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Interactions between polystyrenes of different tacticities and thermal evidence for miscibility

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Abstract

Various evidence of thermal behavior was probed to discuss the miscibility in atactic polystyrene (a-PS) with syndiotactic polystyrene (s-PS), which was not trivial owing to the small difference of only 10°C between the T_gs of these two isomeric polystyrenes. The preliminary morphology characterization using optical and scanning electron microscopies indicated that no discernible heterogeneity existed in the a-PS/s-PS blend. Composition dependence of peak temperature of cold crystallization for the quenched a-PS/s-PS blend samples also supported that inter-segmental interactions existed. The crystallinity of s-PS in a-PS/s-PS mixtures showed a minor negative deviation from linearity, which suggests favorable, albeit weak, interactions between the chain segments of s-PS and a-PS. These results provide evidence that this isomeric pair of polystyrenes of different tacticities are mixed in the molecular scales. The melting behavior of semicrystalline s-PS in the a-PS/s-PS mixtures was analyzed using the Flory–Huggins approach. In measuring the equilibrium melting point of s-PS in the a-PS/s-PS mixtures, the complex multiple melting peaks of s-PS were also discussed. A small negative value for the interaction parameter ($\chi = \backsim -0.11$) was found, further suggesting that miscibility is likely favored. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Interaction parameter; Melting; Syndiotactic polystyrene (s-PS)

1. Introduction

It is usually difficult to assess the miscibility of polymers in mixtures differing only in tacticity owing to proximity in their glass transition temperatures. Polymers with the same repeat units but different tacticities (i.e. stereoisomers) are not all miscible. For examples, Maier et al. [1] have concluded that polypropylenes (PPs) of different tacticity (a, i, or s) are not all miscible with each other, with a-PP/i-PP blend being miscible, but a-PP/s-PP system being incompatible. Another example can be given by polystyrenes of different tacticities. Binary miscibility of polystyrenes of isotacticity and atacticity has never been proven beyond doubt. Yeh et. al. [2] tentatively proposed miscibility in atactic polystyrene (a-PS)/isotactic polystyrene (i-PS) based on the results of a crystallization kinetic study. They, however, did not provide more direct evidence than an analysis of the crystallization kinetics of the blend. Syndiotactic polystyrene (s-PS), being a relatively newcomer into industrial scales [3], has also been a focus of various studies since it was reported. However, miscibility of s-PS with PS of other tacticities has not been proven conclusively. Very recently, Ermer et al. [4] tentatively proposed that s-PS and a-PS might be at least partially miscible based on the results of solvent diffusion behavior in the blends. In their study of diffusion measurements on the syndiotactic s-PS and deuterated atactic PS, Ermer et al. have concluded that there might be at least partial miscibility between a-PS and s-PS but they could not positively prove miscibility in a-PS/s-PS. Although they did not rule out the possibility of miscibility in a-PS/s-PS, direct evidence for miscibility was yet to be searched.

The small glass transition difference of only 10°C between s-PS and a-PS makes it especially difficult or inconclusive to confirm the true phase behavior of a-PS/s-PS blend. Other analytical techniques had to be employed to examine the blends of s-PS with atactic a-PS. Examination of the interaction parameter from measurements of the equilibrium melting point was considered as a valid approach from the point of view of thermodynamics. However, multiple melting peaks in s-PS are known to be complex. There are at least three melting peaks (Peak-I, -II, and -III) in an isothermally-crystallized neat s-PS, with the different melting peaks possibly associated with the α or β crystal forms [5]. Relative stability of the α vs. β forms has also been shown to be dependent on the temperature of crystallization

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[6]. Measurements and extrapolation of the melting temperatures for s-PS, thus, might not be straightforward. Furthermore, the behavior of s-PS chains in miscible states might most likely be influenced by another polymer chain if these two polymer chains are in miscible state with molecular-scale interactions. For example, s-PS has been earlier proved to be miscible with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, $T_g = 210°C$) [7,8].

We have earlier proved that as a result of intermolecular interactions, the multiple melting behavior of s-PS is influenced greatly by the miscible PPO molecules [5]. Our earlier studies have tentatively proposed that the a-PS/s-PS blend could be miscible [5] which was based on the analysis of the multiple melting behavior of neat s-PS in comparison with that of the a-PS/s-PS mixtures. For isothermally-crystallized a-PS/s-PS blends of most intermediate compositions, Peak-II is not seen, leaving only two melting peaks (Peak-I and -III). At higher crystallization temperatures, only single melting peak is observed in a-PS/s-PS blends, which has been attributed to Peak-I. Apparently, the intermolecular mixing of s-PS as expected in a miscible state with a large volume fraction of a-PS is unfavorable for generation of less-stable crystal entity under the same conditions of melt crystallization. Nevertheless, more direct evidence for miscibility in a-PS/s-PS had to be searched. By performing a thorough and carefully designed thermal analysis scheme on a-PS/s-PS samples, this study attempted to search for sufficient evidence to clarify the true phase state of the blends whose constituents possess closely-spaced T_gs.

2. Experimental

2.1. Materials and preparation

Additive-free atactic polystyrene was supplied by Chi-Mei, Inc. (Taiwan), with $M_w = 192\,000$ g/mol (GPC), P.I. = 5.1 and T_g (onset) of 87.5°C. Due to the relatively high polydispersity, this a-PS has a comparatively low T_g. Semicrystalline syndiotactic polystyrene (s-PS) was obtained as a courtesy sample material from Idemitsu Petrochemical Co., Ltd. (Japan) with a high $M_w = 241\,000$ g/mol and PI (M_w/M_n) = 2.31, and T_g (onset) of 95°C.

Melt-mixing was used for preparing blend samples of s-PS with a-PS. The constituent polymers were ground into fine powder, dried and pre-mixed. The mixed fine powdery polymers were then placed into the miniature chamber (a small cylindrical cavity ca. 2 g capacity) inside a laboratory-designed aluminum mold preheated to 320°C. Temperature control was provided by placing the mold-chamber assembly on a hot plate with controlled heating (set at 320°C). Blending of the polymers (small quantities ca. 1 g) could be easily accomplished in short time by manually hand-stirring the mixtures of polymer melts within the chamber. During melt-blending, a continuous purge of dry nitrogen was maintained to provide an inert-gas blanket on the mixing chamber in order to minimize possible thermal degradation/oxidation at high temperatures. Samples so prepared had minimal thermal degradation.

2.2. Apparatus and procedures

A polarized-light microscope (Nikon Optiphot-2, POL) was used for characterizing optical homogeneity of blends. A small quantity of the melt-blend samples was transferred between micro-glass slides, heated and pressed into thin film on a heating stage, and examined using the optical microscope. Additionally, morphology (fracture surface) of blends was examined using a scanning electron microscope (SEM) (Model JEOL JXA-840). The as-blended a-PS/s-PS mixtures were molded into a film between metal plates and quenched into ice water (or liquid nitrogen) to obtain amorphous samples with virtually no crystallinity. Quenched samples (amorphous glassy solids) were used for SEM characterization because s-PS crystals, if present, might obscure observation of phase morphology of blends. The quenched film samples were fractured across thickness and coated with gold by vapor deposition using vacuum-sputtering.

T_g transitions of the blend samples were measured with a differential scanning calorimeter (DSC-7, Perkin–Elmer) equipped with an intracooler (−70°C). Prior to DSC runs, the temperature and heat of transition of the instrument were calibrated with indium and zinc standards. During thermal annealing or scanning, a continuous nitrogen flow in the DSC sample cell was maintained to ensure minimal sample degradation. For determining the T_g transition temperatures, a heating rate of 20°C/min was used unless otherwise specified. For measurements of the melting points, a heating rate of 10°C/min was used instead.

3. Results and discussion

3.1. Morphology

The a-PS/s-PS blends of several compositions were first examined using an optical microscope. The quenched blends or at the melt state appeared visually transparent and were free of any heterogeneity or domain boundaries at the maximum magnification of optical microscope (ca. 1000 ×). The quenched blends were first examined at ambient temperature, then the temperature was raised to T_m and gradually up to where degradation occurred in order to observe whether or not there was a cloud-point transition. No lower critical solution point (LCST) phenomenon was observed up to above 350°C where they started to thermally degrade. In addition, the morphology of the quenched a-PS/s-PS blends in comparison with neat s-PS or a-PS was examined using SEM to provide further evidence of phase homogeneity. For brevity, the micrographs are not shown, but the morphology revealed that the quenched blends

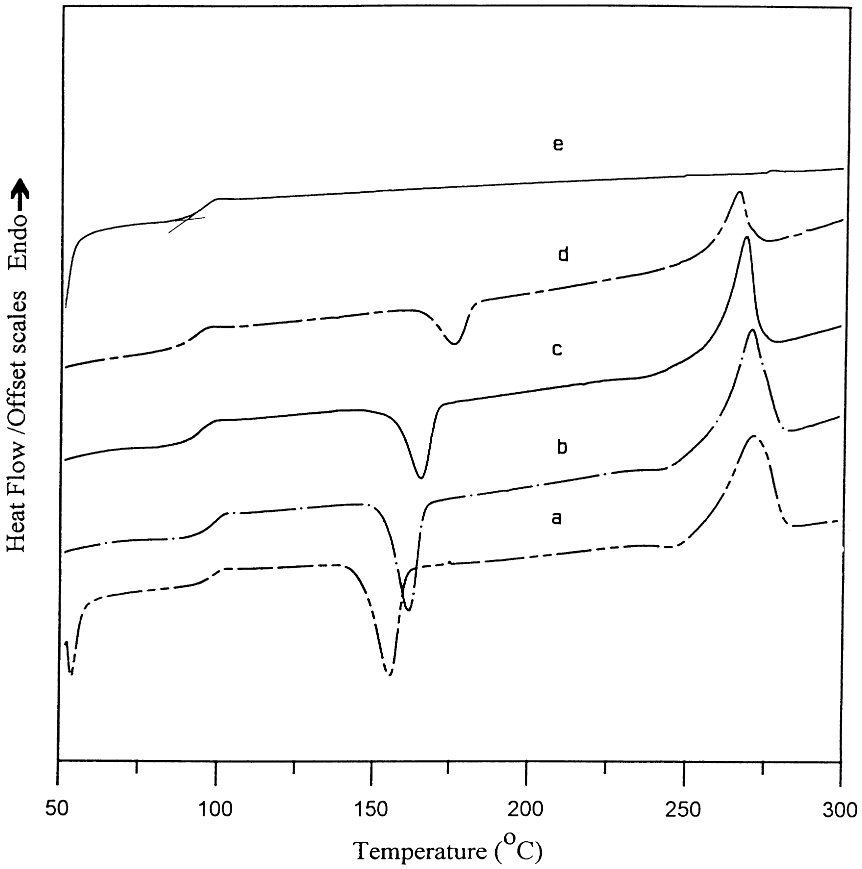

Fig. 1. DSC thermograms of as-quenched a-PS/s-PS blend samples: (a) neat s-PS; (b) 25/75; (c) 50/50; (d) 75/25; and (e) neat a-PS.

within a wide composition range exhibited no discernible heterogeneity within the resolution limit of SEM.

3.2. Glass transition behavior and other thermal transitions

All a-PS/s-PS samples for T_g characterization were initially heated to 320°C for melting the crystals and then quenched from the melt state before DSC scanning. Note that prior to scanning in DSC up to the temperature where the T_g was identified, the quenched blends were initially amorphous glasses with virtually no crystallinity. Fig. 1 shows the DSC thermograms with clearly one single T_g in each of the as-quenched a-PS/s-PS blends of various compositions, as indicated on the curves. However, it is not a certain evidence of homogeneity even though a single T_g is observed for the blends where the constituent polymers possess closely-spaced T_gs. A small glass transition difference of only 10°C between s-PS and a-PS makes it inconclusive regarding the true phase behavior of a-PS/s-PS blend showing a single T_g. Other thermal characteristics were also examined. First, the cold crystallization peak (T_{cc}) for each composition as shown in the DSC curves (in Fig. 1) was compared. The figure shows that the cold crystallization peak temperature (T_{cc}) upon DSC scanning is the lowest for neat s-PS ($T_{cc} = 155$°C). However, at increasing volume fractions of a-PS in the blend, T_{cc} (for the s-PS segment) increases steadily, suggesting that the molecular segment of non-crystallizing a-PS may intimately interact with the s-PS segment. Inter-segmental interactions between a-PS and s-PS chain segments existed and the non-crystalline (amorphous) nature of a-PS might have made it difficult for the s-PS chains to crystallize. This segmental interaction results in a higher T_{cc} needed for the s-PS segment to be packed into a crystalline domain in the a-PS/s-PS blend than what it would be for neat s-PS.

Table 1
Thermal transitions of as-quenched a-PS/s-PS blend samples

Composition (a-PS/s-PS)	T_g(°C)	Δ(°C)[a]	T_{cc}(°C)[b]
0/100	92.4	7.1	153
25/75	90.7	8.9	160
50/50	88.4	8.6	163
75/25	85.6	9.0	174
100/0	85.6	11.5	none

[a] Δ: transition breadth.

[b] T_{cc}: peak temperature of cold crystallization.

The numerical values of T_{cc} and other thermal transitions of the a-PS/s-PS blends are summarized in Table 1. The T_g transition breadth was measured and compared. Although only a small glass transition difference (10°C) is between the constituent polymers of s-PS and a-PS, the extents of glass

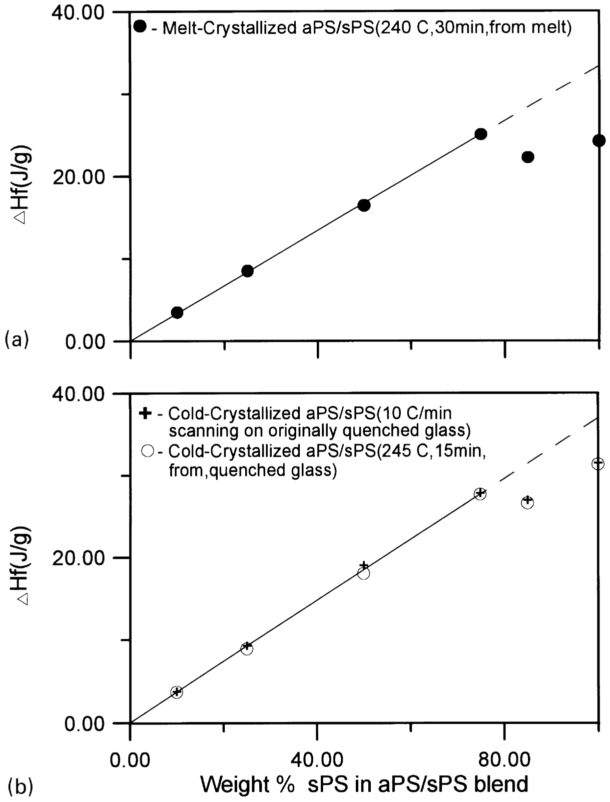

Fig. 2. Heats of fusion as functions of wt.% of s-PS in the a-PS/s-PS blend samples, which have been melt-crystallized and cold-crystallized, respectively.

transition breadth may be used as evidence if there are overlapped T_gs for individual phase domains or aggregated homo-molecular chains. The transition breadth was estimated from the DSC thermograms, and the result showed that the breadth remained quite constant ($\Delta = 8$–10°C) for all the blend compositions, indicating that the single T_g was not likely a partial superposition of two closely-spaced glass transitions.

Fig. 2(a) and (b) shows the heats of fusion (ΔH_f), as functions of wt.% of s-PS in the a-PS/s-PS blend samples melt-crystallized and cold-crystallized, respectively. Dependence of the enthalpy of transitions on blend composition can give some clues of intermolecular interactions. For non-compatible components, the changes of heat of melting (propotional to blend crystallinity) with respect to composition is expected to be linear, suggesting two separated domains. For two weakly-interacted miscible pairs with similar T_gs, dependence on composition can also be expected to be nearly linear. For strongly-interacted polymer pairs, negative deviation is usually observed, owing to the disruption of the crystallizing polymer chains by the interacting amorphous polymer chains. For examples, the crystallization of a crystallizing poly(ϵ-caprolactone) in miscible blends with poly(vinyl chloride) can be significantly disturbed (depressed), presumably by favorable molecular/segmental polar interactions [9]. If one ignores data of the experimentally measured ΔH_f for the neat s-PS, the trend indicates that, for most intermediate blend compositions, the heats of fusion or crystallization decrease almost linearly with s-PS weight fraction. This fact can be explained. s-PS and a-PS possess nearly the same T_g and the same chain stiffness (in rubbery amorphous state). In addition, the segmental interactions between a-PS and s-PS are weak and thus the amorphous (non-crystallizing) a-PS has a minimal effect on suppressing the crystallization tendency of crystallizing s-PS in the blends.

Interestingly, exceptions are observed for the neat s-PS and a-PS/s-PS blends of extremely high s-PS contents (e.g. >75 wt.%). These few data (for pure s-PS and compositions near) exhibit an apparent positive deviation. This peculiar behavior for a-PS/s-PS has also been earlier reported by de Rosa et al. [8], who provided no explanations at that time. We believe that the multiple crystal forms in s-PS has made interpretations complicated and the polymorphism is responsible for the peculiar deviation of the experimentally measured ΔH_f of s-PS in comparison to those of a-PS/s-PS blends. It has been earlier reported [5,6] that, depending on the thermal treatments, melt-crystallized s-PS can contain various crystal forms, mostly co-existing α-crystal (yielding Peak-II) and β forms (yielding Peak-I and -III). More specifically, s-PS melt-crystallized at high temperatures (e.g. >250°C), only β form (with minimal or no α form) can develop predominantly. In contrast, lower temperatures (210–245°C) melt-crystallization leads to various fractions of co-existing α and β form crystals. Thus, in experimental measurements of ΔH_f for the pure s-PS, the value of measured ΔH_f represented co-existing $\alpha + \beta$ forms, unless the neat s-PS sample has been melt-crystallized at sufficiently high temperatures (e.g. 250°C and up) to develop full crystallinity of β form only. Upon DSC scanning, a sample containing $\alpha + \beta$ forms for measurement of its ΔH_f, the α(crystal (Peak-II) could feasibly melt and re-organize (i.e. re-crystallized upon scanning to 260–275°C). Therefore, partial portion of endothermic heat of melting (of α from) was nulled by the exothermic heat of re-crystallization (α into β form). Thus, the measured heat of fusion for the samples (neat s-PS or its blends of high s-PS wt.%) containing $\alpha + \beta$ forms would be less than what would have been for the same samples containing only β form crystal (which melts upon heating but does not re-crystallize to other forms). By contrast, the a-PS/s-PS blends of most intermediate compositions (25–90 wt.% a-PS) develop, upon melt-crystallization, predominantly β form at most accessible temperatures [5]. The heat of fusion for the a-PS/s-PS blends of the intermediate compositions (containing only β form crystal) is largely linear, as shown in Fig. 2, with the extrapolated value to the *y*-axis coordinate (s-PS = 100 wt.%) representing the ΔH_f for the s-PS containing only β form crystal. Thus, the "positive deviation" in the plot of ΔH_f vs. composition does not necessarily indicate absence of interactions in a-PS/s-PS, but actually reflects that a transition of co-existing dual crystals in s-PS

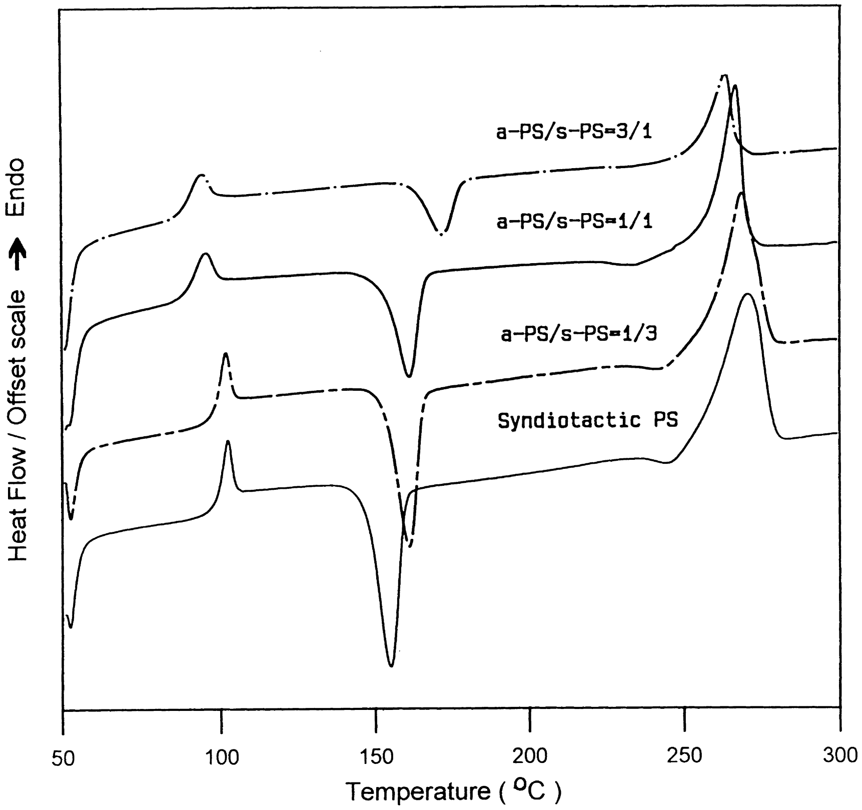

Fig. 3. DSC thermograms of physically-aged blends of a-PS/s-PS of various compositions, revealing a distinctly sharp enthalpy relaxation peak.

to predominant α crystal in a-PS/s-PS under the conditions of same temperature of thermal treatments. This fact suggests that the intimate interaction exists between the a-PS and s-PS polymer chains and is responsible for the observed transition from co-existing α crystal (kinetically favored) and β crystal (thermodynamically favored) in neat s-PS to dominating β crystal (thermodynamically favored) in a-PS/s-PS blends, when crystallized at the same conditions.

A technique of enhancing the resolution of transition by physical aging was employed in order to distinguish if there were partially overlapped thermal transitions. Resolution of T_g transitions is generally limited to about 15–20°C. However, physical aging can significantly enhance the resolution power by revealing the enthalpy relaxation peaks. Note that physical aging occurred only at below T_g, thus, the treatment would not induce any crystallization. Samples of a-PS/s-PS were physically-aged at 80°C (just 5–10°C below T_g) for 2 h each, which were then scanned in DSC to reveal the transitions. Fig. 3 shows the DSC thermograms of the physically-aged a-PS/s-PS blends of various compositions (0/100, 25/75, 50/50, and 75/25). As a result of physical aging, a peak of enthalpy relaxation is seen on top of the T_g in each of the DSC curves. Apparently, there is only one identifiable enthalpy relaxation peak, suggesting that only one T_g transition is involved in each of the blend samples. The relatively sharp endothermic peak indicate that it is not possible that multiple T_g transitions may be involved. Note that as a result of aging treatment, the T_gs of blend samples were slightly elevated, but otherwise appeared to be a distinctly single transition. The result clearly revealed only one enthalpy relaxation peak, which more positively suggested only one T_g transition in each of the aged blend samples. Note that the a-PS component again led to increase in T_{cc} of the s-PS in the aged a-PS/s-PS blends, in agreement with the cold crystallization behavior observed in the as-quenched a-PS/s-PS blend samples.

3.3. Melting behavior and interaction parameters

Melting point depression must be determined using T_m data that are a function of only the thermodynamic contribution. Variation of lamellae thickness in the spherulites of a-PS/s-PS blend of different composition can also influence the apparent melting point and thus must be taken out. Relationship of T_m vs. T_c for each of the samples was first determined. Extrapolation gives prediction of the trend at infinite time by means of classical Hoffman–Weeks procedure [10]. As one of the two components is semicrystalline and crystallizable, the classical Flory–Huggins theory on melting point depression for miscible polymer solutions can be used to estimate the intermolecular interaction strength. For polymers with a single melting peak, plotting of data is straightforward. Plotting of equilibrium temperature measurements on neat s-PS was not straightforward as there are two multiple melting peaks.

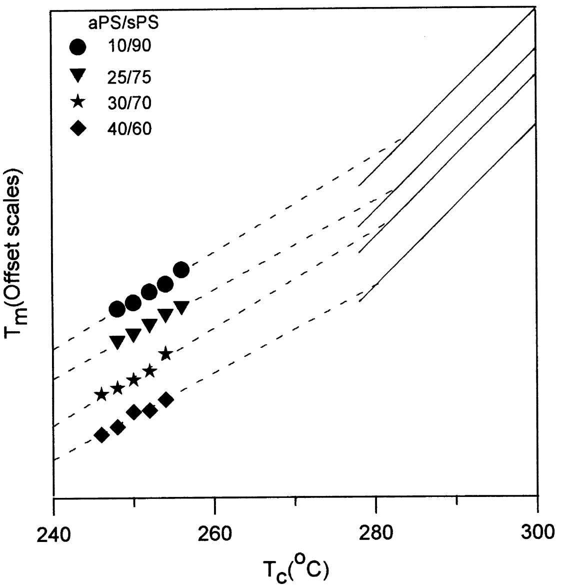

Fig. 4. Hoffman–Weeks plot of the melting Peak-I (in offset *y*-axis) of a-PS/s-PS blend samples isothermally crystallized at various temperatures.

Although the equilibrium melting temperature of s-PS has been earlier reported [5,11], we performed double checks in this study. Different values (from 275 to 287°C) for the T_m^0 of s-PS, depending on different thermal treatments, have been reported in literature [12–14]. We performed experimental measurements on T_m^0 of s-PS again in this study, because consistency in calibrating the DSC as well as consistent thermal treatment was critical to ensure minimal scattering. The difference between the equilibrium melting points of the pure s-PS and s-PS in the a-PS/s-PS blend was expected to be relatively small, thus a minor experimental error in T_m^0 of neat s-PS can lead to significant scattering in the slopes of Hoffman–Weeks plots. Each of the s-PS samples was first heated to 320°C and quenched (in DSC) to melt-crystallize at a designated temperature (T_c) for 4 h. Hoffman–Weeks plots were generated. For brevity, the figure is not shown here as it is similar to that already previously reported [5]. It is worth mentioning, however, extrapolation may be performed using either of the two distinct melting peaks. When crystallized at relatively lower temperatures, neat s-PS exhibited three multiple melting peaks; however, when crystallized at higher temperatures or for longer times, only two melting peaks were observed upon DSC. The temperature of the third peak (highest-melting Peak-III) remained quite constant with time of annealing and eventually diminished in intensity or disappeared completely [5]. Extrapolation of these two sets of data (upper and lower melting peaks) yielded a intercept with the $T_m = T_c$ line. The intercept point gave the equilibrium T_m^0 for neat s-PS, which was 285.5°C if extrapolated for Peak-II, or 286.6°C if extrapolated for Peak-I. An intercept with $T_m = T_c$ near 285.5–286.6°C was obtained, suggesting that the lamella crystals representing these two peaks eventually became the same upon extended annealing. If an average of these two value is taken, the equilibrium melting point for s-PS is about 286.0°C. This result for the neat s-PS is slightly different from the previously reported values, but still in reasonable agreement with the earlier reported literature value of 285.0°C by an earlier study in this laboratory [5], as well as by Arnauts and Berghmans ($T_m^0 = 285.5$°C) [11]. For the investigation of T_m–T_c plotting for the neat s-PS sample, one must be careful in avoiding polymorphism in s-PS, as extrapolation from the T_m–T_c plots would become less accurate. In addition, the melting/recrystallization of α crystal in the presence of β form may likely to interfere with the accurate determination of melting peaks of β form (Peak-I and III). The temperature range (250–260°C) for crystallizaiton of s-PS was chosen such that the β form was the dominating species (Peak-I and III). By comparison, isothermal melt-crystallization at lower temperatures (<250°C) would yield α(β forms in s-PS.

As mentioned earlier, the crystal forms and associated melting behavior of a-PS/s-PS blend are different from those of neat s-PS, suggesting the likelihood of a certain level of interactions between the s-PS and a-PS molecular chains. Again, for measurements of T_m^* of s-PS in a-PS/s-PS blends, similar isothermal treatments were imposed on the blend samples. The blend samples were first melt at above their respective T_m and then cooled (in DSC cell) to a series of isothermal holding temperatures for crystallization to full extent. Subsequently, DSC scanning was performed on the isothermally crystallized blend samples to reveal their melting peak(s). Isothermal temperatures of 245–255°C (slightly lower than those for the neat s-PS) were chosen for melt-crystallization of the a-PS/s-PS blends. When crystallized at temperatures lower than 250°C, neat s-PS would have exhibited three multiple melting peaks (α(β forms); while the a-PS/s-PS blend samples of most compositions yield only the dominating β form crystal (Peak-I and -III). Furthermore, when crystallized at higher temperatures, the higher-melting peak (Peak-III) quickly diminished in intensity and became merged with the fast-elevating Peak-I. Thus, in general, only one peak (Peak-I) was available for extrapolation for the a-PS/s-PS blend.

Fig. 4 shows Hoffman–Weeks extrapolations of the lower melting Peak-I of a-PS/s-PS blend samples (10/90, 25/75, 30/70, and 40/60 weight ratios). Note that for most compositions annealed for 4 h in the selected temperature range, the second peak (Peak-II) either disappeared or exhibited a much depressed intensity and was partially merged with the quickly elevating Peak-I (originally the lowest-melting peak). Thus, only one melting peak (Peak-I) was available for extrapolation. The intercepts at the $T_m = T_c$ lines gave the equilibrium melting temperature (T_m^*) for each of the blend compositions. There is some scattering for the T_m vs. T_c plot for the a-PS/s-PS sample of 30/70 and 40/60, but not much for 10/90 and 25/75 compositions. The extrapolation might lead to deviation if scattering is significant. However, it was extremely difficult to experimentally measure the T_m of blend samples crystallized at higher

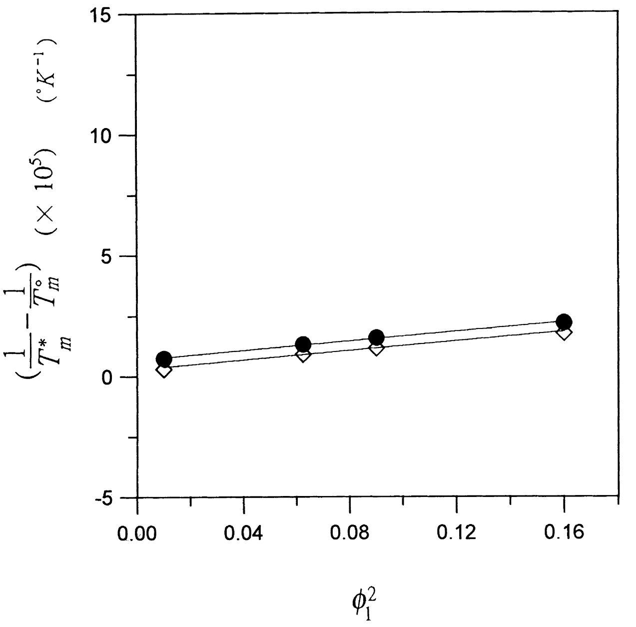

Fig. 5. Melting point depression of a-PS/s-PS blend according to the Flory–Huggins relationship. (Solid circle) based on $T_m^0 = 286.6$°C; (diamond) based on $T_m^0 = 285.5$°C.

temperatures. Possibility of thermal degradation at high T_c for long times is something one must care about. Errors in measured T_m caused by thermal degradation might outweight the error in long extrapolation.

From the T_m^* of each blend composition, the interaction parameter (χ) between s-PS and a-PS was estimated from the Flory–Huggins relationship [15]:

$$\left(\frac{1}{T_m^*}-\frac{1}{T^\circ{}_m}\right)=-\left(\frac{RV_2}{\Delta H_f V_1}\right)\times\left[\frac{\ln\phi_2}{n_2}+\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\phi_1+\chi\phi_1^2\right] \quad (1)$$

where in this equation, χ is the Flory–Huggins interaction parameter. T_m^* and $T^\circ{}_m$ are the equilibrium melting points of s-PS in the polymer mixture and neat crystallizable polymer (s-PS), respectively. The subscript "1" indicates the non-crystallizing (amorphous) polymer (a-PS), and "2" indicates the crystallizing polymer (s-PS). V_1 and V_2 are the molar volumes of the repeat units of the non-crystallizable and crystallizing polymers, and n_1 and n_2 are degrees of polymerization of these two polymer components, respectively. $V_1 = 99$ cm^3/mol for a-PS [16]. V_2 (for s-PS) is not readily known, but is assumed to be approximately the same as that of i-PS within some experimental errors [17]. Thus, V_2 was taken as 92.9 cm^3/mol. ΔH_f is the heat of fusion (melting) of the fully crystalline polymer (s-PS) per mole repeat unit. The enthalpy of fusion for s-PS has been reported to be $\Delta H_f = 2050 +/- 100$ cal/mol (or 82.5 J/g) [18]. ϕ_1 is the volume fraction of the non-crystallizing polymer (a-PS), which is same as the weight fraction if the density of s-PS and a-PS is assumed to be approximately equal (both in amorphous state).

The first two terms in the left-hand-side bracket of the above equation are due to entropic contribution to melting point depression, while the last term is enthalpic contribution to melting point depression. It can be expected that the contributions from the first two terms are small due to relatively large n_1 and n_2. For high-molecular-weight blends, the first two terms (entropic contribution) drop out and the above equation can be approximated by:

$$\left(\frac{1}{T_m^*}-\frac{1}{T^\circ{}_m}\right)=-\left(\frac{RV_2}{\Delta H_f V_1}\right)\chi\phi_1^2. \quad (2)$$

Fig. 5 shows a plot of the left-hand-side of Eq. (2) vs. ϕ_1^2, yielding a fairly consistent straight line. From the plot, the interaction parameter between a-PS and s-PS (χ) was found to be −0.11. This value, though not large, indicates additional thermal evidence for miscibility in a-PS/s-PS. The low interaction parameter suggests that although the molecular segments of s-PS and a-PS are favored to form a miscible state, the scales of interaction between the s-PS and a-PS molecules of different configurations are about comparable to those between homopolymer chains of s-PS or a-PS of the same configuration. As discussed earlier, there is some scattering for the T_m vs. T_c plot (Fig. 4) for a-PS/s-PS sample of 30/70 and 40/60. Extrapolation for obtaining T_m^* of blends thus might involve some errors. The deviation for the 30/70 and 40/60 a-PS/s-PS blends was about ±0.5°C. The measured difference between $T^\circ{}_m$ of pure s-PS and T_m^* of a-PS/s-PS (40/60) was about 9°C, thus the amount of deviation (scattering) was tolerable. One must also realize that error in T_m of blends of high a-PS contents is less sensitive than the error in T_m of blends of small a-PS contents (due to the square effect of ϕ_1^2) in Hoffman–Weeks plotting.

Alternatively, to evaluate the effect of possible data scattering, a self-consistency check was performed by an alternate plotting. Eq. (2) may be rearranged for a different plotting scheme:

$$\left(\frac{1}{T_m^*}-\frac{1}{T^\circ{}_m}\right)/\phi_1=-\left(\frac{RV_2}{\Delta H_f V_1}\right)\chi\phi_1 = -\left(\frac{\chi R T^\circ{}_m}{V_1}\right)\left(\frac{V_2}{\Delta H_f}\right)\frac{\phi_1}{T_m^0} = -B\left(\frac{V_2}{\Delta H_f T_m^0}\right)\phi_1. \quad (3)$$

A plot of the left-hand-side of Eq. (3) vs. ϕ_1 yielded a fairly consistent straight line. For brevity, the plot is not shown. This plot yielded an interaction parameter between a-PS and s-PS (χ), which was found to be −0.04. This value is slightly smaller than the value estimated from Eq. (2); however, it indicates that miscibility in a-PS/s-PS is likely favored. Note that the interaction parameter is a small negative value; thus, the method of plotting may induce slight errors. Nevertheless, the self-consistency check by these two different graphic methods suggests that the interaction parameter assumes a small negative value most likely between -0.04 and -0.10.

Runt [17] investigated a classically known miscible blend system of a-PS/iPS (M_w ca. 50 000 g/mol for both) and found that the polymer–polymer interaction parameter (χ) for the a-PS/iPS pair is about -0.003, which essentially is zero. This study shows that the interaction parameter in the a-PS/s-PS system is similarly a small negative, but slightly higher ($\chi = \sim -0.1$) than that for the a-PS/iPS system. By comparison, the miscible iPS/PPO blend system exhibits a much larger interaction parameter $\chi = -0.22$, as also reported by Runt [17].

4. Conclusion

Experimental proof for binary miscibility in the isomeric a-PS/s-PS blend has been difficult owing to proximity of T_gs in these two polymers. In this study, optical microscopy revealed that the polymeric mixtures of a-PS/s-PS remained optically homogeneous and free of phase separation up to a high temperature of 350°C, but no temperature-induced phase separation associated with the lower critical solution temperature (LCST) phenomenon was observed. The SEM morphology also indicated that no discernible heterogeneity existed in the a-PS/s-PS blend. Other evidence of thermal transition behavior was also examined. The cold crystallization of the s-PS component in the blend was analyzed. The peak temperature of the cold-crystallization exotherm increased with increasing a-PS content in the a-PS/s-PS blend, which indicated that inter-segmental interactions existed between the s-PS and a-PS molecular chains. The fact that significantly suppressed heat of fusion of the s-PS component in the a-PS/s-PS blend in comparison to the pure s-PS also suggests that segmental interactions between a-PS and s-PS in molecular scales are likely responsible.

In addition, the melting behavior of s-PS in the a-PS/s-PS blend was analyzed and compared to the pure s-PS. A small negative value for the interaction parameter ($\chi = -0.04 - -0.10$) was found, which provides additional evidence for a favorable condition leading to binary miscibility in this isomeric pair. The various thermal transition approaches utilized in this study have led to a reasonable conclusion that miscibility exists in the a-PS/s-PS blend.

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