

Effect of HIPS on Polymorphism, Melting, and Crystallization Behavior of sPS Crystallized Dynamically from Melting State

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Received 21 April 2006; accepted 14 September 2006

DOI 10.1002/app.25481

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Syndiotactic polystyrene/highly-impact polystyrene (sPS/HIPS) blends were prepared with a twin-screw extruder. Differential scanning calorimetry and wide angle X-ray diffractometry were used to investigate the effect of the maximal melting temperature, the content of HIPS and cooling rates on the melting and crystallization behavior and crystal forms of sPS. The experimental results indicated that the addition of low content of HIPS induced the formation of more α -crystal, whereas the addition of high content of HIPS favored the formation of β -crystal for sPS/HIPS blends crystallized dynamically from low melting temperature. Both sPS and its blends produced only β -crystal as crystallized from high melting temperature.

The crystallization temperatures of sPS and its blends decreased as the melting temperature increased, favoring the formation of β -crystal. Higher temperature of sPS crystallization favored the formation of more content of α -crystal while lower temperature of sPS crystallization produced more content of β -crystal. Cooling rates showed no significant effect on the crystal form of sPS and its blends, but influenced the melting behavior of both sPS and its blends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3353–3361, 2007

Key words: syndiotactic polystyrene; highly-impact polystyrene; melting and crystallization behavior; crystal form

INTRODUCTION

Syndiotactic polystyrene (sPS) is known for its high heat-resistance and modulus of elasticity, excellent resistance to chemicals, and relatively fast crystallization rate, which qualify it to be used as a potential engineering plastic. Since its synthesis by Ishihara in 1985, it has gained increasing academic and industrial interests. The sPS has complex polymorphisms such as α , β , γ , and δ crystal forms depending on the conditions of sPS crystallization. Because physical and mechanical properties of crystalline polymer depend on the crystal forms, numerous studies have focused on the polymorphic behavior of sPS.

In the melt crystallization, factors controlling the crystal forms of sPS include premelting temperatures, crystallization temperatures, crystallization times, cooling rates, the addition of the second component, etc.^{1–13} It is well known that more β -crystals are obtained for sPS melted at higher temperatures and higher isothermal crystallization temperatures. Moreover, fast cooling rates seemed to induce the formation of more α -crystals for sPS crystallized dynamically. However, the time

duration in the molten state showed no significant effect on the polymorphism of sPS. The differences of α - and β -crystals such as the crystalline structure, crystallization kinetics, crystal morphology, melting behavior, and crystallization behavior were summarized by Woo et al.¹⁴

However, the addition of the second component such as PPO or aPS was found to reduce the crystal growth rate and the overall crystallization rate, leading to the formation of more β -crystals. In the sPS/aPS blending system, Sun et al.¹⁵ found that the components were completely miscible in the molecular level. Chiu and Peng¹⁶ investigated the effect of molecular weight of aPS on the thermal properties and crystalline structure of sPS/aPS blends, showing that aPS with the lower molecular weight reduced the temperature of sPS crystallization. The crystallization kinetics, lamellar morphology, and crystal growth rates in sPS/aPS blends were analyzed by Wang et al.^{17–19} The effect of the temperature and composition in the cold-crystallization of sPS/aPS blend was studied by Ya and Woo.²⁰ In the sPS/PPO blending system, the two components were also found to be miscible by the analysis of the glass transition temperature and the phase behavior.^{21,22} The correlation between polymorphism and melting behavior was studied by Hong et al.,²³ suggesting that the lowest and middle melting endotherms are attributed to melting of the β - and α -crystal forms. The polymorphism of sPS in the amorphous

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state was found to be modified by the incorporation of PPO.²⁴ The compatibility, morphology, tensile properties, crystallization and melting behavior of other blending systems such as sPS/PVME,²⁵ sPS/SEBS,²⁶ sPS/HDPE,^{27,28} sPS/EPR,^{29,30} sPS/PA6,^{31–33} sPS/PP,³⁴ sPS/PMMA,³⁵ etc., were also investigated.

The multiple melting behavior correlating to the polymorphism and morphology of sPS was analyzed.^{1,36,37} Generally speaking, when four melting peaks appeared, Peak I and Peak III were ascribed to the melting of β -crystal, Peak II and Peak IV were recognized as the contribution of α -crystal. However, the multiple melting phenomenon concerned with melting–recrystallization–melting behavior and different crystalline structure is still in debate.

Because of the high toughness of highly-impact polystyrene (HIPS), the blending of sPS with HIPS is a reasonable way to improve the brittleness of sPS. Blends of sPS with HIPS have not been reported in literature. In this paper, sPS blends with different content of HIPS were prepared by melt extrusion. The effect of the maximal melting temperature, the content of HIPS, and cooling rates on the melting and crystallization behavior and crystal forms of dynamically crystallized sPS were investigated by differential scanning calorimetry (DSC) and wide angle X-ray diffractometry (WAXD).

EXPERIMENTAL

Materials and blends preparation

The sPS is Questra F2250 from Dow Chemical Co. (Taiwan) M_w and M_n were characterized by GPC and were 2.3×10^5 and 9×10^4 g/mol respectively. The highly-impact polystyrene (HIPS) is MS 500, the product of the Idemitsu Co. (Malaysia). 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 a SJS-H-Z-30 twin-screw extruder (Factory of rubber and plastic of Nanjing China). The rate of the main machine was 100 rpm. The composition of sPS/HIPS blends was 10/0, 9/1, 7/3, 5/5, and 3/7, respectively.

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 heat flow and temperatures of DSC were calibrated with standard materials, indium and zinc. The weights of the specimens ranged from 4 to 5 mg. For dynamical crystallization experiments, 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 cooled at

different rates to 50°C. The crystallized specimens were subsequently heated at rate of 10°C/min to investigate the corresponding melting behaviors.

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.

RESULTS AND DISCUSSIONS

Effect of content of HIPS on crystal forms and melting behavior of sPS

Figure 1 shows the WAXD spectra of sPS and sPS/HIPS blends. It can be seen that sPS and its blends exhibited diffraction peaks at $2\theta = 6.8, 10.4, 11.8, 13.7, 14.2, 15.7, 18.0^\circ$ and $2\theta = 6.2, 10.5, 12.4, 13.8, 18.8, 21.3^\circ$. Although the peaks moved slightly as compared with the data from literature,¹³ it is still recognized that the characteristic peaks of the former are attributed to the formation of α -crystal and the peaks of the latter are attributed to the formation of β -crystal, respectively. According to the literature,¹³ the relative fraction of α -crystal could be roughly calculated by the equation as follows:

$$P_\alpha(\%) = \{[1.8A(11.6)/A(12.2)]/[1 + 1.8A(11.6)/A(12.2)]\} \times 100\% \quad (1)$$

where $A(11.6)$ refers to the area of the α -crystal diffraction peak at 11.6°, and $A(12.2)$ refers to the area of the diffraction peak at 12.2° corresponding to β -crystal.

As a consequence, the fraction of α -crystal was 86.8%, 97.8%, 97.6%, and 72.4% respectively, for sPS and sPS/HIPS = 9/1, 7/3, and 5/5 blends crystallized dynamically from the melting temperature of 280°C. For the sPS/HIPS = 3/7 blend, high content of HIPS increases the noise level of the diffraction peaks, making it inadequate to obtain the fraction of α -crystal to use the equation. However, the melting behavior in later section indicated that more content of β -crystal was formed for sPS/HIPS = 3/7 blend as compared with the other blends during the crystallization process. Only β -crystals were obtained for sPS and its blends crystallized dynamically from the melting temperature of 320°C. Apparently, addition of HIPS and the content of HIPS affected the relative fraction of α -crystal of sPS crystallized from 280°C. Addition of low content of HIPS increased the relative fraction of α -crystal of sPS. When the content of

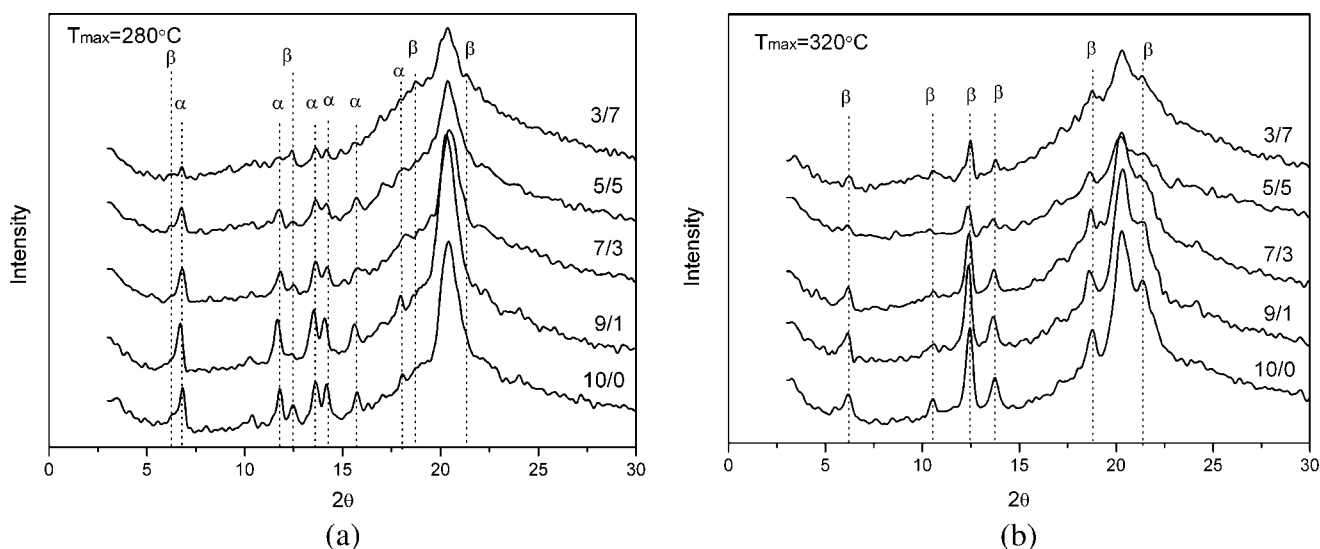


Figure 1 X-ray diffractogram for sPS and sPS/HIPS blends crystallized dynamically at cooling rate of 10°C/min after melting at (a) 280°C and (b) 320°C for 10 min.

HIPS was higher than 50 wt %, the relative fraction of α -crystal of sPS decreased with increasing the content of HIPS. However, addition of HIPS and the content of HIPS had no influence on the relative fraction of α -crystal of sPS crystallized dynamically from the melting temperature of 320°C. In sPS/aPS blends,^{15–19} the addition of aPS generally induced the formation of β -crystal of sPS. But the relative fraction of α -crystal of sPS first increased and later decreased with increasing the content of HIPS for sPS/HIPS blends crystallized dynamically from 280°C. The increase in the relative fraction of α -crystal of sPS might be concerned with the existence of rubber phase in HIPS and the interaction between the sPS and the rubber phase.

When the content of HIPS was higher than 50 wt %, the relative fraction of β -crystal of sPS increased with increasing the content of HIPS as the same as in sPS/aPS blends.

DSC melting curves are shown in Figure 2 for sPS and its blends crystallized from temperatures of 280°C and 320°C, respectively. For the sPS melted at temperature of 280°C, three melting peaks were observed. The low temperature peak was ascribed to the melting of β -crystal of sPS and the middle peak was corresponded to the melting of α -crystal of sPS.^{1,2} The high temperature peak was the contribution of melting of α - and β - crystals. For the sPS/HIPS = 9/1 and 7/3 blends, only one melting peak was observed which

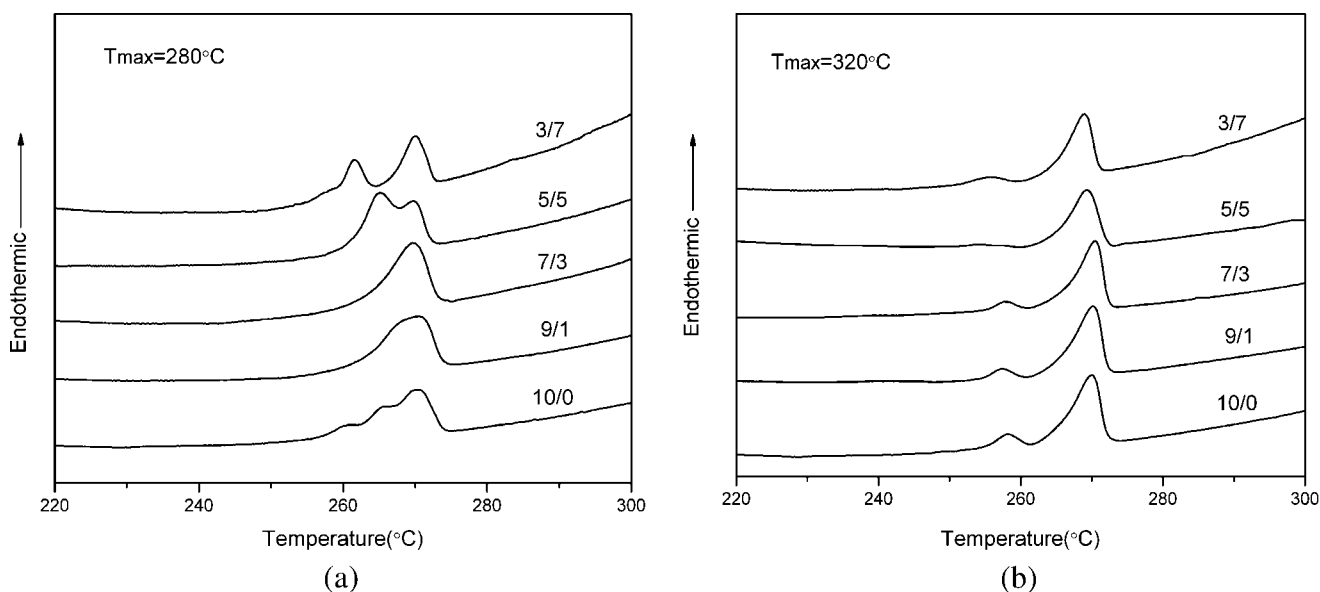


Figure 2 DSC melting curves for sPS and sPS/HIPS blends crystallized dynamically at cooling rate of 10°C/min after melting at of (a) 280°C and (b) 320°C for 10 min.

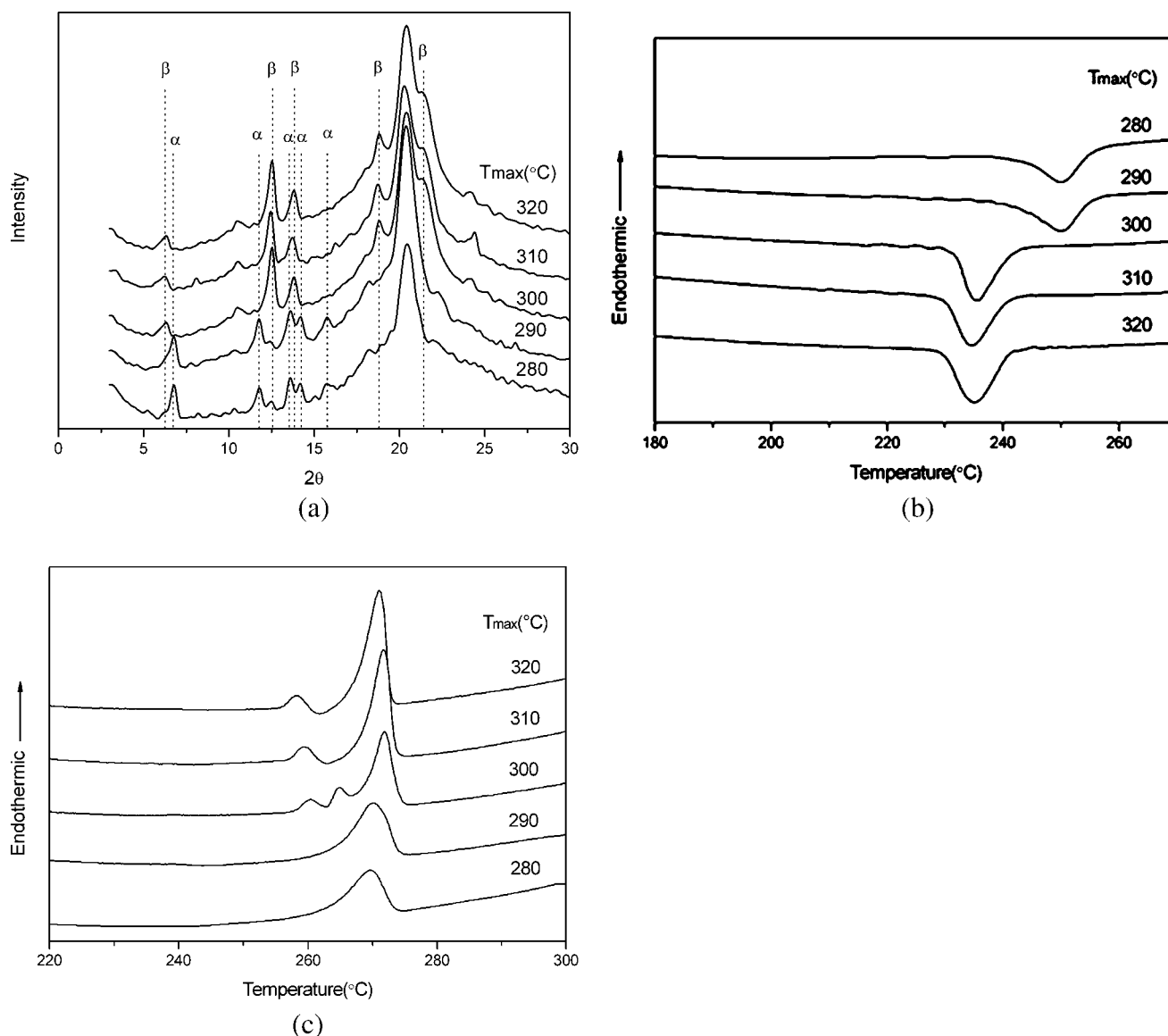


Figure 3 X-ray diffractogram (a), DSC crystallization curves (b), and DSC melting curves (c) for sPS/HIPS=7/3 blend crystallized dynamically at cooling rate of $10^\circ\text{C}/\text{min}$ after melting at different temperatures for 10 min.

might be attributed to the formation of higher content of α -crystal. For the sPS/HIPS = 5/5 blend, two melting peaks were observed and the low temperature peak exhibited higher intensity. For the sPS/HIPS = 3/7 blend, two major melting peaks and a small shoulder peak at low temperature were observed. On the basis of the temperature of the melting peaks, the low temperature peak was recognized as the melting of β -crystal and the middle peak as the melting of α -crystal. The high temperature peak should ascribe to the melting of both α - and β - crystals. In general, sPS/HIPS = 3/7 blend seemed to produce more content of β -crystal as compared with other blends. For the sPS and its blends melted at temperatures of 320°C , two melting peaks were observed which should be corresponded to the melting of β -crystal. The addition of

low content of HIPS had no influences on the temperatures of lower and higher melting peak of sPS. However, the addition of high content of HIPS resulted in the depression of the temperatures of lower and higher melting peak of sPS. It is suggested that the less perfect β -crystal was formed because of the dilute effect of HIPS.

On the basis of the results of DSC and WAXD, it is suggested that the addition of a small amount of HIPS resulted in the formation of more α -crystal and the addition of high content of HIPS facilitated the formation of more β -crystal of sPS melted at low temperature. For the sPS melted at high temperature, the addition of HIPS and the increase in the content of HIPS had no significant effect on the crystal forms and melting behaviors of sPS.

Effect of melting temperatures on crystal forms and melting behaviors of sPS/HIPS blends

Figure 3(a) shows the WAXD spectra of sPS/HIPS = 7/3 blend crystallized from different melting temperatures. It can be seen that the relative fraction of α -crystal of the blend crystallized dynamically decreased with increasing the melting temperature. The majority of β -crystal was obtained for the blend melted at temperature above 300°C. When crystallized dynamically after melting at 280°C and 290°C, sPS/HIPS = 7/3 blend seemed to produce more content of α -crystal. Generally, it is suggested that the melting temperature is a major factor controlling the crystalline structure of sPS. De Rosa⁵ reported the existence of the memory effect of α -crystal and the memory effect of α -crystal induced the formation of α -crystal during the cooling process. For sPS and its blends crystallized dynamically after melting at temperature below 290°C, there should be α -crystal nuclei existed because of low melting temperature. The memory effect of α -crystal induced the formation of α -crystal during the cooling process. However, for sPS and its blends crystallized dynamically after melting at temperature above 300°C, α -crystal nuclei were completely melted and disappeared because of high melting temperature. As a result, only β -crystal was formed.

DSC crystallization thermographs of sPS/HIPS = 7/3 blend are shown in Figure 3(b) and the crystallization data is listed in Table I. It can be observed from Figure 3(b) that only one crystallization peak is obtained for sPS/HIPS = 7/3 blend crystallized dynamically at the cooling rate of 10°C/min after melting at different temperatures. However, the crystallization peak temperatures (T_c^p) and crystallization enthalpy (ΔH_c) of sPS and its blends depended upon the melting temperatures. For sPS/HIPS = 7/3 blend crystallized dynamically after melting at temperature

below 290°C, it exhibited a higher crystallization temperature and a lower crystallization enthalpy. The crystallization temperatures and the crystallization enthalpy were dependant of melting temperatures. As the melting temperature increased from 290°C to 300°C, the crystallization temperatures of sPS/HIPS = 7/3 blend significantly decreased and the crystallization enthalpy greatly increased. The decrease of the crystallization temperatures was about 3.0°C, 14.7°C, and 4.8°C and the increase of the crystallization enthalpy was about 3.4 J/g, 6.8 J/g, and 3.4 J/g for sPS, sPS/HIPS = 7/3 and 3/7 blends crystallized dynamically after melting at temperature from 290°C to 300°C, respectively. As the melting temperature was above 300°C, the crystallization temperatures and crystallization enthalpy of sPS and its blends showed no serious change with increasing the melting temperatures. Further investigation of the crystallization enthalpy and melting enthalpy indicated that the crystallization enthalpy was lower than the melting enthalpy of sPS and its blends crystallized dynamically after melting at temperature below 290°C. However, the crystallization enthalpy was almost equal to the melting enthalpy of sPS and its blends crystallized dynamically after melting at temperature above 300°C.

It is believed that the presence of unmelted α -crystal increased crystallization temperatures of sPS crystallized dynamically after melting at low temperature due to the self-nucleation of un-melted α -crystal. Because the remained crystal was not melted, it had no contribution to the crystallization enthalpy during the crystallization process. Therefore, sPS and its blends exhibited a higher crystallization temperature and a lower crystallization enthalpy. As the melting temperature increased from 290°C to 300°C, α -crystal was completely melted. The decrease in temperature of sPS crystallization was attributed to the absence of self-nucleation of α -crystal due to complete melting of α -crystal.⁵ The completely melted sPS led to higher crystallization enthalpy as crystallized from high melting temperatures.

It is generally accepted that the melting temperature is an important factor in determining the crystal forms of sPS. In this paper, we consider that the crystal forms of sPS actually depend on the temperature of sPS crystallization. The results of the above research indicated that the temperature of sPS crystallization decreased with the increase of melting temperature, favoring the formation of β -crystal. For sPS/HIPS blends, the temperature of sPS crystallization in its blends was not only affected by the melting temperature but also concerned with the effect of HIPS. Above results indicated that more α -crystal was observed when the addition of HIPS increased the temperature of sPS crystallization. For example, sPS/HIPS = 7/3 blend had higher temperatures of sPS crystallization and a higher content of α -crystal was produced when melted at temperatures

TABLE I
The DSC Crystallization and Melting Data for sPS and sPS/HIPS Blends Crystallized Dynamically at the Cooling Rate of 10°C/min after Melting at Different Temperatures

sPS/HIPS	T_{\max} (°C)	T_c^p (°C)	ΔH_c (J/g)	ΔH_m (J/g)
10/0	280	241.4	20.70	23.90
	290	239.9	21.60	23.25
	300	236.9	24.95	23.29
	310	236.2	24.19	23.94
	320	235.8	24.86	23.28
7/3	280	249.9	20.23	26.54
	290	250.1	21.24	26.01
	300	235.4	28.09	27.07
	310	234.8	27.43	27.09
3/7	280	229.6	28.07	30.43
	290	228.4	28.40	30.50
	300	224.8	31.50	30.07
	310	225.0	30.00	30.53
	320	224.2	31.57	30.83

below 290°C. In contrast, more content of β -crystal were obtained when the addition of HIPS decreased the temperature of sPS crystallization. For example, sPS/HIPS = 3/7 blend had lower temperature of sPS crystallization and more β -crystals were produced when melted at temperatures between 280°C and 290°C. Therefore, it is suggested that the crystal forms of sPS depend on the temperatures of sPS crystallization. The increase in the temperature of sPS crystallization favored the formation of α -crystal and the decrease in the temperature of sPS crystallization would produce more β -crystal.

It can be seen from Table I that the effect of melting temperatures on the temperature of sPS crystallization in its blends was larger than that of sPS. At the melting temperatures of 280°C and 290°C, the temperature of sPS crystallization in sPS/HIPS = 7/3 blend was higher than that of sPS. However, the temperature of sPS crystallization in sPS/HIPS blends was lower than that of sPS melted at temperatures above 300°C. For the sPS/HIPS = 3/7 blend melted at different temperatures, the temperature of sPS crystallization in sPS/HIPS blends was lower than that of sPS. Above result indicated that addition of low content of HIPS increased the temperature of sPS crystallization, which might be contributed to the existence and interaction of the rubber phase in the blends.

The corresponding DSC melting curves are shown in Figure 3(c). It can be seen that only one melting peak at temperature of about 270°C appears for sPS/HIPS = 7/3 blend crystallized dynamically after melting at temperature of 280°C and 290°C, which is different from sPS crystallized from 280°C. For sPS, three melting peaks corresponded to different crystal forms were observed as melted at 280°C. The addition of HIPS greatly influenced the melting behavior of sPS, which might be originated from the change of the fraction of different crystal forms and the formation of less perfect crystals. As crystallized dynamically after melting at temperature of 300°C, three melting peaks were observed for the sPS/HIPS = 7/3 blend. The middle one should be attributed to the melting of α -crystal,¹ which also confirms that the addition of a small amount of HIPS induced the formation of more α -crystal. As the melting temperature increased to 320°C, the sPS/HIPS = 7/3 blend showed two melting peaks and the low melting peak shifted to lower temperature because of the formation of less perfect β -crystal.

Effect of cooling rates on the crystal forms and melting behaviors of sPS and its blends

DSC melting curves for sPS and sPS/HIPS blends crystallized dynamically at different rates after melting at 320°C are shown in Figure 4. The results of

WAXD spectra of sPS and its blends showed specific diffraction peaks at $2\theta = 6.2, 12.4, 13.8, 18.8, 21.3^\circ$, suggesting that all the samples produced only β -crystal no matter how the cooling rates changed. The melting behaviors depended upon the cooling rates and the content of HIPS. For the sPS, two melting peaks were observed at all cooling rates; a small recrystallization peak was appeared between the two melting peaks. Although the cooling rates had no influence on the temperature of higher melting peak, the temperature of lower melting peak shifted to lower temperatures and the intensity of the peak decreased with increasing cooling rates. For the sPS/HIPS = 7/3 blend, a similar melting behavior was observed as that of sPS. However, the temperature of higher melting peak at cooling rate of 40°C/min was lower than that of sPS. For sPS/HIPS = 3/7 blend, the temperature of higher melting peak shifted to lower temperatures and the lower melting peak disappeared at fast cooling rate because of the effect of high content of HIPS. Moreover, the melting peaks of the sPS/HIPS = 7/3 and 3/7 blends became more wider than those of sPS, indicating that the high content of less perfect of crystal was formed because of the addition of high content of HIPS.

The above results indicate that the lower melting peak shifted to lower temperature and finally disappeared with increasing cooling rates. It is believed that the formation of less perfect crystal resulted in the depression of melting temperature of β -crystal for sPS and its blends crystallized dynamically after melting at temperature of 320°C with increasing cooling rates. During the heating process, the β -crystals with lower melting temperature were first melted and then recrystallized to form more perfect β -crystal with high melting temperature.^{1,36} It is suggested that the polystyrene in HIPS is miscible with sPS, the dilution effect of polystyrene and the interactions between HIPS and sPS restricted the growth of β -crystal, leading to form less perfect lamellae crystal. The effect of HIPS on the formation of β -crystal increased with increasing cooling rates. Therefore, the melting behavior of sPS/HIPS blends is greatly affected by the cooling rates.

Figure 5 shows the melting curves of sPS and sPS/HIPS blends crystallized dynamically from 280°C at different cooling rates. Since sPS and its blends produced the majority of α -crystal at lower melting temperature because of the higher temperature of sPS crystallization, the cooling rates seemed to have no serious effect on the WAXD spectra of sPS and its blends except for sPS/HIPS = 3/7 blend. However, the melting behavior of sPS and its blends was strongly affected by the cooling rates. For sPS, three melting peaks were observed as the cooling rate was at 5°C/min and 10°C/min, which corresponded to the results of melting of α - and β -crystals. Two melting

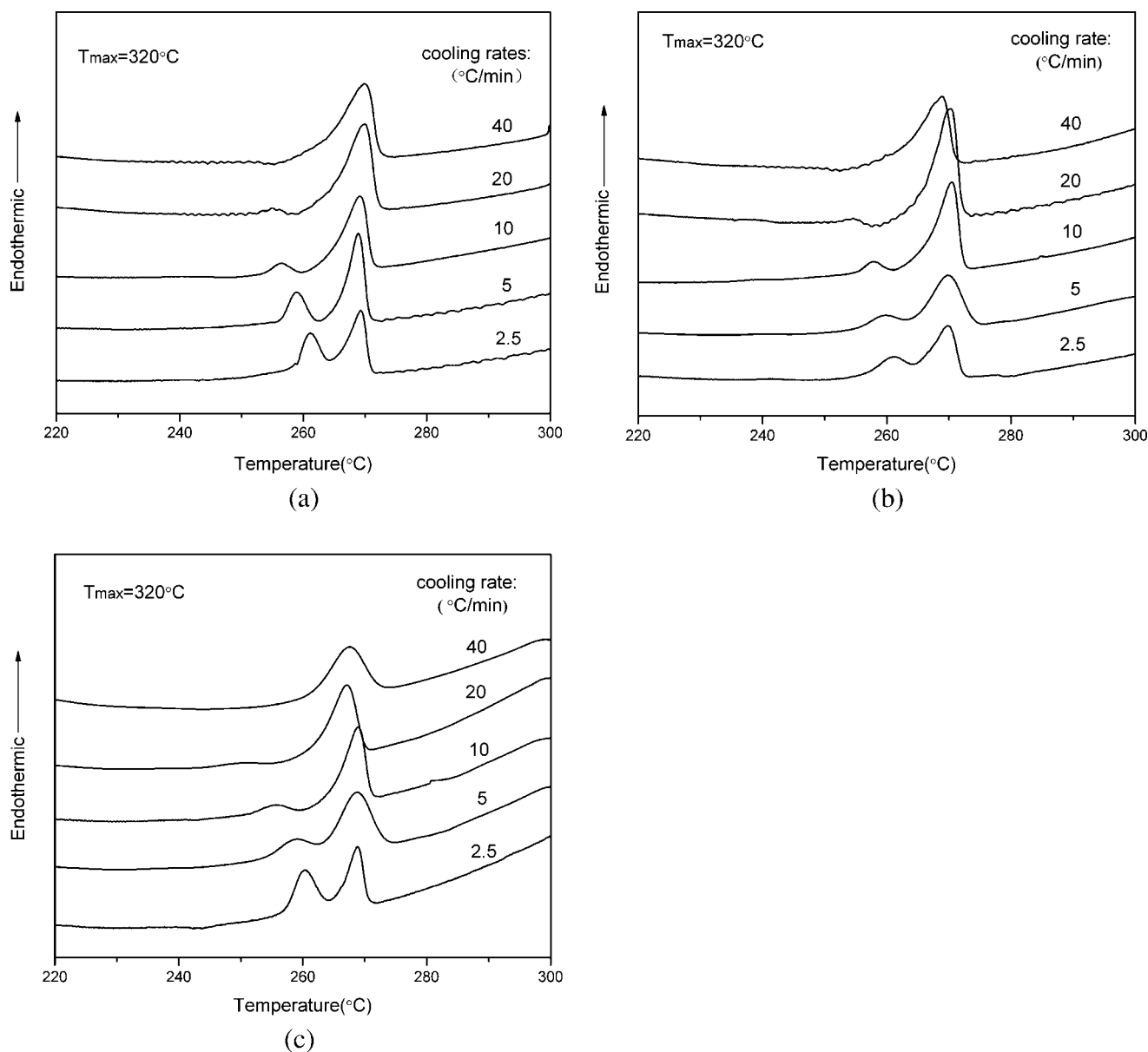


Figure 4 DSC melting curves for sPS/HIPS blends crystallized dynamically at different rates after melting at 320°C for 10 min. (a) 10/0, (b) 7/3, and (c) 3/7.

peaks were observed as the cooling rate was at 20°C/min and 40°C/min. The higher melting peak shifted to higher temperature and the lower melting peak shifted to lower temperature with increasing cooling rate. sPS/HIPS = 7/3 blend seemed to have one major melting peak at various cooling rates and the melting peak shifted to a higher temperature as crystallized at the cooling rate of 40°C/min. For sPS/HIPS = 3/7 blend, three melting peaks were obtained as crystallized at 5°C/min and the lower melting peak disappeared with increasing cooling rate. Two melting peaks were observed with increasing cooling rate. The lower melting peak shifted to lower temperature with its relative intensity decreasing, and the higher melting peak showed no serious change in temperature

position with increasing cooling rate except for the increase of the relative intensity.

Sun and Woo¹ reported that the increase of the cooling rate finally facilitated the formation of α -crystal in both sPS and sPS/aPS blends. However, the result of our experiment showed that cooling rate had no serious effect in the formation of α - and β -crystals as the cooling rate increased from 2.5°C/min to 40°C/min. Ho et al.¹¹ found that the effect of cooling rate was not so profound for the polymorphic behavior. Above results indicated that although the same crystal form of sPS is formed, the melting temperatures, the content of HIPS, and the cooling rate play an important role in determining the shape of the melting curves.

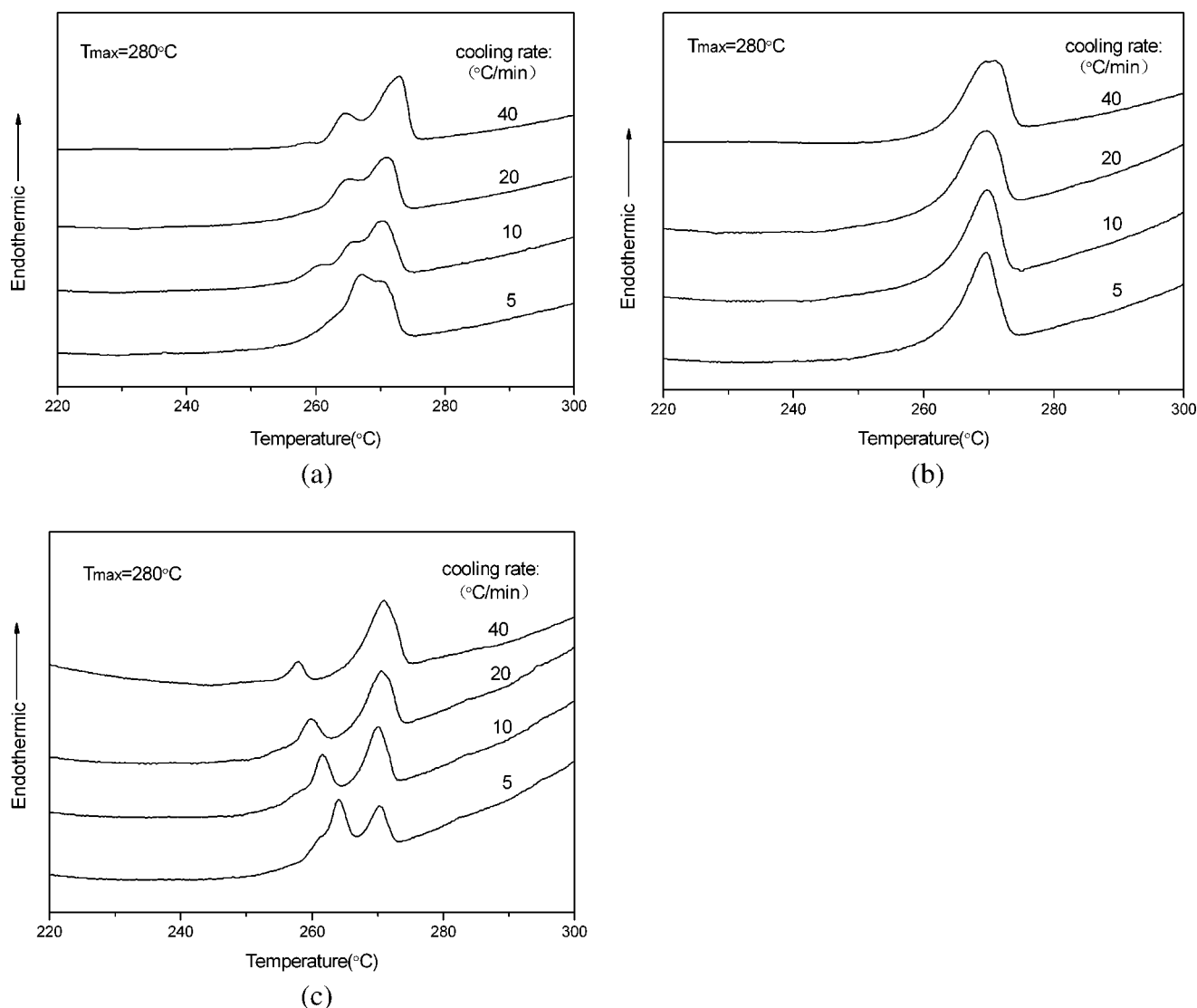


Figure 5 DSC melting curves for sPS/HIPS blends crystallized dynamically at different rates after melting at 280°C for 10 min. (a) 10/0, (b) 7/3, and (c) 3/7.

CONCLUSIONS

Syndiotactic polystyrene/highly-impact polystyrene (sPS/HIPS) blends were first prepared. The investigation of melting behaviors and crystal forms of sPS and its blends crystallized dynamically after melting at different temperatures and cooling rates indicated that melting behaviors and crystal forms of sPS and its blends depended on the HIPS content and the melting temperatures. The addition of a small content of HIPS induced higher fraction of α -crystal and high content of HIPS led to the formation of more β -crystal as crystallized from 280°C. However, the content of HIPS had no significant effect on the crystal form and melting behavior of sPS as crystallized from 320°C. The temperatures of sPS crystallization in sPS and sPS/HIPS blends decreased with increasing melting temperature, favoring the formation of β -crystals of sPS. The temperatures of sPS crystallization were also

affected by the content of HIPS, which increased with a small content of HIPS and then decreased as the content of HIPS increased as the melting temperature was below 290°C. Low melting temperature facilitated the formation of α -crystals due to the nucleation of memory effect of α -crystal. Therefore, the temperature of sPS crystallization is another main factor affecting the development of α - and β -crystals. Although the same crystal form of sPS was obtained, the sPS and its blends exhibit different melting behavior when crystallized at various cooling rates.

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