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# Polymer Blends Containing Isotactic Polystyrene: Thermal Behavior of Model Systems

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ABSTRACT: Model blends containing isotactic polystyrene were prepared by embedding i-PS single crystals in both compatible and incompatible polymer matrices. The melting point of the i-PS crystals was monitored for each blend system. Blends prepared with incompatible matrix polymers exhibited melting behavior significantly different from that of the pure i-PS crystals. This is interpreted in terms of the physical constants of the matrix polymers. Significant changes in $T_m$ were found to occur in the incompatible blends only when the matrix was glassy. Blends consisting of i-PS crystals with compatible polymer matrices exhibited, in general, somewhat larger $T_m$ depressions. Analysis of the depression of the $T_m$ via the Flory-Huggins treatment yielded values for the polymer-polymer interaction parameter. Considering both the physical nature of the matrix and finite molecular weight effects, it is concluded that the interaction parameter for the compatible systems studied is virtually zero.

## Introduction

A potentially powerful method for determining the interaction between component polymers in a compatible blend where one of the constituents is crystalline uses the experimentally determined melting point ($T_m$) depression. Unfortunately, there are a number of factors which can complicate this analysis. The lamellar thickness of the crystalline component may change on blending relative to the pure crystallizable polymer prepared under the same conditions. One therefore has the problem of separating $T_m$ changes due to variations in the crystal thickness from that resulting from surface interactions. A number of recent publications[1-7] have analyzed the $T_m$ depression in crystalline compatible blends in terms of diluent effects. However, only rarely have the authors directly monitored the lamellar thickness of the crystallizable polymer in the blend.[8] In most cases it has been assumed that this thickness remains invariant upon blending.

A more direct approach to determining polymer-polymer interactions by depression of $T_m$ would be to disperse single crystals of one polymer in a matrix of another appropriate polymer. This approach has been used for incompatible systems (polyethylene crystals dispersed in polystyrene, polybutadiene, and poly(1,4-dimethylphenylene oxide)) in which one would expect no $T_m$ depression (i.e., no significant interactions and certainly no lamellar thickness changes on blending).[9] Nevertheless, it was shown that the physical nature of the matrix changes the overall melting behavior of the polyethylene crystals. For normal sample sizes (~5-10 mg) it was shown that $T_m$ depressions of up to 5 °C can be obtained, depending on the nature of the incompatible matrix.

In this paper we report the results of an extension of this study of isotactic polystyrene (i-PS) crystals embedded in both incompatible and compatible polymer matrices. By maintaining constant lamellar thickness and from knowledge of the physical matrix effects for the incompatible systems, we have obtained estimates of the polymer-polymer interactions ($\chi$) between i-PS and the compatible matrix polymers.

## Experimental Section

The i-PS used in this study had $\bar{M}_w = 4.54 \times 10^5$ and $\bar{M}_n = 9.90 \times 10^4$ as determined by high-pressure size exclusion chromatography. Single crystals of this polymer were grown isothermally at 85 °C from dimethyl phthalate (DMP).[10] After the preparation was washed isothermally at the crystallization temperature with fresh DMP, it was cooled and toluene was exchanged for the mother liquor by centrifugation and decantation. The resulting toluene/crystal suspension was divided into several parts and each was further centrifuged to give a "sludge" which contained approximately 0.5-1% polymer crystals. A 10% solution of the appropriate matrix polymer in toluene was also prepared. Six different matrix polymers were studied. Three of these are considered to be compatible with i-PS: two different molecular weight atactic polystyrenes (a-PS)[11] and poly(2,6-dimethylphenylene oxide) (PPO).[12,13] *cis*-1,4-Polybutadiene (PB)[14], poly(methyl methacrylate) (PMMA),[14] and poly(vinyl methyl ether) (PVME)[15] were also used and are believed to be incompatible with i-PS at its melting point. The PB was obtained from B.F. Goodrich Co. (CB 220) and is reported to have a concentration greater than 98% cis-1,4 placements. The a-PS's were obtained from Pressure Chemical Co. and are reported to have narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \doteq 1.1$); the two samples used had molecular weights of $5 \times 10^4$ ($T_g = 100$ °C) and 2200 ($T_g = 54$ °C). PMMA was obtained from E. I. du Pont de Nemours and Co., Inc. (Lucite 147), PVME from Polysciences, Inc., and PPO from General Electric Co.

Equal volumes of the "sludge" and matrix polymer solution were mixed and a small quantity of the mixture (20 $\mu$L) was placed in aluminum pans. In order to ensure a random distribution of the i-PS cyrstals in a particular matrix, the solvent was removed rapidly at room temperature under vacuum and the samples were left under vacuum for at least 24 h. For mixtures containing glassy matrices (PPO, PMMA, a-PS), the samples were further placed under vacuum at 80 °C for at least 24 h to completely remove the solvent. The resulting "blends" therefore had a concentration of approximately 5-10% i-PS crystals in the various polymer matrices.

The melting behavior of all samples was determined with a Perkin-Elmer DSC-2 differential scanning calorimeter. Total sample sizes were approximately 1 mg (approximately 0.1 mg of i-PS) and all samples were run on a sensitivity of 0.2 (mcal/s)/10 in. Each blend was run a minimum of two times. Samples were initially heated from 80 to 230 °C at 20 °C/min, held at 230° C for 1 min, and cooled at 10 °C/min to 80 °C. They were then reheated at 20 °C/min. The reported melting points were determined by superimposing the leading edge of a calibration standard (indium) on the i-PS melting peak. The intersection of the indium leading edge with the constructed sample base line was designated as $T_m$. This value was also corrected for deviation of the indium from its reported melting point.

## Results and Discussion

The initial melting behavior of i-PS single crystals in the absence of any polymer matrix ("air") is shown in Figures 1 and 2. This dual melting behavior has been reported previously.[10,16] The first peak (lower $T_m$) has been shown to be indicative of the $T_m$ of the as-formed crystals ($T_{m_1}$). The second peak ($T_{m_2}$) is associated with the melting of

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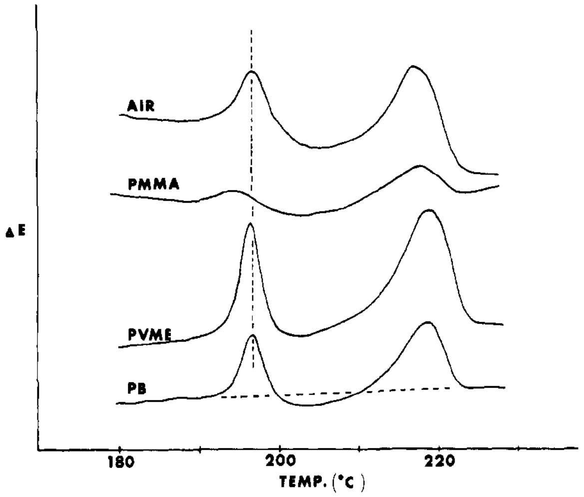

**Figure 1.** DSC traces of the initial melting of the i-PS crystals in the absence of matrix polymer (air) and of the incompatible model blends.

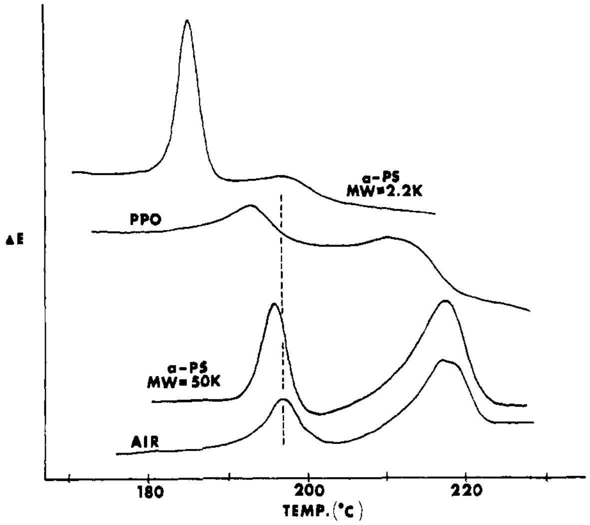

**Figure 2.** DSC traces of the initial melting of the i-PS crystals in the absence of matrix polymer (air) and of the compatible model blends.

material which has undergone annealing (lamellar thickening) while heating in the DSC-2. This latter assignment is also supported by the observation in some of our samples of an exotherm at a temperature between that of the first and second melting peaks (Figure 1). Close examination of the thermograms of the air sample (Figures 1 and 2) also suggests that the "second" peak is composed of two components ($T_m \doteq 217$ and 219 °C). We have used very small sample sizes (0.1 mg of i-PS) and, as such, expect better peak resolution[17–19] than is obtained for samples of the usual sizes (5–10 mg). These two components are not seen in the thermograms of the blends (Figures 1 and 2), presumably because the sample sizes are a factor of 10 larger (~0.1 mg of i-PS + ~0.9 mg of matrix polymer). In order to directly compare the blend and air samples, we will take $T_{m_2}$ of the air sample to be an average value of ca. 218 °C.

**1. Incompatible Blends.** Both PB and PMMA have been reported to be incompatible with high molecular weight polystyrene[14] and one initially would not expect a $T_m$ depression in the absence of morphological (lamellar thickness) changes. Our results substantiate this conclusion for the PB/i-PS blend system (Figure 1 and Table I) but the melting of the as-formed crystals in the PB/i-PS system (first peak) appears to be somewhat sharper than for the crystals in air (width at peak half-height approximately 30% less than that of the air sample). This is reminiscent of the differences reported for polyethylene (PE) between dry crystals and crystals maintained in suspension in a low molecular weight nonsolvent.[16–19] Furthermore, the same behavior is observed when PE crystals are embedded in PB.[9] PB will provide a more thermally conductive matrix than air and, as a consequence, one would expect to observe more clearly resolved or sharper melting endotherms.

Table I
Initial Melting Points of the Incompatible and Compatible Model Blends

| sample | $T_{m_1}$, °C (±0.4 °C) | $T_{m_2}$, °C (±0.4 °C) |
|---|---|---|
| i-PS | 196.7 | ~218 |
| PB/i-PS | 196.5 | 218.4 |
| PMMA/i-PS | 195.3 | 218.3 |
| PVME/i-PS | 196.2 | 218.6 |
| a-PS/i-PS (MW = 5 × 10$^4$) | 195.1 | 216.8 |
| a-PS/i-PS (MW = 2200) | 185.0 | 197.0 |
| PPO/i-PS | 191.9 | ~209.9 |

The PMMA/i-PS blend (Figure 1), although apparently incompatible, exhibits a $T_m$ (first peak) approximately 1 °C lower than that of the air sample. Like the case of PE crystals embedded in glassy matrices at room temperature,[9] this presumably arises from deformation of the crystals on sample preparation. When toluene is evaporated from the PMMA/i-PS blend, a glassy matrix is formed around the i-PS crystals as soon as the solvent concentration decreases sufficiently that the PMMA/toluene mixture has a $T_g$ of approximately room temperature. Continued loss of solvent will increase $T_g$ of the matrix and result in a volume contraction of the matrix. The magnitude of the resulting forces is presumably large enough to cause disruption of the i-PS crystals. Clearly, the nature of the matrix must be considered prior to any analysis of the $T_m$ depression and subsequent calculations of $\chi$.

PVME and polystyrene have been shown to be compatible at room temperature under certain preparation conditions.[15,20,21] However, this system has a lower critical solution temperature at ca. 120 °C; above this temperature these polymers are incompatible.[15] It is important to remember that in our case we are concerned with compatibility at ca. 200 °C (i.e., at the i-PS melting point) and PVME/i-PS would therefore be expected to be incompatible. Like the PB/i-PS blend, the first peak in the PVME/i-PS thermogram (Figure 1, Table I) is significantly narrower than that of the air sample. However, there is little change in the breadth of the remelting endotherm. Since PVME is rubbery at room temperature ($T_g$ = −29 °C), the matrix effects discussed above for PMMA/i-PS would presumably be absent from the PVME/i-PS system. One observes a small $T_m$ depression (0.5 °C) but this is within the error limits of the experiment.

**2. Compatible Blends.** Blends prepared from a-PS (MW = 5 × 10$^4$) show a depression of the melting point of 1.6 °C (Figure 2, Table I). However, one must consider that a-PS is a glass at room temperature and disruption of the crystals is possible upon evaporation of the solvent due to volume contraction of the matrix. The observed depression is almost identical with that found in PMMA/i-PS and we therefore believe that the $T_m$ decrease can be attributed primarily to disruption of the i-PS single crystals on sample preparation rather than surface inter-

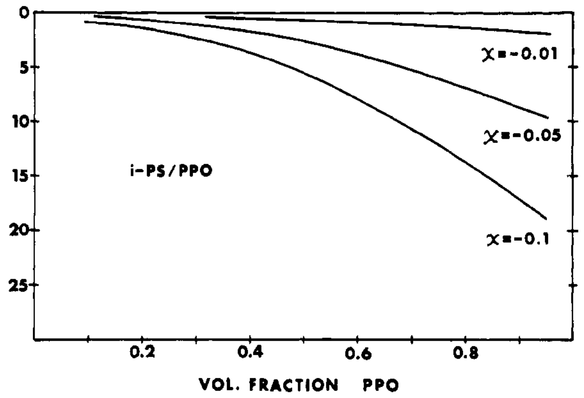

**Figure 3.** Plot of the predicted depression of the equilibrium $T_m$ of i-PS (from the Flory–Huggins treatment) as a function of the volume fraction of PPO in the blend.

actions. On the other hand, the overall melting behavior of the a-PS (MW = 2200)/i-PS blend is markedly different from that observed for the other systems (the ratio of the areas under the first and second peaks is considerably different from that of the other systems studied). In addition, the $T_m$ of the as-formed crystals (first peak) is 11.7 °C less than the corresponding endotherm of the air sample. This depression is larger than the effect of matrix contraction/crystal disruption alone and will be discussed more fully in the next section.

The final blend prepared, PPO/i-PS, is also well-known to be compatible.[12,13] Here again we see that the observed $T_m$ depression (first peak) is somewhat larger than what one would expect simply from crystal disruption (total $T_m$ depression $\doteq$ 4.8 °C). However, PPO possesses a relatively relatively high $T_g$ ($\doteq$209 °C) and $T_m$ ($\doteq$267 °C). If the first melting endotherm contains some contribution from reorganizational effects (i.e., if the peak is not due solely to the melting of the as-formed crystals), then the presence of rigid PPO around the crystals at $T_m$ could prevent lamellar thickening from taking place and result in a lowering of $T_{m_1}$.[9] Unfortunately, whether this endotherm is actually composed of the melting of annealed material along with the melting of the as-formed crystals is unknown at this time.

**3. Polymer–Polymer Interaction Parameter.** One method by which one can analyze the $T_m$ depression in a blend where one component is crystalline is by the simplified Flory–Huggins treatment.[22] Other more comprehensive relationships are available (e.g., Flory–Prigogine[23]) but these tend to be relatively intractable. According to the Flory–Huggins treatment, the equilibrium melting point of the crystalline material in the blend ($T_m'$) is related to the polymer–polymer interaction parameter ($\chi$) by the relation

$$\frac{1}{T_m'} - \frac{1}{T_m^\circ} = \frac{-R\bar{V}_2}{\Delta H_f^\circ \bar{V}_1}\left[\frac{\ln \phi_2}{M_2} + \left(\frac{1}{M_2} - \frac{1}{M_1}\right)\phi_1\right] + \frac{-R\bar{V}_2}{\Delta H_f^\circ \bar{V}_1}(\chi\phi_1^2) \quad (1)$$

where $\bar{V}$ is the molar volume of the polymer repeat unit, $\phi$ the volume fraction of the component in the blend, $\Delta H_f^\circ$ the perfect crystal heat of fusion of the crystallizable polymer, $M$ the degree of polymerization, $R$ the universal gas constant, and $T_m^\circ$ the equilibrium melting point of the pure crystallizable component. The subscripts 1 and 2 denote the amorphous and crystalline components, respectively. The first term on the right-hand side of eq 1 reflects the entropy of mixing contribution to the equilibrium melting point depression while the second term reflects the enthalpy of mixing contribution. For blends where both components are of high molecular weight the entropy term becomes negligible and the $T_m$ depression is then dependent primarily on $\chi$ and $\phi_1$.

Table II
Observed Melting Point Depression and Polymer–Polymer Interaction Parameter of the Compatible Model Blends

| sample | obsd $\Delta T_m$ | $(\Delta T_m)_S$ | $(\Delta T_m)_H$ | $\chi$ |
|---|---|---|---|---|
| a-PS/i-PS (MW = 50 000) | 1.6 | 0.9 | 0.7 | -0.003 |
| a-PS/i-PS (MW = 2200) | 11.7 | 11.2 | 0.5 | -0.002 |
| PPO/i-PS | 4.8 | 0.9 | 3.9 | -0.022 |

Figure 3 shows the expected change in the equilibrium melting point of i-PS ($T_m^\circ - T_m' = \Delta T_m^\circ$) as a function of the volume fraction of PPO for three values of $\chi$ (−0.01, −0.05, and −0.1). In the construction of these curves we have taken $\bar{V}_1$ = 116.7 cm³/mol, $\bar{V}_2$ = 92.9 cm³/mol, $\Delta H_f^\circ$ = 1.91 kcal/mol,[24] $T_m^\circ$ = 513 K (240 °C),[16,25] and $M_1$ and $M_2 = \infty$. Notice that at high volume fractions of PPO (remember than in our system $\phi_1 \doteq$ 0.9–0.95) and values of $\chi$ less than −0.01 the predicted depression (which we take to a first approximation as corresponding to the observed nonequilibrium $T_m$ depression) can be quite large. The curves for the other compatible i-PS blend systems are very similar to that shown in Figure 3.

Let us assume for the sake of argument that physical matrix effects are not sufficient to cause any changes in $T_m$. From the observed $T_m$ depression data for the blends which are known to be compatible with i-PS and the Flory–Huggins relationship one may derive values for $\chi$. However, for our samples, one must take into account the entropy of mixing contribution. For the a-PS (MW = 5 × 10⁴) blend over half of the observed depression of the melting point can be attributed to finite molecular weight ($(\Delta T_m)_S$). Determination of the $\chi$ from the remainder ($(\Delta T_m)_H$) yields a very small value (−0.003). For the PPO blends (taking $\bar{M}_w \doteq 46\,000$[4,26]) the entropy of mixing contribution is relatively smaller and a slightly larger value of $\chi$ is found (−0.022). The a-PS (MW = 2200)/i-PS system possesses the largest experimental $T_m$ depression but this can be attributed almost entirely to the entropy of mixing on melting. Therefore, for all the compatible blends studied, $\chi$ is quite small. In addition, both a-PS's and the PPO are glassy at room temperature and in light of earlier results (PMMA/i-PS blend and ref 9), we would expect some disruption of the i-PS crystals upon preparing the blend. We would therefore expect $\chi$ to be even greater than that reported in Table II, i.e., virtually zero.

## Remelts

Figures 4 and 5 show the thermograms of all blends after melting and subsequent cooling at 10 °C/min to 80 °C. The air sample recrystallizes on cooling and exhibits a $T_m$ of approximately 218 °C. The PMMA and PVME blends (incompatible) also show a recrystallization endotherm at approximately this temperature but these appear to be somewhat smaller. On the other hand, the PPO and a-PS blends (compatible) exhibit no discernible melting. We envision this situation as follows. Our blend samples as prepared are essentially two-phase systems. Above $T_m$, the i-PS will be molten but if the matrix polymer is incompatible with i-PS at these temperatures, a domain structure

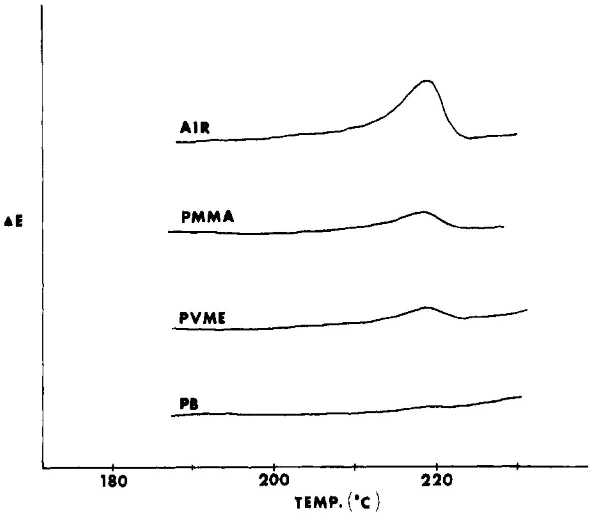

**Figure 4.** DSC traces of the remelting behavior of the i-PS crystals and the incompatible model blends.

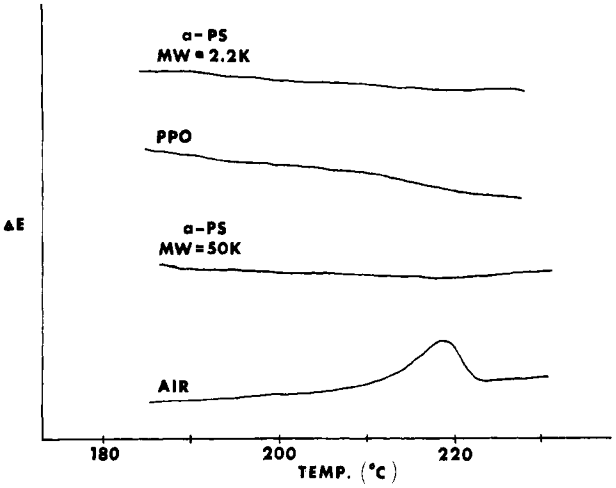

**Figure 5.** DSC traces of the remelting behavior of the i-PS crystals and the compatible model blends.

will still be present. Since the i-PS molecules will be in close proximity to each other, the chains may crystallize on cooling, provided the experimental cooling rate is not unduly high. The fact that the PVME/i-PS system exhibits a discerible recrystallization endotherm lends further support to the observation that this blend is incompatible at elevated temperatures. For the compatible systems, the i-PS (at temperatures greater than the melting point) apparently diffuses into the compatible matrix polymer. The time available for it to diffuse back and recrystallize is presumably insufficient under the conditions imposed in this study.

The observed remelting behavior for the PB/i-PS blend was unexpected; it is indicative of a compatible rather than an incompatible system. The explanation for this behavior is unclear. One possibility is that on heating to above $T_m$, the system passes through an upper critical solution temperature, rendering the polymers compatible at high temperatures.

## Conclusions

1. In the absence of any chemical interactions it is shown that the nature of the melting behavior of a crystalline polymer in an incompatible blend is affected by the physical constants of the matrix polymer. For the systems studied, a significant change in $T_m$ (at least 1 °C) occurs only in incompatible blends where the matrix is glassy in nature.

2. Model blends consisting of compatible polymer matrices have been used to obtain estimates of the polymer–polymer interaction parameter. Considering both the finite molecular weight of the constituent polymers and the physical nature of the matrix, $\chi$ is found to be nearly zero for the systems studied.

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