Thermodynamics of isotopic mixtures of syndiotactic poly(methyl methacrylate) from small-angle neutron scattering

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Mixtures of high-molecular-weight hydrogenous, syndiotactic poly(methyl methacrylate) with two lower-molecular-weight deutero poly(methyl methacrylate)s have been investigated over a range of temperatures and compositions using small-angle neutron scattering. Effective interaction parameters have been obtained which have been used to estimate the Flory–Huggins interaction parameter. Spinodal temperatures have been defined from the temperature dependence of these effective interaction parameters and other parameters of the mixtures. The conclusion is that these isotopic mixtures are incompatible at ambient temperatures and have an upper critical solution temperature. The influence of local stereochemistry on the polymer configuration is evident in the scattering cross-section variation with scattering vector. This variation is compared with the scattering obtained from Monte Carlo rotational isomeric state calculations.

(Keywords: polymer mixtures; interaction parameters; molecular configuration)

INTRODUCTION

Although polymer blends have been the focus of intense experimental activity for some 15 years[1–3], the number of systems for which extensive thermodynamic information is available is still limited. In part this is due to the difficulty of obtaining such fundamental data as the enthalpy of mixing for high-molecular-weight polymers. Furthermore, it is well known that a rigorous description of a polymer blend requires the use of equation of state theories and these theories require many additional parameters that are often difficult to obtain[4].

Recourse is usually made to evaluating the Flory–Huggins interaction parameter of the polymer blend, χ_{FH}. Despite the fact that the Flory–Huggins theory is *not* sufficiently general to describe completely the phase behaviour of polymer blends (notably it fails to predict the existence of lower critical solution temperatures), nonetheless the theory can provide the approximate location of phase boundaries (associated with upper critical solution temperatures) if the temperature dependence of χ_{FH} is known. De Gennes[5] has discussed the location of phase boundaries and the value of χ_{FH} in relation to these boundaries. The applicability of this relatively straightforward approach has been demonstrated by the experiments of Bates and Wignall[6] and others[7,8]. A notable feature of this work was the observation of a positive value of χ_{FH} (i.e. unfavourable for mixing) between deutero and hydrogenous isomers of the same polymer. This is a manifestation of the isotopically driven phase segregation predicted theoretically by Buckingham and Hentschel[9] on the basis of larger molar volume anticipated for C–^{2}H bonds based on the zero point oscillations of C–^{1}H and C–^{2}H bonds.

In addition to determining the bulk miscibility of polymer blends, χ_{FH} also has a role in determining the near surface depth profile in polymer mixtures[10]. It is this aspect which was the motivation for the experiments discussed here. Factors which determine the surface composition of a binary polymer mixture, in the absence of specific surface interactions, are: (1) the difference in surface tension between the two components; (2) the magnitude and sign of χ_{FH}; and (3) the bare surface energy of the polymer–air interface. Of these three components, the first two are of greatest influence and Jones and Kramer[10] have suggested that in certain circumstances, it is χ_{FH} which is the most important of all the three parameters. We have been investigating the surface composition in mixtures of hydrogenous and deuterated poly(methyl methacrylate), where the molecular weight of the hydrogenous polymer was fixed at a high value ($\sim 10^6$) and that of the deuterated polymer varied[11]. We

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report here the use of small-angle neutron scattering (SANS) to determine molecular parameters of two of these *asymmetric* blends; a special focus of interest was the value of χ_{FH} and its temperature variation.

THEORY

Interaction parameter

Application of the Flory–Huggins lattice theory to a binary polymer mixture results in the following expression for the Gibbs free energy of mixing, ΔG_m:

$$\frac{\Delta G_m}{RT}=\frac{\phi}{N_A}\ln\phi+\frac{(1-\phi)}{N_B}\ln(1-\phi)+\phi(1-\phi)\chi_{FH} \quad (1)$$

where ϕ is the volume fraction of polymer A which has a degree of polymerization N_A, polymer B has a degree of polymerization N_B and all other symbols have their usual meaning. The binodal or co-existence curve is defined by $(\partial\Delta G_m/\partial\phi)_{T,p}=0$ and the spinodal curve by $(\partial^2\Delta G_m/\partial\phi^2)_{T,p}=0$; thus at the spinodal boundary we have:

$$\chi_s=\frac{1}{2N_A\phi}+\frac{1}{2N_B(1-\phi)} \quad (2)$$

where χ_s is the value of the interaction parameter for the polymer mixture at the spinodal.

The original Flory–Huggins definition of χ_{FH} has been the subject of much adjustment in recent years. There have been discussions of the dependence of χ_{FH} on temperature, composition, molecular weight and, where SANS has been used, on scattering vector, Q (ref. 12). An exhaustive consideration of such dependences (except Q dependence) has been published by Muthukumar[13] and efforts at experimental investigation of these predictions have been made by Bates *et al.*[14]. To incorporate the possibility of a molecular weight and composition dependence of χ_{FH} in equation (1), the last term is replaced by Γ and the effective interaction parameter $\tilde{\chi}=-\frac{1}{2}(\partial^2\Gamma/\partial\phi^2)$. Only when there is no dependence of χ_{FH} on molecular weight or composition does $\tilde{\chi}=\chi_{FH}$. Muthukumar[13] has shown that monomer density fluctuations in the mixture lead to corrections to the original Flory–Huggins theory and a shift in the locus of the coexistence curve. The resultant expression for $\tilde{\chi}$ is complex but contains both molecular weight and composition dependence. SANS on polymer mixtures provides values of $\tilde{\chi}$.

SANS

The coherent scattering cross-section $(\mathrm{d}\Sigma/\mathrm{d}\Omega)$ obtained from the intensity of neutrons scattered from a mixture of deuterated and hydrogenous polymers is given by[15]:

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q)=K(\rho_D-\rho_H)^2S(Q) \quad (3)$$

where K is a factor containing instrumental parameters (e.g. incident intensity neutrons $\mathrm{cm^{-2}\,s^{-1}}$, cross-sectional area of beam and the sample thickness amongst others), and ρ_i is the scattering length density for the deuterated (subscript D) or hydrogenous (subscript H) polymers. An expression for the scattering law, $S(Q)$, has been provided by de Gennes using the random-phase approximation:

$$S(Q)^{-1}=\frac{1}{N_D\phi g_D(R_{gD},Q)}+\frac{1}{N_H(1-\phi)g_D(R_{gH},Q)}-2\tilde{\chi} \quad (4)$$

with $g_D(R_{gi},Q)$ being the Debye equations describing the variation of scattered intensity with scattering vector Q for a single Gaussian polymer molecule with radius of gyration R_{gi}:

$$g_D(R_{gi},Q)=(2/u^2)(\exp(-u)+u-1) \quad (5)$$

$$u=Q^2R_{gi}^2 \quad (6)$$

$$Q=(4\pi/\lambda)\sin\theta$$

where λ is the radiation wavelength and 2θ is the scattering angle.

Depending on the value of Q *vis à vis* R_{gi}^{-1}, different limiting forms of equation (5) are obtained and may be used to obtain useful expressions for $S(Q)$. Hence, when $Q=0$, $g_D(R_{gi},Q)=1$ and thus $S^{-1}(0)=(\partial^2\Delta G_m/\partial\phi^2)_{T,p}$ (ref. 5); consequently at the spinodal temperature for the mixture the value of $\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(0)$ is infinite. In the region where Q is small, more particularly for the range $Q\leqslant R_{gi}^{-1}$, then

$$g_D(R_{gi},Q)=1-\frac{Q^2R_{gi}^2}{3} \quad (7)$$

Equation (7) forms the basis for determining the radius of gyration of polymers in bulk. If the polymer molecule has a statistical step length of a_i then $R_{gi}^2=N_ia_i^2/6$ and we can define a correlation length, ξ, for the composition fluctuations in the mixture as:

$$\xi=\frac{a_i}{6}[\phi(1-\phi)(\chi_s-\tilde{\chi})]^{-1/2} \quad (8)$$

then we obtain:

$$S(Q)=\frac{1}{2(\chi_s-\tilde{\chi})(1+Q^2\xi^2)} \quad (9)$$

and we note from equation (8) that as $\tilde{\chi}$ approaches χ_s then ξ approaches a value of infinity. Where $QR_{gi}>1$ then $\tilde{\chi}$ has a negligible influence on $S(Q)$ and we anticipate;

$$S(Q)\approx\phi(1-\phi)(12/(Q^2a_i^2)) \quad (10)$$

The use of equations (4), (9) and (10) depends on the extent to which the scattering law is 'sampled' by the range of Q available in the small-angle diffractometer. In principle, $\tilde{\chi}$, R_{gD}, R_{gH} and $S(0)$ could be obtained using equation (4). As long as the Guinier condition $(Q\leqslant R_{gi}^{-1})$ is fulfilled then equation (9) can be used to extract values of ξ and χ. Equation (10) may be used to obtain values of a_i, the statistical step length, but some caution may need to be exercised since steric effects may also have an influence in this region of the scattering vector.

EXPERIMENTAL

Polymers

Deuterated and hydrogenous poly(methyl methacrylate) (DPMMA and HPMMA, respectively) were prepared by anionic polymerization of the purified monomers in tetrahydrofuran solution at 195 K using 9-fluorenyllithium as initiator. After termination by addition of degassed methanol, the polymers were isolated by precipitation in hot hexane, filtered off, washed and dried under vacuum at 313 K for 1 week. Molecular weights were determined by size-exclusion chromatography using chloroform as the eluting solvent, ^{13}C n.m.r. was used to obtain the tacticity and the glass transition temperatures (T_g) were obtained from differential scanning calorimetry. Details of the three polymers used here are given in *Table 1.*

Small-angle neutron scattering

The high-molecular-weight HPMMA was used as the 'base' polymer for all the mixtures. Three mixtures of each of the DPMMA polymers were made with the HPMMA, the range of volume fractions of the DPMMA being between 0.1 and 0.49. Precise details and sample codings are given in *Table 2.* Each mixture was prepared by dissolving deuterated and hydrogenous polymer in the desired proportions in toluene such that the total polymer concentration was ~5 wt%. The polymer was precipitated in chilled methanol and dried under vacuum for 1 week at 313 K. Clear bubble-free plaques, 1 mm thick and 12 mm in diameter, were prepared by compression moulding at 453 K under vacuum. Each plaque was then mounted between quartz windows in cylindrical brass cells which were mounted in a heated cell-holder on the small-angle diffractometer, LOQ, on the ISIS pulsed neutron source at the Rutherford–Appleton Laboratory, Chilton, Oxfordshire, UK.

Scattered neutron intensities were collected for all samples for selected temperatures in the range $408\,K \leqslant T \leqslant 473\,K$; in this temperature range separate thermogravimetric analyses showed there was no weight loss due to degradation. For the purpose of subtracting the background, scattered intensities were recorded for pure HPMMA and pure DPMMA420. The range of neutron wavelengths used was $0.5 \leqslant \lambda \leqslant 12$ Å and the scattering vector range accessible was $\sim 0.01 \leqslant Q \leqslant 0.2$ Å^{-1}. All the scattered intensities recorded were radially isotropic about the incident beam direction and were corrected for transmission and thickness before subtraction of background using the appropriately volume fraction-weighted sum of the flat scattering of DPMMA420 and HPMMA. The corrected intensities were placed on an absolute scale by calibrating the instrument using a blend of deuteropolystyrene and hydrogenous polystyrenes with matched molecular weights and for which the molecular weights and mixture composition are known accurately. The molecular weight of this calibrant mixture (71.1×10^3) is sufficiently low that the isotopically driven phase boundary is at a much lower temperature than ambient[6]. The background scattering for this calibrant mixture was obtained using a random copolymer of hydrogenous and deuterated styrene of the same composition and molecular weight as the calibrant mixture.

Table 1 Characteristics of poly(methyl methacrylate) polymers

Polymer	$\bar{M}_w$ (g mol^{-1} × 10^3)	$\bar{M}_w/\bar{M}_n$	T_g (K)	Syndiotactic (%)
HPMMA	994.0	1.26	403.6	76
DPMMA420	417.0	1.26	397.6	74
DPMMA25	25.4	1.14	376.7	76

Table 2 Mixtures of HPMMA and DPMMA

Code	$\bar{M}_w$ (g mol^{-1} × 10^3) DPMMA	ϕ_{DPMMA}	$\bar{M}_w$ (g mol^{-1} × 10^3) HPMMA
HD251	25.4	0.48	994.0
HD252	25.4	0.28_6	994.0
HD253	25.4	0.09_4	994.0
HD4201	417.0	0.48	994.0
HD4202	417.0	0.28_7	994.0
HD4203	417.0	0.09_6	994.0

RESULTS

Typical plots of $d\Sigma/d\Omega$ are given in *Figure 1* for each mixture. For the HD25 mixtures, the influence of the volume fraction composition is clearly evident and the molecular weight of DPMMA25 is such that almost all of the scattering law is being sampled. Only the region at very low values of Q is absent because of the finite area of the beam stop and the intrinsic Q range of the diffractometer. The situation does not appear to be so encouraging for the HD420 mixtures since the influence of volume fraction appears to have little influence on $d\Sigma(Q)/d\Omega$, although the value at $Q=0$ will clearly differ for each mixture. We attribute this to insufficient sampling of the scattering law by the diffractometer because of the high molecular weight of DPMMA420. That there are differences between each composition will be shown later.

For the present we consider the DPMMA25 mixtures only. *Figure 2* shows $d\Sigma/d\Omega$ values for the range $0.01 \leqslant Q \leqslant 0.04$ Å^{-1} plotted in the Ornstein–Zernicke

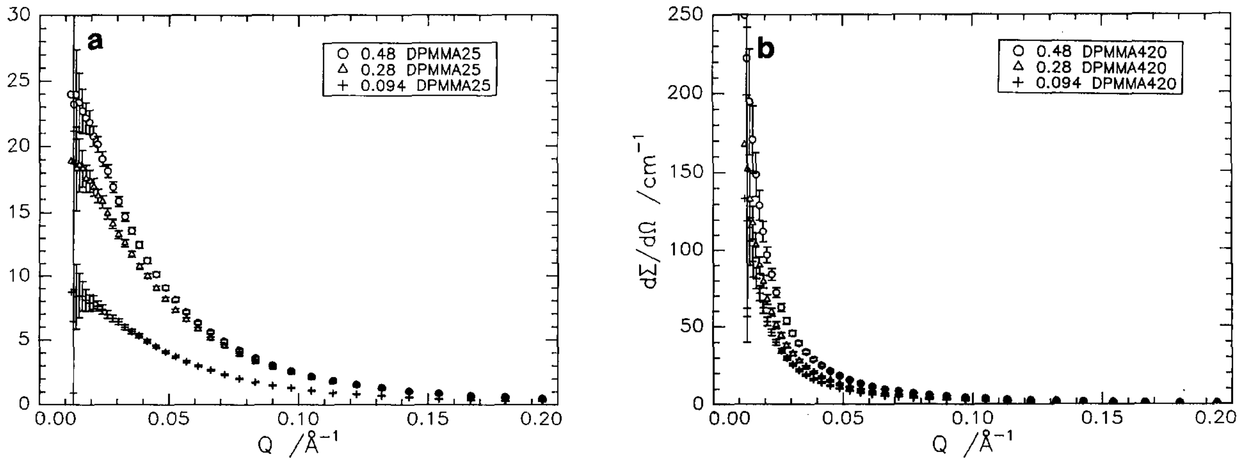

Figure 1 Scattering cross-section for (a) HD25x mixtures and (b) HD420x mixtures. Volume fraction of deutero polymer in each mixture is indicated, in both cases the temperature was 453 K

mode ($1/I$ *versus* Q^2) suggested by equation (9). Values of the fluctuation correlation length ξ, were obtained from the slopes and the value of the intercepts was used to evaluate $\tilde{\chi}$ for each mixture at each temperature. For this purpose values of χ_s were calculated using equation (2) and the known molecular weights of HPMMA and DPMMA25 in conjunction with the volume fractions. Furthermore, the values of $d\Sigma/d\Omega$ at $Q=0$ were also obtained from these plots. Values of $\tilde{\chi}$, $d\Sigma/d\Omega$ at $Q=0$ and ξ obtained are given in *Table 3*. *Figure 3* shows $\tilde{\chi}$, $(d\Sigma/d\Omega)^{-1}$ and ξ^{-2} plotted as a function of T^{-1}. Extrapolation of these data provides estimates for the spinodal temperatures of each mixture; i.e. $(d\Sigma/d\Omega)^{-1}$ and ξ^{-2} are extrapolated to a value of zero and $\tilde{\chi}$ is extrapolated until it intersects a line indicating the value of χ_s. From these extrapolations the spinodal temperatures obtained were:

$$\phi_{\mathrm{DPMMA}}=0.48 \qquad T_s=377\pm 20\,\mathrm{K}$$

$$\phi_{\mathrm{DPMMA}}=0.28 \qquad T_s=380\pm 50\,\mathrm{K}$$

$$\phi_{\mathrm{DPMMA}}=0.09 \qquad T_s=350\pm 20\,\mathrm{K}$$

Values of $\tilde{\chi}$ were also obtained by non-linear least-squares fitting of equation (3) to the data using equation (4) as the expression for $S(Q)$. The adjustable parameters of the fit were $\tilde{\chi}$, R_{gH} and R_{gD}, and the equation was fitted over the Q range 0.01–0.1 Å^{-1}. The values of $\tilde{\chi}$ obtained in this manner were, within experimental error, the same as those quoted in *Table 3*; *Figure 4* shows examples of the quality of fit obtained by this procedure. In *Figure 4*, both data and fitted line have been plotted over the whole range of Q used. For determination of the parameters the actual fit was confined to the Q limits given above. Discrepancies between fitted line and data are apparent at higher values of Q, this is commented upon later. *Figure 5* collects the values of $\tilde{\chi}$ obtained at each temperature from the SANS data and plots them as a function of the volume fraction of DPMMA25 in the mixture, also included on this figure is the spinodal curve calculated from equation (2). For any fixed temperature, it is seen that the dependence of $\tilde{\chi}$ on volume fraction has the same qualitative behaviour as that of the spinodal curve. Generally, the dependence of $\tilde{\chi}$ on temperature is given by an equation of the form:

$$\tilde{\chi}=A+\frac{B}{T} \tag{11}$$

Table 3 Parameters obtained from Ornstein–Zernicke plots for HD25 mixtures

Temperature (K)	ϕ	$\frac{d\Sigma}{d\Omega}(Q=0)$	χ (10^{-3})	ξ (Å)
408	0.48_6	85 ± 2	-1.3 ± 0.2	42 ± 1
	0.28_6	123 ± 5	3.6 ± 0.1	50 ± 2
	0.09_4	39 ± 2	10.5 ± 1	36 ± 2
435	0.48_6	86 ± 1	-1.2 ± 0.5	29 ± 4
	0.28_6	58 ± 1	-1.0 ± 0.1	25 ± 8
	0.09_4	24 ± 1	2.4 ± 0.2	20 ± 1
453	0.48_6	58 ± 1	-4.1 ± 0.1	27 ± 5
	0.28_6	44 ± 1	-3.8 ± 0.1	24 ± 1
	0.9_4	20 ± 1	-2.2 ± 0.5	22 ± 1
473	0.48_6	32 ± 1	-11.0 ± 2	24 ± 1
	0.28_6	26 ± 1	-12.0 ± 2	23 ± 1
	0.09_4	17 ± 1	-6.8 ± 0.2	23 ± 8

Values of A and B obtained for each of the HD25 mixtures are given in *Table 4*; the temperature dependence of $\tilde{\chi}$ for all compositions from these values is, within experimental error:

$$\tilde{\chi}=-0.12+\frac{52}{T} \qquad (T\ \text{in K}) \tag{12}$$

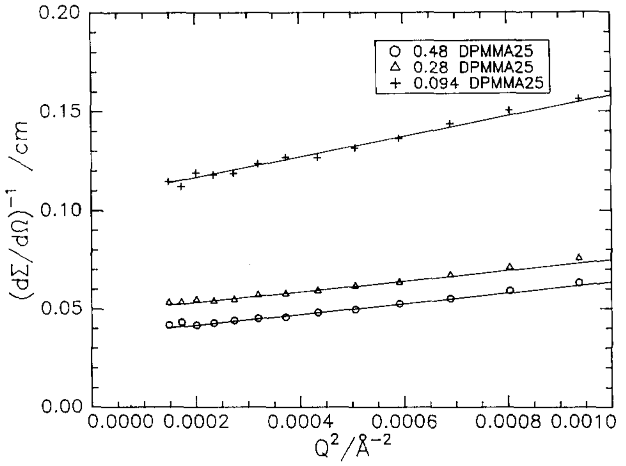

Figure 2 Ornstein–Zernicke plots of the scattering cross-section for the HD25 mixtures at 453 K. Volume fraction of deutero polymer in each mixture is indicated

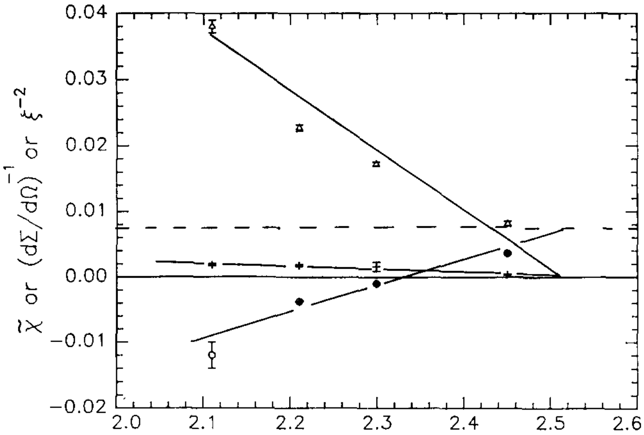

Figure 3 Values of (○) $\tilde{\chi}$, (△) $(d\Sigma/d\Omega)^{-1}$ and (+) ξ^{-2} as a function of T^{-1} for the HD252 mixture (DPMMA25 volume fraction $=0.28_6$). (– – –) χ_s

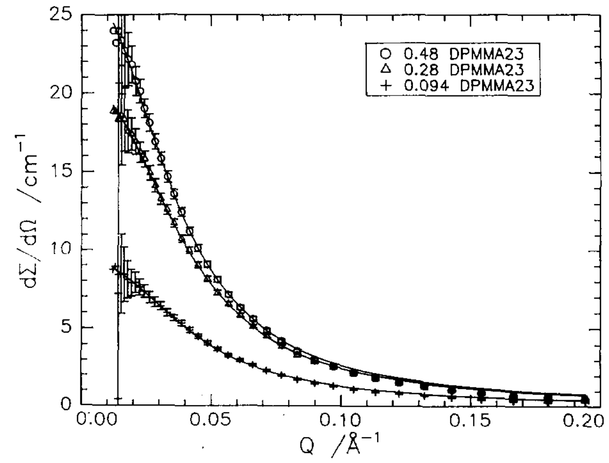

Figure 4 Fit of random-phase expression for scattering law (equation (4)) to the scattering cross-section for all HD25*x* mixtures at 453 K

Table 4 Values of A and B parameters in the temperature dependence of χ

Code	ϕ_{DPMMA}	A	B
HD251	0.48	-0.12 ± 0.03	50 ± 10
HD252	0.28_6	-0.13 ± 0.03	57 ± 14
HD253	0.09_4	-0.11 ± 0.03	48 ± 2
HD4201[a]	0.48_1	-0.32×10^{-2}	1.86
HD4202[a]	0.28_7	-0.20×10^{-2}	0.98
HD4203[a]	0.09_6	0.40×10^{-2}	1.84

[a] These values were obtained from values of χ at only two temperatures and should be regarded as tentative values only

We now consider the values of radius of gyration of DPMMA25 in its mixtures with HPMMA. Values of the mean square radius of gyration were obtained from the fitting of the reciprocal of equation (4) to the absolute SANS intensity values in the region $0 < Q \leqslant 0.11$ Å^{-1} and the value obtained was $1.8 \times 10^3 \pm 0.2 \times 10^3$ Å^2 over the whole temperature and composition range used. No dependence on either temperature or composition was evident from the values of the radii of gyration for each specimen investigated. Assuming a Gaussian distribution of segments and noting that literature values[17] for $(\langle r^2 \rangle_0 / M)^{1/2}$ for atactic PMMA are in the region of 0.55 Å, then the value of the mean square radius of gyration, $\langle s^2 \rangle$, predicted is $\sim 1.3 \times 10^3$ Å^2. Our experimental value is somewhat larger but the tacticity of the polymers from which the literature values have been obtained may have been considerably different. When the larger values of $(\langle r^2 \rangle_0 / M)^{1/2}$ amongst the values quoted are used, then a value of $\sim 1.6 \times 10^3$ Å^2 is expected for $\langle s^2 \rangle$, which is closer to the value we observe here.

Turning now to the PMMA mixtures with DPMMA420, then from the molecular weight (*Table 1*) we anticipate that $\langle s^2 \rangle$ should be in the region of 20×10^3 Å^2. This value suggests that to obtain ξ, the correlation length, via equation (9), the appropriate Q range is $0 \leqslant Q \leqslant 6 \times 10^{-3}$ Å^{-1}, which is not within the current usable range of the LOQ diffractometer. Consequently we have not attempted to obtain values of ξ for the HD420x mixtures. However, we have fitted the reciprocal of equation (4) to the data in an attempt to estimate values of $\tilde{\chi}$ and the radius of gyration of DPMMA420. Only the fits to the scattered intensity at 453 K and 435 K are discussed here, the results obtained for the 408 K data were anomalous. This may be due to the specimens being insufficiently distant from the T_g of DPMMA420 and hence inhomogeneities of the glassy state may be contributing to the observed scattering intensity. The average mean square radius of gyration obtained was 2.4×10^4 Å^2 ($\pm 10^4$ Å^2) which is reasonably close to the anticipated value. However, the large errors arising from insufficient sampling of the Guinier region of the scattering from the mixtures mean that confidence in this value should not be high. By contrast, the values of $\tilde{\chi}$ obtained are of the same order of magnitude as those for the HD25 mixtures and are plotted as a function of composition in *Figure 6*, together with the spinodal value of $\tilde{\chi}$ anticipated. The values of A and B in equation (11) for the HD420x mixtures are given in *Table 4* and the average values suggest that

$$\tilde{\chi} = -0.3 \times 10^{-2} + \frac{1.56}{T} \qquad (13)$$

However, since this relation is based on only two values of $\tilde{\chi}$ at each composition it should only be viewed as a tentative value for this molecular weight combination. In conjunction with equation (2), this relationship suggests that the spinodal temperatures for these mixtures are: HD4201, 460 K; HD4202, 440 K; and HD4201, 350 K.

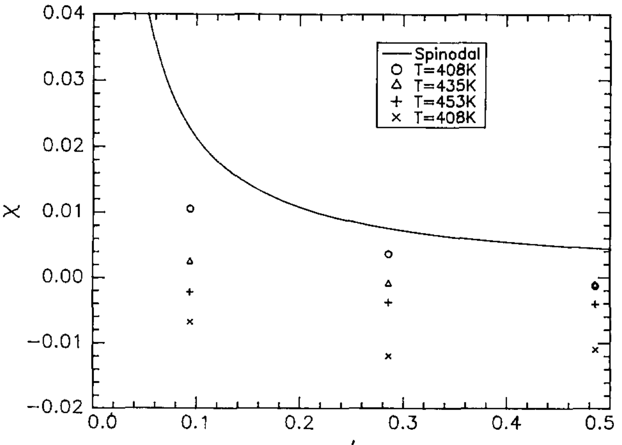

Figure 5 Dependence of $\tilde{\chi}$ on volume fraction of deuterated polymer in HD25x mixtures. (——) Value of the interaction parameter at the spinodal boundary, χ_s

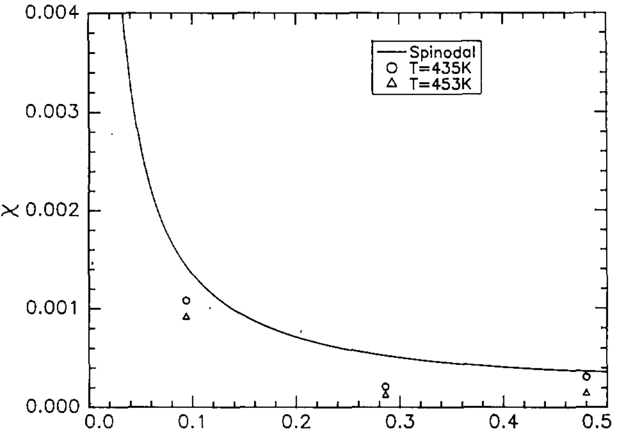

Figure 6 Dependence of $\tilde{\chi}$ on volume fraction of deuterated polymer for HD420x mixtures

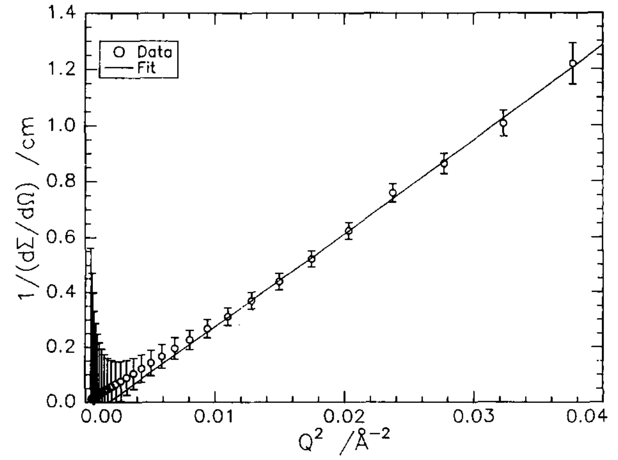

Figure 7 Typical plot used to obtain values of the statistical step length. Particular data set used here pertains to HD4202 at 435 K. The linear least-squares fit was confined to $0.01 \leqslant Q \leqslant 0.04$ Å^{-1} but has been extended to lower Q values to illustrate the deviations

Although the molecular weight of DPMMA420 is such that the Guinier region of the scattering law is not probed to a sufficient degree, it does allow us to extract values of the statistical step length, a, by using equation (10). *Figure 7* shows the data plotted in this way, and the value of the statistical step length obtained from all such plots at both 435 K and 453 K was 6.5 ± 0.5 Å.

DISCUSSION

In the original definition of the interaction parameter, χ_{FH}, there is no composition dependence; however, most of the experimentally determined values of what are stated to be χ_{FH} values clearly display some dependence on composition[6,14,16]. Correlations between density fluctuations have been cited as the source of this apparent concentration dependence, there being two types of density fluctuations in polymer systems: composition fluctuations and spatial correlations of monomer units on the same molecule. Muthukumar[13] has formulated a theory of the thermodynamics of polymer solutions which incorporates these correlations and essentially states that the experimentally measured interaction parameter is an effective interaction parameter, $\tilde{\chi}$. For polymer–polymer mixtures, three-body interactions and excluded-volume effects are negligible[14] and the Gibbs free energy of mixing is given by:

$$\frac{\Delta_m G}{k_B T} = \frac{\phi}{N_D} \ln \phi + \frac{(1-\phi)}{N_H} \ln(1-\phi) + \chi_{FH}\phi(1-\phi) + (24\pi\xi^3)^{-1} \tag{14}$$

and we make the following identity;

$$\Gamma(T, \phi, N) = \chi_{FH}\phi(1-\phi) + (24\pi\xi^3)^{-1} \tag{15}$$

where ξ is defined by equation (8). Equation (14) predicts the same general thermodynamic behaviour as does the original Flory–Huggins theory, equation (1), except that the dependence of the free energy on composition predicted by equation (14) is very slightly displaced from that of the Flory–Huggins theory. However, neither the loci of the coexistence and spinodal curves nor the position of the critical point are altered by the use of equation (14).

Since $\tilde{\chi} = -\frac{1}{2}\frac{\partial^2 \Gamma}{\partial \phi^2}$, then for a polymer–polymer mixture we have:

$$\begin{aligned}\tilde{\chi} = \chi_{FH} - \frac{27}{4\pi}(\chi_s - \chi_{FH})^{1/2}\Big\{&\frac{3}{2}\left(\frac{1}{N_H(1-\phi)^2} - \frac{1}{N_D\phi^2}\right)\\ &\times(\phi^{1/2}(1-\phi)^{3/2} - \phi^{3/2}(1-\phi)^{-1/2}) + \tfrac{1}{2}(\chi_s - \chi_{FH})\\ &\times(\phi^{-1/2}(1-\phi)^{3/2} + \phi^{3/2}(1-\phi)^{-1/2}) - 6\phi^{1/2}(1-\phi)^{1/2}\\ &+\left(\frac{1}{N_D\phi^3} + \frac{1}{N_H(1-\phi)^3}\right)(\phi^{3/2}(1-\phi)^{3/2})\\ &+\tfrac{1}{8}(\chi_s - \chi_{FH})(\phi^{3/2}(1-\phi)^{3/2})\left(\frac{1}{N_H(1-\phi)^2} - \frac{1}{N_D\phi^2}\right)^2\Big\}\end{aligned}$$

Figure 8 shows the dependence of $\tilde{\chi}$ on volume fraction ϕ for the situation where $N_D = N_H$. Consequently, if values of $\tilde{\chi}$ are available over a sufficiently wide range of ϕ, then equation (17) could be fitted to these data using χ_{FH} as the only adjustable parameter. For the limited number of values of $\tilde{\chi}$ available here such a procedure is not advisable in view of the complexity of equation (17). However, we have attempted to estimate values of χ_{FH} by adjusting values of χ_{FH} until the theoretical curve of equation (17) is in reasonable agreement with the values of $\tilde{\chi}$ obtained. *Figure 9* shows the agreement attainable by this empirical process and *Figure 10* plots the values of χ_{FH} obtained as a function of $1/T$; the equations which

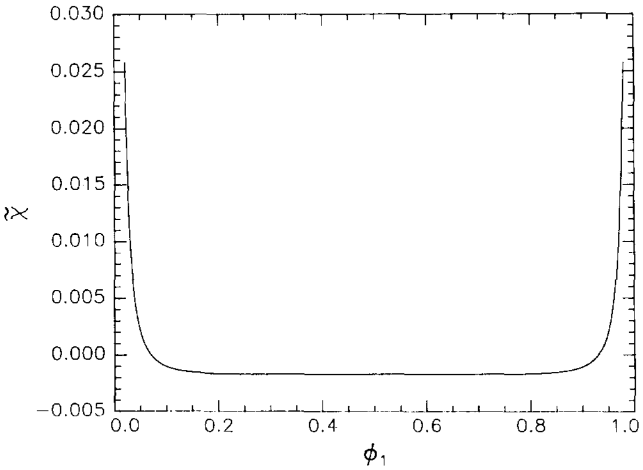

Figure 8 Variation of $\tilde{\chi}$ predicted by equation (17) for a polymer mixture with $N_D = N_H = 1000$ and $\chi_{FH} = -1 \times 10^{-3}$

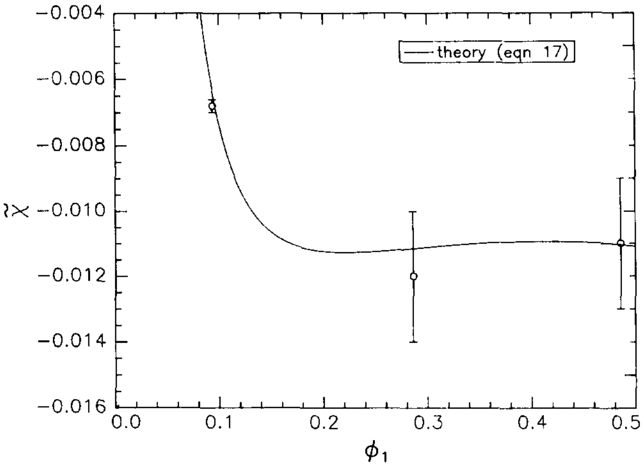

Figure 9 Values of $\tilde{\chi}$ at 473 K for HD25x mixtures. (——) Variation predicted by equation (17) with $\chi_{FH} = -1.6 \times 10^{-2}$

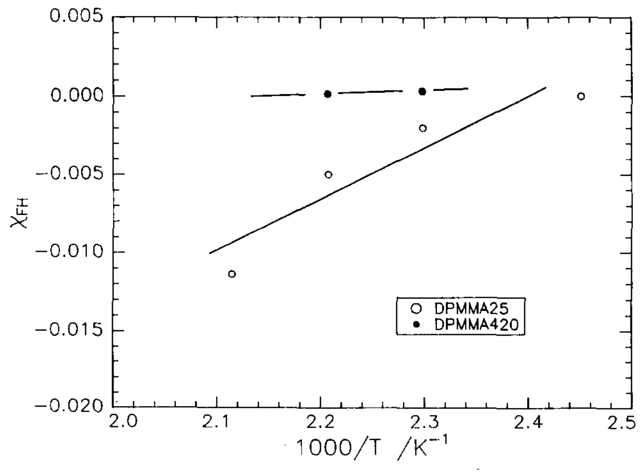

Figure 10 Dependence of χ_{FH} (obtained by the empirical method shown in *Figure 9*) as a function of T^{-1}

describe these temperature dependences are:

$$\chi_{FH} = -0.1 + \frac{43.7}{T} \qquad \text{(DPMMA25)}$$

$$\chi_{FH} = -4 \times 10^{-3} + \frac{1.86}{T} \qquad \text{(DPMMA420)}$$

These two relations are reasonably close to the temperature dependences obtained for $\tilde{\chi}$ (equations (12) and (13)) and thus they suggest that $\tilde{\chi} = \chi_{FH}$ and hence the DPMMA/HPMMA mixtures are similar in behaviour to the poly(vinyl ether)/polyethylethylene mixtures discussed by Bates *et al.*[14].

What is more surprising is the evident molecular weight dependence of χ_{FH} that is displayed. Again, we emphasize that the temperature dependence of χ_{FH} for DPMMA420 is based on only two values and the remarks made here are therefore somewhat tentative. Notwithstanding these comments, the two sets of parameters are so markedly dependent that it is reasonable to suspect a molecular weight dependence of χ_{FH}. The original definition of χ_{FH} is[17]

$$\chi_{FH} = \frac{(z-2)}{k_B T} \Delta\varepsilon_{12} \qquad (18)$$

where $\Delta\varepsilon_{12}$ is the exchange interaction energy in a mixture of components 1 and 2 and z is the lattice co-ordination number. Since the exchange interaction energy is not molecular weight dependent then only the effective co-ordination number of the lattice can be adjusted to encompass the molecular weight dependence of χ_{FH}. This may be reconcilable by adjustments in the expressions for the density correlation functions being needed for the asymmetric (in terms of the molecular weights of H and D species) polymer mixtures studied here. Alternatively, the molecular weight dependence of χ_{FH} may be due to the thermal expansivity of the polymers and/or the entropic factor, Q, in the equation of state theory[18] of polymer–polymer mixtures also being molecular weight dependent. Evidence for such behaviour is extremely scarce, but for both polyethylene and poly(dimethyl siloxane) a weak molecular weight dependence does seem to be evident for the volume parameters used in equation of state theory[19].

In the analysis of the SANS data, depending on the parameters being sought, the coherent scattering cross-section used has been confined to particular ranges of Q. Thus, in the Ornstein–Zernicke analysis of HD25x mixtures, the region where $QR_g \leqslant 1$ was used. In the determination of the Kuhn statistical step length, a, data from the large Q region for HD420x mixtures were used. Lastly, in the fitting of the random-phase expression (equation (4)) to the scattered cross-section, the region of the fit was confined to $0 \leqslant Q \leqslant 0.1$ Å^{-1}. The reasons for such selectivity become apparent when the cross-section data are plotted as a Kratky plot (*Figure 11*). This form emphasizes the deviations in the scattering from that predicted for a Gaussian distribution of segments as predicted by equation (5). Furthermore, the Debye equation fails to account for the stereochemistry of the substituents on the main chain, and this is particularly significant for poly(methyl methacrylate). Yoon and Flory[20] rationalized this behaviour nearly 20 years ago when discussing scattering data for poly(methyl methacrylate). There is a preference for particular stereochemical sequences along the molecule and these lead to maxima in the characteristic ratio for particular sequence lengths. Three discrete scattering centres can be identified in poly(methyl methacrylate), the methylene groups on the main chain backbone, the α-methyl groups, and the ester methyl groups. There will also be contributions to the scattering cross-section from cross-correlations between each of these centres. To calculate the separate contributions to the scattering, a Monte Carlo rotational isomeric state calculation was made using the BIOSYM Polymer modelling software suite[21]. The model molecule contained 470 main chain bonds with 75% syndiotacticity in the whole molecule. The scattering functions were calculated from a total of 400 configurations at a temperature of 450 K. After calculation the scattering functions were normalized by division by the calculated scattering function at $Q=0$, thus the scattering law had a value of 1 at $Q=0$, which conforms to the protocol adopted for the definition of scattering laws. For comparison purposes we have used the data set corresponding to a volume fraction of 0.48_6 DPMMA25 at 453 K and these data have been divided by the cross-section obtained by extrapolating to $Q=0$. *Figure 12* shows the data plotted in Kratky form and the individual contributions from the separate scattering centres. Clearly the substituents have a dominant influence on the observed scattering, since the

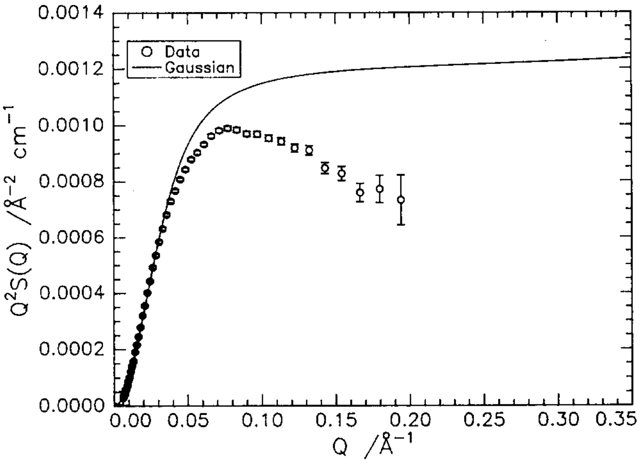

Figure 11 Kratky plot for HD251 (volume fraction of DPMMA25 = 0.48) at 453 K. (——) Behaviour predicted by the Debye equation (equation (5)) for a Gaussian segment distribution

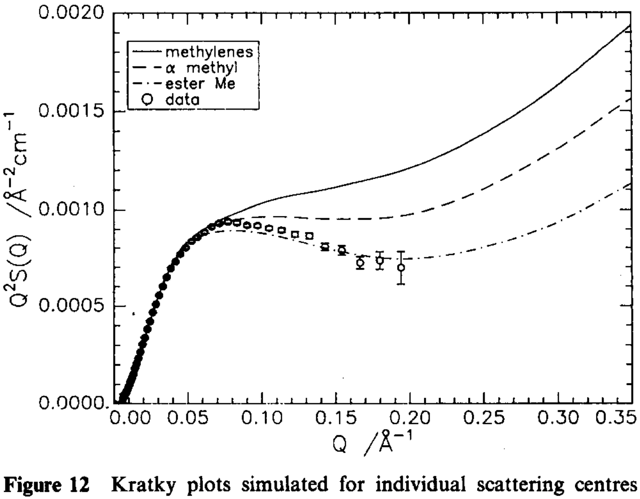

Figure 12 Kratky plots simulated for individual scattering centres compared with data for DPMMA25 at 450 K

experimental data lie closer to the curves obtained from the substituent scattering than to that from the methylene backbone scattering. Although the agreement between experiment and simulation suggests that the ester methyl group is the dominant contribution to the scattering, the experimental data do not extend to a sufficiently high value of Q to be able to make a definitive statement to this effect. It should be noted that all the calculated curves show an upturn at $Q \sim 0.2\ \text{Å}^{-1}$, corresponding to the reciprocal length scale where the contiguous scattering units are behaving as a set of short, thin rods. The Q value where this upturn is observed suggests that the persistence length of poly(methyl methacrylate) with this level of syndiotacticity is ~ 10 Å.

CONCLUSIONS

SANS has been used to ascertain the thermodynamics of the interaction between deuterated and hydrogenous syndiotactic poly(methyl methacrylate). Two different molecular weights of deutero poly(methyl methacrylate) were used, the hydrogenous matrix being of considerably higher molecular weight. From the variation with temperature of the scattered intensity, values of the effective interaction parameter, $\tilde{\chi}$, have been obtained for both polymers. For the lower-molecular-weight polymer, values of the composition fluctuation correlation length and scattering cross-section at zero scattering vector have also been calculated. From the temperature variation of all these parameters it has been possible to define the spinodal temperatures of the mixtures. The values of $\tilde{\chi}$ have been interpreted using Muthukumar's theory which explicitly includes the composition dependence of the Flory–Huggins interaction parameter, χ_{FH}. The temperature dependences of $\tilde{\chi}$ and χ_{FH} are almost identical, suggesting that any additional composition-dependent contributions to $\tilde{\chi}$ are very weak. There does, however, appear to be a strong molecular weight dependence of χ_{FH} and the causes of this have been the subject of speculation.

Deviations from the theoretical scattering for a Gaussian segment distribution were noted and with the aid of molecular modelling, the stereochemically significant contributions to the scattered intensity have been discussed. A complete identification of the dominant contribution has been prevented because of the absence of experimental data at sufficiently high values of the scattering vector Q.

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REFERENCES

1 Paul, D. R. and Newman, S. 'Polymer Blends' Vols 1 and 2, Academic Press, New York, 1978

2 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

3 Walsh, D. J., Higgins, J. S. and Maconnachie, A. (Eds) 'Polymer Blends and Mixtures' Nijhoff, Dordrecht, The Netherlands, 1985

4 Sanchez, I. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vols 1 and 2, Academic Press, New York, 1978, Ch. 3

5 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, London, 1979

6 Bates, F. S. and Wignall, G. D. *Macromolecules* 1986, **19**, 1938

7 Schwahn, D., Hahn, K., Streib, J. and Springer, T. *J. Chem. Phys.* 1990, **93**, 8383

8 Sakurai, S., Jinnai, H. and Hashimoto, T. *Macromolecules* 1991, **24**, 4839

9 Buckingham, A. D. and Hentschel, H. G. E. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 853

10 Jones, R. A. L. and Kramer, E. J. *Polymer* 1993, **34**, 115

11 Hopkinson, I. and Richards, R. W. unpublished results

12 Brereton, M. G., Fischer, E. W., Herkt-Maetzky, Ch. and Mortensen, K. *J. Chem. Phys.* 1987, **87**, 6144

13 Muthukumar, M. *J. Chem. Phys.* 1986, **85**, 4722

14 Bates, F. S., Muthukumar, M., Wignall, G. D. and Fetters, L. J. *J. Chem. Phys.* 1988, **89**, 535

15 Richards, R. W. 'Polymer Characterisation' (Eds B. J. Hunt and M. I. Jones), Blackie, Glasgow, 1993, Ch. 8

16 Ito, H. and Russell, T. P. *Macromolecules* 1987, **20**, 2213

17 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953, p. 509

18 Rostami, S. in 'Multicomponent Polymer Systems' (Eds I. S. Miles and S. Rostami), Longman, Harlow, UK, 1992, Ch. 3

19 Zoller, P. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), Sect. VI, Wiley, New York, 1989, pp. 475–483

20 Yoon, D. Y. and Flory, P. J. *Macromolecules* 1976, **9**, 299

21 Computational results obtained from Biosym Technologies (San Diego) Polymer Module, version 5.1