

Isothermal crystallization, melting behavior and crystalline morphology of syndiotactic polystyrene blends with highly-impact polystyrene

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Abstract

Syndiotactic polystyrene (sPS) blends with highly-impact polystyrene (HIPS) were prepared with a twin-screw extruder. Isothermal crystallization, melting behavior and crystalline morphology of sPS in sPS/HIPS blends were investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarized optical microscopy (POM). Experimental results indicated that the isothermal crystallization behavior of sPS in its blends not only depended on the melting temperature and crystallization temperature, but also on the HIPS content. Addition of HIPS restricted the crystallization of sPS melted at 320 °C. For sPS melted at 280 °C, addition of low HIPS content (10 wt% and 30 wt%) facilitated the crystallization of sPS and the formation of more content of α -crystal. However, addition of high HIPS content (50 wt% and 70 wt%) restricted the crystallization of sPS and facilitated the formation of β -crystal. More content of β -crystal was formed with increase of the melting and crystallization temperature. However, α -crystal could be obtained at low crystallization temperature for the specimens melted at high temperature. Addition of high HIPS content resulted in the formation of sPS spherulites with less perfection.

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1. Introduction

Syndiotactic polystyrene (sPS) is known for its complex polymorphism, including α , β , γ and δ , four different crystal forms. In addition, α - and β -crystal forms are always generated through bulk crystallization process while γ - and δ -crystal forms could be obtained by the treatment of solvents [1–8].

Many studies have been devoted to understand the crystallization effects on polymorphic behavior of sPS. Complex crystallization and polymorphic behavior have been found. The formation of α -crystal was believed to be either the result of the kinetically controlled process or the memory effect of α nuclei. The formation of the thermally stable β -crystal was dependent on the thermal histories and crystallization

conditions. The parameters affecting the formation of α - and β -crystal forms of sPS included the maximum temperature at the melt, the permanent time at the melt, the crystallization temperature, the crystallization time, the starting material, the cooling rate and so on [2,9–13]. The maximum temperature at melt was found to be the most intrinsic factor in affecting the polymorphism of sPS [14,15]. In addition, He et al. [16] found that there existed the process of transformation of α -crystal to β -crystal as sPS was in supercritical carbon dioxide.

sPS based blends such as sPS/aPS (atactic polystyrene) [17–25] and sPS/PPO poly(phenylene oxide) [26–31] were also extensively studied. The corresponding results showed that these blends were miscible and the addition of second component facilitated the formation of more content of β -crystal and affected the melting behavior of sPS. Chiu and Peng [19] found that the incorporation of aPS decreased the non-isothermal crystallization peak temperature and reduced the crystallization rate of sPS. Similar phenomenon was also

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observed in other blending systems of sPS/PPE (polyphenylene ether) [32], sPS/TMPC (tetramethyl polycarbonate) [33] and so on. For the other partly miscible and immiscible blends of sPS/SEBS (atactic polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-atactic polystyrene) [34], sPS/HDPE (high-density polyethylene) [35,36], sPS/iPP (isotactic polypropylene) [37], sPS/PA6 (polyamide 6) [38,39], sPS/PA66 (polyamide 66) [40], sPS/EPR (ethylene-propylene rubber) [41,42] and so on, researchers focused on the improvement of compatibility of the blends, and on the morphology, thermal properties, mechanical properties of the blends.

sPS is known for its high melting point, resistance to chemicals and good mechanical properties, however, the low impact strength of sPS restricts the application in more fields. Highly-impact polystyrene (HIPS) is composed of rubber phase of 1,4-polybutadiene and atactic polystyrene. It is known for its good toughness and the relatively high impact strength. Addition of HIPS is expected to be a reasonable way to improve the impact strength of sPS. Generally, the mechanical properties of crystallized polymers and its blends not only depend on the crystallization behavior and morphology, but also on the blend ratio and interfacial interaction between the components. Therefore, sPS blends with different contents of HIPS were prepared by a twin-screw extruder. The isothermal crystallization and melting behaviors of sPS and its blends were investigated by differential scanning calorimetry (DSC), and the corresponding polymorphism was analyzed by the wide-angle X-ray diffraction (WAXD). Polarized optical microscopy (POM) was also used to observe the crystalline morphology of sPS and its blends.

2. Experimental

2.1. Materials and blends preparation

The sPS is Questra F2250 from Dow Chemical Co., M_w and M_n were characterized by GPC and were 2.3×10^5 g/mol and 9×10^4 g/mol, respectively. The HIPS is MS 500, the product of the Idemitsu Co. The sPS and HIPS were first dried in a vacuum oven at 80 °C for 24 h before blending. All the blends were prepared by melt extrusion at 280 °C with an SJSH-Z-30 twin-screw extruder (Factory of Rubber and Plastic of Nanjing, China). The rate of the main machine was 100 rpm. The weight composition of sPS/HIPS blends was 10/0, 9/1, 7/3, 5/5 and 3/7.

2.2. Differential scanning calorimetry (DSC)

The characterization of crystallization and melting behaviors was carried out with the DSC-7 Perkin–Elmer instrument under a nitrogen atmosphere. The corresponding parameters of crystallization and melting enthalpies (ΔH_c and ΔH_m), crystallization peak time (t_p) and melting peak temperature (T_m) were involved. The heat flow and temperatures of DSC were calibrated with standard materials, indium and zinc. The weights of the specimens ranged from 4 mg to 5 mg. All the specimens were heated rapidly at a rate of 200 °C/min to various

maximum melting temperatures (T_{max}) and melted for 10 min to erase the thermal history and then the specimens were rapidly cooled at 200 °C/min to different designed crystallization temperatures (T_c) for 30 min. The crystallized specimens were subsequently cooled to room temperature at 200 °C/min and then heated at rate of 10 °C/min to investigate the corresponding melting behaviors.

2.3. Wide-angle X-ray diffraction (WAXD)

The wide-angle X-ray diffraction patterns of the specimens were recorded at room temperature using a Rigaku D/Max 2200 unit equipped with Ni-filtered Cu K α radiation in the reflection mode with a wavelength of 0.154 nm. The scanning 2θ angle ranged between 3° and 40° with a step scanning rate of 2°/min. For direct comparison, the specimens were thermally treated as those for DSC experiments.

2.4. Polarized optical microscope (POM)

The specimens pressed between two glass slides were first heated to 280 °C or 320 °C for 10 min and then were rapidly quenched to designated crystallization temperatures (240 °C) on the microscopic heating stage (Linkam THMS-600 with TP-92 temperature programmer) for 30 min. Then, the specimens were rapidly cooled to room temperature to observe the morphology.

3. Results and discussion

3.1. The crystallization behavior of sPS and sPS/HIPS blends

DSC curves of sPS and sPS/HIPS 7/3 blend crystallized isothermally at various temperatures after melting at 320 °C and 280 °C are shown in Fig. 1, respectively. As anticipated by the nucleation-controlled crystal growth theory, the time needed to complete crystallization was longer for the specimens crystallized at higher crystallization temperature (T_c). While at the same T_c , the time needed to complete the crystallization for sPS and sPS/HIPS 7/3 blend after melting at 320 °C was longer than that at 280 °C. That is to say, sPS and its blend exhibited faster crystallization rate at lower T_{max} . Furthermore, at the same T_c , the t_p for sPS was shorter than that for sPS/HIPS 7/3 blend melted at 320 °C, and the t_p for sPS was longer than that for sPS/HIPS 7/3 blend melted at 280 °C. It is indicated that the crystallization rate of sPS was affected with the addition of HIPS.

Table 1 lists the t_p and ΔH_c for sPS and its blends. The relationship of reciprocal crystallization peak (i.e. t_p^{-1}) versus T_c for sPS and its blends is shown in Fig. 2. Generally, the t_p^{-1} is proportional to the crystallization rate. It is observed from Table 1 and Fig. 2 that the crystallization rate of sPS and its blends decreased with increase of crystallization temperatures. For the specimens melted at 320 °C, the crystallization rate of sPS decreased with increase of HIPS content,

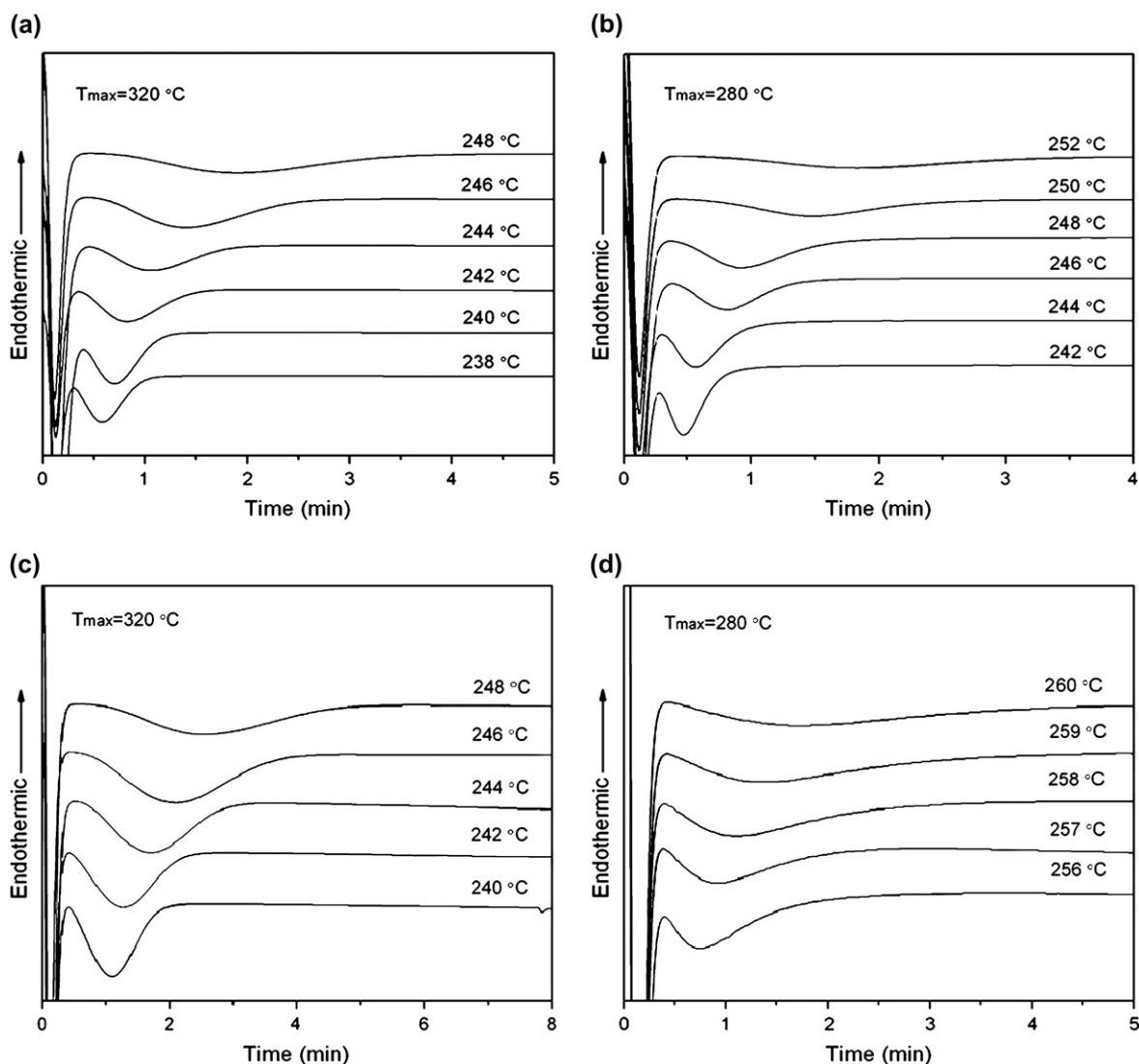


Fig. 1. DSC curves for sPS (a, b) and sPS/HIPS 7/3 blend (c, d) isothermally crystallized at different temperatures after melting at 320 °C and 280 °C for 10 min.

which was similar to the sPS/aPS blends [19]. However, for the specimens melted at 280 °C, the crystallization rate of sPS first increased and then decreased with increase of HIPS content. Therefore, sPS/HIPS 9/1 and 7/3 blends showed faster crystallization rate than that of sPS, and sPS/HIPS 5/5 and 3/7 blends exhibited slower crystallization rate. It is observed from Table 1 that the ΔH_c of sPS was almost the same as that of the blends melted at 320 °C. The value of ΔH_c ranged from about 25.90 J/g to 26.94 J/g, showing that the content of HIPS had little influence on the crystallization enthalpy. However, the ΔH_c of sPS was different from that of the blends melted at 280 °C. The ΔH_c of sPS was about 23 J/g, and the ΔH_c of sPS/HIPS 9/1 and 7/3 blends was lower than that of sPS. However, the sPS/HIPS 3/7 blend showed the largest value of about 25 J/g. The ΔH_c first decreased and then increased with increase of HIPS content. The T_{max} was an important factor in affecting the value of ΔH_c . The ΔH_c of sPS and its blends melted at 280 °C was lower than that at 320 °C. And the change of

ΔH_c for sPS melted at 320 °C and 280 °C was lower for blends containing low HIPS content and higher for blends containing high HIPS content. Therefore, it is suggested that the crystallization rate and enthalpy of sPS were related with HIPS content and T_{max} . For the specimens melted at 280 °C, addition of low content of HIPS increased the crystallization rate and decreased the ΔH_c of sPS. However, addition of HIPS decreased the crystallization rate but did not change the ΔH_c of sPS in its blends melted at 320 °C. The increase of crystallization rate led to the decrease in the crystallization enthalpy for sPS in its blends melted at low temperature. However, the change of crystallization rate showed little influence on the crystallization enthalpy for sPS in its blends melted at high temperature. It is suggested that the change of crystallization rate and enthalpy might be originated from the difference in crystallization mechanisms, such as the different nucleating and growth pattern.

According to Turnbull and Fisher [43,44], the crystallization rate of the polymer could be described as follows:

Table 1

The data of the crystallization peak time (t_p) and crystallization enthalpy (ΔH_c) for sPS and its blends crystallized at various temperatures (T_c) after melting at 280 °C and 320 °C

| T_{max} (°C) | 280 | | | 320 | | |
|----------------|------------|-------------|--------------------|------------|-------------|--------------------|
| | T_c (°C) | t_p (min) | ΔH_c (J/g) | T_c (°C) | t_p (min) | ΔH_c (J/g) |
| 10/0 | 252 | 1.83 | 23.67 | 248 | 2.00 | 26.21 |
| | 250 | 1.45 | 23.40 | 246 | 1.40 | 26.94 |
| | 248 | 0.91 | 22.13 | 244 | 1.12 | 26.84 |
| | 246 | 0.81 | 23.31 | 242 | 0.82 | 26.44 |
| | 244 | 0.56 | 23.00 | 240 | 0.71 | 26.25 |
| | 242 | 0.47 | 22.34 | 238 | 0.57 | 25.93 |
| 9/1 | 260 | 2.00 | 19.47 | 246 | 1.70 | 26.26 |
| | 259 | 1.60 | 19.18 | 244 | 1.26 | 26.79 |
| | 258 | 1.30 | 19.80 | 242 | 1.01 | 26.86 |
| | 257 | 1.05 | 18.46 | 240 | 0.81 | 26.84 |
| | 256 | 0.91 | 18.86 | 238 | 0.67 | 26.81 |
| 7/3 | 260 | 1.80 | 19.47 | 248 | 2.51 | 26.61 |
| | 259 | 1.40 | 19.03 | 246 | 2.08 | 26.44 |
| | 258 | 1.15 | 19.39 | 244 | 1.78 | 26.71 |
| | 257 | 0.94 | 19.29 | 242 | 1.27 | 26.06 |
| | 256 | 0.77 | 19.43 | 240 | 1.08 | 26.03 |
| 5/5 | 258 | 9.49 | 23.14 | 242 | 1.65 | 26.00 |
| | 256 | 5.71 | 23.90 | 240 | 1.37 | 26.66 |
| | 254 | 3.81 | 23.60 | 238 | 1.10 | 26.18 |
| | 252 | 2.50 | 23.12 | 236 | 1.07 | 26.10 |
| | 250 | 1.68 | 23.32 | 234 | 0.95 | 26.12 |
| 3/7 | 242 | 2.17 | 25.80 | 231 | 1.30 | 26.47 |
| | 240 | 1.97 | 25.33 | 230 | 1.25 | 26.70 |
| | 238 | 1.66 | 25.07 | 228 | 1.15 | 25.90 |
| | 236 | 1.39 | 25.73 | 226 | 1.10 | 26.77 |
| | 234 | 1.23 | 24.30 | 224 | 1.00 | 26.73 |
| | | | | 222 | 0.95 | 26.43 |

$$G = G_0 \exp(-\Delta F/kT_c) \exp(-\Delta\Phi/kT_c) \quad (1)$$

where G is the crystallization rate, G_0 is a pre-exponential factor, ΔF is the transport activation energy and $\Delta\Phi$ is the nucleating activation energy. Obviously, isothermal crystallization rate of polymers basically depends on two energetic terms. One is the activation energy (ΔF) required for transportation of the chain molecules across the melt–crystalline interface. The other is the free energy ($\Delta\Phi$) required for the formation of a nucleus of critical size, which contains enthalpic and entropic terms. The addition of the non-crystalline polymer to a crystalline polymer may influence both the energetic terms. The influence of ΔF depends on the variation of T_g with blend composition. The specimens with a lower T_g possess a higher molecular mobility and a lower ΔF value at the same crystallization temperature. Therefore, the crystallization rate of specimens with lower T_g will be faster if the influence of $\Delta\Phi$ term is negligible [20]. However, our results indicated that the T_g of sPS and sPS/HIPS 9/1, 7/3, 5/5, 3/7 blends was 97.4 °C, 98.1 °C, 97.8 °C, 99.9 °C and 100.3 °C, respectively. The difference of T_g was less than 3 °C and the influence of ΔF term could be neglected at the same T_c . Therefore, the influence of $\Delta\Phi$ term should play a dominant role in controlling the isothermal crystallization of sPS and its blends. As discussed above, the increase of the HIPS

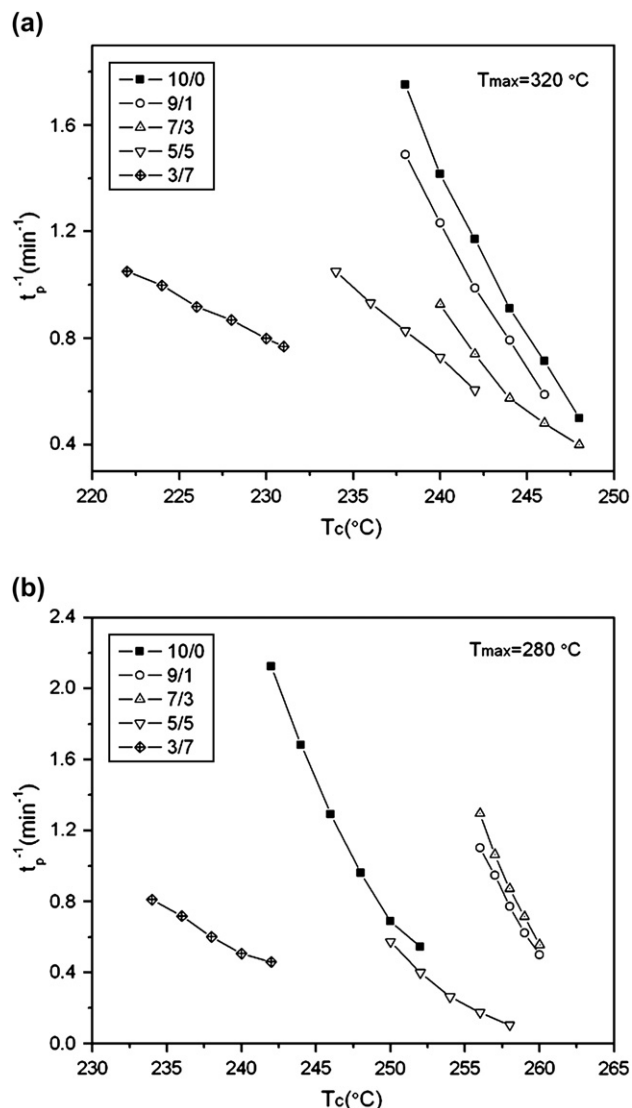


Fig. 2. Reciprocal crystallization peak time versus T_c for sPS and its blends crystallized at different temperatures after melting at 320 °C (a) and 280 °C (b) for 10 min.

content decreased the crystallization rate of sPS melted at 320 °C. It is believed that the decreased crystallization rate of sPS was relative to the depression of the equilibrium melting temperature (T_m^0) of sPS. Our results indicated that the addition of HIPS decreased the T_m^0 of sPS in its blends melted at 320 °C. The decreased equilibrium melting temperature resulted in the increase in the $\Delta\Phi$ term. For the blends melted at 280 °C, addition of lower HIPS content might decrease the value of $\Delta\Phi$ term, which resulted in the easy formation of nucleus of critical size and increased the crystallization rate of sPS. However, addition of higher HIPS content might increase the value of $\Delta\Phi$ term as the same as the blends melted at 320 °C. Therefore, the effect of HIPS on the crystallization rate of sPS might be attributed to the change of $\Delta\Phi$ in blends.

It is suggested that the crystallization rate of sPS also depended on the formation of different crystal forms. Previous study [2,45] confirmed that lower T_{max} facilitated the

formation of α -crystal while higher T_{\max} facilitated the formation of β -crystal. And the variation of the crystallization rate influenced by both T_{\max} and HIPS content should be originated from the formation of different crystal forms.

Fig. 3 shows the X-ray spectra of sPS and its blends crystallized at 240 °C after melting at 320 °C and 280 °C. The reflection peaks were observed at $2\theta = 6.2^\circ, 10.5^\circ, 12.4^\circ, 13.8^\circ, 18.8^\circ, 21.3^\circ$ (Fig. 3a). It is indicated that only β -crystal was produced for sPS and its blends melted at 320 °C [2]. However, sPS and its blends melted at 280 °C exhibited main reflection peaks at $2\theta = 6.8, 10.4^\circ, 11.8^\circ, 13.7^\circ, 14.2^\circ, 15.7^\circ, 18.0^\circ$ (Fig. 3b), and weak reflection peaks at $2\theta = 6.2^\circ$ and 12.4° could also be observed. It is indicated that the majority of α -crystal and low content of β -crystal were formed. For sPS/HIPS 3/7 blend, the stronger intensity of the reflections of β -crystal ($2\theta = 6.2^\circ$ and 12.4°) showed that more content of β -crystal was produced. According to Woo et al. [9],

α -crystal exhibited faster crystallization rate than that of β -crystal. It is easy to understand that the crystallization rate was higher for sPS and its blends melted at 280 °C due to the formation of more content of α -crystal. De Rosa et al. [2] believed that there existed the memory effect of α -crystal. The un-melted α -crystal played the role of nucleating agent and facilitated the formation of α -crystal. As a consequence, the low crystallization enthalpy was obtained due to the existence of un-melted α -crystal. For example, the content of α -crystal for sPS/HIPS 9/1 and 7/3 blends was higher than that for sPS melted at 280 °C [46], and the blends exhibited faster crystallization rate and lower crystallization enthalpy. However, only β -crystal was produced for sPS and its blends melted at 320 °C. The crystallization enthalpy showed no serious change although the crystallization rate decreased with increase of HIPS content. Therefore, it is suggested that the crystallization rate and crystallization enthalpy of sPS and its blends depended on the formation of different crystal forms and the content of α -crystal.

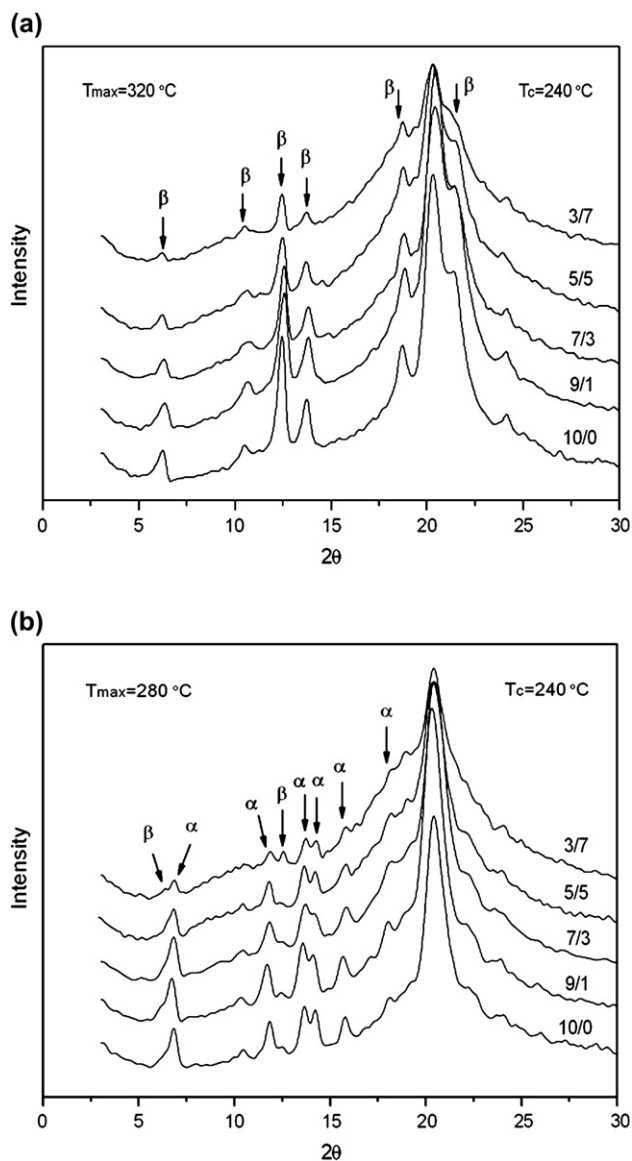


Fig. 3. X-ray spectra of sPS and its blends crystallized at 240 °C for 30 min after melting at 320 °C (a) and 280 °C (b) for 10 min.

3.2. Polymorphism and melting behaviors of sPS and sPS/HIPS blends

It is generally accepted that T_{\max} and T_c play vital role in determining the crystal forms and the corresponding melting behaviors of sPS [2]. Our results indicated that the majority of α -crystal was produced for sPS and its blends melted at temperatures below 290 °C. Only β -crystal was produced at temperatures above 305 °C. The content of α -crystal gradually decreased and the relative content of β -crystal increased with increase of melting temperatures.

Fig. 4 shows the X-ray spectra and the corresponding DSC melting curves for sPS and its blends crystallized at 240 °C after melting at 295 °C. It could be seen that both α -crystal and β -crystal were produced during the crystallization process. The relative reflection peak intensity of α -crystal ($2\theta = 6.8^\circ$ and 11.8°) for sPS/HIPS 9/1 and 7/3 blends was stronger than that for pure sPS. However, the relative reflection peak intensity of β -crystal ($2\theta = 12.4^\circ$) increased with increase of HIPS content. The corresponding DSC melting curves exhibited multiple melting behaviors and the data are listed in Table 2. According to the results of Woo and Sun [47,48], peak I and peak III should be ascribed to the melting of β -crystal while peak II and peak IV were attributed to the melting of α -crystal. As sPS was concerned, the melting peaks at 260.2 °C and 271.9 °C were attributed to the melting of β -crystal and the melting peaks at 266.0 °C and 273.8 °C were ascribed to the melting of α -crystal. For the blends, three melting peaks were observed. As compared with sPS, peak III and peak IV merged into one major peak for the blends. The relative intensity of peak I increased with increase of HIPS content, indicating that addition of HIPS facilitated the formation of β -crystal. However, the relative intensity of peak I for sPS/HIPS 9/1 and 7/3 blends was lower than that for sPS, showing that low content of HIPS facilitated the formation of more α -crystals, which further confirmed the X-ray results. The melting enthalpy (ΔH_m) for sPS and its blends was close

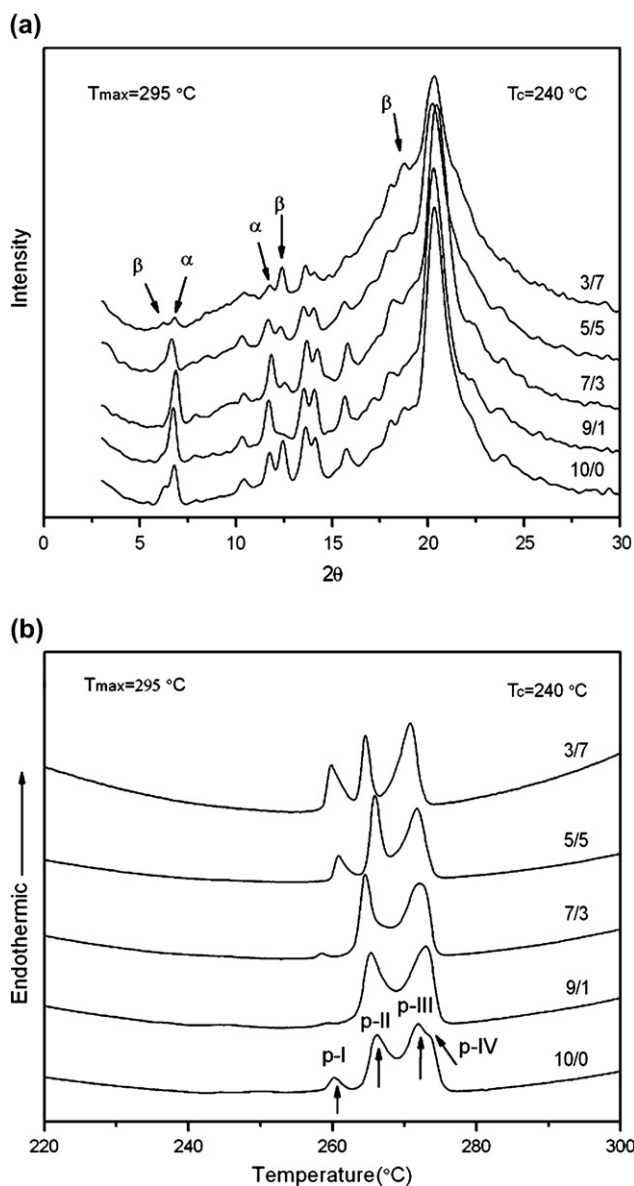


Fig. 4. X-ray spectra (a) and DSC melting curves (b) for sPS and its blends crystallized at 240 °C for 30 min after melting at 295 °C for 10 min.

to each other, ranging from 28.09 J/g to 28.76 J/g. It is believed that addition of HIPS had no serious influence on the value of ΔH_m and the crystallinity of sPS in its blends.

Fig. 5 shows the X-ray spectra and DSC melting curves for sPS and its blends crystallized at 260 °C for 120 min after melting at 280 °C and the corresponding data are listed in

Table 2
DSC melting data for sPS and its blends crystallized at 240 °C for 30 min after melting at 295 °C for 10 min

| sPS/HIPS | T_{p1} (°C) | T_{p2} (°C) | T_{p3} (°C) | T_{p4} (°C) | ΔH_m (J/g) |
|----------|---------------|---------------|---------------|---------------|--------------------|
| 10/0 | 260.2 | 266.0 | 271.9 | 273.8 | 28.76 |
| 9/1 | | 265.3 | 272.9 | | 28.09 |
| 7/3 | 258.4 | 264.5 | 272.2 | | 28.70 |
| 5/5 | 260.8 | 265.9 | 271.8 | | 28.60 |
| 3/7 | 259.8 | 264.6 | 270.7 | | 28.60 |

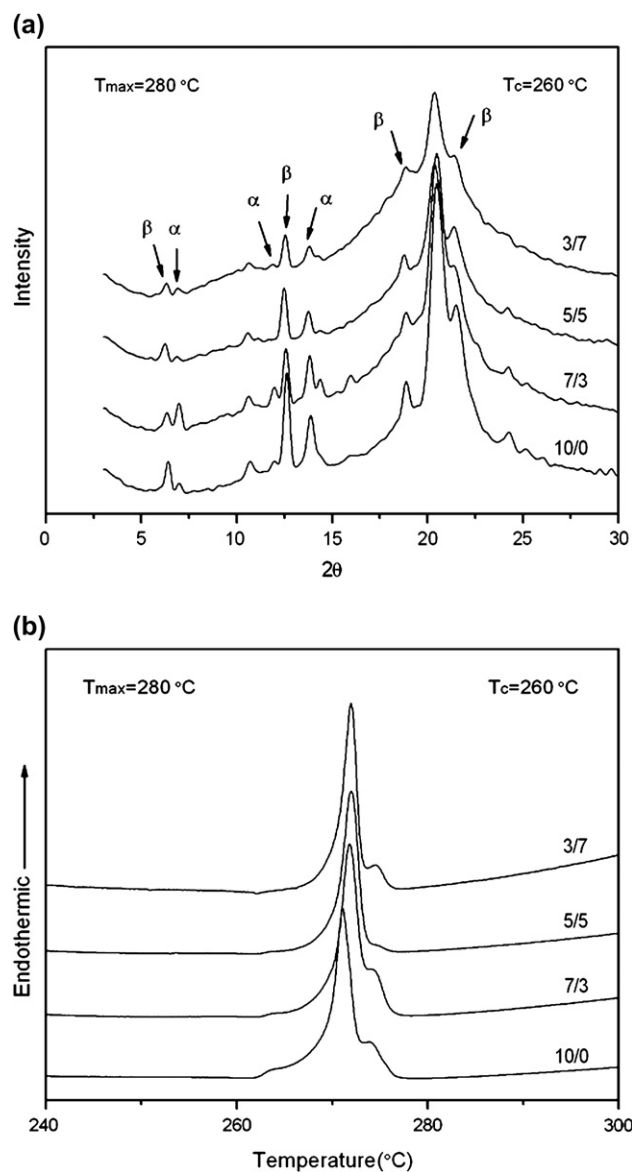


Fig. 5. X-ray spectra (a) and DSC melting curves (b) for sPS and its blends crystallized at 260 °C for 120 min after melting at 280 °C for 10 min.

Table 3. Characteristic reflection peaks of β -crystal and the relatively weak reflection peaks of α -crystal were observed. The sPS/HIPS 7/3 blend exhibited stronger reflection peaks at $2\theta = 6.8^\circ$ and 11.8° , indicating that more α -crystal was produced. The corresponding DSC melting curves of sPS and its blends showed one major melting peak and two shoulder peaks. Combined with the results of X-ray spectra, it is

Table 3
DSC melting data for sPS and its blends crystallized at 260 °C for 120 min after melting at 280 °C for 10 min

| sPS/HIPS | T_{p1} (°C) | T_{p2} (°C) | T_{p3} (°C) | ΔH_m (J/g) |
|----------|---------------|---------------|---------------|--------------------|
| 10/0 | 263.6 | 271.1 | 274.2 | 28.89 |
| 7/3 | 263.8 | 271.8 | 274.6 | 28.41 |
| 5/5 | | 272.0 | | 28.54 |
| 3/7 | | 272.0 | 274.7 | 28.27 |

suggested that the major melting peak at around 272 °C was attributed to the melting of β -crystal. The high temperature melting shoulder peak at around 274 °C should be ascribed to the melting of α -crystal, and the low temperature melting shoulder peak at around 263.6 °C should correspond to the melting of less perfect β -crystal. The corresponding ΔH_m of sPS and its blends was close to each other and the value was similar to that of sPS and its blends melted at 295 °C. Although the melting temperature (280 °C) was low, the high T_c and the long crystallization time favored the formation of β -crystal. Furthermore, addition of low content of HIPS (30 wt%) facilitated the generation of more α -crystal.

Fig. 6 shows the X-ray spectra and the DSC melting curves for sPS and its blends crystallized at 200 °C after melting at 320 °C and the corresponding data are listed in Table 4. It is observed that the majority of β -crystal was produced for sPS and its blends. And the characteristic reflection peaks at $2\theta = 6.8^\circ$ and 11.8° indicated the formation of a small amount

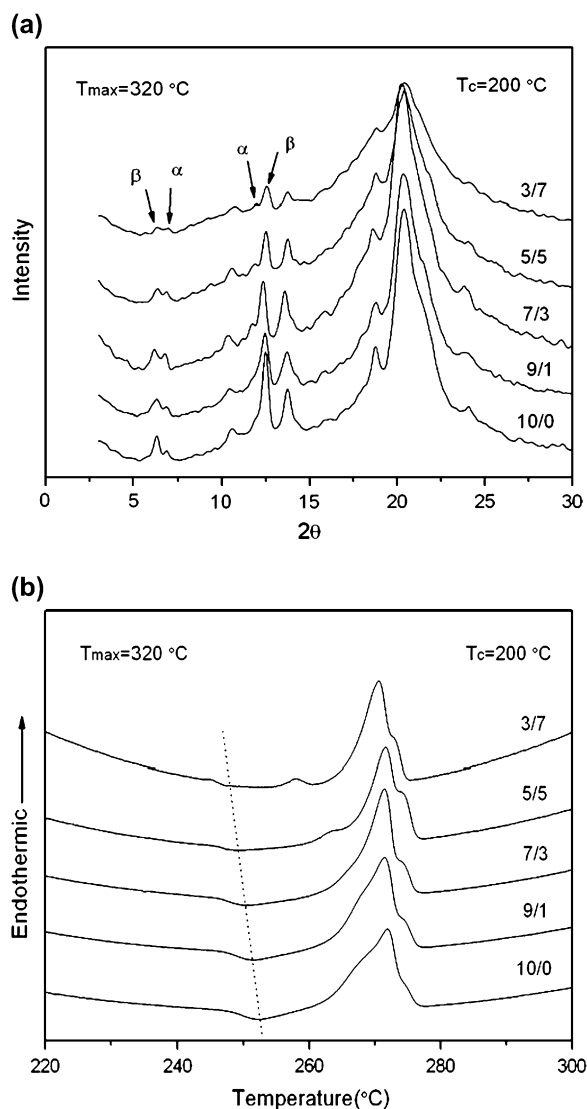


Fig. 6. X-ray spectra (a) and DSC melting curves (b) for sPS and its blends crystallized at 200 °C for 30 min after melting at 320 °C for 10 min.

Table 4

DSC melting data for sPS and its blends crystallized at 200 °C for 30 min after melting at 320 °C for 10 min

| sPS/HIPS | T_{p1} (°C) | T_{p2} (°C) | T_{p3} (°C) | T_{p4} (°C) | ΔH_m (J/g) |
|----------|---------------|---------------|---------------|---------------|--------------------|
| 10/0 | | 267.2 | 271.9 | 274.0 | 28.43 |
| 9/1 | | 267.8 | 271.4 | 274.6 | 28.29 |
| 7/3 | | | 271.4 | 274.7 | 28.92 |
| 5/5 | 263.2 | | 271.6 | 274.5 | 28.32 |
| 3/7 | 258.1 | | 270.6 | 273.2 | 28.68 |

of α -crystal. The corresponding DSC melting curves exhibited different melting behaviors. Four melting peaks were observed for sPS specimen. The weak peak at around 248 °C and the major peak at 271.9 °C were attributed to the melting of β -crystal. The other two peaks at 267.2 °C and 274.0 °C corresponded to the melting of α -crystal. An exothermic peak at about 252 °C was attributed to the re-crystallization of less perfect crystals. sPS/HIPS 9/1 and 7/3 blends exhibited similar melting behaviors as those of sPS. For sPS/HIPS 5/5 and 3/7 blends, the discernible peaks at 263.2 °C and 258.1 °C were due to the melting of β -crystal. The melting enthalpy of sPS and its blends was also close to each other, showing that HIPS had little influence on the crystallinity of sPS. It is believed that the addition of HIPS affected the melting behaviors of sPS, such as the melting temperatures, the shape of the melting peaks, and the number of the melting peaks.

Both the X-ray analysis and the DSC results indicated that addition of a small amount of HIPS (less than 30 wt%) induced the formation of more content of α -crystal of sPS. To our knowledge, the phenomenon that addition of the second component increased the crystallization rate of sPS and induced the formation of more content of α -crystal has not been found in sPS blends. In the sPS/aPS [19], sPS/PPO [26,28,29] and sPS/poly(styrene-co- α -methyl styrene) [20] blends, addition of the second component always inhibited the crystallization of sPS and facilitated the formation of β -crystal due to the dilution effect. It is suggested that the formation of more content of α -crystal was related with the rubber phase in HIPS. The rubber phase in HIPS induced the easy formation of α -crystal of sPS melted at low temperatures. However, the dilution effect of aPS eventually led to the formation of more β -crystal with increase of HIPS content. For the blends melted at high temperatures, the memory effect of α -crystal of sPS was completely erased and the rubber phase had no effect on the crystallization of sPS.

Despite of the effect of T_{max} , T_c was another important factor in determining the crystal forms of sPS. He et al. [10,11] believed that crystallization temperature was the intrinsic factor controlling the formation of α - and β -crystal of sPS, and α -crystal could be obtained with decrease of crystallization temperature. For the specimens melted at low temperature of 280 °C, higher T_c at 260 °C favored the formation of β -crystal. For the specimens melted at high temperature of 320 °C, lower T_c at 200 °C induced the generation of a small amount of α -crystal. Therefore, it is suggested that α -crystal could be obtained at low crystallization temperature and β -crystal can be formed at high crystallization temperature.

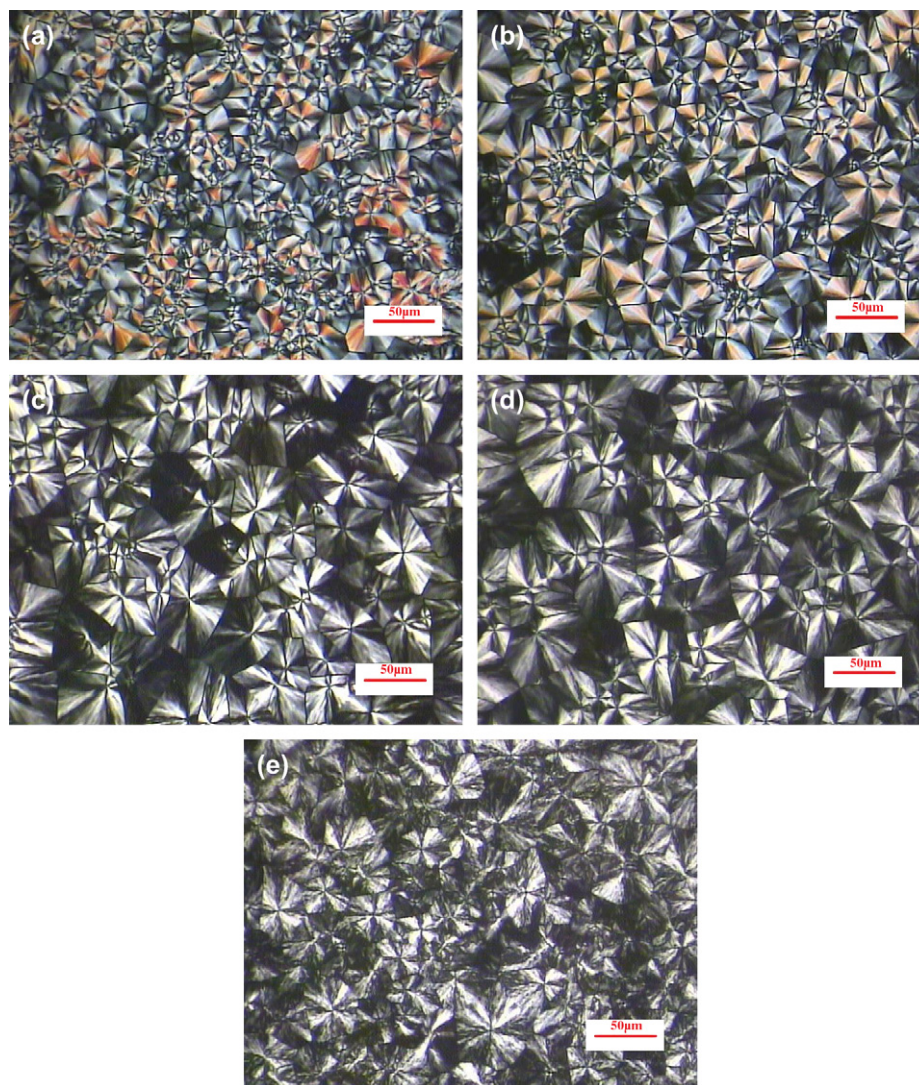


Fig. 7. Polarized optical micrographs of sPS (a), and sPS/HIPS 9/1 (b), 7/3 (c), 5/5 (d) and 3/7 (e) blends crystallized at 240 °C for 30 min after melting at 320 °C for 10 min; the scale bar is 50 μm.

3.3. Crystal morphology

Fig. 7 depicts the representative POM micrographs of sPS and its blends crystallized at 240 °C after melting at 320 °C. Maltese-cross spherulites were obtained for sPS and its blends. For sPS, the optical birefringence in the spherulites caused different light diffraction leading to various colors, with yellow and blue birefringence being the dominant pattern in the spherulites. With increase of HIPS content, the color of the spherulites gradually decreased and finally disappeared. The density of the spherulites decreased and size of the spherulites increased with increase of HIPS content. It is suggested that the addition of HIPS decreased the nucleating ability of sPS in its blends. The boundaries of sPS spherulites were less clear for sPS/HIPS 3/7 blend, showing that the addition of HIPS led to the formation of less perfect spherulites. However, spherulites with clear boundaries were still observed for sPS/HIPS 5/5 blend. It is suggested that HIPS should stay between the lamellae or crystal fibers.

The T_{\max} played a vital role in determining the crystalline morphology of the sPS and sPS/HIPS blends. Tiny crystals were obtained for sPS and its blends melted at 280 °C (Fig. 8). However, sheaf-like crystals were observed for sPS/HIPS 3/7 blend and the sizes of crystals were larger than those of sPS and the other blends. From the results of X-ray analysis, only β -crystal was obtained for sPS and its blends melted at 320 °C. The majority of α -crystal was formed as T_{\max} was at 280 °C except for 3/7 blend. The β -crystal was observed for sPS/HIPS 3/7 blend melted at 280 °C. Therefore, it is believed that the larger spherulites corresponded to β -crystal, and the tiny spherulites corresponded to α -crystal [9]. The larger size of sPS was attributed to the formation of β -crystal for sPS/HIPS 3/7 blend melted at 280 °C.

4. Conclusions

The isothermal crystallization and melting behaviors, crystalline morphology of sPS and sPS/HIPS blends were

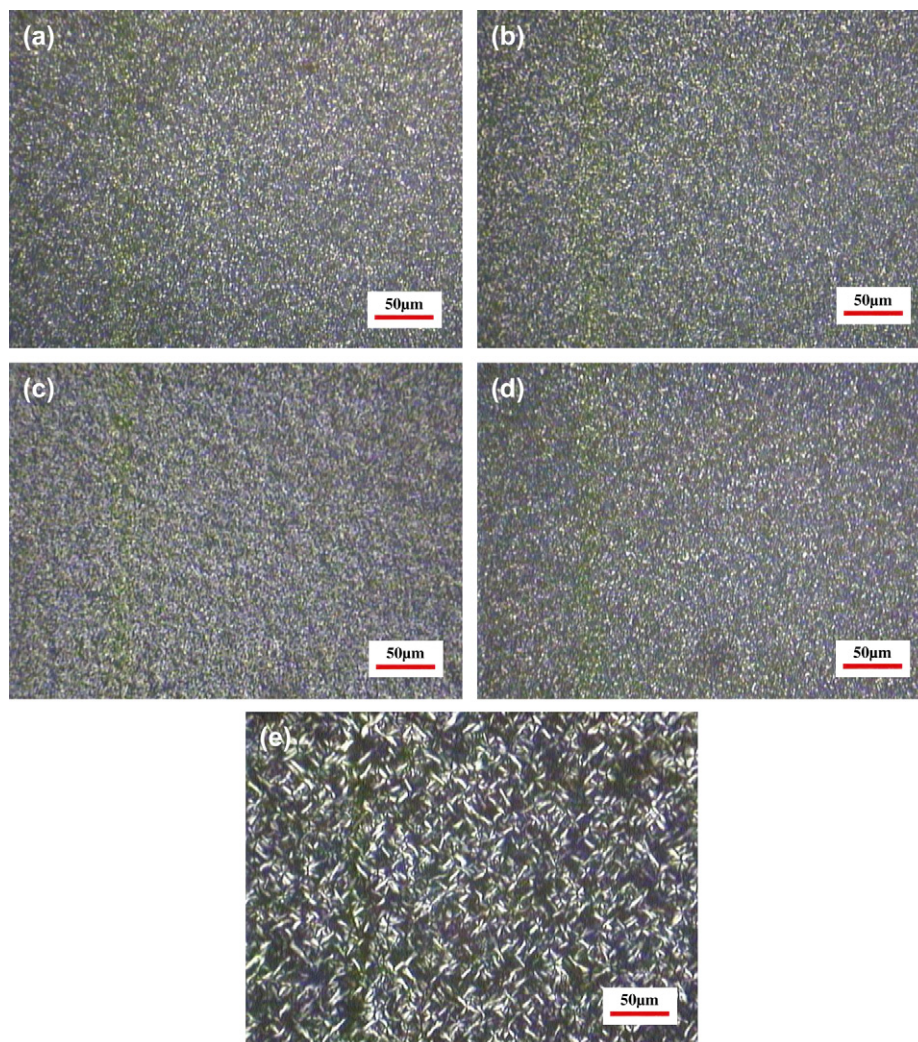


Fig. 8. Polarized optical micrographs of sPS (a), and sPS/HIPS 9/1 (b), 7/3 (c), 5/5 (d) and 3/7 (e) blends crystallized at 240 °C for 30 min after melting at 280 °C for 10 min; the scale bar is 50 μm.

investigated. The isothermal crystallization rate of sPS and its blends not only depended on the melting temperature and crystallization temperature, but also on the HIPS content. For sPS blends melted at high temperatures, the addition of HIPS decreased the crystallization rate of sPS due to the dilution effect of the second component and the formation of β -crystal with lower crystallization rate. For sPS blends melted at low temperatures, addition of low HIPS content facilitated the formation of more content of α -crystal, increased the crystallization rate and decreased the crystallization enthalpy of sPS. However, addition of high content of HIPS facilitated the formation of β -crystal, resulting in the decreased crystallization rate and increased crystallization enthalpy of sPS. Therefore, it is suggested that the effect of HIPS on crystallization of sPS in its blends melted at different T_{\max} may be originated from the different contents of α -crystal and β -crystal. The crystalline forms and the corresponding melting behaviors of sPS and its blends were affected by the maximum melting temperature and crystallization temperature. High T_{\max} and T_c facilitated the formation of β -crystal. However,

α -crystal could be obtained for specimens crystallized at lower temperature after melting at high T_{\max} . More α -crystal could be obtained for sPS blends with low HIPS content. The sPS and its blends melted at 320 °C produced large spherulites due to the formation of β -crystal. Addition of high HIPS content resulted in the formation of spherulites with less perfection. The spherulite size of sPS/HIPS 3/7 blend was higher than that of sPS and other blends melted at 280 °C due to the formation of β -crystal.

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