

Synthesis of Novel Biodegradable Poly(butylene succinate) Copolyesters Composing of Isosorbide and Poly(ethylene glycol)

Licheng Tan, Yiwang Chen, Weihua Zhou, Junchao Wei, Suwen Ye

Department of Chemistry, Institute of Polymers, Nanchang University, Nanchang 330031, China

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ABSTRACT: A series of biodegradable isosorbide-based copolyesters poly(butylene succinate-co-isosorbide succinate-co-polyethyleneoxide succinate) ($PB_xI_yE_zS$) were synthesized via bulk polycondensation in the presence of dimethyl succinate (DMS), 1,4-butanediol (BDO), poly(ethylene glycol) (PEG) and isosorbide (ISO). The crystallization behaviors, crystal structure and spherulite morphology of the copolyesters were analyzed by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and polarizing optical microscopy (POM), respectively. The results indicate that the crystallization behavior of the copolyesters was influenced by the content of iso-

sorbide succinate (IS) and polyethyleneoxide succinate (PEOS) units, which further tuned the mechanical and biodegradable properties of the copolyesters. The $PB_xI_yE_zS$ copolyesters, compared to pure poly(butylene succinate), showed lower crystallization temperature, melting temperature, degree of crystallinity and degradation rate while a significant increase in glass transition temperature with increasing isosorbide content. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2291–2300, 2011

Key words: poly(butylene succinate); isosorbide; polycondensation; crystallization; enzymatic degradation

INTRODUCTION

Poly(butylene succinate) (PBS) is a biodegradable aliphatic polyester that is used in a wide range of engineering applications. PBS has a relatively high melting temperature similar to that of the low density polyethylene, so that it can be processed with conventional equipments commonly used for polyolefins. However, PBS possesses a low glass transition temperature ($T_g \approx -38^\circ\text{C}$),^{1,2} which makes it without glass fibers or other fillers less suitable for applications at elevated temperature. Moreover, the insufficient mechanical properties of PBS, especially its poor elongation at break, have prevented it from being used in diverse application, and so various techniques such as blending and copolymerization with various aromatic polyesters have been explored to improve these weaknesses. In particular, aromatic polyesters normally including poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET) and so on, usually provide chain rigidity and thus suffi-

ciently high T_g ,^{3–7} but these polyesters are originated from fossil feedstock and have the disadvantage that they are less susceptible to biodegradation.^{8,9}

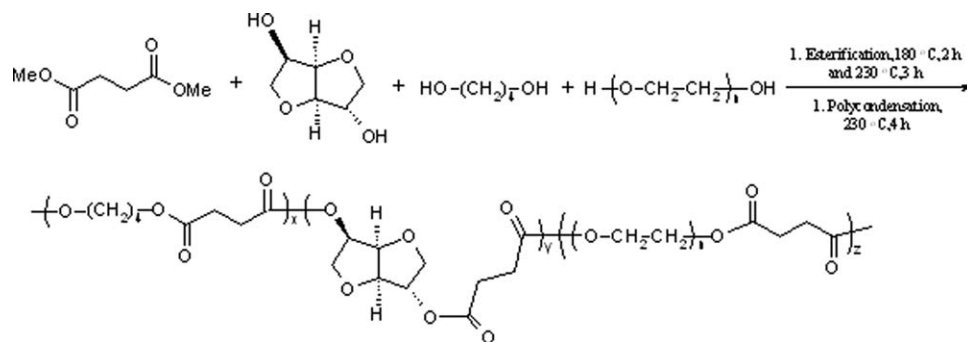
The development of biobased, especially cereal-based, chemicals has the potential to reduce the amount of petroleum consumed in the chemical industry and also to open new high-value-added markets to agriculture.¹⁰ 1,4 : 3,6-Dianhydro-D-glucitol (isosorbide) is an example of such chemicals, which was prepared by hydrogenation and subsequent dehydration from D-glucose.¹¹ It was easily accessible from natural feedstock (starch) and could thus advantageously replace compounds from the petroleum industry.¹² Isosorbide has a melting temperature between 61 and 64°C and it is known to be thermally stable up to 270°C.¹³ The use of isosorbide in polymer systems for coating applications has been previously reported by several authors,^{14–18} and direct incorporation of isosorbide into commercial polyesters such poly(ethylene terephthalate) (PET) can raise their glass temperatures¹⁹ allowing a new range of applications including hot-fill containers.²⁰ In spite of the increasing interest in isosorbide use in aromatic (co)polyesters,^{21–23} relatively little is known about its effect on aliphatic copolyesters.^{24,25}

The aim of this work is to prepare a series of isosorbide-based copolyesters with relatively higher glass transition temperature and sufficient mechanical properties via bulk polycondensation. Monomers such as 1,4-butanediol, poly(ethylene glycol) and

Correspondence to: Y. Chen (ywchen@ncu.edu.cn) or W. Zhou (dramzwh@126.com).

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Scheme 1 Synthesis route of $\text{PB}_x\text{I}_y\text{E}_z\text{S}$ copolyesters.

dimethyl succinate (DMS), in combination with renewable isosorbide, were used in the polymer synthesis. Poly(ethylene glycol) was used as the component of improving the degradation rate of the copolymers. The effect of isosorbide on crystallization behavior, crystal structure, morphology, as well as the mechanical and degradation properties of the copolyesters was also explored.

EXPERIMENTAL

Materials

1,4 : 3,6-Dianhydro-D-glucitol (isosorbide) (ISO) and DMS was purchased from Aldrich (Shanghai, China), and Alfa Aesar, (Tianjin, China), respectively. The 1,4-butanediol (BDO) was purchased from Sinopharm Chemical Reagent, (Shanghai, China). The reagents were used as received without further purification. Hydroxyl end-capped poly(ethylene glycol) 1000 (PEG, $M_n = 1000$) was purchased from Lancaster and dried by vacuum at 40°C before use. The Titanium (IV) butoxide ($\text{Ti}(\text{OBU})_4$) catalyst was purchased from Acros and the lipase of *Pseudomonas cepacia* was purchased from Fluka. All the other chemicals and solvents of analytical grade were used as received without further purification.

Synthesis of copolyesters

The aliphatic copolyesters poly(butylene succinate-co-isosorbide succinate-co-polyethyleneoxide succinate) ($\text{PB}_x\text{I}_y\text{E}_z\text{S}$) were synthesized by the two-stage melt polycondensation method composing of esterification and polycondensation in the presence of DMS, 1,4-butanediol (BDO), isosorbide (ISO) and poly(ethylene glycol) (PEG) as shown in Scheme 1. The total molar ratio of BDO and ISO to the molar ratio of DMS was 1.2 to 1. In the first stage, the reaction mixture was charged into a 250 mL glass reactor under nitrogen, followed by the addition of $\text{Ti}(\text{OBU})_4$ (0.025 mol % of the total chemicals). The mixture was heated to 180°C and reacted for 2 h under nitro-

gen protection and vigorous stirring. The esterification was complete when the theoretical amount of byproduct was yielded; a second portion of catalyst $\text{Ti}(\text{OBU})_4$ (0.025 mol % of the total chemicals) was then added. The temperature was slowly increased to 230°C and continued for 3 h for all prepared polyesters. In the second step of polycondensation, a vacuum (50 Pa) was applied slowly over a period of time of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation. Vacuum was applied for 4 h, after which the polymer was allowed to cool to room temperature, dissolved in 50 mL of chloroform, isolated by precipitation in 800 mL of methanol, and collected on a filter. The polymer was then dried at 40°C for 24 h under vacuum.

Measurements

The proton nuclear magnetic resonance (^1H NMR) spectra were collected on a Bruker AV 600 NMR spectrometer with deuterated CDCl_3 as the solvent and with tetramethylsilane ($\delta = 0$) as the internal standard. The gel permeation chromatography (GPC) was conducted with a Breeze Waters system using polystyrenes as the standard and chloroform as the eluent at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) measurements of copolyesters were carried out on a Shimadzu DSC-60 under a nitrogen flow. The calibration of the temperature was performed using indium as the standard before the measurement. About 5 mg of samples encapsulated in the DSC aluminum pan, were heated quickly to 150°C and held for 3 min to erase thermal history. Then, the samples were cooled to -50°C and subsequently heated to 150°C at $10^\circ\text{C}/\text{min}$. The corresponding glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) were recorded, respectively. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen with a sample size of 8–10 mg. The wide angle X-ray diffraction (WAXD) study was

TABLE I
Chemical Composition, Yield and MolecularWeights of the Copolyesters

Sample	Feed molar ratio DMS/BDO/ISO/PEG	Feed composition DMS/BDO/ISO/PEG	Composition ^a BS/IS/ES	Yield (%)	$\overline{M}_n \times 10^{-4}$ (g/mol)	$\overline{M}_w/\overline{M}_n$
PB ₁₀₀ I ₀ E ₀ S	1.0/1.2/0/0	45.5/54.5/0/0	100/0/0	89.4	8.80	1.47
PB ₈₆ I ₁₄ E ₀ S	1.0/0.96/0.24/0	45.5/43.6/10.9/0	85.9/14.1/0	70.9	1.85	1.67
PB ₁₁ I ₈₉ E ₀ S	1.0/0.24/0.96/0	45.5/10.9/43.6/0	10.6/89.4/0	64.8	1.37	1.64
PB ₀ I ₁₀₀ E ₀ S	1.0/0/1.2/0	45.5/0/54.5/0	0/100/0	56.3	1.34	1.57
PB ₇₀ I ₁₂ E ₁₈ S	1.0/0.96/0.24/0.2	41.7/40.0/10.0/8.3	70.4/11.9/17.5	74.1	5.02	1.86
PB ₅₅ I ₈ E ₃₇ S	1.0/0.96/0.24/0.5	37.0/35.6/8.9/18.5	54.9/7.9/37.2	78.5	8.63	1.75
PB ⁴⁴ I ⁸ E ₄₈ S	1.0/0.96/0.24/0.8	33.3/32.0/8.0/26.7	44.1/8.4/47.5	70.2	3.25	1.62

^a The molar ratio of BS, IS, and ES units in the copolyesters calculated from ¹H-NMR.

adopted to analyze crystalline structure of the samples by a Bruker D8 Focus X-ray diffractometer, operating at 30 kV and 20 mA with a copper target ($\lambda = 0.154$ nm) and in the 2θ angle range of $5\text{--}40^\circ$ at a scanning rate of $0.5^\circ/\text{min}$. The crystal morphology of the copolyesters was analyzed by a Nikon E600POL polarizing optical microscope (POM) equipped with an Instec HS 400 heating and cooling stage. Mechanical properties of the copolyesters were determined by a SANS WDW universal test system with electronic data evaluation on specimen of 70×25 mm with a thickness in the range of 0.04 to 0.06 mm determined by a vernier caliper. The specimens were cut from melt-pressed films by a mold equipped with knives. The values of tensile strength, elongation at break and tensile modulus were determined. Data were taken as the average value of at least five measurements. The surfaces of degraded samples after the enzymatic degradation were observed with Quanta 200F scanning electron microscopy (SEM) after gold vapor deposition onto the samples in an Edwards Auto 306.

Enzymatic degradation

The copolyesters films ($50 \times 20 \times 0.06$ mm) prepared by melt-pressed were placed in vials containing 20 mL of phosphate buffer solution (pH 7.4 at 25°C) with 0.30 mg/mL *Pseudomonas cepacia* lipase at constant temperature of 37°C . To retain the activity of the enzyme, the phosphate buffer solution was replaced with fresh buffer solution every week. At predetermined degradation time intervals, the specimens were removed from the medium, rinsed with distilled water, dried under vacuum at room temperature for one week and weighed. Weight loss percentages of the copolyesters were obtained according to the relationship:

$$\text{Weight loss (\%)} = (W_0 - W_r)/W_0 \times 100\% \quad (1)$$

where W_0 is the initial weight, and W_r is the dry weight of the specimens after degradation.

RESULTS AND DISCUSSION

Structure of copolyesters

The isosorbide-based copolyesters were synthesized via the two-stage polycondensation process as shown in Scheme 1. The reactions were carried out in bulk at 230°C with different DMS/butanediol/isosorbide/poly(ethylene glycol) feed ratios in the presence of titanium (IV) butoxide ($\text{Ti}(\text{OBU})_4$) as a catalyst. Terpolyesters based on 1,4-butanediol (BDO), poly(ethylene glycol) (PEG) and isosorbide (ISO) were colorless to pale yellow materials, as the increasing the feed ratio of ISO. The sensitivity of isosorbide to thermooxidation at high temperature needed to polymerize polyesters is the cause for this yellowing. In the $\text{PB}_x\text{I}_y\text{E}_z\text{S}$ copolyesters, the "B" in the sample code represents for the butylene succinate (BS) unit, the "I" in the sample code represents for the isosorbide succinate (IS) unit, and "E" represents for polyethyleneoxide succinate (PEOS) unit. The subscript numbers at the end of each initial indicate the actual molar fractions (%) of BS, IS and PEOS units in the copolyesters.

Table I lists the feed molar ratio, composition, yield, number-averaged molecular weight (\overline{M}_n) and polydispersity ($\overline{M}_w/\overline{M}_n$) of the copolyesters. It is noticed that the number-averaged molecular weights (\overline{M}_n) is ranging from 1.34×10^4 to 8.80×10^4 g/mol with the polydispersity between 1.47 and 1.86. Moreover, \overline{M}_n decreases with increasing isosorbide content owing to the low reactivity of ISO. The values obtained indicate that the $\text{PB}_x\text{I}_y\text{E}_z\text{S}$ copolyesters synthesized from three different diol moieties (BDO, ISO and PEG) have high molecular weights and they are suitable to be used in fields where flexible materials are needed.

Figure 1 shows the ¹H NMR spectra of the $\text{PB}_{55}\text{I}_8\text{E}_{37}\text{S}$ copolyester, and the peaks corresponding to the BS, IS and PEOS units are observed. The peak at 2.67 ppm (proton a) is assigned to protons from the CH_2 of succinate. The peaks at 4.12 ppm (proton b) and 1.71 ppm (proton c) are attributed to the

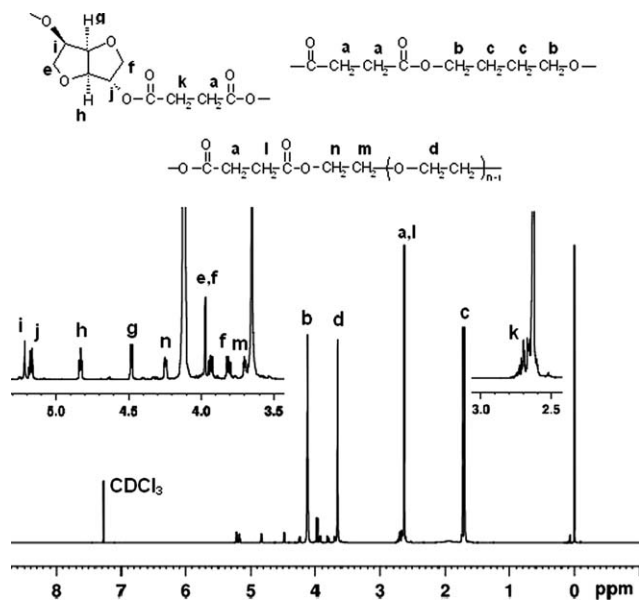


Figure 1 600 MHz^a H-NMR spectrum of the PB55I8E37S copolyester.

side and central CH₂ protons of the butylene, respectively. The peak at 3.65 ppm (proton **d**) is ascribed to the CH₂ of polyethyleneoxide. Furthermore, the peaks at 3.97 ppm (proton **e**), 3.81 ppm (proton **f**), 4.48 ppm (proton **g**), 4.83 ppm (proton **h**), 5.18 ppm (proton **i**), and 5.16 ppm (proton **j**), are correspond to the protons of isororbide. The differences in shifts between peaks **e** and **f** as well as between peaks **i** and **j** are direct results of the *endo* and *exo* positioning of the two OH groups of isororbide. The broadening of the CH₂ protons of succinate at 2.6–2.7 ppm (peaks **a**, **k** and **l**) is caused by the esterification with three different diol moieties (BDO, ISO and PEG), as well as by the *endo* and *exo* character of the isororbide OH groups, leading to different chemical environ-

ments. Besides, the peak at 3.70 ppm (proton **m**) and 4.25 ppm (proton **n**) are assigned to the CH₂ protons of the ethyleneoxide linking to succinate. The above results suggest that the BS, IS and ES units are built into the molecular chains of the copolyesters due to the transesterification.

The composition of the copolyesters is calculated on the basis of the corresponding resonance peak integrals of the protons of the butylene succinate (BS) units, isororbide succinate (IS) units, and polyethyleneoxide succinate (PEOS) units by the following equations:

$$x_{\text{BS}} = \frac{I_c/4}{I_c/4 + I_g + (I_d + I_m)/4} \quad (2)$$

$$x_{\text{IS}} = \frac{I_g}{I_c/4 + I_g + (I_d + I_m)/4} \quad (3)$$

$$x_{\text{PEOS}} = \frac{(I_g + I_m)/4}{I_c/4 + I_g + (I_d + I_m)/4} \quad (4)$$

where, x_{BS} , x_{IS} and x_{PEOS} are the molar fractions of BS, IS and PEOS units, I_c , I_d , I_g , and I_m are the integrals of the corresponding peaks, respectively. It is found that the BS units content decrease as the IS and PEOS units content increasing.

Thermal properties of copolyesters

The crystallization and melting behaviors of the copolyesters were investigated by the DSC analysis, and the heating and cooling curves are shown in Figure 2. Table II provides a summary of the DSC results from two scans, revealing the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), as well as crystallization enthalpy (ΔH_c). It is noticed that all the copolyesters exhibit only one glass

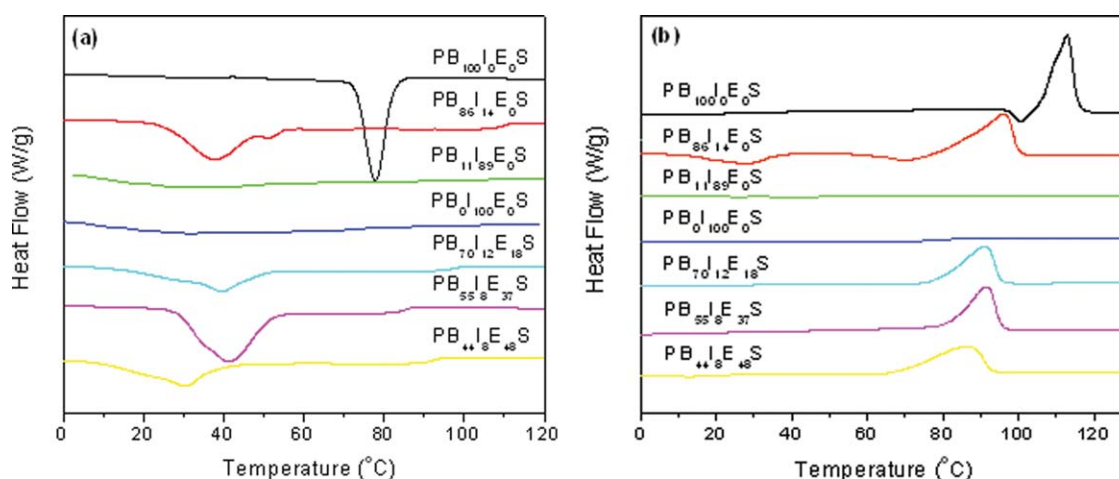


Figure 2 DSC (a) cooling and (b) second heating curves for the copolyesters. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE II
Thermal Properties and Degree of Crystallinity of the Copolyesters

Sample	T_g (C)	T_m (C)	H_m (J/g)	T_c (C)	H_c (J/g)	T_d (C)	X_{c-DSC} (%)	X_{c-WAXD} (%)
PB ₁₀₀ I ₀ E ₀ S	-26.7	112.9	73.6	77.9	68.4	317.1	66.6	54.5
PB ₈₆ I ₁₄ E ₀ S	37.5	96.1	64.2	37.8	49.4	341.0	58.1	48.5
PB ₁₁ I ₈₉ E ₀ S	45.3	-	-	-	-	219.7	-	-
PB ₀ I ₁₀₀ E ₀ S	56.4	-	-	-	-	129.8	-	-
PB ₇₀ I ₁₂ E ₁₈ S	23.5	91.2	46.2	39.6	31.7	333.2	41.8	40.9
PB ₅₅ I ₈ E ₃₇ S	19.7	91.5	48.3	41.3	54.2	352.2	43.7	44.5
PB ₄₄ I ₈ E ₄₈ S	20.9	86.4	47.2	30.5	39.3	314.3	42.7	41.5
PB ₆₅ I ₀ E ₃₅ S	-40.8	110.3	57.5	70.1	57.0	298.3	52.1	50.9

Glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) were registered by DSC at a cooling rate of 10°C/min or at a second heating rate of 10°C/min. Thermal decomposition temperature (T_d) (-5 wt %) was measured by TGA at a heating rate of 20°C/min. The crystallinity degree (X_{c-DSC}) was obtained from DSC cooling run according to $X_{c-DSC} = \Delta H_m / \Delta H_m^0$, where ΔH_m^0 is the theoretical value of the melting enthalpy of 100% crystallized PBS homopolymer as 110.5 J/g. The crystallinity degree (X_{c-WAXD}) was determined by the X-ray diffraction method.

transition temperature, showing the formation of homogeneous phase without significant phase separation. According to Noordover et al.,²⁶ a minimum isosorbide content of approximately 60–70% of the total diol amount is required to obtain materials with T_g values above the boundary (>45°C) for coating applications. In this study, the T_g of the PB_xI_yE_zS copolyesters is varied from 19.7 to 56.4°C. Compared to pure PBS, a significant increase in T_g with increasing isosorbide content can be observed. The results demonstrate that it is possible to synthesize aliphatic copolyesters containing isosorbide with sufficiently high T_g values, which are potential candidates for different application.

The crystallization temperature and melting temperature decreased as the IS units content increasing, and increased as the incorporating of PEOS units into the copolyesters. However, the T_c of the copolyester decreased as the content of PEOS units was more than 40% and became the dominant component of the copolyester. In the cases of PB₁₁I₈₉E₀S and PB₀I₁₀₀E₀S, in which the IS units were the dominant component, no crystallization peak was observed. It is indicated that PB₁₁I₈₉E₀S and PB₀I₁₀₀E₀S copolyesters were completely amorphous. Moreover, it is noticed that the corresponding ΔH_c and ΔH_m values is the similar as those of the crystallization temperature. The degree of crystallinity of copolyesters could be calculated by the following equation:

$$X_{c-DSC} = \frac{\Delta H_m}{\Delta H_m^0} \quad (5)$$

where ΔH_m^0 is the theoretical value of the melting enthalpy of 100% crystallized PBS homopolymer, calculated on the basis of the group contribution method,²⁷ and the value was determined to be 110.5 J/g.

The T_c , in accordance with T_m , ΔH_c , and ΔH_m , was mainly determined by the degree of crystallinity of

copolyesters, causing by the different content of IS and PEOS units in the copolyesters. Due to the IS units with large steric hindrance decreasing the crystallinity of copolyesters, the copolyesters crystallize at lower crystallization temperatures lead to the formation of less perfect crystals which eventually melt at lower temperatures. As increasing the content of PEOS units leading to the decreasing of IS units, the effect of IS units on the crystallinity became less significant. Conversely, the more content of PEOS units increased the mobility of copolyester chain, resulting in the orderly arrangement of copolyester chain and increasing of crystallinity. As the content of PEOS units became the dominant component of the copolyester, the crystallinity decreased, which is due to the ability of crystallization of PEOS units lower than BS units in the copolyesters.

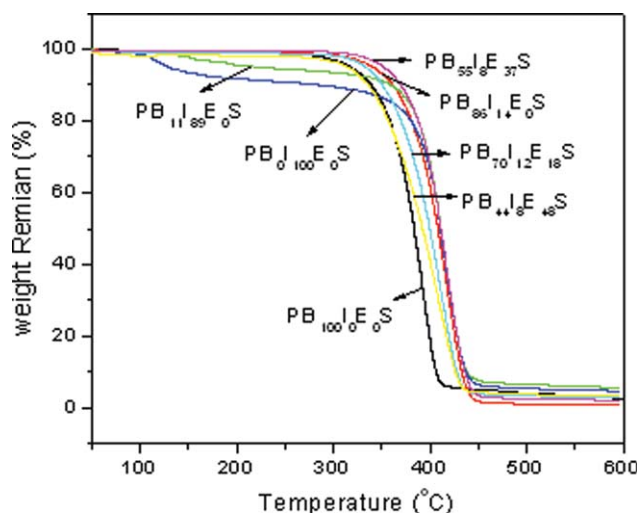


Figure 3 TGA traces of copolyesters (heating rate of 20°C/min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

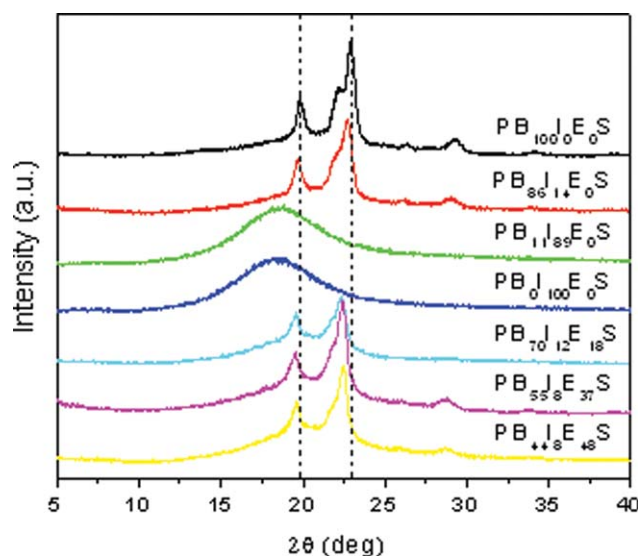


Figure 4 WAXD spectra of the copolyesters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The TGA measurements were conducted in a nitrogen atmosphere in the 50–600°C temperature range to evaluate the thermal stability of the copolyesters (Fig. 3). Classic one-step degradation curves are obtained for all samples, indicating that there is no significant difference in the mechanism of thermal degradation. Table II compares decomposition temperatures (T_d), measured at 5% weight loss of all copolyesters. Except that the T_d of $PB_{11}I_{89}E_0S$ and $PB_0I_{100}E_0S$ decreased markedly, the T_d of the rest $PB_xI_yE_zS$ copolyesters increased slightly compared to pure PBS, revealing that incorporating IS and PEOS units slightly improved the thermal stability of the $PB_xI_yE_zS$ copolyesters containing isosorbide in total diol less than 89 mol %.

Crystal structure and morphology of copolyesters

The nature of the crystallize phase in the copolyesters of this study was investigated with WAXD. Figure 4 shows the WAXD patterns of the $PB_xI_yE_zS$ copolyesters, crystallized during cooling in the air at room temperature for 24 h. Except for the $PB_{11}I_{89}E_0S$

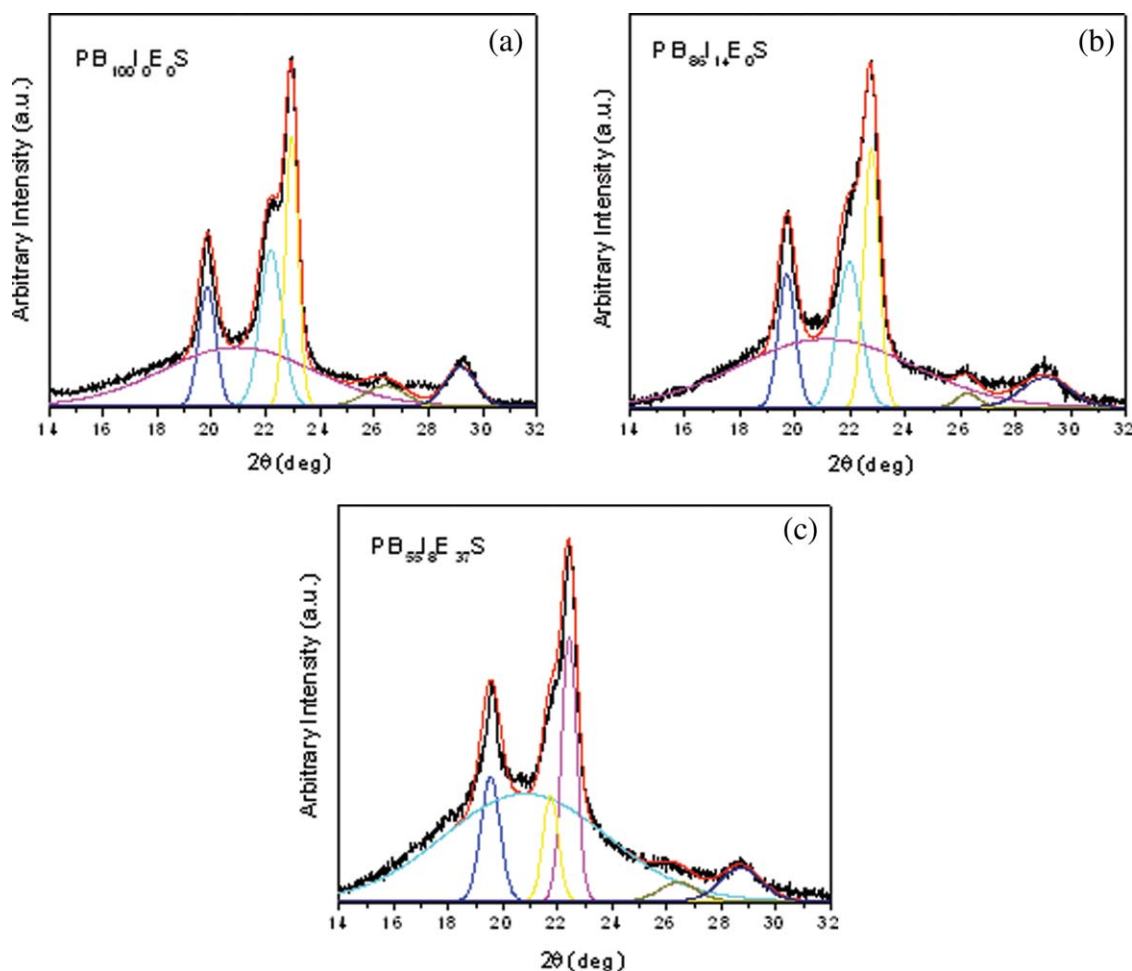


Figure 5 Peak-separation diagrams of the copolyesters by WAXD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

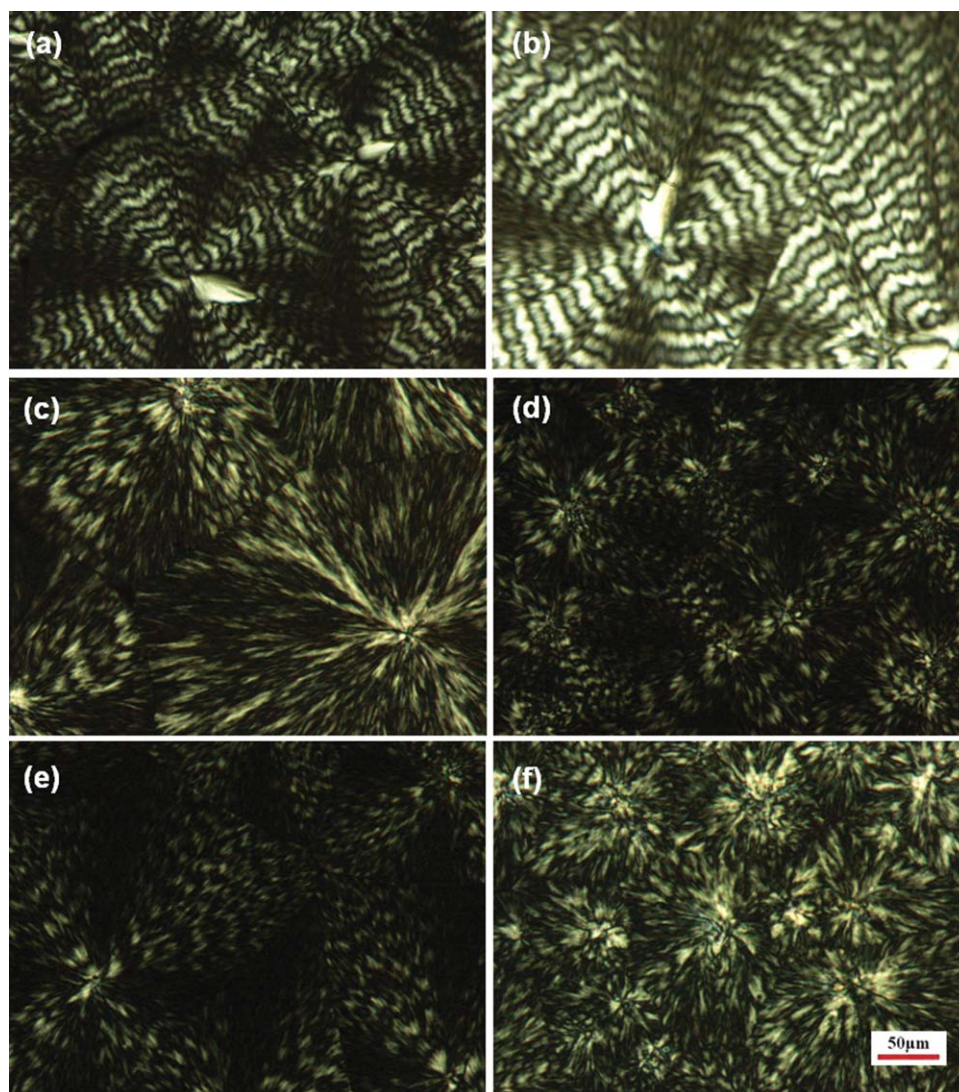


Figure 6 POM graphs for copolyesters of (a, b) PB100I0E0S crystallized at 75 and 80°C, (c) PB86I14E0S crystallized at 45°C, (d) PB70I12E18S crystallized at 45°C, (e) PB55I18E37S crystallized at 50°C, (f) PB44I18E48S crystallized at 40°C, respectively. The scale is the same for all photos. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and $PB_0I_{100}E_0S$, which were amorphous, in the WAXD patterns of the copolyesters, crystalline reflection peaks can be observed. As reported,²⁸ the PBS tended to form the monoclinic crystal lattice. In this study, the $PB_xI_yE_zS$ copolyesters containing isosorbide in total diol less than 89 mol %, exhibit two major reflection peaks at $2\theta = 19.6^\circ$ and 22.3° . As compared with pristine PBS, the reflection peaks of the other copolyesters shifted toward a low angle region as the IS and PEOS units content increased. It is suggested that the crystalline $PB_xI_yE_zS$ copolyesters formed the crystals similar to pristine PBS, and d -spacing of the $PB_xI_yE_zS$ copolyesters increased when IS and PEOS units introduced.

The crystallinity was also calculated using a basic method for the differentiation between crystalline and amorphous scattering in the X-ray diffraction.

Figure 5 shows peak-separation diagrams of diffraction pattern of the copolyesters. The percentage crystallinity (X_{C-WAXD}) of the $PB_xI_yE_zS$ copolyesters in Table II can be obtained by the multiple peak-separation method. The results of X_{C-WAXD} are consistent with that of X_{C-DSC} determined by the DSC analysis.

The polarizing optical microscope (POM) was further used to investigate the morphology of the copolyesters after crystallizing from melt at different crystallization temperatures, and the results are illustrated in Figure 6. In pure PBS, the spherulites exhibit a well-defined fibrillar pattern with an apparent Maltese cross, which is true to type with many polymers.²⁹ It is found that the $PB_xI_yE_zS$ copolyesters having relative less content of BS units form the incomplete spherulites, which lose part of the spherical shape and become very coarse. It is revealed

TABLE III
Mechanical Stabilities of the Copolyesters

Sample	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)
PB ₁₀₀ I ₀ E ₀ S	30.9	10.1	522.3
PB ₇₀ I ₁₂ E ₁₈ S	9.8	125.1	217.6
PB ₅₅ I ₈ E ₃₇ S	13.0	136.4	258.6
PB ₄₄ I ₈ E ₄₈ S	9.0	57.9	278.3

that the IS and PEOS units seem to interfere with the crystallization of BS units and the differences in spherulite morphology may eventually lead to the change of mechanical and degradable properties.

Mechanical properties of copolyesters

The effects of the chemical composition and the degree of crystallinity on the mechanical properties of the PB_xI_yE_zS copolyesters are summarized in Table III. It is observed that the tensile strength and modulus of the PB₇₀I₁₂E₁₈S, PB₅₅I₈E₃₇S and PB₄₄I₈E₄₈S copolyesters are lower than pristine PBS. The increase of the IS and PEOS units content in the copolyesters, as well as the decrease of the BS unit content made copolyesters with decreased the crystallinity of the copolyesters, leading to the decrease of the tensile strength and tensile modulus. However, the elongation at break of the copolyesters is higher than that of PBS, indicating the higher flexibility of the copolyesters. The increased elongation at break indicates that the toughness of PBS is improved effectively with the addition of flexible ES units, so that the copolyesters can be used as flexible materials in many fields.

Enzymatic degradation of copolyesters

To evaluate the biodegradability of the copolyesters in a short time scale, enzymatic degradation was performed. It is well known that the biodegradability of polyesters is influenced not only by the chemical structure, especially the presence of functional groups and a hydrophilicity/hydrophobicity balance, but also by a highly ordered structure, such as crystallization, orientation, and other morphologies.³⁰ In this study, enzymatic degradation is expressed as the percentage of weight loss, and the lipase of *Pseudomonas cepacia* was utilized for analysing the enzymatic degradation of copolyesters at constant temperature of 37°C.

The weight loss of the PB_xI_yE_zS copolyesters during enzymatic degradation process is presented in Figure 7. It is clear that all copolyesters were degraded through the action of microorganisms. Besides, PB₇₀I₁₂E₁₈S and PB₅₅I₈E₃₇S showed a low degradation rate, due to the incorporation of isosorbide with rigid cyclic structure.

These results were further confirmed by microscopic surface characterization of the copolyesters after enzymatic degradation for 1 and 3 weeks (Fig. 8). After 1 week of degradation, the majority surface of PBS showed conspicuous biodegradation with holes [Fig.8(a)]. In the case of PB₇₀I₁₂E₁₈S and PB₅₅I₈E₃₇S, the rough surface with no significant change developed [Fig.8(c,e)] confirmed the biodegradation rate measured by the weight loss. After 3 weeks, the interior portions of PBS with a large number of deep pits were exposed because the surface was completely digested [Fig.8(b)]. For PB₇₀I₁₂E₁₈S and PB₅₅I₈E₃₇S, shallow crevices and holes could be observed, and the surface became rougher [Fig.8(d,f)]. It is well known that copolymers with a low degree of crystallinity degrade faster.³¹ However, in this study, PB₇₀I₁₂E₁₈S and PB₅₅I₈E₃₇S with lower degree of crystallinity compare to PBS showed low degradation rate, demonstrating that the rigid cyclic structure of isosorbide is the main factors influencing the enzymatic degradation rate of the copolyesters with comparison to degree of crystallinity.

CONCLUSIONS

Biodegradable copolyesters based on renewable resources were successfully synthesized by the transesterification and polycondensation in the melt from poly(butylene succinate), poly(ethylene glycol) and isosorbide. Compared to pure PBS, the PB_xI_yE_zS copolyesters showed lower crystallization temperature, melting temperature and crystallinity while a significant increase in glass transition temperature with

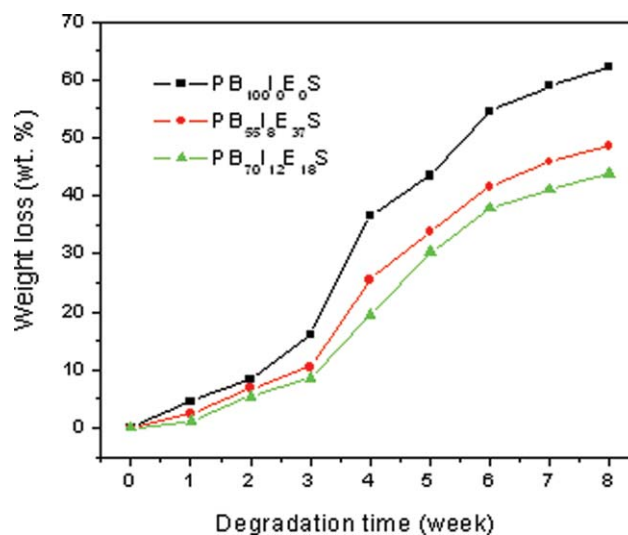


Figure 7 Weight loss versus time during enzymatic degradation for the copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

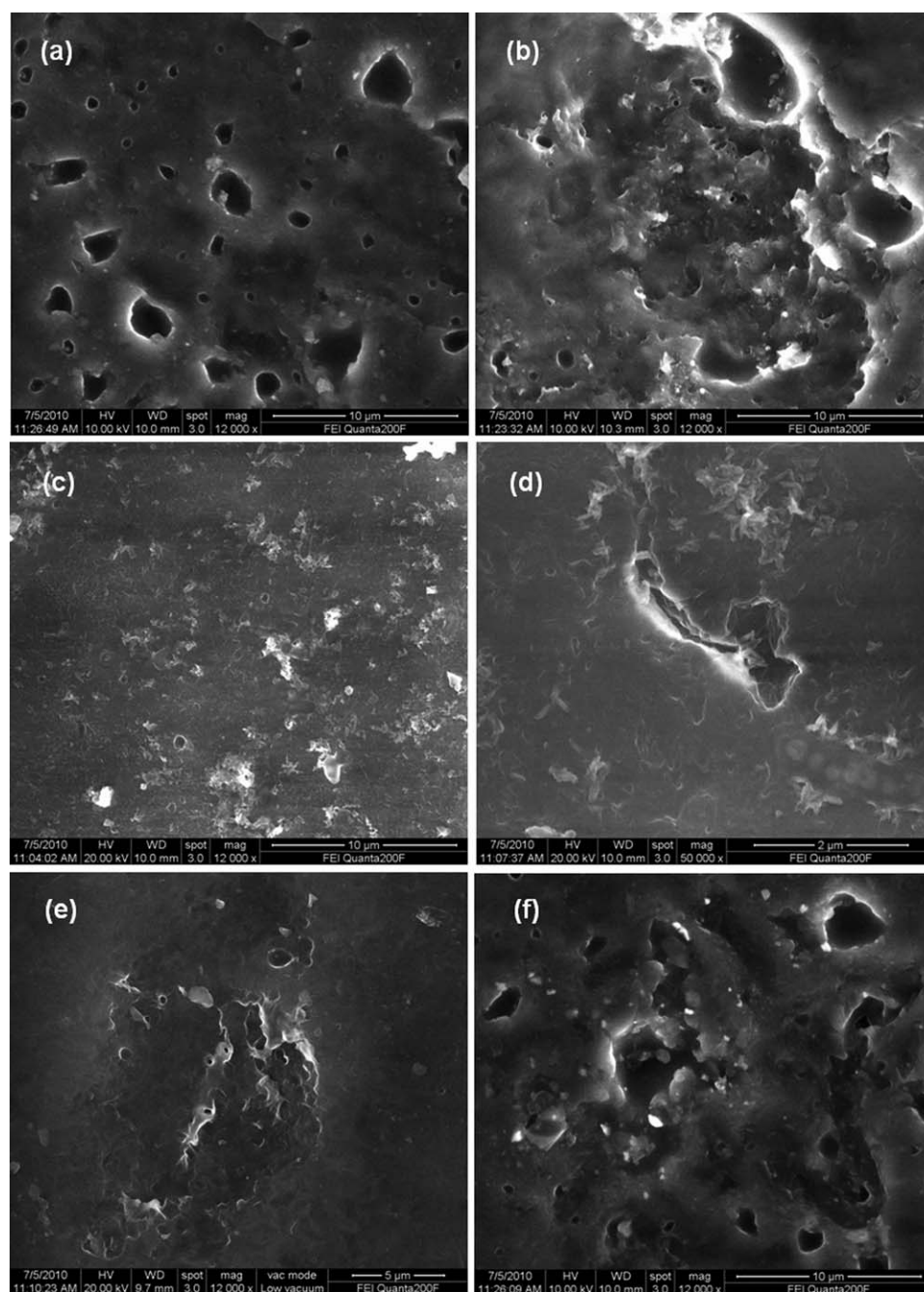


Figure 8 SEM graphs of the copolyester films surface after enzymatic degradation of (a, b) PB100I0E0S, (c, d) PB70I12E18S, and (e, f) PB55I8E37S for 1 week and 3 weeks, respectively.

increasing isosorbide content. PB₁₁I₈₉E₀S and PB₀I₁₀₀E₀S copolyesters, in which the IS units were the dominant component, were completely amorphous. PB_xI_yE_zS copolyesters having relative less content of BS units form the incomplete spherulites, which lose part of the spherical shape and become very coarse. The elongation at break of the copolyesters is enhanced insignificantly than that of PBS as the incorporation of IS and PEOS units. PB₇₀I₁₂E₁₈S and PB₅₅I₈E₃₇S showed a low degradation rate, indicating that the rigid cyclic structure of isosorbide is the main

factors influencing the enzymatic degradation rate of the copolyesters with comparison to degree of crystallinity. Because of the increased thermal stability and high attainable T_g values, these renewable polyesters can even be used in engineering plastics.

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