

Compatibility and neutron scattering studies of mixtures of polystyrene with poly(2,6-dimethyl 1,4-phenylene oxide) and its brominated derivatives

A. Maconnachie

Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7, UK

and R. P. Kambour and R. C. Bopp

Polymer Physics and Engineering Branch, Corporate Research and Development, General Electric Company, Schenectady, New York 12301, USA

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Several narrowly disperse polystyrenes (PS) were mixed with three series of random copolymers of 2,6-dimethyl phenylene oxide (also known as xylenyl ether (XE)) and 3-bromo-2,6-dimethyl phenylene oxide (BrXE), each series having a fixed chain length. The critical BrXE comonomer concentration necessary to induce phase separation, x_c , was characterized for each blend series by a number of techniques. x_c was extrapolated to a value of about 0.5 at infinite chain lengths of each polymer of the blend. This finding supports the negative heat of mixing of PS with PXE reported by other workers. Small-angle neutron scattering studies were carried out using small amounts of perdeuteropolystyrene in several matrices for which single phase behaviour had been shown to exist. The radius of gyration R_g and the second virial coefficient A_2 were greatest in the pure PXE matrix reflecting the goodness of this material as a 'solvent' for PS. In matrices containing 50% PS/50% copolymer, A_2 extrapolated to zero at $x_c \geq 1$ which was consistent with the phase behaviour of this series of blends.

Keywords Compatibility; small-angle neutron scattering; polystyrene-poly(2,6-dimethyl 1,4-phenylene oxide) blends; brominated blends; phase separation

INTRODUCTION

Mixtures of polystyrene (PS) and poly(2,6-dimethyl 1,4-phenylene oxide), trivially named poly(xylenyl ether) (PXE), have long been known to exhibit a single, composition-dependent glass transition temperature (T_g) from which molecular miscibility has been inferred¹. These mixtures appear to be miscible in all proportions and because of this and other unusual properties a great deal of research has been carried out on them. Mixtures of PS and PXE form the basis of a set of technologically important thermoplastics².

The combinatorial entropy of mixing of two high molecular weight polymers is very small, and therefore the magnitude of the free energy of mixing is essentially dictated by the heat of mixing. Thus, a negative heat of mixing would tend to suggest that the free energy of mixing is also negative and thus favourable. For the mixture PS/PXE a negative heat of mixing, although small, has been reported³. This negative heat of mixing is thought to arise from a specific interaction involving the aromatic rings of the polymers⁴. As well as a negative heat of mixing there is a negative volume of mixing which together are thought to be the underlying cause of the observed positive deviations from additivity in modulus and yield stress of the mixtures⁵. Another study that suggests that PS and PXE are miscible has focused on chemical modifications of the styrene resin as a means of bringing about two-phase behaviour. This approach has

resulted in the observation of critical solution temperatures in several systems⁶.

During the past few years small-angle neutron scattering (SANS) has been used to investigate the miscibility of polymer blends at the molecular level⁷⁻⁹. Using SANS it is possible to observe the conformation of the polymer chains in the blend and thus establish the extent of miscibility of the chains¹⁰. Through measurement of the second virial coefficient, A_2 , the interaction parameter χ can be calculated and thus the extent of compatibility predicted.

The purpose of this paper is to combine traditional compatibility measurements, e.g. glass transition measurements and microscopy, with those of SANS in order to investigate the effect of bromination of PXE on the compatibility of PS and PXE.

EXPERIMENTAL

Materials

The PXE samples were supplied by the General Electric Company. The PS samples were purchased from the Pressure Chemical Company and Polymer Laboratories Ltd. The perdeuteropolystyrene (PSD) was purchased from Polymer Laboratories Ltd. Details of the molecular weights and molecular weight distributions of all the polymers are given in *Table 1*.

PXE bromination was effected in chloroform solution

Table 1 Molecular weights and molecular weight distributions of the polymers used in the blends

Sample	Polymer	$\bar{M}_w \times 10^{-4}$	\bar{M}_w/\bar{M}_n
PS1	Polystyrene	86.0	—
PS2	Polystyrene	74.0	<1.1
PS3	Polystyrene	9.7	<1.06
PS4	Polystyrene	5.1	<1.06
PS5	Polystyrene	3.15	<1.05
PS6	Polystyrene	2.0	<1.06
PSD	Perdeuteropolystyrene	2.3	<1.05
PXE1	Poly(2,6-dimethyl 1,4-phenylene oxide)	9.3	2.97
PXE2	Poly(2,6-dimethyl 1,4-phenylene oxide)	4.4	2.18
PXE3	Poly(2,6-dimethyl 1,4-phenylene oxide)	3.7	2.50

(10 vol% solids) in Erlenmeyer flasks covered with aluminium foil. The resin was dissolved, stirring begun and then the requisite amount of bromine dribbled into the flask. Bromination levels were set by the molar ratio of xlenol residues to added bromine. After several hours the polymer was isolated by pouring the reaction mixture into methanol in a high-speed blender. Yields of dried polymer were typically 95% of theoretical yield calculated by assuming complete reaction of the bromine.

^{13}C and ^1H n.m.r. were used to determine the concentration and position of the bromine in the aromatic ring in the resins. No aromatic ring contained more than one bromine atom and bromination occurs only in the 3-position. Comparison of the ^{13}C spectra with those obtained from random copolymers formed by oxidative coupling of 2,6-xlenol with 3-bromo-2,6-xlenol has shown that bromination occurs randomly along each chain¹¹. The molecular weight of the brominated PXE resins (PBr_xXE) ($0 \leq x \leq 1$) was measured using osmometry and no change in the chain length was found to have occurred during bromination.

Blend processing

Blends were formed by codissolution in chloroform followed either by film casting or by coprecipitation in methanol in a high-speed blender. The fibrous powders resulting from coprecipitation were dried in vacuum at 125°C. Specimens for neutron scattering were cold pressed from these powders. The resultant discs were subsequently hot-pressed in the same mould at temperatures of 280° to 300°C for approximately 10 min. The mould used (Figure 1) was designed in such a way that four specimens could be hot-pressed at one time and the conical inner part of the mould could be easily knocked out once the mould was removed from the press. The inner section was then placed under pressure in a cold press and the samples allowed to cool.

Subsequently, samples were reloaded into the mould and annealed at certain temperatures (see Table 3). The inner section was quenched with water in an attempt to freeze-in the chain conformation existing at the annealing temperature. It is estimated that it took 30 s for the temperature of the sample to drop below its glass transition temperature.

Cast films used for the miscibility measurements were dried *in vacuo* at 125°C. No effects due to the presence of solvent were observed.

Tests of miscibility

Phase behaviour was characterized in three ways: (1) cast film clarity; (2) measurement of the glass transition temperatures by scanning calorimetry; and (3) inspection of the films using scanning electron microscopy and/or transmission electron microscopy.

Cast film clarity proved to be a reliable indicator of single-phase behaviour. Portions of the films were characterized in a Perkin-Elmer DSC II scanning calorimeter. Generally the three methods give consistent results. The success of these methods results from the marked increases in, respectively, refractive index, T_g , secondary electron emission yield and electron density caused by the addition of bromine to the PXE (Table 2).

Neutron scattering

SANS measurements were carried out using the small-angle diffractometer, D17, at the Institute Laue-Langevin, Grenoble, France. The sample-to-detector distance was 2.82 m and the neutron wavelength, λ , was 15 Å, giving a q -range of 10^{-2} to $5 \times 10^{-2} \text{ \AA}^{-1}$ ($q = (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle). The basic SANS experiment has been described elsewhere¹².

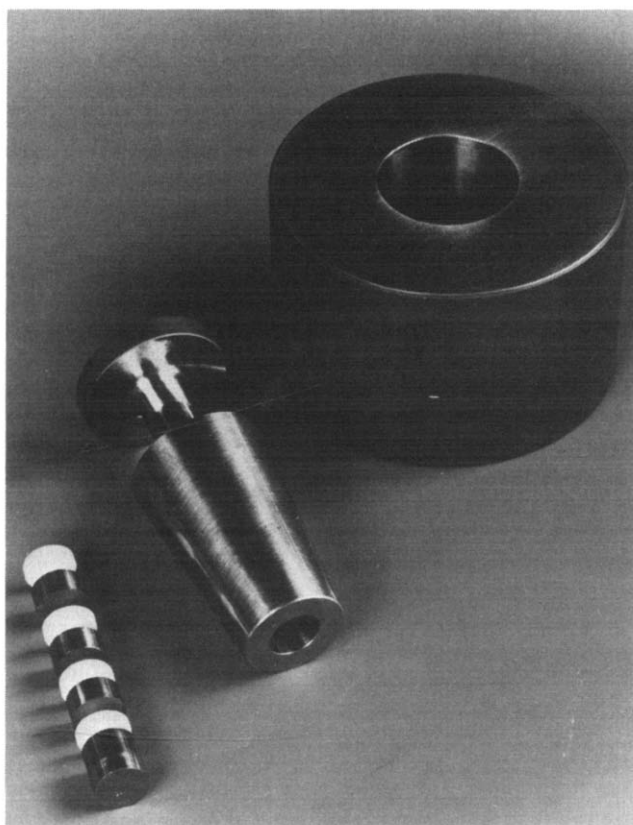


Figure 1 Multicavity mould used for fabricating SANS specimens (white discs). Conical inner section easily removed for fast cooling

Table 2 Selected properties of PS, PXE and PBr_1XE

	PS	PXE	PBr_1XE
Refractive index	1.585	1.570	1.60
Density (g cm^{-3})	1.04	1.07	1.49
Electron density $\times 10^{-23}$ (electron/cm^3)	3.37	3.44	4.65
T_g ($^{\circ}\text{C}$)	100	210	280

Measurements were made of the scattering from mixtures of PSD in a number of different matrices. The matrices consisted of mixtures of PS5 and $\text{PBr}_x\text{XE3}$ and their compositions are listed in Table 3. For each matrix measurements were made on four concentrations of PSD in the matrix. The concentrations of PSD were in the range 3 to 9 vol%. Only one concentration of PSD (3%) was used for sample V.

RESULTS

Miscibility measurements

Scanning calorimetry traces for a set of films all containing 30 wt% PS3 and 70 wt% of variously brominated derivatives of PXE3 are shown in Figure 2. Single T_g transitions are seen at low values of x , the degree of bromination, whilst two transitions are seen for $x > 0.75$. In Figure 3 the measured T_g values are plotted as a function of x and compared with the T_g values obtained for the pure PBr_xXE used in the blends.

In Figure 4, T_g is plotted versus x for a similar series of blends in which the PS3 is replaced by a lower molecular weight polystyrene, PS5. In this case the existence of one

Table 3 Matrix compositions of the samples used for the SANS measurements

Sample	Matrix composition (vol%)	Annealing temperature (°C)
I	100% PXE3	220
II	50% PXE3/50% PS5	230
III*	50% $\text{PBr}_{0.4}\text{XE}/50\%$ PS5	230
IV*	50% $\text{PBr}_{0.84}\text{XE}/50\%$ PS5	230
V	100% PS5	150†

*Parent resin PXE3

†Moulding temperature of specimen, not annealed

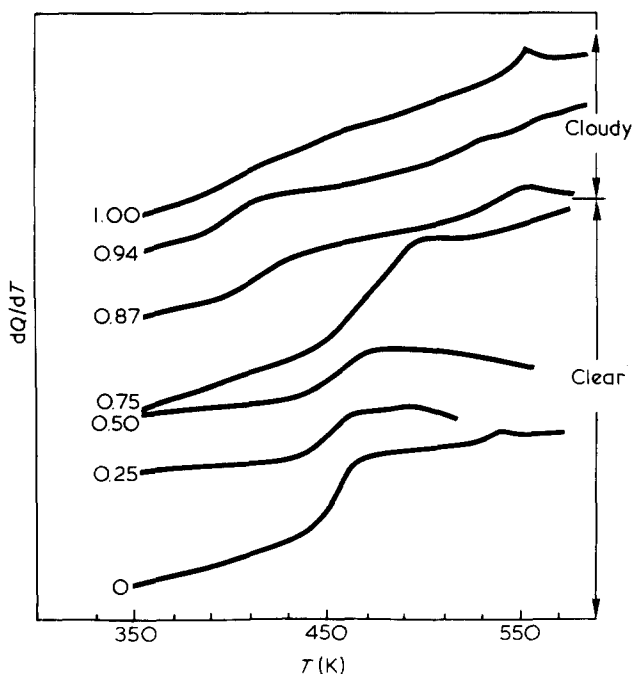


Figure 2 Scanning calorimetry traces for a set of cast films each containing 30 wt% PS3 and 70 wt% PBr_xXE based on PXE3. Inset numbers indicate values of x . dQ/dT is the heat flux in arbitrary units

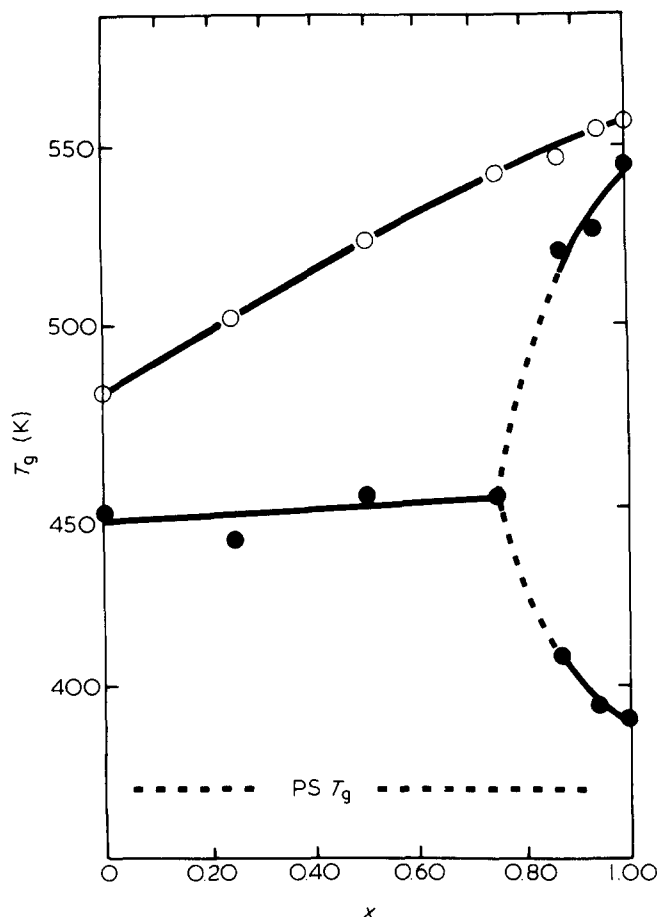


Figure 3 The dependence of the glass transition temperature, T_g , obtained from Figure 2 on x , the number of bromine atoms per XE monomer unit

T_g at all values of x suggests miscibility of all blends of this blend composition regardless of x . The experimental T_g values in Figure 4 depart increasingly with x from those calculated from the Fox equation using the experimental T_g values of the PS and the individual PBr_xXE values. In the conventional T_g plot for blends of a homopolymer with copolymers that differ from each other only in comonomer concentration, T_g would be plotted as a function of blend composition at each of several fixed copolymer compositions. However, in Figure 4, T_g is plotted against copolymer composition at one fixed blend composition. The departure from the theoretical prediction plotted in Figure 4 is tantamount to successively greater negative deviations of the plots of T_g versus blend composition as the parameter x is increased. The cause of this ultimately large deviation is not known at present. With regard to the number of phases present for a given x the calorimetric results for 30/70 blends generally agreed well with clarity results for 50/50 cast films.*

In the rare event that a conflict occurred between the results of the first two methods of detecting phase separation, this would be resolved through inspection of

* For two-phase blends the calorimetric transition associated with the PBr_xXE rich phase tended to be obscure. Related studies^{13,14} have shown that this obscurity arises from two sources: (1) a progressive reduction in ΔC_p at T_g for PBr_xXE with increasing x and (2) an increase in the temperature interval over which the transition occurs in mixed, arylene oxide rich phases. The obscurity of the 'upper' T_g could be counteracted by changing the PS/ PBr_xXE ratio from 50/50 to 30/70; cast film results *vis-à-vis* phase separation were insensitive to such a change.

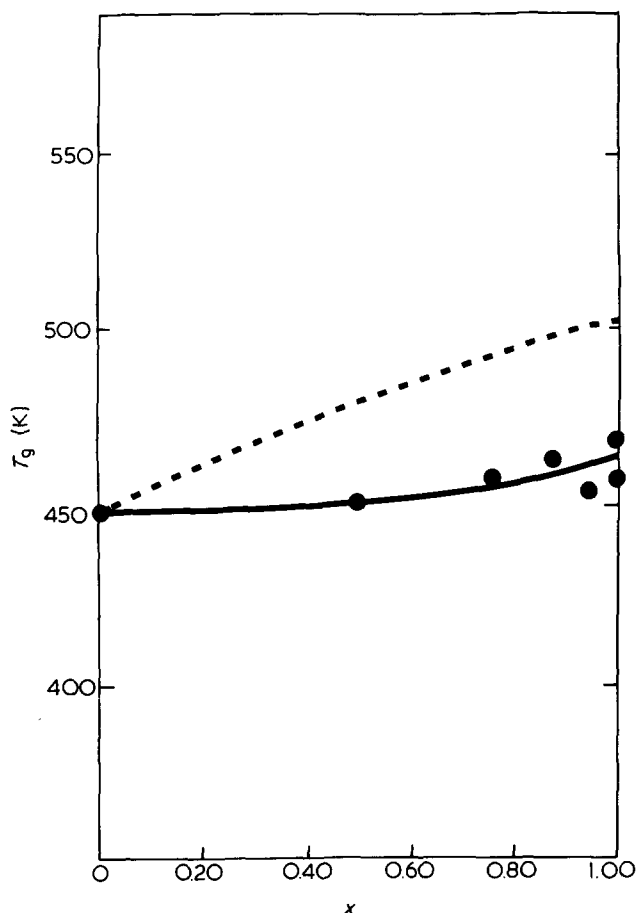


Figure 4 The dependence on x of the glass transition temperatures obtained from calorimetry traces of films containing 30 wt% PS5 and 70% PBr_xXE. The PBr_xXE polymers are based on PXE3. The broken line was calculated using the Fox equation

the films by scanning electron microscopy (Figure 5) or transmission electron microscopy (Figure 6). The existence of heterogeneity of contrast in the specimen would be taken as *prima facie* evidence for the existence of two phases.

Based on these experimental results the dependence on molecular weight of the critical level of bromination required to cause phase separation, x_c , in blends of 50 wt% PS and 50 wt% PBr_xXE was characterized for several PS/PXE parent molecular weight combinations. The values of x_c are shown in Table 4.

Small-angle neutron scattering

The excess scattering, I , of PSD over the blend matrix was analysed using the following equation:

$$\frac{K^*c_2}{I} = \frac{1}{M_2} [1 + 4\gamma A_2(c_1)c_1M_1] + \frac{q^2R_2^2}{3M_2} + 2A_2(c_1)c_2 \quad (1)$$

Equation (1) is based on Yamakawa's equation for the scattering from a multicomponent solution¹⁵ and its derivation is given in the Appendix. c_1 and c_2 are the concentrations and M_1 and M_2 are the molecular weights of PS5 and PSD, respectively. R_2 is the radius of gyration of PSD. $A_2(c_1)$ is the second virial coefficient for PSD in the 'solvent' at concentration c_1 of PS5. γ is the ratio v_2/v_1 ,

where v_i is the neutron contrast between component i and the 'solvent' component O. Equation (1) reduces to the well known Zimm equation for a two-component mixture (samples I and V) since $\gamma=0$ and $c_1=0$, thus

$$\frac{K^*c_2}{I} = \frac{1}{M_2} \left(1 + \frac{q^2R_2^2}{3} \right) + 2A_2(0)c_2 \quad (2)$$

The data were plotted as a function of c_2 and q^2 for samples I to IV and the resulting Zimm plots are shown in Figures 7-10 respectively. Values of A_2 and R_2 were calculated from the plots using the values of the neutron contrasts shown in Table 5. The calculated values of A_2 and R_2 are listed in Table 6. Since it has already been established that PSD in a bulk sample of PS adopts its unperturbed dimensions and A_2 is zero¹⁶ measurements were made on only one concentration of PSD in PS5 (sample V).

In Figures 11 and 12, A_2 and R_2 are plotted as a function of the concentration of PS5 in the matrix and the degree of bromination of the PXE respectively. A_2 is positive except for sample V where it is assumed to be

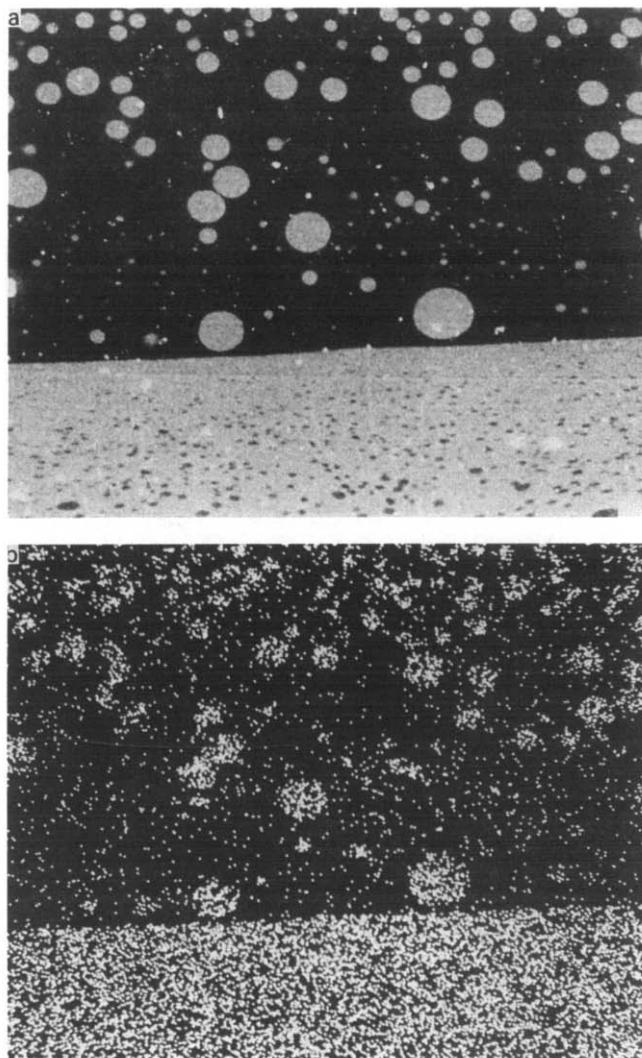


Figure 5 Scanning electron micrographs of a cross-section of cast film of 30 wt% PS3 and 70 wt% PBr₁XE (parent PXE3). Images of the same area formed by (a) secondary electron modulation (magnification x490), and (b) bromine X-ray emission (magnification x490). The light areas are bromine-rich. The morphology is a kinetic artefact of the casting process

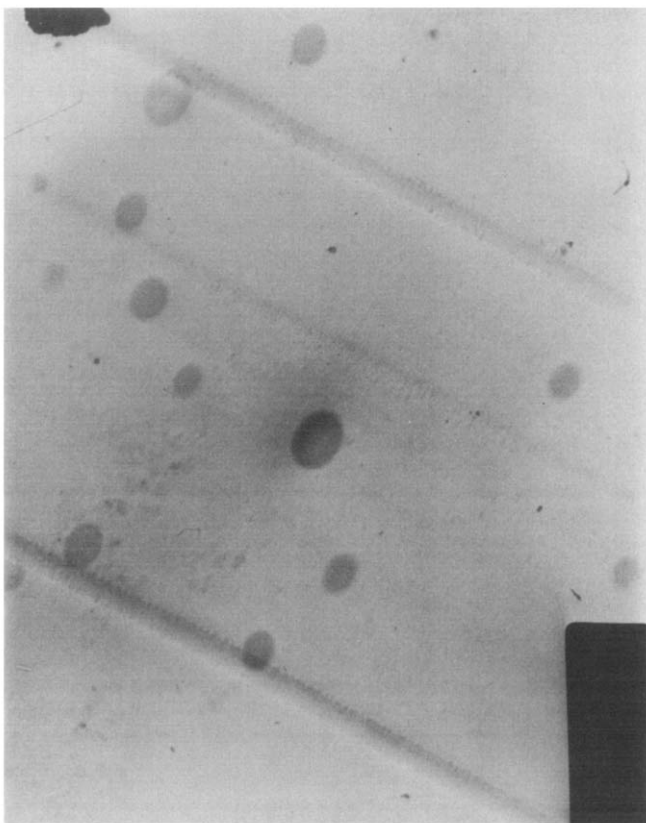


Figure 6 Transmission electron micrograph of an ultrasection of a phase-separated cast film showing bromine-rich inclusions (dark areas) (magnification x8888)

Table 4 Molecular weight dependence of the critical bromination level for phase separation, x_c , in PS/PBr_xXE blends (50/50 wt%)

PS	Parent PXE		
	PXE1	PXE2	PXE3
PS1	0.65	0.71	0.79
PS2	—	—	0.84
PS3	0.75	0.75	0.87*
PS4	0.80	0.88	0.90
PS5	0.86	0.92	>1.0
PS6	0.94	0.97	>1.0

* 30/70 wt% PS/PBr_xXE blends

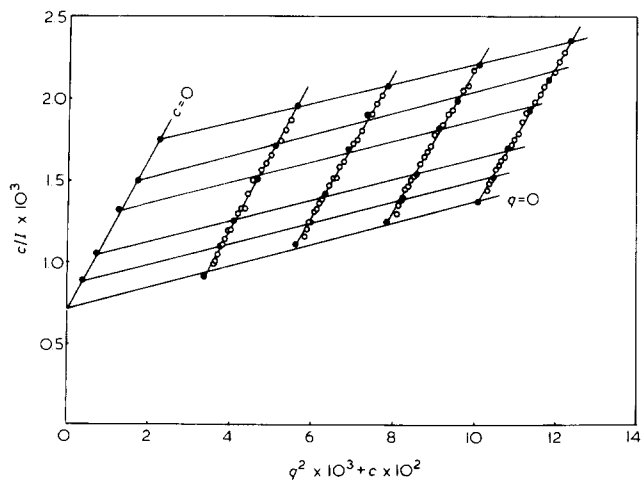


Figure 7 Zimm plot for PSD in PXE3

zero. The radius of gyration of the PSD chains decreases as the proportion of polystyrene in the matrix increases. The value of R_2 in 50% PS/50% PXE has dropped to that of the unperturbed chains ($R_2(V)$). Bromination of the PXE in the 50% PS/50% PXE matrix to a level of 0.4 Br/monomer has little effect on R_2 . However, when the

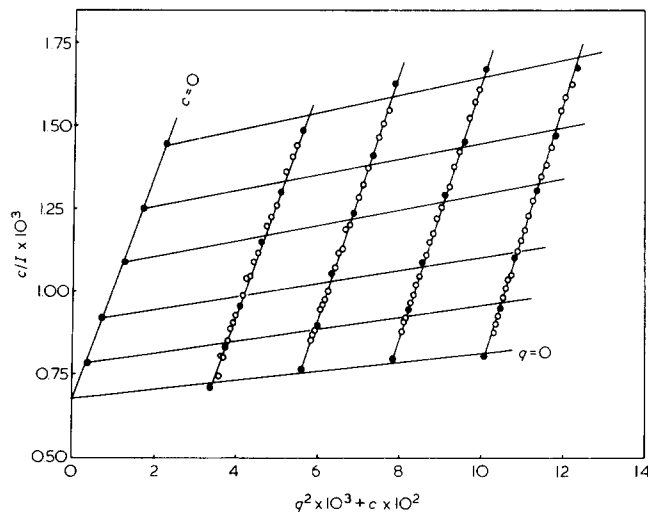


Figure 8 Zimm plot for PSD in 50 vol% PXE3/50 vol% PS5

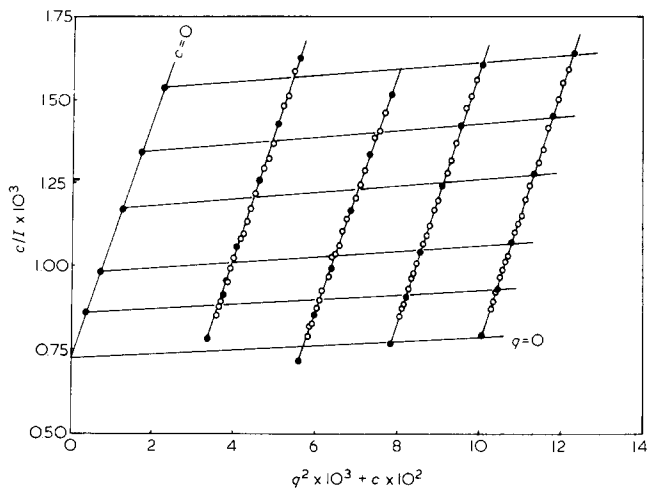


Figure 9 Zimm plot for PSD in 50 vol% PBr_{0.4}XE/50 vol% PS5

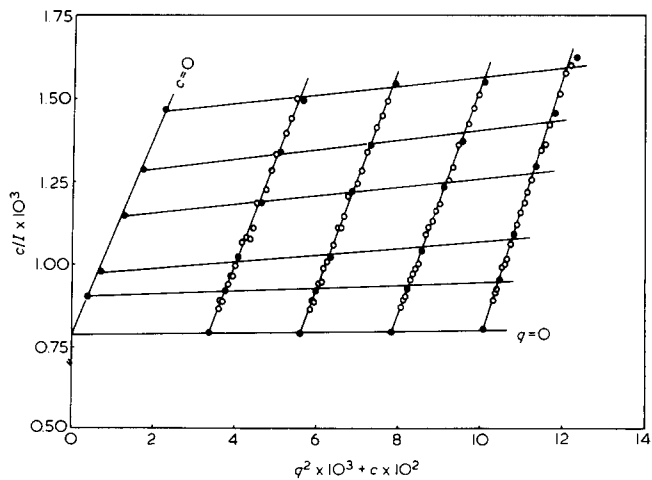


Figure 10 Zimm plot for PSD in 50 vol% PBr_{0.84}XE/50 vol% PS5

Table 5 Neutron contrasts for various polymer pairs

Polymer 1/polymer 2	$\nu \times 10^{12}$ (cm)*	$\nu^2 \times 10^{24}$ (cm ²)
PSD/PSH	8.328	69.36
PSD/PXE	8.076	65.23
PSD/PBr _{0.4} XE	7.895	62.33
PSD/PBr _{0.84} XE	7.736	59.85
PSH/PXE	-0.252	0.063
PSH/PBr _{0.4} XE	-0.433	0.188
PSH/PBr _{0.84} XE	-0.592	0.350

* $\nu = [\Sigma b_{1j} - (V_1/V_2) \Sigma b_{2j}]$ where Σb_{1j} and Σb_{2j} are the coherent scattering lengths of monomer 1 and monomer 2, respectively. V_j is the molar volume of polymer i

Table 6 Neutron scattering results

Sample	R_2 ($\pm 5\%$) (Å)	α^*	$A_2 \times 10^4$ (cm ³ g ⁻² mol)	x
I	44	1.16	1.51 \pm 0.2	-0.020
II	37	0.97	0.32 \pm 0.15	-0.0029
III	37	0.97	0.14 \pm 0.15	-0.0005
IV	33	0.87	0.033 \pm 0.7	0.0011
V	38	1	0	

* $\alpha = R_2/R_2(V)$

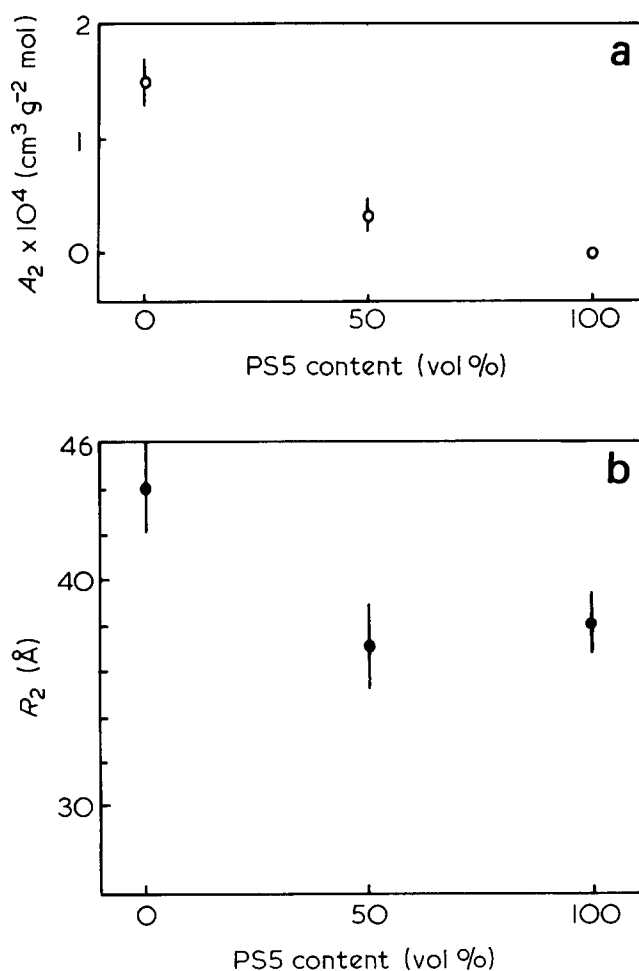


Figure 11 Plots of (a) A_2 and (b) R_2 as a function of PS5 content in PXE3/PS5 blends

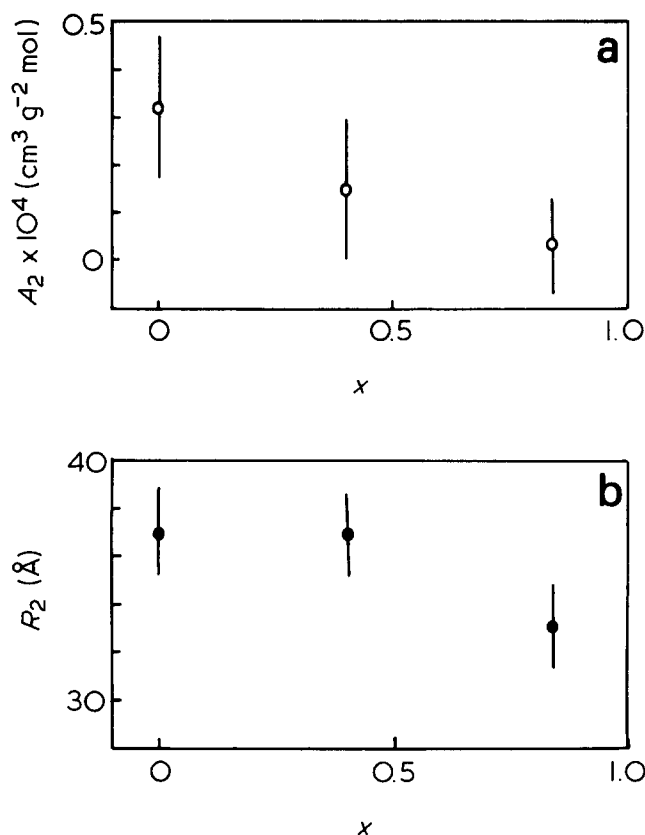


Figure 12 Plots of (a) A_2 and (b) R_2 as a function of bromine content, x , in the PBr _{x} XE/PS5 blends

level of bromination is increased to 0.84 Br/monomer R_2 decreases and A_2 goes essentially to zero, indicating that the PSD chains should be adopting an unperturbed conformation.

DISCUSSION

The miscibility measurements show that the compatibility of PS and PBr _{x} XE can be altered by changes in both the molecular weights of the polymer pair and the degree of bromination of the PXE. In keeping with the standard thermodynamic theory of phase behaviour in two-component polymer blends¹⁷ x_c is displayed in Figure 13 versus the sum of reciprocal weight average chain lengths of the two resins used for each blend series. The data fit a straight line approximately. Extrapolation to infinite molecular weight suggests a limiting bromine tolerance, x_c , of roughly 0.6. This result is qualitatively consistent with calorimetric results that suggest a small but favourable heat of mixing of the two parent resins. The very favourable interactions between PS and PXE are also confirmed by the SANS measurements. The values of A_2 and α , the expansion coefficient, for sample I (see Table 6) both indicate that PXE is a good solvent for PS. A_2 is large and positive for sample I and decreases with increasing concentration of PS in the blend. Similar behaviour has been observed for polymer solutions^{18,19}. Measurements on semi-dilute solutions showed that A_2 for PS in CS₂ tends to zero as the polymer concentration reaches 40 to 50%. Unlike polymer solutions the radius of gyration in the blend has already attained its unperturbed value when A_2 drops to zero.

The initial addition of bromine to the PXE has only a

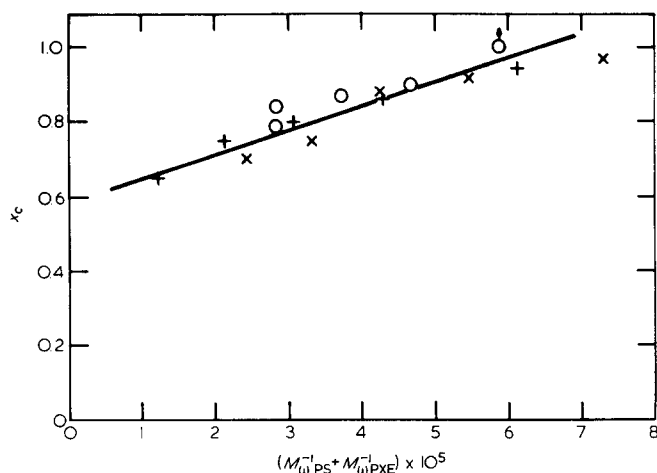


Figure 13 The dependence of x_c on the sum of the reciprocal weight average molecular weights of the PS and the parent PXE of each 50/50 blend series: +, PXE1; x, PXE2; o, PXE3

marginal effect on the values of A_2 and R_2 although increasing the level of bromine does cause these parameters to decrease further and R_2 drops below the unperturbed value. Assuming that phase separation will tend to occur when A_2 has dropped below zero then the data indicate that, for the molecular weights of the resins in the neutron scattering blends, x_c must be greater than 1, confirming the miscibility results for this polymer pair.

The unperturbed value for R_2 in matrix IV is less than that obtained for PSD in pure polystyrene. The decrease in R_2 is outside experimental error. The chains are molecularly dispersed as there is no sign of aggregation since the molecular weight of PSD measured by SANS is the same within experimental error in all the different matrices. The unperturbed value of the radius of gyration of PSD in matrix IV indicates that the PSD chains have adopted an unperturbed conformation which is more compact than in pure polystyrene. The reason for this change in conformation is not known but it may be associated with the presence of specific interactions between the polymers.

Since PSD and PS are assumed to be equivalent in a SANS experiment, it is possible to obtain a value for the interaction parameter, χ , between the polystyrene and the 'solvent' polymer. $A_2(c_1)$ is defined (see the Appendix) as the second virial coefficient for PSD or PS in the 'solvent', PBr_{x}XE . For a two-component polymer mixture²⁰ A_2 is defined as

$$A_2 = \frac{V_2^2}{V_0 M_2^2} (0.5 - P_0 \chi) \quad (3)$$

where V_2 and V_0 are the molar volumes of PSD and the 'solvent' polymer, respectively. P_0 is the degree of polymerization of the 'solvent'. χ has been calculated assuming that equation (3) holds not only at infinite dilution, but also at finite concentrations. The values of χ are listed in Table 6. Negative values of χ indicate that the polymers are completely miscible at that particular temperature. If the χ values are positive then the polymers are partially miscible and a change in molecular weight will cause phase separation. For all the blends, except IV, the values of χ are negative, confirming miscibility. However, for blend IV, χ is positive, indicating that at this level of bromination the polymers are only partially compatible and that a change in the molecular weight of

the components above a certain critical value will cause phase separation. If the degrees of polymerization of the polymers are approximately the same then this critical value can be defined as²¹:

$$P_{cr} = 2/\chi$$

for $\chi > 0$, so that for PS and $\text{PBr}_{0.84}\text{XE}$, $P_{cr} \approx 10^3$. This is equivalent to a molecular weight for the PS and the parent PXE of about 10^5 . The closest match to a blend of these molecular weights would be a blend of PS3 and PXE1. In fact, the level of bromination required to cause phase separation in this blend is 0.75, slightly lower than the predicted 0.84. However, considering that the molecular weights are only approximately matched, the agreement is very reasonable.

In the interests of completeness it should be pointed out that, while our SANS results, our blend results and the cited calorimetry results are internally consistent *vis-à-vis* free energies and heats of mixing, a contradiction may exist with the results of Jelenic *et al.*⁷ These workers determined a value of χ of 0.0018 for PSD and PXE at infinite dilution. For both their polymers $M \sim 5 \times 10^5$. If the results of the two SANS studies were both valid, the fact that their χ is lower than the present value by a factor of 10 might suggest that $\chi \rightarrow 0$ as $M \rightarrow \infty$, i.e. that PS and PXE are immiscible at infinite molecular weight. At present, however, the favourable heats of mixing and the miscibility results obtained in the current study make such a conclusion doubtful. Thus the resolution of the question of the χ dependence on M will have to await a further study.

CONCLUSIONS

Both the miscibility measurements and the SANS measurements of the current study suggest that miscibility in PS/PXE blends occurs at all molecular weights. Phase separation can be induced by brominating the PXE component to a sufficiently high level. Values of χ calculated from SANS measurements serve to predict the onset of phase separation at molecular weights and levels of bromination consistent with the results of miscibility studies.

APPENDIX

The scattering has been analysed using the equation developed for multicomponent systems by Yamakawa¹⁵. The excess scattering, I , from a multicomponent solution comprising $n + 1$ components over that from the solvent can be written as:

$$\frac{I}{K} = \sum_{i=1}^n v_i^2 P_{1,i}(qc) M_i c_i - 2 \sum_{i=1}^n \sum_{j=1}^n v_i v_j M_i M_j P_{2,ij}(qc) A_{2,ij}(c) c_i c_j \quad (\text{A.1})$$

where K is a normalization constant, M_i and c_i are the molecular weight and concentration in g ml^{-1} of component i , respectively. v_i is the neutron contrast between component i and the solvent, component 0. $P_{1,i}(qc)$ is the intramolecular interference function for component i . $P_{2,ij}(qc)$ is the intermolecular interference function for

components i and j . Both P_1 and P_2 are functions of q , where $q = (4\pi/\lambda) \sin(\theta/2)$ and θ is the scattering angle, and the set of concentrations c , i.e. c_1, c_2, \dots, c_n . $A_{2,ij}(c)$ is the osmotic second virial coefficient for components i and j at concentrations c .

Consider a ternary solution of three polymers, PBr_xXE (component 0), PS (1) and PSD (2). The excess scattering from components 1 and 2 can be written as:

$$I/K = v_1^2 M_1 P_{1,1}(qc_1 c_2) c_1 + v_2^2 M_2 P_{1,2}(qc_1 c_2) c_2 - 2v_1^2 M_1^2 P_{2,11}(qc_1 c_2) A_{2,11}(c_1 c_2) c_1^2 - 2v_2^2 M_2^2 P_{2,22}(qc_1 c_2) A_{2,22}(c_1 c_2) c_2^2 - 4v_1 v_2 M_1 M_2 P_{2,12}(qc_1 c_2) A_{2,12}(c_1 c_2) c_1 c_2 \quad (\text{A.2})$$

Similarly, the excess scattering from the two-component system PS (1) and PBr_xXE (0) can be written as

$$I/K = v_1^2 M_1 P_{1,1}(qc_1) c_1 - 2v_1^2 M_1^2 P_{2,11}(qc_1) A_{2,11}(c_1) c_1^2 \quad (\text{A.3})$$

In order to simplify these equations the following assumptions have been made for $c_2 \gg c_1$:

$$P_{1,1}(qc_1 c_2) = P_{1,1}(qc_1)$$

$$P_{2,11}(qc_1 c_2) = P_{2,11}(qc_1)$$

and

$$A_{2,11}(c_1 c_2) = A_{2,11}(c_1)$$

In order to reduce the number of variables further the deuterated and hydrogenous PS are considered to be identical in every way except for their neutron scattering lengths; therefore

$$A_{2,11}(c_1 c_2) = A_{2,22}(c_1 c_2) = A_{2,12}(c_1 c_2) = A_2(c_1)$$

and

$$P_{2,11}(qc_1 c_2) = P_{2,22}(qc_1 c_2) = P_{2,12}(qc_1 c_2) = P_2(qc_1)$$

Subtracting (A.3) from (A.2) and incorporating the above assumptions the following equation is obtained:

$$I/K = v_2^2 M_2 P_{1,2}(qc_1) c_2 - 2v_2^2 M_2^2 P_2(qc_1) A_2(c_1) c_2^2 - 2v_1 v_2 M_1 M_2 P_2(qc_1) A_2(c_1) c_1 c_2 \quad (\text{A.4})$$

At low c_2 and low q , $P_2(qc_1) \approx 1$ and equation (A.4) can be rearranged and inverted to give:

$$\frac{Kv_2^2 c_2}{I} = \frac{1}{M_2} [P_{1,2}(qc_1)^{-1} + 4\gamma A_2(c_1) c_1 M_1] + 2A_2(c_1) c_2 \quad (\text{A.5})$$

where $\gamma = v_1/v_2$. At low q , $P_{1,2}(qc_1)^{-1}$ can be written as:

$$P_{1,2}(qc_1)^{-1} = 1 + \frac{q^2 R_2^2}{3} \quad (\text{A.6})$$

where R_2^2 is the mean square radius of gyration of component 2 (PSD). Substituting (A.6) into (A.5), the final equation is:

$$\frac{K^* c_2}{I} = \frac{1}{M_2} [1 + 4\gamma A_2(c_1) c_1 M_1] + \frac{q^2 R_2^2}{3M_2} + 2A_2(c_1) c_2 \quad (\text{A.7})$$

where $K^* = Kv_2^2$. Equation (A.7) is essentially the same as the equation for an ordinary ternary solution composed of two polymers in a solvent, with the difference that $A_2(c_1)$ is the virial coefficient for the two-component system PS (or PSD) and 'solvent' PBr_xXE . $A_2(c_1)$ and R_2 can be obtained from the normal Zimm plot of c_2/I versus q^2 and c_2 . It should be noted that the intercept of this plot, which normally yields the molecular weight, is modified by the function in the square brackets.

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