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Equilibrium Melting Point Depression for Blends of Isotactic Polystyrene with Poly(2,6-dimethylphenylene oxide)

Joaquin Plans,[†] William J. MacKnight,* and Frank E. Karasz

Polymer Science and Engineering Department and Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003. *Received June 22, 1983*

ABSTRACT: The melting behavior of pure isotactic polystyrene (iPS) and blends with poly(2,6-dimethylphenylene oxide) (PPO) have been investigated by differential scanning calorimetry (DSC). Evidence for interaction between the blend components has been detected from melting point depression studies and by examining the composition dependence of the glass transition temperature. The interaction parameter has been evaluated via the Flory–Huggins approximation of the thermodynamic mixing of two polymers, which yielded an average value of $\chi = -0.17$ for the range of compositions analyzed. This result is in agreement with the interaction parameter values derived from the negative heat of mixing for a-PS/PPO liquid blends previously reported in the literature.

1. Introduction

The melting temperature of a crystalline polymer is often lowered when it is blended with another polymer that is compatible with it in the liquid state.[1–4] On the basis of thermodynamic theory[5,6] this melting point depression is attributed[1] to the entropy of mixing and to the energetic interaction between both components, the source of an enthalpic term. Thus a study of the melting point depression of the crystallizable component in a binary polymer blend can lead to an assessment of the interaction between the blend components.[1]

The system polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been the subject of several investigations.[2,4,7–11] A negative enthalpy of mixing for atactic-PS/PPO blends as a function of composition referred to the liquid state of the components was reported by Weeks, Karasz, and MacKnight,[7] suggesting the presence of interaction between the polymers. Therefore, one should expect a corresponding melting point depression for crystalline isotactic-PS (i-PS) in blends with PPO, assuming the influence of tacticity to be negligible. Melting point depression for i-PS/PPO blends has been observed in the literature,[2,4] but no equilibrium melting point depression data are available for this system. It is the scope of the present paper to show that equilibrium melting point depressions for i-PS/PPO blends result from extrapolating Hoffman–Weeks plots, revealing the presence of interactions between both components. The existence of such interactions is also concluded from a consideration of the composition dependence of the glass transition temperature.

2. Sample Preparation

Isotactic polystyrene (i-PS) was received in the form of pellets from Polysciences Inc. ($\bar{M}_w \sim 10^6$). It was purified by dissolving in boiling toluene followed by filtration and precipitation at room temperature with vigorous stirring into a large excess of ethanol. The precipitated material was then collected, cut into small pieces, and extracted in a Soxhlet apparatus with boiling 2-butanone for 40 h in order to remove the atactic component. The remaining i-PS was then redissolved in toluene in order to make the material homogeneous and reprecipitated in an excess of ethanol. The i-PS obtained was dried in a vacuum oven at 60 °C for 24 h. The final yield was 70%.

Powdered PPO (General Electric Co.) was purified by dissolving in toluene slightly above room temperature and reprecipitating from an excess of methanol. Viscosity measurements gave a molecular weight of $\bar{M}_v = 2.3 \times 10^4$.

Blends of i-PS and PPO were made by dissolving the appropriate weight fraction of the polymers in hot chlorobenzene and precipitating from ethanol. The dried material was compression molded between steel plates of 10 000 lbs and 280 °C under nitrogen. Uniform films of about 0.4-mm thickness were obtained.

3. Experimental and Crystallization Procedure

Blend compositions of 85/15, 75/25, 65/35, and 50/50 by weight of i-PS/PPO were prepared by the procedure described in section 2. Small circular samples were cut and introduced into aluminum pans for crystallization and DSC experiments. The equipment used was a Perkin-Elmer DSC-II equipped with a Thermal Analysis Data Station (TADS). All the samples were crystallized in the DSC sample container.

Prior to a run, each sample was heated up to 260 °C for 5 min in order to eliminate crystalline residues formed during the preparation procedure. The samples were then quenched at a rate of 160 °C/min to the desired crystallization temperatures and held there for 12 h unless specified differently. Annealing at 260 °C was also imposed before measuring the respective glass transition temperatures followed by quenching at 160 °C/min to room temperature, which is well below the T_g of the blend in all cases. Each measurement was repeated at least twice.

4. Results

4.1. Glass Transition Temperatures. A single T_g appears for all the i-PS/PPO blends prepared. The composition dependence of T_g is shown in Figure 1. The glass transition temperature was taken at the midpoint of the heat capacity increment ΔC_p. The dashed line in Figure 1 corresponds to the theoretical relation[12]

$$\ln T_g = \frac{W_1 \Delta C_{p1} \ln T_{g1} + W_2 \Delta C_{p2} \ln T_{g2}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2}} \qquad (1)$$

where W_1 and W_2 are the weight fractions of the components, ΔC_{p1} and ΔC_{p2} are the heat capacity increments at T_g, and T_{g1} and T_{g2} are the transition temperatures of the pure constituents. Equation 1 was derived based on thermodynamic arguments for the entropy of mixing of two polymers, assuming temperature-independent heat capacity increments and also assuming that miscibility approached the segmental level.

The following values were obtained for pure i-PS: $T_{g2} = 371$ K and $\Delta C_{p2} = 0.074$ cal g^{-1} deg^{-1}. The corresponding values for pure PPO were $T_{g1} = 489$ K and $\Delta C_{p1} = 0.0597$ cal g^{-1} deg^{-1}. In our case eq 1 yields nearly the same composition dependence as the Fox expression.[14]

4.2. Melting Temperatures. At low heating rates three different endotherm peaks appear for pure i-PS crystallized at temperature below 190 °C. The influence of the heating rate on the DSC curves is illustrated in Figure 2. It has been suggested that the lowest temperature (endotherm I) peak is due to a secondary crystallization process between the lamellae, probably correlated with intercrystalline links.[15] The highest temperature peak

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[†] Permanent address: Instituto de Estructura de la Materia, CSIC, Serrano 119, Madrid, Spain.

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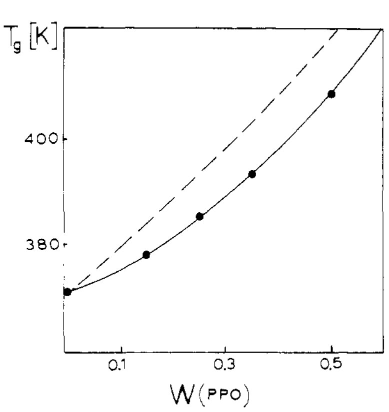

Figure 1. Composition dependence of T_g. The dashed line corresponds to eq 1.

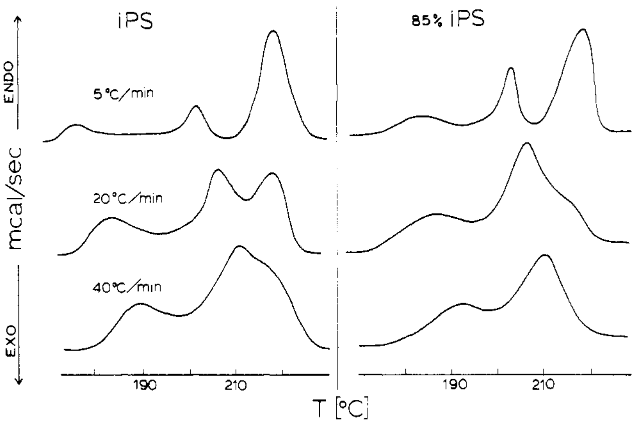

Figure 2. Influence of the heating rate on the DSC thermograms corresponding to T_c = 160 °C for i-PS and 85% i-PS blend.

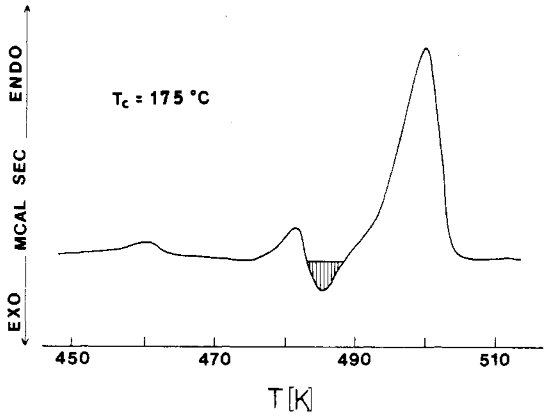

Figure 3. DSC thermogram of pure i-PS crystallized at T_c = 175 °C for 1 h. An exotherm appears between peak II and peak III. (Scanning rate: 1.25 °C/min.)

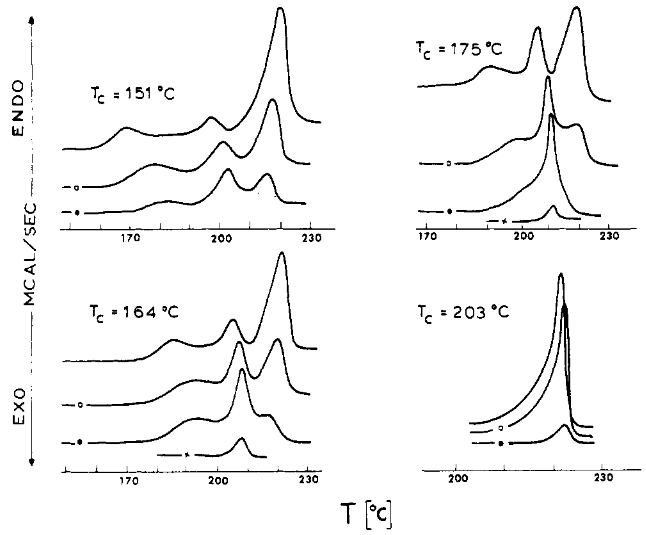

Figure 4. DSC thermograms obtained after crystallizing at different temperatures for pure i-PS, 85% i-PS blend (○), 75% i-PS blend (●), and 65% i-PS blend (×). (Scanning rate: 5 °C/min.)

(endotherm III) corresponds to the melting of crystallites formed at T_c but reorganized during heating.[8,15] We are actually concerned with the intermediate peak (endotherm II), which corresponds to the melting of crystallites formed at T_c by a primary crystallization process. The use of the maximum peak temperature as the melting point (T_m) was preferred because the accuracy of its determination is greater when multiple melting peaks are present, especially when a reorganization process is taking place. In such a case, the temperature associated with the return to the base line of endotherm II can be controlled by melting of reorganized crystals or even by the presence of a masked exotherm due to recrystallization. As a matter of fact the existence of an exotherm was observed by Lemstra et al.[15] in i-PS. The appearance of a slight exotherm between endotherm II and endotherm III has also been confirmed in our samples by using very low heating rates. Figure 3 shows the presence of this exotherm for pure i-PS at T_c = 175 °C and a heating rate of 1.25 °C/min. For these reasons it was thought that the peak maximum temperature was the most representative of the melting of primary crystals formed at T_c. Moreover, taking the maximum peak temperature as T_m, the Hoffman–Weeks plots can be drawn for a larger range of crystallization temperatures since for $T_c \gtrsim 180$ °C the third peak appears very close to the second one, masking the last trace of endotherm II. We chose 5 °C/min as the optimum heating rate since, as noted above, lower heating rates produced an exotherm between peaks II and III and higher heating rates produced too much overlapping between peaks II and III.

Figure 2 shows that overlapping between endotherm II and endotherm III occurs at lower heating rates for the blends compared to pure i-PS. On the other hand, Figure 4 shows that the degree of reorganization as evidenced by reduction in the magnitude of endotherm III is also reduced with increasing PPO content. In Figure 4 one also observes that the higher the PPO content, the higher the T_m of endotherm II. The DSC thermogram in Figure 4 corresponds to several crystallization temperatures and a heating rate of 5 °C/min. A heating rate as low as 5 °C/min was chosen for scanning in order to approach equilibrium conditions for melting. Lower heating rates were not employed since the intensity of peak II is greatly reduced under these conditions. Moreover, the dependence of T_m on heating rate for such low scanning rates was observed to be negligible. The Hoffman–Weeks plots of T_m vs. T_c corresponding to pure i-PS, 85% i-PS, 75% i-PS, and 65% i-PS are presented in Figure 5. Extrapolation of the different straight lines to the intersection with $T_m = T_c$ yields the equilibrium melting temperatures: An equilibrium melting point of $T_m{}^\circ$ = 240 °C is obtained by a least-squares fit for pure i-PS, and the following equilibrium melting point depressions (see Figure 5) are found for the blends: $\Delta T(85\%)$ = 2.1 °C, $\Delta T(75\%)$ = 2.9 °C, and $\Delta T(65\%)$ = 4 °C. It is noted that the experimental T_m's in Figure 5 for the blends are higher than those for pure i-PS, yet the extrapolated curves cross at high T_c and lead to a depression of the equilibrium T_m. This behavior may result from the fact that crystals of i-PS in the blends may be more stable than in pure i-PS due to the nature of their

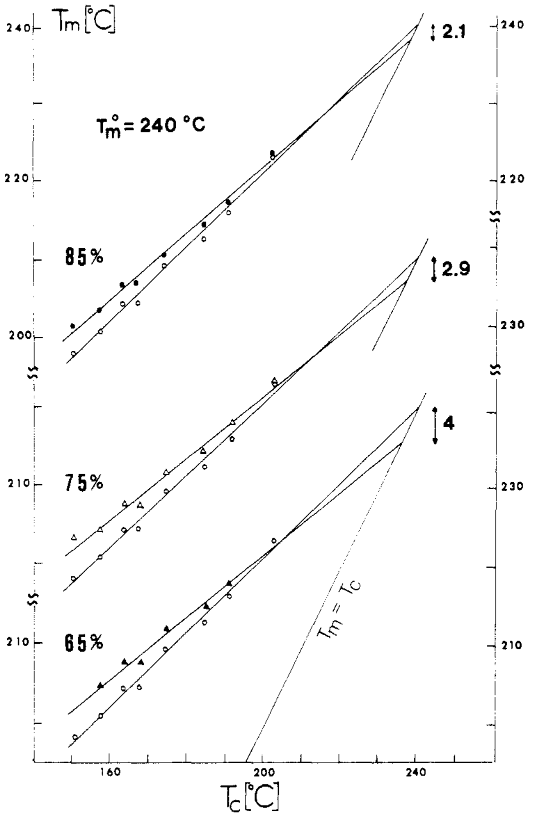

Figure 5. Hoffman–Weeks plot corresponding to pure i-PS (○), 85% i-PS (●), 75% i-PS (△), and 65% i-PS (▲) blends.

Table I
Dependence of the Total Heat of Fusion H_f (cal/g) with Crystallization Temperature[a]

	T_c, °C							
	151	159	164	168	175	185	192	203
H_f(i-PS)	4.6	5.1	5.5	5.6	5.7	5.6	5.4	4.5
H_f(85%)	3.3	3.6	4.5	4.5	4.6	4.5	4.4	2.7
H_f(75%)	0.5	1.3	3.2	3.6	3.6	3.6	3.6	1.7
H_f(65%)		0.1	0.2	0.2	0.2	0.1	0.1	

[a] Error limits ±0.1 cal/g.

surfaces in the former case. The extrapolated Hoffman–Weeks plots yield the equilibrium melting points of crystals of infinite size where surface effects are negligible.

Finally, Table I shows the total areas in cal/g for the different crystallization temperatures and the different blends.

5. Discussion

5.1. Composition Dependence of T_g. Usually the appearance of a single transition temperature in blends is taken as a powerful criterion of compatibility between the components. Most of the theoretical relations that attempt to describe the composition dependence of T_g for blends are derived from thermodynamic arguments assuming random mixing at a segmental level.[12-14] If the mixing of both polymers is not random a single T_g will still appear unless phase separation occurs. Specific interactions between both components may introduce orientation factors, resulting in a deviation from random mixing. Therefore it is very useful to compare the experimental blend T_g's with the theoretical curves in order to infer the presence of interaction between the components.

From the present results it is clear that the glass transition temperatures of i-PS/PPO blends fall below the theoretical curve resulting from eq 1. These results are in very good agreement with the previous ones obtained by Neira-Lemos[4] on the same kinds of blends prepared by the same procedures described in section 2. However, it is worth noting that the preparation procedure of the blends is a very important factor to be considered when comparing results from different authors. It was shown,[8] for example, that samples obtained by freeze-drying display three different T_g's at low i-PS concentrations unless they are previously annealed at 260 °C. Sample preparation and post thermal treatment may modify the degree of mixing, causing apparent discrepancies between results from different laboratories.

The low T_g values obtained for i-PS/PPO blends compared to the predicted ones (see Figure 1) are very likely due to a specific interaction between PS and PPO. As a matter of fact, a negative enthalpy of mixing for a-PS/PPO liquid blends as a function of composition was reported by Weeks, Karasz, and MacKnight,[7] suggesting the presence of a specific interaction between both polymers. The negative value of the heat of mixing is in accordance with evidence for phenyl group coupling presented by other authors.[16,17] This interaction could be the cause of the nonrandom mixing in our blends. It seems reasonable to assume that when the intimate mixing takes place, i-PS molecules are more mobile than PPO due to the very low T_g of pure i-PS and they are then driven by the interaction force to surround PPO monomer units. The presence of a high number of i-PS monomer units neighboring PPO monomer units as compared to random mixing would explain the observed depression of the T_g experimental values. On the other hand, a single T_g should still be expected, as is in fact confirmed by experiments.

Although we did not obtain results for blends of i-PS concentrations below 50%, it is worth noting Neira-Lemos[4] obtained a better fit with the Fox equation[14] for blends of high PPO content. This could be related to the composition dependence of the interaction parameter which seems to decrease with increasing PPO content, as will be shown in section 5.3. The better fit with eq 1 would suggest that the mixing is nearly random (absence of specific interaction) for this range of compositions.

5.2. Melting Behavior. From the theory of polymer crystallization one expects a linear relation when plotting T_m vs. T_c, corresponding to the equation[18]

$$T_m = T_m^\circ(1 - 1/n) + T_c/n \qquad (2)$$

where T_m° is the equilibrium melting temperature and $n = l/l^*$ is the ratio of the lamellar thickness l to the thickness l^* of the critical nucleus at T_c. From our results it is clear that the linear relation predicted by eq 2 is obeyed by i-PS and i-PS/PPO blends, as is shown in Figure 5. Thickening of the lamellae with increasing crystallization temperature was also found by X-ray studies on i-PS.[8]

The original crystals formed at T_c undergo a reorganization during heating to form more stable structures. The melting of these more stable crystals corresponds to endotherm III. The identification of endotherm III with the melting of reorganized crystals follows from the influence of the heating rate on the relative intensities of endotherms II and III. At fast heating rates the original crystallites have a shorter time to reorganize, and hence the ratio of area III to area II is lowered, as illustrated in Figure 2. In addition, the total heat of fusion (II + III) is approximately independent of the heating rate. One also observes a shift of T_m(III) to lower values if the heating rate is increased, which is to be expected since crystals III are less perfect. Alternatively, stopping the scan at an intermediate temperature between peak II and peak III and scanning again after quenching results in the appearance of a single endotherm with an area nearly equal to the sum (II + III) of both areas appearing in the first scan. For all these reasons we conclude that crystals III result from a reorganization during scanning of crystals II. However, the nature of the reorganization taking place is not yet well understood although it is probably due to a secondary crystallization after the melting of the original crystals.[15] From Figure 4 it can be seen that the temperature T_r at which reorganization starts is around $T_r \leq 200$ °C, where T_r is taken as the onset of endotherm III. For crystallization temperatures $T_c \gtrsim T_r$ a single sharp endotherm appears, which very likely corresponds to the more stable and perfect crystals III and not the crystals II, which grow at $T_c < T_r$. This interpretation is supported by the findings of other authors[8] who argue that in the high crystallization temperature range ($T_c > 175$ °C) the end free energy σ_e decreases noticeably with increasing T_c but the lamellar thickness remains constant. However, at low cyrstallization temperatures σ_e does not change but the lamellar thickness increases systematically with T_c. It is very likely that for $T_c > 175$ °C some of the crystals present already belong to the second and more perfect crystal type III. The higher chain mobility at higher crystallization temperatures probably favors folding so that the surface of the crystals becomes more perfect, and hence the melting temperature increases despite the constancy of the lamellar thickness.[8]

Another interesting feature is that the higher the PPO content, the higher the melting temperature of the crystals at a given T_c. This phenomenon was also observed[19] for PVF$_2$/i-PEMA blends with composition of 95% PVF$_2$ as compared to pure PVF$_2$. In this case it was proved that the higher melting point of PVF$_2$ crystals in the blend results from thicker lamellae. However, Hammel, Karasz, and MacKnight[20] showed by X-ray analysis that in i-PS/PPO blends the lamellar thickness decreases with increasing PPO content.

Another feature is that the amount of reorganization is observed to be lower in the blends than in pure i-PS. One reason for this is that the viscosity of the amorphous phase surrounding the crystallites increases with increasing PPO content, reducing the rate of diffusion of chain segments and hence the rate of reorganization. A second possible cause for this phenomenon is that crystals originally grown in the blends are more stable than those in the pure i-PS; therefore they do not so easily undergo reorganization.

From the total heats of fusion shown in Table I one notices that the maximum crystallinity for all the samples is reached at crystallization temperatures $T_c = 175$ °C. This fact is in agreement with the observations of other authors who showed that the spherulitic growth rate is a maximum at 175 °C for pure i-PS as well as for i-PS/PPO blends.[8]

5.3. Equilibrium Melting Point Depression. The thermodynamic mixing of two polymers was treated by Scott[21] using the Flory-Huggins approximation.[5] It was later shown that if two polymers are compatible in the molten state, the same approximation can be used for the solid blend.[1,3] The melting point depression of the crystallizable polymer is then given by

$$\frac{1}{T_{mb}{}^{\circ}} - \frac{1}{T_m{}^{\circ}} = -\frac{RV_2}{\Delta H_f V_1}\left\{\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1 + \chi\phi_1{}^2\right\} \quad (3)$$

where V is the molar volume of the polymer repeat unit, ϕ is the volume fraction of the component in the blend, ΔH_f is the perfect crystal heat of fusion of the crystallizable polymer, m is the degree of polymerization, R is the universal gas constant, and $T_m{}^{\circ}$ and $T_{mb}{}^{\circ}$ are the equilibrium melting temperatures of the pure crystallizable component and of the blend, respectively. The interaction parameter between both components χ can be easily derived from eq 3 if one knows the equilibrium melting point depression for a given composition. The following parameter values have been used in our calculations:[22] $V_1 = 16.7$ cm^3/mol, $V_2 = 92.9$ cm^3/mol, and $\Delta H_f = 1.91$ kcal/mol. The densities of both polymers have been assumed equal to unity.

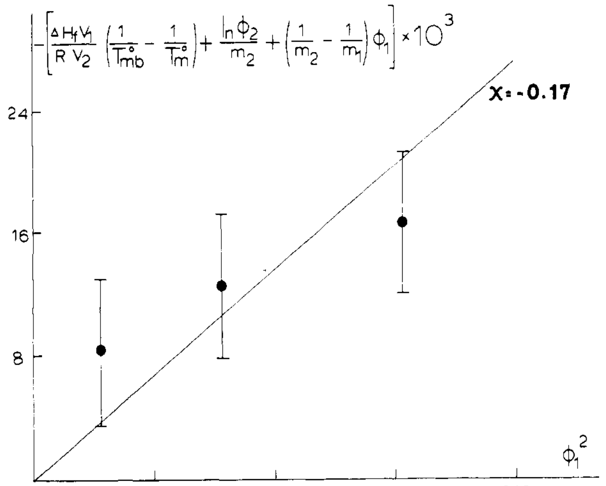

Figure 6. Plot of $\{(V_1\Delta H_f/RV_2)(1/T_{mb}{}^{\circ} - 1/T_m{}^{\circ}) + (\ln \phi_2)/m_2 - 1/m_2 - 1/m_1)\phi_1\}$ vs. $\phi_1{}^2$ for the melting point depression data obtained in i-PS/PPO blends.

In Figure 6 the plot $\{(V_1\Delta H_f/RV_2)(1/T_{mb}{}^{\circ} - 1/T_m{}^{\circ}) + (\ln \phi_2)/m_2 - (1/m_2 - 1/m_1)\phi_1\}$ vs. $\phi_1{}^2$(PPO) is shown, where the entropic contribution to the melting point depression has been subtracted using $\bar{M}_v$(PPO) = 2.3 × 10^4. Assuming the interaction parameter to be composition independent, such a plot must result in a straight line passing through the origin, the slope of which gives directly the χ value. From the present results (see Figure 6) one obtains an average interaction parameter value of $\chi = -0.17$ in i-PS/PPO blends. By an average χ value we mean the value that results from assuming χ to be constant. However, from the results in Figure 6, one could infer a certain composition dependence for the interaction parameter, i.e., a tendency to lower χ values for blends of higher PPO content. Other blend systems are known to have a concentration-dependent interaction parameter, and therefore a composition-dependent χ for i-PS/PPO blends is very likely. This is probably the reason for the small difference between our value of -0.17 and the value of -0.1 reported by Kambour et al.[24] In the latter case also a kind of composition average is obtained. However, a composition-dependent χ cannot be rigorously concluded from the present results due to the large error bars associated with the experimental equilibrium melting points.

The existence of an equilibrium melting point depression is in accordance with the negative heat of mixing for liquid a-PS/PPO blends reported in the literature. It is known that tacticity has an important influence on compatibility and hence the interaction between components of some polymeric blends such as poly(ethyl methacrylate)/poly(vinyl fluoride).[25] However, this kind of influence is not expected to be so significant in our case since PS/PPO blends have been shown to be compatible for the whole range of composition[4] whatever the tacticity of the polystyrene involved. Therefore, from the heat of mixing reported by Weeks, Karasz, and MacKnight, one can derive

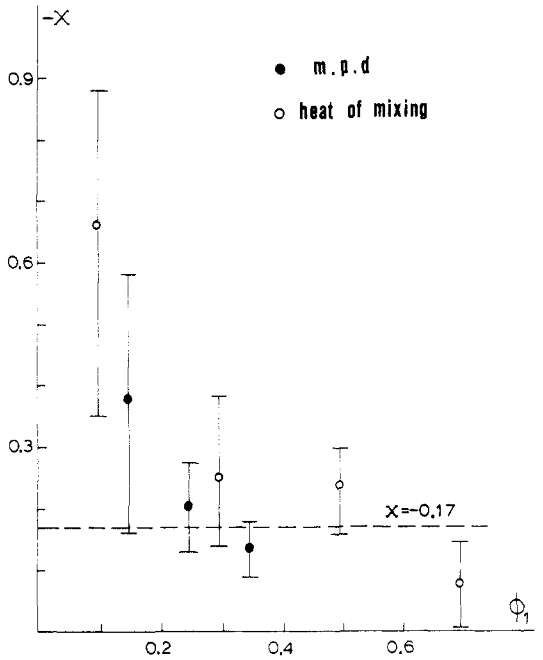

Figure 7. Plot of the interaction parameter values obtained from the melting point depression data of i-PS/PPO blends using eq 3 (●) and from the heat of mixing of a-PS/PPO liquid blends using eq 4 (○).

the corresponding interaction parameter χ assuming that χ is primarily enthalpic:[5]

$$\Delta H_m = RT\chi\phi_1\phi_2 \tag{4}$$

where ΔH_m represents the heat of mixing per mole of segments.

In Figure 7 the empty circles represent the χ values as a function of composition obtained from eq 4 for a-PS/PPO liquid blends. The filled circles represent the values that result from eq 3 using the equilibrium melting point depression data from our i-PS/PPO solid blends. One notices from Figure 7 that there is good agreement between both kinds of measurements. Moreover, the composition dependence of χ, which reaches values as low as -0.1 for high concentrations of PPO, is apparent from Figure 7.

The presence of a slight interaction between the components in blends of high concentrations of PPO (95%) was also detected by Runt[2] by melting point depression measurements. Runt avoided[2] the influence of kinetic factors by embedding i-PS single crystals in the blend matrix, obtaining a melting point depression of 4.8 °C, corresponding to an interaction parameter value of $\chi = -0.022$. There are several reasons that could explain the small χ value obtained by Runt compared to $\chi = -0.17$ derived in the present paper: (i) Runt is dealing with blends of extremely high PPO concentration. If the interaction parameter for this system is composition dependent as has been shown to be likely, the parameter χ could reach values as small as -0.022 on increasing PPO content. (ii) Runt prepared the blend by mixing i-PS single crystals with PPO in solution. The solvent (toluene) was then removed at room temperature under vacuum. With such a procedure solvent evaporation could leave a "free volume" in the dried material, lowering the degree of contact between PPO molecules and i-PS crystals, as compared to our samples, which were compression molded under pressure (10 000 psi) at high temperature before being isothermally crystallized from the melt. (iii) Runt is dealing with nonequilibrium melting temperatures.

It would be very interesting to find a way to apply the procedure of Runt to blends of higher i-PS concentration in order to test the composition dependence of χ.

6. Conclusions

Melting point depression studies are not expected to be very accurate for evaluating the interaction parameter of polymeric blends where one of the components crystallizes only if it is present in high concentrations, as is the case with i-PS/PPO. For such high concentrations of crystallizable polymer and reasonable χ values, very small melting point depressions are predicted by eq 3. Moreover, the use of the Hoffman–Weeks plots for evaluating χ has the disadvantage of neglecting the possible influence of temperature on the interaction parameter.

Despite these sources of error, it is clear from the present study that an equilibrium melting point depression of up to 4 °C is found in our blends, corresponding to an interaction parameter value of $\chi \simeq -0.1$. On the other hand, one concludes by examining the composition dependence of the glass transition temperature that mixing between components occurs at a very intimate level but not in a random way, in accordance with the presence of specific interactions. Moreover, the presence of a specific interaction between components in i-PS/PPO blends is in agreement with the negative heat of mixing reported[7] for a-PS/PPO liquid blends and also with evidence for phenyl group coupling present by other authors.[16,17]

Reorganization of crystals during heating makes it difficult to obtain equilibrium melting points from DSC data.

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Registry No. iPS (homopolymer), 25086-18-4; PPO (SRU), 24938-67-8; PPO (homopolymer), 25134-01-4.

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