

Isotopic labelling and composition dependence of interaction parameters in polyethylene oxide/polymethyl methacrylate blends

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Mixtures of deuterated polyethylene oxide with hydrogenous polymethyl methacrylate and hydrogenous polyethylene oxide with deuterated polymethyl methacrylate have been investigated using small angle neutron scattering. The range of temperatures used was 423–473 K and the volume fraction of polyethylene oxide in the mixtures varied from ca. 0.1 to ca. 0.27. Values of the effective interaction parameter (χ_{eff}) were obtained using the incompressible random phase approximation. Both temperature dependence and composition dependence were noted in the values of χ_{eff} . The temperature dependence observed was compared with that predicted by equation of state theory. A notable feature of the composition dependence of χ_{eff} was the change in behaviour as temperature increased. Changes in the excess volume of mixing have been cited as a possible source of this behaviour, but the currently available data do not allow us to confirm this. Using the relation between χ_{eff} and a composition independent interaction parameter proposed from Monte Carlo simulations, approximate values of the composition independent interaction parameter have been obtained.

(Keywords: isotopic labelling; interaction parameters; PEO/PMMA blends)

INTRODUCTION

Attempts at quantifying the stability (at a molecular level) of blends of both chemically different and isotopically distinct polymers have generally used the Flory–Huggins mean field lattice theory to express the Gibbs free energy of mixing. Although it is recognized that the theory is insufficient to describe completely the thermodynamics of polymer blends, its simplicity compared to the more rigorous equation of state theories has fostered its use. In a mixture composed of polymers 1 and 2, the Gibbs free energy of mixing in the Flory–Huggins theory¹ is given by

$$\frac{\Delta G_{\text{mix}}}{k_B T} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi \phi_1 \phi_2 \quad (1)$$

where ϕ_i and N_i are the volume fraction and degree of polymerization of polymer i and χ is the polymer–polymer interaction parameter. Miscibility is usually controlled by the value of χ , small or negative values favouring miscibility. As originally defined, χ was independent of composition and molecular weight and arose purely from enthalpic interactions between the polymers.

Because of its importance in controlling polymer miscibility, there has been much effort in determining values of χ ^{2–10}. Additionally, apart from controlling polymer miscibility, the interaction parameter also plays an important role in determining the shape of the near-surface concentration profile of surface-segregated polymer mixtures^{11–13}. Consequently, quantitative information on the value of χ is of value in more than one area. There are some complicating factors. A dependence of χ on the concentration and molecular weight of the blend components has been observed in many blends. Additionally, determination of χ using small angle neutron scattering (SANS) requires that one component of the blend be deuterium labelled. Since the length and polarizability of a C–D bond are both smaller than those of the equivalent C–H bond¹⁴, deuterium labelling influences the value of χ . Proof of this has been amply demonstrated by the existence of a finite value of χ between isotopic isomers of homopolymers and the shifting of cloud point curves when one of the components is deuterated¹⁵. An additional aspect which may influence the value of χ obtained by SANS is the locus of deuteration, i.e. which of the components in the blend is deuterated.

As part of a larger research programme we have been investigating the near-surface depth profiles in mixtures

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of polyethylene oxide (PEO) and polymethyl methacrylate (PMMA). Different surface behaviour was observed depending on which of the two molecules was deuterated¹⁶. Blends of PEO and PMMA have been extensively studied by a variety of techniques, including differential scanning calorimetry^{17–25}, small angle X-ray scattering²⁶, optical microscopy²⁷, electron spin resonance²⁸, ¹³C n.m.r.²⁹ and i.r. spectroscopy³⁰. For low volume fractions of PEO, up to a value of ca. 0.4, a single glass transition temperature is observed which decreases as the amount of PEO increases, the lowest value being ca. 340 K. At higher volume fractions of PEO, crystallinity is evident and the melting point is depressed from that of pure PEO. This melting point depression has been used to determine χ values and the negative values of χ obtained are indicative of miscibility. Although the position of a coexistence curve has been deduced from some of these data, the exact position is not clear because crystallization intervenes before the coexistence curve is crossed. The general conclusions are that these two polymers are miscible in the melt state and remain miscible in the solid state for PEO volume fractions less than 0.4. Apart from one published paper (referred to later), there has been no systematic application of SANS to this blend to obtain values of the interaction parameter. We have used SANS to determine the interaction parameter for mixtures of deuterated polyethylene oxide (DPEO) with hydrogenous polymethyl methacrylate (HPMMA) and for mixtures where the labelling has been switched, i.e. HPEO/DPMMA mixtures. A limited range of compositions has been examined and both the composition dependence and temperature dependence of χ are discussed here.

THEORY

The measured coherent elastic scattered neutron intensity $I(Q)$ at any value of the scattering vector $Q (= (4\pi/\lambda)\sin\theta)$ for neutrons of wavelength λ and scattering angle 2θ is given by³¹

$$I(Q) = FN_p \frac{d\Sigma}{d\Omega}(Q) \quad (2)$$

where F is a factor which corrects for instrument geometry, sample thickness, transmission and cross-sectional area. N_p is the number of scattering particles (molecules) per unit volume and $d\Sigma(Q)/d\Omega$ is the differential scattering cross-section per unit volume. This last term is directly related to the structure factor $S(Q)$ of the scattering sample, i.e. the density correlation function for the specimen. For SANS the relevant density fluctuation responsible for scattering is the scattering length density and

$$\frac{d\Sigma}{d\Omega}(Q) = (\rho_1 - \rho_2)^2 S(Q) \quad (3)$$

where ρ_i is the scattering length density of a segment of polymer i . For a two-component blend where the segments have the same volume, the incompressible random phase approximation³² gives

$$S(Q)^{-1} = \frac{1}{\phi_1 N_1 g_{1D}(Q)} + \frac{1}{\phi_2 N_2 g_{2D}(Q)} - 2\chi \quad (4)$$

where N_i is the degree of polymerization of polymer i and $g_{iD}(Q)$ represents the single-molecule form factor, which for a polymer molecule with a Gaussian segment density distribution is given by the Debye equation³³

$$g_{iD}(Q) = \frac{2}{[Q^2(R_{ig})^2]^2} \left\{ Q^2(R_{ig})^2 + \exp[-Q^2(R_{ig})^2] - 1 \right\} \quad (5)$$

where R_{ig} is the z -average root mean square radius of gyration of polymer i . Where the segment volumes of the two polymers in the mixture may be different, a reference volume ν_0 is introduced together with the segment volumes of each polymer (ν_1 and ν_2). Hence we have

$$\frac{1}{S(Q)} = \frac{(\rho_1 - \rho_2)^2}{d\Sigma(Q)/d\Omega} = \frac{1}{\phi_1 N_1 \nu_1 g_{1D}(Q)} + \frac{1}{\phi_2 N_2 \nu_2 g_{2D}(Q)} - \frac{2\chi_{\text{eff}}}{\nu_0} \quad (6)$$

and commonly $\nu_0 = \sqrt{\nu_1 \nu_2}$ where we introduce an effective interaction parameter χ_{eff} in equation (6) to account for the possible concentration dependence and any other influences not incorporated in the original Flory–Huggins theory. It is equation (6) that we have used subsequently to analyse our SANS data for values of χ_{eff} .

EXPERIMENTAL

Polymer synthesis

Hydrogenous and deuterated isomers of polymethyl methacrylate were prepared by anionic polymerization of the respective monomers in tetrahydrofuran solution. The initiator used was 9-fluorenyllithium and high vacuum conditions at ambient temperature were used throughout. Degassed methanol was added after polymerization had been under way for 15 h. Each polymer solution was then poured into a large excess of well-stirred methanol and the precipitate filtered off. After washing and drying to constant weight at 313 K under vacuum, the deuterated and hydrogenous polymethyl methacrylate (DPMMA and HPMMA) were stored in the dark until required.

Polyethylene oxide polymers were also prepared by anionic polymerization using diphenylmethylpotassium as the initiator. Hydrogenous ethylene oxide was obtained from Fluka and deuterated ethylene oxide purchased from Greef (Croydon, UK). In addition to the usual drying over calcium hydride and freeze–thaw cycles, it was necessary to use additional purification procedures for both hydrogenous and deuterated ethylene oxide. After drying over calcium hydride, each isomer of ethylene oxide was exposed to several freshly prepared sodium mirrors until no tarnishing of the mirror was observed. The required amount of ethylene oxide was then distilled into the reaction flask together with tetrahydrofuran. After cooling the flask and contents to acetone/solid carbon dioxide temperature, a solution of diphenylmethylpotassium in tetrahydrofuran was injected and the temperature allowed to increase to room temperature overnight. The temperature of the flask and contents was then raised to 343 K and maintained at that temperature for one week. After this

Table 1 Molecular weights and polydispersities of the polymers used

Polymer	$10^{-5} \bar{M}_w$ (g mol ⁻¹)	\bar{M}_w/\bar{M}_n
Deuterated polyethylene oxide	1.022	1.2
Hydrogenous polymethyl methacrylate	1.476	1.3
Hydrogenous polyethylene oxide	1.243	1.1
Deuterated polymethyl methacrylate	1.179	1.2

time polymerization was terminated by injection of degassed glacial acetic acid and the polymer recovered by pouring the solution into a large excess of hexane. The recovered hydrogenous polyethylene oxide (HPEO) and deuterated polyethylene oxide (DPEO) were dried under vacuum at 313 K to constant weight and subsequently stored in the dark. Molecular weights of these polymers obtained by size exclusion chromatography are given in Table 1.

Small angle neutron scattering

Blends of DPEO with HPMMA and HPEO with DPMMA were prepared by co-dissolving the two polymers in each blend in chloroform such that the total concentration of polymer in solution was ca. 5% (w/v). The blends were precipitated by pouring each solution into excess hexane. After filtering and drying, each blend was compression moulded at 423 K to form a cylindrical specimen of 20 mm diameter and between 1.0 and 1.2 mm thickness. The volume fraction of PEO in the blend mixtures explored was in the range $0.100 \leq \phi_{\text{PEO}} \leq 0.275$. In addition to these blend samples, specimens of the D and H homopolymers were also compression moulded. It was found necessary to use a lower moulding temperature of 373 K for HPEO and DPEO.

Each specimen so prepared was placed between two quartz windows in a brass cell which could be placed in a temperature-controlled sample changer on the LOQ small angle neutron diffractometer at the UK pulsed neutron source, ISIS, at the Rutherford Appleton Laboratory, Chilton, UK. Small angle neutron-scattering data were collected for each blend and the individual homopolymers at temperatures of 423, 438, 458 and 473 K. The range of scattering vector used was $0.01 \text{ \AA}^{-1} \leq Q \leq 0.2 \text{ \AA}^{-1}$ and the instrument was calibrated using a mixture of hydrogenous and deuterated polystyrene (PSH and PSD) of known composition and molecular weight. All scattering patterns were isotropic and consequently the raw data were radially averaged before being corrected for transmission and thickness. Incoherent background scattering was subtracted from each data set for the blends using the volume fraction weighted sum of the scattering intensities of the pure homopolymers in each blend.

RESULTS

Analysis of these blends using differential scanning calorimetry showed that no melting point existed, and hence within the sensitivity of this technique the blends were non-crystalline at ambient temperatures. During the time that the blends were in the temperature range 423–473 K, it was noted that voids formed in some samples. In some cases these voids were small and located at the periphery of the sample, in others they

were somewhat larger. It is noteworthy that these voids only appeared when the temperature was greater than the moulding temperature. The conclusion is that incomplete removal of solvent may be responsible for the formation of the voids. However, the two homopolymers were treated in exactly the same way and no voids were observed for any of the temperatures used in the SANS measurements on these two polymers. Although transmission measurements correct, to some extent, for the presence of voids in the sample, this correction will be incomplete. We foresee two effects coming from voids in the sample which are in the path of the incident neutron beam. Firstly, the incoherent background scattering will be reduced owing to the absence of polymer from the beam. Secondly, the coherent elastic scattering will also be reduced from that which would prevail if there were no voids. Consequently, the use of the volume fraction weighted sum of the scattering intensities from the two homopolymers as the background may result in an over-subtraction of the background scattering. Furthermore, as long as the voids in the beam path are sufficiently large that any scattering from them is essentially located at $Q = 0 \text{ \AA}^{-1}$, then the absolute coherent elastic scattering cross-section can be obtained by including the calibration constant as an adjustable parameter in the fitting procedure to extract a value for χ_{eff} , the polymer–polymer interaction parameter (see later).

Figure 1 shows the absolute scattering cross-section ($d\Sigma(Q)/d\Omega$) for DPEO/HPMMA blends at 423 K for the range of ϕ_{DPEO} values explored. Figure 2 shows the influence of temperature on the HPEO/DPMMA blend where the volume fraction of HPEO is 0.24. In both cases, the values of $d\Sigma(Q)/d\Omega$ are those obtained after normalization and background subtraction, i.e. any corrections required owing to the presence of voids have not been made. As anticipated, as the volume fraction of the PEO in the blend increases, the scattering cross-section increases. Because the PEO is the minor component in both DPEO/HPMMA and HPEO/DPMMA blends, the form of the scattering law is determined by the composition fluctuations in the blend caused by this minor component.

SANS data were analysed using the random phase expression set out earlier in equation (6), where

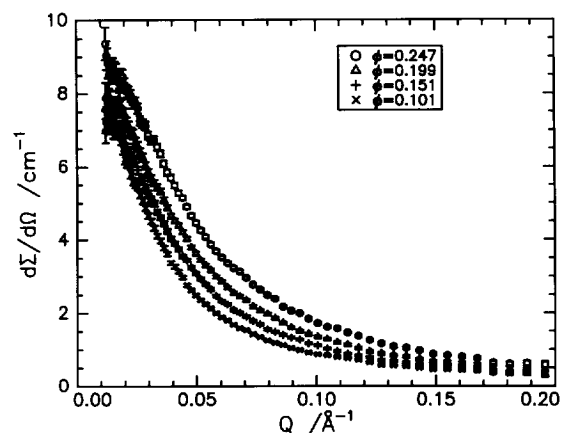


Figure 1 Coherent scattering cross-section at 423 K for DPEO/HPMMA blends. Volume fractions of DPEO are indicated

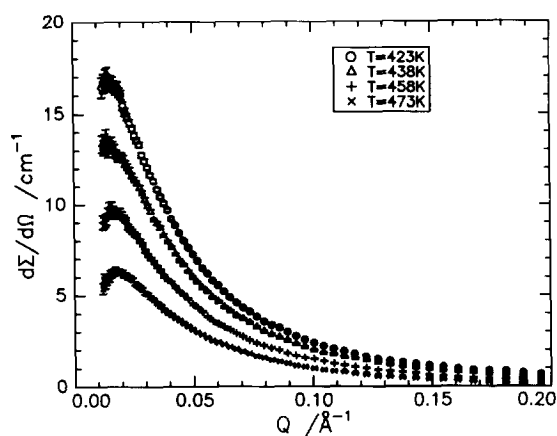
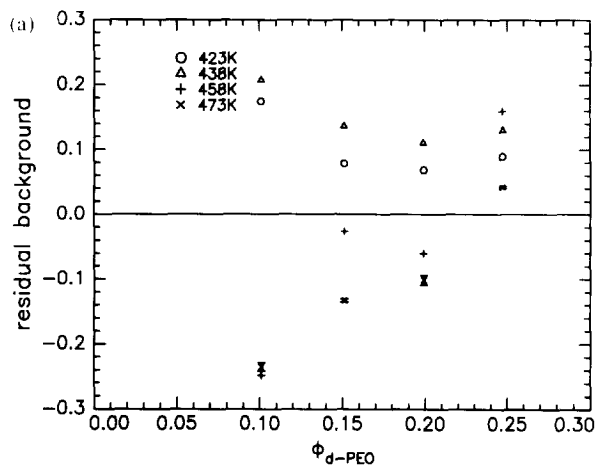


Figure 2 Coherent scattering cross-section for an HPEO/DPMMA blend with a volume fraction of HPEO of 0.24. Temperatures of blends are indicated

allowance has been made for the different segment volumes of PMMA and PEO in both deuterated and hydrogenous versions. The radii of gyration of the polymers were fixed at the unperturbed dimensions calculated^{34,35} from the molecular weights of the polymers used and literature values of $(\langle s^2 \rangle_0 / M_w)^{1/2}$. To account for the presence of voids which would influence the background scattering and the absolute coherent scattering cross-section, a multiplicative calibration constant and an additive background contribution were included in the fitting equation. The additional background contributions resulting from the fit were all small in magnitude and the values obtained are displayed in *Figures 3a* and *3b* for each temperature and blend composition investigated. Values of χ_{eff} were extracted from the data using both a fixed calibration constant (i.e. that obtained from the PSD/PSH blend) and a 'floating' calibration constant. Comparison of the values of χ_{eff} obtained showed that for the majority of cases the difference between the two values was ca. $\pm 5\%$; in one case only was the difference ca. 16%. Consequently, it appears that the corrections required owing to possible errors in the absolute cross-sections due to voids are within errors arising from sources other than the small angle neutron scattering (values of molecular weight and $(\langle s^2 \rangle_0 / M_w)^{1/2}$). The



values of χ_{eff} reproduced here are those obtained where an adjustable calibration constant and the background have been retained.

Figure 4 shows the coherent scattering intensities plotted in Kratky form ($Q^2 d\Sigma(Q)/d\Omega$) as a function of Q with the fits (using equation (6)) to these data overlaid. This form of plotting the data is used because any deviations from scattering described by the Debye equation (equation (5)) become very evident. Such deviations generally appear in the Q region covered by the plateau in *Figure 4* and are generally due to preferred stereochemical configurations of substituents along the main chain. In contrast to our earlier SANS results on polymethyl methacrylate isotopic homopolymer blends³⁶, no deviations are observed in the current data since the coherent scattering is dominated by the polyethylene oxide.

The values of χ_{eff} obtained are presented as a function of the reciprocal absolute temperature in *Figures 5a* and *5b*. In general, the χ_{eff} values for the DPEO/HPMMA combinations are more negative than the values for the HPEO/DPMMA blends. This is an example of the 'label-switching' effect that has been noted in other systems and which has been extensively discussed by Krishnamoorti *et al.*^{37,38} in relation to their SANS results on saturated hydrocarbon polymers. The fact that the DPEO/HPMMA blends have more negative values of χ_{eff} suggests that these blends are more distant from the coexistence curve than the HPEO/DPMMA blends. Since positive slopes are evident for the data as plotted in *Figures 5a* and *5b*, an upper critical solution temperature is indicated for both sets of blends. The temperature dependence of χ_{eff} for polymer blends is usually described by a relation of the form

$$\chi_{\text{eff}} = A + \frac{B}{T}$$

where A is identified with the entropy contribution to χ_{eff} and B is an enthalpy contribution. The values of A and B obtained from the best linear least squares fits to the data of *Figures 5a* and *5b* are given in *Table 2*. From the values of A and B given in *Table 2* it appears that the enthalpic parameter (B) is more influenced by the label-switching effect.

The value of χ_{eff} at the spinodal temperature (below

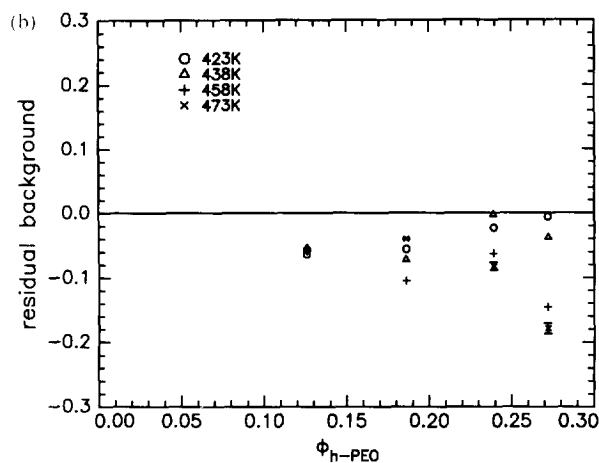


Figure 3 (a) Residual background resulting from fitting the random phase approximation expression to neutron-scattering data for DPEO/HPMMA blends. (b) Residual background for HPEO/DPMMA blends

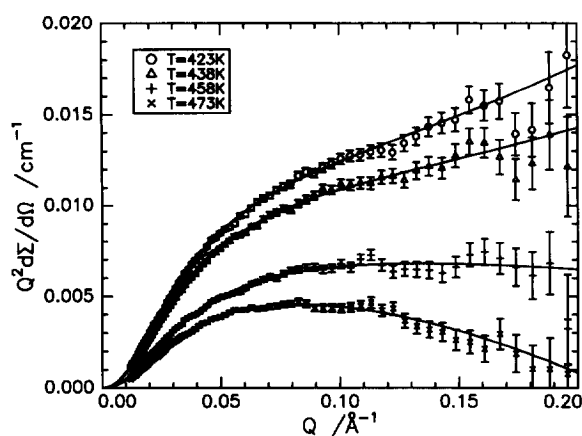


Figure 4 Small angle neutron-scattering data for DPEO/HPMMA blends plotted in Kratky form together with the best fits to these data (solid lines) ($\phi_{\text{DPEO}} = 0.151$)

which the blends phase separate spontaneously) is given by

$$\chi_{\text{eff}}^{\text{sp}} = \frac{\nu_o}{2} \left(\frac{1}{\nu_{\text{PEO}} \phi_{\text{PEO}} N_{\text{PEO}}} + \frac{1}{\nu_{\text{PMMA}} \phi_{\text{PMMA}} N_{\text{PMMA}}} \right) \quad (7)$$

Using the values of A and B given in *Table 2* and the values of $\chi_{\text{eff}}^{\text{sp}}$ calculated from equation (7), we obtain 350 ± 50 K and 320 ± 100 K as the spinodal temperatures of the HPEO/DPMMA and DPEO/HPMMA blends, respectively. The errors included in the values of the spinodal temperature do not permit us to observe any composition dependence in the values (and thus define partially the spinodal curve), but they do suggest that the spinodal curve may have a rather flat dependence on composition in the range explored by us.

While the temperature dependence of χ_{eff} for the PEO/PMMA blends has no differences from the behaviour observed for other polymer blends, the composition dependence is quite different and in one case marked (*Figures 6a* and *6b*). For the DPEO/HPMMA blends, there is only a very small composition dependence of χ_{eff} for temperatures of 423 and 438 K. At 458 K there may be evidence of some slight downward curvature in the value of χ_{eff} at low values of ϕ_{DPEO} . This downward

curvature becomes very evident for the χ_{eff} values obtained at 473 K. Composition dependence is evident at all temperatures in the HPEO/DPMMA blends. At low values of ϕ_{HPEO} and for the two lower temperatures investigated, upward curvature in χ_{eff} is observed. At the two higher temperatures, this behaviour is transformed to a downward curvature in χ_{eff} . Although a composition dependence of χ_{eff} has been observed in other polymer blends, this is generally an upward curvature only. In their work on blends of hydrocarbon polymers, Krishnamoorti *et al.*³⁸ obtained a composition dependence of χ_{eff} which had upward curvature, but this curvature became much attenuated as the temperature of the blend increased.

DISCUSSION

Comparison of the values of χ_{eff} obtained for both DPEO/HPMMA and HPEO/DPMMA systems with values quoted for other polymer blends where the components are chemically dissimilar shows that they are of the same magnitude where the blends are miscible. Ito *et al.*³⁹ report values of χ_{eff} for PEO in a mixture of HPMMA and DPMMA as a function of MMA monomer fraction. These values range from -0.005 to ca. 0.001 over the MMA monomer fraction range 0.3 – 0.9 . The values were reported for a temperature of 350 K, and the authors remark that no temperature dependence was observed over an 80 K range. The absolute temperatures at which these data were collected were not stated. Extrapolating our data to 350 K produces values of χ_{eff} of the same order of magnitude as those of Ito *et al.* Evidently there is disagreement over the temperature dependence since we clearly have a temperature dependence of χ_{eff} for all blend compositions. Ito *et al.* point out that they have ignored the possibility of a non-zero χ_{eff} between the H and D isomers of the PMMA, and we have shown in an earlier publication that there is a finite value of χ_{eff} between these two isotopic forms of PMMA. For mixtures of H and D isotopes of PMMA we found that χ_{eff} has a positive slope in its dependence on $1/T$, and consequently the absence of any temperature dependence of χ_{eff} in the data of Ito *et al.* is puzzling. In an attempt to resolve this point we have turned to equation of state parameters for the PEO/PMMA blend, which have been reported by

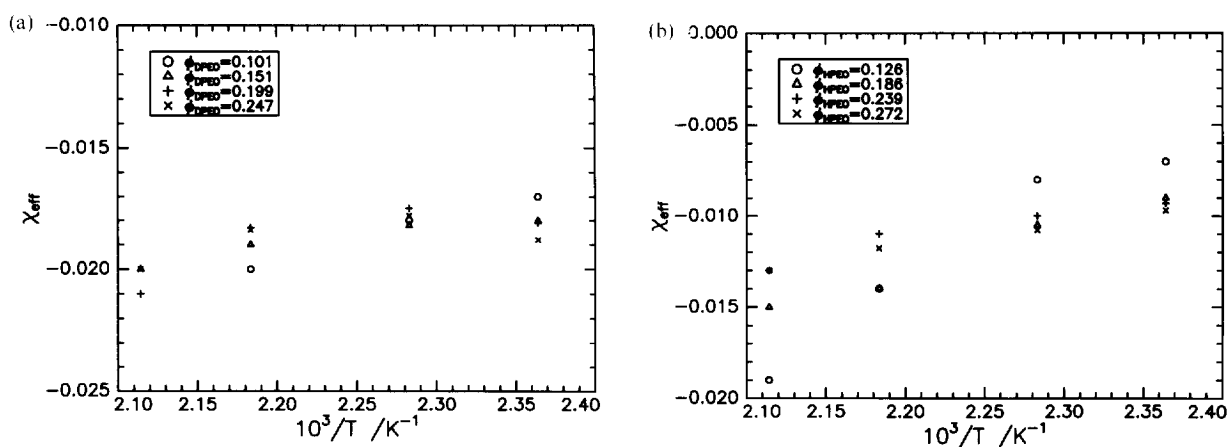


Figure 5 Plots of χ_{eff} as a function of the reciprocal absolute temperature: (a) DPEO/HPMMA blends; (b) HPEO/DPMMA blends

Table 2 Parameters of the temperature dependence of χ_{eff} for DPEO-HPMMA and HPEO/DPMMA blends

DPEO-HPMMA			HPEO/DPMMA		
ϕ_{DPEO}	A	B/(K ⁻¹)	ϕ_{HPEO}	A	B/(K ⁻¹)
0.101	-0.12	44 ± 18	0.126	-0.12	47 ± 8
0.151	-0.03	7 ± 2	0.186	-0.07	25 ± 4
0.199	-0.04	11 ± 8	0.239	-0.04	14 ± 1
0.247	-0.03	5 ± 5	0.272	-0.04	13 ± 1

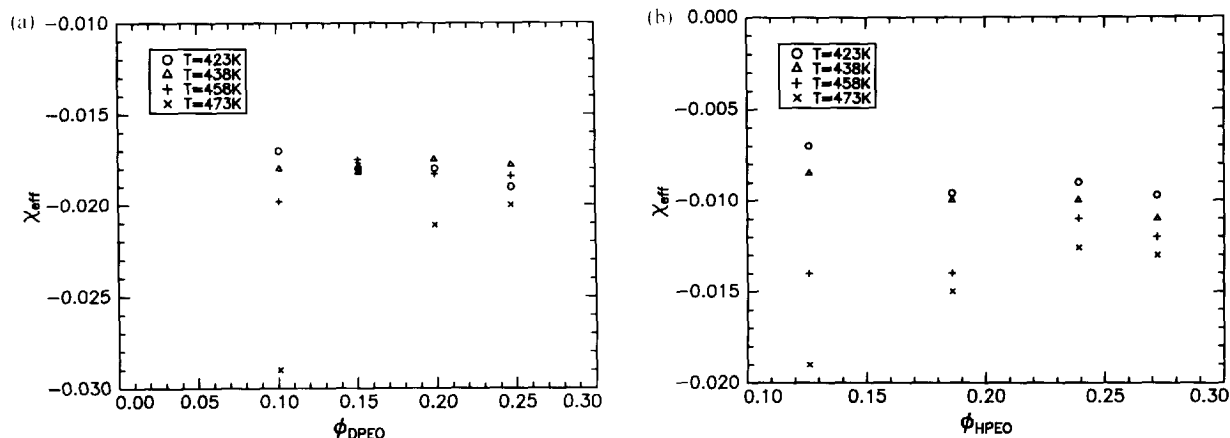
Pedemonte and Burgisi⁴⁰ and Martuscelli *et al.*⁴¹. The Flory-Huggins interaction parameter may be expressed in terms of the parameters of the corresponding equation of state theory as

$$\chi = \frac{P_1^* V_1^*}{RT_1^*} \left[\frac{\tilde{V}_1^{1/3}}{\tilde{V}_1^{1/3} - 1} \left(\frac{X_{12}}{P_1^*} \right) + \frac{\tilde{V}_1^{1/3}}{2(4/3 - \tilde{V}_1^{1/3})} \tau^2 \right] \quad (8)$$

where $\tau = 1 - (T_1^*/T_2^*)$ and T_i^* , P_i^* and V_i^* are the characteristic parameters of polymer i . The X_{12} parameter is the contact energy term between polymers 1 and 2 and \tilde{V}_i is the reduced volume of polymer i . Values of \tilde{V}_i , V_i^* , T_i^* and P_i^* have been provided by Pedemonte and Burgisi⁴⁰ in a recent publication where they also present values of χ for the PEO/PMMA mixture. Values of X_{12} required for this calculation were obtained by two methods: firstly from the reduced temperature of the mixture, and secondly from values of the heat of mixing of the two polymers (obtained indirectly from measurements on solutions). A value of -0.54 J cm^{-3} for X_{12} was obtained by the first method, whereas the more direct heat of mixing data gave a value of -11.7 J cm^{-3} . This latter value was rejected by Pedemonte and Burgisi on the basis that the interactions between the two polymers were weak. Moreover, an earlier estimate of X_{12} using available values of χ (amongst them the values of Ito *et al.* referred to above) gave a value of -0.3 J cm^{-3} . Calculation of values of χ from the characteristic parameters and the value of X_{12} favoured by Pedemonte and Burgisi as a function of temperature shows that χ does indeed have a temperature dependence. However, the values of χ , although negative, are ca. 10–20 times larger in magnitude than those obtained by us or Ito *et al.* The dependence of χ so calculated on temperature is such that an upper critical solution temperature is

predicted for the PEO/PMMA system, which appears to be in agreement with our findings here. (At this point we remark that our recalculated values of χ and the temperature dependence using Pedemonte and Burgisi's data are completely at variance with those given by Pedemonte and Burgisi. Notably, Pedemonte and Burgisi show a temperature dependence which predicts a lower critical solution temperature! This cannot be so if Pedemonte and Burgisi have used the data set given in their paper to calculate X_{12} .)

On the basis of the independence of χ_{eff} on temperature (and on the concentration dependence of χ_{eff}), Ito *et al.* concluded that entropic contributions were dominant in the mixture; however, our data clearly show that this is not the case. Enthalpic interactions are more dominant, and from the values of B in Table 2 it is also evident that the enthalpic contribution is more influenced by the label switching of the deuterium in the blend. It has been proposed that the intermolecular interactions between PEO and PMMA are between the negatively charged ether oxygens in PEO and the positively charged carbonyl carbon atoms of PMMA. However, this attractive interaction is weakened by repulsions from the negatively charged oxygen atoms in the PEO, and consequently the interaction between the two polymers is thought to be weak and of the same order of magnitude as van der Waals forces. Let us now attempt to predict the effect of replacement of hydrogens by deuterium on these interactions and confront these predictions with the values of χ_{eff} obtained experimentally. On replacing a hydrogen atom by deuterium both the length and polarizability of the bond to carbon are reduced. In PEO, deuterium labelling should render the ether oxygens rather more negative and thus favourably increase the interaction with the carbonyl carbon

**Figure 6** Plots of χ_{eff} as a function of polyethylene oxide volume fraction: (a) DPEO-HPMMA blends; (b) HPEO-DPMMA blends

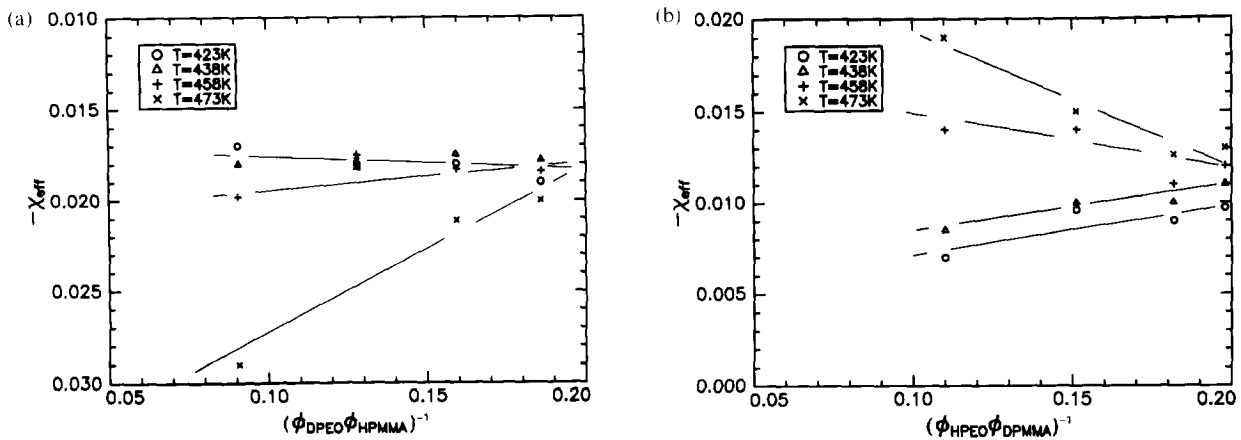


Figure 7 Values of χ_{eff} plotted according to equation (9): (a) DPEO-HPMMA blends; (b) HPEO/DPMMA blends. Lines are guides to the eye

atoms of hydrogenous PMMA. Deuterium substitution in PMMA should also make the ester oxygens slightly more negative and hence increase the repulsion felt by the PEO on close approach to the PMMA. Consequently, on this qualitative argument we anticipate that χ_{eff} for DPEO/HPMMA should be more negative (i.e. favourable to mixing) than for HPEO/DPMMA mixtures. This conclusion is consistent with the experimental values of χ_{eff} shown in Figures 5 and 6.

We turn now to the observed concentration dependence of the interaction parameter χ_{eff} . As originally defined by Flory and Huggins the interaction parameter should have neither composition dependence nor molecular weight dependence. There has been plentiful evidence that χ_{eff} displays a composition dependence, and in some cases a molecular weight dependence has also been asserted³⁹. This composition dependence has been attributed (separately) to several sources. The most commonly given explanation is that there are excess volumes of mixing when the two polymers are mixed which are not accounted for in the original Flory-Huggins theory. Another invalidity in the Flory-Huggins theory which has been cited as leading to a composition dependent χ_{eff} is the absence of any accounting for concentration fluctuations. Muthukumar⁴² has thoroughly discussed this aspect and the theory compared with experimental data by Bates *et al.*⁴³ with apparently satisfactory agreement. Unfortunately, the equation (equation (4) in their paper) quoted by Bates *et al.* is incorrect and cannot give the upward curvature seen in their experimental data. All of these attempts at explaining the composition dependence of χ_{eff} predict a downward curvature of the values at the extremes of the composition range. Another aspect that has been the focus of attention as a possible cause of a composition dependence of χ_{eff} values obtained by SANS is the use of the random phase approximation with the assumption of incompressibility of polymer melts. This and other facets have been discussed in a recent paper by Kumar⁴⁴. Kumar used a Monte Carlo simulation of off-lattice chains of a polymer blend to calculate the chemical potential of one component in the blend, from which χ_{eff} can be obtained. He points out that departures from either the original Flory theory or the assumption of incompressibility in the random phase approximation

can lead to composition dependence in χ_{eff} . From his simulations it is concluded that the chemical potentials of blends held at constant pressure follow Flory-Huggins theory with a composition independent interaction parameter. If constant molar volume conditions in the blend are used, then only by using a composition dependent interaction parameter is it possible to describe the variation in chemical potential as a function of composition using Flory-Huggins theory. Consequently, any composition dependence in χ_{eff} is due to the assumption of incompressibility in the random phase approximation. The relation between χ_{eff} and the composition independent interaction parameter χ obtained by Kumar is

$$-\chi_{\text{eff}} = \frac{1}{2N\phi_1\phi_2} \left[\frac{1}{4\rho^2} \left(\frac{1}{\bar{V}_1} + \frac{1}{\bar{V}_2} \right)^2 - 1 \right] - \frac{\chi}{4\rho^2} \left(\frac{1}{\bar{V}_1} + \frac{1}{\bar{V}_2} \right)^2 \quad (9)$$

where N is the degree of polymerization of the polymers in the blend (a symmetric blend is assumed for the simulations), ρ is the blend density, ϕ_i is the volume fraction of component i and \bar{V}_i is the partial molar volume of that component. Kumar shows by simulation of data that the dependence of χ_{eff} on composition is strongly controlled by the volume changes that occur on mixing the two polymers.

Values of χ_{eff} are plotted according to equation (9) for all the data in Figures 7a and 7b. Although the data for any one temperature are sparse, each set is essentially linear in $(\phi_{\text{PEO}}\phi_{\text{PMMA}})^{-1}$, the slopes changing from positive to negative as the temperature increases. The change in slope from positive to negative is associated with the change of curvature from upward to downward in the dependence of χ_{eff} on ϕ_{PEO} . Kumar has shown that volume changes on mixing as small as 0.05% produce a significant composition dependence of χ_{eff} at the extremes of the composition range. Where the excess volume of mixing is positive, χ_{eff} has upward curvature dependence on composition and constitutes what Kumar terms a 'repulsive' blend. Negative excess volumes occur in 'attractive' blends and lead to a downward curvature in the dependence of χ_{eff} on composition in the wings of

the composition range. Privalko *et al.*⁴⁵ report specific volumes as a function of composition for PEO/PMMA mixtures at 393 K. For PEO of molecular weight $125 \times 10^3 \text{ g mol}^{-1}$ the data presented suggest that there is a negative volume change on mixing of up to 2%, i.e. the blend is attractive. However, the dependence of the specific volume on composition displays extremely strange behaviour, i.e. an abrupt change from a negative excess volume of mixing to essentially zero excess volume of mixing for blends with high MMA content. (We note that the ordinate axis scale in *Figure 2a* of the paper by Privalko *et al.*⁴⁵ is incorrect.) Pedemonte and Burgisi⁴⁰ state that they have determined the volume of a 50/50 mixture of PEO and PMMA but they have not reported the value; consequently, we are unable to estimate the partial molar volumes needed in equation (9) to extract values of χ . However, Pedemonte and Burgisi remark that the equation of state parameters (P^* , T^* and V^*) have a temperature dependence in PEO/PMMA mixtures. Consequently, the change in composition dependence with temperature observed by us may be due to the excess volumes of mixing changing from slightly positive at low temperature to slightly negative at higher temperatures.

CONCLUSIONS

The effective interaction parameter in polyethylene oxide/polymethyl methacrylate mixtures has been shown to be dependent on which of the polymers is deuterated. Over the temperature range investigated, 423–473 K, the blends are compatible no matter which molecule is deuterated. However, the blend with deuterated polyethylene oxide has the more negative values of the interaction parameter and is thus further from any possible phase separation boundary. A rationale for this observation has been given knowing the influence that D for H substitution has on bond polarity. The temperature dependence of the interaction parameter suggests an upper critical solution temperature of ca. 350 K for both blends. A composition dependence of the interaction parameter has been observed for both systems even though the volume fraction range of polyethylene oxide has been restricted to prevent crystallization of the polyethylene oxide in the blend.

The shape of this concentration dependence changes as the blend temperature changes. At each temperature the relation proposed by Kumar to account for volume changes on mixing affecting the interaction parameter is a suitable description of the dependence of the interaction parameter on blend composition. Polyethylene oxide/polymethyl methacrylate mixtures appear to form repulsive blends at low temperatures and attractive blends at higher temperatures. This lends some support to the expressed view that interactions between polyethylene oxide and polymethyl methacrylate are weak. The absence of sufficient volumetric data on mixtures of the two polymers prevents evaluation of the composition independent value of the interaction parameter using Kumar's equation. Similar, albeit weaker, behaviour has been noted in blends of hydrocarbon polymers where the interaction parameter is an order of magnitude smaller than noted here.

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