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# Crystallization, Thermal Behavior, and Compatibility in Isotactic Polystyrene / Poly(*o*-chlorostyreneco-*p*-chlorostyrene) Blends

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# **Synopsis**

The dependence of the kinetics of crystallization and melting behavior in isotactic polystyrene/poly-o-chlorostyrene-co-p-chlorostyrene (iPS/P(o-ClS-co-p-ClS) blends on temperature, thermal history, and blend composition has been investigated. The crystallization rate at a given temperature and copolymer composition decreases with increasing copolymer content in the blend when the samples are premelted. These effects can be ascribed to the reduction of mobility of the crystallizable chains due to the presence of the copolymer and to the decrease in the number of heterogenous iPS nuclei as a result of the premelting process. The Avrami exponent values and the analysis of the blend morphology indicate that the growth mechanism of the crystals is strongly influenced by thermal treatment. There is no measurable change in the melting temperature of iPS in the blends, with composition indicating that, on the basis of the Flory-Huggins approximation of the thermodynamics of polymer mixing, the net interaction parameter at the melting temperature is close to zero. From the comparison of the phase diagram for the isotactic polystyrene-containing blend with that of the atactic-containing blend, it can be concluded that in the amorphous state polystyrene with a regular configuration is slightly less compatible with the P(o-ClS-co-p-ClS) than is polystyrene with random configuration.

# INTRODUCTION

The system consisting of atactic polystyrene and random poly(o-chloro-styrene-co-p-chlorostyrene) has been extensively investigated.<sup>1-4</sup> In this system miscibility can be found for a range of copolymer compositions and molecular weights of aPS up to a maximum temperature, the lower critical solution temperature (LCST). Miscibility in these homopolymer/copolymer systems is due not to any specific interaction between the two polymers but rather to a repulsion between different monomer units of the copolymer.<sup>1</sup> When miscibility is depicted in a diagram of temperature versus copolymer composition (for 50:50 wt% blends), the regions of miscibility for blends containing polystyrenes of different molecular weights all show a maximum at the copolymer composition of 85 mol% o-chlorostyrene.

In this study we have examined the behavior of blends of isotactic polystyrene (iPS) with poly(o-chlorostyrene-co-p-chlorostyrene) containing 85 mol% o-chlorostyrene (COP85) under two different sets of thermal conditions.

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It is expected that the use of a polymer with regular configuration, e.g., iPS, in polymer blends can provide not only additional information about the polymer-polymer interaction but can also broaden and supplement our knowledge of individual polymers. In particular the aim of this study is to analyze the influence of blend composition and thermal history on crystallization, melting behavior, and compatibility in iPS/(COP85) blends.

# **EXPERIMENTAL**

# **Materials and Preparation of Blends**

The codes, sources, and molecular characteristics of the samples used in this study are listed in Table I. The aPS and COP85 were used as received, whereas the iPS was purified by dissolving in toluene followed by filtration and precipitation at room temperature into a large excess of methanol. As indicated in Table I, the weight average molecular weights of aPS and iPS are similar. The precipitated material was dried in a vacuum oven at 70°C for 3 days. The blends of iPS and COP85 were prepared by dissolving the appropriate weight fractions of the two polymers in toluene and coprecipitating in methanol. The materials were dried in vacuo at 70°C for 3 days.

#### **Calorimetric Measurements**

The kinetics of crystallization and the thermal properties of the homopolymers and of the blends were analyzed by differential scanning calorimetry using a Perkin-Elmer DSC-4 equipped with a thermal data station.

Before isothermal crystallization the samples were subjected to two different thermal treatments schematically illustrated in Figure 1. After drying at 70°C, the samples were directly heated to selected crystallization temperatures,  $T_c$ , ranging from 140 to 200°C (non-premelted samples); in the second case, the samples were first melted for 2 min at 250°C and then rapidly cooled in liquid nitrogen and held at -195°C for 3 min and finally annealed at the

TABLE I Characteristics of the Polymers Used			
	Isotactic polystyrene	Atactic polystyrene	Poly( <i>o</i> -chlorostyrene- co- <i>p</i> -chlorostyrene)
Code	iPS	aPS	COP85
Source	Polymer Laboratories, Ltd.	Pressure Chemical Co.	Polymer Laboratories, Ltd.
Molecular mass <sup>a</sup>			
<i>М</i> <sub>"</sub> ь	$3.3 \times 10^5$	$3.9  imes 10^5$	$8.0 \times 10^{4}$
$M_{\rm n}^{\rm "b}$	$7.3 \times 10^{4}$	$3.6  imes 10^5$	$5.2  imes 10^4$
Polydispersity	4.6	1.1	1.54
Percent isotacticity	> 95%	_	. —
Percent			
o-chlorostyrene	_	—	85 mol%

<sup>a</sup> Determined by GPC.

 $^{\rm b}$  Molecular masses of the iPS were measured after the purification process described in the experimental section.

## CRYSTALLIZATION IN BLENDS



Fig. 1. Schematic representation of the thermal treatments to which samples were subjected.

desired  $T_{\rm c}$  ("premelted samples"). The kinetics of crystallization were studied by measuring the heat evolved during the crystallization process as a function of time. The weight fraction  $X_{\rm t}$  of the material crystallized at time t was calculated from the ratio of the heat generated at that time and the total heat generated upon completion of crystallization.

After completion of the crystallization process, the samples were cooled to room temperature and then heated at  $10^{\circ}$ C/min both to determine the miscibility and to study the melting behavior of the blend as a function of thermal history.

From the DSC thermograms one or two glass relaxations were found depending on whether or not phase separation had taken place at the crystallization temperature. The observed calorimetric melting temperatures were obtained from the maxima of the endothermic peaks. The maximum peak temperature was considered to be the melting temperature  $(T_m)$ , because the accuracy of its determination is greater when multiple peaks are present and reorganization is taking place during scanning, as was the case for our samples.

#### **RESULTS AND DISCUSSION**

Typical crystallization isotherms, obtained by plotting  $X_t$  versus time, are shown in Figure 2 for pure iPS and for a 88/12 wt% iPS/COP85 blend crystallized at different  $T_c$  (premelted samples). From these curves the half time of crystallization  $\tau_{\frac{1}{2}}$ , defined as the time required for half of the final crystallinity to develop, was obtained.

Plots of  $\tau_{\frac{1}{2}}$  versus blend composition for different crystallization temperatures and thermal treatments are shown in Figure 3. From these figures it is clear that  $\tau_{\frac{1}{2}}$  is strongly dependent on the composition, crystallization temperature, and thermal history of material. In particular it can be noted:

1. For all samples the crystallization rate displays a maximum between 170 and 180°C, in agreement with results reported in the literature for pure iPS. $^{5-7}$ 

2. For a given  $T_c$ , the addition of the copolymer to the pure iPS causes a reduction in the overall rate of crystallization. The rate decreases with



# TIME (min)

Fig. 2. Crystallization isotherms of pure iPS and 88/12 wt% iPS/COP85 blend, crystallized at different  $T_c: \circ, T_c = 170^{\circ}$ C;  $\blacktriangle, T_c = 160^{\circ}$ C;  $\Box, T_c = 150^{\circ}$ C.

increasing COP85 content in the blend because of the reduction of mobility of the crystallizable chains due to the presence of the copolymer. In fact, the viscosity of the material surrounding the crystallites increases slightly with the increase of COP85 content, reducing the rate of diffusion of the macromolecules to the growing crystals and hence the overall rate of crystallization.

3. For the samples crystallized without prior melting, the crystallization rate at a given  $T_c$  and blend composition is approximately one order of magnitude higher than that of the samples crystallized after melting. Such a marked dependence on thermal history presumably arises from a variation in the number of preformed nuclei present before crystallization. An extensive study of the influence of thermal history on the nucleation density in isotactic polystyrene has been reported by Boon et al.,<sup>8</sup> who deduced that nucleation in iPS appears to be largely heterogeneous. They made a distinction between nuclei that continue to be present above the melting point ("resistant" nuclei) and those nuclei created by undercooling ("induced" nuclei). Heating the sample at  $T > T_m$  decreases the number of resistant nuclei and completely

# 2535 CRYSTALLIZATION IN BLENDS Non - premelted samples Premelted samples 2.0 .20 1/ <sub>7/12</sub> (min<sup>-1</sup> 1.5 0.1 05 0.5 Ø 150 170 190 200 200 160 180 150 160 170 180 190 T<sub>c</sub> ( °C )

Fig. 3. Half-time of crystallization  $\tau_{\frac{1}{2}}$  as a function of  $T_c$  for non-premelted and premelted samples at different blend compositions:  $\bigcirc$ , pure iPS;  $\blacktriangle$ , 88/12 wt%;  $\Box$ , 75/25 wt%;  $\blacklozenge$ , 50/50 wt%;  $\triangleright$ , 25/75 wt%;  $\triangleleft$ , 10/90 wt%.

destroys the induced nuclei which are again created by supercooling the sample in amounts depending on time and undercooling temperature.

Thus the lower crystallization rate observed for premelted samples is explained by assuming that melting at 250°C destroys the induced nuclei and some of the resistant nuclei. It is probable that cooling in liquid nitrogen for 3 min is not sufficiently long to permit the reformation of all the nuclei originally present in the samples.

The bulk kinetics of crystallization of iPS and its blends with COP85 were analyzed using the Avrami treatment<sup>9</sup> for the kinetics of phase change.

Avrami's equation is written

$$\log[-\log(1 - X_t)] = \frac{1}{2.3}\log K + n\log t$$
 (1)

where n, Avrami's exponent, and K, the kinetic rate constant, depend on the nucleation and growth mechanism of the crystals.

The experimental data appear to fit Avrami's equation. In fact, for any composition,  $T_c$ , and thermal treatment, plots of  $\log[-\log(1 - X_t)]$  versus  $\log t$  are linear except for long time periods when secondary crystallization takes place and for premelted samples at short time periods during which a different crystal growth mechanism may occur. The values of n determined from the slope of the above-mentioned straight lines, are about 3 and 2 for the premelted and non-premelted samples, respectively.

If the nucleation mechanism is heterogeneous, as discussed by Boon et al.,<sup>8</sup> then according to Avrami there is a three-dimensional growth of the crystals for premelted samples and a two-dimensional growth regime for the non-premelted samples.

Analysis of the morphology of the samples by optical microscopy shows that the premelted samples crystallize according to a spherulitic morphology. In non-premelted samples there are no resolvable spherulites, indicating that the density of nucleation for these samples is higher than that of the premelted samples. It should be noted that it was not possible to use electron microscopy to examine the crystals because of the very brittle nature of the non-premelted samples.

The dependence of n, morphology, and crystallization rate on thermal history allows us to formulate the hypothesis that the crystal growth process of iPS begins with the formation of lamellar quasi-two-dimensional crystals. Aggregates of these crystals subsequently develop rapidly into growing spherulites. Thus if the nucleation density is sufficiently high, as in the case of the non-premelted samples, the lamellar crystals are unable to develop into spherulites before termination of their growth due to impingment. Several examples in the literature regarding the occurrence of single-crystal lamellae in bulk polymers<sup>10-13</sup> provide further confirmation of this hypothesis. In particular, Keith,<sup>10</sup> using optical microscopy, has reported direct evidence for the growth of single crystals, lamellar in habit, with simple polyhedral outlines in thin films of isotactic polystyrene. Moreover, recently Bassett and Vaughan<sup>13</sup> have shown that spherulites of isotactic polystyrene, crystallized from the melt, have two dimensional, lamellar, sheaflike precursors. These lamellae grow into spherulites essentially by a splaying and branching mechanism.

#### **Glass Transition Temperature: Miscibility**

Except for the 88/12 wt% iPS/COP85 blend, the premelted blends always displayed two  $T_g$ 's after the crystallization protocols discussed above. This implies that the blends are phase separated around 250°C (i.e., they display an LCST). The samples may not have become rehomogenized upon reheating (see Fig. 1), because they were not heated to temperatures sufficiently higher than the  $T_g$ 's for those particular blends to allow rehomogenization to take place.

•

One or two  $T_{\rm g}$ 's are observed for the non-premelted samples depending on  $T_{\rm c}$ and composition. A phase diagram, Figure 4, was constructed using as a criterion of miscibility the presence of one or two  $T_{\rm g}$ 's in the thermograms. Also shown in Figure 4 is the phase diagram for the aPS/COP85 blends of nearly the same molecular weight components. Both systems display LCST behavior with a minimum at a blend composition of about 75 wt% copolymer. For the aPS/COP85 blends, the boundary between the one and two phase regions is 20–30°C lower than that of the system containing iPS. Therefore, these results indicate that in the amorphous state polystyrene with regular configuration is less miscible with COP85 than polystyrene with random configuration. However, it should be noted that the decrease in miscibility of

# CRYSTALLIZATION IN BLENDS

2537



Fig. 4. Phase diagrams for the aPS/COP85 blend  $(0, \bullet)$  and the iPS/COP85 blend  $(\Delta, \blacktriangle)$  in the amorphous state;  $0, \Delta$ , one phase;  $\bullet, \blacktriangle$ , two phases.

iPS/COP85 blends, compared with aPS/COP85, could also be due to the different molecular weight distributions of the isotactic and atactic polysty-renes.

# **Melting Behavior**

Figure 5 shows three endotherms typically observed for the isothermally crystallized pure iPS and iPS/COP85 blends. It has been suggested<sup>14-17</sup> that the peak occurring at the lowest temperature, labeled Peak I in Figure 5, is due to the melting of material crystallized by secondary crystallization. Peak II corresponds to the melting of crystallites formed at  $T_c$  by a primary crystallization process. The highest temperature peak, Peak III, is related to the melting of crystallites formed at  $T_c$  but which became reorganized during heating. The reorganization phenomenon has been attributed to melting followed by recrystallization.

It can be seen in Figure 5 that the ratio of Peak II to Peak III increases with increasing copolymer content in the blend and that the exotherm present between Peaks II and III seems to disappear as COP85 is added, to pure iPS, indicating that the degree of reorganization during scanning is lower in blends than in pure iPS. This result was also obtained by Plans, MacKnight, and Karasz<sup>17</sup> for iPS/PPO blends. We believe that this phenomenon can be attributed to the fact that the viscosity increases somewhat in the amorphous phase with increasing copolymer content and to the presence of entanglements between the two phases which reduce the diffusion rate of chain segments and hence the rate of reorganization.

The dependence of melting temperature  $(T_m)$  on  $T_c$  for iPS is illustrated in Figure 6. For pure iPS the melting peak occurring at the highest temperature,



Fig. 5. DSC thermograms for pure iPS and iPS/COP85 blends crystallized at  $T_c = 170$  °C. The heating rate was 10 °C/min.



Fig. 6. Observed calorimetric melting temperature  $T'_{\rm m}$  versus crystallization temperature  $T_{\rm c}$  for pure iPS. I, II, and III correspond to the endotherms accordingly labeled in Figure 5.

# CRYSTALLIZATION IN BLENDS

Peak III, remains constant with crystallization temperature, the temperature of Peak I is always about 10°C above  $T_{\rm c}$ , and the temperature of the intermediate peak increases with the increasing  $T_{\rm c}$ . The addition of COP85 to iPS does not influence  $T_{\rm m}$ .

Thermodynamic considerations predict that the chemical potential of a polymer will be decreased by the addition of a miscible diluent.<sup>18</sup> If the polymer is crystallizable, the decrease in chemical potential will result in a depression of the equilibrium melting point. Nishi and Wang<sup>19</sup> derived the relation for the melting point of a crystalline polymer in the presence of a polymeric diluent:

$$\frac{1}{T_{\rm m}} - \frac{1}{T_{\rm m}^0} = -\frac{R\overline{V}_{\rm c}}{\Delta H^0\overline{V}_{\rm a}}\chi V_{\rm a}^2 \tag{2}$$

where  $T_{\rm m}^0$  and  $T_{\rm m}$  are the equilibrium melting points of the pure crystallizable component and of the crystalline material in the blend, respectively,  $\Delta H^0$  is the heat of fusion of the crystallizable polymer, and  $\overline{V}_{\rm c}$  and  $V_{\rm a}$  are the molar volumes of the repeat units of the crystalline and amorphous material, respectively;  $V_{\rm a}$  is the volume fraction of the amorphous component in the blend, and  $\chi$  is the polymer-polymer interaction parameter.

On the basis of eq. (2), if favorable interactions occur between the two components, the equilibrium melting temperature of the crystallizable polymer in the blend should be lower than that of the pure polymer. In addition, the degree of the  $T_{\rm m}$  depression should depend on the magnitude of the polymer-polymer interaction and on the concentration of the crystallizable component in the blend.

As discussed above, the systems iPS/COP85 and aPS/COP85 may be compatible or phase separated depending on  $T_c$  and blend composition. The blends containing more than 12 wt% copolymer are essentially immiscible at the  $T_c$ 's examined. In this case it is expected that iPS molecules are surrounded by additional iPS molecules, and thus crystallization and melting are similar to that in the pure state. For the 88/12 wt% iPS/COP85 blend the phase diagram shows the least miscibility for all ranges of  $T_c$  studied. According to eq. (2), no decrease in the equilibrium melting temperature should be observed for this blend.

The equilibrium melting temperatures for pure iPS and for the 88/12 wt% iPS/COP85 blend were obtained using the Hoffman–Weeks equation:<sup>20</sup>

$$T'_{\rm m} = T_{\rm m} \left( 1 - \frac{1}{\gamma} \right) + \frac{T_{\rm c}}{\gamma}$$
 (3)

where  $\gamma = l/l^*$  is the ratio of the lamellar thickness l to the thickness  $l^*$  of the critical nucleus at  $T_c$ , and  $T'_m$  is the observed melting temperature of crystallites formed at  $T_c$  (Peak II). The equilibrium melting temperature  $T_m$  can be determined from a plot of  $T'_m$  versus  $T_c$ .  $T_m$  is the intercept of the extrapolated  $T'_m$ s with the line defined by  $T'_m = T_c$ .

The linear relation predicted by eq. (3) is obeyed by both pure iPS and the 88/12 wt% iPS/COP85 blend. A constant value of  $T_{\rm m}$  of  $238 \pm 2^{\circ}$ C is found

for the two systems. The constancy of  $T_{\rm m}$  may indicate that there is no specific interaction between the blend components, thus agreeing with the results reported for the blend containing aPS and COP85.<sup>3</sup> Miscibility in this blend occurs because of the so-called "repulsion effect" between the two different monomer units comprising the copolymer.<sup>1-3</sup>

It should be noted that the determination of the "true" crystalline melting points can be complicated by processes such as lamallar thickening which may occur during crystallization and thermal analysis and which can be influenced unpredictably by the presence of a noncrystallizable phase.<sup>21</sup>

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