

# Multiple Melting Behavior of Polyphenylene Sulfide Blends with Polyamide 6

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**ABSTRACT:** Although there are many studies on the multiple melting behavior of polyphenylene sulfide (PPS) homopolymer, similar investigations on PPS component in PPS blends with thermoplastics are relatively rare. In the present paper, the multiple melting behavior of PPS blends with polyamide 6 (PA6) have been investigated by differential scanning calorimetry (DSC). The double melting peaks are also observed for PPS in the blends. Although the annealing temperature and time as well as the heating rate of DSC scanning are different, the lower melting peak temperature of PPS in the blend is higher than that of pure PPS and the higher melting peak temperature is lower than that of pure PPS. It is suggested that PA6 can accelerate the cold-crystallization of amorphous PPS due to the possible presence of interfacial interaction between the component polymers to induce the heterogeneous nucleation, and increase the perfection of PPS crystals. The multiple melting behavior of PPS in the blends are explained by recrystallization. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1579–1585, 2000

**Key words:** polyphenylene sulfide; polyamide; melting behavior; differential scanning calorimetry; polymer blends

## INTRODUCTION

Multiple melting peaks are generally observed on differential scanning calorimetry (DSC) of polyphenylene sulfide (PPS) that have been crystallized either from the melt or from the rubbery amorphous state. The multiple melting behavior is usually interpreted in terms of a pre-existing morphology and/or of reorganization, which has been discussed extensively before for PPS and for other polymers. Both causes for the multiple

melting often cooperate with each other to make the melting characteristics very complex and sometimes it is very difficult to differentiate these two affects. Sometimes more than one reason has been suggested as being responsible for the multiple melting behavior. Chung and Cebe<sup>1–4</sup> had reported a systematic investigation of multiple melting behavior of a single-stage melt- and cold-crystallization, and multiple-stage melt-crystallization of PPS. They found that the multiple melting behavior and the dependence of melting temperature on the crystallization temperature cannot be explained solely on the basis of either a reorganization- or a morphology-based model. They presented a model, in which the distribution of crystal perfection created during crystallization controls the multiple melting behavior, to explain the observation of multiple melting behavior and crystallization temperature dependency of the melting peaks. They suggested that

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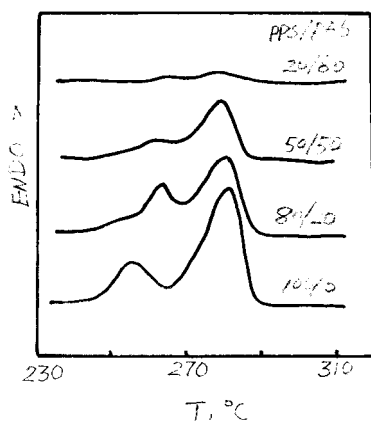
the degree of undercooling determines whether the existence of performed crystals or reorganization of imperfect crystals dominates the observed endothermic response. At high undercooling, a broad distribution of crystals can form, a part of which may melt and reorganize during the normal DSC scan. The melting point of the uppermost endotherm becomes independent of the crystallization temperature. The ability of the material to reorganize during the scan depends upon the initial state of perfection of the crystals. At low undercooling conditions, a bimodal distribution of crystals can form, which eventually may become two morphologies. The pre-existing crystals are much more perfect and less susceptible to reorganization. Multiple stage crystallization indicated that it is possible to generate many distinct crystal populations by step-wise crystallization from the melt, which display their own melting points.

Although there are many studies in the literature on the multiple melting behavior of PPS homopolymer, similar investigations on PPS component in its blends with thermoplastics are relatively rare. In polymer blends, upon crystallization of the first polymer, the second polymer should be rejected from the crystal growth front. Depending upon the extent of rejection, there are three possible morphologies<sup>5,6</sup>: (i) interlamellar segregation, in which the second polymer is located in the crystalline interlamellar regions of the first polymer; (ii) interfibrillar segregation, in which the second polymer can be expelled by a greater distance to regions between branches of spherulites of the first polymer; and (iii) interspherulitic segregation, in which the second polymer is expelled by the greatest distance so that it is not within the crystalline spherulites of the first polymer. If a complete rejection of the second polymer from the first polymer crystalline interlamellar zones occurs, the reorganization of the first polymer crystals before melting should be identical to that of pure polymer. On the other hand, if the second polymer is located in the interlamellar regions, the crystal reorganization of the first polymer should be changed. Chen and Porter<sup>5</sup> establish a method, based on the investigation of polyether ether ketone (PEEK) crystal reorganization in PEEK/polyether imide (PEI) blends, to examine the existence of PEI in the interlamellar zones of PEEK crystals. They found that reorganization of PEEK crystals during heating is hindered by PEI, suggesting the PEI is located in the interlamellar zones of PEEK lamel-

lae. Chem et al.<sup>7</sup> had also studied the multiple melting behavior of polyethylene terephthalate (PET) in PEI/PET blend and found that the extent of reorganization during DSC heating decreased with increasing PEI composition. The reduction in extent of reorganization of PET upon blending with PEI was attributed to the remixing between PEI and PET after the initial melting. The PET crystals exhibited a slower annealing in the blends than in the pure state. It was also found that the multiple melting behavior was seen to disappear and the melting endotherm shifted to a lower temperature due to prevention of reorganization by cross-linking in the amorphous phase.

In order to investigate the multiple melting behavior of PPS, we have embarked on a comprehensive study of effects of blending on the multiple melting behavior of PPS polymer.<sup>8-10</sup> In the PPS blends with amorphous PSF (bisphenol A polysulfone) and PEK-C (polyether ketone with phthalidylidene), we found that, with a rise in melt temperature and melt time, the intensities of the lower melting peaks of pure PPS increase whereas those of the upper ones decrease or disappear in some cases. This can be attributed to the obstructive effect of branching or cross-linking of PPS macromolecules on the crystallization of PPS at higher temperature. As the annealing crystallization temperature increases, both the peak temperatures and intensities of the lower melting peak of PPS increase. PSF and PEK-C have no influence on the lower melting peaks but are unfavorable to the crystallization of the higher melting species. The multiple melting behavior of PPS component in the blends is much more susceptible to the changes in melt temperature and melt time than that of pure PPS. In a PPS blend with PEEK, the intensity of the upper melting peak of PPS decreases significantly by addition of PEEK. The multiple melting peaks of PPS can be observed when PPS and their blends are crystallized dynamically from the melt state.

In the present study, we report, for the first time, an investigation of the multiple melting behavior of PPS in its blends with polyamide 6 (PA6) cold-crystallized from the rubbery amorphous state. DSC is used to study the melting behavior after annealing. The effect of blend composition, annealing temperature and time, and heating rate on the multiple melting behavior of PPS in its blends will be discussed.



**Figure 1** Melting endotherms of pure PPS and PPS in PPS/PA6 blends annealed at 240°C for 3 hours.

## EXPERIMENTAL

### Preparation of Blends

Powdered PPS with a number average molecular weight of 2200 g/mol used in this study was produced by the Changshou Chemical Factory, China. PA6 was obtained from UBE Industries Ltd. Japan (UBE 1013B). Powder of PPS and PA6 pellets were dried at 100°C for 3 hours prior to use, and mechanically mixed at different compositions at room temperature. The mixture was added to a preheated roll mill (Model xss-300 Shanghai P. R. China) at 300°C and then mixing was continued for 8 min with a rotor speed of 32 rpm. After mixing thoroughly, the mixture was removed from the mixing head and cooled to room temperature.

### Isothermal Crystallization and Thermal Analysis

Isothermal crystallization of PPS and PPS/PA6 blends were carried out using a mode CDR-1 DSC made by the Shanghai Balance Instrument Factory (China). PPS and PPS/PA6 blends were melted at 320°C for 10 min to eliminate crystalline residues formed during sample preparation. After this melting, the samples were quenched in ice water. Then quenched samples were annealed in DSC at various temperature for a certain period of time, and the annealed samples were removed from DSC and cooled to room temperature in air.

The melting behavior of the cold-crystallized PPS and PPS/PA6 blends was examined using a Perkim-Elmer DSC-7 between 50 and 320°C at a heating rate of 20°C/min in a nitrogen atmo-

sphere. The melting peak temperature and the heat of fusion were calibrated by using an indium standard. The heat of fusion has been normalized on per gram of PPS vs. per gram of sample.

## RESULTS AND DISCUSSION

### Effect of PA6 Content on Multiple Melting Behavior of PPS

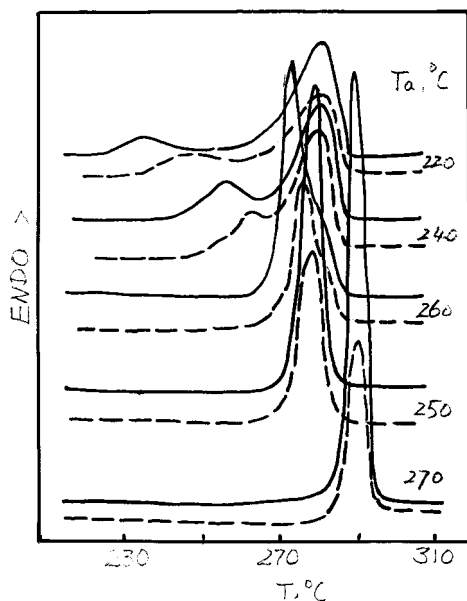
Figure 1 shows DSC melting curves of PPS and PPS/PA6 blends annealed at 240°C for 3 hours. The melting temperatures and the heat of fusion of PPS are shown in Table I. The double melting peaks were observed for PPS and PPS/PA6 blends. It can be seen that the lower melting peak temperatures ( $T_{m1}$ ) of PPS in the blends are ca. 7°C higher than that of pure PPS. The higher melting peak temperatures ( $T_{m2}$ ) of PPS in the blends, on the other hand, are ca. 1°C lower than that of pure PPS. These results are different from the multiple melting behavior of PPS in the presence of amorphous polymer, PSF, and PEK-C with high  $T_g$ , and in the presence of crystalline polymer, PEEK with  $T_m$  higher than that of PPS.<sup>8-10</sup> There, no change in the  $T_{m1}$  of PPS and the decrease in the intensity of  $T_{m2}$  peak was observed. The increase in the  $T_{m1}$  of PPS may be attributed to acceleration of the crystallization of PPS by addition of PA6 and increase of the crystal perfection of PPS as the PPS crystallized in the presence of PA6 melt. In our previous studies<sup>11</sup> of the nonisothermal crystallization and melting behavior of PPS/PA6, we found that the crystallization parameters for PPS became modified to a greater extent than those for PA6 in the blends. PPS and PA6 crystallized at a high temperature as a result of blending. The PPS crystallization peak became narrower and the crystallization temperature shifted to higher temperature, suggesting a faster rate of crystallization as a result of blending with PA6. This enhancement in the

**Table I** DSC Melting Data of PPS in PPS/PA6 Blends Annealed at 240°C for 3 Hours

PPS/PA6	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$\Delta H_m$ (J/g)
100/0	256.2	280.7	48.7
80/20	263.0	279.5	47.3
50/50	261.4	279.0	40.3
20/80	264.9	280.4	17.2

nucleation of PPS could be attributed to the possible presence of the interfacial interactions between the component polymers to induce the heterogeneous nucleation. Similar results were observed in PEEK/PEI blends. Chen and Porter<sup>5</sup> compared the melting behavior of pure PEEK with that of PEEK in PEEK/PEI blends crystallized at  $T_c < 305^\circ\text{C}$ . They found that  $T_{m1}$  of PEEK in the blends was higher than that of pure PEEK at the same  $T_c$ , whereas  $T_{m2}$  of PEEK in the blend was lower than that of pure PEEK. They suggested that reorganization of PEEK crystals in the blends was hindered and that PEI was located in the interlamellar zones of PEEK lamellae, and established a method, based on the investigation of PEEK crystal reorganization in PEEK/PEI blends, to examine the existence of PEI in the interlamellar zones of PEEK crystals.

In PPS/PA6 blends, if a complete rejection of PA6 from the PPS crystalline interlamellar zones occurs, the reorganization of PPS crystals before melting should be identical to that of pure PPS, since the crystals are exposed to a pure PPS amorphous matrix. On the other hand, if PA6 is located in the interlamellar regions, the entanglements of the chain segments of PA6 with the segments of PPS in the interphase can restrict the cooperative motion of the crystalline chains in the subsequent lamellar thickening during reorgani-



**Figure 2** Melting endotherms of pure PPS (—) and PPS in PPS/PA6 = 80/20 blends (---) annealed at different temperatures for 3 hours.

**Table II** Melting Temperatures and Heat of Fusion of Pure PPS and PPS in the Blends Annealed for 3 Hours at Different Temperatures

	$T_a$ ( $^\circ\text{C}$ )	$T_{m1}$ ( $^\circ\text{C}$ )	$\Delta H_{m1}$ (J/g)	$T_{m2}$ ( $^\circ\text{C}$ )	$\Delta H_{m2}$ (J/g)
PPS	180	199.7	1.41	282.8	41.3
	200	217.0	2.36	279.7	40.3
	220	236.5	3.38	280.3	37.2
	240	256.2		280.7	(48.7)
	250	273.2		Shoulder	(51.6)
	260	277.6			(51.4)
	270			289.1	(48.2)
PPS/PA6 = 80/20	180	208.1	15.9	277.3	33.5
	200	210.5	11.7	280.2	35.0
	220	249.3	5.6	279.1	45.8
	240	263.0		279.5	(47.3)
	250	277.8		Shoulder	(33.7)
	260	278.0			(44.6)
	270			287.9	(39.8)

Data for heat of fusion:  $\Delta H_{m1} + \Delta H_{m2}$

zation. The perfection of PPS crystal reorganization should be decreased and the  $T_{m2}$  of PPS in the blends is lower than that of pure PPS. It can be seen from Table I that the heat of fusion of PPS decreased with increasing of PA6 content, indicating the existence of interfacial interaction between PPS and PA6.

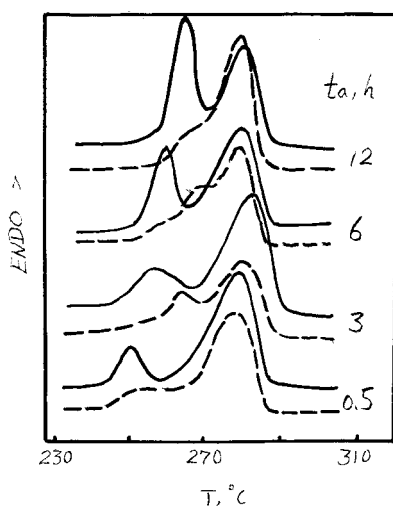
In crystalline PEEK and amorphous PEI blends, PEEK and PEI are miscible over the whole composition range.<sup>12</sup> The lamellar thickening of PEEK in the PEEK/PEI blends during reorganization is more difficult than that of PPS in the PPS/PA6 blends. Therefore the decrease in the  $T_{m2}$  of PEEK in PEEK/PEI blends is more significant than that of PPS in PPS/PA6 blends.

#### Effect of Annealing Temperature on Multiple Melting Behavior of PPS in the Blends

Figure 2 shows DSC melting curves of PPS and PPS/PA6 blends annealed for 3 hours at various temperatures. The melting temperatures and the heat of fusion of PPS are shown in Table II. For the PPS annealed at the temperature below  $250^\circ\text{C}$ , two melting peaks are observed. The temperature and area of  $T_{m1}$  peak increase, and the heat of fusion of  $T_{m2}$  peak decrease with increasing the annealing temperatures. The  $T_{m2}$  remains constant and independent of the annealing

temperatures, which is attributed to the reorganization. The  $T_{m2}$  then increases as  $T_a$  increases. When  $T_a = 250^\circ\text{C}$ – $260^\circ\text{C}$ , the two melting peaks merge into one peak. Only one single melting peak can be observed, which shifts to higher temperature as  $T_a$  increases to higher temperature due to the increase in the perfection of crystals during the annealing process. For the PPS/PA6 blend annealed at  $180^\circ\text{C}$  and  $200^\circ\text{C}$ , because the  $T_{m1}$  of PPS is close to the  $T_m$  of PA6, the  $T_{m1}$  of PPS overlaps with the  $T_m$  of PA6 to form a single melting peak and can no longer be separately distinguished. When annealed between  $220^\circ\text{C}$  and  $250^\circ\text{C}$ , we observe two melting peaks.  $T_{m1}$  of PPS in the blends is always higher than that of pure PPS, suggesting the increase in the perfection of crystals during annealing process due to the interfacial nucleation induced by interfacial interaction between PPS and PA6. When  $T_a$  is between  $250^\circ\text{C}$  and  $260^\circ\text{C}$ , two melting peaks merge together forming one single melting peak, similar to the behavior of pure PPS. For the  $T_a$  higher than  $260^\circ\text{C}$ , we only observe a single melting peak, which shifts to higher temperature as  $T_a$  increases above  $260^\circ\text{C}$ .

It can be seen from Table II that the  $T_{m2}$  of PPS in the blends is  $5^\circ\text{C}$  lower than that of pure PPS annealed at  $180^\circ\text{C}$ . It is suggested that at low annealing temperatures, more imperfect crystals can be formed and are susceptible to reorganization. Therefore,  $T_{m2}$  shifts to a lower temperature because the reorganization of PPS crystals during heating is hindered by PA6. At high annealing



**Figure 3** Melting endotherms of pure PPS (—) and PPS in PPS/PA6 = 80/20 blends (---) annealed at  $240^\circ\text{C}$  for different times.

**Table III** Melting Temperatures and Heat of Fusion of Pure PPS and PPS in PPS/PA6 Blend Annealed at  $240^\circ\text{C}$  for Different Times

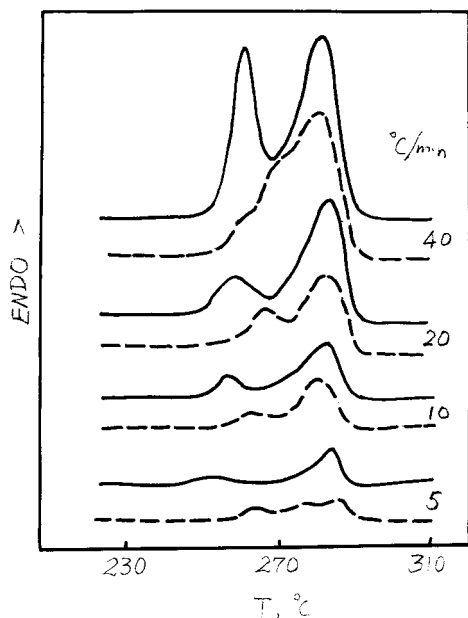
	$t_a$ (h)	$T_{m1}$ ( $^\circ\text{C}$ )	$T_{m2}$ ( $^\circ\text{C}$ )	$\Delta H_m$ (J/g)
PPS	0.5	250.9	280.2	46.9
	3.0	259.1	280.9	47.2
	6.0	256.2	278.9	45.9
	12.0	264.3	278.9	53.3
PPS/PA6 = 80/20	0.5	256.5	279.7	51.6
	3.0	263.0	279.5	47.3
	6.0	268.3	277.7	46.9
	12.0	Shoulder	278.6	52.0

temperatures, the crystallization proceeds at a slower rate resulting in more perfect crystals and the fractions which would undergo reorganization during heating decreases. The effect of blending on the  $T_{m2}$  of PPS in the blends is not significant in the presence of PA6.

#### Effect of Annealing Time on Multiple Melting Behavior of PPS in the Blends

Figure 3 shows DSC melting curves of PPS and PPS/PA6 blends annealed at  $240^\circ\text{C}$  for various times. The melting temperatures and the heat of fusion of PPS are shown in Table III. For the PPS,  $T_{m1}$  shifts to a higher temperature and the intensity of  $T_{m1}$  peak increases with increasing the annealing time, although the intensity of  $T_{m1}$  peak is lower than that of  $T_{m2}$  peak as annealed at  $240^\circ\text{C}$  for below 6 hours. The intensity of  $T_{m1}$  peak is higher than that of  $T_{m2}$  peak as annealed at  $240^\circ\text{C}$  for 12 hours. The decrease in the  $T_{m2}$  and the intensity of  $T_{m2}$  peak were observed with increasing the annealing times. This may be explained by the reduction in extent of reorganization of PPS due to the increase in the perfection of PPS crystals during annealing process and the shorter time of reorganization during heating due to the increase in the  $T_{m1}$  of PPS.

The multiple melting behavior of PPS in the blends is different from that of pure PPS annealed at  $240^\circ\text{C}$  for various times. Although the  $T_{m1}$  of PPS in the blends is always higher than that of pure PPS, the intensity of  $T_{m1}$  peak of PPS in the blends is always lower than that of  $T_{m1}$  peak of pure PPS and that of  $T_{m2}$  peak of PPS in the blends. This may be explained by the interfa-



**Figure 4** Influence of heating rate on the melting endotherms of pure PPS (—) and PPS in PPS/PA6 = 80/20 blends (---) annealed at 240°C for 3 hours.

cial nucleation between PPS and PA6 to accelerate the crystallization and increase the perfection of PPS crystals. Because the annealing temperature (240°C) is higher than the  $T_m$  of PA6, much more crystals with  $T_{m2}$  can be formed during annealing process and the intensity of  $T_{m1}$  peak decreases with increasing the annealing times as PPS annealed-crystallized in the presence of PA6.

#### Effect of Heating Rate on Multiple Melting Behavior of PPS in the Blends

Figure 4 shows the results of a heating rate study on PPS and PPS/PA6 blends annealed at 240°C for 3 hours. The melting temperatures and the heat of fusion of PPS are shown in Table IV. It can be seen from Figure 4 and Table IV that the melting behavior of PPS is different from that of PPS in the blends. The  $T_{m1}$  of PPS shifts to higher temperature and the  $T_{m2}$  shifts to lower temperatures as the heating rate increases. The intensities of  $T_{m1}$  and  $T_{m2}$  peak increase. The ratio of the intensity of  $T_{m1}$  peak to  $T_{m2}$  peak increases as the heating rate increases, consistent with a mechanism based on melting, recrystallization, and subsequent remelting. Triple melting peaks of PPS in the blends may be observed. The intensities of triple melting peaks also increase

with increasing the heating rates. The  $T_{m2}$  of PPS and PPS in the blends shifts to lower temperature with increasing the heating rates. This is generally explained by the reorganization of imperfect crystals formed at annealing process during the normal DSC scan. A third melting peak between  $T_{m1}$  and  $T_{m2}$  of PPS can easily be formed in the presence of PA6. The third middle peak,  $T_m^*$ , located in the front shoulder of the higher melting peak have been observed by Chung and Cebe<sup>1</sup> when PPS, Ryton V-1, was melt crystallized below 230°C. They suggested that this third melting peak may result from the melting of a more perfect type of crystal present in the material at room temperature, and  $T_{m1}$  represents the melting of a less perfect type of crystal, also present in the material at room temperature.  $T_{m2}$  would then come from the melting and recrystallization of these types of crystals during DSC scan.

The crystal structure and morphology of crystalline polymers are strongly affected by the crystallization kinetics. The balance of between the nucleation rate and chain mobility will be very important to determine the perfection of the crystal structure. Chung and Cebe<sup>1</sup> suggested that if the PPS was crystallized at a lower crystallization temperature, at which the nucleation rate and subsequent growth are very fast and chain mobility is very low, the resulting crystal perfection has a broad distribution and its crystal structure is relatively imperfect. The appearance of dual melting peaks is dominated by reorganization. However, when the PPS was crystallized at a higher crystallization temperature, at which the nucle-

**Table IV** Melting Temperatures and Heat of Fusion of Pure PPS and PPS in the Blends Annealed at 240°C for 3 Hours at Different Heating Rates

	Scan. Rate (°C/min)	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$\Delta H_m$ (J/g)
PPS	5	245.5	281.3	42.8
	10	255.5	280.9	43.3
	20	256.2	280.6	47.2
	40	260.1	279.7	48.2
PPS/PA6 = 80/20	5	260.1	284.3	51.5
	10	261.8	281.7	46.0
	20	263.0	279.5	47.3
	40	268.6	278.9	44.3

ation rate and subsequent crystal growth are slow, but chain mobility is high, two kinds of crystal populations can be formed. The cause of dual melting peaks is the existence of two kinds of crystal perfection. In the PPS/PA6 blends, the nucleation rate of PPS increases by the interfacial nucleation induced by interfacial interaction between PPS and PA6 and chain mobility of PPS is high in the presence of PA6 melt, when the annealing temperature is 240°C. A broad distribution of imperfect crystals and two kinds of crystal population can be formed. Therefore, three melting peaks of PPS can easily be formed in the PPS/PA6 blends.

Although the heating rates are different, the  $T_{m1}$  of PPS in the blends is always higher than that of pure PPS due to the increase in the perfection of crystals in the blends. However, the  $T_{m2}$  of PPS in the blends is higher than that of PPS heating rates below 10°C/min. PPS crystals may be reorganized to more perfection in the presence of PA6 melt because slower heating allows more time for the annealing process to proceed. However, at higher heating rates, the melting peak shifts to a lower temperature in the presence of PA6 melt due to prevention of reorganization of PPS crystals by blending. The higher heating rate suppresses the reorganization, since less time is available for the imperfect crystals to change.

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