

Synthesis and Characterization of Biodegradable Poly(butylene succinate-co-propylene succinate)s

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ABSTRACT: Biodegradable polyesters such as poly(butylene succinate) (PBS), poly(propylene succinate) (PPS), and poly(butylene succinate-co-propylene succinate)s (PBSPSs) were synthesized respectively, from 1,4-succinic acid with 1,4-butanediol and 1,3-propanediol through a two-step process of esterification and polycondensation in this article. The composition and physical properties of both homopolyesters and copolyesters were investigated via ^1H NMR, DSC, TGA, POM, AFM, and WAXD. The copolymer composition was in good agreement with that expected from the feed composition of the reactants. The melting temperature (T_m), crystallization temperature (T_c), crystallinity (X), and thermal decomposition

temperature (T_d) of these polyesters decreased gradually as the content of propylene succinate unit increased. PBSPS copolyesters showed the same crystal structure as the PBS homopolyester. Besides the normal extinction crosses under the polarizing optical microscope, the double-banded extinction patterns with periodic distance along the radial direction were also observed in the spherulites of PBS and PBSPS. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1881–1889, 2008

Key words: biodegradable aliphatic polyesters; polycondensation; poly(butylene succinate-co-propylene succinate)s; banded spherulites

INTRODUCTION

The gradual depletion of nonrenewable resources and the serious environmental problems from the waste polymers have been attracting considerable attention since the last decades of the 20th century. Many countries have put much effort and emphasis on recycling polymer waste and, at the same time, on developing alternative biodegradable materials. Among them, aliphatic polyesters made from renewable sources are one of the most promising biodegradable materials. Besides the high molecular weight polyesters produced by micro-organisms or by ring-opening polymerization of lactones or lactides,^{1–3} aliphatic polyesters from diols and dicarboxylic acid are also expected to be one of economically competitive biodegradable polymers and attracted the attention of many researchers in the recent years.^{4–8} Limiting factors for a normal use of these polyesters with low molecular weight are their poor mechanical properties and low melting temperatures. To improve their mechanical properties, the high molecular weight polyesters have been synthesized by the use of very effective esterification catalysts, high vacuum technique, and chain extenders.^{9,10} Also, the incorporation of rigid aromatic structures into aliphatic copolyesters was used for the synthesis

of polymers with improved mechanical and thermal properties and controlled biodegradability.^{11–15}

Properties of these polyesters, such as melting temperature, crystal structures, crystallinity, mechanical properties, as well as biodegradability, closely depend on their chemical structure, the molecular weight, and the physical morphology. It has been recognized that poly(butylene succinate), PBS, from 1,4-butanediol and succinic acid possesses excellent properties.⁵ Therefore, many studies have been carried out to improve the properties of PBS, i.e., to enhance its mechanical properties, thermal properties, and biodegradability properties.^{16–18} One way of modifying the properties of biodegradable PBS is to prepare polyesters copolymerized with different diacids or diols. The investigations showed that either the mechanical or thermal properties deteriorated with copolymerization, but that generally copolymerization is a good method for tailoring the biodegradability properties of polyesters. Up to now, more attention has been paid on the so-called “even”-numbered copolyesters such as poly(ethylene succinate-co-butylene succinate), poly(butylene succinate-co-butylene adipate), and poly(butylene succinate-co-hexylene succinate).^{19–25} However, the “odd”-numbered polyesters, for example, poly(propylene succinate) (PPS) with three methylene groups in the polymer's repeating unit and copolyesters with PBS remained obscure polymers.^{26–28} The expensive raw material, 1,3-propanediol, was once a bottleneck for the application of these polyesters. Now, 1,3-propanediol can be conveniently obtained

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from biological fermentation in the presence of a number of microbial strains, for instance, by cultivation of *Clostridium butyricum* in glycerol.²⁹ Therefore, PPS and their copolyesters constitute a family of polymers of great potential interest.³⁰

It has been established that the polyesters with an odd number of methylene groups in the glycol or in the acid segment adopt an orthorhombic unit cell, while those with an even number of methylene groups in the glycol and in the acid part all crystallize with a monoclinic unit cell.³¹ Although there are many reports regarding the relationships between crystallization behaviors and their chemical structure of the two types, few results have been reported for their copolymers. As to PBS and PPS, there is only one methylene difference between propylene unit and butylene unit, but the "odd-even" effect of the number of methylene groups in the chemical repeating unit may result in different properties of the polyesters.³²

Many research results verified that PPS has some different properties such as higher biodegradation rate, compared with the two familiar polyesters, poly(ethylene succinate) and PBS.³³ To widen the field of practical applications, we thought it interesting to modify the chemical structure of polyesters by copolymerizing butylene succinate (BS) with propylene succinate (PS). The properties of the copolyesters would vary with the content of the comonomers. In the present article, the high-molecular weight aliphatic polyesters were synthesized from succinic acid with 1,4-butanediol and 1,3-propanediol through a two-step process of esterification and polycondensation in the presence of a highly effective catalyst tetra-*n*-butyl-titanate Ti(OBu)₄. The effect of polymer composition on the thermal properties and crystalline morphology of the copolyesters was further investigated.

EXPERIMENTAL

Materials

1,4-Succinic acid was provided by Tianjin Chemical (China) and was used as received. 1,3-Propanediol and 1,4-butanediol from Shanghai Chemical (China) too

was used as received. Tetra-*n*-butyl-titanate Ti(OBu)₄ as a catalyst was obtained from Beijing Chemical (China). Other chemicals and solvents were used without further purification.

Synthesis

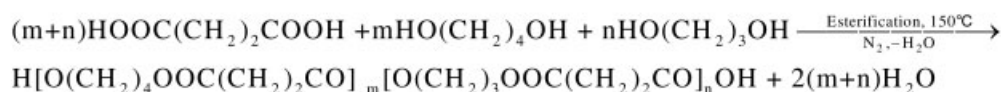
Aliphatic homopolyesters, poly(butylene succinate) (PBS) and poly(propylene succinate) (PPS), as well as their copolyesters poly(butylene succinate-*co*-propylene succinate) (PBSPS) were synthesized by a two step reaction of esterification and polycondensation in the melt. As an example, the synthesis of copolyester with 10 mol % of 1,3-propanediol is described. In the process of esterification, the reactor was a three-necked flask with a mechanical stirrer, nitrogen inlet, and a condenser in a well controlled oil bath. The reaction mixtures, 1,4-butanediol (62.4 g, 0.693 mol), 1,3-propanediol (5.8 g, 0.077 mol), and 1,4-succinic acid (82.7 g, 0.70 mol), were added into the reactor. The temperature was increased slowly to 140–150°C until the acid component melted completely under N₂ gas atmosphere. H₂O was collected using a trap device. When no more water was distilled out under the normal pressure, this reaction was assumed completed. The volume of H₂O collected was around 95% of its theoretical value. For the polycondensation process, the catalyst Ti(OBu)₄ was added first and the temperature was gradually raised to the final reaction temperature of 200°C at pressure below 1.0 mmHg. When the viscosity of reaction mixture was no more increasing, the reaction was assumed to be completed. The viscous resultant was cooled in the reactor under nitrogen atmosphere.

The synthesized copolyester was dissolved in chloroform and then precipitated into a 10-times amount of stirred ice-cold methanol. The precipitate was washed with methanol and dried in vacuum at room temperature for 24 h. All the other polyesters were synthesized following the same procedure.

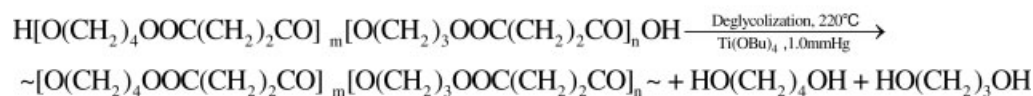
Measurements

¹H NMR spectra were taken by Varian VXR-Unity (500 MHz) using CDCl₃ as solvent, with tetramethylsi-

First step:



Second step:



Scheme 1 Synthesis of PBSPS from succinic acid with 1,4-butanediol and 1,3-propanediol.

TABLE I
Composition and Average Molecular Weight of the Synthesized Polyesters

Polymer	Composition		Intrinsic viscosities, [η] (dL g ⁻¹)	Molecular weight (g mol ⁻¹) ^b		
	Feed ratio BS/PS	Polymer ratio ^a BS/PS		M_n	M_w	M_w/M_n
PBS	100.0/0	100.0/0	0.496	21,400	39,800	1.86
PBS/PS-5	95.0/5.0	93.2/6.8	0.444	18,800	37,000	1.97
PBS/PS-10	90.0/10.0	89.7/10.3	0.415	14,500	29,700	2.05
PBS/PS-15	85.0/15.0	82.3/17.7	0.371	14,300	25,600	1.79
PBS/PS-20	80.0/20.0	78.1/21.9	0.352	15,000	26,000	1.73
PBS/PS-30	70.0/30.0	69.6/30.4	0.349	13,000	24,600	1.89
PBS/PS-40	60.0/40.0	61.4/38.6	0.264	8,100	15,400	1.90
PBS/PS-50	50.0/50.0	50.5/49.5	0.261	7,000	14,200	2.03
PPS	0/100.0	0/100.0	0.321	11,300	20,500	1.82

^a Determined by ¹H NMR.

^b Measured by GPC with chloroform as the eluent and polystyrene standards.

lane as the internal standard of chemical shift. Weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) of the resulting polymers were measured by gel permeation chromatography (Viscotek-M302 TDA), which calibrated with polystyrene standards. Eluent solvent was chloroform with a flow rate of 1 mL/min. The concentration of the tested sample was around 0.5% w/v. The intrinsic viscosity [η] was measured using an Ubbelohde viscometer in chloroform at 25°C. Differential scanning calorimetry (Shimadzu, TA-60WS) was used to measure the thermal properties of polymers. The heating and cooling rates were 10°C/min under nitrogen atmosphere. The thermal decomposition temperature (T_d) was obtained with a heating rate of 20°C/min at a weight loss of 50%. Wide-angle X-ray diffraction (WAXD) for PBS, PPS, and PBS/PS was measured using an X-ray diffractometer (Rigaku D/max-RB) with Cu K α radiation. A polarizing optical microscope (Olympus BH-2) was used to observe the spherulitic morphology of the polyesters. A SPM-9500 J3 model AFM from Shimadzu was used in the tapping mode.

RESULTS AND DISCUSSION

Polymer synthesis

A series of polyesters PBS, PPS, and PBS/PS were synthesized by a two step reaction process in the bulk. The first step, esterification reaction, was carried out in the temperature range of 140–150°C at normal pressure with a 4–10% stoichiometric excess of diol in the feeding composition. In the second step, the reaction was carried out by heating the mixture at 200°C under vacuum to remove the excess glycol and produce the chain extension. This step was maintained for 1.5–2.5 h depending on the feeding composition. The reaction scheme for the synthesis of the PBS/PS copolyesters is shown in Scheme 1.

The viscosity of the reaction mixture increased with the increasing reaction time. Table I shows the change in the intrinsic viscosities and molecular weight of PBS, PPS, and PBS/PS with various BS unit and PS unit compositions after the polycondensation reaction.

All the synthesized polyesters were purified by dissolving them in chloroform and precipitated into ice-cold methanol to remove low-molecular part as well as traces of the catalyst. The polyesters with intrinsic viscosities between 0.26 and 0.50 dL g⁻¹ were obtained. The number-average molecular weights of the polyesters ranged from 7000 to 21,400 g mol⁻¹, and the polydispersity index was in the range of 1.73–2.05. Both the intrinsic viscosity and average molecular weight of PBS/PS decreased with the increasing 1,3-propanediol

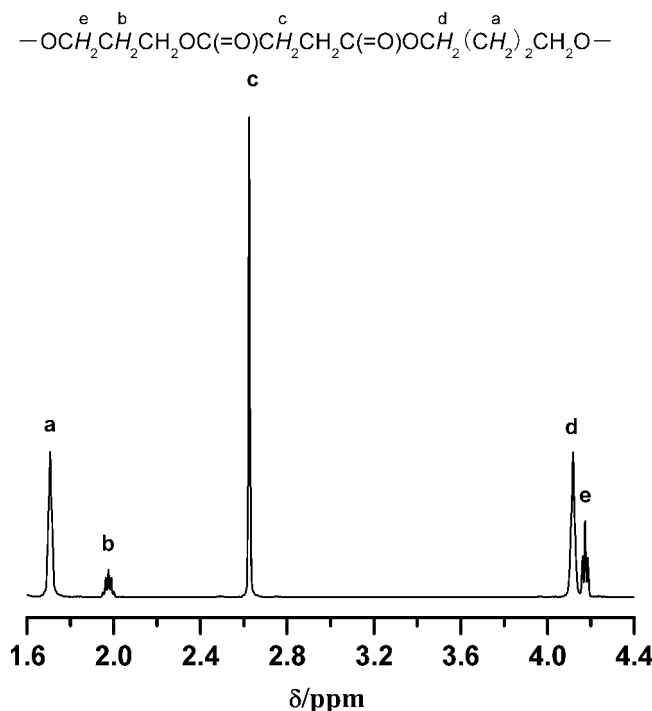


Figure 1 ¹H NMR spectrum of the PBS/PS-20.

TABLE II
Thermal Properties of the Synthesized Polyesters

Polymer	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	T_g (°C)	T_m^0 (°C)	X_{C-DSC} (%) ^a	X_{C-WAXD} (%) ^b	T_d (°C) (50 wt %)
PBS	113	69.8	76	-30.0	132	63.2	52.8	404
PBSPS-5	111	57.2	69	-31.3	124	51.8	49.9	385
PBSPS-10	105	56.0	60	-32.9	118	50.7	49.3	377
PBSPS-15	100	49.7	56	-33.5	114	45.0	47.7	368
PBSPS-20	96	43.4	52	-33.9	108	39.3	46.0	374
PBSPS-30	84	39.8	40	-34.8	103	36.0	43.9	371
PBSPS-40	76	37.3	39	-35.1	99	33.8	40.2	362
PBSPS-50	63	20.9	- ^c	-35.5	89	18.9	37.3	361
PPS	50	36.4	-	-36.0	-	-	44.6	378

^a X_{C-DSC} was calculated from DSC method (110.5 J/g) for a 100% crystalline PBS.³⁵

^b X_{C-WAXD} was calculated from the X-ray method.

^c (-) indicated that no crystallization peak was observed by DSC at the cooling rate of 10°C/min.

proportion. The molecular weight has an important effect on the properties of polyesters, but in the molecular weight range discussed in this article, molecular weight variation is not considered to have an important role in the crystallization behavior.³⁴ Therefore, their possible influence was not considered in the following discussion.

¹H NMR characterization

The composition of PBSPS copolyesters was determined from the ¹H NMR spectra using the relative intensities of the proton peaks arising from BS and PS repeating units. As a sample, the ¹H NMR spectrum of the PBSPS-20 is shown in Figure 1: O—CH₂— and C—(CH₂)₂—C from the BS unit at δ 4.12 and δ 1.71; O—CH₂— and C—CH₂—C from the PS unit at δ 4.17 and δ 1.98. They are identical to the signals of BS and PS unit. The molar composition of PBSPS was measured as the area ratio of δ 4.12 peak to δ 4.17 peak, or δ 1.71 peak to δ 1.98 peak. The PS unit is incorporated into the copolyesters in an amount about 2% less than that of the feed proportion. These results showed that the composition of the copolyesters is in good agreement with that expected from the feed proportion.

Thermal properties

The thermal properties of the polyesters were obtained from DSC analysis, as shown in Table II. The crystallization temperature was determined at a cooling rate of 10°C/min after the polymers were melted at 160°C for 5 min to eliminate the thermal and mechanical history. The melting temperature was determined at a heating rate of 10°C/min.

The crystallinity (X_{C-DSC}) of copolymers was determined by dividing the observed heat of fusion by the theoretical value of perfectly (100%) crystalline polymer. The crystallinity of the polyesters were in the range of 18.9–63.2%. Overall, the T_m , T_g , T_c , ΔH_m , and X_c of polyesters were decreased with increase of the

PS unit content. In addition, the T_g decreased with the increasing [PS] units content in Figure 2. In particular, all the copolyesters were found to exhibit a single T_g rather than two T_g s, regardless of the composition. It suggested that random PBSPS copolyesters were synthesized all over the compositions.

The results of decomposition temperature of the polyesters, namely the temperatures corresponding to polyester weight losses of 50% in nitrogen atmosphere, are also given in Table II. The on-set temperatures of weight loss are well above 200°C, the temperature of synthesis process. Thermal degradation of the copolyesters hardly takes place during synthesis process, so there is no need to use a heat stabilizer during the synthesis of these copolyesters. From

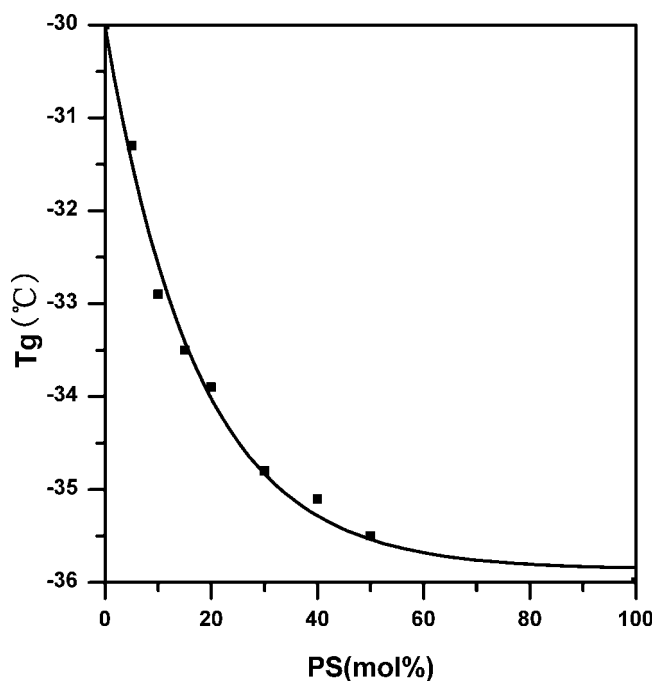


Figure 2 A plot of glass transition temperature (T_g) versus PS unit content in the polyesters.

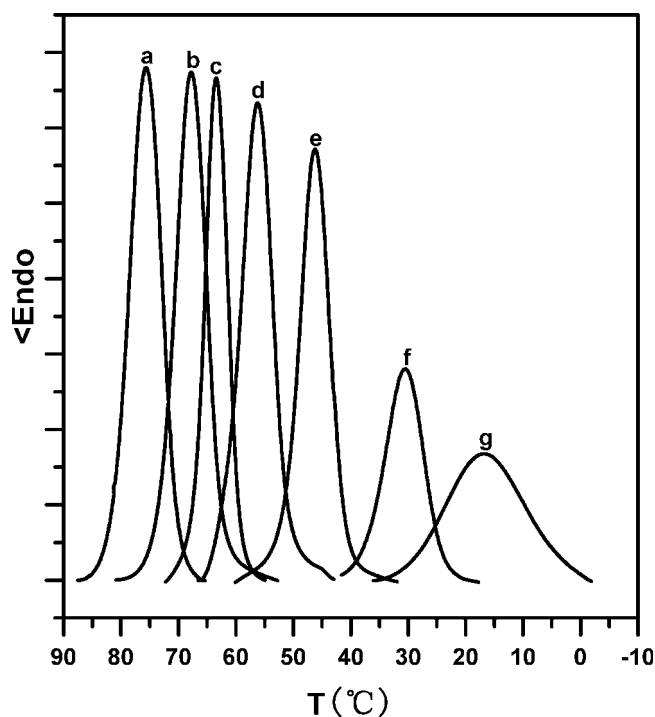


Figure 3 Crystallization curves of the polyesters at a cooling rate of $10^{\circ}\text{C}/\text{min}$: (a) PBS, (b) PBS-5, (c) PBSPS-10, (d) PBSPS-15, (e) PBSPS-20, (f) PBSPS-30, (g) PBSPS-40.

the values of the temperatures of 50% weight loss of the polyesters in nitrogen atmosphere, it is obvious that the PBSPS are less stable than the PBS.

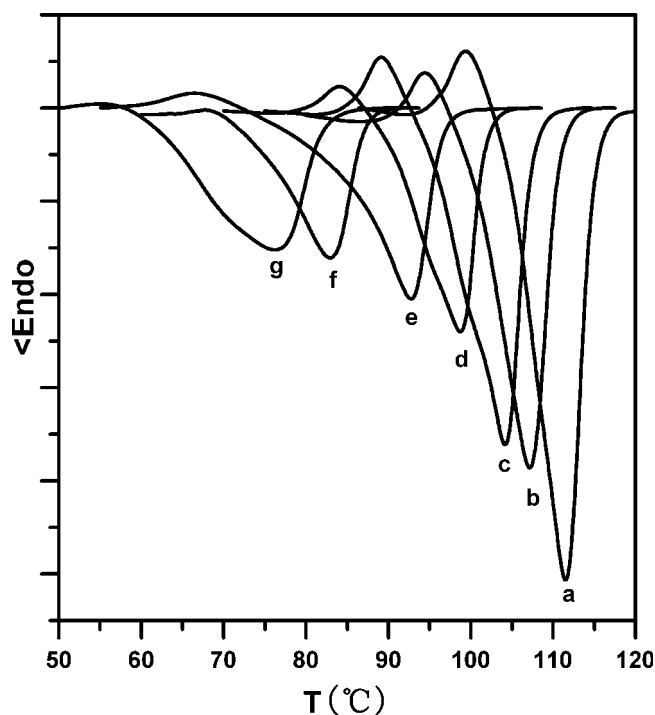


Figure 4 Melting curves of the polyesters at a heating rate of $10^{\circ}\text{C}/\text{min}$: (a) PBS, (b) PBS-5, (c) PBSPS-10, (d) PBSPS-15, (e) PBSPS-20, (f) PBSPS-30, (g) PBSPS-40.

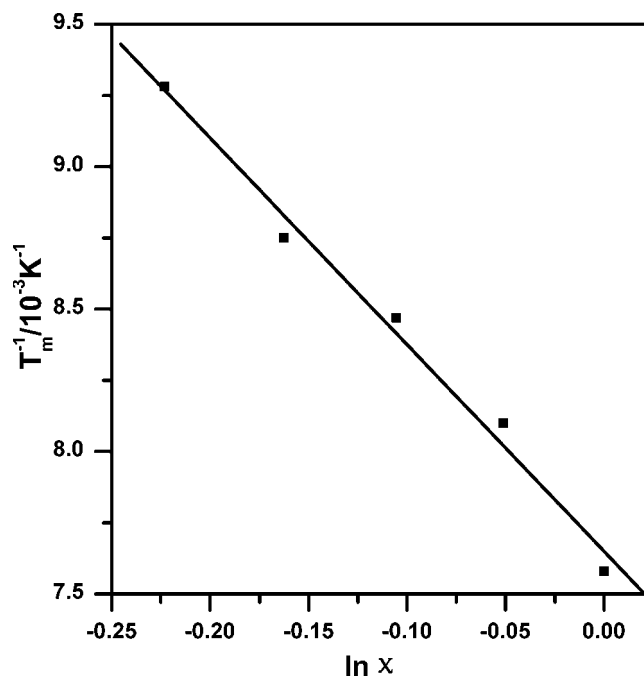


Figure 5 Relationship between $1/T_m^0$ and $\ln X_A$ of the polyesters.

Crystallization and melting behaviors

Figure 3 shows the crystallization curves of the polyesters at a cooling rate of $10^{\circ}\text{C}/\text{min}$. The crystallization temperatures decreased with the increasing of PS unit content at the same cooling rate. The melting

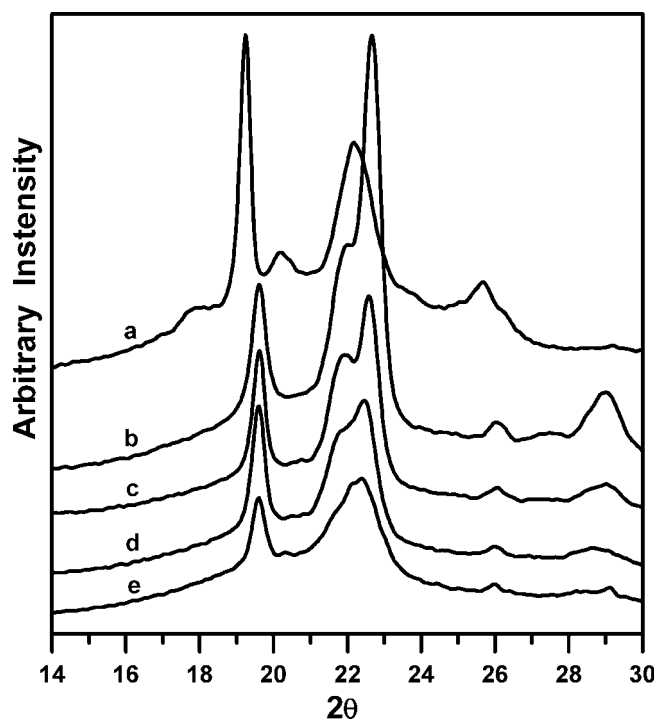


Figure 6 X-ray diffraction diagrams of the polyesters: (a) PPS, (b) PBS, (c) PBSPS-15, (d) PBSPS-30, (e) PBSPS-50.

temperatures also decrease with the increasing of PS unit content, as seen in Figure 4. These results are due to the lowered regularity of the copolyester's main chain caused by the introduction of the PS unit into PBS.

Equilibrium melting point T_m^0 , the melting temperature of infinitely thick lamellae, is one of the important parameters for the analysis of crystallization process. According to a theory derived by Hoffman and Weeks,³⁶ it can be obtained from the relationship between the observed melting point T_m and the isothermal crystallization temperature T_c . The T_m^0 of PBSPS decreases with the increasing PS unit content, as listed in Table II. In general, the melting temperature depression implies a reduction in the thickness of

lamellar crystals as well as an increase in the level of crystal defects. Therefore, it was concluded that the incorporation of PS unit into the PBS chain reduces the lamellar crystal thickness and increases the crystal defects to a certain level. The estimated $T_{m,co}^0$ of copolyesters was analyzed further by the Flory equation:

$$1/T_{m,co}^0 - 1/T_m^0 = -R/\Delta H_f \ln \chi \quad (1)$$

where T_m^0 is the equilibrium melting temperature of PBS homopolymer, χ is the molar fraction of PS unit, and R is the gas constant. The T_m^0 of the polyesters is plotted against $\ln \chi$ in Figure 5. It was noted here that the reciprocal plot of T_m^0 s against $\ln \chi$ shows a good

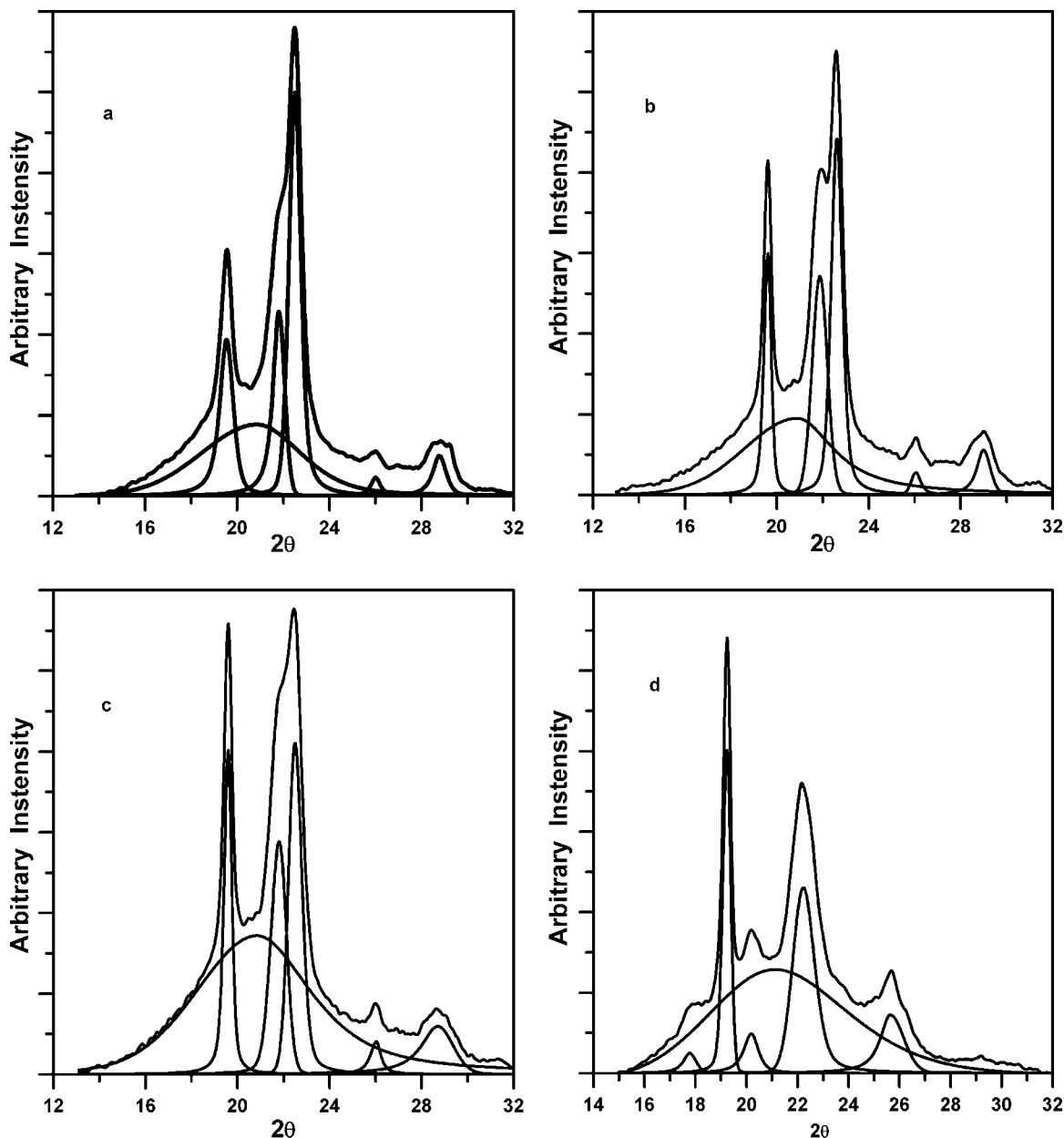


Figure 7 Peak-separation diagrams of (a) PBS, (b) PBSPS-15, (c) PBSPS-30, (d) PPS by WAXD.

linearity. This result supports positively that the PBSPS copolyesters are random copolymers, which have been proposed earlier from their T_g variation with the composition.

X-ray analysis

Further information on the crystal structure and the crystallinity of the polyesters were obtained from WAXD measurements. Figure 6 indicates the diffrac-

tion diagrams of the polyesters with different PS unit content. The crystal unit cell of PBS was monoclinic crystal and diffraction peaks of (020), (021), and (110) planes were observed at 2θ of 19.4, 21.5, and 22.5°, respectively.³⁷ From the crystal lattice of PBS and PPS, up to the 50 mol % of PS unit, the copolyesters show the same X-ray diffraction patterns as PBS. This indicates that although PPS homopolymer is crystallizable, the PS units are excluded from the crystalline region of the lamellae in the

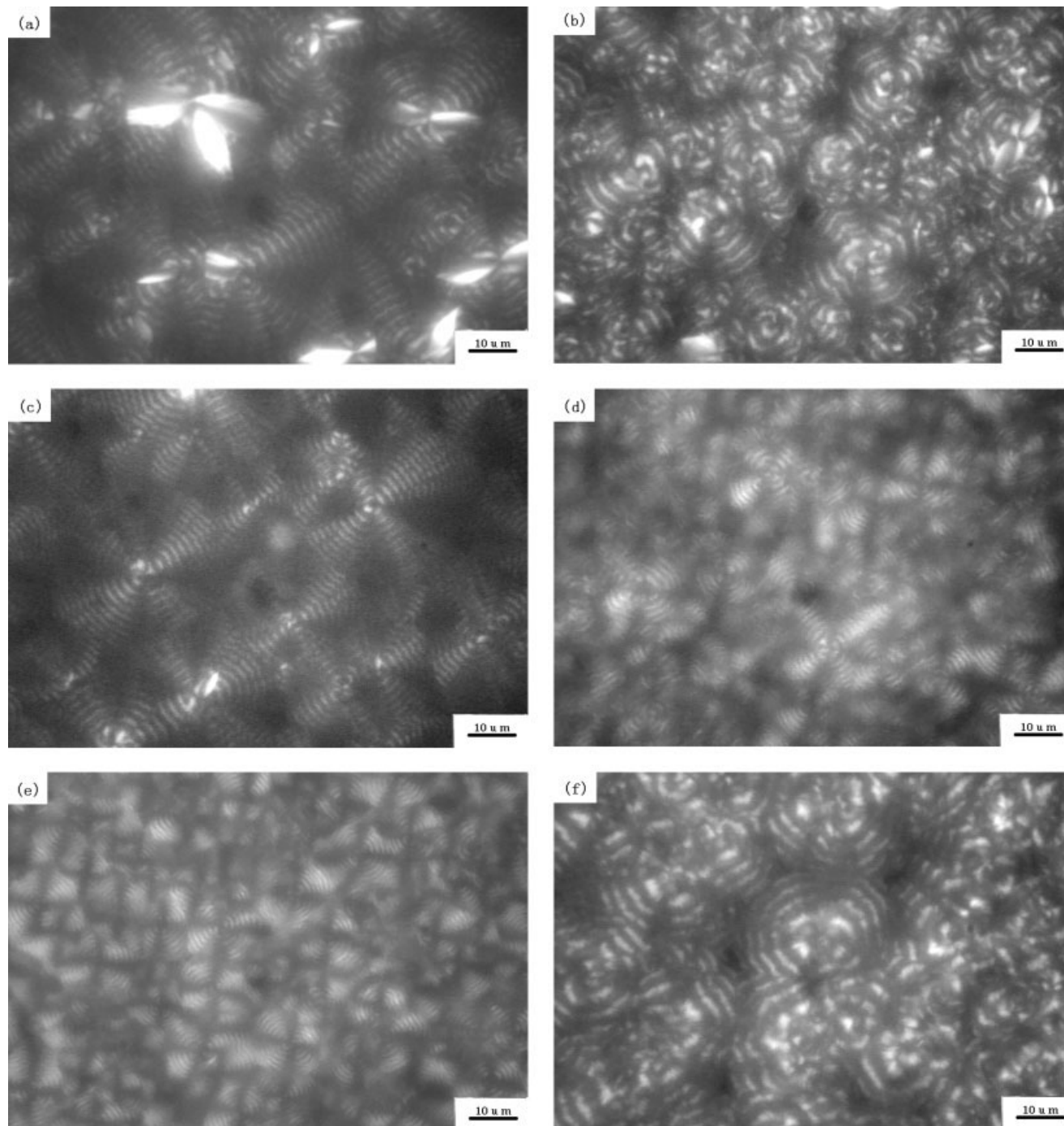


Figure 8 Polarizing optical micrographs of PBSPS copolymers: (a) PBS, (b) PBSPS-5, (c) PBSPS-10, (d) PBSPS-20, (e) PBSPS-30, (f) PBSPS-50.

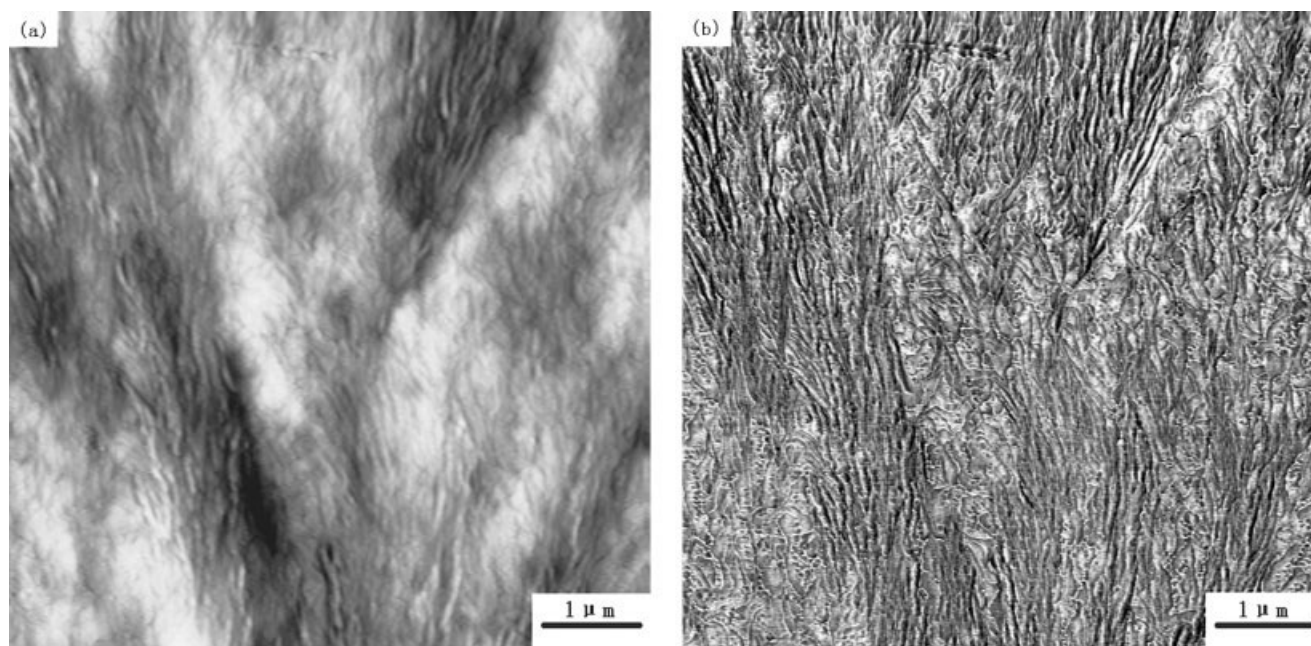


Figure 9 AFM height image (a) and phase image (b) of PBSPS-15 crystallized at 70°C.

crystallized copolyester when the PS units are minor component. As a result, there is no “odd–even” effect in PBSPS, just as the copolyester poly(butylene succinate-*co*-adipate).³⁸

The crystallinity was calculated using a basic method for the differentiation between crystalline and amorphous scattering in the X-ray diffraction. As seen in Figure 7, the percentage crystallinity (X_{C-WAXD}) of PBS, PPS, and PBSPS in Table II can be obtained by the multiple peak-separation method. The X-ray diffraction patterns were resolved into crystalline peaks and amorphous peaks by peak-separation software in WAXD, and the crystallinity was determined by the area ratio of crystalline peaks and amorphous peaks. The existence of PS unit in an amorphous state results in a decrease of the crystallinity of PBSPS comparing with that of PBS.

Crystallization morphology

Figure 8 shows the spherulitic morphology of melt-crystallized PBS, PPS, and PBSPS observed under polarizing optical microscope. The samples were fused between coverslip and glass slide at the same temperature of 160°C, and then cooled naturally until completely crystallized. Besides the normal extinction crosses (i.e., Maltese cross) under the polarizing optical microscope, the double-banded extinction patterns with periodic distance along the radial direction are observed in the spherulites of PBS and PBSPS.

It is generally believed that the formation of banded spherulites is attributed to lamellar twisting about the direction of radial growth.³⁹ As seen in Figure 9, the AFM research indicates that the lamel-

lar structures of PBSPS-15 appeared to adopt an alternative flat and edge-on orientation, just as the PET and PTT.^{40,41} The origin of lamellar twisting of PBSPS will be investigated in future work.

CONCLUSIONS

PBS, PPS, and PBSPS were synthesized from 1,4-butanediol and 1,3-propanediol with succinic acid by a two-step reaction process of esterification and polycondensation using $Ti(OBu)_4$ as a catalyst. The chemical proportion of a dicarboxyl unit and diol unit had a 1.0:1.04–1.10 mol ratio. T_g of PBSPS copolyesters decreased with the increasing of PS unit content. From the relationship of T_g and T_m with the composition of PBSPS, it can be concluded that the BS unit and PS unit in the copolyesters chain are randomly distributed. From the polarizing optical microscope observation, besides the normal extinction crosses, the double-banded extinction patterns are observed in the spherulites of PBS and PBSPS. The WAXD patterns of PBSPS had the same patterns as PBS with the content of PS unit up to 50 mol %. The existence of PS unit did not change the crystal structure of BS unit. But the crystallinity of PBSPS decreased with the increasing of PS unit content.

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