Thermal transitions in cold-crystallized blends of isotactic and static polystyrene

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Solution-cast blends of isotactic and atactic polystyrene were stripped of casting solvent and heated above the glass transition temperature to temperatures below the equilibrium melting point of the respective blends to induce the development of crystallinity of the isotactic polystyrene. The samples, maintained at these crystallization temperatures for various times, were subsequently characterized by differential scanning calorimetry. The amount of crystallinity, the crystalline melting point, and the rate of crystallization were determined for each of the blends from the d.s.c. scans. The development of crystallinity, characterized by increased melting points, resulted from annealing at progressively higher temperatures. The maximum rate of crystallization for each of the blends was observed at a temperature corresponding closely to 8/9 of the absolute equilibrium melting temperature. The decrease in the melting point of the isotactic polymer, crystallized in the presence of atactic diluent, resulted primarily from weak enthalpic interactions between isotactic and atactic polystyrene homopolymers. Scanning electron photomicroscopy revealed that atactic-rich blends, immersed in n-hexane at $40°C$, developed a non-intercommunicating network of microvoids. Similar solvent treatment of isotactic rich blends had little effect on the samples. D.s.c. measurements confirmed recently published results which indicated that n-hexane, at modest temperatures, does not induce the development of crystallinity in isotactic polystyrene.

INTRODUCTION

There has not been significant growth in the commercial development of products based upon isotactic polystyrene, presumably because the isotactic polymer is relatively high-melting ($228°C$) and, therefore presents processing difficulties without offering significantly improved mechanical and optical properties. Similar considerations regarding processing difficulties limited the development of poly(phenylene oxide) homopolymers; however, blends of poly(phenylene oxide) with atactic polystyrene are essentially miscible and the glass transition temperatures of the blends are monotonically dependent on blend composition. There has been a great deal of fundamental and commercial interest in poly(phenylene oxide)—polystyrene blends since significant processing and, in turn, economic advantages accrue from blending the extremely tough poly(phenylene oxide) with the inexpensive, albeit compatible, polystyrene[1-3].

These considerations, regarding the potential utility of blending an intractable polymer with atactic polystyrene motivated the study of solvent removal and vapour sorption in blends of atactic and isotactic polystyrene[4]. Earlier studies had demonstrated that isotactic polystyrene crystallizes slowly from the melt upon cooling with the attendant development of spherulitic structure[5-7]. Overbergh, Berghman, and Smets[8,9] subsequently demonstrated that crystallinity is induced in isotactic polystyrene by swelling with either dichloromethane or acetone.

The work reported here represents an extension of the earlier study of the isotactic/atactic polystyrene blend system. This study emphasizes the effect of blend composition and thermal history on the rate and extent of crystallization of the isotactic polymer in solution cast blends of the tactic polymers. Whereas Kieth and Padden[5,6] used crystallization from the melt and Overbergh and coworkers[8,9] induced crystallinity by swelling with organic vapours, crystallization was induced in the blends by heating to temperatures between the glass transition and the crystalline melting point.

This work also includes a systematic description of the morphological changes induced in polystyrene blends by isothermal immersion of the blends in liquid n-hexane. The possible development of solvent craze resistance in isotactic polystyrene-containing blends[4] motivated an investigation of the relationship between crazing and crystallization in these tactic polystyrene blends.

EXPERIMENTAL

Materials

Atactic polystyrene ($\bar{M}_w$ = 207 000, Dow Chemical Company Midland, Michigan) and isotactic polystyrene
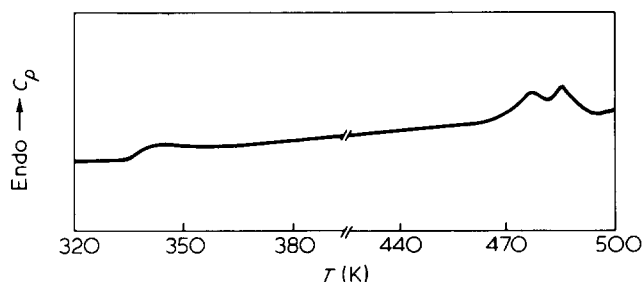
Figure 1 Typical differential scanning calorimetry thermogram for isothermally crystallized homopolymers and blends of isotactic polystyrene and atactic polystyrene

(M_w = 590 000, Arco Polymers Inc, Pittsburgh, Pennsylvania) were used as received to prepare the casting solutions. *o*-Chlorotoluene (b.p. 159°C, Carlo Erba, Milan, Italy) was selected as a suitable high boiling solvent to permit relatively rapid dissolution of the isotactic component of the blend at elevated temperatures. n-Hexane supplied by Carlo Erba S.p.A. (>99% molar purity) was used as received, as a swelling solvent for the cast films.

Apparatus and procedures

Film casting. Polystyrene films, containing either homopolymer or tactic blends, were cast from 10% solutions (w/v) onto glass plates at ambient temperature. The films were dried at room temperature for 48 h and subsequently stripped from the plate by immersion of the plate and film in water at room temperature. The films were then placed in a vacuum oven at 40°C for at least 1 month prior to calorimetric characterization. This protocol was imposed in an attempt to strip the last traces of casting solvent from the films without subjecting the films to temperatures which would permit the development of crystallinity in the isotactic-rich blends. Subsequent differential scanning calorimetric (d.s.c.) characterization of the as-cast and dried films was performed to determine whether the cast and dried films were indeed free of residual solvent. Moreover, these scans revealed that there was no evidence of crystallinity in the as-cast and dried films.

Thermally induced crystallization. Approximately 10 mg of polymer sample were placed in an hermetically sealed sample pan in a Perkin–Elmer DSC-2 differential scanning calorimeter. The sample was rapidly heated at a rate of 320°C/min to temperatures in the range 140–190°C to induce the development of crystallinity in samples which had not previously experienced temperatures in excess of the crystalline melting range. The samples were maintained at these crystallization temperatures for various times. Subsequent d.s.c. scans of these samples *in situ* were performed to determine the rates and extents of crystalline development in the various blend samples.

Solvent-induced morphological changes. Film samples were immersed in liquid-n-hexane at 40°C for times ranging from 20 min to 28 h. The films were subsequently placed in a vacuum oven for 1 month at 40°C to remove the imbibed swelling solvent. The development of solvent-induced crazing and the suspected development of solvent-induced crystallinity were investigated by scanning electron photomicroscopy and differential scanning calorimetry.

Differential scanning calorimetry. D.s.c. scans were performed at a heating rate of 20°C minute in the Perkin–

Elmer DSC-2 differential scanning calorimeter. Typical results are represented by the scan presented in *Figure 1*.

RESULTS AND DISCUSSIONS

Thermal transitions in the isotactic/atactic polystyrene blends and homopolymers were characterized by d.s.c. scans performed at 20°C/min. The scan presented in *Figure 1* for pure isotactic polystyrene exhibits the general features of the various scans. An inflection, characteristic of a glass transition, is apparent at 345K and a twin-peaked endotherm characteristic of complex melting accompanied by partial recrystallization is present over the temperature range 465 to 495K. The baseline-corrected areas under the melting peaks were used to estimate the percentage crystallinity in the various blends using the literature value of 19.9 cal/g for the enthalpy of fusion of 100% crystalline isotactic polystyrene[10]. This calculation implicitly includes the conservative assumption that the enthalpy of fusion is independent of lamellar thickness and, therefore, the recrystallization exotherm is cancelled quantitatively by the subsequent remelting of the recrystallized material.

Scans were run for several crystallization temperatures over the range 140° to 190°C for the pure isotactic and atactic homopolymers and for blends containing 90, 75, and 50% by wt of the isotactic polystyrene. The glass transition temperatures of the isotactic rich blends varied monotonically from 78°C for the pure homopolymer to 73°C for the 50% isotactic blend. These low values, and the slight superimposed endotherm in the glass transition region, suggest that trapped casting solvent in the blends depresses the measured T_g and is liberated at and slightly above the glass transition temperature. Repeated scans also exhibit a low T_g since the polymer was hermetically sealed in tightly fitting sample pans. An atactic sample, which was maintained under laboratory conditions for 1 year exhibited a glass transition of 83°C suggesting that most of the previously trapped casting solvent was liberated after long-time exposure to infinite sink conditions.

Interpretation of the scan in the crystalline melting region is not confounded by trapped solvent since the solvent would certainly be liberated during the protracted exposure (>6 min) to temperatures above T_g and below incipient melting. This assumption is confirmed by the d.s.c. scan for the atactic homopolymer which initially exhibited an anomalously low value of T_g; however, no detectable endotherm was apparent in the melting region.

The time dependence of the fractional crystallinity, developed at various crystallization temperatures, is plotted for the isotactic polystyrene homopolymer, and for blends containing 90, 75 and 50% isotactic polystyrene in *Figures 2–5*, respectively. For each of the blends, the rate of crystallization is maximized at temperatures in the range of 160–170°C. This result is readily apparent from the superimposed plots in *Figure 6* of reciprocal half-time for crystallinity development $(1/\tau_{1/2})$ *versus* crystallization temperature for the various blends. These results are quite similar to the observed maxima in spherulite growth rate observed by Keith and Padden[6] and Yeh and Lambert[7] for crystallization from the melt. The observed maximum results from the competition between nucleation rate and growth rate as supercooling is varied. The subtle variation in the temperature at which the maximum rate is observed is most likely a consequence of competitive homogeneous and heterogeneous nucleation, kinetic limitations on the fractionation of various
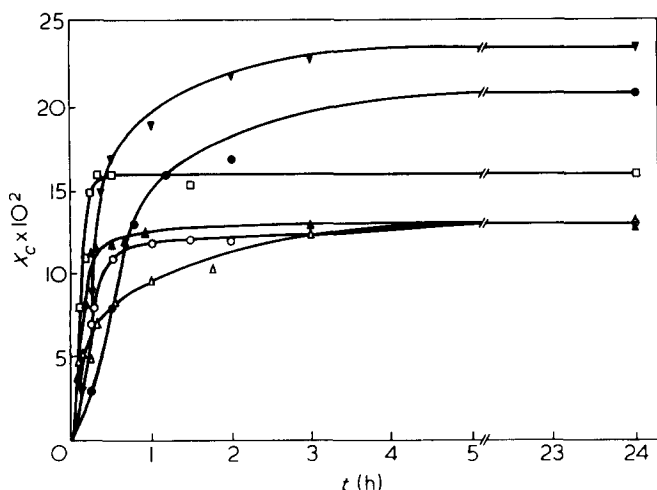
Figure 2 Effect of crystallization temperature on the crystallization kinetics of isotactic polystyrene homopolymer. ○, 413; △, 423; □, 433; ▲, 443; ▲, 453; ●, 463K
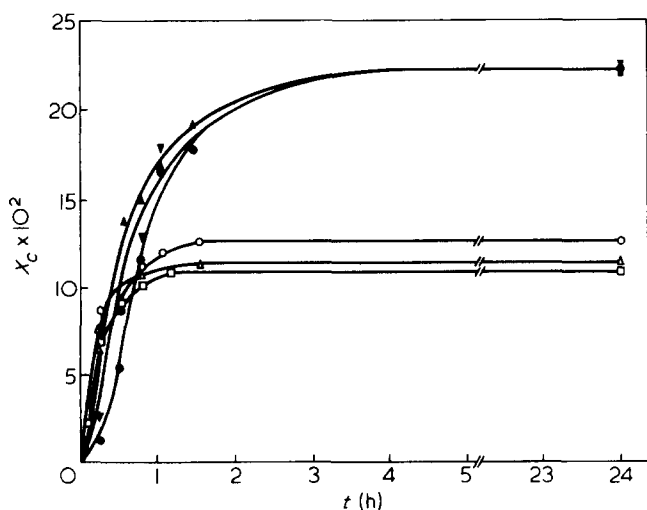

Figure 3 Effect of crystallization temperature on the crystallization kinetics of a 90% isotactic/10% atactic polystyrene blend. Key as in *Figure 2*
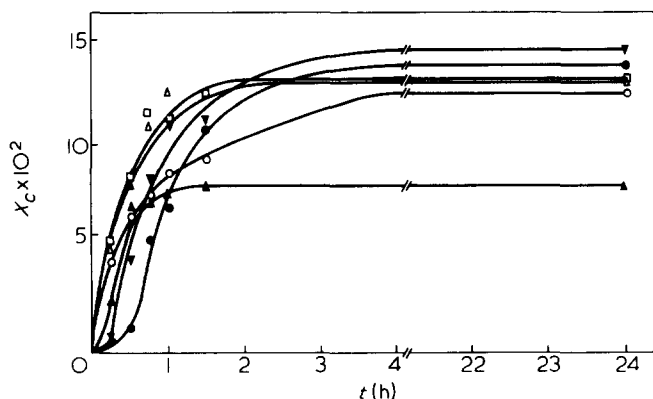

Figure 4 Effect of crystallization temperature on the crystallization kinetics of a 75% isotactic/25% atactic polystyrene blend. Key as in *Figure 2*

The melting points corresponding to both melting peaks are plotted *versus* crystallization temperature for the isotactic homopolymer and for the blends containing 90, 75 and 50% by wt of the isotactic polystyrene in *Figures 7–10*, respectively. For all compositions the peaks converge toward the single equilibrium melting point of the respective individual blend, suggesting more perfect crystalline development as the crystallization temperature is increased[12]. The intersection of the extrapolated lines correlating the individual melting peaks with the 45° line (corresponding to crystallization at the equilibrium melting temperature) provides a reasonable estimate of the equilibrium melting points of the various blends[12]. These values and the corresponding melting point depressions are presented in *Table 1*.

The monotonic decrease in melting point of the isotactic polymer with added atactic polymer suggests that the atactic polymer is acting simply as a compatible diluent for the crystallizable isotactic polymer. A quantitative analysis of this effect has been presented by Nishi and Wang[13] and later by Imken, Paul and Barlow[14], based upon the earlier treatment offered by Scott[15] based upon assumed Flory–Huggins behaviour[16]. The analysis begins by equating the chemical potentials of the crystalline polymer with the chemical potential of the crystallizable polymer which is diluted in the contiguous equilibrium amorphous melt by the atactic poly-
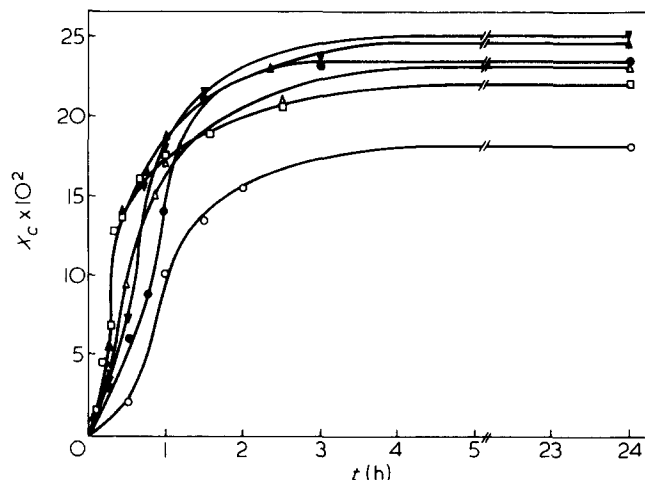

Figure 5 Effect of crystallization temperature on the crystallization kinetics of a 50% isotactic/50% atactic polystyrene blend. Key as in *Figure 2*
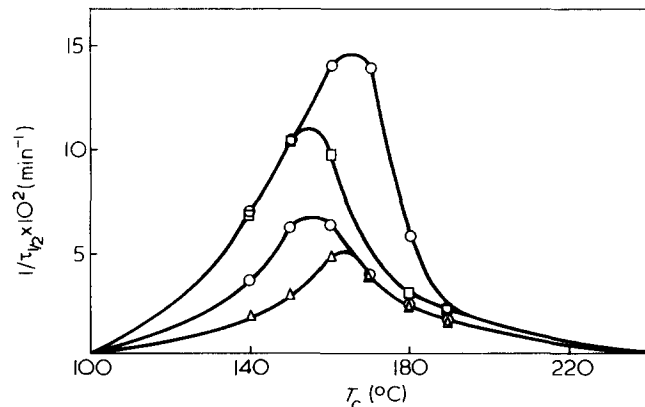

Figure 6 Effect of crystallization temperature on the reciprocal half-time for crystallization of isotactic/atactic polystyrene blends. ○, 100%; □, 90%; ●, 75%; △, 50% iso

molecular weight species of the isotactic polymer between the crystalline and amorphous phases, as well as systematic variations in the melting point of the blends with blend composition. In this regard, the maximum rate of crystallization corresponds rather closely to 8/9 of the absolute equilibrium melting temperature[11].
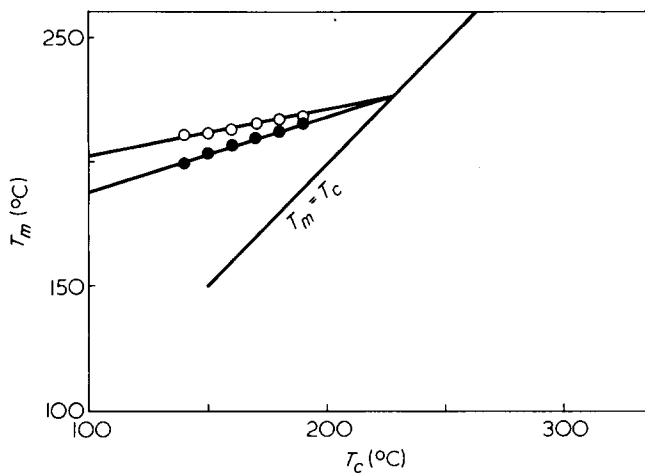
Figure 7 Effect of crystallization temperature on the peak temperatures of the melting recrystallization endotherm of isotactic polystyrene (100%)
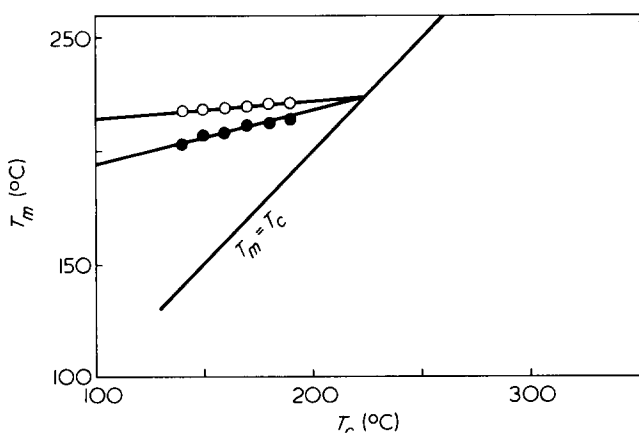

Figure 8 Effect of crystallization temperature on the peak temperatures of the melting–recrystallization endotherm of 90% isotactic/10% atactic polystyrene blends

mer. The treatment assumes that the chemical potential of the isotactic polymer in the liquid melt is described by the Flory–Huggins equation. The subscript 2 denotes the crystallizable isotactic component and the subscript 1 denotes the atactic polystyrene. The resulting relationship for the melting point depression making use of classical thermodynamic arguments[13-15] is given by equation (1):

$$\frac{1}{T_M^\infty} - \frac{1}{T_{M_0}^\infty} = \frac{-R}{V_{1u}} \frac{V_{2u}}{\Delta H_{2u}} \left[\frac{\ln \nu_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) \nu_1 + \chi_{12} \nu_1^2 \right] \quad (2)$$

where T_M^∞ is the equilibrium melting point of the blend, $T_{M_0}^\infty$ is the equilibrium melting point of the pure isotactic homopolymer, V_{1u} and V_{2u} are the molar volumes of the repeat units; m_1 and m_2 are the degrees of polymerization of the polymers comprising the blend; ν_1 and ν_2 are volume fractions of atactic and isotactic polymer in the melt; R is the gas constant and χ_{12} the polymer–polymer interaction parameter Since the degrees of polymerization, m_1 and m_2 are high, the first two terms in the brackets vanish in comparison with the third term involving the interaction para-

meter. This algebraic simplicliation is equivalent to describing the melting point depression entirely by enthalpic effects rather than the entropic effects described by the first two terms in brackets. This simplification leads to:

$$\frac{1}{T_m^\infty} - \frac{1}{T_{m_0}^\infty} = \frac{T_{m_0}^\infty - T_m^\infty}{T_{m_0}^\infty T_m^\infty} = -\frac{R}{V_{1u}} \left(\frac{V_{2u}}{\Delta H_{2u}} \right) \chi_{12} \nu_1^2 \quad (2)$$

Therefore

$$\Delta T_m = T_{m0}^\infty - T_m^\infty = \frac{-RT_{m_0}^\infty}{V_{1u}} \left(\frac{V_{2u}}{\Delta H_{2u}} \right) \chi_{12} T_m^\infty \nu_1^2 \quad (3)$$

As suggested by Imken et al.[14] a plot of ΔT_m versus ν_1^2 should be linear with an intercept at the origin if there are no entropic contributions to ΔT_m. The slope of a ΔT_m versus ν_1^2 plot is equal to

$$-\frac{RT_{m_0}^\infty}{V_{1u}} \left(\frac{V_{2u}}{\Delta H_{2u}} \right) \chi_{12} T_m^\infty$$

All of the component parameters of the slope are essentially constant except for the assumed constancy of χ_{12}. A plot of ΔT_m versus ν_1^2 is presented in *Figure 11*. The volume fractions were calculated from weight fractions, assuming addi-
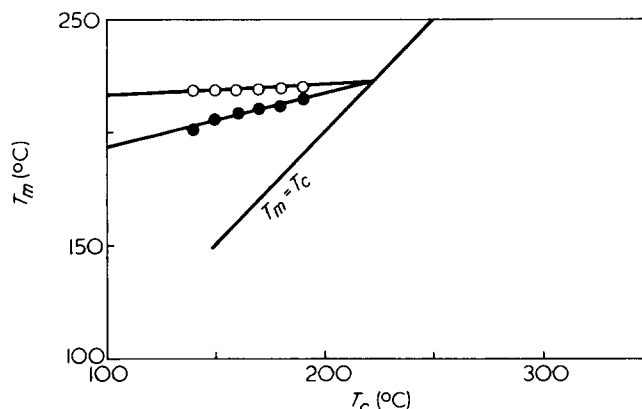

Figure 9 Effect of crystallization temperature on the peak temperatures of the melting–recrystallization endotherm of 75% isotactic/25% atactic polytyrene blends
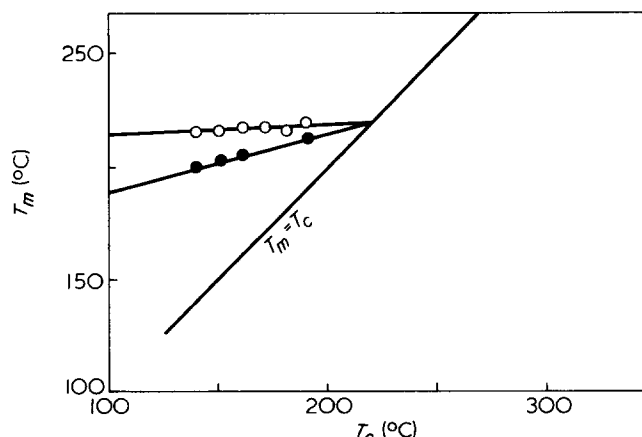

Figure 10 Effect of crystallization temperature on the peak temperatures of the melting–recrystallization endotherm of 50% isotactic/50% atactic polystyrene blends

Table 1 Melting point depression in isotactic/atactic polystyrene blends

| Weight fraction atactic polystyrene	Equilibrium melting point (°C)	Melting point depression (°C)
0.0	228	0
0.10	224	4
0.25	222	6
0.50	220	8
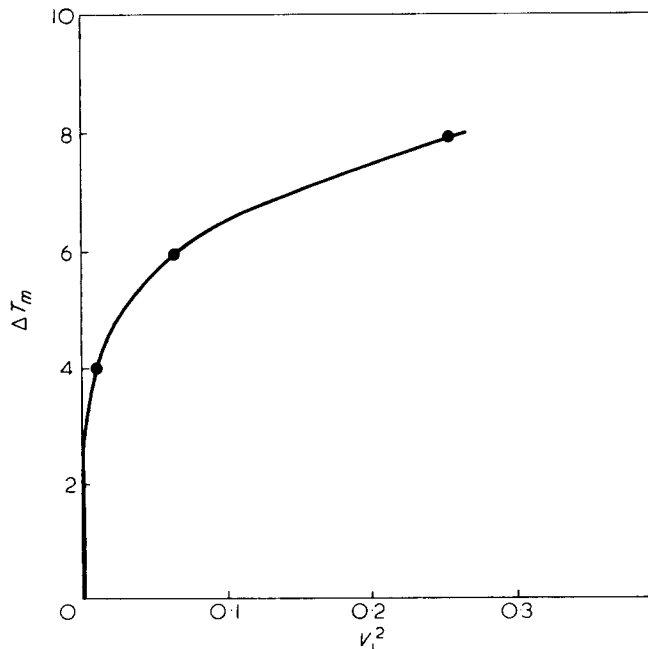
Figure 11 Composition dependence of the melting point depression of isotactic/atactic polystyrene blends

tivity of volumes using the density data for annealed films reported by Faulkner[6] and the maximum fractional crystallinity values presented here in *Figures 2–5*.

The large and positive melting point depression may be explained by a relatively strong exothermic interaction between the isotactic and atactic polymers upon mixing. The non-linearity of the plot may result either from a significant variation of χ_{12} with ν_1 or from non-compliance with the assumptions inherent in the construction of the Hoffman–Weeks plots[12].

The interaction parameters corresponding to the varying slope of *Figure 11* range from −0.04 at low atactic concentration to 0.4 over the concentration range $0.25 > \nu_1^2 > 0.05$. Although the algebraic sense of the concentration dependence of χ_{12} is reasonable, the magnitude of the melting point depression and the magnitude of the variation of χ_{12} are surprisingly large. These striking results might be explained by subtle steric effects which permit relatively strong π electron interactions between pendant phenyl groups upon blending the atactic and isotactic polymer. Although unexpected, these provocative results may relate to the disruption of chain coiling in the isotactic polymer resulting from mixing with the uncoiled atactic component of the blend. The coiling in the amorphous phase of the pure isotactic homopolymer may serve to preclude phenyl–phenyl interactions in the homopolymer which are subsequently facilitated in the lower density and, therefore, destructured blended amorphous phase.

The measured enthalpy of fusion is plotted *versus* crystallization temperature in *Figure 12* for the various blend compositions. This plot provides a useful summary of the effects of blend composition and crystallization temperature on the tendency of these blends to develop crystallinity under these conditions of cold crystallization. Alternatively, film samples of the blends were soaked in liquid n-hexane at 40°C for times sufficient to equilibrate the films with the n-hexane (24 h). After removal of the solvent by protracted evacuation at 40°C, the identical cold crystallization protocol was imposed upon the solvent-soaked samples and subsequently d.s.c. thermograms were obtained for the various samples. The results relating to development of crystallinity are summarized in *Figure 13*. There is no significant difference between the results summarized in *Figures 12* and *13* suggesting that no additional crystallinity, over and above the crystallinity induced thermally, is induced by the n-hexane. These results are consistent with the recently published conclusion of Overbergh and Berghmans indicating
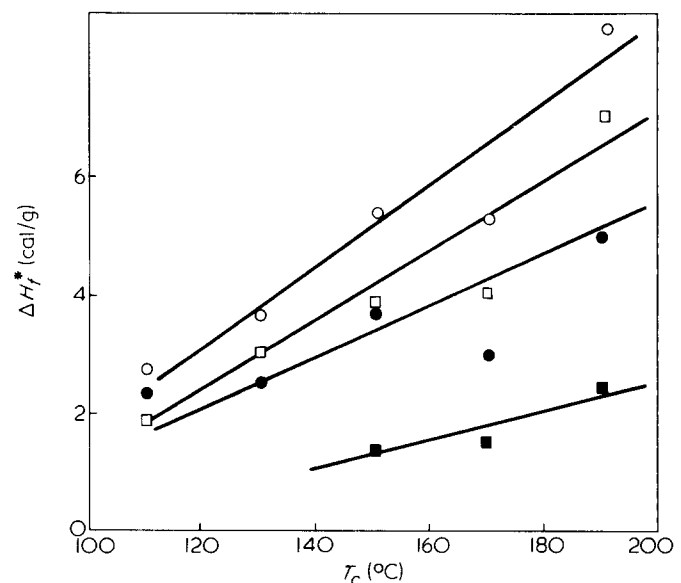
Figure 12 Effect of crystallization temperature on the enthalpy change associated with crystallization of isotactic/atactic polystyrene blends. ○, 100%; □, 75%; ●, 50%; ■, 25%
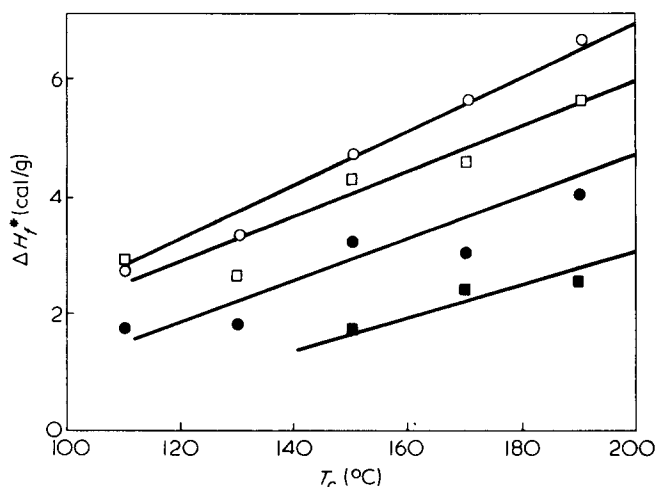
Figure 13 Effect of crystallization temperature on the enthalpy change associated with crystallization of n-hexane pretreated isotactic/atactic polystyrene blends. Key as *Figure 12*
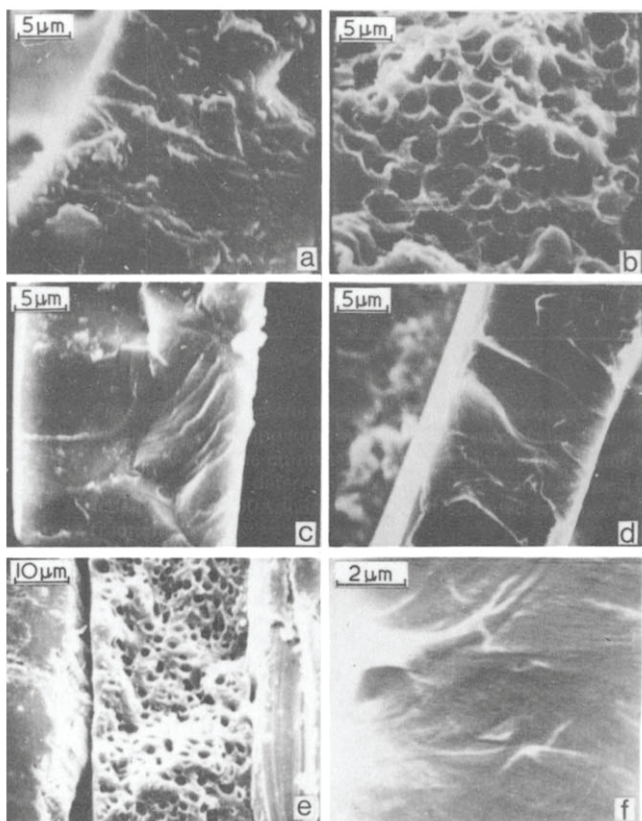
Figure 14 Scanning electron photomicrographs of cross-sections of n-hexane treated homopolymers and blends of isotactic and atactic polystyrene. (a) 100% atactic polystyrene, untreated, 1800X; (b) 100% atactic polystyrene, soaked 20 min in n-hexane at 40°C, 2200X; (c) 100% isotactic polystyrene, untreated, 2200X; (d) 100% isotactic polystyrene, soaked 20 min in n-hexane at 40°C, 2100X; (e) 25% isotactic polystyrene, soaked 20 min in n-hexane at 40°C, 1000X; (f) 75% isotactic polystyrene, soaked 20 min in n-hexane at 40°C, 1800X

that n-hexane at modest temperature does not induce crystallinity in isotactic polystyrene[9].

Crystallinity development induced by n-hexane immersion was suspected since the immersed and dried samples developed a white opalescence. Liquid nitrogen fractured films of untreated and n-hexane-immersed samples were viewed by scanning electron photomicroscopy under varying magnification. Scanning electron photomicrographs of the fracture surfaces are presented in *Figure 14* for the untreated and treated homopolymers as well as for treated intermediate

blends. The opalescence appears to be related to solvent-craze-induced development of non-intercommunicating microvoids in the atactic rich samples. There is no evidence for void development in the isotactic sample nor in the isotactic-rich specimen. These results suggest that inclusion of isotactic polystyrene in atactic-containing blends may significantly improve the resistance to solvent attack characteristic of the atactic homopolymer.

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