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Temperature and Concentration Dependence of the Interaction Parameter in Oligomeric Polymer Blends from Small-Angle Neutron Scattering and Calorimetric Measurements

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ABSTRACT: Small-angle neutron scattering has been used to determine the concentration and temperature dependence of the interaction parameter χ in a blend of two polymers. The interaction parameter can be obtained either by analyzing the angular dependence of the scattering in terms of an apparent radius of gyration or by extrapolation of the data to zero scattering angle. We present here a comparison of these two methods for two blends of oligomeric polystyrene with polybutadiene. One blend containing labeled (deuteriated) polystyrene with hydrogenous polybutadiene and the other deuteriated polybutadiene with hydrogenous polystyrene. The temperature dependence of the interaction parameter has also been determined for a blend of oligomeric methoxylated poly(ethylene glycol) with methoxylated poly(propylene glycol) where the latter component contains a percentage of labeled chains. The availability of heat of mixing data for these systems has also enabled us to assess in part the enthalpic and entropic contributions to the interaction parameter.

1. Introduction

In several recent papers[1-6] it has been shown that small-angle neutron scattering measurements from a single-phase two-component polymer blend containing concentration fluctuations may be used to determine the Flory–Huggins interaction parameter. The concentration fluctuations in such a system were originally shown by Einstein[7] to depend on the concentration gradient of the chemical potential which Debye and Bueche[8] subsequently related to interactions in the system using the Flory-Huggins equation.[9]

In the first neutron scattering papers on this subject[2,4] only the intensity of the scattering extrapolated to zero angle was analyzed in order to obtain the interaction parameter. However, in a recent publication, Benoit et al.[6] have argued that a more precise value of the interaction parameter can be obtained by analyzing the angular dependence of the scattering in terms of an apparent radius of gyration. Shibayama[5] et al have also analyzed their scattering data as a function of angle using a complex nonlinear regression in order to obtain both the interaction parameter and a correlation length for the fluctuations.

In this paper we have analyzed the concentration fluctuations in low molecular weight blends of polystyrene with polybutadiene and of methoxylated poly(propylene glycol) with methoxylated poly(ethylene glycol) using small angle neutron scattering. These blends show upper critical solution temperatures,[10-12] and by labeling one or other component by deuteriation the intense scattering resulting from concentration fluctuations may be observed in the single-phase region at elevated temperatures. We have extracted the interaction parameters as a function of temperature and concentration by systematically analyzing both the intensity extrapolated to zero angle and the apparent radius of gyration following the Benoit method. This allows us to compare the two approaches and to explore the sensitivity of the analyses to the molecular parameters required for their application. The values of the interaction parameters are then compared with the functional dependences predicted by current thermodynamic theories. In some cases values of the enthalpy of mixing are available for similar systems and correlation of these data with the neutron results allows the entropic and enthalpic contributions to the interaction parameter to be assessed in more detail.

2. Small-Angle Scattering from Binary Blends

The scattering from a binary blend composed of polymers 1 and 2 has been shown to be given by[1]

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

where polymer 1 contains a fraction c of chains labeled by

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deuteriation. The first term in this equation represents the scattering due to concentration fluctuations and the second is due to the scattering from single labeled chains. d and h are the net neutron scattering lengths for the deuteriated and hydrogenous monomers of polymer 1; b is the scattering length for a hydrogenous monomer of polymer 2. The lattice model of Flory–Huggins requires a repeat unit cell to be defined, which we have chosen to be a segment of polymer 1; the ratio β ($\beta = V_1/V_2$ where V_1 and V_2 are the respective specific volumes) allows polymer 2 to occupy the same unit cell as polymer 1, its scattering length b being modified accordingly ($b' = \beta b$). U is the mean-field expression for the interaction between two segments. The single-chain scattering factor $P_n(Q)$ is defined by

$$P_n(Q) = \phi_n' N_n f_D(Q\mathrm{Rg}_n) \qquad (2)$$

where Q is a wavevector which is related to the neutron wavelength λ and the scattering angle θ by

$$Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \qquad (3)$$

$f_D(x)$ is the Debye scattering function for ideal polymers, which for values of $x \ll 1$ reduces to

$$f_D(Q\mathrm{Rg}_n) \rightarrow 1 - \frac{(Q\mathrm{Rg}_n)^2}{3} \qquad Q\mathrm{Rg} < 1 \qquad (4)$$

N_n is the degree of polymerization, ϕ_n' the segment concentration of component n, and Rg_n its radius of gyration. The volume fraction

$$\phi_n = \phi_n' \left(\frac{M_n}{\rho_n N_A} \right) \qquad (5)$$

where M_n is the monomer mass and ρ_n the density of component n. N_A is Avogadro's number.

If we extrapolate eq 1 to zero Q and write it in terms of volume fractions we obtain:

$$V_1 S(0) = \frac{(cd + (1-c)h - b')^2}{(N_1\phi_1)^{-1} + \beta(N_2\phi_2)^{-1} - 2\beta U/V_1} + c(1-c)(d-h)^2 N_1 \phi_1 \qquad (6)$$

The denominator in the first term is now directly identifiable with the second differential of the free energy of mixing (see section 3). The interaction parameter $\beta U/V_1$ ($\equiv U/V_2$) can be determined as a function of temperature and concentration provided that N_1 and N_2 are known.

In the design of experiments the relative values of the contrast factors $(cd + (1-c)h - b')^2$ and $c(1-c)(d-h)^2$ can be adjusted by using different proportions of labeled polymer 1 chains in the mixtures. Thus the contribution to the scattered intensity from either term can be controlled. The single-chain term is eliminated by manufacturing blends where $c = 0$ and all the polymer 1 chains are hydrogenous or when $c = 1$ and all the polymer 1 chains are deuteriated. It is worth noting that for the condition $c = 0$ to be useful there must be sufficient contrast between the hydrogenous polymers.

The concentration fluctuation term is eliminated by adjusting the value of c such that the numerator in the first term of eq 1 goes to zero. (In a single-component system where a proportion of the chains are labeled, this term disappears because $P_2(Q)$ is zero and the denominator in (1) becomes infinite.)

Recent literature contains several examples of deuteriation shifting phase boundaries.[10,11,13] As a consequence comparisons between different blend compositions (ϕ_1, ϕ_2) containing differing amounts of deuterium (c) should be made with caution—in the present work we have mainly concentrated on systems with $c = 1$. In situations where one is confident that deuteriation has little or no effect on the phase boundary as for the PEGM/PPGM blend[2] the terms in eq 1 can be separated by weighted subtraction of data with different values of c for fixed ϕ_1.

Benoit et al. also considered eq 1 with either $c = 1$ or 0 but now without the condition $Q \rightarrow 0$ and for a special case where $\beta = 1$. Defining

$$N_1 + N_2 = 2\bar{N} \qquad N_1 - N_2 = 2W\bar{N} \qquad (7)$$

and

$$\mathrm{Rg}_1^2 = R^2(1 + Y) \qquad \mathrm{Rg}_2^2 = R^2(1 - Y) \qquad (8)$$

we can write the single-chain scattering factors $P_1(Q)$ and $P_2(Q)$ as

$$P_1(Q) = \bar{N}(1 - W)\phi_1 \left[1 - \frac{Q^2R^2}{3}(1 + Y) \right] \qquad (9)$$

$$P_2(Q) = \bar{N}(1 - W)\phi_2 \left[1 - \frac{Q^2R^2}{3}(1 - Y) \right] \qquad (10)$$

Then the scattering pattern is analyzed in terms of an apparent radius of gyration $\mathrm{Rg}_{\mathrm{ap}}^2$, i.e.,

$$S(Q) = S(0)\left(1 - \frac{Q^2\mathrm{Rg}_{\mathrm{ap}}^2}{3} \right) \qquad (11a)$$

or for a conventional Zimm plot

$$S^{-1}(Q) = S^{-1}(0)\left(1 + \frac{Q^2R_{\mathrm{ap}}^2}{3} \right) \qquad (11b)$$

in this case $S(0)$ becomes identical with eq 6.

Benoit et al.[6] derived an expression for $\mathrm{Rg}_{\mathrm{ap}}^2$ in terms of W, Y, and U for the special case mentioned above where $\beta = 1$, which when $\beta \neq 1$ becomes

$$\mathrm{Rg}_{\mathrm{ap}}^2 = R^2\{(1 - W)(1 + Y) + \phi_1[\beta(1 - Y) \times (1 + W) - (1 + Y)(1 - W)]\}[(1 - \phi_1)(1 - \beta) + W(\phi_1 + \beta\phi_1 - 1) - \frac{2U\bar{N}}{V_2}\phi_1(1 - \phi_1)(1 - W^2)]^{-1} \qquad (12)$$

Benoit et al.'s method of determining the interaction parameter is to calculate the dependence of $\mathrm{Rg}_{\mathrm{ap}}^2$ on ϕ_1 for different values of U/V_2 and then choose the best fit of the data to the calculated curves. If U/V_2 is concentration dependent, however, as we shall see, the value of U/V_2 must be determined separately for each value of ϕ_1.

The problem with this approach is its requirement for values of both the degrees of polymerization for the two components N_1 and N_2 and the corresponding radii of gyration Rg_1 and Rg_2. N_1 and N_2 can be obtained from the molecular weight values as measured by gel permeation chromatography (GPC). As explained earlier, in some cases the concentration fluctuation term can be made to vanish by adjusting c. In these cases we have directly determined the value of Rg for the labeled components *in the blend* using small-angle neutron scattering.[2,3] Where this is not possible the radius of gyration of the deuteriated chains dispersed in a hydrogenous matrix of the *same* polymer have been determined and can be used as a first approximation for the blend values. The radius of gyration of polymer 2, the unlabeled species, is difficult to determine although values for deuteriated polymer 2 chains of a similar molecular weight dispersed in a hydrogenous matrix of polymer 2 may possibly be found in the litera-

Table I
Sample Characteristics

polymer	M_w	M_w/M_n	% cis	% trans	% vinyl
		Series A			
PB	2660	1.30	41 ± 2	49 ± 2	10 ± 2
PBD6	2360	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			
		Series C			
PEGM	600	narrow			
PPGM	2200	1.07			
PPGMD	2200	1.11			

ture. For very low molecular weight polymers, where molecules may no longer be Gaussian, extrapolation from the Rg values measured for higher molecular weights must be undertaken with caution.[14]

3. Thermodynamics

The simplest expression for the free energy of mixing ΔG_m per lattice segment of a binary polymer blend is given by the Flory–Huggins lattice model[9] where

$$\Delta G_m/RT = N_1^{-1}\phi_1 \ln \phi_1 + N_2^{-1}\phi_2 \ln \phi_2 + \phi_1\phi_2\chi_{12} \quad (13)$$

This leads to the following expression for the second differential responsible for scattering

$$\frac{\partial^2}{\partial \phi_2^2}\left(\frac{\Delta G_m}{RT}\right) = (N_1\phi_1)^{-1} + \beta(N_2\phi_2)^{-1} - 2\chi_{12} \quad (14)$$

This expression should be compared with the denominator of the first term in eq 6. (The lattice as mentioned previously is defined by monomers of polymer 1 and the parameter β compensates for the fact that monomers of polymer 2 in general have a different volume.) The interaction parameter χ_{12} introduced by Flory was independent of concentration and varied with temperature as T^{-1}. However, such a simple description of the interaction is unable to account for the behavior of many polymer blends close to the spinodal. The model improves if the interaction parameter is also allowed to be concentration dependent.

Koningsveld[15] has defined such an interaction parameter as $g_{12}(\phi,T)$ which is both concentration and temperature dependent. When $g_{12}(\phi,T)$ is substituted in eq 14 then the χ_{12} term is replaced by $\partial^2 g_{12}\phi_1\phi_2/\partial\phi_2^2$.

Since the denominator of the first term in eq 6 is directly identifiable with the second differential of the free energy of mixing, then

$$\chi_{12} = \frac{\beta U}{V_1} = \frac{U}{V_2} = -\frac{1}{2}\frac{\partial^2 g_{12}\phi_1\phi_2}{\partial \phi_2^2} \quad (15)$$

In the current work of Koningsveld et al.[15,16] the expression for g_{12} is given as

$$g_{12} = \alpha + \frac{\beta_s + \beta_H/T}{1 - \gamma\phi_2} \quad (16)$$

Discussion of the molecular basis for introducing the parameters used in this expression is given in ref 15. Here we give only a brief summary.

β_H is related to the internal energy per contact of occupied sites in the lattice and $\gamma = 1 - \sigma_2/\sigma_1$ where σ_2/σ_1 is the ratio of surface areas of polymer segments from species 1 and 2. α and β_s are empirical parameters included by Koningsveld and his colleagues in order to fit the observed phase behavior of partially miscible systems. They can be related to a disparity in contact numbers in the contact statistics due to differences in molecular size and shape. Experimentally, for a polymer/solvent system it was found[15] that they may be both molecular weight and temperature dependent. From the neutron experiments we therefore measure $\partial^2 g_{12}\phi_1\phi_2/\partial\phi_2^2$. If we express this as

$$\frac{U}{V_2} = -\frac{1}{2}\frac{\partial^2 g_{12}\phi_1\phi_2}{\partial \phi_2^2} = a + \frac{b}{T} \quad (17)$$

Then from eq 16

$$a = \alpha + \frac{\beta_s(1-\gamma)}{(1-\gamma\phi_2)^3} \quad (18)$$

is the entropic part and

$$b = \frac{\beta_H(1-\gamma)}{(1-\gamma\phi_2)^3} \quad (19)$$

is the enthalpic contribution to the second derivative of the excess free energy of mixing with respect to concentration. Use of eq 16 leads to the following expression for the enthalpy of mixing:

$$\frac{\Delta H}{R} = \phi_1\phi_2\frac{\beta_H}{1-\gamma\phi_2} \quad (20)$$

Thus both the heats of mixing data and the temperature dependence of the small-angle neutron scattering should lead to values of γ and β_H, while the neutron data alone carry information on α and β_s.

4. Experimental Section

Sample Preparation. The interaction parameters reported here are for two different oligomeric systems, namely, polystyrene/polybutadiene (PS/PB) and methoxylated poly(ethylene glycol)/methoxylated poly(propylene glycol) (PEGM/PPGM). Blends containing fully deuteriated polybutadiene (PBD6) are referred to as series A and those containing fully deuteriated polystyrene (PSD) as series B. Series C samples refer to the PEGM/PPGM blends with deuteriated PPGM as the labeled species. The molecular characteristics of the components of each series are given in Table I, their phase boundaries having been published elsewhere.[10,11,12,17]

The hydrogenous PS samples were obtained from Polymer Laboratories Ltd. (U.K.). PSD was synthesized in our laboratory by 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 Tire and Rubber Co. (Akron, OH). PBD6 was synthesized according to the method of Morton and Fetters,[18] using the same initiator and polymerization solvent as for PSD. The active center concentration was such as[11] to yield a microstructure close to that of PB CDS-B-3.

The poly(propylene glycol) (PPG) was synthesized from propylene oxide by heating it with a catalytic amount of sodium dissolved in ethane-1,2-diol at about 95 °C under pressure for 48 h. The deuteriated polymer PPGd was prepared as previously described[19] by a four-stage synthesis starting from propan-2-one-d_8. Methoxylation of the poly(propylene glycols) and the poly(ethylene glycol) (obtained from Shell Chemicals Ltd.) was carried out as previously described[20-22] by reacting the hydroxyl end groups with methyl iodide in an alkaline medium.

Small-Angle Neutron Scattering Experiments. Small-angle neutron scattering (SANS) experiments were performed on the D17 spectrometer at the Institut Laue-Langevin (Grenoble, France), using a sample detector distance of 1.4 m and neutrons of wavelength 15 Å. The components of the blends used in these experiments were weighed into flat-sided quartz cells of dimensions 15 × 20 mm and path length 2 mm. The incorporation of a small metallic strip prior to the samples being degassed and sealed under vacuum facilitated magnetic stirring. Antioxidants were not used. Data were normalized for geometric and flux factors using the isotropic incoherent scattering from water. The

Table II

Relative Values of the Intercept $I(0)$ and Apparent Radii of Gyration Rg_{app} for Blends of PPGMd-PPGM/PEGM as a Function of Temperature and Composition[a]

temp, ±0.25 °C	ϕ_1	W_D, g/g	C	Rg_{app}, Å	$I(0)$	$U/V \times 10^2$
39.5	0.319	13.30	0.417	46.1	3.03	8.07
51.0	0.319	13.30	0.417	29.3	1.71	7.47
58.0	0.319	13.30	0.417	25.2	1.41	7.12
63.0	0.319	13.30	0.417	23.2	1.27	6.91
73.0	0.319	13.30	0.417	21.2	1.10	6.53
39.5	0.336	12.63	0.373	35.6	1.94	7.82
51.0	0.336	12.63	0.373	24.9	1.30	7.25
58.0	0.336	12.63	0.373	21.4	1.10	6.77
63.0	0.336	12.63	0.373	21.4	1.02	6.38
73.0	0.336	12.63	0.373	19.3	0.90	5.78
58.0	0.719	7.89	0.103	10.5	0.47	14.6
73.0	0.719	7.89	0.103	10.5	0.45	14.5
58.0	0.717	9.68	0.127	10.2	0.56	15.5
73.0	0.717	9.68	0.127	10.5	0.54	14.9
70.0[b]	1.0	7.14	0.065	10.4		

[a] Values of U/V_1 have been determined by analyzing $I(0)$ in terms of eq 6. [b] The molecular weight of deuteriated PPGM in a hydrogenous PPGM matrix was found to be 1958 amu.

Table III

Relative Values of the Intercept $I(0)$ and Apparent Radii of Gyration Rg_{app} Obtained for a Blend of PSD/PB[a]

temp, ±0.25 °C	ϕ_1	W_D, g/g	$I(0)$	$U/V_1 \times 10^2$ [b]	Rg_{app}, Å	$U/V_1 \times 10^2$ [c]
110.0	0.275	30.8	14.00	6.53	48.4	6.58
	0.463	50.3	49.75	7.11	77.8	7.10
	0.662	69.7	29.94	9.54	52.2	9.49
118.0	0.275	30.8	10.67	6.38	40.8	6.38
	0.463	50.3	31.45	7.00	60.5	6.99
	0.662	69.7	22.83	9.40	45.2	9.34
125.0	0.275	30.8	9.09	6.17	37.5	6.26
	0.463	50.3	24.45	6.91	53.6	6.91
	0.662	69.7	18.25	9.19	39.7	9.17
130.0	0.275	30.8	8.00	6.17	34.5	6.11
	0.463	50.3	20.04	6.86	47.9	6.82
	0.662	69.7	16.61	9.22	37.5	9.07
140.0	0.275	30.8	7.19	6.00	33.1	6.02
	0.463	50.3	16.86	6.76	44.6	6.76
	0.662	69.7	14.49	9.09	34.7	8.93
150.0	0.275	30.8	5.99	5.76	29.8	5.78
	0.463	50.3	12.71	6.54	37.6	6.55
	0.662	69.7	11.11	8.68	29.6	8.55

[a] $c = 1$ for all compositions. [b] Values of U/V_1 obtained by analyzing $I(0)$ in terms of eq 6. [c] Values of U/V_1 obtained by analyzing Rg_{app} in terms of eq 12 with $Rg_1 = 15.45$ Å (the average of two experimentally obtained values of 14.9 and 16.0 Å) and $Rg_2 = 10.3$ Å (calculated).

incoherent backgrounds for each sample were removed as described previously[2,3] in some detail. As has been pointed out[23] the incoherent cross section is strongly temperature dependent so backgrounds were determined over the whole temperature range of these experiments.

Heats of Mixing Measurements. All the heats of mixing data, ΔH, were reported in ref 24, where the experimental details are also given. The data for the PEGM/PPGM system were also published in ref 25. Briefly, the two components of the desired final blend were separately preheated prior to mixing inside a microcalorimeter where the enthalpy of mixing was directly determined via thermoelectric modules.

5. Results

SANS. Figure 1a shows a typical set of scattering curves with the intensity increasing as the temperature of the blend falls toward its phase boundary T_c. In Figure 1b the same curves are plotted as $S^{-1}(Q)$ against Q^2 (see eq 11b). There is a pronounced curvature, so to proceed with analysis in terms of eq 11b a quadratic was fitted to obtain the limiting slope and intercept.

Tables II, III, and V summarizing the analysis of such sets of data for all three systems in terms of eq 6 and 12. The values of N_1 and N_2 required for the analysis in terms of eq 6 were determined from GPC measurements. The value of Rg_1 and Rg_2 required for eq 12 were determined from SANS measurements wherever possible, the remaining values being obtained from the literature as described in section 2. In each case the radius of gyration used for the unlabeled component carries the highest uncertainty since we are unable to measure it experimentally.

Table IV

Values of the Single-Chain Parameters for a Mixture of Deuteriated Polystyrene Chains in a Hydrogenous Polystyrene Matrix

temp, °C	wt % PS	wt % PSD	ϕ_1	C	R_g, Å	M_w
90.0[a]	100.0	9.15	1	0.085	14.9	4167
150.0	100.0	9.15	1	0.085	16.0	4040

[a] Previously published values.[3]

Binary mixtures of deuteriated PPGM with PEGM were not available therefore the data for the system shown in Table II have only been analyzed in terms of eq 6.

Data in Table III are for a series B blend of deuteriated polystyrene with polybutadiene where the scattering arises from concentration fluctuations. Mixtures of PSD:PS:PB for which the single-chain term contribution to the scattering is dominant cannot be made due to the relative numerical values of d, h, and b' which preclude the numerator in eq 6 going to zero. Measurements of the radius of gyration and molecular weight of the deuteriated polystyrene chains have therefore only been made with the labeled chains dispersed in a hydrogenous polystyrene matrix. These results are summarized in Table IV.

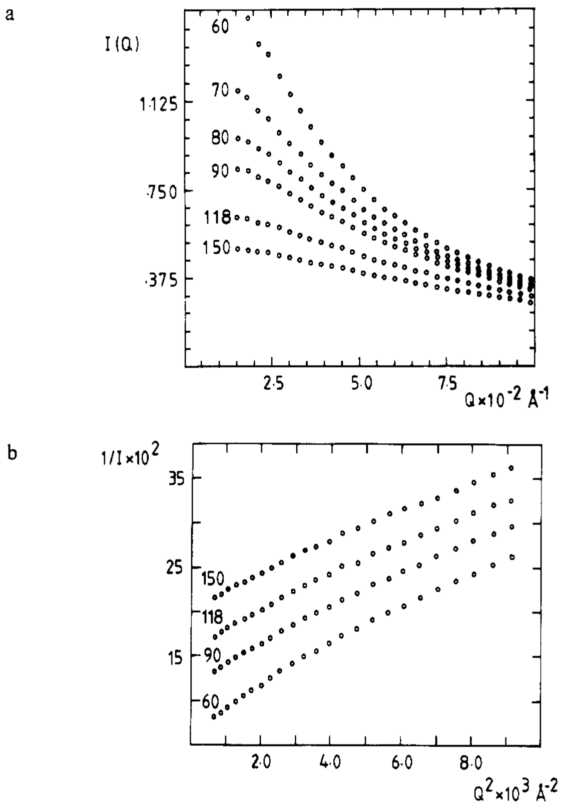

Figure 1. (a) Typical set of scattering curves for a series A blend of PBD6/PS showing the increase in relative intensity as the temperature of the blend (as indicated on the figure (°C)) falls toward its phase boundary. (b) Some of the scattering curves shown in (a) plotted as $1/I$ against Q^2 (see eq 11b) where $I(Q)$ is again relative.

Data in Table V are for a series A blend of deuteriated polybutadiene with polystyrene where the scattering arises from concentration fluctuations. By adding a suitable amount of hydrogenous polybutadiene to such a mixture the single-chain contribution to the scattering can become dominant. Table VI lists the values for the radius of gyration and molecular weight for dispersed single chains of deuteriated polybutadiene in such a blend together with those values for labeled chains in a hydrogenous polybutadiene matrix. The effect of a relatively small uncertainty in the values of Rg_2 used can be seen in the last column of Table V where the value for PS has been changed from its calculated value of 10.5 Å to 8 Å.[14] At these low M_w values the chains are certainly non-Gaussian[14] and the dimensions are experimentally difficult to measure. At higher molecular weight these effects would not be important. Nevertheless, it would be advisable to extract the single-chain term for each component by weighted subtraction of samples with two different values of c in eq 1 in order to have precise values of Rg_1 and Rg_2 (as in ref 2) in the blend itself. This approach, however, relies on deuteriation not affecting the thermodynamics of the blends—an assumption known not to be valid in many cases of interest including the PS/PB systems described here.[10,11]

Benoit et al.[6] suggest that values of Rg_{ap} should be fitted to eq 12 in order to obtain the best value of U/V_2. Figures 2 and 3 show the experimental values of R_{ap} for systems A and B as a function of ϕ_1 compared to eq 12, calculated for various values of U/V_2. Clearly no one curve can fit all the data for a given blend system, confirming that the interaction parameter must be concentration dependent.

Figures 4–6 show the temperature dependence of the interaction terms determined from $I(0)$ for the three sys-

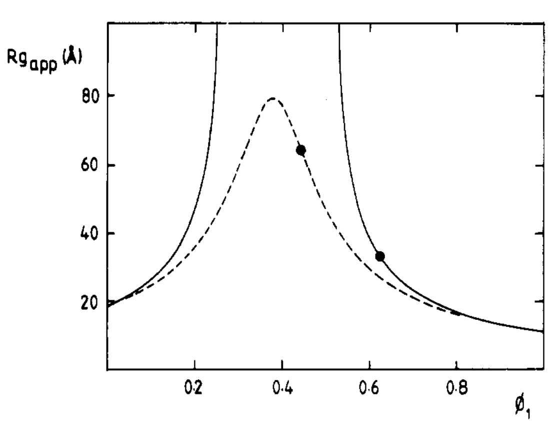

Figure 2. R_{app} as a function of ϕ_1 for a series A blend of PBD6/PS at 70 °C calculated by using eq 13 for volume fractions of 0.432 (---) and 0.625 (—); (●) measured values.

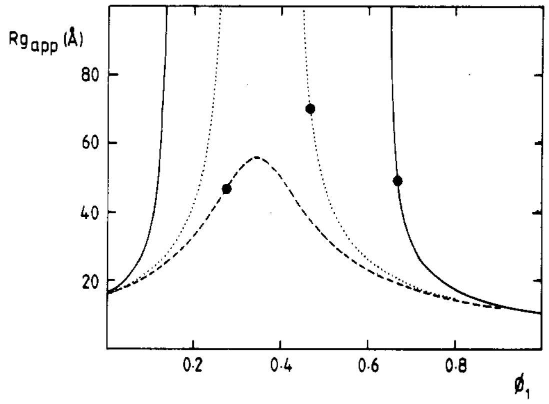

Figure 3. R_{app} as a function of ϕ_1 for a series B blend of PSD/PB at 110 °C calculated by using eq 13 for volume fractions of 0.275 (---), 0.463 (···), and 0.662 (—); (●) measured values.

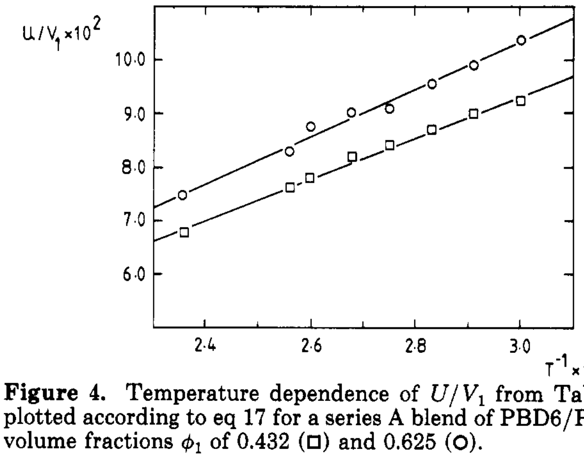

Figure 4. Temperature dependence of U/V_1 from Table V plotted according to eq 17 for a series A blend of PBD6/PS for volume fractions ϕ_1 of 0.432 (□) and 0.625 (○).

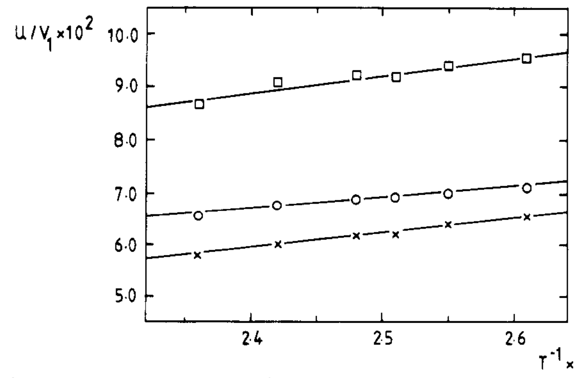

Figure 5. Temperature dependence of U/V_1 from Table V plotted according to eq 17 for a series B blend of PSD/PB for volume fractions ϕ_1 of 0.275 (×), 0.463 (○), and 0.662 (□).

Table V
Values of the Intercept $I(0)$ and Apparent Radii of Gyration Rg_{app} Obtained for a Blend of PBD6/PS[a]

temp, ±0.25 °C	ϕ_1	W_D, g/g	$I(0)$	$U/V_1 \times 10^2$ [b]	Rg_{app}, Å	$U/V \times 10^2$ [c]	$U/V_1 \times 10^2$ [c]
60.0	0.432	39.3	97.09	9.29	114.9	9.28	9.30
	0.625	58.7	16.21	10.40	37.8	10.41	10.71
70.0	0.432	39.3	38.91	9.02	71.9	9.07	9.13
	0.625	58.7	12.21	9.92	31.9	9.90	10.33
80.0	0.432	39.3	23.75	8.73	55.5	8.84	8.93
	0.625	58.7	10.18	9.57	28.7	9.48	10.01
90.0	0.432	39.3	16.92	8.44	46.2	8.58	8.71
	0.625	58.7	8.62	9.13	25.6	8.91	9.58
100.0	0.432	39.3	13.66	8.22	40.5	8.32	8.50
	0.625	58.7	7.94	9.04	24.2	8.59	9.34
112.0	0.432	39.3	9.90	7.81	31.6	7.62	7.91
	0.625	58.7	6.94	8.79	22.6	8.13	8.99
118.0	0.432	39.3	9.43	7.63	33.7	7.84	8.09
	0.625	58.7	6.41	8.30	21.7	7.83	8.77
151.0	0.432	39.3	6.29	6.79	27.1	6.98	7.37
	0.625	58.7	5.00	7.45	18.3	6.27	7.59

[a] $c = 1$ for all compositions. [b] Values for U/V_1 obtained by analyzing $I(0)$ in terms of eq 6. [c] Values of U/V_1 obtained by analyzing Rg_{app} in terms of eq 12 with $Rg_1 = 18.98$ Å (the average of the experimentally obtained values in Table VI) and $Rg_2 = 10.5$ Å.

Table VI
Measurement of Single-Chain Parameters in a Series A Blend of PBD6/PS and in a Mixture of PBD6/PB

temp, ±25 °C	wt % PB	wt % PBD_6	ϕ_1	C	R_g, Å	M_w
80	58.25	12.50	0.621	0.197	19.0	3421
90	58.25	12.50	0.621	0.197	19.1	3346
100[a]	58.25	12.50	0.621	0.197	18.9	3620
112[a]	58.25	12.50	0.621	0.197	18.8	3643
118	58.25	12.50	0.621	0.197	19.1	3239
130[a]	100.00	10.32	1.0	0.094	22.1	3331
90	100.00	10.32	1.0	0.094	20.4	3113

[a] Previously published values.[3]

Table VII
Entropic and Enthalpic Contributions *a* and *b* to the Interaction Parameter for Systems A, B, and C Obtained by Analyzing Figures 4, 5, and 6 in Terms of Equation 17[a]

blend pol$_1$/pol$_2$	ϕ_2	a ± 50%	b ± 20%, K	β_H ± 20%, K	Bondi γ
PBD6/PS	0.375	−0.030	44	51	−0.542
	0.568	−0.024	39	57	
PSD/PB	0.338	0.014	31	33	0.35
	0.537	0.014	22	18	
	0.725	−0.013	30	19	
PPGM/ PEGM	0.6	−0.13	68	50	0.29
	0.30	0.11–0.01	10–46	11–50	

[a] If $\gamma = 0$ in eq 18, then $b \equiv \beta_H$. Values of β_H are also listed for the γ values from Bondi.[26]

tems studied. In each case there is a good linear variation with T^{-1} over the temperature range investigated. Analysis of these data in terms of eq 17 leads to values of a and b (eq 18 and 19) that are listed in Table VII. It is worth noting that for $\gamma = 0$ then from eq 19 $b \equiv \beta_H$. We also include the values of β_H calculated by using values of γ obtained from Bondi[26] ($\sigma_{PS} = 7.25$, $\sigma_{PB} = 4.7$, $\sigma_{PPGM} = 4.64$, $\sigma_{PEGM} = 3.3 \times 10^9$ cm^2/mol).

The error in the values of Rg_{ap} and the absolute values of $I(0)$ have two components, one arising from fitting a quadratic to the data when plotted as $S(Q)^{-1}$ against Q^2 and the other attributable to the normalization procedure. The error in fitting a quadratic to the data lies between 1 and 2%. The error in normalization is of order 5% for the apparent radii of gyration since this is only affected by subtraction of the appropriate incoherent background.[3] For $I(0)$ values the error lies close to 10% since these values depend not only on background subtractions but also on other parameters such as density and degree of polymerization. A more detailed discussion of error analysis can be found in ref 2 and 3.

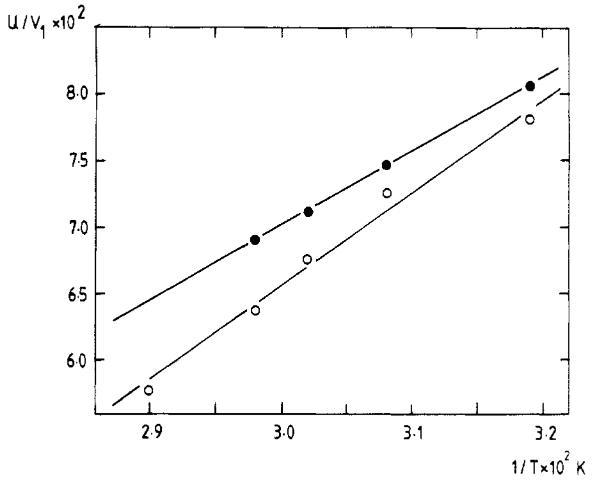

Figure 6. Temperature dependence of U/V_1 from Table II plotted according to eq 17 for a series C blend of PPGMd/PPGM/PEGM for volume fractions ϕ_2 of 0.33 (○) and 0.32 (●).

Heats of Mixing Data. Figure 8 shows data plotted as $\phi_1\phi_2/\Delta H$ against ϕ_2 (a linear form of eq 20) for blends of hydrogenous polystyrene molecular weight 1010 with two hydrogenous polybutadienes of molecular weights 2360 and 960 (here the PS has been defined as component two). The molecular weights although close to those used in the neutron experiments unfortunately do not match them exactly. There is a small difference between the sets of data which may be due to the increased importance of end groups in the lower molecular weight mixture. The straight lines are the result of a least-squares fit to the data which lead to values of γ (and hence σ_2/σ_1) and β_H from eq 20.

These values and those obtained from the same data by treating polybutadiene as component 2 are all listed in Table VIII. (The units of β_H have been converted to per segment mole for comparison with values in Table VII.)

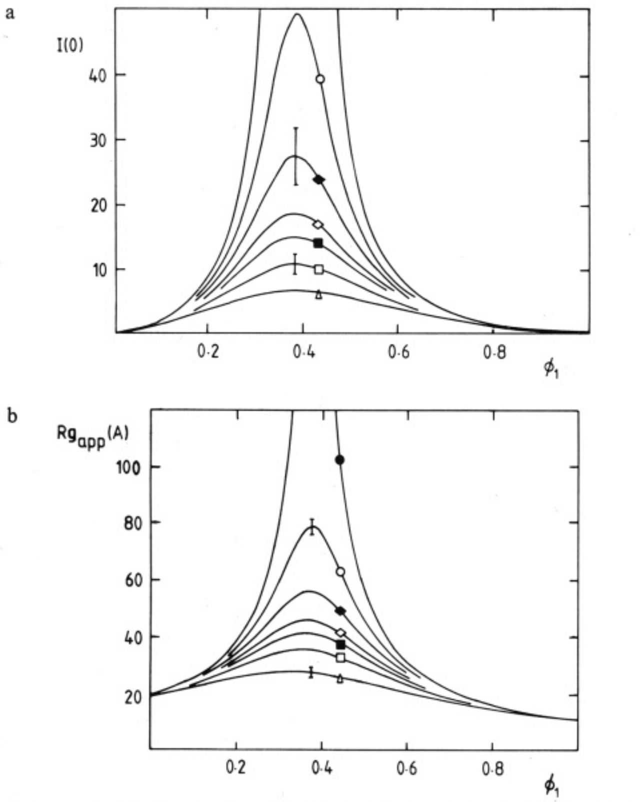

Figure 7. (a) Sensitivity of $I(0)$ to U/V_1 for a blend of PBD6/PS ($\phi_1 = 0.432$) compared with the experimental uncertainty in determining this parameter at the following temperatures (°C): (●) 60; (○) 70; (◆) 80; (◇) 90; (■) 100; (□) 112; (△) 151. (b) Sensitivity of R_{app} to U/V_1 for the same blend as in (a) compared with the experimental uncertainty in determining this parameter. The notation is identical with that used in (a).

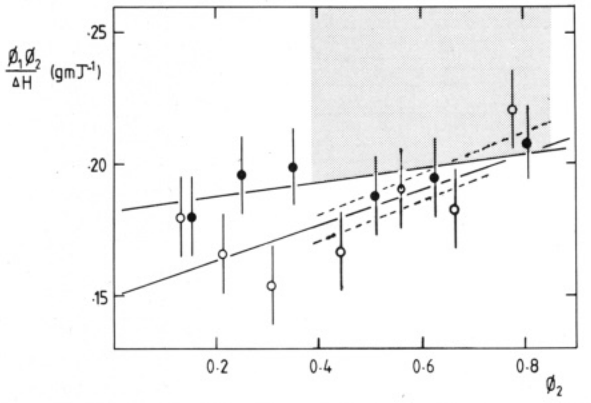

Figure 8. Heats of mixing data plotted according to eq 20 for the systems PB_{2360}/PS_{1010} (●) and PB_{960}/PS_{1010} (○). Concentrations greater than c^* for either component are indicated by the shaded areas. The solid lines are least-squares fits to the data. The dashed lines have the Bondi values for γ and a suitable intercept to pass through data in the shaded areas.

The values for γ compare reasonably well with those from Bondi.[26]

On the other hand Koningsveld has pointed out that an analysis based on the mean field theory is not applicable when either polymer becomes dilute with nonoverlapping chains. Thus the overlap concentrations, C^*_1 and C^*_2, define limits within which the analysis is valid. Values of C^* have been calculated by using

$$C^* = \frac{3M_w}{N_A 4\pi R_g^{\,3}} \tag{21}$$

i.e., assuming each molecule occupies a sphere of radius R_g and M_w is the molecular weight. The composition ranges lying between C_1^* and C_2^* correspond to shaded areas in Figure 8. Within the limits defined by these values, Figure 8 shows that there is not enough precision in the data to extract meaningful values of γ. The dashed lines are from the Bondi value combined with a reasonable β_H as listed in Table VII (last column).

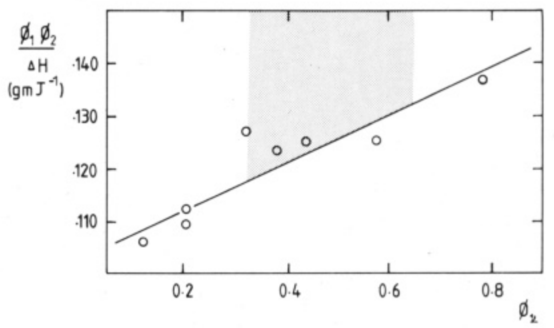

Figure 9. Heats of mixing data plotted according to eq 20 for a series C blend of PPGM/PEGM. Concentrations greater than c^* for either component are indicated by the shaded areas. The line is a least-squares fit to the data.

Table VIII
γ and β_H Determined from Figures 8 and 9 by Using Equation 2

		fit over whole ϕ range		fit between C^*_1 and C^*_2	
	blend pol_1/pol_2	$\beta_H \pm 5\%$, K	γ	$\beta_H \pm 5\%$, K	Bondi γ
compare	PS/PB_{960}[a]	107	0.24	148	0.351
PSD/PB	PS/PB_{2360}	80	0.13	127	
compare	PB_{960}/PS	42	−0.32	50	−0.542
PBD6/PS	PB_{2360}/PS[a]	36	−0.16	43	
	PPGM/ PEGM	94	0.29		0.29

[a] Previously published values.[3]

Figure 9 shows the ΔH data for the PPGM/PEGM system (with PPGM = component 2 and the same molecular weights as for the SANS experiment). Again, within the range C^*_1 to C^*_2 it is unrealistic to fit any ϕ_2 dependence of the ordinate. In this case the value of γ obtained for the least-squares fit is very close to the Bondi value.

6. Discussion

One of the aims of this work has been to test the reliability of obtaining interaction parameters from SANS experiments and to assess the desirability of analyzing data as a function of Q as opposed to using only the zero angle intensity. The latter method requires that the data be absolutely normalized (as in a molecular weight determination), while the former requires a knowledge of the molecular conformation in the blend (for Rg_1 and Rg_2). Both require accurate values of the component molecular weights and both require $QRg_1 < 1$ so that a linear Zimm plot can be observed. The data in Tables III and V show that if care is taken good agreement between the two methods can be achieved. For higher molecular weight blends the uncertainty in the Rg values of the unlabeled component may be less than in the current work since at least the chains may be assumed to be Gaussian.[14] However, assumptions would still have to be made about the behavior of labeled chains in the blend. For example, in Table VI there is some evidence to suggest that the radius of gyration of labeled polybutadiene chains in a series A blend is slightly smaller than the values measured for the same chains in a hydrogenous polybutadiene matrix. As a rule, determination of the interaction term from the zero angle intensity requires fewer parameters and therefore should give the most reliable value, which can, however, be usefully checked by analyzing the apparent radius of gyration. Any gross discrepancy in the values obtained should result in careful checks being made on the absolute calibrations used. It is evident from Figures 3 and 7 that at the limits of ϕ both $\mathrm{Rg}_{\mathrm{ap}}$ and $I(0)$ are sufficiently insensitive to temperature that any variations are unlikely to be resolved experimentally. This effectively restricts the concentration range over which the interaction parameter can be effectively studied.

The second aim was to investigate in more detail than previously the temperature and concentration dependence of the interaction parameter. Figures 4–6 show that a good linear of variation U/V_1 with T^{-1} is observed over the temperature range studied, in agreement with eq 17 for all three blends. We therefore proceed to analyze the concentration dependence of the interaction parameter in terms of a and b, the entropic and enthalpic components, following Koningveld's development and using eq 18 and 19. For the one blend where data at three concentrations are available (PBD6/PS) a parabolic dependence on ϕ_2 is observed for the slope, b, in contradiction to the variation predicted by eq 19. For this case it is not possible to fit the three values of b to eq 19 with a concentration-independent γ and β_{H}. If we take the value of γ obtained from Bondi,[26] then a dependence of β_{H} on ϕ_2 is also observed as shown in Table VII. This observed variation with ϕ_2 is at the limits of error estimated for the experiment although similar behavior has been observed for other systems.[27] It is worth therefore considering possible reasons. As mentioned in the previous section, Koningsveld has pointed out that theories based on the mean-field approximation require that each polymer should be at least in semi-dilute solution in the other. The calculated C^* values for these molecular weights are 0.39 for PS and 0.19 for PB and the samples used in the neutron experiments lie within these limits. Equations 16–20 might therefore be expected to apply to these data. One possible explanation as to why they are not applicable is that the entropic contributions (α and β_{s}) are temperature as well as concentration dependent. These would then contribute to the temperature dependence of U/V_1 observed in the SANS experiments and give an extra apparent concentration dependence of β_{H}. As previously mentioned such a temperature dependence for the entropy of mixing has been found for polymer solvent systems.[15] The fact that the scattering experiment is a free energy measurement allows more thermodynamic information to be obtained than from measurements sensitive to ΔH alone. Comparison with the values of β_{H} obtained by the two methods shows agreement, considering the relatively large differences in molecular weights and the known effect on g_{12} of deuteriation.[10,11,13] In Table VIII the starred systems form the best M_{w} match to those in Table VII. It is noticeable that the values for the PBD/PS system (3260/1460) are reasonably close to the value from heat of mixing data for PB/PS (2360/1010), while there is a much larger discrepancy between the neutron data for PSD/PB (3800/920) and the enthalpy measurements for PS/PB (1010/920), where there is a larger mismatch of the molecular weights in the two experiments. While the question of deuteriation altering g_{12} undoubtedly plays a part in this discrepancy it is masked by the obvious effect of molecular weight. From these data we can merely deduce the advantage to be obtained by comparing data from ΔH and SANS using identical samples. (For the PPGM/PEGM system the molecular weight match for the two experiments is good, however, and earlier experiments detected no effect of deuteriation on the cloud points.[2] For this system the discrepancy in β_{H} values may arise from the same causes as the concentration effects discussed above.)

Finally, it is worth commenting on the values for the entropy of mixing included in factor a in Table VII and expressed in terms of α and β_{s} in eq 17. Several of the values listed are negative. For reasonable values of γ the factor $(1-\gamma)(1-\gamma\phi_2)^{-3}$ is always positive. Thus negative values of a imply negative values for α and/or β_{s}. While the values for PS/PB are all numerically small and barely significant, those for PPGM/PEGM are large. The implication of such a favorable entropy of mixing is not clear at present. It should be remarked that the heats of mixing data for PPGM/PEGM imply that the system should be immiscible to much higher temperatures than observed if only the combinatorial entropy is considered, implying extra favorable entropic contributions. In a previous analysis of some SANS data at one temperature[2] we also concluded that a favorable entropy contribution to the free energy of mixing was required at low PPGM concentrations exactly as shown by the value for a in Table VII.

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Registry No. PS, 9003-53-6; PB, 9003-17-2; PEG methyl ether, 9004-74-4; PPG methyl ether, 37286-64-9; neutron, 12586-31-1.

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