A Study of Compatible Polymer Mixtures

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ABSTRACT: The compatibility of various compositions of polystyrene (PS)–poly(vinyl methyl ether) (PVME) films and the thermally induced phase separation of such mixtures have been studied using several methods. Density measurements indicate extensive mixing of the PS and PVME chains in compatible PS–PVME films. Vapor sorption measurements have enabled calculation of the PS–PVME interaction parameter χ'_{23} as a function of composition and temperature. The parameter χ'_{23} is negative for compatible PS–PVME films in the composition range 35–65 wt % PVME satisfying the thermodynamic criterion for stability in a binary mixture. The temperature dependence of χ'_{23} for the PS–PVME system suggests the existence of a lower critical solution temperature (lcst) and an upper critical solution temperature (ucst). Vapor sorption measurements also indicate that the diffusion of benzene into a 45.3:54.7 PVME–PS film is Fickian, supporting the notion of extensive mixing of PS and PVME chains in the compatible mixture. Temperature-dependent measurements of spin-lattice relaxation time T_1 component, spin-spin relaxation time T_2 and fraction of long T_2 component by pulsed nmr indicate that compatible PS–PVME films can be described as microheterogeneous, in which PVME and PS chains, although being extensively mixed, are not completely mixed on the segmental scale. This is to be expected based on excluded volume and geometrical considerations.

Among polymers which are chemically dissimilar, there are only a few pairs in which compatibility is demonstrated over the whole range of compositions. One such example is the mixture of polystyrene (PS) with poly(vinyl methyl ether) (PVME) recently reported in the literature. Both compatible and incompatible films of PS–PVME can be obtained by choosing suitable solvents[2a] for the film casting process. However, phase separation can be induced in a compatible film simply by heating the mixture to about 150°.[2b,3] Subsequent slow cooling of the phase-separated film to room temperature again results in a compatible mixture.[2b] On the other hand, an incompatible film cast from chlorinated solvents cannot be converted into a compatible film by thermal treatment.[2b] Thus, the question remains whether the compatible or the incompatible mixture represents the thermodynamically preferred state. We have therefore undertaken an investigation to determine the interaction parameter of these two polymers. Furthermore, the unusual properties of the PS–PVME pair offer an opportunity for us to test the applicability of several methods of studying polymer compatibility. The following approaches were used.

1. Specific Volume. Although dilatometry is an established technique for studying polymer mixtures and expressions for excess volume of mixing have been derived many years ago, it occurs to us that the following approach (We are indebted to R.-J. Roe for his valuable suggestions leading to this approach.) may provide additional information in studying mixtures in which the two polymers have glass transition temperatures widely separated from each other. A schematic representation of the volume–temperature curves of the individual polymers is depicted in Figure 1. We are primarily concerned with a mixture where a single glass transition is observed, for example, by mechanical, dielectric, calorimetric, or other commonly used techniques. However, the existence of microscopic domains in such a mixture cannot be completely ruled out because the transition is often broadened. A case in point is the pair poly(vinyl chloride)–acrylonitrile butadiene rubber. While dynamic mechanical measurements identified a single T_g,[4] electron microscope observations indicated the presence of microdispersed domains.[5] We propose that the specific volume data can be used to our advantage in the following manner. Because partial molar volumes depend on interactions between molecules as well as on glassy or rubbery environments, the following example is given to illustrate our reasoning. The temperature of the experiment, T, is chosen so that $T_{gB} > T > T_g$ (mixture). If the mixing of the two polymers occurs on a molecular scale, then the chains of polymer B in the mixture will be in a rubbery environment. The partial molar specific volume of polymer B in the mixture is expected to be closer to V_{lB}, the extrapolated specific volume from the liquid state to T, than to V_{gB}, the specific volume in the glass state at T. On the other hand, if microscopic domains of sufficient size exist, the partial molar specific volume of polymer B in the mixture will be essentially identical with V_{gB}. The partial molar specific volume of polymer A is V_{lA} in either case. Similar reasoning can be applied to the partial molar specific volume of polymer A in the mixture if $T_g > T$. The PS–PVME pair is ideally suited for testing our approach because $T_g(\mathrm{PS}) \simeq 100°$, $T_g(\mathrm{PVME}) \simeq -29°$ and the T_g of the mixture can be varied over the whole range of composition.

2. Interaction Parameter of χ. In the study of the interaction parameter between two polymers, we make use of the polymer solution theory applied to ternary systems consisting of one solvent and two polymers. The activity of the solvent in a ternary solution is[6]

$$\ln a_1 = \ln \varphi_1 + (1 - \varphi_1) + (\chi_{12}\varphi_2 + \chi_{13}\varphi_3)(1 - \varphi_1) - \chi'_{23}\varphi_2\varphi_3 \quad (1)$$

where the subscript 1 refers to the solvent and the subscripts 2 and 3 refer to the two polymers. The activity of the solvent is a_1, and φ is the volume fraction of each component in the mixture. The symbol χ represents the binary interaction parameter and χ'_{23} is the interaction per segment of polymer 2 ($\chi'_{23} = \chi'_{23}(\mathrm{Flory})x_1/x_2$, where x is the number of segments in the molecule).

Although eq 1 was derived more than 25 years ago, it was seldom used without simplifying assumptions. During the past 3 years, only one publication using the unabridged equation for the ternary system came to our attention and it dealt with the melting of poly(2,6-dimethyl-1,4-phenylene oxide) in ternary mixtures with toluene and polystyrene.[7] Since the solvent acts only as a probe to permit the use of eq 1, we choose to conduct our study with only a minor amount of solvent in the ternary system so that the information obtained from our experiments may reflect closely the property of a binary polymer mixture. The technique of our choice is the vapor sorption measurement. The application of the vapor sorption data to determine the solvent–polymer interaction parameter with the use of eq 2 is

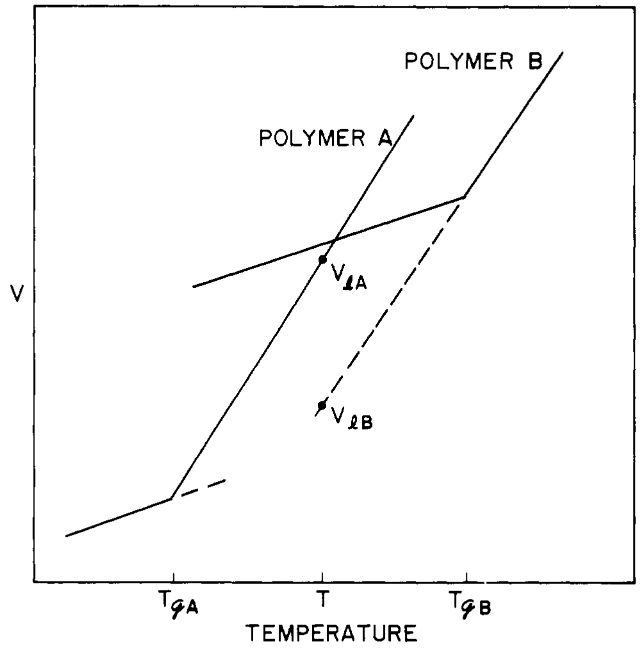

Figure 1. Schematic representation of volume–temperature curves of two polymers having glass temperatures widely separated from each other.

a well-established method.[8]

$$\ln a_1 = \ln \varphi_1 + \varphi_2 + \chi_{12}\varphi_2^2 \qquad (2)$$

Thus, we can determine χ_{12} for benzene (component 1)–polystyrene (component 2) and χ_{13} for benzene–poly(vinyl methyl ether) (component 3) in separate experiments. With a knowledge of χ_{12} and χ_{13}, the parameter χ'_{23} can be readily calculated from vapor sorption data of the polymer mixture with the use of eq 1.

3. **Diffusion of Organic Vapor.** The diffusion of organic vapor molecules in rubbery polymers generally obeys Fick's law[9] while diffusion in glassy polymers is non-Fickian.[10] (The square root time relationship is usually used as a convenient criterion.) Let us again choose the experimental temperature, T, such that $T_{gB} > T > T_g$. If domains of polymer B exist in the mixture and the diameter of the domain is much larger than the characteristic jump distance for diffusion, one would expect to observe non-Fickian diffusion.

4. **Nuclear Magnetic Resonance.** The application of the nmr method to the study of polymer mixtures appears to be a natural extension of the numerous previous nmr studies of pure polymers. A recent example is the work by Davis and Slichter[11] on the system poly(vinyl chloride) and poly(tetramethylene glycol dimethacrylate). For the PS–PVME pair, the nmr method is particularly attractive in the study of phase separation induced by thermal treatment. It is our expectation that two relaxation times should appear as phase separation occurs. This offers an advantage not achievable by other conventional methods.

Table I
Densities of PS–PVME Mixtures

Wt % PVME	ρ23°	T_g (°C)	ρ(calcd) PS and PVME Densities at 23°	Extrapolated PVME Density	Extrapolated PS Density
0	1.0505	102			
10.00	1.0562	80	1.0495	1.0508	
35.06	1.0661	18	1.0470		1.0654
45.30	1.0615	−18	1.0459		1.0614
70.00	1.0525[a]	−23	1.0434		1.0520
100	1.0404	−29			

[a] Measured 1 day after film preparation.

Table II
Interaction Parameter χ'_{23}

T (°C)	Wt %PVME in the Film	φ_1	χ'_{23}
30	35.06	0.0967	−0.78
		0.1388	−0.73
		0.2006	−0.73
			av −0.75
30	45.30	0.0478	−0.67
		0.1104	−0.69
		0.1693	−0.72
			av −0.69
30	55.00	0.0389	−0.59
30	65.00	0.0698	−0.17
50	45.30	0.0367	−0.59
		0.0438	−0.60
		0.0516	−0.61
			av −0.60
50	65.00	0.0405	−0.47
		0.0498	−0.56
		0.0918	−0.36
			av −0.46

Experimental Section

Materials. Polystyrene from Sinclair-Koppers Co., Dylene 8, was purified by precipitating twice from methyl ethyl ketone solution to a large volume of methanol. The intrinsic viscosity of the purified material was 0.94 in benzene at 25°. Poly(vinyl methyl ether) was obtained from Cellomer Associates, Inc.; it was precipitated twice from benzene solution to methanol. The intrinsic viscosity was 0.51 in benzene at 25°.

Film Preparation. Films containing PS, PVME, and their mixtures were cast from toluene solution on glass or mercury surfaces at room temperature. Initial polymer concentration in toluene was about 3 g/100 ml. The ratio of PS to PVME is reported here on a weight basis. Toluene was very slowly evaporated under a stream of air for at least 1 week and the resulting film was dried further under vacuum at 60° for at least 1 week. (A higher drying temperature, 90°, was used for polystyrene.) Film thicknesses of 7–15 × 10^{-3} cm were used for the density, sorption, and diffusion studies. Thicker films, about 0.03 cm, were used for nmr measurements.

Density. The densities of the films were measured in a density gradient column at 23°.

Sorption and Diffusion. The measurement of vapor sorption was accomplished using a Cahn electric balance. Both sorption and desorption experiments were conducted to ensure that equilibrium was attained.

Nmr Measurements. Approximately 0.2 g of the film, cut into small pieces, about 4 mm^2 in area, was packed in a nmr sample tube of 5-mm diameter. The sample tube was evacuated and sealed under vacuum in order to exclude oxygen. The pulsed nmr apparatus has been described elsewhere.[12] The resonance frequency for protons was 30 MHz. For T_1 measurements, a 180°-τ-90° pulse sequence was applied, where τ was changed over a wide range to obtain the completely recovered signal, the unrecovered signal and their intermediates so that multiple T_1 components could be resolved. Free induction decay after a 90° pulse was analyzed for T_2 measurements. The width of a 90° pulse was about 2 μsec and the system recovery time after a 90° pulse was about 6 μsec. For every measurement, phase detection was employed to obtain data on exact resonance and to resolve multiple T_2 or T_1 components.

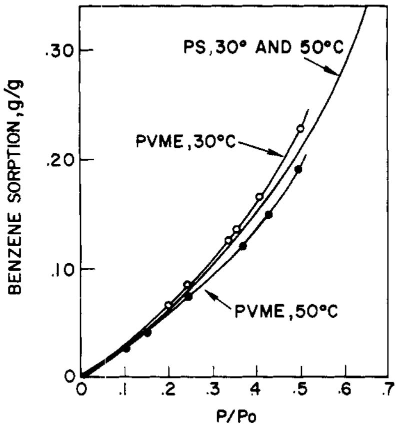

Figure 2. Isotherms for the sorption of benzene vapor in PS and PVME.

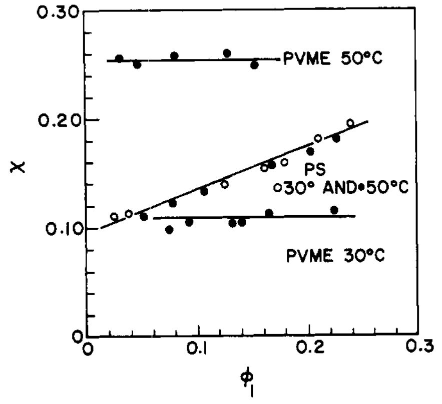

Figure 3. Benzene volume fraction ϕ_1 dependence of interaction parameter χ for PS and PVME systems.

Sample temperatures were changed from liquid N_2 temperature to 170° by controlling the ambient temperature around the sample tube with a stream of air which was guided through liquid N_2 and an electrical heater. Temperature was monitored by chromel–alumel thermocouple placed near the sample tube and the temperature fluctuation was within ±0.5° of the preset temperature.

After the samples were heated to 170°, they were quenched by immersing the sample tube in ice water. Again, nmr results for the quenched samples were obtained from liquid N_2 temperature to 160°.

The decomposition of the T_1 data into two components was performed by plotting the time interval τ between 90 and 180° pulses and the logarithm of fully recovered signal intensity minus partially recovered signal intensity at τ for various τ's. For the decomposition of the free induction decay curves they were photographed and digitized with an Autotrol digitizer. Then the data were analyzed by a nonlinear regression routine. The details are described elsewhere.[13]

Results

1. Density. The densities of PS–PVME films containing from 10.0 to 70.0% by weight of PVME are listed in Table I. Their densities exceed the values for either PS or PVME by a substantial amount.

2. Interaction Parameters χ_{12} and χ_{13}. The isotherms for the sorption of benzene vapor in PS and PVME are shown in Figure 2. The quantities χ_{12} and χ_{13} derived from these isotherms are plotted against the volume fraction of benzene φ_1 in Figure 3. The value of χ_{12} for benzene–PS increases linearly with φ_1 and its temperature coefficient is near zero, or perhaps slightly negative. In contrast, χ_{13} appears to be independent of φ_1 in the range studied and has a positive temperature coefficient. The partial molar heat of solution of benzene in PVME, $\Delta\bar{H}_1$, from $R\partial \ln a_1/\partial(1/T)$, is −0.92 ± 0.02 kcal/mol. If one assumes that the pair contact energy for benzene and PVME segment is similar to that for PS and PVME segments, then the energetic contribution to χ'_{23} is likely to be negative also.

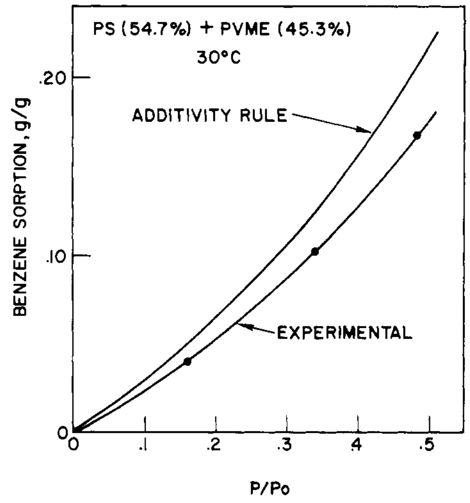

Figure 4. Comparison of isotherms for the sorption of benzene vapor in PS and PVME mixture between experimental and predicted based on additivity rule.

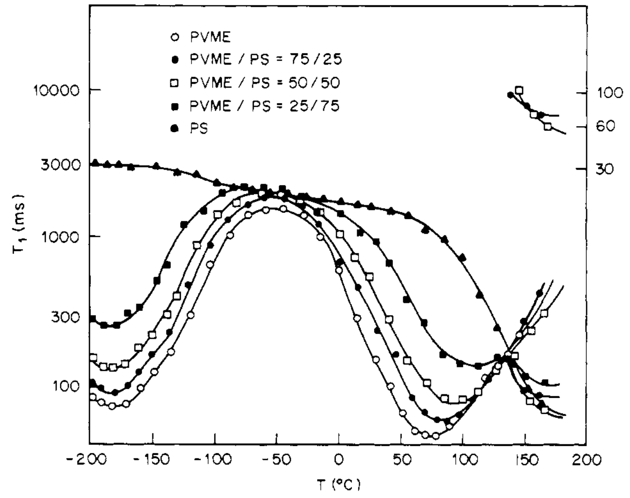

Figure 5. Temperature dependence of T_1 and fraction of long T_1 component (%) for PVME (○): PVME–PS = 75:25 (●), PVME–PS = 50:50 (□), PVME–PS = 25:75 (■), and PS (▲).

3. Interaction Parameter χ'_{23}. The quantity of benzene absorbed by a mixture is always smaller than the amount predicted from the simple rule of additivity (Figure 4). In the application of eq 1 to determine χ'_{23}, (1) the extrapolated density of PS was used to calculate the volume fractions for reasons given in the Discussion section and (2) the appropriate value of χ_{12} at a given vapor pressure was obtained from a plot of χ_{12} *vs.* vapor activity for the binary system. The results of our calculations are shown in Table II.

4. Nmr. The temperature dependence of spin–lattice relaxation time T_1 and fraction of long T_1 component for PVME, PS, and their mixtures are given in Figure 5. Only one T_1 was observed for every sample except for PVME–PS = 75:25 and 50:50 above 140°.

There are two distinct minima in T_1 for PVME and for the three mixtures below 140°. The T_1 minimum value, the temperature at which T_1 minimum occurs, and the apparent activation energy ΔE^* calculated from eq 3[14] are listed in Table III.

Table III
***T_1* Minimum Temperature, *T_1* Minimum Value, and Apparent Activation Energy for PVME, PS, and Their Mixtures**

	T_1 Minima					
	Low			High		
Sample	Temp (°C)	T_1 (msec)	ΔE^* (kcal/mol)	Temp (°C)	T_1 (msec)	ΔE^* (kcal/mol)
PVME	−182	72	2.2	73	45	8.2
PVME–PS = 75:25	−181	88	2.5	84	58	8.6
PVME–PS = 50:50	−182	130	1.9	92	82	9.5
PVME–PS = 25:75	−182	250	1.8	114	140	8.4
PS				~180	~65	13.4

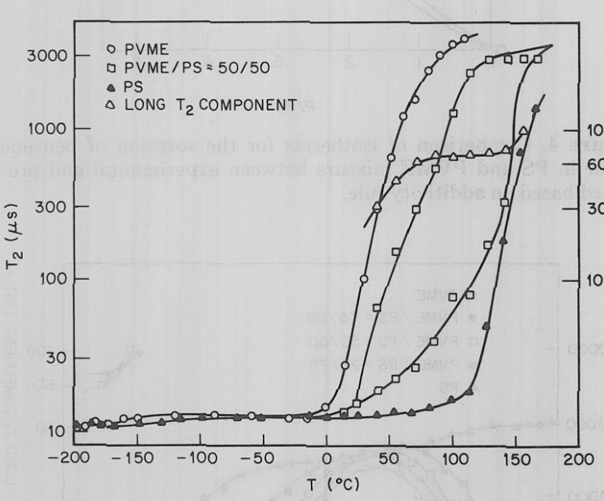

Figure 6. Temperature dependence of T_2 for PVME (○) PVME–PS = 50:50 (□) and PS (▲). Temperature dependence of fraction of the long T_2 component (%) for PVME–PS = 50:50 is also indicated (△).

$$\Delta E^* = \pm R[(\partial \ln T_1)/\partial(1/T)] \tag{3}$$

for $\omega_0\tau_c \gg 1$ or $\omega_0\tau_c \ll 1$. Here, ω_0 is the nmr frequency (30 MHz) and τ_c is the correlation time for molecular motion.

Above 150°, there appear two T_1's for PVME–PS = 75:25 and 50:50. Each T_1 is close to that of pure PVME and PS (Figure 5) showing the occurrence of phase separation.

Figure 6 shows the temperature dependence of spin–spin relaxation time T_2 for PVME, PS, and PVME–PS = 50:50. Two T_2's are observed for PVME–PS = 50:50 above 25°. The temperature dependence of the long T_2 component is also shown in Figure 6. The other mixtures also show two T_2's in this temperature range. The data have been abbreviated for the purpose of clarity. The T_2 data for the mixtures below 0° are also presented in the same figure.

The T_2 transition is associated with the onset of large-scale molecular motion with $\tau_c < 10^{-5}$ sec $\simeq (\gamma\langle\Delta H^2\rangle)^{-1/2}$, where $\langle\Delta H^2\rangle$ is the second moment of the nmr absorption line and γ is the gyromagnetic ratio. For PVME and PS, T_2 transitions occur at about 30 and 140°, respectively, which can be ascribed to the glass transition of each polymer. The apparent activation energies are calculated from eq 4 to be 16.7 and 35.2 kcal per mol for PVME and PS, respectively.

$$\Delta E^* = -R[(\partial \ln T_2)/\partial(1/T)] \tag{4}$$

for $\tau_c \ll (\gamma\langle\Delta H^2\rangle)^{-1/2}$. These values are higher than the activation energies calculated from T_1 (Table III) reflecting the nonlinear relationship between the inverse of absolute temperature and the correlation frequency for primary relaxation associated with glass transition.[15]

For PVME–PS = 50:50, the temperature dependence of each T_2 is different from either that of pure PVME or PS and the long T_2 component shows a plateau region of about 70% between 80 to 140°. Above 150°, it was difficult to resolve two T_2's because of the very long T_2 for each component and the inhomogeneity in magnetic field.

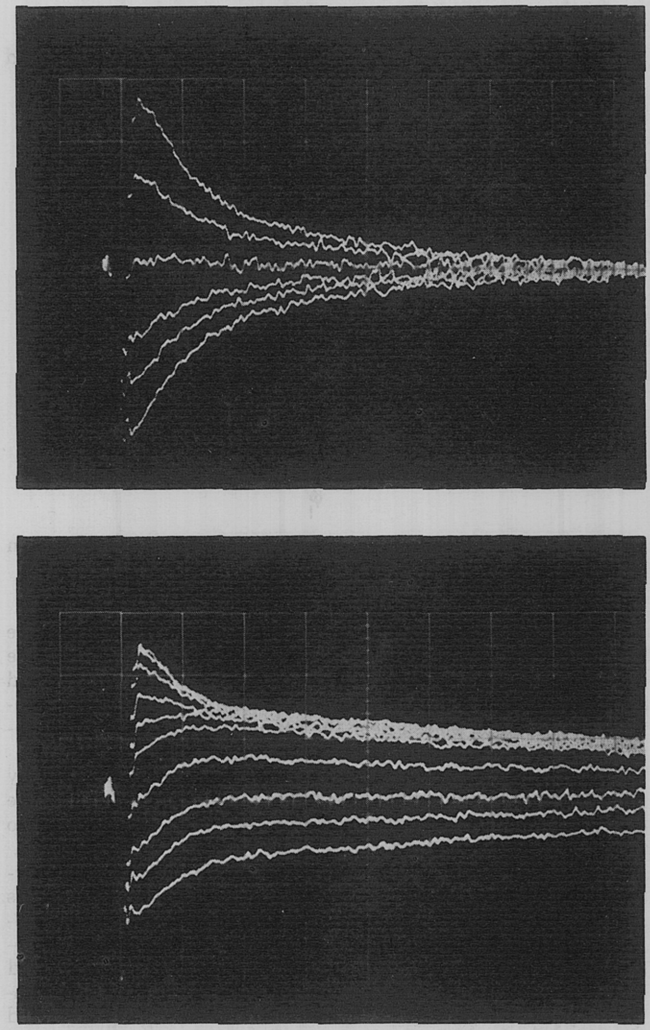

Figure 7. Typical decay curves following the 90° pulse in the T_1 measuring sequence (180°-τ-90°) for PVME–PS = 50:50 before and after phase separation. (a, top) Before phase separation: 40°, horizontal—20 μsec/u; τ = 0.5, 50, 100, 200, 400, 9000 msec. T_1 = 280 msec; T_2 = 18.5 and 68 μsec; long T_2 component ~30%. (b, bottom) After phase separation: 38°, horizontal—20 μsec/u; τ = 0.5, 30, 60, 120, 250, 500, 1000, 2000, 4000, 9000 msec; T_1 = 100 and 1150 msec; long T_1 component ~45%; T_2 = 11.0 and 260 μsec; long T_2 component ~56%.

It is apparent that phase separation occurred when the samples were heated above 150°. After the nmr measurements were completed above 160°, the samples were

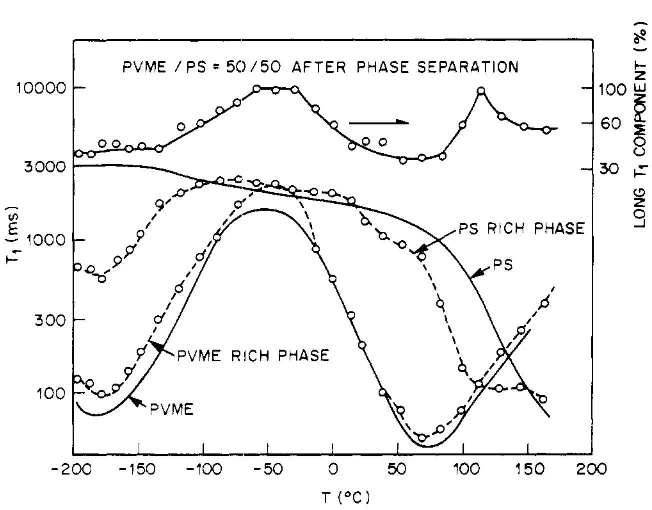

Figure 8. Temperature dependence of T_1 and fraction of long T_1 component for phase separated PVME–PS = 50:50. Full lines correspond to that of pure PVME and PS.

quenched in an ice–water mixture. Then, measurements were carried out again for these samples from liquid N_2 temperature to 170°. This process can provide a unique opportunity to study the nmr behavior of compatible (at least optically transparent) and incompatible (visually whitish) polymer system under the same condition.

Typical nmr results for PVME–PS = 50:50 before and after phase separation are shown in Figure 7. There are two T_1's for the phase-separated sample. One of them is shorter and the other longer than that of compatible sample. The long T_1 component contributes about 45% of the signal. The difference between two T_2's becomes more prominent for the phase-separated sample than in the compatible sample and the long T_2 component increases from 30 to 50% after phase separation.

The overall temperature dependence of the two T_1's, the long T_1 component (%), the two T_2's and the long T_2 component (%) are shown in Figures 8 and 9. The data for pure PVME and PS are also shown in full line for comparison. It is clear that the sample has separated into a PVME-rich phase and a PS-rich phase. However, phase separation is not complete since the two T_1's and two T_2's are different from those of pure PVME or PS. The amount of the PS-rich phase is estimated to be approximately 35% (from T_1 measurement) or 30% (from the plateau region of long T_2 component which corresponds to the amount of PVME-rich phase).

Discussion

1. **Density.** In column 4 of Table I the calculated density values based on volume additivity are given. It is quite evident that the excess volumes of mixing are negative for all four mixtures. Although the excess volume is directly related to molecular properties through the use of reduced variables, the latter are not available for PVME. Therefore, we direct our effort to the simple approach outlined previously. Column 3 in Table I gives the glass transition temperatures of the polymer mixtures.[2a] For the mixtures in the rubbery state we recalculate the additive volume with the use of the extrapolated density of PS at 23°. The data of Fox and Flory[16] give the specific volume of PS at temperatures between its T_g and 160° as

$$V = 0.913 + 5.5 \times 10^{-4}T + (53/M) \quad (5)$$

where M is the molecular weight of the PS fraction and T is the temperature in degrees Centigrade. Extrapolation of the above equation to 23° gives V(extr) = 0.9259 cm^3 g^{-1}. (There is some uncertainty about the appropriate molecular weight average which should be used in applying eq 5 to a polydisperse sample; however, only the fourth decimal place is affected.) These calculated values are given in column 5 of Table I. Their agreement with the experimental results is gratifying. For the glassy film containing 10% by weight of PVME, we extrapolate the glass state specific volume of PVME to 23° by using a $\Delta\alpha$ value of 2.2×10^{-4} deg^{-1}[17] ($\Delta\alpha$ being the difference in thermal expansion coefficients above and below glass transition). The extrapolated specific volume is 0.9502 cm^3 g^{-1}. The calculated density for the mixture is 1.0507 g cm^{-3}, compared with the experimental value of 1.0562 g cm^{-3}. Although the agreement is not perfect for this film, the point is that both the calculated and the measured densities exceed the value predicted from ordinary rule of additivity. This is possible only when extensive mixing of the two different polymer chains has taken place, although increased density over and above additivity does not necessarily indicate the presence of a single phase.

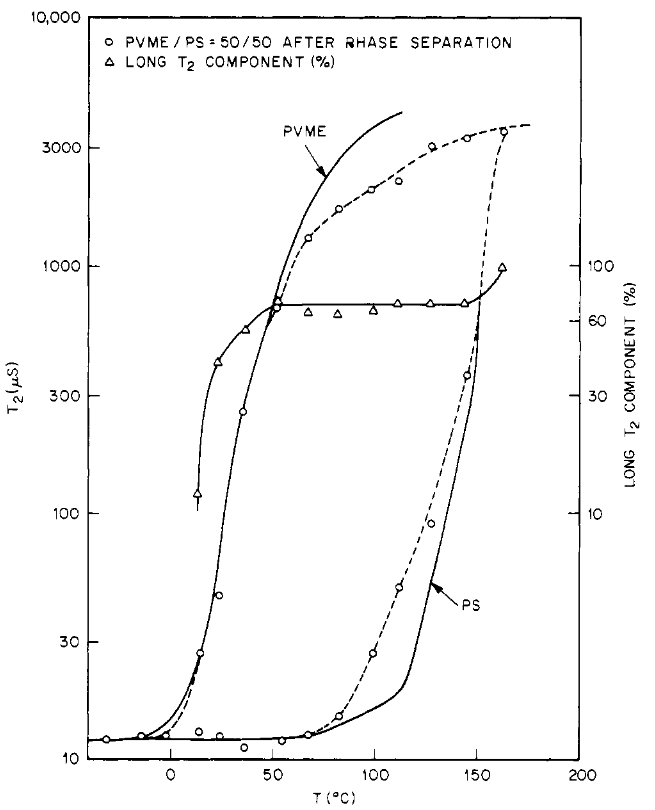

Figure 9. Temperature dependence of T_2 (O) and fraction of long T_2 component (%) (Δ) for PVME–PS = 50:50 after phase separation. Full lines correspond to that of pure PVME and PS.

2. **Interaction Parameter χ'_{23}.** Several features are evident from an inspection of the χ'_{23} values in Table II. First, the quantity χ'_{23} does not vary significantly with φ_1. The same χ'_{23} value therefore applied to a solid film containing no solvent. Secondly, the negative value of χ'_{23} is a sufficient, though not necessary, condition which satisfies the criteria of stability in binary mixtures.[18] To our knowledge, this is the first instance in which a negative χ'_{23} value has been obtained from experimental results in a polymer–polymer system. The third point of interest is the dependence of the interaction parameter on composition. There is a rapid increase in the χ'_{23} value at 30° when the weight fraction of PVME exceeds 0.5 (Figure 10). If one extrapo-

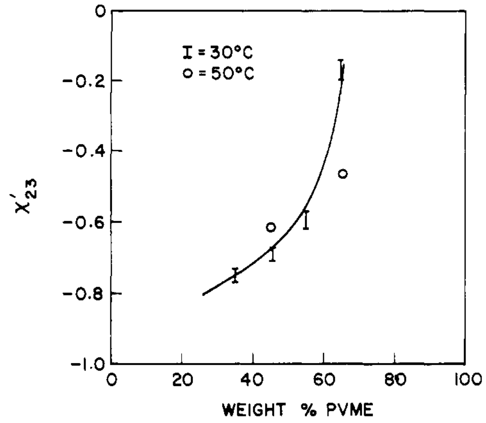

Figure 10. PVME weight fraction dependence of interaction parameter χ'_{23}.

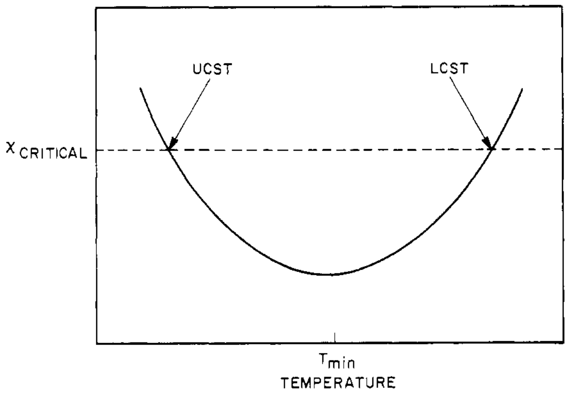

Figure 11. Schematic representation of temperature dependence of χ and existence of ucst and lcst.

lates the experimental data to higher PVME content, it appears that χ'_{23} would become positive at a PVME weight fraction of about 0.7. Indeed, a film of this composition was initially clean but turned opaque after standing at room temperature for several months. Films containing 75% PVME became opaque after 3 weeks. Thus, the change in interaction parameter with composition is in good accord with experimental observations. However, the reason for the rapid change of χ'_{23} in certain composition range is not obvious and a partial explanation will be offered in later discussion.

A fourth important point is the temperature dependence of the interaction parameter. For the 45.3% PVME film, χ'_{23} increases from 30 to 50°. But the trend is reversed for the 65% PVME film. The interaction parameter decreases from −0.17 at 30° to −0.46 to 50°. This apparent contradiction can be understood in light of the following observations. A 50% PVME film which was initially compatible separated into two phases at elevated temperatures. This was described in ref 2b and is confirmed by our nmr measurements. The thermally induced phase separation was also reported to be reversible.[2b] It appears therefore that there exists a lower cloud point temperature (lcpt) for the mixtures. (The word "lower" or "upper" follows the nomenclature of lower or upper critical solution temperature.) The positive temperature coefficient of χ'_{23} obtained for the 45.3% PVME film is consistent with the existence of a lcpt. For the 65.0% PVME film, the observation of the lcpt[2b] would indicate that χ'_{23} should increase at high temperatures. But our experimental result of an increase in χ'_{23} from 50 to 30° suggests that χ'_{23} would also increase at low temperatures, *i.e.*, an upper cloud point temperature (ucpt) is predicted. While we have not carried out a study of the phase separation of this film at low temperatures, the ucpt was easily discerned for the 75% PVME film. As mentioned previously a 75% PVME film became opaque upon standing at room temperature for several weeks. The opaque film, after being heated at 47° for about 40 hr, turned transparent again. Upon further elevation of temperature to 150°, the film once again became opaque and nmr data indicated conclusively that phase separation had taken place. This is a convincing demonstration of both upper and lower cloud point curves[19-21] (Figure 11). We believe that the existence of both ucpt and lcpt for polymer mixtures has not been observed previously. As can be seen in Figure 11 the temperature coefficient of χ'_{23} can be either positive or negative depending on the temperature range of the experiment. For the 65% PVME film, the ucpt is probably near 30°; as temperature increases from 30 to 50°, χ'_{23} becomes more negative. On the other hand, the same temperature 30° probably lies between T_{min} and lcpt for the 45.3% PVME film; as temperature increases from 30 to 50°, χ'_{23} becomes less negative. Thus, we can visualize a set of χ *vs.* T curves for mixtures of different compositions. As the weight percentage of PVME in the mixture increases, lcpt decreases.[2b] But ucpt increases, and the position of T_{min}, most likely, also shifts to a higher temperature. When the interaction parameters of mixtures are compared at a fixed temperature, one may very well be comparing different portions of the χ *vs.* T curves. At 30°, the rapid increase of χ with PVME content merely reflects the proximity of the ucpt's of these compositions to the temperature of the experiment.

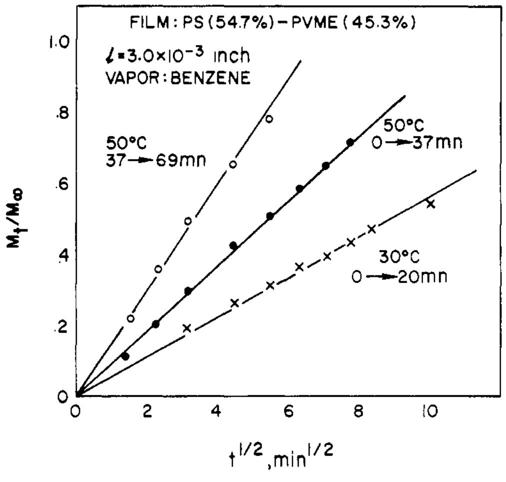

Figure 12. Rate of diffusion of benzene vapor in PS and PVME mixtures.

Aside from thermodynamic requirements, the chain segments must retain sufficient mobility at low temperatures for phase separation to occur at a ucpt within a reasonable time period. Therefore, we expect the glass transition temperature of the mixture to play an important role in the kinetics of phase separation. For the 75% PVME mixture, the T_g is low, about −26°, while the ucpt lies slightly above room temperature. Consequently, phase separation can be detected with relative ease after 3 weeks. On the other hand, the experimental detection of ucpt might become nearly impossible if the T_g of the mixture exceeds the ucpt. Kinetic considerations are likely to prevail in these systems.

4. Diffusion. The rate of diffusion of benzene vapor in a 45.3% PVME film obeys the square-root time relationship, as shown in Figure 12. Diffusion in PS is non-Fickian under identical conditions.[10] The diffusion results therefore are consistent with the idea that extensive mixing of PS and PVME chains has occurred, although the diffusion data are not, by themselves, sufficient criteria. The results are included in this paper because there appears to be very little information about diffusion of organic vapors in polymer mixtures.

5. Nmr. There are three regions of interest in the nmr data: the low-temperature relaxation near −180°, the relaxation around 70–110°, and the behavior at temperatures above 150°. Our discussion will be focused on the first two regions.

At temperatures near −180°, T_2 is very short compared to T_1 in all the samples. There is almost no change in molecular mobility in PS in this temperature range and T_1 is very long, about 3000 msec. The low-temperature T_1 minimum for PVME may be ascribed to methyl group reorientation[22] as judged from the very low T_1 minimum temperature and the small apparent activation energy, 2.2 kcal/mol. (The slight decrease in T_1 for PS around −100° may arise from the reorientation of methyl groups at chain ends.[23]) As PS is added to PVME, the position of the T_1 minimum remains unchanged.

It has been reported for *n*-alkanes, at low temperatures, that spin–lattice relaxation of the whole spin system is controlled by the spin diffusion process, in which the energy of the methylenic spin system is conveyed to the methyl sites where the dissipation to the lattice is effective.[24] In this case, the methyl T_1 minimum value is shown to be proportional to the relative number of methyl protons.

In our mixtures, the same process can be expected to take place *via* methyl group reorientation in the PVME chain if the PS and PVME segments are mixed thoroughly or at least within the spin diffusion distance and three-dimensional spin diffusion is effective.

Figure 13 shows the methyl T_1 minimum values in PVME and PVME–PS mixtures as a function of the relative number of methyl protons. They are proportional to

$$T_1(\mathrm{min}) \propto \frac{(n_2/m_2)(1 - x) + (n_1/m_1)x}{(n_1/m_1)_r x} \tag{6}$$

each other within experimental error showing that eq 6 is obeyed. In eq 6 *m* is the molecular weight of a monomer unit, *n* is the number of protons in one monomer unit, *x* is the weight fraction of polymer 1 in the mixture, and the subscript **r** denotes the relaxing proton.

On the other hand, two T_1's are observed for the phase separated 50:50 sample as shown in Figure 8. It should be noticed, however, that the two T_1's are not exactly the same as that of pure PS or PVME. There is a slight minimum in the long T_1 around −180°. This indicates the presence of PVME chain in the PS-rich phase.

If one assumes complete spin diffusion within each phase and no coupling between the two phases, the PVME concentrations in the PS- and PVME-rich phases for the phase-separated samples are calculated to be about 10 and 71%, respectively. From these figures the weight percentage of PS-rich phase is estimated to be 34%. This value predicts about 30% signal intensity for the long T_1 component or 70% signal intensity for the long T_2 component. Figures 8 and 9 indicate 35 (from long T_1 component) and 30% (from 100 − long T_2 component) signal intensity for the PS-rich phase and the agreement is very good if one considers that the relative intensities as determined from the decomposition of free induction decay (T_2 measurement) curves give better results than those from T_1 measurements.[25] On the other hand, if one assumes complete phase separation for this sample, the signal intensity for PS phase would have been 43%, which is the percentage of protons attached to PS chain in the mixture. Clearly, the nmr results indicate only partial phase separation in this specimen.

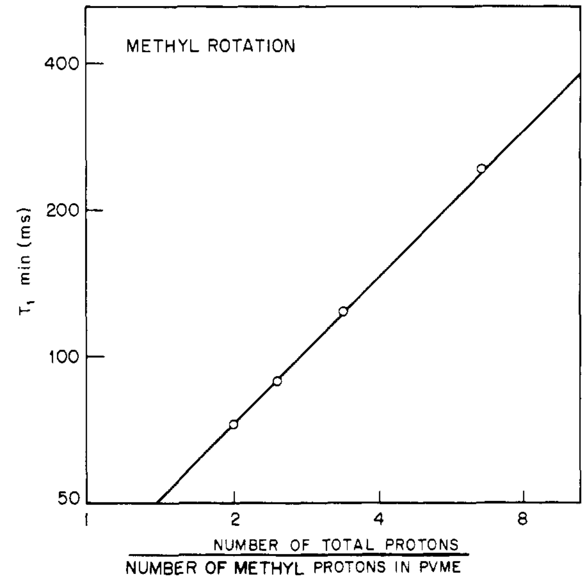

Figure 13. The methyl T_1 minimum value of PVME and its mixtures with PS as a function of the relative number of methyl protons in PVME chain.

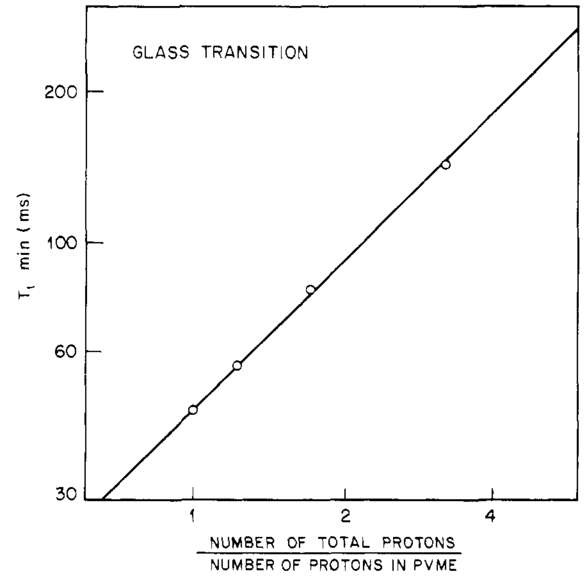

Figure 14. The glass transition T_1 minimum value for PVME and its mixtures with PS as a function of the relative number of protons in PVME chain.

The high-temperature T_1 minimum at ~75° for PVME has an activation energy of 8.2 kcal/mol, indicative of segmental motion of a larger scale than the low-temperature relaxation. Furthermore, the increase in the temperature of T_1 minimum with PS content in the mixture parallels the trend observed for glass transition determined by the DSC method.[2a] Therefore, these T_1 minima are associated with the glass transition phenomena at 30 MHz. Although there is only one T_1 for each mixture, which suggests a high degree of homogeneity of the sample, the T_1 minimum value increases from 40 to 140 msec as the PS content increases from 0 to 75%. The latter is not anticipated if the system is completely homogeneous since the T_1 minimum value of pure PS is not greatly different from that of pure PVME.

Finally in Figure 6, the two T_2's observed for the 50:50 mixture are different from the T_2 observed for either pure PS or pure PVME. This shows the existence of PS- and PVME-rich regions, each of which is almost homogeneous. In this regard, it is known that T_2 is more sensitive to the detection of a multicomponent system than is T_1 since T_2 is free from the spin diffusion effect.

From these experiments the system can be described as microheterogeneous, where PVME and PS chains, although being relatively well mixed, are not completely mixed on a segmental scale. There are regions where PVME chains and PS chains interpenetrate one another, but interpenetration is inevitably limited by excluded volume and geometrical effects. It is useful to recall that even in mixtures of simple liquids, clustering of like molecules does occur and indeed the clustering function can be calculated from thermodynamic data.[26] The clustering of polymer segments is aggravated by the connectivity of the chain segments and local fluctuation in the density of the two species is thus unavoidable.

Since our analysis of the free induction decay assumed one or two exponential decays, the results in Figure 6 may be rationalized by describing the microheterogeneous phase as (1) PS segments plus an interpenetrating region, and (2) an interpenetrating region plus PVME segments. Again, the size of these phases must be very small because of the effectiveness of spin diffusion at low temperatures and the adherence of the vapor diffusion data to the square-root time relationship.

Presumably these two phases give rise to the two T_2's observed at temperatures above 25° for the 50:50 sample. It also appears that the micro-Brownian motion in the PVME-rich phase, which is the more mobile phase, can induce similar motion in the PS-rich phase. Since the phases are finely mixed, the average correlation time lies between those of pure components and the T_1 minimum temperature increases as the PS content increases. As for the T_1 minimum value, the spin diffusion is as effective as that shown in the low-temperature range. In this case, however, the relaxing group should be the segment of PVME chain. Figure 14 shows the relation between the value of T_1 minimum at glass transition and the ratio of total protons to PVME protons in the mixture. A linear dependence is indicated. This correlation suggests that the motion of the PVME chain plays a dominant role in the mechanism of glass transition of the mixture. Moreover, the magnitude of the apparent activation energies for the higher temperature relaxation which is about the same for the mixtures as for pure PVME also supports this interpretation.

Conclusions

Inasmuch as various methods have been used in the present study in an attempt to elucidate the nature of compatibility of the PS–PVME pair, it is gratifying that consistent results have been obtained. The density, χ'_{23}, diffusion, and nmr T_1 results all indicate that extensive mixing has taken place in the case of compatible PS–PVME films even though complete interpenetration of PS and PVME chains does not occur because of physical restrictions as evidenced by the nmr T_2 results.

The negative value of χ'_{23} obtained for the PS–PVME pair not only satisfies the thermodynamic criterion for a stable binary mixture but is also, to our knowledge, the first instance in which a negative χ'_{23} has been obtained from experiment for a polymer–polymer mixture. Furthermore, the temperature dependence of χ_{23} suggests the existence of both lcpt and ucpt for the PS–PVME pair. We believe that this phenomenon has not been previously identified in other polymer–polymer mixtures.

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