Tacticity Effects on Polymer Blend Miscibility

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ABSTRACT: The miscibility of amorphous, vinyl polymers depends upon the molecular weights and tacticities of the blend components. In this investigation blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) were studied. Three isotactic poly(vinyl methyl ether) (PVME) samples, synthesized in our laboratories, and one heterotactic PVME sample have been characterized by GPC, NMR, X-ray diffraction, and DSC. Atactic PS of three molecular weights were used. Cloud-point measurements were made with a light scattering apparatus. It was found that isotactic PVME is less miscible with atactic PS than heterotactic PVME.

Introduction

It has been shown by Challa and co-workers[1] that tacticity can have an effect on the phase diagram of a binary mixture. In work on poly(methyl methacrylate) (PMMA) of varying tacticities blended with poly(vinylidene fluoride) (PVF_2) it was concluded that the 5_1 helical form of isotactic PMMA (i-PMMA) interfered with specific interactions between the two blend components. Syndiotactic PMMA (s-PMMA) has a planar zigzag conformation. Prud'homme et al.[2] have also observed substantial tacticity effects in the system PMMA/poly(vinyl chloride) (PVC). In disubstituted vinyl polymers, such as PMMA, tacticity also has a large effect on the glass transition temperature (T_g). i-PMMA has a T_g of about 50 °C whereas s-PMMA has a T_g of about 130 °C.[1] For monosubstituted vinyl polymers such as poly(vinyl methyl ether) (PVME), tacticity does not significantly effect T_g.[3] Stereoregularity in the vinyl polymers affects the local conformation, which, in turn, affects specific group interactions with other constituent polymers and hence the miscibility. It is of interest to study systems of varying tacticity with similar thermal behavior (i.e., T_g) in order to distinguish the effect of tacticity on conformation and intermolecular interaction from that on more local segmental mobility (related to T_g).

There have been extensive studies in this and other laboratories of the system polystyrene/heterotactic poly(vinyl methyl ether) (PS/h-PVME) where the observation of the cloud point serves to conveniently define the limits of miscibility. Additionally, the system i-PVME shows a partial degree of crystallinity (usually less than 10% as polymerized). The material forms imperfect crystallites, which are detectable by X-ray diffraction and DSC analysis.

A preliminary study of the miscibility of the i-PVME/PS system was undertaken by Bank et al.[4] Bank and coworkers studied high molecular weight i-PVME (6.5×10^5), which had a relatively low degree of isotacticity. They found that this material showed some degree of miscibility with polystyrene. The phase behavior of the heterotactic system exhibits a LCST. The phase diagrams for the low molecular weight isotactic and heterotactic materials occur at convenient temperatures for study.

Experimental Section

Sample Identification. PVME samples are identified by "i" or "h" followed by the molecular weight in thousands; e.g., i40 is a predominantly isotactic PVME of weight average molecular weight 40 000 and h99 refers to a predominantly heterotactic PVME of 99 000 molecular weight. Blends are identified by the PVME component followed by the PS molecular weight; e.g., i40/214 is a blend of i40 with a PS of molecular weight 214 000. Molecular weights of all polymers are reported as measured by GPC in terms of polystyrene standards. A Mark–Houwink analysis of the isotactic and heterotactic PVME indicated that this led to errors in the molecular weight of less than 5%, which is within the accuracy of the measured values.

Synthesis of i-PVME. Isotactic poly(vinyl methyl ether) was produced by homogeneous cationic polymerization using $BF_3{\cdot}O(C_2H_5)_2$ as catalyst.[5] The polarity of the solvent and temperature of polymerization were used to manipulate the tacticity via the degree of association of the reactive ionic end groups.[6]

Sample Preparation by the Amherst Group. PVME sample i89 was prepared by cationic polymerization of vinyl methyl ether (Matheson Gas) at −78 °C under nitrogen using a 43:57 hexane/chloroform mixture as solvent (solvents were distilled over CaH_2; monomer was dried over CaH_2 and distilled into the reaction vessel). The concentration of $BF_3{\cdot}O(Et)_2$ was 7.7 mmol/L. Polymerization proceeded for 2 h, by which time gelation had occurred. The reaction was terminated by using ammoniated methanol. The product was dried in a rotovac and stored at room temperature under vacuum for at least 3 days. i89 was purified by fractionation using toluene as a solvent and heptane as a nonsolvent.

PVME sample h99 was purchased from Scientific Polymer Products, Inc., and fractionated by using toluene as a solvent and heptane as a nonsolvent. This treatment removed the heat stabilizer present in the commercial material and narrowed the molecular weight distribution.

Sample Preparation by the Kyoto Group. PVME samples i40 and i32 were prepared by cationic polymerization at −78 °C under high vacuum using toluene as a solvent. The solvent was washed with concentrated H_2SO_4, a 10% aqueous solution of NaOH, and distilled water in that order, dried with CaH_2, distilled under atmospheric pressure, and sealed in vacuo. The concentration of $BF_3{\cdot}O(Et)_2$ was 10 mmol/L for i32 and 2 mmol/L for i40. Gelling of the polymerization mixture was observed for i32 and i40. The polymerization reaction was terminated with $NH_3/MeOH$. The polymerized products were precipitated by

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Table I
PVME Triad Tacticity (by Proton NMR)

		triad tacticities, %		
		isotactic	hetero-tactic	syndio-tactic
predominantly heterotactic (amorphous)	hAld	34	55	11
	h99	31	69	0
	i89	55	40	5
predominantly isotactic (crystalline)	i40	64	32	3
	i32	59	38	3

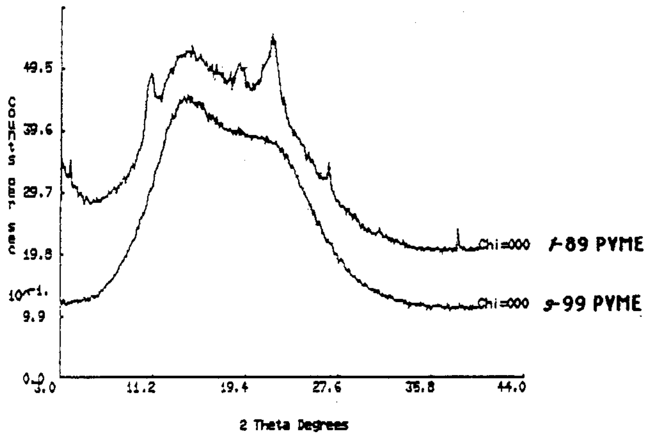

Figure 1. X-ray 2θ scan of isotactic (i89BF) and heterotactic (h99) PVME.

pouring the polymerization mixtures into a large quantity of petroleum ether. The precipitated polymers were vacuum dried. The appearances of the dried polymer samples were slightly turbid solids for i32 and i40.

The polystyrene used in blends h99/120 and i89/120 was purchased from Polymer Laboratories (Amherst, MA; $M_w = 1.20 \times 10^5$, $M_w/M_n = 1.03$). The PS of molecular weight 2.33×10^5 was also purchased from Polymer Laboratories ($M_w = 2.33 \times 10^5$, $M_w/M_n = 1.05$). The polystyrene used in blends i40/214 and i32/214 was anionically polymerized by using *sec*-BuLi in benzene ($M_w = 2.14 \times 10^5$, $M_w/M_n = 1.05$).

Test specimens of the PVME/PS mixtures were cast from toluene solutions at 30 °C and dried further in a vacuum oven at room temperature.

Results and Discussion

Characterization of i-PVME Samples. Triad tacticities were determined by proton NMR following the procedure of Dombroski.[7] The triad tacticities of the synthesized i-PVME samples and of the commercially purchased heterotactic PVME are presented in Table I. (The triad tacticity of PVME obtained from Aldrich Chemical (hAld), which was not used in this study due to its high polydispersity, is also included for comparison.) The NMR experiments were run at least three times for each sample. The reported tacticities were reproducible to ±1 of the indicated percentages.

Figure 1 shows X-ray 2θ scans for an isotactic (i89) and a heterotactic (h99) PVME sample.

Corradini and Bassi[8] have analyzed the rhombohedral crystalline structure of i-PVME using X-ray diffraction. The three strong crystalline peaks at $2\theta = 10.84$, 18.92, and 21.66° shown in Figure 1 correspond to diffraction layer spacings of 2.05, 2.35, and 4.08 Å, agreeing well with Corradini and Bassi's analysis.

Differential scanning calorimetry measurements were also made on several of the above samples. The corresponding glass transition and melting point data as well as the degree of crystallinity in the isotactic samples are presented in Table II.

It is of note that T_g is not significantly affected by the tacticity of the PVME sample in accord with the findings of Karasz and MacKnight.[3]

The literature gives contradictory values for the melting point of i-PVME. A value of 140–144 °C (determined by loss of birefringence) is reported by Vandenberg et al.[9] Vandenberg[10] later showed DTA plots, which indicate multiple melting points for i-PVME, one of which occurs at about 56 °C. Bank[4] reports a melting point for i-PVME (6.50×10^5 molecular weight and a low degree of isotacticity) at 63 °C. The observed melting points occurred between 35 and 80 °C depending on the crystallization conditions. Imperfect crystallites are probably present in these materials.

Phase Diagram for Polystyrene/Poly(vinyl methyl ether). The differences in the index of refraction for PS and PVME make possible an optical determination of the phase-separation point. When an initially clear film of a PS/PVME blend is heated to the phase-separation point, the film becomes opaque. This is termed the cloud point for the blend and has been related to the binodal line on the phase diagram. The location of the cloud-point curve is dependent on such factors as the molecular weight, the tacticity of the components, and the heating rate of the experiment, as well as the film thickness.[11] Figure 2 is a diagram of the cloud-point apparatus used by the Amherst group to determine the phase diagram for the PS/PVME blends. In this apparatus, the blend is cast on a glass slide. A laser beam passes through the film. If the blend is miscible, the light passes through the sample.

When the blend phase separates, domains of differing composition (and index of refraction) form. For thin films (10–15 μm) a scattering pattern resembling a halo is observed due to the presence of phase-separated domains. The characteristic size of these domains is related inversely to the radius of the halo. At early stages of phase separation, the domains are small and the halo is large. As phase ripening occurs, the domains become larger and the halo radius decreases. The cloud point pertains to early stages of phase separation and is thus studied at wide angles.

Heating rates of 10, 2, and 0.2 °C/min were used by the Amherst group, and the cloud point at zero heating rate, T_{CP}, was estimated from a plot of these three points.

The Kyoto group determined T_{CP} by measuring the scattering intensity $I(q,T)$ at $q = 5.0 \times 10^{-3}$ nm^{-1} with a photometer as described elsewhere[13] as a function of temperature, T. For this purpose the temperature is raised at a rate of 0.1 °C/min from a temperature well below T_{CP} to that above T_{CP}. At $T = T_{CP}$, $\mathrm{d}I(q,T)/\mathrm{d}T$ changes from approximately zero to a constant positive value. T_{CP} was determined as a temperature at which the two straight lines of $I(q,t)$ vs T for $T < T_{CP}$ and $T > T_{CP}$ intersect.

Figure 3 compares data obtained by the two techniques. The darkened points were obtained by the Amherst group using a slightly higher molecular weight polystyrene, and the open points were obtained by the Kyoto group. Near the critical composition (about 25% polystyrene) the two techniques agree fairly well.

The as-cast films from toluene solutions showed two general types of behavior.

(I) The blends with no crystallinity (heterotactic PVME) were homogeneous as cast (transparent) and became turbid as their temperature was raised through the cloud point (this behavior was reversible).

(II) For the blends of higher crystallinity (i32 and i40) the as-cast samples were turbid. Figure 4a shows the

Table II
Characterization of PVME Samples

		$M_w \times 10^{-3}$	M_w/M_n	T_g, °C	T_m, °C	crystallinity (by X-ray), %
predominantly heterotactic	h99	99	3	−22.3		0
	hAld	NM[a]	NM[a]	NM[a]		0
predominantly isotactic	i89	89	1.8	−22.3	35.5[b]	3.0[b]
	i40	40.2	1.6	−26.1[c]	54.3[c]	56.4[c]
	i32	31.9	1.6	−31.3	49.7	NM

[a] Not measured. [b] As polymerized. [c] Precipitated from toluene by addition of *n*-hexane and dried.

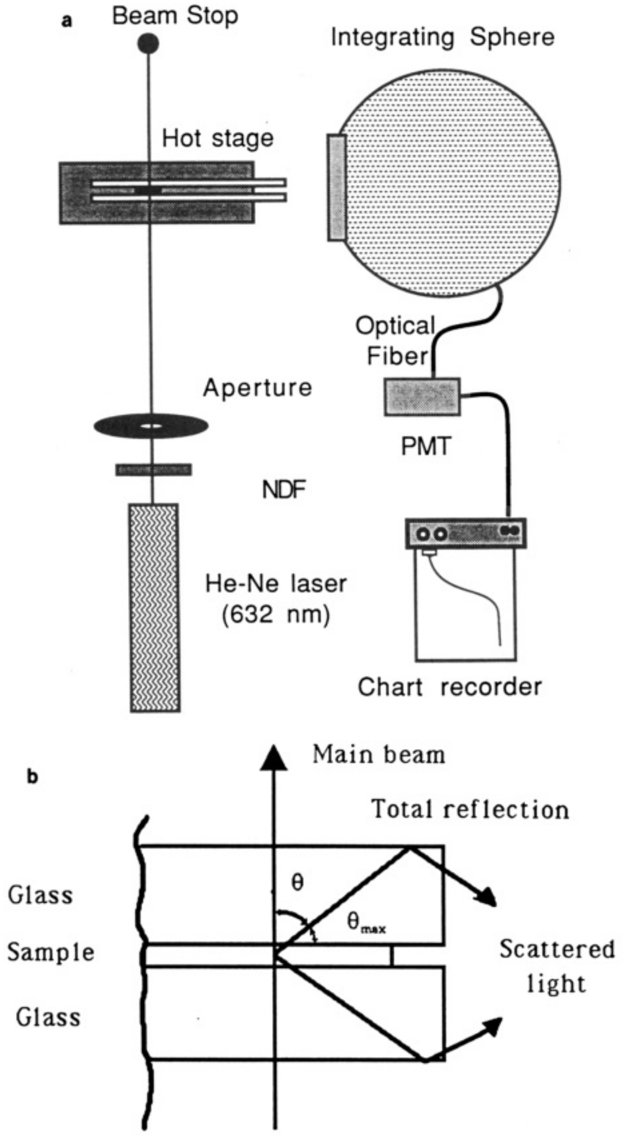

Figure 2. (a) Cloud-point apparatus used for i89/120, h99/120, i40/120, and i40/233 blends. (b) Expanded view of the cloud point apparatus.

change in turbidity as observed upon heating the as-cast film. Figure 4b presents a possible structural model for the turbidity behavior. In these cases the turbidity was observed to decrease initially with heating (Figure 4a). Initially the blends display crystallization-induced phase separation (A of Figure 4a,b), the phase-separated regions comprising crystalline PVME domains (D_{PVME}) in a homogeneous matrix of PS/PVME (M). At the melting point of the i-PVME the turbidity first decreases (B), followed by complete clearing (clearing temperature) at the glass transition temperature, $T_{g,cl}$ of the homogeneous matrix of PS/PVME. This is because above $T_{g,cl}$ the

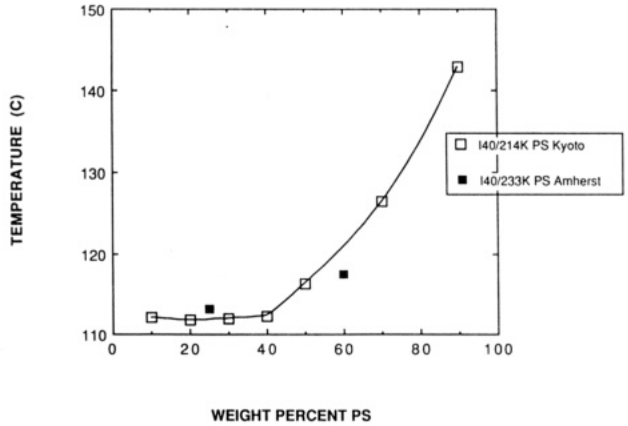

Figure 3. Comparison of cloud-point techniques: solid points, Amherst group; open points, Kyoto group.

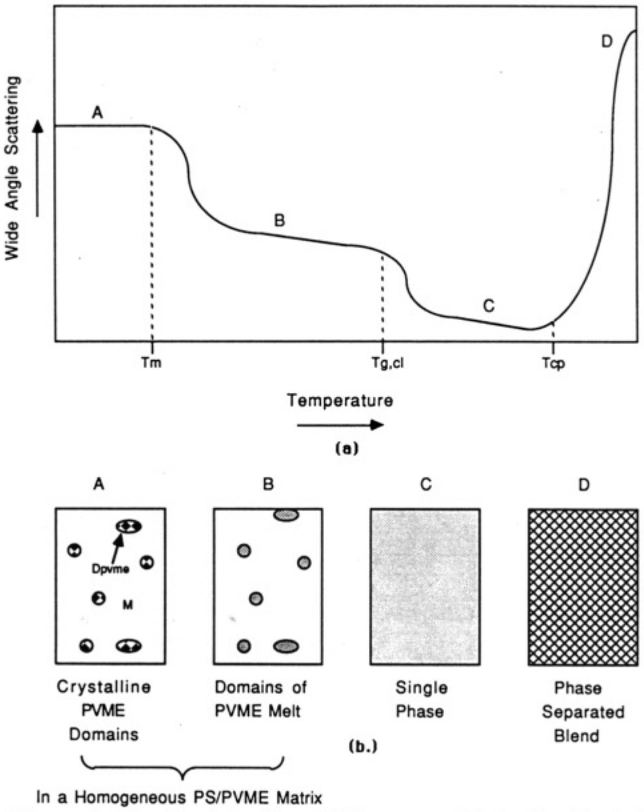

Figure 4. Clearing behavior of higher crystallinity blends. (a) Wide-angle scattering versus temperature. (b) Schematic of phase behavior.

blends can achieve thermodynamic equilibrium and can become truly homogeneous.

An example of type II blend behavior is shown in Figure 5. The clearing temperatures, $T_{g,cl}$, and T_{CP}'s for i40 are given as a function of the weight fraction of polystyrene. $T_{g,cl}$ for the mixture with $\phi_{PS} = 0$ corresponds to the melting

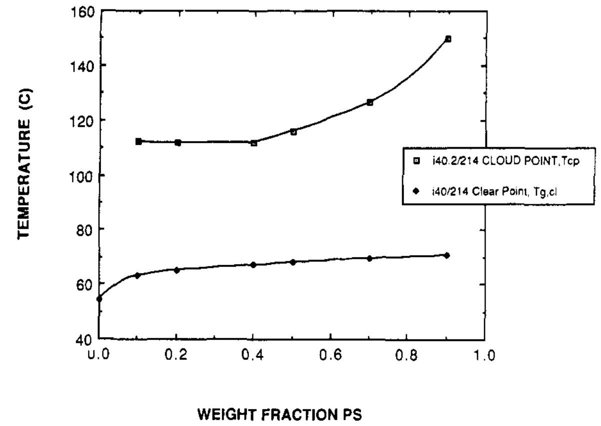

Figure 5. Clearing temperature ($T_{g,cl}$) and cloud points (T_{CP}) for blend i40/214 as a function of the volume fraction of PS.

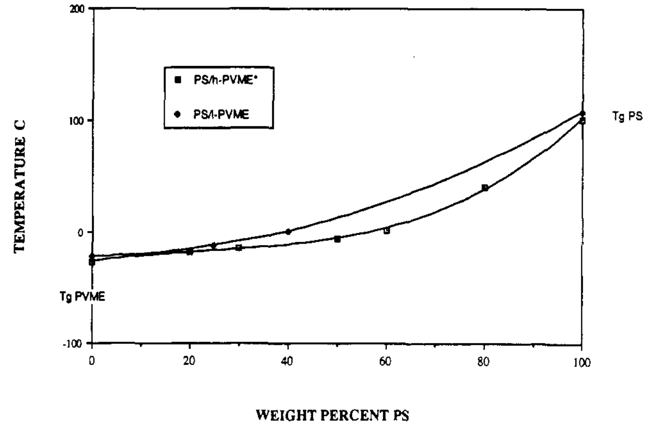

Figure 6. T_g versus weight percent PS for isotactic (solution-cast) and heterotactic (data from Yang et al., ref 12b, Table I) PVME/PS blends.

temperature of pure PVME (i40). It should be noted that this $T_{g,cl}$ depends on the crystallization conditions and therefore on the thermal history of the test specimens. The $T_{g,cl}$ should correspond to the glass transition temperature of the matrix phase, in the structure shown as B in Figure 4b, and should be different from T_g observed by lowering the temperature from the single-phase state below T_{CP} (C in Figure 4) because of the difference in composition. A reversible change in the turbidity associated with the cloud point, T_{CP}, was observed above $T_{g,cl}$ and is associated with the change of the structures between C and D of Figure 4. Upon rapidly lowering the temperature from the temperature below but close to T_{CP}, the miscible blend structure could be locked in below T_g without further crystallization. The T_g for the single-phase state may depend on tacticity[14] even under this situation. However, if we ignore a small variation of the T_g with tacticity of PVME, the T_g for the i89/120 blend may have a T_g similar to h99/120 reported in Table I of ref 12b (Yang et al.). Figure 6 shows a relationship between Yang's T_g for the heterotactic blend (h99/120) and the T_g for the isotactic blend (i89/120).

Figure 7 is the cloud-point curve (CPC) for the i89/120 and h99/120 blends. Both blends contain the same molecular weight PS but a different M_w for the two PVME's. In spite of the fact that the molecular weight of the PVME in h99/120 is higher than that for i89/120, the cloud-point curve for h99/120 is higher than that for i89/120, implying a tacticity effect. Thus the isotactic PVME is less miscible with PS than with the heterotactic PVME.

Figure 8 is the CPC for i40/214, i32/214, and h99/233 blends. The relation between the cloud-point curves for i32/214 and i40/214 may be explainable in terms of a combination of the molecular weight effect and the tacticity effect, since i32 and i40 have isotactic triad contents of 59 and 64%, respectively. If one considers purely molecular weight effects, h99/233 should be less miscible than i40/214. The opposite is observed, implying a tacticity effect.

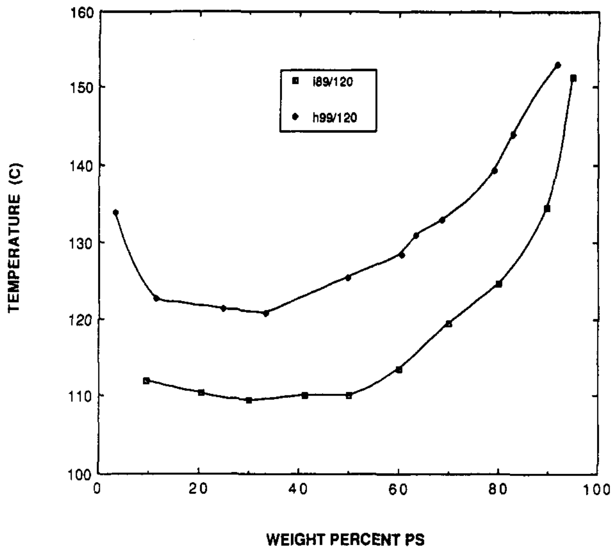

Figure 7. Cloud-point curves for i89/120 and h99/120 blends.

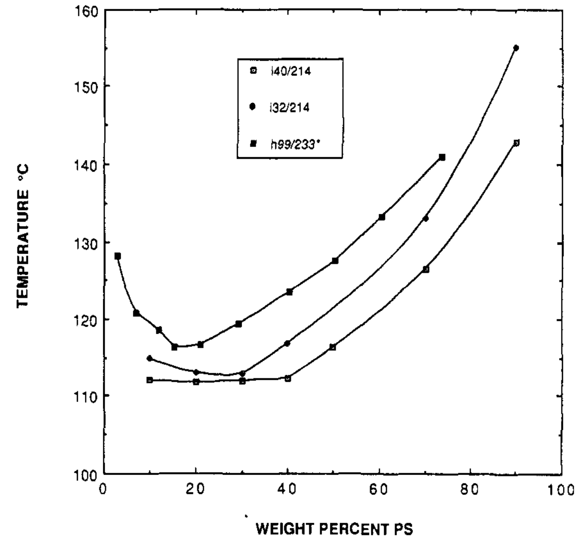

Figure 8. Cloud-point curves for i40/214, i32/214, and h99/233 (data of Yang[12a,b]) blends.

In all of the cases the CPC of the blend is lower than expected in the isotactic PVME samples. This conclusion becomes somewhat clearer after separating the molecular weight effect and the tacticity effect (see the analysis given in Figure 9).

Qualitative Analysis of the Tacticity Effect. We shall attempt to qualitatively separate the tacticity effect and the molecular weight effect on the cloud-point curves. The analysis is based on the following assumptions:

(i) The lowest cloud-point temperature gives the critical temperature, T_c.

(ii) The Flory–Huggins mean-field approximation will be used; i.e., we use the following equation for the χ parameter at the critical point, χ_c

$$2\chi_c = 1/(N_{w1}\phi_{1c}) + 1/(N_{w2}(1 - \phi_{1c})) \qquad (1)$$

where N_{w1} is the weight-average polymerization index for component 1 (PVME in this case) and ϕ_{1c} is the volume

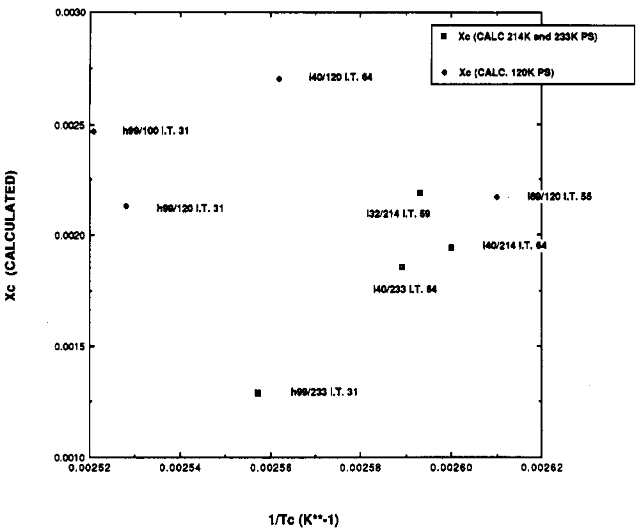

Figure 9. Calculated χ_c vs $1/T_c$ ($T_c = T_{CP}$ at $\phi_{PVME} = \phi_1 = 0.75$) for various molecular weight blends. Isotactic PVME triad tacticities are indicated by IT followed by a percentage.

Table III
$\chi_{c,calcd}$, T_c(measd), $1/T_c$(measd), and Percent Isotactic Triad Content for Various Blends

blend composition	$\chi_{c,calcd}$, ±0.000 05	T_c(measd), ±0.1 °C	$1/T_c$(measd), ±0.000 001 K^{-1}	isotactic triad content, %
i32/214	0.002 19	112.4	0.002 593	59
i40/214	0.001 94	111.4	0.002 600	64
i40/233	0.001 86	113.1	0.002 589	64
i40/120	0.002 70	117.2	0.002 562	64
i89/120	0.002 17	109.9	0.002 610	55
h99/100	0.002 47	123.4	0.002 521	31
h99/120	0.002 13	122.4	0.002 528	31
h99/233	0.001 29	117.9	0.002 527	31

fraction of component 1 for the critical mixture. Here, the correction for the difference in molar volumes of 1 and 2 was ignored in order to pursue qualitative analyses.

(iii) ϕ_{1c} cannot be evaluated by Flory–Huggins theory since the composition dependence of χ for i-PVME/PS is not known. ϕ_{1c} is taken as the value at which the cloud point becomes minimum. Thus, ϕ_{1c} is taken to have a value of 0.75 for all of the blends.

Table III gives the calculated χ_c values for the 11 blends studied, derived using eq 1. The weight-average degree of polymerizations are obtained by dividing the molecular weights by the corresponding monomer molecular weight, i.e., 58.08 for PVME and 104.16 for PS. The T_c values are the cloud-point temperatures at a 0.75 weight fraction for PVME (i.e., $T_c = T_{critical}$).

Figure 9 gives a plot of the calculated χ_c values versus the measured values of $1/T_c$ ($1/T_{CP}$ at a 0.75 weight fraction for PVME).

Blends of h99 (isotactic triad percentage, IT, of 31%) and i40 (IT = 64%) showed the expected decrease in χ_c with $1/T_{CP}$ (Figure 10). Blend i89 did not have sufficient data to determine this plot. With the estimated values for χ_c and the values of T_c obtained from the CPC's the values of the constants A and B in the empirical equation describing the temperature dependence of the Flory interaction parameter χ per monomer unit

$$\chi_c = A + B/T_c \tag{2}$$

can be estimated for the isotactic (i40) and heterotactic (h99) PVME blends. For the isotactic blends, i40, the estimated values are $A \cong 0.080$ and $B \cong -30$. For the heterotactic blends, h99, these parameters have estimated values $A \cong 0.078$ and $B \cong -30$ (see Figure 10). The slope of χ_c versus $1/T_c$, B, did not appear to significantly change within the accuracy of the calculation with a change in tacticity of 31–64%. The intercept did appear to show a significant shift.

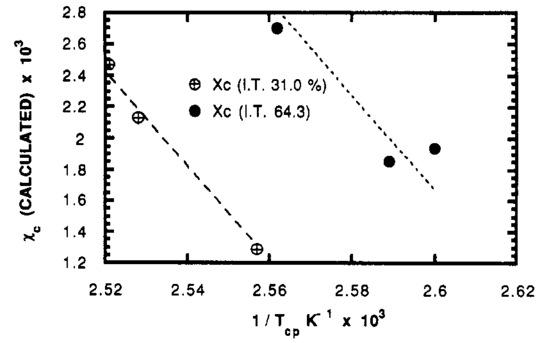

Figure 10. χ_c versus $1/T_{CP}$ (measured at 25% PS) for isotactic triad percentages (IT) of 31 (h99) and 64 (i40).

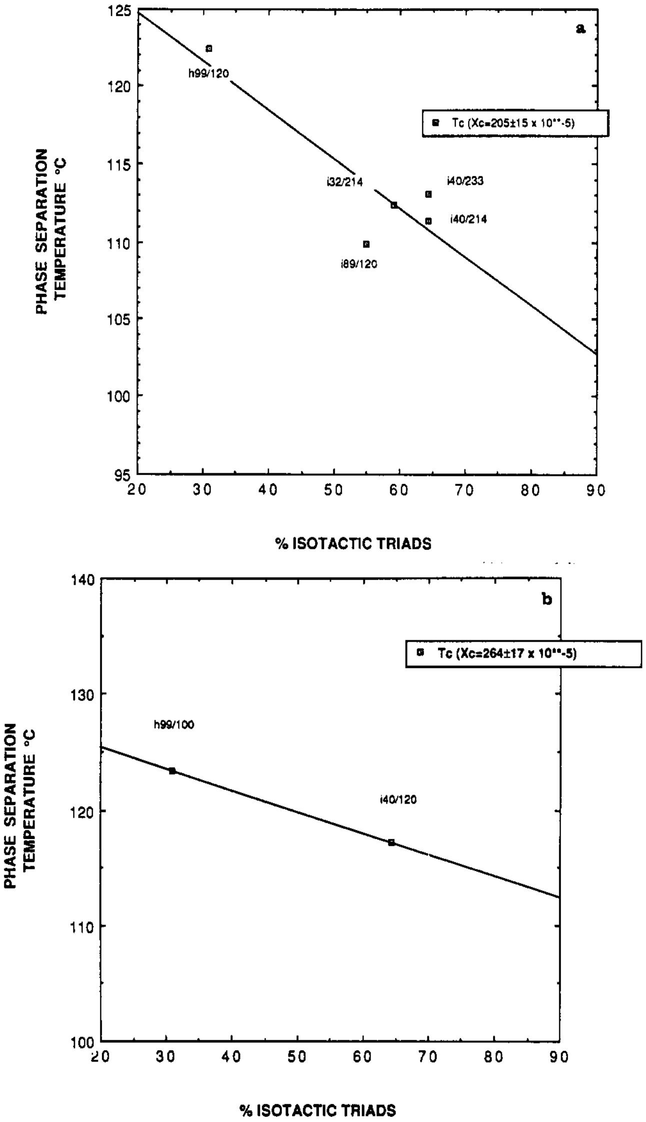

Figure 11. (a) Cloud-point for a 25% PS blend versus percent isotactic triad content of PVME for $\chi_{c,calcd} = 205 \times 10^{-5} \pm 15 \times 10^{-5}$. (b) Cloud-point for a 25% PS blend versus percent isotactic triad content of PVME for $\chi_{c,calcd} = 264 \times 10^{-5} \bullet 17 \times 10^{-5}$.

The data support the view that increasing isotacticity increases the χ values at a given temperature. Hence, at a given χ_s value, i.e., at a given set of molecular weights, the critical temperatures drop with increasing isotacticity. (An increased χ values decreases the miscibility and lowers the LCST curve.)

The tacticity effects are most clearly demonstrated by comparison of the T_c values between the h99/120 and i89/120 points of Figure 9, as they have equal χ_c values. The molecular weight effects are most clearly demonstrated by comparison of the i40/120 and i40/214 (or i40/233) points for the isotactic material and the h99/100, h99/120, and h99/233 points for the heterotactic material.

Parts a and b of Figure 11 show the effect of tacticity on the cloud point at 25% PS (approximately the critical composition) for blends of $\chi_{c,calcd} = 2.05 \times 10^{-3} \pm 1.5 \times 10^{-4}$ (a) and $\chi_{c,calcd} = 2.64 \times 10^{-3} \pm 1.7 \times 10^{-4}$ (b) (these results are determined from Table III or Figure 9). In both cases a negative slope is indicated, implying the tacticity effect. The slope appears to be about −0.18 °C/isotactic triad %. Thus a 10% change in tacticity would be expected to produce a shift in T_{CP} at 25% PS of about 2 °C.

The tacticity effect should be quantitatively investigated by measuring χ directly as a function of temperature. We plan to perform this experiment in the future by using neutron scattering. This point will be further clarified quantitatively on the basis of the copolymer effects.[15,16]

Conformational Effects in the PS/PVME Blend System. Short-range ordering of the isotactic sequences may have an effect on the phase behavior of the i-PVME/PS blend. Such correlations of molecular orientation (CMO) above the crystalline melting point have been postulated as an explanation for aberrant LCST behavior of polyolefins in concentrated solution.[17,18] Delmas explained the lower LCST for polyethylene (PE) when compared to polypropylene (PP) in concentrated solutions as due to short-range ordering, which can occur in PE above the crystalline melting point but not in PP. Copolymers of PP and PE show intermediate behavior.

Schurer, de Boer, and Challa[1] have noted that conformational differences between polymers of differing tacticities can have an impact on blend phase behavior. For the system PMMA/PVF_2, the 5_1 helical conformation of the isotactic PMMA may cause a steric interference to ester group interactions. Isotactic PVME occurs in a 3_1 helical conformation[19] with similar steric interferences to interactions for the methoxy group.

Conclusions

A shift in the phase diagram of PS/PVME blends is observed due to changes in the tacticity of PVME resulting in lower miscibility for more isotactic PVME. Additionally, solution-cast blends of lower molecular weight isotactic PVME show crystallization-induced phase separation below the CPC, and a clearing point is observed for these blends that seems to correspond to a crystalline melting point and/or a matrix phase glass transition. We have qualitatively separated the molecular weight and tacticity effects. Further studies aimed at quantitatively determining the χ parameter from neutron scattering results should clarify the effect of PVME tacticity on miscibility with PS.

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