Deuterated polystyrene–poly(α-methylstyrene) blends: range of miscibility and determination of the interaction parameter by small angle neutron scattering

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The range of miscibility of deuterated polystyrene–poly(α-methylstyrene) blends (PSD–PαMS) as a function of the molecular weights of the two polymeric components has been established by differential scanning calorimetry and phase contrast optical microscopy. The analysis of small angle neutron scattering measurements (1) in terms of an apparent radius of gyration, (2) from the intensity of scattering extrapolated to zero angle and (3) from the method which consists in replacing part of the PSD chains by PSH chains has allowed the determination of the dimensions of deuterated polystyrene dispersed in poly(α-methylstyrene) and of the interaction parameter χ between the two polymers ($\chi = 5.0 \times 10^{-3}$).

(Keywords: polymer blends; small angle neutron scattering; deuterated polystyrene; poly(α-methylstyrene); range of miscibility; Flory interaction parameter)

INTRODUCTION

The thermodynamics of polymer blends has been intensively studied recently[1,2]. In particular, several recent papers have been devoted to the investigation of the concentration fluctuations in the one-phase region and the determination of the interaction parameter by scattering methods[3–8].

We have considered the particular case of a mixture of two polymers, deuterated polystyrene–poly(α-methylstyrene) (PSD–PαMS), which should exhibit, like the hydrogenated polystyrene–poly(α-methylstyrene) (PSH–PαMS) pair[9–13], an upper critical solution temperature (UCST). In the first part of this Paper, we present results concerning the complete determination of the miscibility diagram of PSD and PαMS. The second part deals with the characterization by small angle neutron scattering (SANS) of the homogeneous phase of PSD–PαMS blends. More precisely, we report on the evaluation of the interaction parameter χ using recent theoretical treatments which relate the intensity scattered by a homogeneous mixture of two polymers to χ and to the structure factors of the two polymeric components.

EXPERIMENTAL

Polymer samples were synthesized by anionic polymerization. Deuterated styrene was polymerized in tetrahydrofuran at −70°C using phenylisopropylpotassium as the initiator. The polymerization of α-methylstyrene was initiated in tetrahydrofuran at 0°C with naphthalene sodium and performed at −30°C. Poly(α-methylstyrene) samples were fractionated from benzene solution by progressive addition of methanol. PαMS fractions and PSD samples exhibit narrow molecular weight distributions. Their molecular weights measured by light scattering and size exclusion chromatography are given in *Table 1*.

The blends were prepared by dissolution of given amounts of polymers in benzene. The blends were freeze dried, then dried under vacuum (1.3 Pa) for 2 days at 60°C to remove residual benzene. The samples were compression moulded under vacuum into discs of 14 mm diameter and 1 mm thickness at 230°C (about 50°C above the T_g of PαMS).

Differential scanning calorimetry (d.s.c.) and phase contrast optical microscopy were used to examine the miscibility of blends. The glass transition behaviour of the blends and of the blend components was characterized using a Perkin–Elmer DSC4 equipped with a microcomputer. A typical measurement consisted of heating the sample to 230°C for a short time and cooling at 80°C min^{-1} to 25°C. The sample was then analysed at a 20°C min^{-1} heating rate. Several runs were made to ensure a uniform thermal history. The third and subsequent scans were reproducible. The glass transition temperature T_g was taken as the temperature corresponding to half of the heat capacity change.

Microscopy measurements were performed with a Zeiss photomicroscope II with a lower limit resolution of about 1 μm.

Small angle neutron scattering experiments were

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Table 1 Polymer characteristics

Sample	$\langle M_i\rangle_w$	$\langle M_i\rangle_n$	$\langle M_i\rangle_w/\langle M_i\rangle_n$
PSD			
A1	29 900	25 800	1.16
A2	37 700	34 000	1.11
A3	46 700	40 300	1.16
A4	55 700	47 200	1.18
A5	66 000	57 900	1.14
A6	90 000	78 300	1.15
PαMS			
B1	39 000	36 100	1.08
B2	49 000	39 800	1.23
B3	56 600	46 000	1.23
B4	64 300	56 000	1.15
B5	77 800	60 300	1.29
B6	102 600	84 100	1.22

carried out on the cameras PACE and PAXY at the Laboratoire Léon Brillouin in Saclay, France. The scattering data were obtained over the range of scattering wavevectors $5\times10^{-3}<q<5.4\times10^{-2}$ Å^{-1}* ($q=4\pi\lambda^{-1}\sin\theta/2$, where λ is the neutron wavelength and θ the scattering angle).

The radially averaged intensities were corrected from sample cell scattering, sample thickness and transmission and normalized by an incoherent flat scatterer (pure water) in order to correct for detector efficiency.

The coherent scattering intensities were obtained by subtracting an appropriate incoherent background, taken as a hydrogenated matrix (poly(α-methylstyrene)) reduced to a thickness $\phi_H t$ (ϕ_H is the volume fraction of PαMS in the blends and t the labelled sample thickness). Although this method does not exactly account for the incoherent scattering intensities, the error involved is insignificant in comparison with the high level of coherent scattering intensities.

The measured intensities were finally converted to an absolute differential scattering cross section per unit solid angle and per unit volume of sample (in units of cm^{-1}) by calibrating the instrument with a secondary standard (partially labelled blends of well characterized monodisperse polystyrene).

THEORETICAL BACKGROUND

The absolute coherent scattering intensity $I(q)$ per unit volume for a homogeneous polymer blend containing two monomers A and B is given by

$$\frac{N(b_A/v_A-b_B/v_B)^2}{I(q)}=S^{-1}(q) \qquad (1)$$

where b_A and b_B, v_A and v_B are, respectively, the coherent scattering lengths per mole and the molar volumes for monomers A and B. For PSD, $b_A=10.656\times10^{-12}$ cm mol^{-1}, $v_A=98.94$ cm^3 mol^{-1}; for PαMS, $b_B=2.245\times10^{-12}$ cm mol^{-1}, $v_B=109.97$ cm^3 mol^{-1}; N is Avogadro's number. $S(q)$ is the structure factor related to the interaction parameter χ_{AB} by the expression[14]

$$S^{-1}(q)=\frac{1}{\phi_A V_A P_A(q)}+\frac{1}{\phi_B V_B P_B(q)}-2\frac{\chi_{AB}}{v_0} \qquad (2)$$

V_A and V_B, ϕ_A and ϕ_B are, respectively, the number average molar volumes and the volume fractions. v_0 is a molar volume of reference that we have defined as

$$1/v_0=\phi_A/v_A+\phi_B/v_B$$

P_A and P_B are Debye functions which, when the polymers are polymolecular, assuming a Zimm–Schultz distribution[15,16], are given by[17]

$$P_i(q)=\frac{1}{q^4\langle R_i^4\rangle_n}\left[q^2\langle R_i^2\rangle_n-1+\left(\frac{1}{1+q^2\langle R_i^2\rangle_n/k}\right)^k\right]$$

where $\langle R_i\rangle_n$ is the number average radius of gyration and

$$k=[\langle M_i\rangle_w/\langle M_i\rangle_n-1]^{-1}$$

i.e.

$$\langle M_i\rangle_w/\langle M_i\rangle_n=(k+1)/k$$

Then

$$\frac{\langle M_i\rangle_z}{\langle M_i\rangle_w}=\frac{\langle R_i^2\rangle_z}{\langle R_i^2\rangle_w}=\frac{k+2}{k+1}$$

where $\langle R_i\rangle_z$, $\langle R_i\rangle_w$ are, respectively, the z average and weight average radii of gyration.

For small q values, i.e. $q\langle R_i\rangle_n\ll1$, one can write equation (2) as:

$$S^{-1}(q)=\frac{1}{\phi_A\langle M_A\rangle_w/D_A}\left(1+q^2\frac{\langle R_A^2\rangle_z}{3}\right)+\frac{1}{\phi_B\langle M_B\rangle_w/D_B}\left(1+q^2\frac{\langle R_B^2\rangle_z}{3}\right)-2\frac{\chi_{AB}}{v_0}$$

where D_A and D_B are the densities of polymers A and B. Then

$$S^{-1}(q)=\frac{2}{v_0}(\chi_s-\chi_{AB})+\left(\frac{\langle R_A^2\rangle_z}{\phi_A\langle M_A\rangle_w/D_A}+\frac{\langle R_B^2\rangle_z}{\phi_B\langle M_B\rangle_w/D_B}\right)\frac{q^2}{3}$$

with

$$\chi_s=\frac{v_0}{2}\left(\frac{1}{\phi_A\langle M_A\rangle_w/D_A}+\frac{1}{\phi_B\langle M_B\rangle_w/D_B}\right) \qquad (3)$$

χ_s is the value of χ at the spinodal.

If we introduce the z average mean square 'apparent radius of gyration' $\langle R_{ap}^2\rangle_z$ for the whole system with two components[18],

$$S(q)=S(0)(1-q^2\langle R_{ap}^2\rangle_z/3$$

where $S(0)$ is the intensity scattered at $q=0$ ($S^{-1}(0)=2\chi_s/v_0$), we obtain

$$\langle R_{ap}^2\rangle_z=\frac{v_0}{2(\chi_s-\chi_{AB})}\left(\frac{\langle R_A^2\rangle_z}{\phi_A\langle M_A\rangle_w/D_A}+\frac{\langle R_B^2\rangle_z}{\phi_B\langle M_B\rangle_w/D_B}\right) \qquad (4)$$

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* 1 Å = 10^{-1} nm

The determination of $\langle R_{ap}\rangle_z$ requires a knowledge of the radii of gyration of the two polymers. For PSD, we have determined R_{PSD} from the well-known law of variation of $\langle R_{PSD}\rangle_w$ *versus* $\langle M_{PSD}\rangle_w$ [19]:

$$\langle R_{PSD}\rangle_w = 0.282\langle M_{PSD}\rangle_w^{0.5}$$

For PαMS, we have calculated $R_{P\alpha MS}$ from the law established by Cowie *et al.* in a theta solvent[20]:

$$\langle R_{P\alpha MS}\rangle_w = 0.269\langle M_{P\alpha MS}\rangle_w^{0.5}$$

For $q\langle R_i\rangle \gg 1$, we have

$$\langle P_i(q)\rangle = \frac{2}{q^2\langle R_i^2\rangle_n}$$

and χ_{AB} becomes negligible. One can write

$$\langle R_A^2\rangle_n = \langle Z_A\rangle_n a_A^2/6$$

$$\langle R_B^2\rangle_n = \langle Z_B\rangle_n a_B^2/6$$

where a_A, a_B are, respectively, the Kuhn length segments; $\langle Z_A\rangle_n$, $\langle Z_B\rangle_n$ are the number average polymerization indices; and

$$\langle M_A\rangle_n/D_A = \langle Z_A\rangle_n v_A$$

$$\langle M_B\rangle_n/D_B = \langle Z_B\rangle_n v_B$$

Equation (2) reduces to

$$S^{-1}(q) = \left(\frac{a_A^2}{\phi_A v_A} + \frac{a_B^2}{\phi_B v_B}\right)\frac{q^2}{12} \qquad (5)$$

RESULTS AND DISCUSSION

The results of d.s.c. and of microscopy experiments are given in *Figures 1–3*. The range of miscibility of PSD–PαMS blends as a function of the molecular weights of the two components is shown in *Figure 1*. The corresponding theoretical curve has been obtained using Flory theory from the conditions for stability and criticality which can

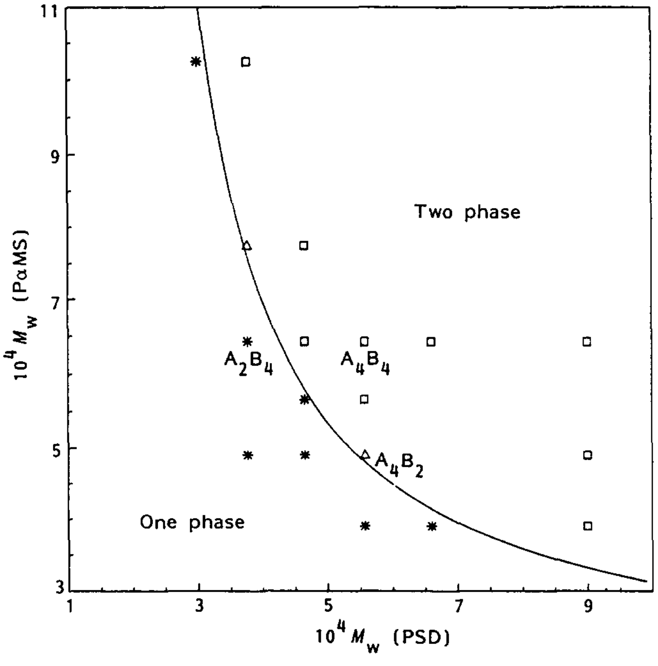

Figure 1 Molecular weight dependence on miscibility range of PSD–PαMS blends at the critical composition (ϕ_c) of each blend. □, phase separated systems; *, homogeneous blends; △, see text. Theoretical curve calculated using equation (6) with $\chi_c = 0.00445$

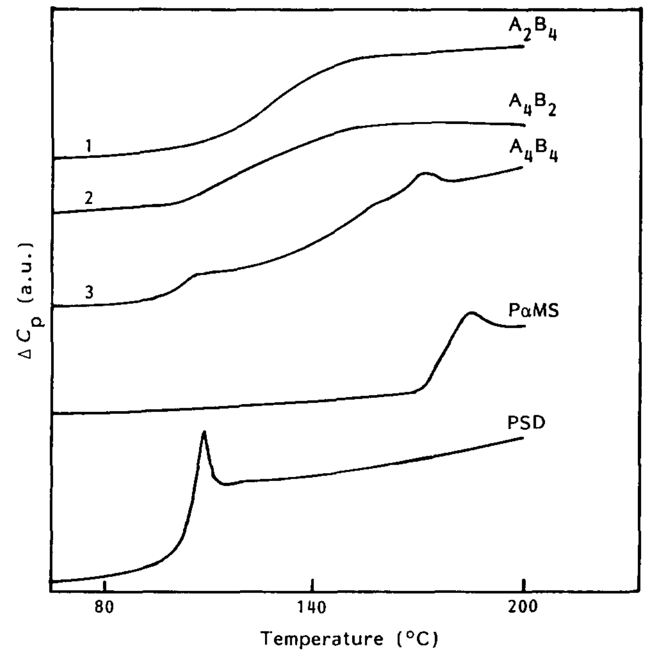

Figure 2 D.s.c. thermograms of PSD–PαMS blends and PSD and PαMS homopolymers

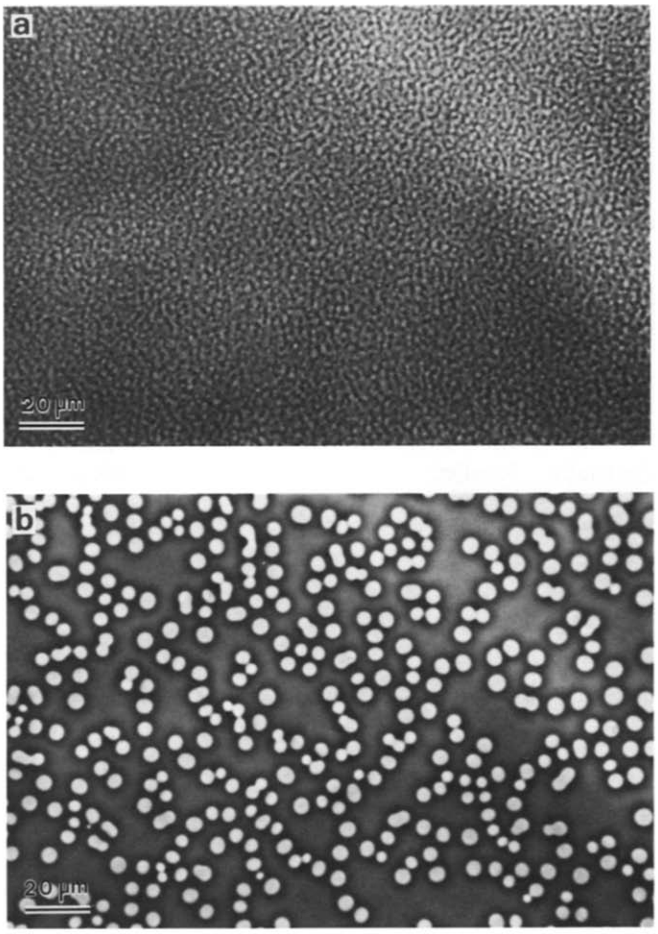

Figure 3 Phase contrast optical micrographs: (a) blend A_4B_2; (b) blend A_4B_4

be expressed in terms of χ_c and ϕ_c:

$$\chi_c=\frac{v_0}{2}\left(\frac{1}{\phi_A^c\langle M_A\rangle_w/D_A}+\frac{1}{\phi_B^c\langle M_B\rangle_w/D_B}\right)$$

$$\phi_A^c=\frac{1}{1+\left(\dfrac{\langle M_A\rangle_w/D_A}{\langle M_B\rangle_w/D_B}\right)^{1/2}}$$

where χ_c is the value of χ at the critical point and ϕ_A^c the critical volume fraction of A.

We obtain

$$\langle M_B\rangle_w=D_B\left[\left(\frac{2\chi_c}{v_0}\right)^{1/2}-\left(\frac{1}{\langle M_A\rangle_w/D_A}\right)^{1/2}\right]^{-2} \qquad (6)$$

The experimental points correspond to the critical composition of each blend and have been determined at room temperature. In fact, they must correspond to the behaviour of the blends above their T_gs since upon passing through the glass transition region the structure of each blend is frozen into a glassy state. (As an example, the values of T_g *versus* the composition of the blend are presented in *Figure 4* for the compatible blend A_2B_4[21].) Note that the blends located near the 'miscibility curve' in the two-phase region (points △; *Figure 1*) become homogeneous only for temperatures of the order of 200°C. *Figure 2* shows the thermograms obtained with three different blends. Curve 1 exhibits a single T_g and corresponds to a compatible blend (A_2B_4). Curve 2 displays a broadening of the glass transition region and corresponds to a blend (A_4B_2) which begins to phase separate, as illustrated by the micrograph of *Figure 3(a)*. Curve 3 displays two T_gs and indicates a phase-separated blend (A_4B_4). This behaviour is confirmed by the microscopy results (*Figure 3b*): the dimensions of the dispersed particles are about 4 μm.

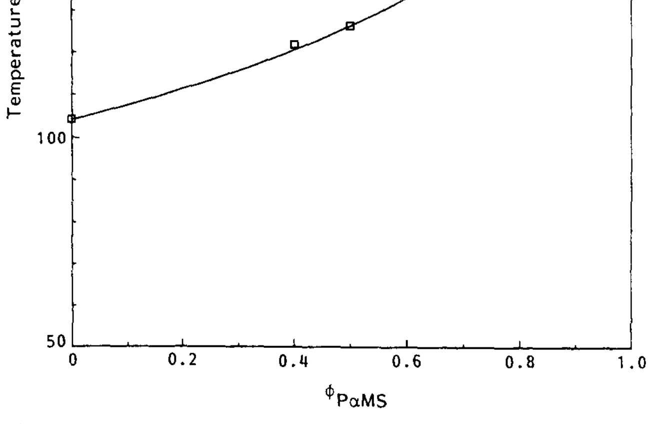

Figure 4 Glass transition temperature (T_g) *versus* composition for blend A_2B_4. □, Experimental points. Theoretical curve calculated from Wood's equation[21] with an adjustable parameter $k=2.3$

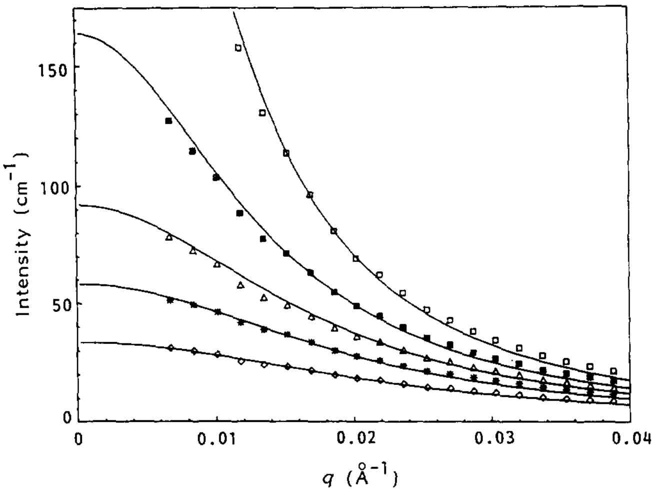

Figure 5 SANS intensity *versus* scattering vector q for blend A_2B_4 at different PSD contents. The solid curves are the predicted scattering profiles calculated from equations (1) and (2) with $\langle\chi\rangle=5.0\times10^{-3}$. ϕ_{PSD} values: □, 0.3872; ⊞, 0.2890; △, 0.2400; ★, 0.1916; ◇, 0.1433

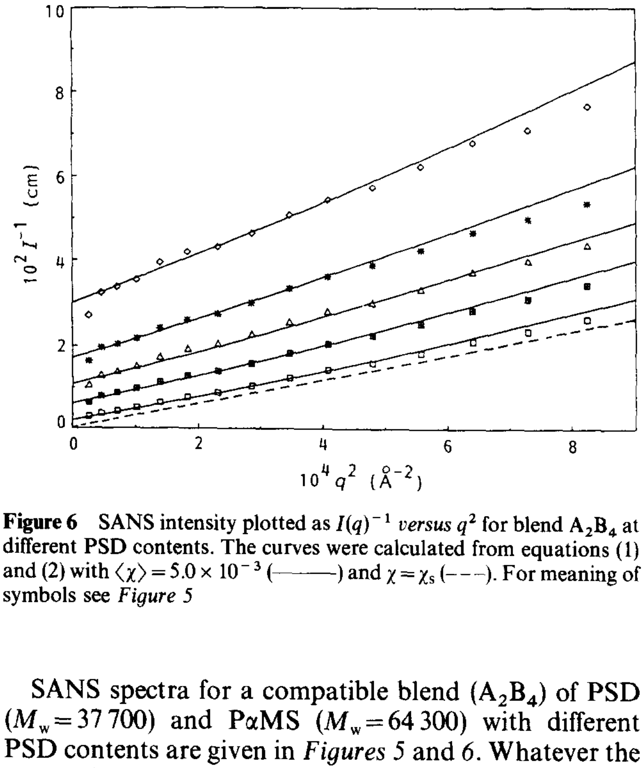

Figure 6 SANS intensity plotted as $I(q)^{-1}$ *versus* q^2 for blend A_2B_4 at different PSD contents. The curves were calculated from equations (1) and (2) with $\langle\chi\rangle=5.0\times10^{-3}$ (———) and $\chi=\chi_s$ (– – –). For meaning of symbols see *Figure 5*

SANS spectra for a compatible blend (A_2B_4) of PSD ($M_w=37\,700$) and PαMS ($M_w=64\,300$) with different PSD contents are given in *Figures 5* and *6*. Whatever the composition of the blend, one observes good agreement between the experimental scattering curves $I(q)=f(q)$ registered at room temperature (*Figure 5*) and the theoretical curves (predicted scattering profiles for homogeneous mixtures). The scattering curves in the Zimm representation (*Figure 6*) allow the determination of the radius of gyration: a linear dependence of $I^{-1}(q)$ as a function of q^2 is obtained. It can be seen that with increasing PSD content the experimental plots tend to the curve calculated from equations (1) and (2) with $\chi=\chi_s$, corresponding to the limit of single phase stability. Moreover $q^2I(q)$ *versus* q plots (*Figure 7*) show that for higher q values ($qR\gg1$), $q^2I(q)$ reaches a constant value, as predicted by equation (5). This means that the PSD chains dispersed in PαMS adopt Gaussian statistics. *Figure 8* represents the experimental values of the apparent radius of gyration as a function of the volume fraction of PSD and the theoretical curves for different

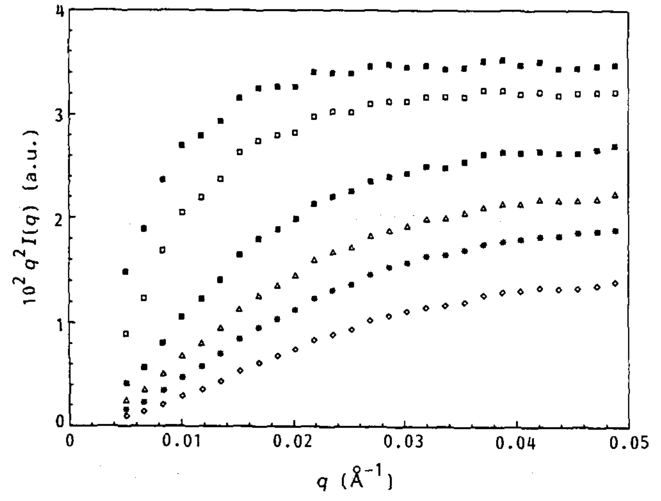

Figure 7 $q^2 I(q)$ *versus* q plot for blend A_2B_4 at different values of ϕ_{PSD}: ◇, 0.1433; ★, 0.1916; △, 0.2400; ⊞, 0.2890; □, 0.3872; ⊠, 0.4370

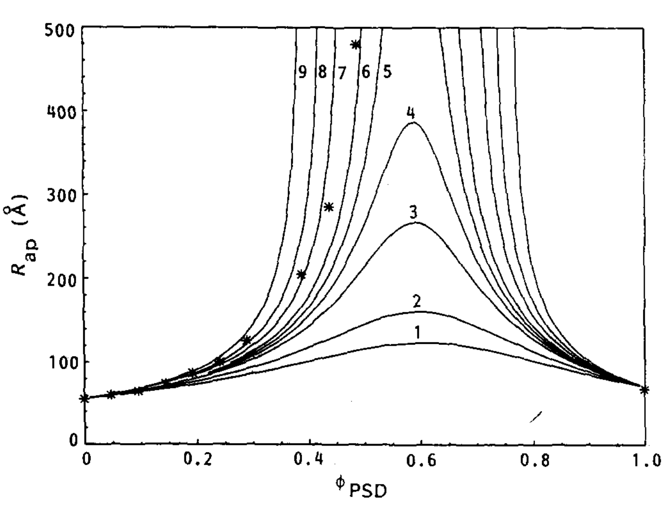

Figure 8 Apparent radius of gyration *versus* blend composition for different values of χ; *, measured values. χ values: curve 1, 0.0035; 2, 0.0040; 3, 0.0045; 4, 0.0046; 5, 0.0047; 6, 0.0048; 7, 0.0050; 8, 0.0052; 9, 0.0055

Table 2 $\chi_{PSD\text{-}P\alpha MS}$ values for binary blend A_2B_4

Φ_{PSD}	$\chi_{PSD\text{-}P\alpha MS}$ $\pm 5\times 10^{-4}$ (at $q=0$)	$\chi\langle Z_{P\alpha MS}\rangle_w$
0.0953	0.0046	2.51
0.1433	0.0047	2.60
0.1916	0.0052	2.84
0.2400	0.0050	2.74
0.2890	0.0052	2.85
0.3872	0.0050	2.73
0.4370	0.0049	2.68
0.4866	0.0048	2.63

values of χ. We have obtained an average value of the interaction parameter: $\langle\chi\rangle = 5.0 \pm 0.3 \times 10^{-3}$ in good agreement with that determined from the intensity scattered at zero angle (*Table 2*).

In terms of the mean field theory of Flory–Huggins, equation (3) corresponds to the limit of stability (spinodal curve) for a mixture of two polymers. This spinodal curve can be represented (*Figure 9*) in terms of the product $\chi_s\langle Z_{P\alpha MS}\rangle = f(\phi_{P\alpha MS})$, where $\langle Z_{P\alpha MS}\rangle$ is the weight average degree of polymerization of PαMS. It confirms that the polymers investigated are compatible, since the blends are located in the homogeneous region of phase space.

It is worth noting that for a given composition of the blend we have not found any significant variation of the radius of gyration and therefore of χ *versus* temperature. This can be explained by the small range of temperatures investigated above the T_g of the blend and above the T_g of PαMS.

It should be emphasized that the radius of gyration measured is an apparent radius of gyration, the value of which increases with increasing PSD content. Thus, for PSD volume fractions ranging from 0.3 to 0.5, the values of R_{ap} are high (> 150 Å). However, it is possible to obtain not only the actual values of the radius of gyration and of PSD molecular weight over the entire phase diagram, but also the interaction parameter χ by using the method developed in References 22–24. This method consists in replacing some of the PSD chains by the corresponding hydrogenated species (PSH) of the same molecular weight. Then the scattered intensity can be expressed as (see equation (13) in reference 22)

$$I(q) = Z_{PS}^2\{[N_D(b_{PSD} - b_{P\alpha MS})^2 + N_H(b_{PSH} - b_{P\alpha MS})^2 P(q) + [N_D(b_{PSD} - b_{P\alpha MS}) + N_H(b_{PSH} - b_{P\alpha MS})]^2 Q(q)\} \quad (7)$$

where $Z_{PS} = Z_{PSH} = Z_{PSD}$ is the weight average degree of polymerization of polystyrene chains; $N = N_H + N_D$ is the total number of H and D polystyrene molecules per unit

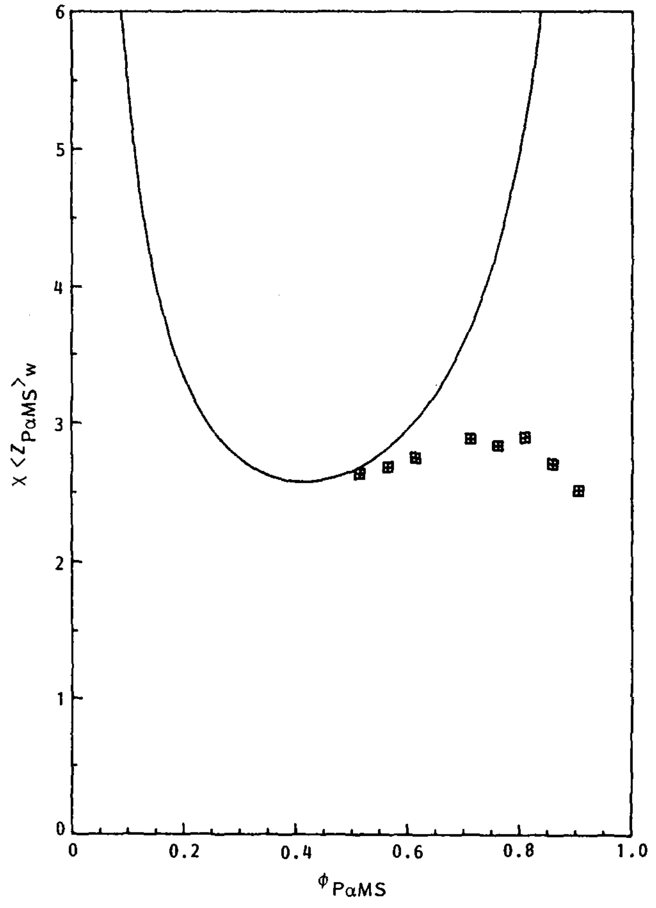

Figure 9 Calculated spinodal curve for blend A_2B_4; see text. ⊞, Experimental points corresponding to $\chi\langle Z_{P\alpha MS}\rangle_w$ given in *Table 2*

volume; and $P(q)$ and $Q(q)$ are, respectively, the single-chain scattering function and the intermolecular correlation function of deuterated or hydrogenated polystyrene.

Relation (7) is only valid if $\chi_{\mathrm{PSD/P\alpha MS}} \simeq \chi_{\mathrm{PSH/P\alpha MS}}$ and $\chi_{\mathrm{PSD/PSH}} \simeq 0$. The latter assumption is reasonable, since $\chi_{\mathrm{PSD/PSH}}$ is very small (of the order of 2×10^{-4} (refs. 5, 6)). Equation (7) can be rewritten as

$$I(q) \simeq [x(b_{\mathrm{PSD}} - b_{\mathrm{P\alpha MS}})^2 + (1-x)(b_{\mathrm{PSH}} - b_{\mathrm{P\alpha MS}})^2] NZ_{\mathrm{PS}}^2 P(q) + [x(b_{\mathrm{PSD}} - b_{\mathrm{P\alpha MS}}) + (1-x)(b_{\mathrm{PSH}} - b_{\mathrm{P\alpha MS}})]^2 N^2 Z_{\mathrm{PS}}^2 Q(q) \qquad (8)$$

with $x = N_{\mathrm{D}}/N_{\mathrm{D}} + N_{\mathrm{H}}$.

From relation (7) or (8), $NZ_{\mathrm{PS}}^2P(q)$ and $N^2Z_{\mathrm{PS}}^2Q(q)$ can be determined by two SANS experiments in which we change only the labelled composition x.

On the other hand, the interaction parameter χ between PS and PαMS can be calculated at zero scattering vector ($q \simeq 0$) from the following relation (see equation (27) in Reference 22), taking into account the difference between the molar volumes of monomers:

$$\chi = \frac{1}{2}\left[-\frac{1}{v_0 N Z_{\mathrm{PS}}^2 [P(0) + NQ(0)]} + v_0 \left(\frac{1}{\phi_{\mathrm{PS}} Z_{\mathrm{PS}} v_{\mathrm{PS}}} + \frac{1}{(1-\phi_{\mathrm{PS}}) Z_{\mathrm{P\alpha MS}} v_{\mathrm{P\alpha MS}}} \right) \right]$$

where $\phi_{\mathrm{PS}} = \phi_{\mathrm{PSH}} + \phi_{\mathrm{PSD}}$ is the volume fraction of PSH + PSD.

We report as an example the results obtained with the compatible blend A_2B_4. In *Figure 10* typical scattering intensities are shown as a function of q for two different compositions of labelled polystyrene maintaining the same overall PS/PαMS composition: 20/80 (w/w). In *Figures 11* and *12* we present the intra- and intermolecular interference functions *versus* q. The radius of gyration and the molecular weight of PS molecules were determined from the plot of the intramolecular interference function against q^2 (*Figure 13*). The values of these parameters and the interaction parameter χ are given in *Table 3*. The radius of gyration and the molecular

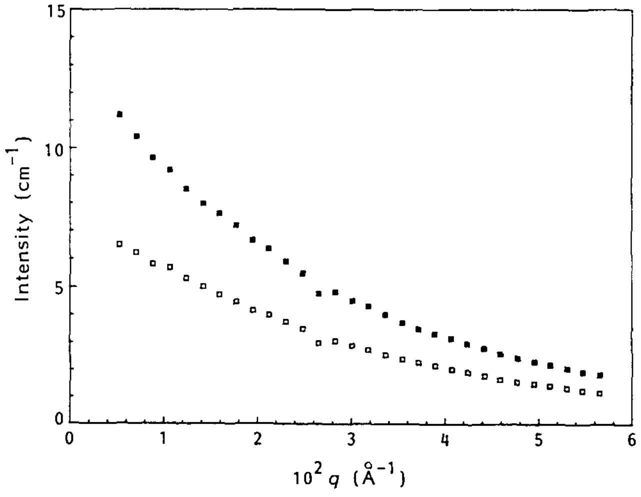

Figure 10 Scattering intensity *versus* q for blend A_2B_4 with 20/80 (w/w) composition in which 4 (□) and 6% (⊞) by weight of the PSD has been replaced with PSH

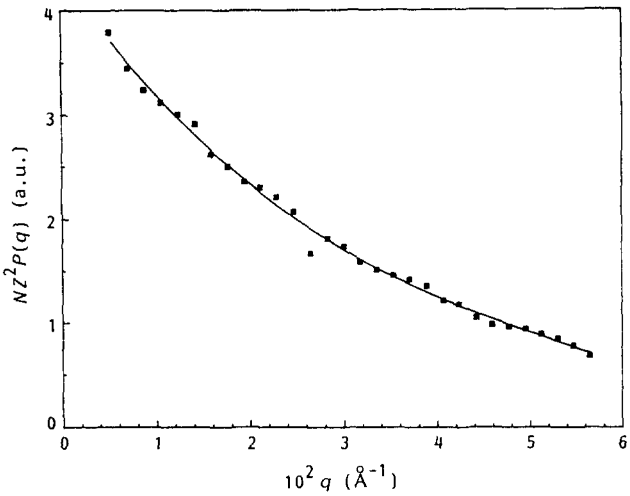

Figure 11 Intermolecular interference function $NZ_{\mathrm{PS}}^2P(q)$ obtained from the scattering data on blend A_2B_4 with (⊞) 20/80 (w/w) composition (*Figure 10*) and (———) equation (8)

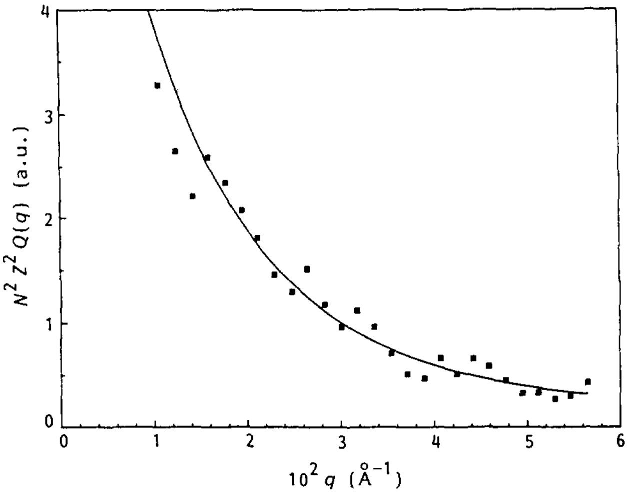

Figure 12 Intermolecular interference function $N^2Z_{\mathrm{PS}}^2Q(q)$ for the PS molecules in the blend A_2B_4 with 20/80 (w/w) composition

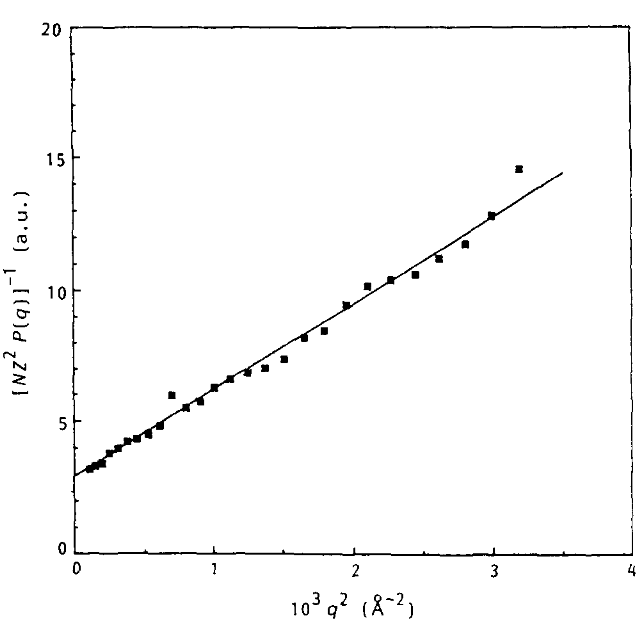

Figure 13 $[NZ_{\mathrm{PS}}^2P(q)]^{-1}$ *versus* q^2 plot. The molecular weight of PS molecules was obtained from the intercept (at $q=0$) and the radius of gyration of PS from the combination of the slope and intercept

Table 3 $\langle M_{\mathrm{PS}}\rangle_w$, $\langle R_{g,\mathrm{PS}}\rangle_z$ and $\chi_{\mathrm{PS-P\alpha MS}}$ for ternary PSD/PSH/PαMS blends (A_2B_4) determined by SANS

	Composition (w/w)	$\langle R_{g,\mathrm{PS}}\rangle_z$ (Å)	$\langle M_{\mathrm{PS}}\rangle_w$	$\chi_{\mathrm{PS-P\alpha MS}}$ $\pm 5\times10^{-4}$
PS/PαMS	20/80	56.1	38000	0.0049
PS/PαMS	40/60	57.4	40000	0.0045
PSD/PSH	5/95	55.8	39000	–

weight of PSD are in good agreement with the values measured in PSD/PSH in the bulk. Moreover the values of χ are similar to those obtained for the binary blend PS–PαMS A_2B_4. This result demonstrates the validity of the assumption made in the theoretical treatment.

CONCLUSIONS

It has been established that, as is the case for the PSH–PαMS pair, blends of PSD and PαMS exhibit an interesting range of miscibilities depending on component molecular weight. However, it should be emphasized that, to be sure of the homogeneity (compatibility) of the blend at a molecular level, one has to determine the molecular parameters of the dispersed polymer chains, such as the radius of gyration and the molecular weight. For this purpose, radiation scattering techniques, in particular small angle neutron scattering, are the most appropriate methods. Neutron scattering studies show first that for the blends located in the one-phase region of the miscibility diagram, the polymer chains are molecularly dispersed, and second that the interaction parameter χ is small and does not display any significant variation with the composition of the blend.

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