Effect of PMR-POI on the Melt Behavior and Isothermal Crystallization of Poly(phenylene sulfide)

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ABSTRACT: The crystallization behavior of neat PPS and PPS in blends with PMR-POI prepared by melt mixing were investigated by differential scanning calorimetry (DSC). It was found that POI was an effective nucleation agent of the crystallization for PPS. The enthalpy of crystallization of PPS in the blends increased compared with that of neat PPS. During isothermal crystallization from melt, the dependence of relative degree of crystallinity on time was described by the Avrami equation. It has been shown that the addition of POI causes an increase in the overall crystallization rate of PPS; it also changed the mechanism of nucleation of the PHB crystals from homogeneous nucleation to heterogeneous nucleation. The equilibrium melting temperature of PPS and PPS/POI blends were determined. The analysis of kinetic data according to nucleation theories shows that the increase in crystallization rate of PPS in the composite is due to the decrease in surface energy of the extremity surface. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 436–442, 2002

Key words: crystallization; blends

INTRODUCTION

Poly(phenylene sulfide) (PPS) is an important high-strength/high-temperature engineering thermoplastic that is finding increasing use in technological applications such as molding resins, fibers, and matrices for thermoplastic composites. Its semicrystalline nature, on the other hand, makes it suitable for accurate studies of its structural and physical properties in either the crystalline or the amorphous state. The crystallization and morphology of PPS and its blends have been studied widely over the last 3 decades. The crystal structure was studied by Tabor,[1] Chung,[2] and Ballirano.[3] Recently, some reports have focused on the crystallization kinetics of PPS[4–7] and its blends.[8–12]

Lovinger et al.[5] found, for example, that the transition for regime II to III is centered at 208°C. They also calculated the fold surface free energy, σ_e, using the Hoffmann and Lauritzen kinetics theory. The effect of molecular weight, branching agent content, and end group counter-atom on the PPS crystallization kinetics was studied by López and Wilkes.[6,7]

When PPS is blended with another polymer such as poly(ether sulfone) (PES),[11] in an isothermal crystallization, the crystallization of PPS is acclerated by blending 10 wt % PES, and further addition results in the retardation.

Another study[9] of the nonisothermal crystallization and melting behavior of PPS blend with polyamide 6 found that PPS and PA6 crystallize at high temperature as a result of blending. The crystallization temperatures of PPS in the blends are always higher than that of pure PPS, and are independent of the melting temperature and the residence time at that temperature. Blending with PA6 also resulted in a faster crystallization rate of PPS compared with that of neat PPS.

In our work, an *in situ* crosslinkable polymerization of monomer reactant-type polyimide (PMR-POI) precursor[13] was initially incorporated into the PPS matrix as a functionalized agent; it also affected the crystallization kinetics of PPS. It has been a challenging subject to functionalize PPS to develop a new class of functional polymers with rigid backbone skeleton. One approach is to react a pre-formed PPS with highly reactive substrates in the solid phase. Another approach is to use functionalized monomer for the polymerization. Here, we attempt to develop a novel method for the functionalization of PPS. We have known that when PPS is heated above its melting point in the presence of air, chain extension, branching, and some degree of crosslinking occur.[18] Crosslinking included oxidative crosslinking and thermal crosslinking. In the case of thermal crosslinking, high temperature leads to the rupture of chemical bonds, macroradicals are generated, and various free radical reactions could be initiated. When PPS was melt blended with PMR-POI, which has double bonds at
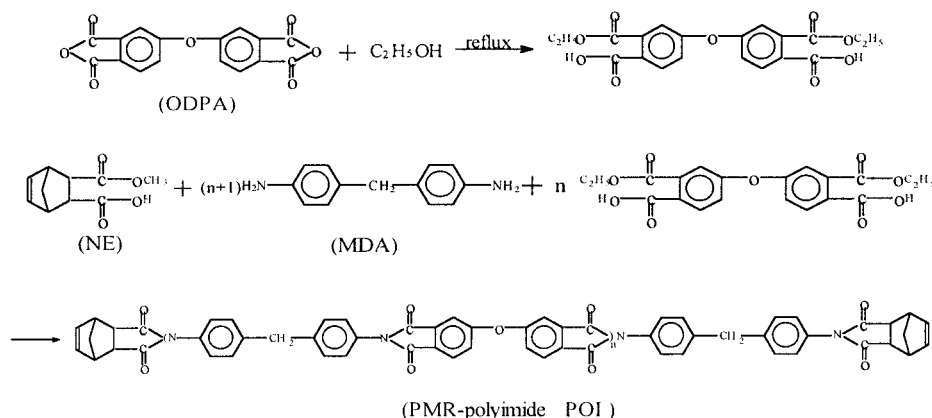
the each end of the molecule, grafting and/or crosslink copolymers of PPS-POI can form through thermally induced radical polymerization.

In this article, the effect of POI on the crystallization and melting behavior of PPS was studied in detail by DSC. The influence of POI on the crystallization of PPS was evaluated by the use of the Avrami equation for the isothermal crystallization process, the equilibrium melt point was estimated by the Hoffman-Weeks method, and the fold surface free energy, σ_e, was calculated by using the Hoffmann and Lauritzen kinetics theory.

EXPERIMENTAL

Materials

PPS used was a commercial grade p-3 manufactured by Sichuan Factory of High-Performance Engineering Plastics. PPS were dried at 90°C for 12 h in a vacuum oven to remove the absorbed water.

The thermally crosslinkable PMR polyimide (POI) precursor was prepared in our laboratory by using three monomeric ingredients of 4,4-oxydiphthalic anhydride (ODPA), 4,4-methylene dianiline (MDA), and the monomethyl ester of norbornene anhydride (NE). The chemical structure is:

(ODPA)

(NE)   (MDA)

(PMR-polyimide POI)

The precursor can form crosslink network or graft with PPS by thermally induced radical polymerization through the double bonds at the each end of the molecule. We can control the molecular weight by controlling the mol ratio of the three ingredients to ensure that the precursor exhibited the excellent mobility in melt blending. In this experiment the mol ratio of ODPA, MDA, and NE was 2 : 3 : 2, and the average molecular weight of the precursor was 1434 ($n = 2$).

ODPA and NE were purified before use; MDA and ethanol were used as received.

Samples preparation

The premixing of POI with polymer was carried out by sopping the PPS powder into the POI ethanol solution homogeneously. After most ethanol evaporated at room temperature, the POI coated powder was dried at 70°C for 12 h. in a vacuum oven. A Brabender internal mixer was employed to prepare the PPS/POI blends at 290°C, 50 rmp for 10 min. The weight ratios of PPS and POI were as follows: 100/0, 100/1, 100/3, and 100/5, which were coded as PPS, POI1, POI3, and POI5. Amorphous samples were made by heating PPS and PPS/POI blends to 300°C on a hot stage, then quenching to 0°C in ice water.

Characterization

The melting behavior and isothermal crystallization behaviors were characterized in a nitrogen atmosphere by a Perkin-Elmer DSC-7 apparatus. The heating and cooling runs were always carried out at a rate of 10°C/min. The first heating trace of amorphous samples were recorded from 50 to 300°C. After holding the specimens at 300°C for 5 min to destroy the crystalline nuclei completely, the cooling traces were recorded from 300 to 50°C, and then the second heating scan was recorded. Isothermal crystallization experiments were carried out with the same instrument. The samples were placed in DSC pans and heated to 300°C at a rate of 20°C/min, held for 5 min at that temperature, and then cooled to appropriate T_C, at a rate of 200°C/min. The heat was generated during the development, and further heat evolution was observed and analyzed according to the usual procedure to obtain the relative degree of crystallinity. The relative degree of crystallinity as function of time was found from eq. (1),

$$\chi_c(t)/\chi(\infty) = \frac{\int_0^t (dH/dt)dt}{\int_o^\infty (dH/dt)dt} \qquad (1)$$
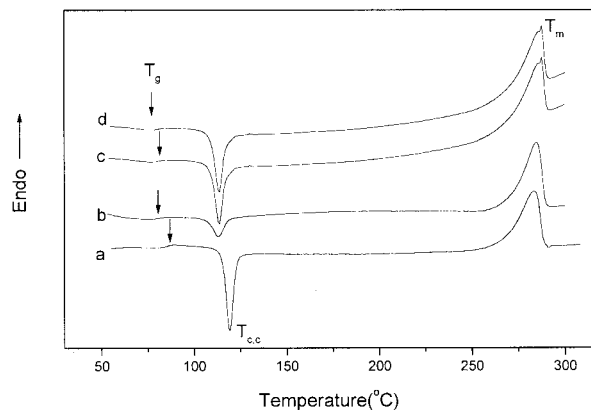
Figure 1 The DSC first heating traces of quenched samples: (a) PPS; (b) POI1; (c) POI3; (d) POI5.

Figure 3 The second heating scan of: (a) PPS; (b) POI1; (c) POI3; (d) POI5.

where t_0 is the time at which the sample attains isothermal conditions, as indicated by a flat baseline after the initial spike in the thermal curve, $\chi_c(t)$ is the degree of crystallinity at time t, $\chi_c(\infty)$ is the ultimate crystallinity at a very long time, and dH/dt is the heat flow rate. At the end of each isothermal experiment, the samples were reheated at heating rate of 10°C/min, for the measuring the melting temperature of the crystals.

RESULTS AND DISCUSSION

Nonisothermal crystallization and melting behavior

The DSC thermograms of PPS and its blends are shown in Figures 1, 2, and 3, respectively. The first heating run of quenched samples showed a glass transition temperature related to PPS at the temperature range of 78 to 84°C, a cold crystallization temperature ($T_{c,c}$) at 119 to 111°C, and a melting temperature (T_m) at 283–287°C. On the cooling trace from melt, a crystallization peak (T_c) was observed at the temperature
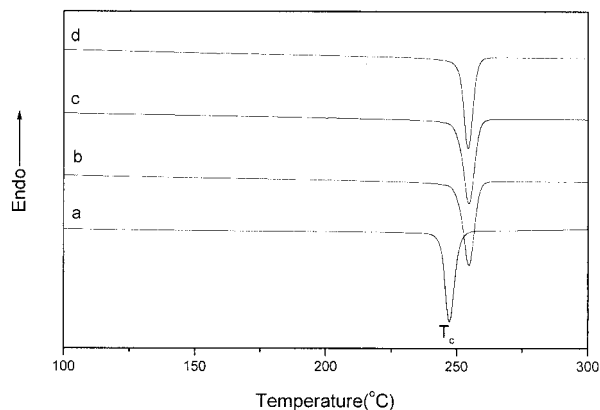

Figure 2 The cooling trace from the melt at 10°C/min: (a) PPS; (b) POI1; (c) POI3; (d) POI5.

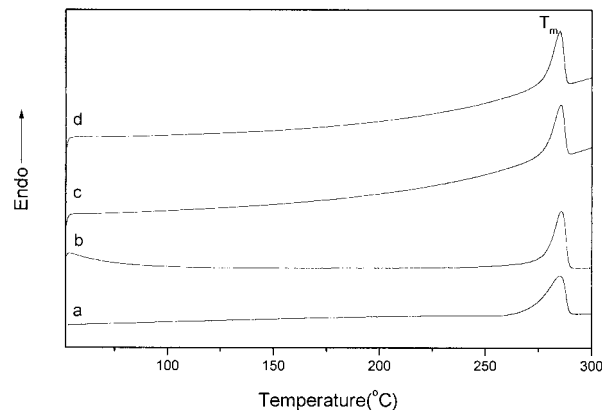range of 247 to 255°C. The second heating scan showed no cold crystallization exotherm and glass transition, indicating that PPS crystallized during the 10°C/min cooling run. All parameters down from the thermal analysis curves, T_g, T_c, $T_{c,c}$, and T_m for PPS and its blends are summarized in Table I. The degree of crystallinity of PPS was calculated according to eq. (2):

$$\chi_c = \Delta H_c / \Delta H_c^0 \ (100\% \text{ crystalline}) \qquad (2)$$

The heat of crystallization ΔH_c^0 for 100% crystalline PPS, 80 J/g, was extrapolated from the data of literature.[14]

Obviously, the glass transition and cold crystallization temperature of PPS decreased when it was blended with POI. On the other hand, the increase of T_m of the first heating scan, the crystallization peak (T_c), and the heat of crystallization (ΔH_c) brought by the addition of POI indicated the promotion of the crystallization of PPS. The precursor POI with little molecular weigh acted as an effective plasticity agent and nucleation agent for PPS simultaneously.

In the first heating trace, the melt temperatures of blends were higher than that of neat PPS. This shows the increase of lamella thickness of the crystals. It was thought that blending with POI promoted the PPS crystals crystallized from glassy state more perfectly. According to the crystallization theory of polymers, the crystallization of polymer from the glass state was controlled by the transference processes. At the front of a growing crystal, the crystallizable molecular segments and noncrystallizable ones interdiffuse to maintain the spherulities growing up. Then the macromolecule mobility is a dominant factor when the polymer crystallized from the glass state. As we discussed above, low molecular weight POI acted as a plasticity agent of PPS. The plastication increased the mobility

TABLE I
Thermal Transition Parameters of the Blends of PPS and POI

Sample	T_g (°C)	$T_{c,c}$ (°C)	$T_{m(1st)}$ (°C)	T_c (°C)	$T_{m(2nd)}$ (°C)	ΔH_c (J/g)	χ_c
PPS	84.6	119.0	283.0	247.3	285.0	57.7	0.72
POI1	81.2	113.0	284.6	253.7	285.7	59.3	0.74
POI3	81.9	113.4	287.5	254.8	285.5	59.1	0.74
POI5	79.0	111.4	284.3	254.4	285.5	59.1	0.74

of the crystallizable segment of PPS; thus, it made the folding of PPS molecular chains more orderly. Furthermore, sample POI5 got the lowest T_g, and the T_m of POI3 was the highest among all samples. POI was not only a plasticizer, it was also a chain extender and/or crosslinking agent that could also form grafting and/or crosslink copolymers of PPS-POI during melt blending. Although more plasticizer could provide more free volume for the PPS molecular chains, farther reaction between PPS and POI weakened the crystallization promoting effect when the content of POI was higher in the blends.

However, neat PPS and its blends have the same melting temperature on the second heating scanning. The melting point observed on the DSC curves resulted from the melting of the crystals, which was created when the samples were cooled from melt. Lamella thickness of the crystal of PPS was mostly determined by the crystallization temperature (undercoolings) and annealing time.[15] In our experiment, all the samples have the same cooling rate 10°C/min.

Equilibrium melting point

According to Hoffman-Weeks theory,[16,17] the dependence of the apparent melting temperature T_m on the crystallization temperature (T_c) is given by:

$$T_m = (1 - 1/\gamma)T_m^0 + (1/\gamma)T_c \quad (3)$$

where T_m^0 is the equilibrium melting point and γ is the lamella thickening factor (the final lamella thickness will be γ times larger than the initial thickness). Equation (3) shows that T_m and γ can be determined from the intersection with the $T_m = T_c$ line and the slope, respectively, in Hofman-Weeks plot of T_m vs. T_c. The T_m measured in the heating DSC scan from T_c were plotted against T_c (Fig. 4).The values of T_m^0 calculated from the plots are also shown in Figure 4. The T_m^0 of neat PPS (305°C) was lower than those of PPS/POI blends. Similar phenomena had been reported elsewhere. For example, Lovinger et al.[5] found that the T_m^0 of PPS with low molecular weight ($\bar{M}w \sim 15,000$) was 303°C and a medium molecular weight sample ($\bar{M}_w \sim 51,000$) had a T_m^0 at 315°C. Lopez and Wilkes[6] studied the effect of molecular weight on the crys-

tallization kinetics of PPS and reported that the T_m^0 of PPS samples with molecular weight 24,000, 49,000 and 63,000 were 304, 308, and 312°C, respectively. It can be concluded that the increase of T_m^0 had something to do with the increase of molecular weight. The effect of POI as a nucleation agent on the crystal perfect of PPS induced the increase of T_m^0 of PPS as mentioned above.

Hawkins[18] has reported that the simultaneous reactions observed with cured PPS may be summaized: (1) chain extension (oligomerization); (2) oxidative crossliking forming unites as shown:
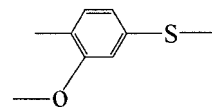
(3) thermal crosslinking forming units:
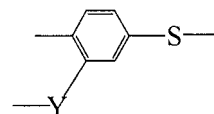
where Y may be aryl or S; (4) oxygen uptake followed by loss of SO_2. Because the blends made in this article were prepared in an intermixer at 290°C, 50 rpm for 10 min, the cased of (2) and (4) were not taken into
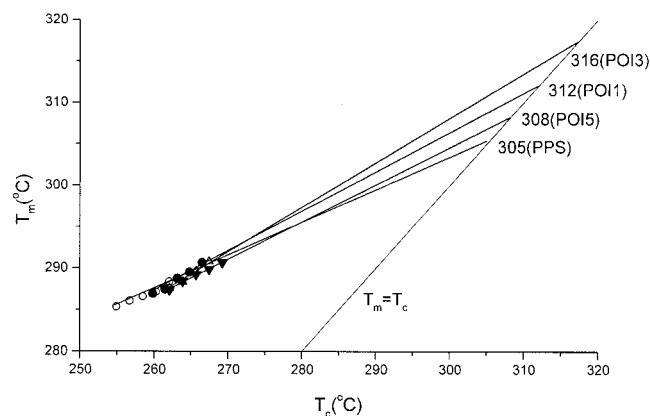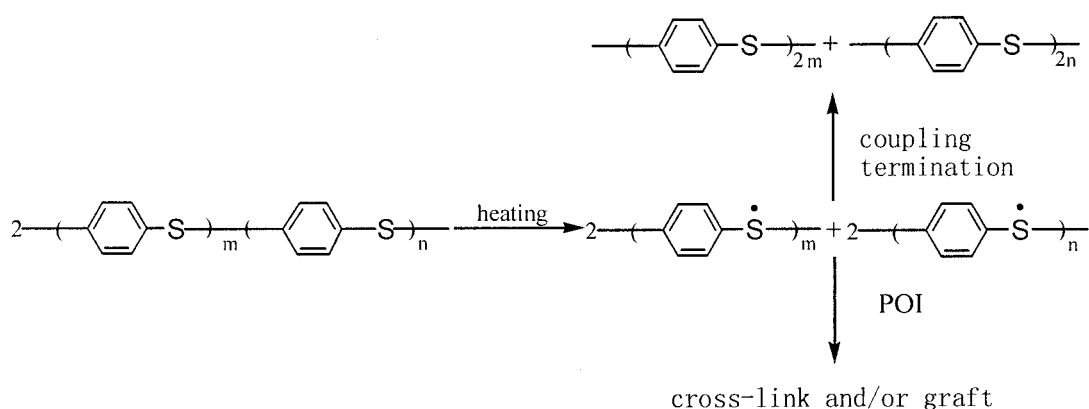

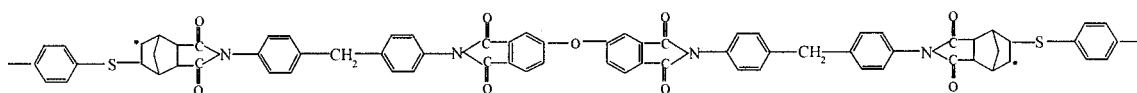**Figure 4** Typical Hoffmann and Weeks plots of PPS and its blends.

accounted. In the presence of POI during melt blending, the reaction between PPS and POI can be described by the following mechanism:

When the POI molecule is reacted with PPS macroradicals in the form of head to head, the following unit is produced:

Here, POI is used as a chain extender. From the result in Figure 4, we can draw the conclusion that when the weight fracture of POI was under 3 wt %, the reaction between PPS and POI was mainly chain extension, and when the composition of POI grew into 5 wt %, the decrease of T_m^0 was given rise to the destruction of the molecular ordered arrangement resulting from the thermal crosslinking between some macromolecules of PPS and POI.

Isothermal crystallization kinetics

The isothermal crystallization kinetics of PPS/POI (100/0–100/5) blends over a temperature range of 252–268°C were analyzed by means of Avrami equation:

$$\chi_c(t)/\chi_c(\infty) = 1 - \exp(-Zt^n) \qquad (4)$$

where Z is the rate constant of crystallization and n is the Avrami exponent, which can be related to the type of nucleation and the geometry of the crystal growth. When the spherulite grows in the form of three dimensionality of growth, $n = 4$ for homogenous nucleation and $n = 3$ for heterogeneous nucleation. From the intercepts and slopes of the plots of $\lg(-\ln[1-\chi_C(t)/\chi_c(\infty)])$ vs. $\lg t$ (Fig. 5), the values of Z and n were calculated, respectively; all these data are summarized in Table II. Each curve has a linear portion followed by a gentle roll-off at longer times, which shows the change to a secondary kinetic process. The Avrami exponents of pure PPS was above 4, whereas the n values of PPS/POI blends were mostly close to 3. It was good evidence of the change of nucleation type from homogenous nucleation to heterogeneous nucleation induced by the incorporation of POI to the PPS matrix. Under the same crystallization temperature, such as 260°C, the overall rate constant Z values of blends were about two orders higher than that of PPS, and the crystallization half times, $t_{1/2}$, decrease with increasing POI content. But the Z and $t_{1/2}$ values of POI3 and POI5 did not change much. Obviously, POI was an effectual nucleation agent for PPS, nucleation competed with the reaction between POI and PPS, and 3 wt % of POI was the sufficient amount for being the nucleation agent of PPS.

Fold surface free energy

According to the nucleation theories, it is possible to discuss the overall crystallization behavior of PPS by using calorimetric data obtained in isothermal conditions. In fact, it can easily be shown that, under isokinetic conditions for nucleation rate, the linear growth rate, G, is related to n and Z by a simple relation:

$$G \propto Z^{1/n} \qquad (5)$$

The theory of surface nucleation can be used to account the effect of nucleating agents on the linear growth rate of the spherulites developing in an under-
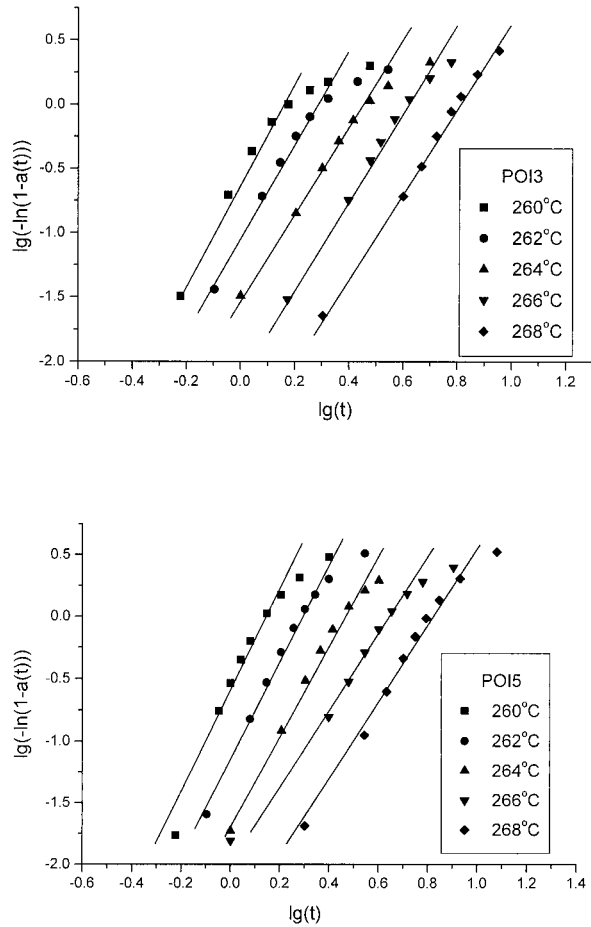
Figure 5 Plots of $\lg(-\ln(1- \chi_C(t)/\chi_c(\infty)))$ vs. $\lg t$ for PPS and PPS/POI blends.

TABLE II
The Effect of POI on the Crystallization Parameters of PPS

Sample	T_c (°C)	n	Z (min^{-1})	$t_{1/2}$ (min)	$\sigma_e \times 10^{-3}$ (J/m^2)
PPS	252	4.5	5.1×10^{-1}	1.07	40.6
	254	4.4	1.2×10^{-1}	1.48	
	256	4.2	4.9×10^{-2}	1.88	
	258	4.1	1.4×10^{-2}	2.64	
	260	4.2	2.4×10^{-3}	3.97	
POI1	258	4.3	3.9×10^{-1}	1.14	34.7
	260	3.8	1.2×10^{-1}	1.58	
	262	3.4	4.7×10^{-2}	2.24	
	264	3.4	1.3×10^{-2}	3.07	
	266	3.6	2.3×10^{-3}	4.47	
POI3	260	3.9	2.6×10^{-1}	1.28	38
	262	3.8	9.2×10^{-2}	1.71	
	264	3.3	3.2×10^{-2}	2.52	
	266	3.5	8.4×10^{-3}	3.56	
	268	3.4	2.1×10^{-3}	5.52	
POI5	260	3.9	2.3×10^{-1}	1.3	31.3
	262	3.8	7.2×10^{-2}	1.78	
	264	3.6	2.4×10^{-2}	2.55	
	266	2.9	1.4×10^{-2}	3.78	
	268	3.1	2.1×10^{-3}	6.21	

on the substrate. $\Delta T = T_m^0 - T_c$ is the undercooling degree.

By combining eqs. (5) and (6), after some rearrangements and set α as:

$$\alpha = \ln(Z)/n + U/R[C_2 + T_c - T_g]$$
$$- [1 + 2\sigma T_m^0/b_0 f\Delta H_m^0 \Delta T] \ln \phi_2$$
$$= \ln G_0 - rb_0\sigma \sigma_e T_m^0/[kf\Delta H_m^0 T_c \Delta T] \quad (7)$$

The straight lines with the slopes, Kg, related to the surface energies of the lamellar crystals were obtained by plotting α as a function of $1/f T_c\Delta T$. The results are shown in Figure 6 for pure PPS and PPS/POI blends. The parameters n and Z in eq. (6) have been evaluated
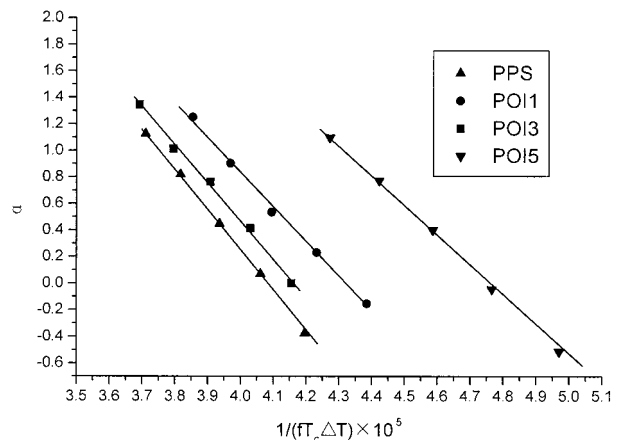
cooling PPS. The equation commonly used describe the linear growth kinetics[19] reads:

$$G = \phi_2 G_0 \exp[-U/R(C_2 + T - T_g)]$$
$$\times \exp[-rb_0\sigma \sigma_e T_m^0/[kf\Delta H_m^0 T_c \Delta T]$$
$$\times \exp[2\sigma T_m^0 \ln\phi_2/b_0 f\Delta H_m^0 \Delta T] \quad (6)$$

where ϕ_2 is the volume fraction of crystallizable component in the blends; U is the activation energy for transport of segments to the crystal front through the subcooled melt; T_g is the glass transition temperature of PPS; C_2 is a constant usually assumed as 51.6°C; and f is the correction factor for the temperature dependence of the entholpy of fusion, and can be expressed as $f = T_c$). σ and σ_e are the lateral and fold surface free energy of the developing crystals, respectively, and b_o is the layer thickness. The parameter r is related to the characteristic of the growth regime: $r = 4$ in regimes I and III, $r = 2$ in regime II. It is expected that transition from regime I to II to III should be observed upon increasing the ratio between the surface nucleation rate and the rate of spreading of the secondary nucleus

Figure 6 Plots of α as function of $1/(fT_c\Delta T)$ for PPS and PPS/POI blends.

from the preceding Avrami analysis and $U = 1400$ cal/mol; $C_2 = 30°C$; $\Delta H_m^0 = 80$ J/g; $b_0 = 0.56$ nm; $\sigma = 1.69 \times 10^{-2}$ J/m^2; and $r = 2$ have been taken from literature.[5] Lovinger[5] found that the transition for regime II to III is centered at 208°C; however, a regime I to II transition was not observed. In our experiment, T_c of all samples were above 252°C, which belonged to the regime II. The equilibrium melting temperature, T_m^0, and the glass transition temperature, T_g, of PPS have been measured as mentioned above.

The experimental data in Figure 6 obey eq. (7) at all samples, regardless of the adding of POI and the contents. The surface free energy of PPS crystals crystallized from melt decreased by the addition of POI in the blends as shown in Table II.

CONCLUSIONS

The crystallization and melting behavior of PPS was affected by adding POI. POI used in this study enhanced the crystallization rate and improved the perfection of the crystals of PPS. The equilibrium melting temperature of the PPS is 305°C, which is lower than that of the PPS/POI blends. The free energy for PPS crystals formed during the crystallization isothermally from melt decreased by incorporating POI in to the matrix.

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