Molecular conformation and interactions in oligomeric mixtures of polystyrene with polybutadiene: a small-angle neutron scattering study

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In this preliminary study we report values of the interaction parameter determined from small angle neutron measurements at two temperatures and three concentrations for two blends of oligomeric polystyrene with polybutadiene. One blend contained labelled (deuterated) polystyrene with hydrogenous polybutadiene and the other deuterated polybutadiene with hydrogenous polystyrene. The results from the latter are compared with predicted values.

INTRODUCTION

A considerable amount of attention is currently being focussed on the problems of understanding the thermodynamic behaviour of partially compatible polymer blends. Although practical applications are more common amongst high molecular weight systems, oligomeric mixtures are generally more amenable to study. One such model oligomeric system is that of polystyrene with polybutadiene. The strong molecular weight dependence of the phase boundaries can be usefully exploited to give mixtures that phase separate in the easily experimentally accessible range between room temperature and 200°C.

In classical Flory–Huggins theory[1-3] the Gibb's free energy of mixing per mole segment, ΔG_m, is expressed as:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi_{12} \phi_1 \phi_2 \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2, N_1 and N_2 being the respective relative chain lengths. χ is an empirical interaction parameter between unlike segments which was originally defined such that it had an inverse temperature dependence and was independent of concentration.

The partial specific volumes of the polymer components tend to alter on mixing causing the total volume of the mixture to change, which subsequently affects both the enthalpic and entropic contributions to the free energy in a way that cannot be predicted by regular solution theory. The equation-of-state developed by Flory and coworkers[4,5], although quantifying such volume changes, still utilizes semi-empirical parameters to describe the excess enthalpy (X_{12}) and entropy (Q_{12}) of the interactions between unlike segments. The entropic parameter Q_{12} is often small and tends to be ignored or incorporated into the definition of X_{12}; to avoid confusion we therefore define $\bar{X}_{12}$ as;

$$\bar{X}_{12} = X_{12} - T\bar{v}Q_{12} \qquad (2)$$

where $\bar{v}$ is the reduced volume of the mixture. An alternative approach to that of equation-of-state theories is to replace χ_{12} in equation (1) with a function g_{12} which is both temperature and concentration dependent; (this function is further discussed in the 'neutron scattering experiments' section).

Interaction parameters are notoriously difficult to measure experimentally although several techniques can be used with varying degrees of success as discussed in a recent paper by Higgins and Walsh[6] and summarized in *Table 1*. It is apparent from *Table 1* that using these methods reliable measurements of $\bar{X}_{12}$ or g_{12} can only be made at fixed temperature composition points. To explore the temperature dependence of the interaction parameters, it is necessary to make measurements away from phase boundaries. This can be achieved by using scattering techniques and in particular small angle neutron scattering (SANS). Conventionally SANS is used to study molecular conformation by labelling a proportion of the molecules with deuterium. However, in the case of a polymer blend this leads to a pseudo three component system consisting of polymer 1 in both deuterated and hydrogenous forms and polymer 2. The scattering from such a system contains not only contributions from the molecular shape function but also from concentration fluctuations. The latter were originally shown by Einstein[7] to depend on the concentration gradient of the chemical potential, and subsequently related by Debye and Beuche[8] to the interactions in the system via the Flory–Huggins expression. Recent papers[9,10] have examined in detail the neutron scattering from blend systems and shown how to separate and analyse the molecular conformation and interaction terms.

Although we have measured interaction parameters by neutron scattering in other systems away from the phase boundaries we have yet to explore their temperature dependence. We present here the first results obtained in this area.

Table 1 A comparison of some methods used to calculate interaction parameters

Technique	Parameter determined	Comments
Measurement of the heat of mixing[11]	X_{12}	Restricted to systems where direct mixing is possible although high molecular weight systems can be modelled using oligomers or small molecule analogues
Inverse gas chromatography[12,13]	$\bar{X}_{12}$	Measurements need to be made not only on the blend but also on the components at temperatures well above their T_g's. Errors arise from non-equilibrium absorption in addition to those from measurements on the individual polymers and can lead to a large error in the result
Pulse induced critical scattering (PICS)[14]	g_{12} (χ_{12} with a concentration dependence)	g_{12} is determined by curve fitting to an experimentally obtained spinodal, i.e. it can only be determined for a particular composition at one temperature. The limitations are the same as those for the heat of mixing measurements
Simulation of phase boundaries[15–17]	$\bar{X}_{12}$	Using values of X_{12} obtained from heat of mixing measurements Q_{12} is adjusted to fit an experimentally obtained cloud point curve. As with PICS the temperature dependence of $\bar{X}_{12}$ away from the phase boundary cannot be inferred. A further uncertainty arises from fitting to the cloud point curve since cloud points can lie anywhere between the binodal and spinodal

EXPERIMENTAL

Samples

The hydrogenous PS samples were obtained from Polymer Laboratories Ltd. (UK). PSD was synthesized in our laboratory using purified butyllithium as the initiator and benzene as the polymerization solvent. The PB standards CDS-B-3 and CDS-B-2 were purchased from the Goodyear Tyre and Rubber Co. (Akron, USA). PBD6 was synthesized according to the method of Morton and Fetters[18] using the same initiator and polymerization solvent as for PSD. The active centre concentration was such[19] as to yield a microstructure close to that of PB CDS-B-3.

For neutron experiments the samples were weighed into flat-sided quartz cells of internal cross-section 15×20 mm and path length 2 mm. A small metallic strip was added to each cell prior to these being degassed and sealed under vacuum to facilitate magnetic stirring. Antioxidants were not used.

Blends containing PBD6 are referred to as series A samples and those containing PSD as series B samples. The phase boundaries for both series A and B have been published elsewhere[20–22]. The molecular characteristics of the components of each series are given in Table 2. The molecular weights of the oligomers were chosen such that

the phase boundaries of A and B blends remain at reasonably low temperatures. An effort was also made to keep the chain lengths of the deuterated molecules comparable with those of their hydrogenous counterparts.

NEUTRON SCATTERING EXPERIMENTS

The small angle neutron scattering (SANS) experiments were performed on the D17 spectrometer at the Institut Laue–Langevin (Grenoble, France). A sample-detector distance of 1.4 m was used with neutrons of wavelength 15 Å. Data were normalized for geometric and flux factors using the isotropic incoherent scattering from water. The corrected scattered intensity is then related to the scattering law $S(Q)$.

$$S(Q) = \frac{I(Q)(1 - Tr_w)g(\lambda)}{4\pi \cdot Tr_s \cdot d} \tag{3}$$

where Tr_s and Tr_w are the transmissions of the sample and water respectively and d is sample thickness. The factor $g(\lambda)$ takes account of effects in the water scattering due to inelastic terms.

We have recently derived an equation[9] to describe the scattering from a sample containing volume fractions ϕ_1 and ϕ_2 of two polymers with a deuterated fraction c, of type 1 segments. A segment is conveniently defined as a monomeric repeat unit. In the expression the polymer species with labelled chains is termed polymer 1.

$$S(Q) = \frac{(cd + (1-c)h - b')^2}{P_1^{-1}(Q) + \beta P_2^{-1}(Q) - 2\beta U}$$
$$+ c(1-c)(d-h)^2 P_1(Q) \tag{4}$$

where d and h are the sums of neutron scattering lengths for deuterated and hydrogenous segments of polymer 1. $b' = \beta b$ where b is the scattering length per segment of polymer 2 and $\beta = V_1/V_2$ where V_1 and V_2 are the respective segment specific volume for polymers 1 and 2. U is a mean field expression for the interaction between two segments.

$$P_n(Q) = \phi_n' N_n f_D(QRg_n) \tag{5}$$

ϕ_n' is the segment concentration, N_n the degree of polymerization and Rg_n the radius of gyration of the nth component. $f_D(QRg_n)$ is the Debye scattering curve for ideal polymers which at low Q can be approximated to

$$f_D(QRg_n) \to 1 - \frac{(QRg_n)^2}{3} \tag{6}$$

In more familiar terms the volume fraction

$$\phi_n = \phi_n'(M_n/\rho_n N_A) \tag{7}$$

Table 2 Sample characteristics

Polymer	M_w	M_w/M_n	% cis	% trans	% vinyl
Series A					
PB	2660	1.3	41 ± 2	49 ± 2	10 ± 2
PBD6	3260	1.16	36 ± 4	54 ± 4	10 ± 2
PS	1460	1.09			
Series B					
PB	920	1.12	36 ± 4	49 ± 4	15 ± 2
PSD	3800	1.12			
PS	3800	1.08			

M_n is the segment mass and ρ_n the density of polymer species n, N_A is Avogadro's number. Substituting $\phi_n = \phi'_n(M_n/\rho_n N_A)$ and removal from both terms of V_1 where $(V_1 = M_1/\rho_1 N_A)$ leads us to the expression at zero Q:

$$V_1 . S(O) = \frac{(cd + (1-c)h - b')^2}{(\phi'_1 N_1)^{-1} + \beta(\phi'_2 N_2)^{-1} - 2\beta U/V_1}$$
$$+ c(1-c)(d-h)^2 \phi'_1 N_1 \qquad (8)$$

The factor β corrects for the fact that we are counting segments of polymer 2 rather than the number of lattice sites (defined by polymer 1) occupied by it.

The first term in equation (8) arises from concentration fluctuations, the second is the scattering from labelled chains. In these calculations the assumption has been made that the d-segments occupy the same volume as the h-segments (i.e. the density of d-polymer = the density of h-polymer × the ratio of the segment weights).

Fitting curves to spinodal points determined by the pulse induced critical scattering technique enabled Atkin et al.[20,21] to derive expressions based on Flory–Huggins theory which describe the free energy behaviour of PB–PS, PBD6–PS and PBD6–PB–PS blends. However, unlike the Flory–Huggins interaction parameter χ_{12}, the parameter g_{12} used in these expressions is both temperature and concentration dependent, i.e.

$$g_{12} = g_{120} + g_{121}/T + g_{122}\phi_2 \qquad (9)$$

the subscripts 1 and 2 refer to polymers 1 and 2. g_{120}, g_{121} and g_{122} are parameters empirically determined. They are constants specific to a given system.

For a binary mixture the free energy of mixing per unit volume is described by

$$\frac{\Delta G}{RT} = \phi_1 N_1^{-1} \ln \phi_1 + \phi_2 N_2^{-1} \ln \phi_2 + g_{122}\phi_1\phi_2 \qquad (10)$$

The relative chain lengths N_1 and N_2 are obtained by dividing the polymer molar masses by the segment mass of polymer 1.

At the spinodal the second derivative of the free energy with respect to composition is zero. Rewriting equation (10) we obtain

$$\frac{\partial^2 \Delta G}{\partial \phi^2} = 0 = (N_1\phi_1)^{-1} + (N_2\phi_2)^{-1}$$
$$- 2g_{120} - 2g_{121}/T + 2g_{122}(1 - 3\phi_2) \qquad (11)$$

The denominator of the first fluctuation term in equation (8) also depends[7,8] on $\partial^2\Delta G/\partial\phi^2$. Comparison of this denominator with equation (11) gives:

$$\beta \frac{U}{V_1}\left(= \frac{U}{V_2}\right) = g_{120} + \frac{g_{121}}{T} - g_{122}(3\phi_2 - 1) \qquad (12)$$

because the appearance in both expressions of $(N_1\phi_1)^{-1}$ and $(N_2\phi_2)^{-1}$ eliminates any scaling problems.

It is worth considering why V_2 appears on the left-hand side of equation (12). As defined U is a mean field expression for the interaction between two segments. To obtain the interaction per unit volume we multiply U by the number of type 1 and 2 segments (per unit volume), i.e. V_1^{-1} and V_2^{-1}. When expressed as the interaction energy per segment 1, i.e. the segment which defines the lattice, we get:

$$U \cdot \frac{1}{V_1} \cdot \frac{1}{V_2} \cdot V_1 = \frac{U}{V_2} \qquad (13)$$

If the lattice is redefined according to polymer 2 (PS) such that it corresponds to that used by Atkin et al. then we obtain $U/V_1 \equiv g_{12}$.

DATA ANALYSIS AND DESIGN OF EXPERIMENTS

Removal of incoherent backgrounds

The value of U eventually obtained from the data is strongly dependent on how accurately the incoherent contribution to the scattering can be removed. The incoherent contribution to the scattering decreases as the concentration of deuterated chains in the blend increases therefore subtracting the scattering from a hydrogenous blend of the same composition will result in too much signal being removed. Although this error is minimal at low deuterium concentrations, it becomes significant for the high levels used in this study. Subtraction of the appropriate hydrogenous blend also relies on the denominator of the concentration fluctuation term being identical to that for a blend of the same composition but containing labelled chains. This requirement is met in those systems where the spinodals are insensitive to deuteration of either component as, for example, in a blend of poly(ethylene glycol)–poly(propylene glycol)[10]. However, the spinodal in the present system is known to be not only sensitive to deuteration but also to which component is labelled. Hence we are unable to use this method of removing the incoherent contribution even at low deuterium concentrations.

An alternative approach to the problem is to estimate the incoherent contribution by summing the relative proportions of the incoherent levels measured for both hydrogenous components, i.e. using a 'sandwich' rather than a blend. It must be emphasized that the scattering from these hydrogenous samples must be measured at the same temperature as the blend containing the deuterated chain, recent results having shown the cross-sections of both components to be very temperature dependent[23] after density changes have been accounted for. This observation is most obviously explained by the well-
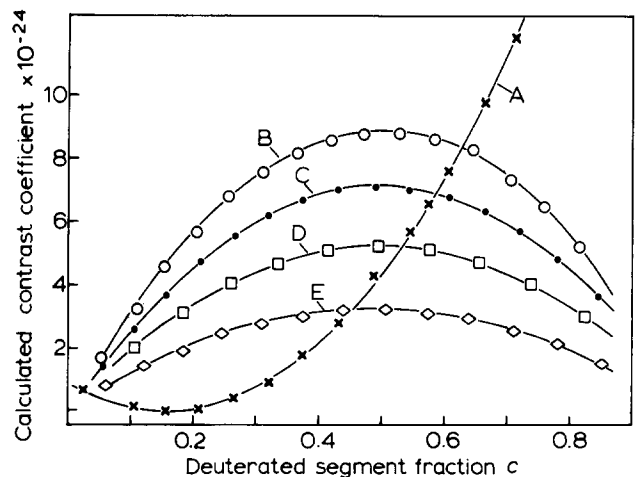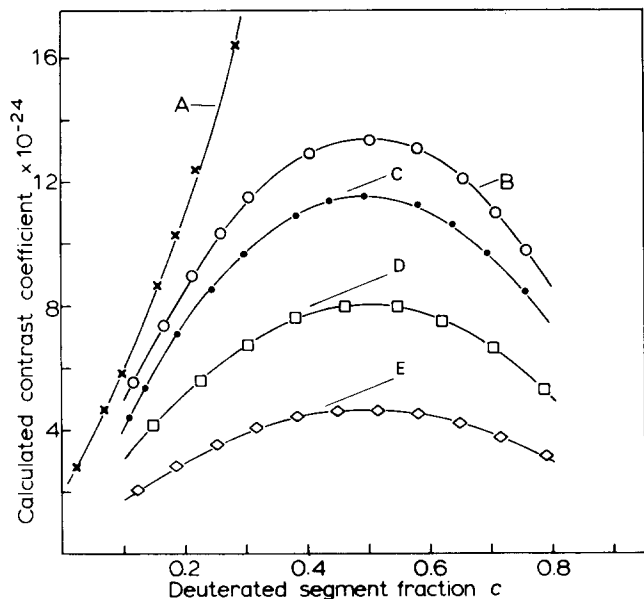

Figure 1 Calculated contrast coefficients for the single chain and concentration fluctuation terms as a function of deuterated segment fraction, c, for the PBD6–PB–PS blend. Curve A represents the concentration fluctuation contrast (equation (8)) and the set of curves B, C, D, E represent the single chain factor, $c(1-c)(d-h)^2\phi_1$. The ϕ_1 values for the single chain terms shown are: ($\bigcirc$): 0.91; ($\bullet$): 0.73; ($\square$): 0.54 and ($\diamond$): 0.34

Figure 2 Calculated contrast coefficients of the single chain and concentration fluctuation terms as a function of deuterated segment fraction c for the PSD–PS–PB blend. Curve A represents the concentration fluctuation contrast (equation (8)) and the set of curves B, C, D, E represent the single chain factor, $c(1-c)(d-h)^2\phi_1$. The ϕ_1 values for the single chain terms shown are: ($\bigcirc$): 0.77; ($\bullet$): 0.66; ($\square$): 0.46 and ($\diamond$): 0.27

known[24] dependence of the total cross-sections on the state of mobility of the H containing groups. Even if changes with temperature of specific segment volume in the blend could be accurately predicted, determining the incoherent contribution to the scattering for a blend by the 'sandwich' method may be inadequate if any changes occur in the chain mobility of either component as a result of blending, i.e. the cross-sections of a given segment are different to those of the pure state.

To be confident of obtaining U or the single chain term care should be taken in selecting the appropriate values of c and ϕ_1 such that the term of interest is dominant. If U is the term of interest then the design of the experiment can be considerably simplified by using a binary mixture of deuterated component 1 with hydrogenous component 2. In such a case the single chain term is zero, hence all the coherent scattering arises from concentration fluctuations.

The concentration fluctuation contrast (i.e. the numerator of the first term in equation (8)) is parabolic in c and has a minimum value close to zero at $c \sim 0.15$ for the system PBD6–PB–PS (Figure 1). Therefore the coherent scattering from any sample with a concentration of deuterated chains ≈ 0.15, such that the contrast factor is zero, is attributable solely to the single chain term. In the converse experiment where the polystyrene is the deuterated component it becomes difficult to extract the single chain term since the minimum in the parabola for the contrast factor occurs at a negative value of c (Figure 2). In such cases where the contrast factor is of the same magnitude as the single chain term the latter could still be obtained by exploiting the as yet unknown temperature dependence of the interaction parameter U. At temperatures close to the spinodal as U approaches its maximum value the scattering from the concentration fluctuations will become infinite, dominating any single chain term. However, away from the spinodal the scattering from the concentration fluctuations will decrease, i.e.

at sufficiently high temperature, the single chain term may dominate.

RESULTS

Blends containing deuterated PB (Series A)

Single chain dimensions. As a demonstration of the temperature invariance of the single chain term measurements were made on a series of PBD6–PB–PS blends where ϕ_1 was allowed to vary but c was kept constant. Attempts were made to keep c close to a value of 0.15, which corresponds to the minimum position of the contrast factor, as shown in *Figure 1*, ensuring that the numerator in the concentration term of equation (8) is essentially zero. In this case we obtain from equation (4) the scattering per monomer

$$S(Q) = c(1-c)(d-h)^2\phi_1 N_1\left(1 - \frac{Q^2(Rg)^2}{3}\right) \quad (14)$$

which allows us to determine the molecular dimensions, Rg and degree of polymerization N_1 in the conventional way.

Figure 3 shows the effect of a 12°C rise in temperature on a typical scattering pattern from a pseudo-ternary blend. It is apparent from the Figure that increasing the temperature has no significant effect on the slope of the plot, i.e. the radius of gyration.

Table 3 lists the values of the radii of gyration and molecular weights obtained from these measurements. The values of Rg are independent of the accuracy of the absolute scattered intensity and concentration, the errors
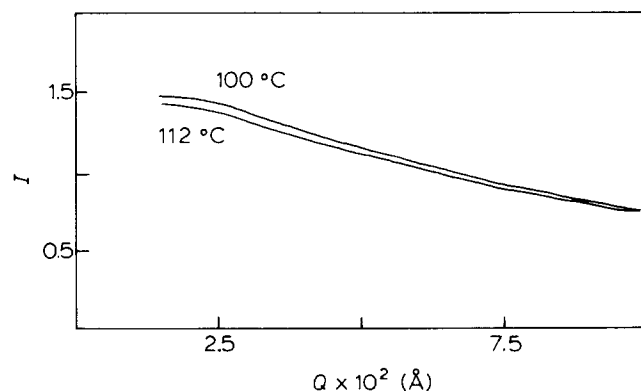
Figure 3 The effect of a 12°C rise in temperature on a typical scattering pattern from a pseudo-ternary blend where the concentration fluctuation contrast is essentially zero
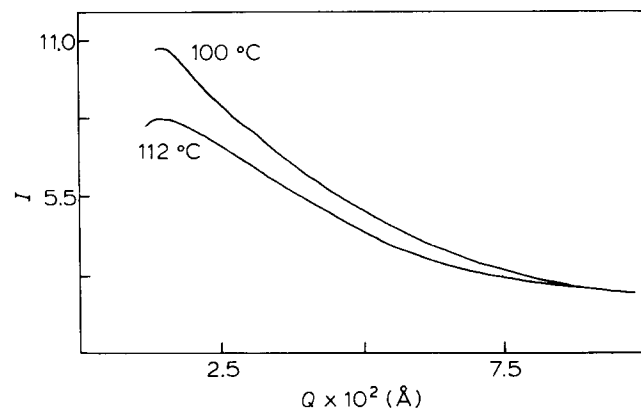
Figure 4 The effect of temperature on a typical scattering pattern from a binary mixture where the single chain term is zero

Table 3 Measurements of the single chain parameters in a blend of PBD6–PB–PS

Temperature (°C)	wt% PB	wt% PBD6	ϕ_1	c ($\pm 5\%$)	Rg ($\pm 3\%$)	M_w ($\pm 10\%$)
100	58.30	12.50	0.621	0.197	18.9	3620
	30.06	6.39	0.335	0.195	18.1	3562
	40.12	8.23	0.440	0.188	18.9	3767
112	58.30	12.50	0.621	0.197	18.8	3643
130	100.00	10.32	1.000	0.094	22.1	3331

are thus smaller than those for the molecular weight. Comparison of the Rg values with that from a sample that does not contain any PS suggests that the PB chains are slightly contracted in its presence.

The interaction parameter. *Figure 4* shows the effect of a 12°C rise in temperature on a typical scattering pattern from a binary mixture of PBD6–PS where the single chain term is zero. The fall in intensity corresponds to a reduction in the amplitude of the concentration fluctuations as the temperature gets further away from the spinodal value. In terms of equation (8) it represents a reduction in the size of the interaction parameter U.

If we analyse the data in terms of equation (14) values of 'Rg', the apparent radius of gyration, can be extracted and compared with that obtained for PBD6 in PB under theta conditions (*Table 3*). Values of U/V_1 are also listed in *Table 4* together with calculated values of g_{12}.

Figure 5 shows the predicted temperature dependence of g_{12} based on the values determined by fitting the spinodal, together with measured values of U/V_1. The calculated values of U/V_1 at the spinodal are of course in agreement with those predicted since both equation (11) and the denominator of equation (8) are equivalent at this point. *Figure 6* contrasts the predicted concentration dependence of g_{12} with measured U/V_1 values.

Blends containing deuterated PS (Series B)

Single chain dimensions. It is apparent from the dominant behaviour of the contrast factor shown in *Figure 2* for a blend of PSD–PS–PB that it is difficult to extract the single chain term. Calculations using an arbitrary value of U suggested that the single chain terms for blends containing low concentrations of deuterium could dominate at high temperatures, i.e. well away from the spinodal. However, measurements made at 130°C and 140°C on samples where c was kept approximately constant at 0.8 show a very significant contribution to the scattering from the concentration fluctuations. Attempts to analyse the data in terms of equation (14) thus lead to values of Rg and M_w which are much larger than the molecular parameters. Values of the apparent Rg and M_w are given in *Table 5*. In a system such as this where the phase boundary is sensitive to c it is not possible to separate the single chain from the concentration term contribution to the scattering unless the relationship between c and U is known (although it is always possible knowing the M_w to obtain U from $I(0)$).

The interaction parameter. Binary mixtures of PSD with PB were again used in preference to tertiary blends to ensure that there was no contribution to the scattering from the single chain term. The data can be analysed in terms of equation (14) to give values of the apparent Rg and M_w. These are compared with the values obtained for a blend of PS under theta conditions in *Table 5*. Values of $\beta U/v_1$ obtained by analysis of the scattering as $Q \to 0$ in terms of equation (8) are also listed. At present the spinodal for this system has not been determined by PICS (although this will be done in the near future) hence there are no g_{12} values available for comparison.

Sources of error. Apart from counting statistics which were very good for these experiments, the two most

Table 4 Apparent molecular parameters 'Rg' and 'M_w' for blends of PBD6–PS where scattering is attributable to only concentration fluctuations

Temperature (°C)	ϕ_1	$I(0)$ ($\pm 10\%$)	'Rg' ($\pm 3\%$)	'Rg'/$Rg(\theta)$	U/V_1	g_{12}[a]
100	0.625	7.96	23.9	1.28	0.0871	0.018
	0.432	13.30	39.6	2.12	0.0850	0.021
	0.328	12.20	43.0	2.30	0.0884	0.023
112	0.625	6.94	22.5	1.19	0.0837	-1.64E-4
	0.432	10.60	34.5	1.84	0.0815	0.0027
	0.328	10.60	36.3	1.94	0.0864	0.0043

[a] Predicted using equation (11) and the experimental PICS value at the spinodal

Table 5 Apparent molecular parameters 'Rg' and 'M_w' for blends of PSD–PB, and for PSD–PD–PB where scattering is attributable to both concentration fluctuations and a single chain contribution

Temperature (°C)	ϕ_1	W_D (g/g)	c	'Rg' ($\pm 3\%$)	'Rg'/$Rg(\theta)$	$I(0)$ ($\pm 10\%$)	$\beta U/V_1$	'M_w'
140	0.463	50.3	1	43.0	2.88	16.68	0.098	
	0.275	30.8	1	33.0	2.21	7.24	0.132	
	0.662	69.7	1	33.3	2.23	14.44	0.086	
	0.461	39.8	0.782	42.2	2.83	12.07	0.099	86 868
	0.268	24.2	0.795	30.8	2.07	5.00	0.138	76 831
	0.665	56.2	0.791	29.3	8.85	8.85	0.085	30 362
130	0.463	50.3	1	50.8	3.41	21.46	0.101	
	0.275	30.8	1	35.6	2.39	8.27	0.136	
	0.662	69.7	1	38.9	2.61	17.25	0.090	
	0.665	56.2	0.791	30.8	2.07	9.88	0.087	35 376
90[a]	1			9.15	14.9	1.00	6.44	–	4 167

[a] For a blend containing PSD ($M_w = 4000$, $M_w/M_n = 1.18$) and PS ($M_w = 4500$, $M_w/M_n = 1.15$)
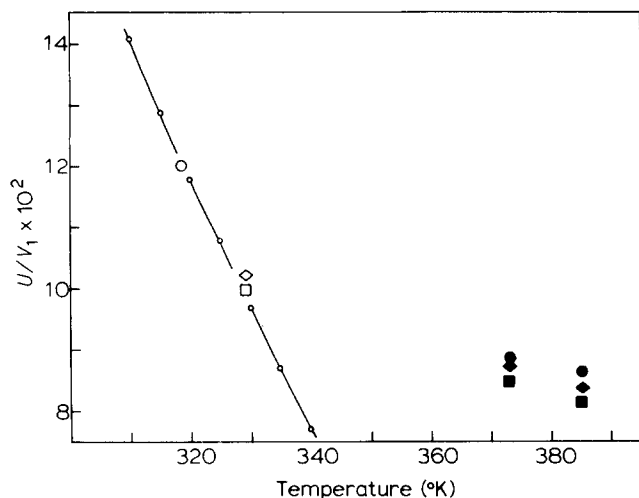
Figure 5 A comparison of the predicted behaviour of g_{12} for $\phi_1 = 0.64$ (— ○) and measured U/V_1 values for the following volume fractions: (●): 0.625; (◆): 0.432 and (■): 0.328. The U/V_1 values indicated by the open symbols which lie on the solid line are those predicted to occur at the spinodal

significant sources of error in the data arise from weighing samples and insufficient temperature equilibration times.

The high viscosity of the polybutadiene can give rise to an error through losses incurred on filling the sample tubes. However, with the high PB concentrations used in the present study this error is considered to be well below 5%.

The quality of the data can be seriously affected by not allowing sufficient time for the samples to achieve thermal equilibrium. The most obvious effect is upon the scattered intensity, which in many of the samples is directly dependent on the amplitude of the concentration fluctuations. This problem is at its worst when experiments are carried out on high flux reactors where measuring times are short. Recent experiments[23] have shown the sensitivity of transmission measurements to temperature, reflecting changes in the effective atomic cross-sections. Errors of 10%, or in some cases less, in a transmission measurement can lead to problems with background subtraction particularly in samples that scatter weakly. In this study samples were allowed to equilibrate at a particular temperature for a minimum of 20 min. Although experiments with a thermocouple and an oil-filled quartz cell showed that a stable temperature was reached in 2–3 min, extra time was allowed for the concentration fluctuations to reach equilibrium. A much longer time should be used in highly viscous systems such as high molecular weight blends. One check that can be made which will serve to indicate whether or not the sample has equilibrated is to measure the sample transmissions before and after a series of experiments. In the present study sample transmission measurements made before and after scattering measurements (which took some 2 h to complete) were well within experimental error.

A further source of error may arise from subtracting manufactured incoherent background levels by the so-called 'sandwich' method (described in 'removal of incoherent backgrounds' section). The manufactured incoherent background for a sample of PBD6–PB–PS containing 6.39% deuterated material accounts for 70% of the sample's scattered intensity at high Q ($Q = 0.1067$ Å^{-1}). This particular blend contains the least

amount of deuterium; hence it is prone to the largest error in background subtraction. However, this blend has been prepared to give single chain scattering only and the molecular weights obtained from the data agree very well with those obtained from a binary mixture of PBD6–PB. In both cases the background subtraction is important in obtaining the correct M_w values from the absolute scattered intensity. The latter sample, being a binary mixture, can be treated in the conventional way. The agreement in the M_w values thus gives confidence in the 'sandwich' method used for the blends. Where we are measuring the scattering from concentration fluctuations the incoherent background falls to a mere 14% at $Q = 0.1067$ Å^{-1} of the scattered intensity for a blend of PBD6–PS containing 58.7% PBD6. Therefore any errors which may occur in the estimation of the flat background will have a minimal effect on the value of U calculated.

DISCUSSION

The conventional way in which molecular weights are calculated requires the scattering per unit volume to be converted to that per monomer (equation (7)). The density value used in this equation is normally taken to be that for the hydrogenous analogue of the labelled species at the measurement temperature. Although this works well for systems such as PBD6 in PB it is not so suitable for systems such as PBD6 in a blend of PB–PS where the blend density will be higher than that of the pure PB. This is clearly shown in *Table 3*, where the molecular weights of the deuterated PB chains appear to be higher when measured in a blend than those measured in a binary system. To obtain molecular weights in the blends that are comparable with those of the pure compound measured at 130° (3300) one would need to use a density of 0.927 in equation (7), which can be compared with a value predicted using relative proportions for the blend density of 0.976.

We have not attempted to apply a correction of this type to the molecular weight data since the blend densities have not been experimentally determined. This point would actually raise the well-known deficiencies of the
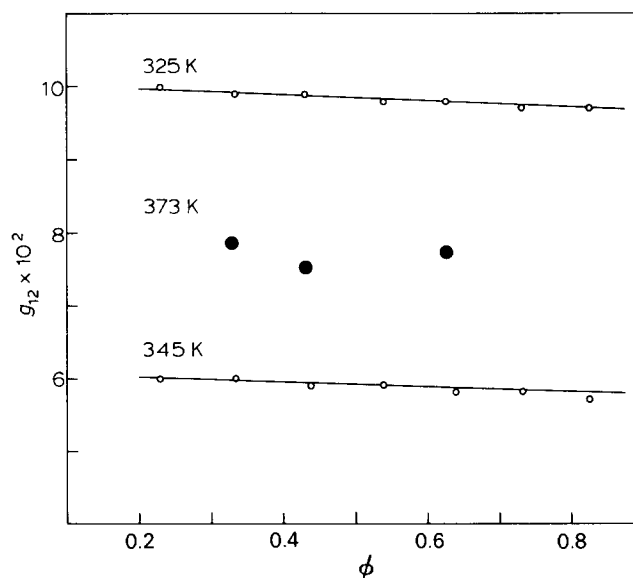
Figure 6 A comparison between the predicted dependence (–○–) of g_{12} upon the volume fraction (ϕ) of PBD6 in a binary mixture of PBD6–PS and measured values (●) at the temperatures stated

Flory–Huggins lattice model in dealing with changes in segment specific volumes in a blend.

The poor agreement between measured U values for a series A system and those predicted by equation (11) suggest that the interaction parameter is much less temperature dependent than previously assumed. The implication of the data is then that Flory's interaction energy per polymer 1 segment (which when divided by RT is more familiarly known as χ_{12})[25] actually increases with temperature for this system. Further experiments are planned in this area in order to obtain a more complete picture. The slight concentration dependence of the interaction parameter as shown in *Figure 6* agrees well with that predicted by equation (11).

ACKNOWLEDGEMENT

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