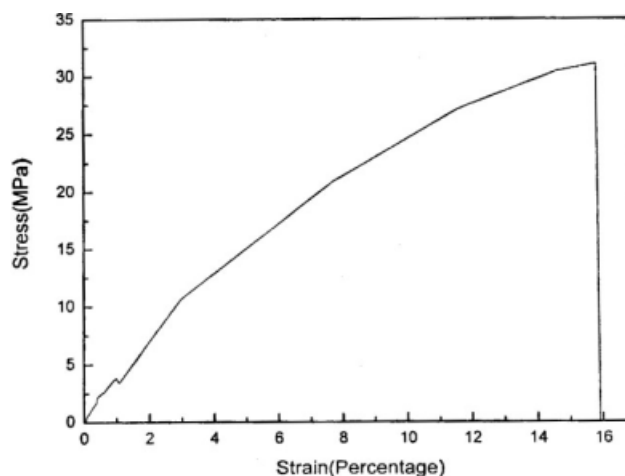


Figure 8 Tensile strain curve of ExtPBS-3.

ments. Figure 7 shows the diffraction curves of PrePBA, ExtPBA, PrePBS, and ExtPBS. As shown in Figure 7, peaks corresponding to PrePBS at a  $2\theta$  of 19.54 Miller indices (111 and 002) 21.79 (012), 22.65 (110), 26.32 (121), and 28.84 (111) and peaks corresponding to PrePBA at a  $2\theta$  of 17.49 (002), 21.58 (110), 22.27 (020), 23.95 (021), and 29.13 (120) were present. The peaks corresponding to ExtPBS and ExtPBA were almost the same as that of PrePBS and PrePBA, respectively. From the X-ray diffraction, it was revealed that PrePBS, PrePBA, ExtPBS, and ExtPBA crystallized in a monoclinic crystal lattice.<sup>26,27,33</sup> The degrees of crystallinity of PrePBA, ExtPBA, PrePBS, and ExtPBS were also calculated from the X-ray patterns and are compiled in Table IV. As shown in Table IV, after chain extension, the degree of the crystallinity determined by X-ray diffraction also decreased. The reason was that the introduction of the different diester amide structural units (III) into the PBA and PBS main chains by the chain extension of PBOX lowered the regularity of the polyesters.

Tensile tests of PBS were also conducted (Fig. 8). Because the PrePBS samples had low molecular weights and were very brittle, their testing bars could not be prepared by the hot-press method. Testing bars of the chain-extended PBS with a  $[\eta]$  of 0.77 dL/g were successfully prepared. Their tensile strength was 31.05 MPa, and their strain at break was 15.73%. ExtPBS obtained from the chain extension had good mechanical properties and may suitably be used as a biodegradable thermoplastic material.

### CONCLUSIONS

Aliphatic polyesters such as PBA and PBS with high molecular weights were successfully synthesized through the chain extension of HOOC-terminated

PBA and PBS prepolyesters with PBOX under the catalysis of *p*-TSA. Compared with those of polyesters without a catalyzed chain extension, the molecular weights of the chain-extended polyesters was much higher. However, a higher amount of *p*-TSA than 0.15 wt % and a higher temperature than 200°C often caused a crosslinking reaction during the chain extension. Under optimal conditions, a chain-extended PBA with an  $M_n$  up to 29,600 and a chain-extended PBS with a  $[\eta]$  of 0.82 dL/g were synthesized. DSC and TGA characterization showed that the chain-extended PBA and PBS had lower melting temperatures and crystallinities and slower crystallization rates and were less thermally stable compared with PrePBA and PrePBS, respectively. The chain extension with PBOX introduced many stiffer diester amide structural units (III), which were different from the major structural units of the PBA and PBS, which made ExtPBA and ExtPBS difficult to crystallize and less thermally stable. However, this deterioration of the properties was not harmful enough to impair their thermal processing properties and obstruct them from being used as biodegradable thermoplastics. After the chain extension, the PBS had good mechanical properties.

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