

Synthesis, characterization and properties of poly(butylene succinate) modified with rosin maleopimaric acid anhydride

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Abstract: Huge hydrogenated phenanthrene ring segments were introduced into the main chain of poly(butylene succinate) by polymerization of succinic acid (SA), 1,4-butanediol (BD) and rosin maleopimaric acid anhydride (RMA), which was obtained from maleic rosin. The chemical structure and composition of the copolyesters were determined with the aid of ¹H-NMR, FTIR and elemental analysis. The thermal properties, crystallization behaviour and mechanical properties of the copolyester were then investigated using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), polarized light microscopy (PLM) and mechanical testing. With increasing content of hydrogenated phenanthrene ring segments, the melting temperature, the crystallization temperature and the relative degree of crystallinity decreased gradually, but the elongation at break and the notched impact strength of poly(butylene succinate) were enhanced without a significant deterioration of tensile strength.

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Keywords: poly(butylene succinate); hydrogenated phenanthrene ring; thermal properties; crystallization; mechanical properties

INTRODUCTION

Synthetic aliphatic polyesters, being the most inexpensive biodegradable plastics, are expected to be one of the most competitive materials in the future^{1,2} because of the global concern about ‘white pollution’ from the use of non-biodegradable polymers. Poly(butylene succinate) (PBS) is one of the best of these aliphatic polyesters and has a relatively high melting temperature (113–115 °C). However, full-scale commercialization has been limited owing to the poorer mechanical properties and higher cost compared with other universal plastics.^{3,4} A number of techniques, such as physical blending^{5–8} or copolymerization,^{9–18} have so far been used to improve their mechanical properties. Chemical modification is a powerful tool for obtaining polymers with new properties. For example, Jin *et al.*^{11,12} introduced phenyl units into the side chain of PBS and found the biodegradability of the copolyesters was increased because of the decrease in the relative degree of crystallinity; Darwin and Kint,⁹ Wilt *et al.*^{10,19,20} and Tokiwa and Suzuki^{17,18} also copolymerized aliphatic polyesters with small aromatic monomers, and found that the mechanical properties and biodegradability were influenced remarkably by the chemical structure.

Aliphatic/alicyclic copolyesters were also synthesized by Jung *et al.*¹³ by using succinic acid (SA), 1,4-butanediol (BD) and 1,4-cyclohexanedimethanol.

In contrast with the existing method of copolymerizing small ring-shaped monomers with SA/BD, in this paper hydrogenated phenanthrene ring segments were introduced into the PBS chain by polymerization of SA, BD and rosin maleopimaric acid anhydride (RMA), which was obtained from maleic rosin. RMA contains huge and rigid hydrogenated phenanthrene rings. The addition of a small quantity of RMA affects the crystallization properties, thermal properties and mechanical performance of the polyesters markedly. The structures and properties of PBS modified with RMA were investigated in detail in this study.

EXPERIMENTAL

Materials

Succinic acid (SA), 1,4-butanediol (BD), chloroform (CHCl₃), *p*-aminobenzoic acid, zinc acetate and Sb₂O₃, all of reagent grade, were purchased from Beijing Chemical Reagents Corp. and used without further purification. Titanium (IV) butoxide, used as a catalyst, was distilled before use. Rosin maleopimaric

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acid anhydride (RMA) was purchased from the Research Institute of Chemical Processing and Utilization of Forest Products, China. It was used after recrystallization from glacial acetic acid solvent.

Synthesis of rosin maleic anhydride imidodicarboxylic acid

To synthesize rosin maleic anhydride imidodicarboxylic acid (RMID),²¹ 40 g (0.1 mol) of RMA, 14.4 g (0.105 mol) of *p*-aminobenzoic acid and 90 mL of dimethylformamide (DMF) were placed in a 250 mL three-necked flask equipped with a mechanical stirrer, a thermometer and a nitrogen inlet tube (Scheme 1). After the mixture was heated for 4 h at 160 °C, it was cooled to room temperature and poured into 300 mL of water. The precipitate was washed with water thoroughly and dried under vacuum at 90 °C. The white product was recrystallized in DMF, washed with diethyl ether and dried in a vacuum oven at 90 °C for 12 h. Yield: 87%; melting point = 284 °C. The chemical structure was determined by FTIR and ¹H-NMR spectroscopy. ¹H-NMR (CHCl₃, δ, ppm): 8.11–8.19 (d 2H), 5.52–5.54 (s 1H), 3.08–3.12 (d 2H); FTIR (KBr, cm⁻¹): 3416.7, 1776.4, 1708.6, 1416.8, 1384.2; elemental analysis for C₃₁H₃₇O₆N: (calculated) C 71.7%, N 2.69%, H 7.11%; (found) C 71.1%, N 2.64%, H 7.04%.

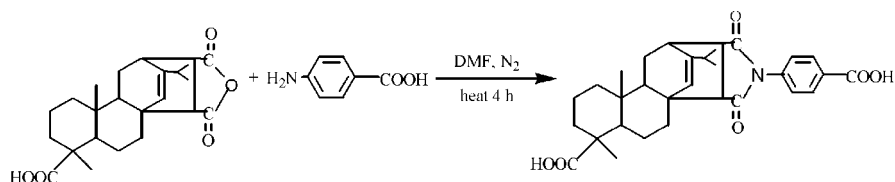
Synthesis of prepolymer and polymer

Poly(BD/SA/RMID) (PBSR) was bulk-polymerized by two-step polycondensation techniques (Scheme 2). In the first step, under a nitrogen atmosphere, RMID (0.05 mol) was reacted with excess BD (0.5 mol) in

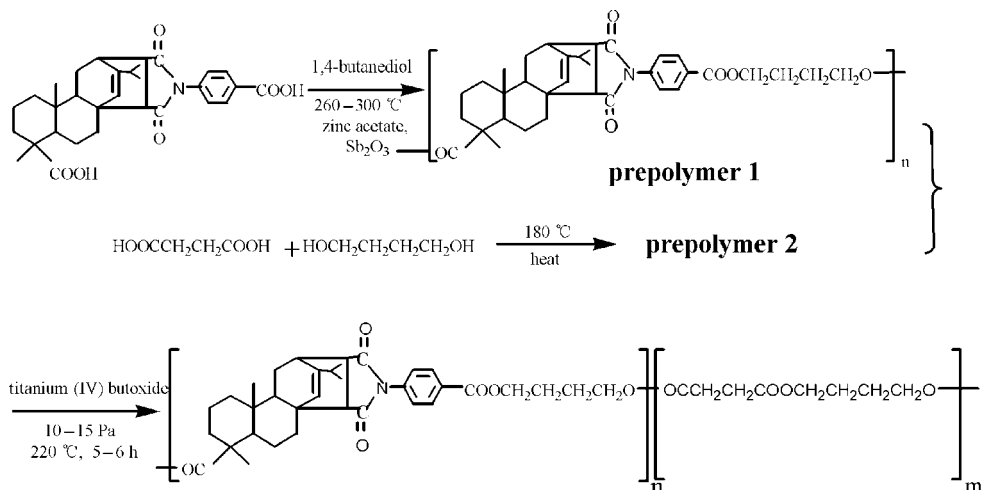
the presence of zinc acetate and Sb₂O₃ as catalysts at 260–280 °C for 4 h and at 300 °C for 1 h. After that, the excess BD was removed by vacuum distillation, and the product (prepolymer 1) was recrystallized in DMF before it was dried in a vacuum oven at 80 °C. The esterification of SA (0.5 mol) and BD (1 mol) was carried out separately at 180 °C in a nitrogen atmosphere. In the second step, when each of the esterification reaction was completed, the above products were mixed and heated at 220 °C for 5–6 h under 10–15 Pa, using titanium (IV) butoxide as a catalyst (0.1 wt% of monomer). The polymers obtained were purified by reprecipitation from chloroform solution by methanol repeatedly, and they were then dried in a vacuum oven for 10 h at 80 °C in order to obtain a constant weight. The polymers were named PBS100R0, PBS98R2, PBS97R3, PBS96R4 and PBS94R6, where the ‘S’ stands for SA and ‘R’ for RMID, and the numbers following those letters represent their respective molar fractions. For example, PBS94R6 represented the polymer synthesized with 94% SA and 6% RMID.

Measurements

The chemical structures and compositions of the copolymer and prepolymer were identified by a 300 MHz Bruker DMX-300 ¹H-NMR spectrometer. Tetramethylsilane was used as the internal reference and CDCl₃ was the solvent. FTIR spectra were obtained with a Perkin–Elmer FTIR system 2000 with KBr pellets and the wavenumber range was 4000–400 cm⁻¹.



Scheme 1. Synthesis of rosin maleic anhydride imidodicarboxylic acid (RMID).



Scheme 2. Synthesis of the PBSR copolyesters.

The inherent viscosity of the polymer was measured with an Ubbelohde viscometer at a concentration of 1 g dL^{-1} . The solvent was metacresol. The temperature was kept at $30 \pm 0.1^\circ\text{C}$.

The molecular weight and molecular weight distribution were determined by gel permeation chromatography (PL-GPC210, UK) at 40°C . The eluent was chloroform at a flow rate of 1.0 mL min^{-1} . The molecular weights and the molecular weight distributions were calculated against polystyrene standards.

The thermal properties were determined by differential scanning calorimetry with a Perkin–Elmer DSC-7 instrument, and calibration of the temperature was performed using indium as the standard before the measurement. Specimens were heated to 150°C at a constant rate of $10^\circ\text{C min}^{-1}$ (first scan) and held there for 5 min to eliminate thermal history, and then the samples were cooled to 30°C at a rate of $10^\circ\text{C min}^{-1}$ to observe the crystallization behaviour. The second-scan thermodiagrams were obtained by reheating the samples at the same rate from 30 to 150°C . All the measurements were conducted under a high-purity helium gas atmosphere.

The spherulitic morphologies of the polymers after melt-crystallization at the stated temperature were examined with a polarized light microscope (PLM, Leica MPS30, Germany). The samples were sandwiched by cover glasses. The polymers were initially heated to 150°C and held there for 5 min to remove the thermal history, and then cooled to 85°C as fast as possible. When the isothermal crystallization was over, the spherulitic morphologies were observed and screened with a video camera.

Wide-angle X-ray diffraction (WAXD) was performed at room temperature with a Ragaku Model D/max-2B diffractometer using $\text{Cu K}\alpha$ radiation (40 kV , 200 mA), and the experimental data were collected from 10° to 40° at a scanning rate of 2° min^{-1} . The samples for this measurement were prepared by moulding at 150°C and then cooling to room temperature naturally.

The tensile testing was carried out on a universal tester (Instron 1122, UK). The tensile properties of the specimens were measured according to ASTM D 638–97 with a crosshead speed of 10 mm min^{-1} . The impact strength was measured with an impact testing machine (CBI-137C, USA) according to ASTM D 256–97. The average value of at least five measurements was calculated in each case. The specimens for these tests were all prepared on an injection moulding machine (SZ-15, Shanghai, China). The temperatures of the upper injection heater and nether injection heater were 110 and 130°C , respectively.

RESULTS AND DISCUSSION

RMID was prepared by the reaction of RMA with *p*-aminobenzoic acid as described earlier and as shown

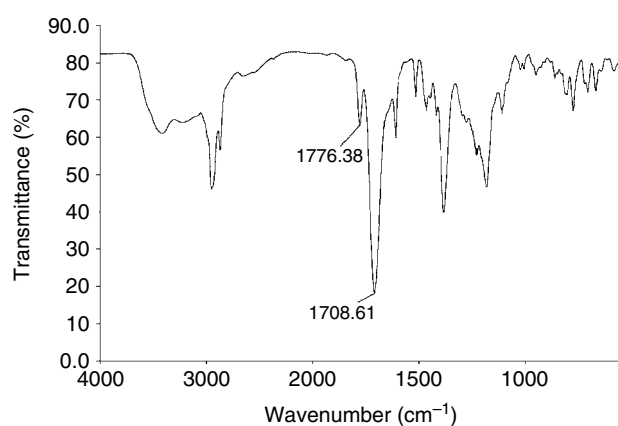


Figure 1. FTIR spectrum of RMID.

in Scheme 1. The structure of RMID was confirmed by FTIR, $^1\text{H-NMR}$ and elemental analysis. The FTIR spectrum (Fig. 1) showed strong absorptions at 1776.4 and 1708.6 cm^{-1} , which were due to C=O stretching vibrations of imide rings.

In the $^1\text{H-NMR}$ spectrum (Fig. 2), the proton at (a) corresponded to the peak at $\sim 5.5 \text{ ppm}$ and the peak at $\sim 8.1 \text{ ppm}$ was assigned to proton (b) in the RMID unit. The elemental analysis values were in good agreement with the calculated ones. From the FTIR and $^1\text{H-NMR}$ results, it could be concluded that the desired product had been obtained.

RMA was introduced into the main chain of PBS by copolymerization of BD, SA and RMID together. Because the carboxyl joined to the hydrogenated phenanthrene ring in RMID is too inactive to be esterified, it is difficult to obtain copolymers with high molecular weight through a simple method of esterification. A special esterifiable approach was thus adopted. RMID was reacted with BD at $260\text{--}280^\circ\text{C}$ for 4 h, and then heated to 300°C for another hour, with zinc acetate and Sb_2O_3 as catalysts. However, the esterification of SA was carried out separately at 180°C without any catalyst (Scheme 2). The chemical structures of the prepolymer 1 and the copolyester (PBSR) were confirmed by $300 \text{ MHz } ^1\text{H-NMR}$ spectra, as shown in Figs 3 and 4, respectively.

In Fig. 3, the proton m and proton n showed chemical shift at $\sim 4.3 \text{ ppm}$ and $\sim 4.1 \text{ ppm}$, respectively. In Fig. 4, the peak at $\sim 5.5 \text{ ppm}$ was assigned to the $=\text{CH}$ proton (proton a) in the RMA unit, the peak at $\sim 8.1 \text{ ppm}$ originated from the CH proton (proton b) in the phenyl unit, and the other specific signals were at $\sim 4.1 \text{ ppm}$ (CH_2 , proton c of the BD unit), $\sim 1.7 \text{ ppm}$ (proton d), $\sim 2.6 \text{ ppm}$ (proton e of the succinate unit) and $\sim 4.3 \text{ ppm}$ (proton f). Based on the above assignments of peaks, the chemical structure of prepolymer 1 and PBSR were confirmed adequately. The ratio of RMA and SA units in the copolymers was calculated on the basis of the corresponding resonance intensities of proton a and proton (Table 1). The RMA proportion calculated in the copolymers was lower than the corresponding feed ratio because of the lower reactivity of RMID compared with SA.

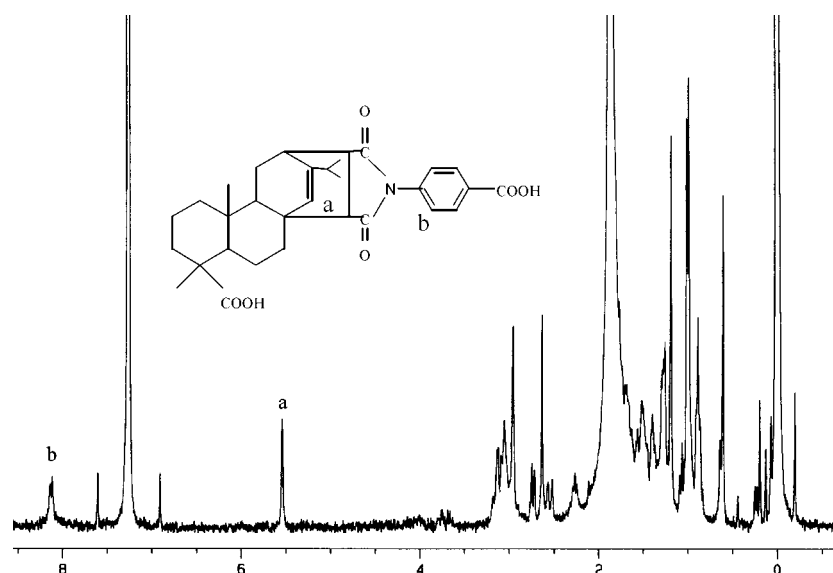


Figure 2. ^1H -NMR spectrum of RMID.

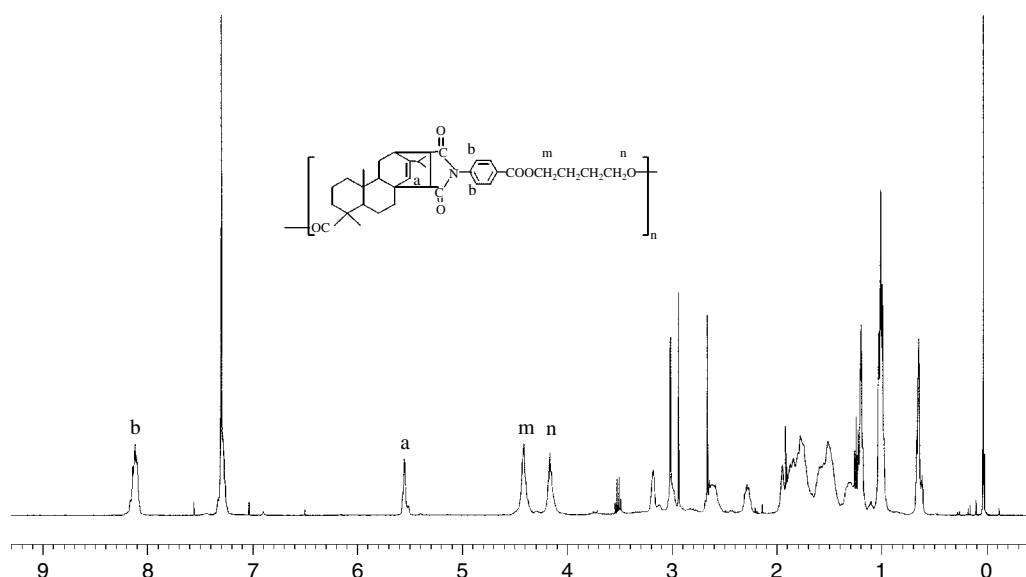


Figure 3. ^1H -NMR spectrum of prepolymer 1.

The inherent viscosities of the copolymers measured with an Ubbelohde viscometer, and the molecular weight and molecular weight distribution determined by GPC are listed in Table 1. The values obtained indicated that the procedures in Scheme 2 were feasible and successful.

The thermal properties of PBSRs were investigated by DSC. Figure 5 shows the second heating curves and cooling curves of the PBSRs. The thermal parameters are listed in Table 2. From Fig. 5, it was found that the PBS100R0 curve had a melting peak at 113.6°C and a crystallization peak at 73.8°C , but when the RMA unit was introduced into the chain of PBS, the T_m and T_c reduced with increasing RMA, to 104.9°C and to 54.9°C , respectively. The degree of supercooling ($\Delta T = T_m - T_c$) is an

important parameter for estimating the crystallizability of polymers.²² Generally speaking, when the ΔT increased, the crystallizability became poorer. In this case, as shown in Table 2, ΔT increased as the content of RMA increased. Table 2 also lists the relative degree of crystallinity of the copolyesters calculated by equation $X_t = \Delta H_m / \Delta H^\circ$, where ΔH° is the thermodynamic melting enthalpy of PBS (110.4 J g^{-1})²³ and ΔH_m is the apparent enthalpy of fusion corresponding to PBSR. The relative degree of crystallinity decreased significantly as the content of the RMA unit was increased. These results implied that the movement of the crystallizable segment was blocked by the huge hydrogenated phenanthrene ring, so the crystallizability and crystallization rate of the copolymers were decreased. This effect became more

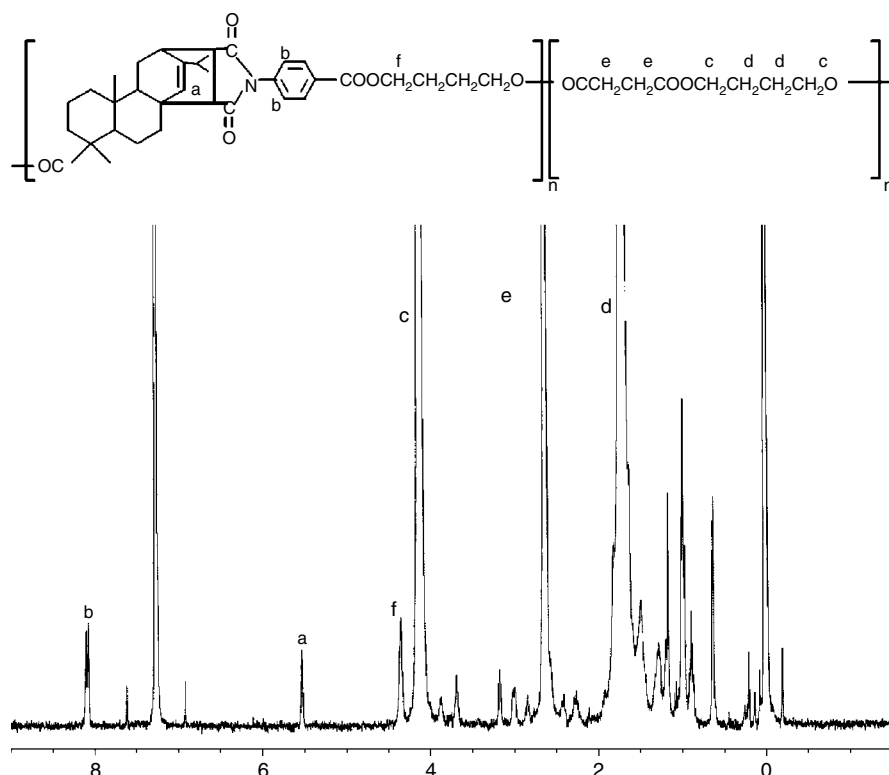


Figure 4. ^1H -NMR spectrum of PBSR copolyester.

Table 1. Composition, molecular weight and intrinsic viscosity of the PBSR copolymers

| Sample | RMID/(RMID+SA) (mol/mol) | | M_n ($\times 10^4$) | M_w ($\times 10^4$) | PDI ^a | $[\eta]$ (dL g^{-1}) |
|----------|--------------------------|-----------|----------------------------|----------------------------|------------------|------------------------------------|
| | Feed (%) | Found (%) | | | | |
| PBS100R0 | 0 | 0 | 4.2 | 6.6 | 1.55 | 1.03 |
| PBS98R2 | 2 | 1.3 | 4.8 | 8.7 | 1.81 | 1.12 |
| PBS97R3 | 3 | 2.1 | 3.8 | 7.7 | 2.02 | 0.86 |
| PBS96R4 | 4 | 2.8 | 4.3 | 8.3 | 1.94 | 1.05 |
| PBS94R6 | 6 | 4.0 | 3.1 | 6.3 | 2.04 | 0.80 |

^a Polydispersity index (molecular weight distribution).

Table 2. Thermal parameters and relative degree of crystallinity of the PBSR copolymers

| Sample | T_m ($^{\circ}\text{C}$) | T_c ($^{\circ}\text{C}$) | ΔT ($^{\circ}\text{C}$) ^a | ΔH_m (J g^{-1}) ^b | X_t (%) ^c |
|----------|---------------------------------|---------------------------------|---|--|---------------------------|
| PBS100R0 | 113.6 | 73.8 | 39.8 | 73.6 | 66.9 |
| PBS98R2 | 112.6 | 70.8 | 41.8 | 70.7 | 64.2 |
| PBS97R3 | 109.9 | 67.3 | 42.6 | 62.6 | 56.9 |
| PBS96R4 | 107.0 | 61.0 | 46.0 | 59.5 | 54.5 |
| PBS94R6 | 104.9 | 54.9 | 50.0 | 56.3 | 51.2 |

^a Degree of supercooling: $\Delta T = T_m - T_c$.

^b Enthalpy of fusion.

^c Degree of crystallinity calculated by DSC.

and more significant with increasing RMA content. The results of crystallization kinetics studies were discussed in detail in our former article.²⁴

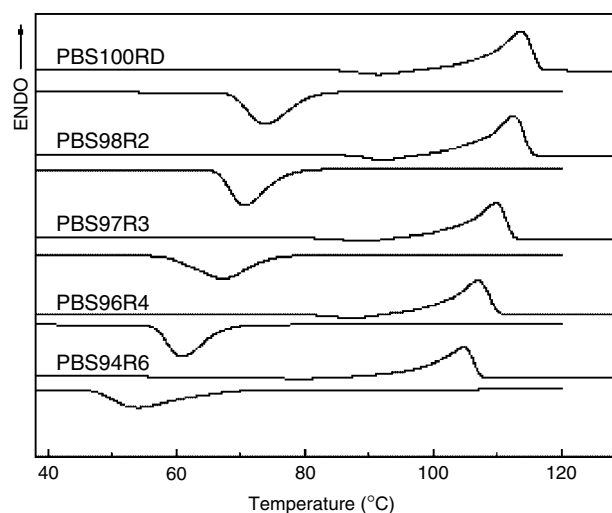


Figure 5. DSC curves of the PBSR copolyesters (second heating curves and cooling curves).

Figure 6 shows the X-ray diffraction patterns for the PBSR copolyesters. PBS showed main peaks at $2\theta = 19.4^{\circ}$, 22.4° and 28.6° , which were the signs of the presence of crystallites.²⁵ Its copolyester also displayed three main peaks in Fig. 6, but the diffraction peaks gradually shifted to lower 2θ angles as the content of RMA increased. This implied that the huge hydrogenated phenanthrene ring disturbed the crystallization of the PBS molecular chain, the basal spacing of crystals was enlarged and the perfection of crystals was reduced.

The above conclusion was confirmed by the PLM observations. The spherulitic morphologies of the

copolymers melt-crystallized isothermally at 85 °C are shown in Fig. 7. The spherulite formed in PBSR had the normal extinction crosses (Maltese cross) and radiating textures could be seen. For PBS100R0 and PBS97R3, the spherulitic interface was very clear. However, for PBS96R4 and PBS94R6, the boundaries became blurry. The diameter of the spherulites reduced with increasing content of RMA units. It should be noted that, although the well-developed spherulites were not seen in PBS94R6, it was also a semi-crystalline polymer. The reason was that when the content of the non-crystallizable member was increased, the perfection of spherulites declined and the crystallizable link of the chain became shorter and shorter.

As far as semi-crystalline polymers are concerned, the size, shape, perfection, orientation and degree of

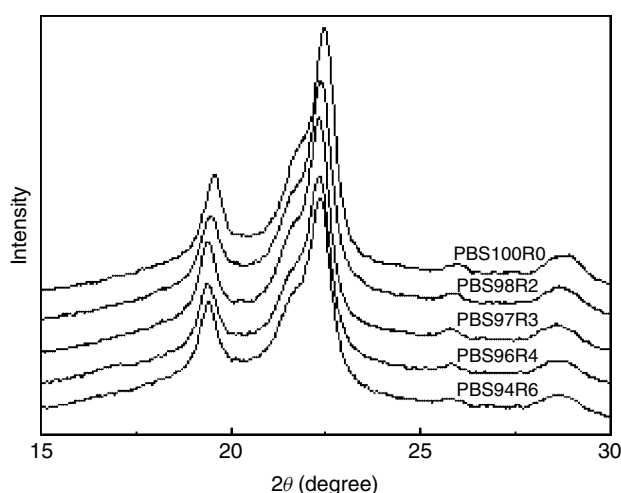


Figure 6. WAXD patterns of the PBSR copolyesters.

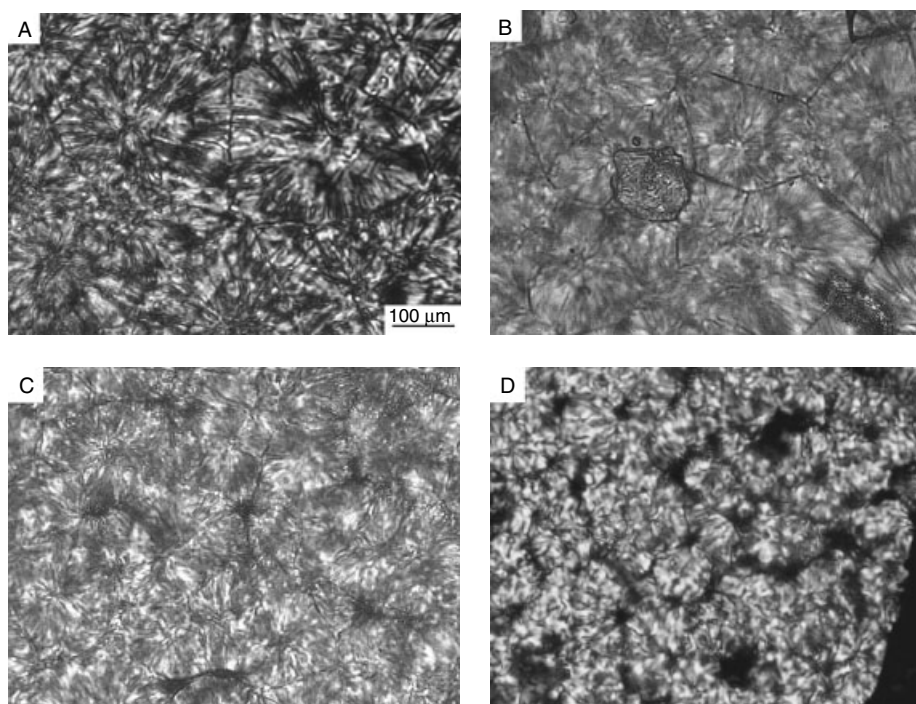


Figure 7. Morphologies of PBSR copolyesters under a polarizing microscope: (A) PBS100R0; (B) PBS97R3; (C) PBS96R4; (D) PBS94R6.

Table 3. Mechanical properties of the PBSR copolyesters

| Sample | Elongation at break (%) | Tensile strength (MPa) | Impact strength (J m^{-1}) |
|----------|-------------------------|------------------------|---------------------------------------|
| PBS100R0 | 272 | 32.7 | 38.9 |
| PBS98R2 | 320 | 30.5 | 41.7 |
| PBS97R3 | 330 | 29.9 | 44.2 |
| PBS96R4 | 360 | 28.3 | 48.5 |
| PBS94R6 | 380 | 26.5 | 50.3 |

crystallinity play an important role in determining the mechanical properties. The mechanical properties of the copolymers are listed in Table 3. It was found that the notched impact strength and elongation at break of the copolymers were enhanced significantly with increasing content of RMA. However, the tensile strength decreased gradually. The notched impact strength increased from 38.9 J m^{-1} for PBS100R0 to 50.3 J m^{-1} for PBS94R6, an increase of 29.3%. It is well known that when the perfection of spherulites and the degree of crystallinity are decreased, the tensile strength will be reduced, but notched impact strength will be increased in some extent. The results of mechanical testing were consistent with those from the crystallization studies.

CONCLUSIONS

For the synthesis of PBS modified by rosin maleopimaric acid anhydride, a special esterifiable approach was adopted. The values of molecular weight, molecular weight distribution and inherent viscosity for the copolymers indicated that our experiments in Scheme 2 were feasible and successful. On the basis of the successful synthesis of PBSR copolyesters,

the thermal, mechanical and crystallization properties were studied. The results indicated the rate of crystallization, degree of crystallinity and dimensions of the spherulites decreased notably. The studies on their mechanical properties showed that the elongation at break and notched impact strength increased accordingly with increasing content of RMA in the copolymers, but the tensile strength was reduced to a certain extent. The main reason for these changes in mechanical properties was the change in crystallization properties.

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