

Predicted miscibility of polystyrene and poly(α -methyl styrene) and comparison with experiment

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The free energy of mixing of polystyrene with poly(α -methyl styrene) has been calculated using the Flory–Huggins expression and the more recent Flory theory which takes account of free volume effects. The double tangents to the free energy–composition curves were used to define phase separation points and hence the expected phase diagram for the system. Both approaches reproduce the observed behaviour reasonably well but in the latter case this is true only if a semi-empirical entropy parameter is included. The interaction of the polymers with the solvents used to prepare the blends is discussed.

(Keywords: miscibility; free energy; phase diagram; polystyrene; poly(α -methyl styrene); mixing theory)

INTRODUCTION

The study of polymer blends is an area which has attracted growing interest in recent years and has led to the discovery of an increasing number of miscible polymer pairs. Such combinations are still relatively unusual and phase separated systems are much more common. The combination of polystyrene (PS) with poly(α -methyl styrene) (PAMS) is one in which 'conditional' miscibility exists, and a one phase system is obtained only over a limited molecular weight range^{1–3}. The phase behaviour of PS–PAMS for a number of different molecular weight combinations, along with the effect of the solvent used to cast the blend, has recently been reported by us⁴. In this paper the thermodynamic state of this system is examined in terms of the free energy of mixing (ΔG_m).

Several schemes for the calculation of ΔG_m have been proposed and are well reviewed^{5,6}. In general, ΔG_m may be written as the sum of a combinatorial and an interaction term. The simplest expression for the free energy of mixing is based on the Flory–Huggins treatment and requires knowledge of the value of the interaction parameter χ_{12} in the expression

$$\Delta G_m = (RT/m)[(\phi_1/x_1) \ln \phi_1 + (\phi_2/x_2) \ln \phi_2 + \phi_1 \phi_2 \chi_{12}] \quad (1)$$

where ϕ_1 and ϕ_2 are segment fractions of polymers 1 and 2 of degrees of polymerization x_1 and x_2 respectively, and m is the mass of a mole of mixture. The value of χ_{12} may be estimated from the solubility parameters (δ_1 and δ_2) through

$$\chi_{12} = (V_{ref}/RT)(\delta_1 - \delta_2)^2 \quad (2)$$

Equation (1) predicts phase separation for non-zero (positive) values of χ_{12} when this outweighs the favourable combinatorial contribution to the free energy of mixing. This latter term is vanishingly small for high molecular weights and small positive values of polymer–polymer heats of mixing are sufficient to ensure incompatibility.

In the more recent Flory treatment^{7,8} of polymer–polymer mixtures the non-combinatorial ('residual') term is composed of two contributions, one from so-called equation of state (free volume) effects, and the other from contact interactions. The residual chemical potential of polymer 1 in a mixture with polymer 2 is expressed⁸ as:

$$(\mu_1 - \mu_1^0)^R = p_1^* v_1^* \{3 \tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 1/\tilde{v}_1 - 1/\tilde{v}\} + v_1^* X_{12} \theta_2^2 / \tilde{v} \quad (3)$$

where p_1^* and v_1^* are the pressure and volume ('hard core' volume) reduction parameters of pure 1, \tilde{v}_1 is its reduced volume, and \tilde{v} is the reduced volume of the mixture which is calculated by numerical solution of equation (8)^{7,8}. The reduced temperature \tilde{T}_1 is equal to T/T_1^* where T_1^* is the temperature reduction parameter. The first term on the right hand side of (3) characterizes the equation of state effects (essentially the differences in expansion between the polymers and their mixtures), while the second term represents contact energy difference characterized by X_{12} .

The site fraction $\theta_2 = (1 - \theta_1)$ is calculated from:

$$\theta_2 = \phi_2 / [(s_1/s_2)\phi_1 + \phi_2] \quad (4)$$

s_i are surface to hard core volume ratios. Equation (3) with the indices 1 and 2 interchanged gives the chemical potential of component 2. The residual free energy (per gram) of mixing follows from:

$$\Delta G_m^R = w_1 (\mu_1 - \mu_1^0)^R + w_2 (\mu_2 - \mu_2^0)^R \quad (5)$$

w_1 and w_2 are weight fractions. The combinatorial free energy of mixing is estimated as before such that:

$$\Delta G_m = \Delta G_m^c + \Delta G_m^R \quad (6)$$

EXPERIMENTAL

The heat of mixing (H^E) for equimolar amounts of ethyl benzene and isopropyl benzene (both 99% pure) was determined at 298.2 K using an LKB batch microcalorimeter. The instrument was calibrated electrically using

the internal current supply. The calibration and mixing runs were displayed on a chart recorder and their respective areas measured by planimeter.

Differential scanning calorimetry (d.s.c.) was performed on PS-PAMS blends as described before⁴.

The demixing of a 50/50 wt% mixture of PS (63 000 g mol⁻¹) and PAMS (55 000 g mol⁻¹) in methylene chloride solution was determined as the onset of visible turbidity on slow (~ 1 K min⁻¹) cooling of the samples sealed in tubes under vacuum.

SYSTEM PARAMETERS

The solubility parameters for PS and PAMS were estimated using Small's group contributions⁹. The values calculated are listed in Table 1. The characteristic equation of state parameters T_1^* , p_1^* and v_1^* for PS(1) have been established by Hoker *et al.*¹⁰ from measurements of the thermal expansion (α) and pressure (γ) coefficients via equations (7), (8) and (9).

$$\tilde{v}_1^{1/3} = [\alpha_1 T / 3(1 + \alpha_1 T)] + 1 \quad (7)$$

$$\tilde{T}_1 = T / T_1^* = \tilde{v}^{-1} (1 - \tilde{v}^{-1/3}) \quad (8)$$

$$p_1^* = \gamma_1 T \tilde{v}_1^2 \quad (9)$$

where $\tilde{v}_1 = v_1 / v_1^*$. The thermal expansion of PAMS(2) has been measured by Cowie and Toporowski¹¹, and extrapolating their V - T data to 298 K gives a value of $\alpha = 5.1 \times 10^{-4}$ K⁻¹. p_2^* for PAMS was calculated by the method of Crescenzi and Manzini¹². All the parameters are gathered together in Table 1.

Heats of mixing for pairs of glassy polymers are experimentally inaccessible and so one must resort to the use of model systems. Here ethyl benzene and isopropyl benzene were chosen to represent the polymer system PS-PAMS. For equimolar quantities of these small molecule analogues H^E was determined calorimetrically to be 124 ± 10 J mol⁻¹.

Alternatively, the polymer solubility parameters may be used to estimate H^E through:

$$H^E = V_{\text{ref}} (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (10)$$

where V_{ref} is taken as the molar volume of PS. On this basis H^E is found to be considerably smaller at only 0.7 J mol⁻¹, for an equimolar mixture, implying that the mixing of PS and PAMS is essentially athermal.

Table 1 Equation of state data for polymers at 298 K

	Polystyrene(1)	Poly(α -methyl styrene)(2)
T^* (K)	7420	8095
p^* (J cm ⁻³)	547	627
v^* (cm ³ g ⁻¹)	0.8098	0.781
v (cm ³ g ⁻¹)	0.9336	0.888
$10^{-8} s$ (cm ⁻¹)	0.474	0.453
δ (J ^{1/2} cm ^{3/2})	18.59	18.31

Table 2 Equation of state data at 298 K for model compounds

	Ethyl benzene(1)	Isopropyl benzene(2)
T^* (K)	5203	5250
p^* (J cm ⁻³)	549	538
v^* (cm ³ g ⁻¹)	0.9278	0.9358
v (cm ³ g ⁻¹)	1.1592	1.1662
$10^{-8} s$ (cm ⁻¹)	0.885	0.845

X_{12} , the interaction parameter can be calculated¹³ from H^E (a) using the model calorimetric value and the equation of state parameters which are listed in Table 2 and (b) using the solubility parameter-derived value with the equation of state data in Table 1. The values are, respectively, $X_{12} = 4.3$ J cm⁻³ and $X_{12} = 0.15$ J cm⁻³.

Another approach is to estimate X_{12} using a group additivity method¹⁴ involving the surface area fractions of dissimilar segments. X_{12} calculated on this basis is 0.7 J cm⁻³. The three methods of estimation yield near zero but positive values as expected from mixing similar and non-polar structural units.

The values of the surface to volume ratios for the two polymers, which are also required for the calculation of ΔG_m , were found by treating the polymer repeat units as right cylinders of lengths 2.5 Å and volumes v_i^* .

METHOD OF CALCULATION

Using equations (1) and (2) or (5) and (6) the free energy of mixing of PS and PAMS was calculated as a function of composition for pairs of equal molecular weights with the aid of an Apple II microcomputer. Thermodynamic stability of a one phase mixture exists only when $(\partial^2 \Delta G_m / \partial \phi^2)_{T,P} \geq 0$ and so the binodal and the spinodal phase boundaries may be constructed as a function of composition and molecular weight from the points of double tangency and inflection respectively.

Equation (1) predicts only upper critical phase boundaries. On the other hand, the Flory equation predicts both upper and lower critical phase boundaries, as a consequence of the additional free volume term. The temperature dependence of reduced volume is predicted from equation (8) and the corresponding temperature dependence of the residual chemical potential follows from equation (3).

RESULTS OF CALCULATIONS

Figure 1 shows the theoretical phase behaviour of PS + PAMS at 298 K based on the simple Flory-Huggins expression for mixing with $\chi_{12} = 0.032$ which was calculated from equation (2).

Also shown are the previously reported experimental phase boundaries for toluene- and propylene oxide-cast blends. The agreement between theory and experiment is reasonable, but exact coincidence of the limiting molecular weights for complete miscibility would require the value of χ_{12} to be slightly different for each of the solvent-cast blends.

The theoretical phase behaviour predicted by the Flory theory depends on the value of X_{12} chosen to characterize the system. With X_{12} at 4.3 J cm⁻³ the system is immiscible for all molecular weight pairs below ~ 1000 g mol⁻¹, quite contrary to experiment. The miscibility limit is increased to ~ 7000 g mol⁻¹ by using $X_{12} = 0.7$ J cm⁻³, but this prediction is still at variance with experiment by an order of magnitude as can be seen from Figure 2.

Examination of the separate contribution to ΔG_m from the equation of state and interaction terms of equation (3) shows that the former, although small, is always unfavourable to mixing, reflecting the differences in thermal expansions of the two components. The contact interaction is also unfavourable for all positive X_{12} . The

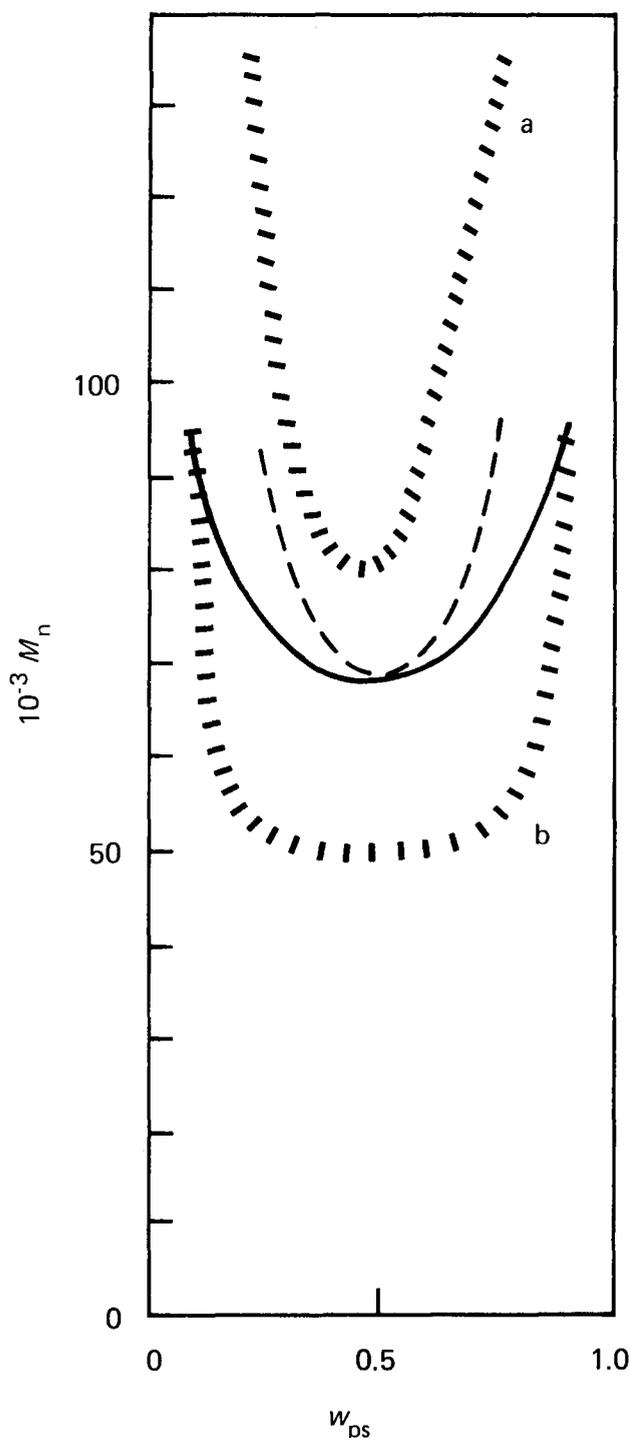


Figure 1 Binodal (—) and spinodal (---) boundaries, as a function of the weight fraction of PS (w_{ps}), for blends of PS and PAMS of equal molecular weight calculated from Flory-Huggins theory with $\chi_{12} = 0.0322$. Experimental phase boundaries (/////) (a) toluene cast and (b) propylene oxide cast blends

experimental phase boundaries can only be satisfactorily reproduced with negative values of the interaction term. In this case values of $X_{12} = -0.174$ and -0.223 J cm^{-3} would reproduce the curves (b) and (c) in Figure 2 but negative values of X_{12} are indicative of some form of favourable specific interaction, which seems unlikely in this system. This contradiction may be reconciled by invoking entropy effects¹⁵ and adding the quantity $-TQ_{1/2}v_1^*\theta_2^2$ to the residual chemical potential (equation (3)), where Q_{12} represents an entropy of interaction⁸. By adjusting this latter parameter, in conjunction with X_{12}

values from heats of mixing, Zhikuan *et al.*¹⁶ were able to simulate the experimental phase boundaries for chlorinated polyethylene-poly(methylmethacrylate) blends. Using a similar strategy in this present system, the phase diagram shown in Figure 3 was calculated using $X_{12} = 0.15 \text{ J cm}^{-3}$ (derived from the solubility parameters) with a value of $Q_{12} = 0.0012 \text{ J cm}^{-3} \text{ K}^{-1}$, chosen such that the miscibility limit at 298 K is $70\,000 \text{ g mol}^{-1}$ (this being the average experimental value). The phase boundaries

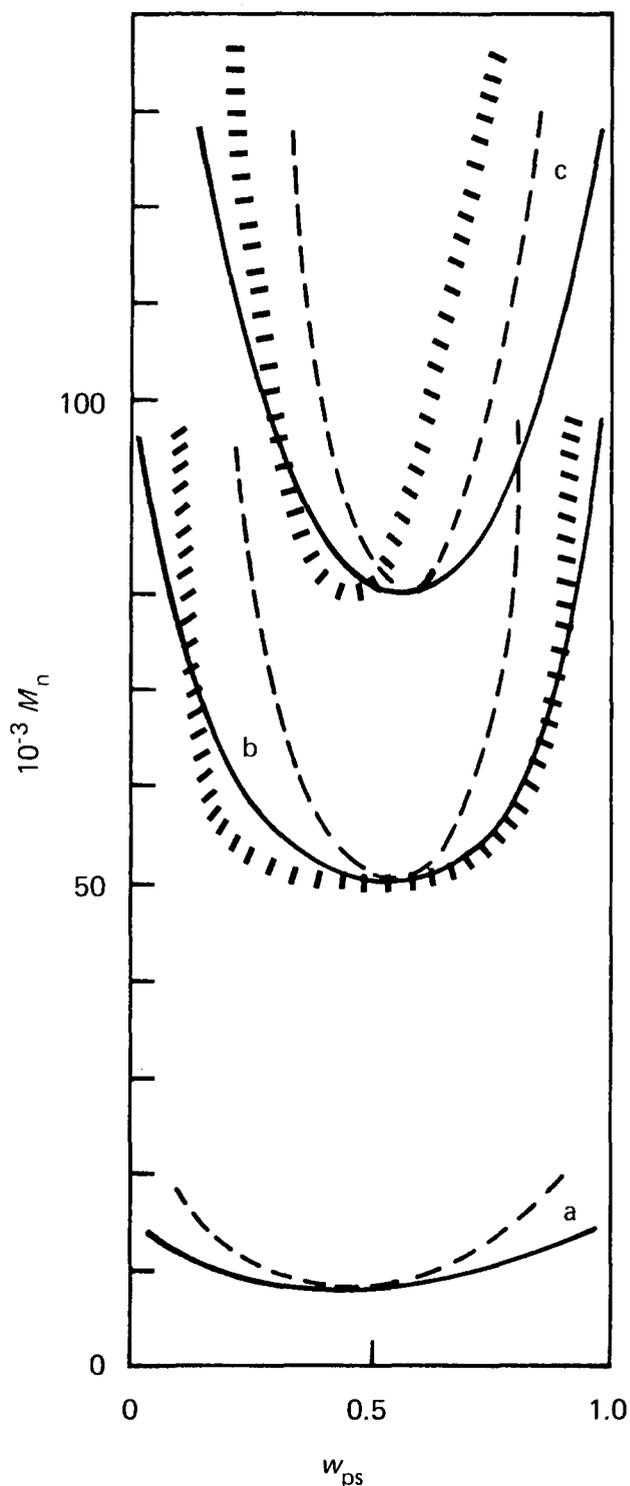


Figure 2 Binodal (—) and spinodal (---) boundaries, as a function of the weight fraction of PS, for blends of PS and PAMS of equal molecular weight calculated from Flory theory with (a) $X_{12} = 0.7 \text{ J cm}^{-3}$, (b) $X_{12} = 0.15 \text{ J cm}^{-3}$ and $Q_{12} = 0.00109 \text{ J cm}^{-3} \text{ K}^{-1}$, (c) $X_{12} = 0.15 \text{ J cm}^{-3}$ and $Q_{12} = 0.00125 \text{ J cm}^{-3} \text{ K}^{-1}$. Experimental phase boundaries (/////) as in Figure 1

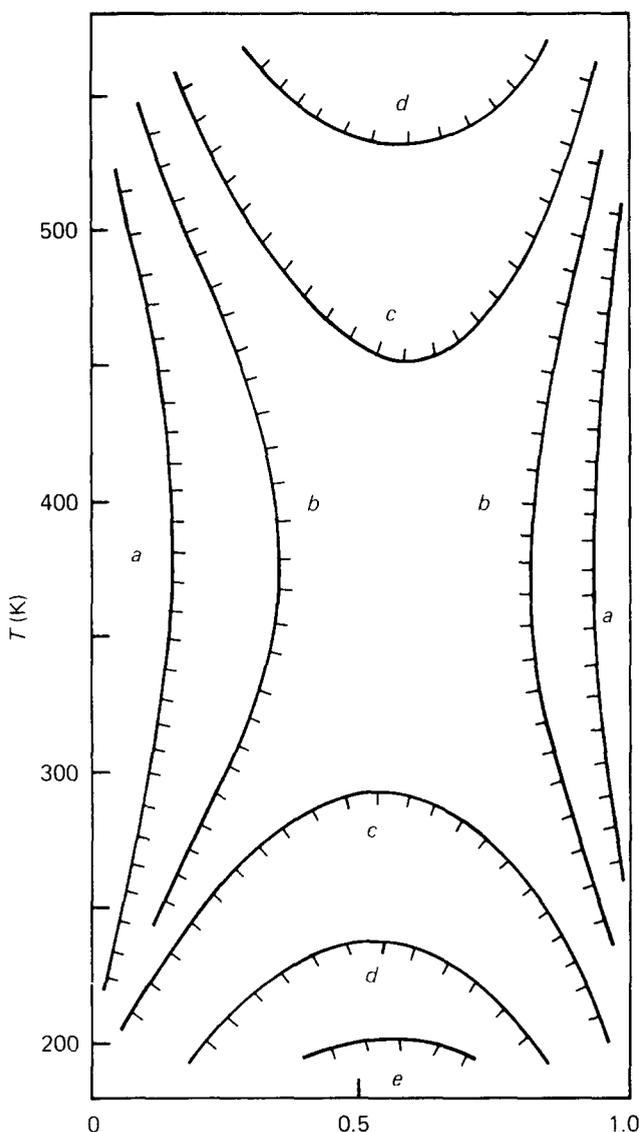


Figure 3 Binodals for PS-PAMS blends of equal molecular weights as a function of temperature and weight fraction of PS. The two-phase regions are on the hatched sides of the boundaries. Calculated with $X_{12} = 0.15 \text{ J cm}^{-3}$ and $Q_{12} = 0.0012 \text{ J cm}^{-3} \text{ K}^{-1}$. (a) $10^{-3} M_n \text{ g mol}^{-1} = 110$, (b) 85, (c) 70, (d) 55 and (e) 40

shown in *Figure 2* correspond to $X_{12} = 0.15 \text{ J cm}^{-3}$ with $Q_{12} = 0.00109 \text{ J cm}^{-3} \text{ K}^{-1}$ and $0.00125 \text{ J cm}^{-3} \text{ K}^{-1}$ respectively.

DISCUSSION

Using the values of the solubility parameters cited, the simple Flory-Huggins theory successfully predicts the observed phase behaviour of PS-PAMS, indicating one-phase behaviour up to a molecular weight limit of $\sim 70\,000 \text{ g mol}^{-1}$. Using the same solubility parameter basis to estimate X_{12} , free volume theory is much less satisfactory. The other estimates of polymer contact interactions give no improvement. The estimation of X_{12} from the heat of mixing of model compounds is especially unsatisfactory and may be because no account of chain length is involved. Predictively, then, the Flory approach to miscibility in the PS-PAMS system is rather unsatisfactory. However, by invoking entropic effects (Q_{12}), and essentially treating this as an adjustable parameter, the theory can simulate the experimental phase boundaries quite satisfactorily. Unfortunately, it is impossible to

predict Q_{12} from any basis at present—and indeed it is unsound to rationalize numerical values obtained from such fitting procedures.

Free volume theory, nevertheless, is capable of describing phase separation resulting from both upper (UCST) and lower (LCST) critical solution phenomena. The latter is essentially a result of differences in expansion between the two components of the mixture. *Figure 3* reproduces the observed miscibility limit of $\sim 70\,000 \text{ g mol}^{-1}$, for blends prepared at 298 K, as an UCST, and also suggests that molecular weights below $\sim 85\,000 \text{ g mol}^{-1}$ will again exhibit two phase behaviour at elevated temperatures. Several experiments were carried out in order to attempt to confirm the UCST nature of the experimental phase behaviour and to observe, if possible, LCST values in this system.

Figure 4 shows the observed turbidity on cooling for a 50/50 wt% mixture of PS and PAMS ($63\,000$ and $55\,000 \text{ g mol}^{-1}$ respectively) at various concentrations in methylene chloride. Neither PS nor PAMS separately were found to demix from methylene dichloride in the temperature range examined. Extrapolation of the data to zero solvent concentration should indicate the phase separation temperature, $\sim 270 \text{ K}$ in agreement with *Figure 3*, for the binary solvent-free system.

The d.s.c. trace for the same mixture cast from methylene chloride at 298 K shows a single T_g characteristic of a miscible blend. If, however, the sample is cast at 200 K, two T_g inflexions are observed, again indicating a phase separated system at low temperatures.

A miscible toluene-cast blend of the same molecular weight pair was annealed at high temperature, quenched

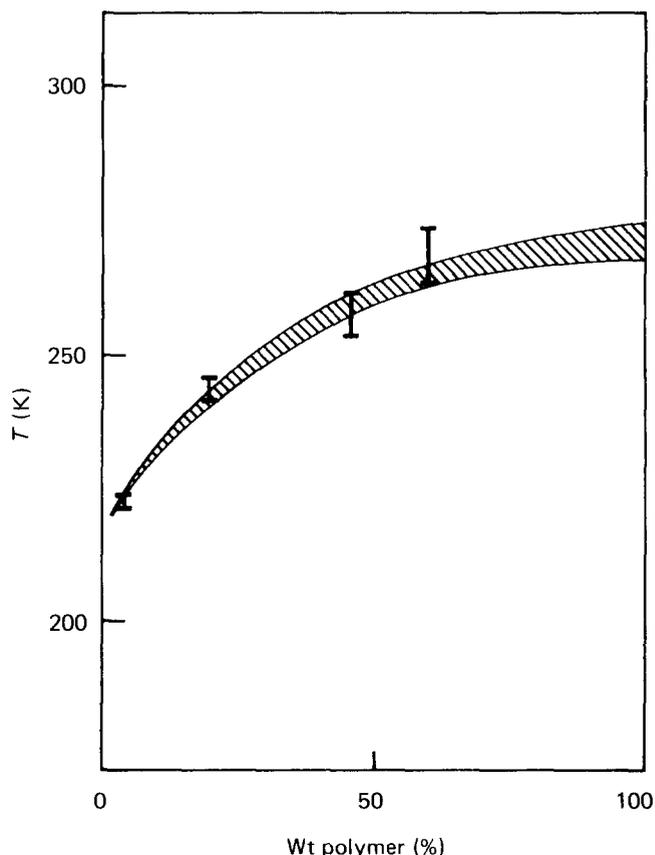


Figure 4 Extrapolation of demixing temperatures for a 50/50 mixture of PS ($63\,000 \text{ g mol}^{-1}$) and PAMS ($55\,000 \text{ g mol}^{-1}$) in methylene chloride solution as a function of weight % total polymer

and scanned by d.s.c. According to *Figure 3* phase separation should occur above about 520 K. Samples were held at various combinations of time and temperature ranging from one minute at 570 K to 16 h at 530 K (these represent the limits imposed by thermal degradation). In no instance was evidence of phase separation obtained.

Although the observed phase behaviour in the UCST region is well represented in *Figure 3*, the predicted LCST phase boundaries cannot be observed, at least in the temperature range examinable. The Flory theory thus appears to have overestimated the importance of the free volume component in the system. Indeed the simpler Flory–Huggins approach, which neglects free volume effects, provides a perfectly adequate description. This cannot be general since polymer–polymer LCST values¹⁶ are known and only explicable by the Flory theory if one considers free volume differences. Nevertheless, where the two components are so similar, as in this case, the simpler approach is the more successful.

Finally, some comment can be made on the difference between the toluene- and propylene oxide-cast phase behaviour shown in *Figures 1* and *2*, and on the differences in the values of either χ_{12} or Q_{12} required by the two theories to reproduce these exactly. During the casting process a ternary (solvent(1) + polymer(2) + polymer(3)) system exists in which the degree of miscibility is suggested by Robard *et al.*¹⁸ to be a consequence of the ' $\Delta\chi$ ' effect as well as polymer(1)–polymer(2) interactions, where:

$$\Delta\chi = |\chi_{12} - \chi_{13}| \quad (11)$$

and χ_{ij} are the Flory polymer–solvent interaction parameters. Toluene is a relatively good solvent for both PS and PAMS and although propylene oxide is also relatively good for PS it is a poorer solvent for PAMS¹⁹. $\Delta\chi$ (propylene oxide) is greater than $\Delta\chi$ (toluene), implying PS and PAMS to be more miscible in the latter.

During the casting process the degree of mixing between the two dissolved macromolecules will, at some stage, become 'locked in' as the solution viscosity rises to

some critical value, and this will be reflected in the final solvent-free blend. On this argument the components in the toluene-cast blends should be more miscible than in the propylene oxide blend, and this is indeed reflected in the experimental phase diagrams.

Thus in polymer blends where there are no specific interactions to assist mixing, the phase separation boundary is more likely to be an upper critical rather than a lower critical separation process. The simple Flory–Huggins approach is therefore adequate, and it is not necessary to consider free volume effects when attempting to describe the phase behaviour in such systems.

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