polymer papers

Small angle neutron scattering studies of interactions and chain dimensions in bimodal polystyrene blends

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The nature of mixing in bimodal polystyrene homopolymer blends has been investigated by using small-angle neutron scattering. Blends were made from deuterated high ($M \approx 110000$) and hydrogenous low ($M \approx 1000$–3000) molecular weight fractions. The interaction parameter χ and the statistical segment length were obtained as a function of blend composition and the molecular weight of the low M component. Blend compositions ranged from 0 to 50% of the high M component in the low M matrix. A significant level of non-ideal mixing was observed for the lowest molecular weight of the low M component, as evidenced by χ values of the order of 0.02 and chain dimensions associated with the high M component that were smaller than those expected for polystyrene in the bulk state. With increasing molecular weight of the low M component, χ decreased toward the value intrinsic to blends of deuterated and hydrogenous polystyrene, and the chain dimensions became essentially ideal. The molecular weight effect and magnitude of χ were consistent with a non-ideal mixing effect associated with the initiator fragment remaining from the polymerization.

(Keywords: polystyrene; blends; neutron scattering; interaction parameter)

INTRODUCTION

A random-coil polymer in dilute solution in a monomeric solvent is swollen due to the excluded volume interactions between monomers within a single chain. The chain dimensions, as measured through the radius of gyration, are determined by the interaction between the chain segment and the solvent. This interaction is expressed by the second virial coefficient or the related Flory χ parameter. The result of increasing the polymer concentration is a reduction of the excluded volume effect by screening. With the advent of small angle neutron scattering (SANS) methods and facilities for polymer studies, investigations of the behaviour of chain dimensions across the semi-dilute and concentrated regimes of concentration have become possible. Because of the contrast enhancement afforded by selective deuteration and the ability to make measurements on non-dilute systems, small angle neutron scattering (SANS) is certainly the method of choice for such studies. It is now generally accepted that random-coil polymers assume dimensions in the bulk state which are identical to those in dilute solution under θ conditions[1–3].

Relatively few experiments have been done in which the solvent is an oligomeric version of the polymer. Certainly, the effects of chain length polydispersity on the relaxation behaviour of polymers are of great interest, particularly in the area of melt rheology. A number of experimental studies have been conducted with polymers having a bimodal molecular weight distribution (MWD), made by blending two narrow MWD fractions of widely differing molecular weight M. For example, bimodal homopolymer blends in which both components have M well above the characteristic entanglement molecular weight have been used to investigate polymer melt dynamics in terms of various aspects of the reptation model[4–7]. In some instances, blends of high molecular weight fractions with homologous oligomers have been studied rheologically. In general, the low molecular weight component acts as a simple diluent in terms of its effect on rheological parameters such as the plateau modulus and zero-shear viscosity[8]. Little experimental work has been done to look at the structure and interactions between components in such blends, particularly at concentrations for which the high M component cannot be considered to be dilute. In this paper, we report on the use of SANS to measure the component interactions and chain dimensions in model bimodal polystyrene (PS) systems in which the component molecular weights are of the order of 100 000 and 1000, i.e. blends of a high M polymer with its oligomer.

The original motivation for this study was our observation of anomalous glass transition behaviour in such bimodal PS blends[9]. The blends showed single T_gs in calorimetric and dielectric measurements. However, the apparent activation energy of T_g, obtained from the temperature dependence of the frequency of maximum dielectric loss, exhibited a minimum at compositions in which the high M component was the minority component. This minimum in the activation energy was lower than the value for either pure component and was seen only in blends having a low M component with

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$M < 2000$. For higher molecular weights, a simple monotonic change of the blend activation energies between the pure component values was observed. It was felt that valuable insight could be gained by studying the static chain properties in these blends by SANS as a function of the molecular weight of the low M component. In particular, it was suspected that chain-end effects most evident for the lowest molecular weight could result in non-ideal mixing.

THEORY

Our data analysis essentially follows that of previous investigations[10,11]. The random-phase approximation (RPA) of de Gennes[12] gives the expression for the scattering structure factor for a single-phase, interacting binary blend as

$$\frac{1}{S(q)} = \frac{1}{N_A \phi_A S_A(q)} + \frac{1}{N_B \phi_B S_B(q)} - 2\chi \tag{1}$$

where N is the degree of polymerization, ϕ is the volume fraction and χ is an interaction parameter related to the mean field interaction potential $U(\phi, T)$ between the two types of monomers at a given ϕ and T. The subscripts A and B denote components A and B of the binary blend. The structure factor S is a function of the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ where λ is the neutron wavelength and θ is the scattering angle. The RPA describes scattering arising from concentration fluctuations in mixtures having $0 \leqslant \chi < \chi_s$, where $\chi = 0$ for ideal mixing and χ_s represents the boundary for stability of a single phase system:

$$\chi_s = \frac{1}{2}\left(\frac{1}{N_A \phi_A} + \frac{1}{N_B \phi_B}\right) \tag{2}$$

Shibayama *et al.*[10] have generalized equation (1) to the form

$$\frac{k_N}{\mathrm{d}\Sigma(q)/\mathrm{d}\Omega} = \frac{1}{N_A v_A \phi_A S_A(q)} + \frac{1}{N_B v_B \phi_B S_B(q)} - \frac{2\chi}{v_0} \tag{3}$$

where $\mathrm{d}\Sigma/\mathrm{d}\Omega$ is the differential scattering cross section, identical to the Rayleigh ratio used in light scattering, v_A and v_B are the segmental molar volumes of A and B, respectively, and v_0 is a reference volume. k_N is given by

$$k_N = N_0\left(\frac{b_A}{v_A} - \frac{b_B}{v_B}\right)^2 \tag{4}$$

where N_0 is Avogadro's number and b_A and b_B are the coherent scattering lengths of the A and B monomers. For a blend of a polymer with its deuterated analogue, $v_A = v_B = v_0$ and the cross section is

$$\frac{\mathrm{d}\Sigma(q)}{\mathrm{d}\Omega} = \frac{(N_0/v_0)(b_H - b_D)^2}{[N_D \phi_D S_D(q)]^{-1} + [N_H \phi_H S_H(q)]^{-1} - 2\chi} \tag{5}$$

where the H and D subscripts denote the hydrogenous and deuterated components. Equation (5) can be used to fit experimental scattering data after correcting the data by a suitable method to give absolute intensities[13].

For random-coil polymers, the single-chain structure factor for component i is given by the Debye function

$$S_i(q) = \frac{2[R_{gi}^2 q^2 + \exp(-R_{gi}^2 q^2) - 1]}{R_{gi}^4 q^4} \tag{6}$$

The radius of gyration R_g is related to the degree of polymerization by

$$R_g = (Na^2/6)^{1/2} \tag{7}$$

which serves to define a statistical segment length a in the manner of Bates and Wignall[14]. For polystyrene in either a θ solvent or the bulk, $R_g^{1/2}/M \approx 0.28$ (References 15, 16), equivalent to $a = 7.0$ Å*. In general, the degrees of polymerization are known from molecular weight measurements. This leaves R_g or equivalently a of the two components and χ as unknowns in equation (5). As noted by others[10,11], the two structure factors in equation (5) are correlated such that the individual a values cannot be treated as statistically independent. In the data analysis to be described below, the statistical segment length for each component in the bimodal blend was assumed to be the same average value a_{av}, leaving χ and a_{av} as the only parameters used in fitting equation (5) to the scattering data. This assumption is justified in terms of both components being polystyrene, although the assumption of ideal chain statistics inherent in the random phase approximation can be questioned for short chains. It will be shown below that for the bimodal blends studied here, the average statistical segment length is affected more by the high M than the low M component because of the stronger q dependence of $S(q)$ for high M. Warner *et al.*[17] extended the RPA to the case of binary blends in which one component is partially labelled with deuterium. For the types of blends considered in this paper, their expression is

$$\frac{\mathrm{d}\Sigma(q)}{\mathrm{d}\Omega} = \frac{(N_0/v_0)[cb_D + (1-c)b_H - b_H]^2}{N_A \phi_A S_A(q) + N_B \phi_B S_B(q) - 2\chi} + c(1-c)(b_D - b_H)^2 N_A \phi_A v_A^{-1} S_A(q) \tag{8}$$

where a fraction c of component A is deuterated and component B is completely hydrogenous. The first term represents the scattering due to concentration fluctuations and the second term is the single chain scattering due to component A. A weighted subtraction of the scattering of two blends with the same ϕ_A and ϕ_B but different cs can be used to eliminate the first term and isolate the single chain scattering of component A.

EXPERIMENTAL

Materials and characterization

Narrow MWD polystyrenes were obtained from Polymer Laboratories Inc. The molecular weight characterization data supplied with the polymers are summarized in *Table 1*. M_w values were obtained by low angle laser light scattering and M_w/M_n values by gel permeation chromatography (g.p.c.). The low M polymers, hydrogenous in all cases, were designated by their M_w values.

Table 1 Molecular weight data for blend components

Component designation	M_w	M_w/M_n
1050 (hydrogenous)	1050	1.16
2150 (hydrogenous)	2150	1.06
2950 (hydrogenous)	2950	1.05
H (hydrogenous)	100 000	1.05
D (deuterated)	110 000	1.05

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* 1 Å = 10^{-1} nm

The high *M* component of the blends had a constant molecular weight of $\approx 110\,000$ in all the blends and was designated by D or H in its deuterated or hydrogenous form, respectively.

Sample preparation

Samples were blended in 5% solutions in methylene chloride. Weight fractions of the high *M* component ranged from 0.1 to 0.5 for blends containing a low *M* component having $M_w = 1050$ and from 0.1 to 0.4 for blends containing a low *M* component having $M_w = 2150$ or 2950. Films of 0.1 mm thickness were cast in aluminium dishes. Films were dried for 5 d at ambient conditions and 2 d at 90–100°C under vacuum. Film fragments were then stacked and compression-moulded at 150°C in aluminium rings into 1.2 mm thick, 15 mm diameter circular specimens. To eliminate microvoids and to ensure a uniform thermal history, a procedure similar to that of Bates and Wignall[14] was used. Specimens were annealed at 170°C under vacuum for 6 h and quenched to room temperature before the SANS measurements at room temperature. The annealing treatment was designed to establish an equilibrium state of concentration fluctuations. Blends were designated by the weight percentages of each component. For example, a designation 2150/D 70/30 describes a binary blend containing 70 wt% of a hydrogenous polymer of $M_w = 2150$ and 30 wt% of a deuterated polymer of $M_w = 110\,000$. The designation 2150/D/H 70/15/15 represents a ternary blend also containing 70% of the hydrogenous $M_w = 2150$ polymer but having the high *M* component made up of equal amounts of its deuterated and hydrogenous forms. The volume fractions required for the data analysis were calculated for each blend from the component densites measured in a density gradient column.

SANS measurements

Scattering measurements were made using the small angle diffractometer[18] at the Intense Pulsed Neutron Source (IPNS) facility at Argonne National Laboratory. Data were collected over a q range from 0.008 to 0.35 Å^{-1}. The two-dimensional detector readings were circularly averaged, corrected for delayed neutrons, and normalized for the specimen thickness and the number of incident neutrons. The data were put on an absolute intensity scale by using a deuterated/hydrogenous polystyrene blend of known absolute cross section as a standard. The scattering was also measured from blends of hydrogenous low *M* and hydrogenous high *M* polymers prepared identically to the deuterium-containing blends. Close examination of the fully hydrogenous blend scattering showed no excess scattering at the lowest angles, confirming the absence of microvoid scattering which might affect the data analysis. Incoherent scattering corrections were done by subtracting a fraction of the scattering from the appropriate fully hydrogenous blend equal to the fraction of hydrogen in the deuterated/hydrogenous blend. This approach assumes that the incoherent contribution from deuterium can be neglected compared to hydrogen. Typical incoherent scattering levels were between 0.3 and 0.6 cm^{-1}.

Non-linear least-squares fitting was performed by using a VAX 8600 computer with RS/1 software (BBN Software Products Corp.). The program uses a Marquardt compromise algorithm.[19]

RESULTS AND DISCUSSION

The accuracy of the scattering measurements was checked by performing a standard analysis of a partially deuterium-labelled high molecular weight sample consisting of 30 wt% d-PS in a nearly identical hydrogenous matrix. The sample was designated H/D 70/30 according to the notation of *Table 1*. The scattering curve is shown in *Figure 1* along with a non-linear least squares fit to the data using the relation[16]

$$\frac{d\Sigma}{d\Omega} = \phi(1-\phi)(b_D - b_H)^2 V^{-1} N S(q) \tag{9}$$

where ϕ is the volume fraction of labelled polymer, $S(q)$ is given by equation (6), and V is the segmental volume of polystyrene (1.64×10^{-22} cm^3), equal to the quantity N_0/v_0 in the equations above. The value of $(b_D - b_H)^2$ was taken as 6.936×10^{-23} cm^2 (Reference 20). Corrections exist for differences between the degrees of polymerization of the hydrogenous and deuterated components[21,22], but the slight difference here made the correction negligible in this case. The $q = 0$ intercept yielded a (weight average) degree of polymerization $N = 980$. The angular dependence gave a value of $R_g = 101$ Å. A value of 90 Å is calculated from equation (7) with $a = 7.0$ Å for PS and $N = 990$. The agreement between the g.p.c. and SANS-derived values of N is perhaps fortuitous in light of the 10% difference between the measured and calculated R_g and the approximately 5–10% uncertainty in the absolute scattered intensities.

RPA analysis

Figure 2 shows the scattering curves and fits to equation (5) for blends having 30% high *M* component as a function of the molecular weight of the low *M* component. These curves are representative of the intensities and data scatter around the fits observed for the blends in this study. Good fits to the RPA form were obtained in all cases, with larger scatter observed for the lower intensities resulting from decreasing the molecular weight of the low *M* component.

The χ values obtained from the fits are summarized in *Table 2* and shown on a logarithmic scale in *Figure 3* as

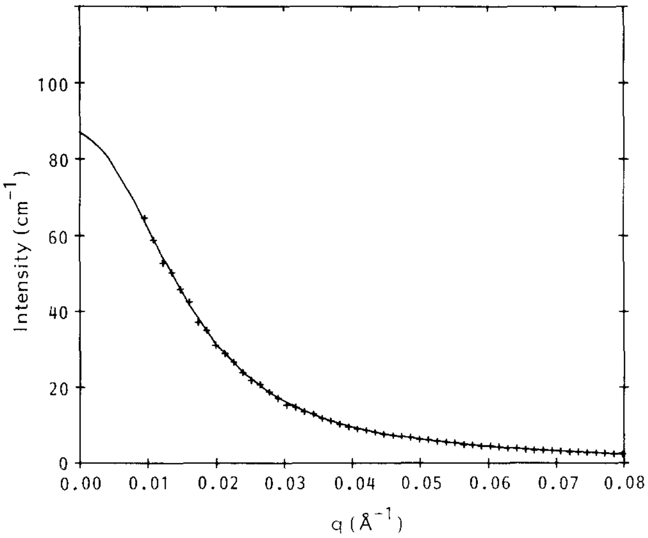

Figure 1 Scattering curve for 70H/30D blend. ———, Fit to the single chain scattering according to equation (9)

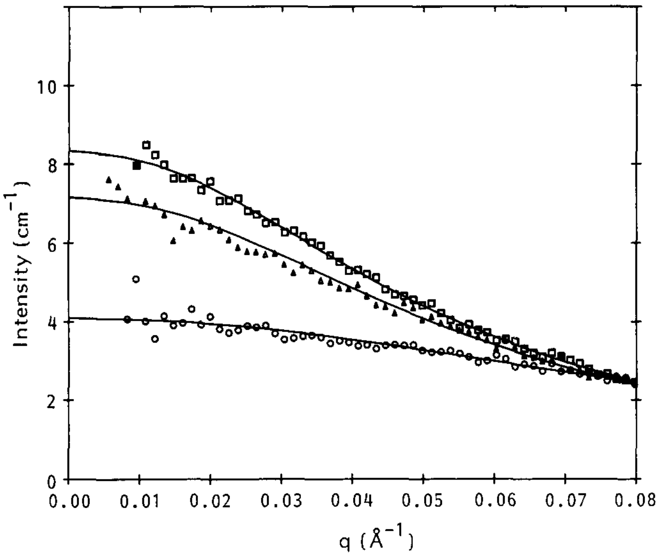

Figure 2 Scattering curves for bimodal blends having 30% high M component for different low M components: ○, 1050/D blend; Δ, 2150/D blend; □, 2950/D blend. ———, Fits to the RPA form according to equation (5)

Table 2 Measured χ and calculated χ_S values

Blend designation	Volume fraction ϕ_D	χ	χ_S
1050/D	0.094	0.023 ± 0.004	0.061
	0.189	0.019 ± 0.004	0.064
	0.285	0.020 ± 0.005	0.072
	0.383	0.017 ± 0.006	0.082
	0.482	0.019 ± 0.008	0.098
2150/D	0.094	$(5.3 \pm 2.7) \times 10^{-3}$	0.032
	0.189	$(3.8 \pm 2.8) \times 10^{-3}$	0.032
	0.285	$(5.5 \pm 2.9) \times 10^{-3}$	0.035
	0.383	$(3.8 \pm 3.6) \times 10^{-3}$	0.040
2950/D	0.094	$(6.3 \pm 24) \times 10^{-4}$	0.025
	0.189	$(2.5 \pm 25) \times 10^{-4}$	0.025
	0.285	$(8.0 \pm 26) \times 10^{-4}$	0.027
	0.383	$(6.7 \pm 29) \times 10^{-4}$	0.030

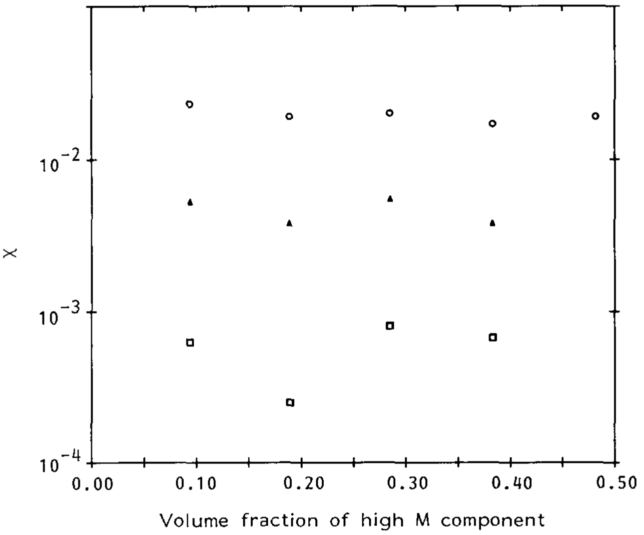

Figure 3 Compositional dependence of the SANS interaction parameter, plotted as a function of the volume fraction of the high M component: ○, 1050/D blends; Δ, 2150/D blends; □, 2950/D blends

a function of the volume fraction of high M component for the 1050/D, 2150/D and 2950/D blends. The error limits reported in *Table 2* were calculated based on an assumed 10% error in molecular weights and absolute intensity calibration. The errors calculated for the three blend systems were all of the same magnitude (2–8×10^{-3}) so that the uncertainty in χ is quite significant for the 2950/D blends. The standard error in χ resulting only from the fitting procedure was an order of magnitude smaller than the error estimates reported in *Table 2*. Two things are notable from *Figure 3*. First, no significant composition dependence of χ was observed for a given blend. Second, the magnitude of χ increases rapidly with decreasing molecular weight of the low M component, from of the order of 6×10^{-4} at $M = 2950$ to 2×10^{-2} at $M = 1050$. As seen from *Table 2*, all χ values were less than the χ_s calculated for each blend, although χ for the 1050/D blends was comparable in magnitude to χ_s. The single-phase nature of the blends predicted by $\chi < \chi_s$ is consistent with the observed single T_g. Obviously the blend can exist as a single phase with a fairly large positive χ because of the favourable combinatorial entropy contributed by the low molecular weight component. The χ values are all greater than the value of 1.7×10^{-4} obtained by Bates and Wignall for high molecular weight PS at 160°C, which can be taken as an estimate of the intrinsic χ between deuterated and hydrogenous PS due to isotopic effects[14].

We believe that the magnitude and molecular weight dependence of χ can be explained by a chain-end effect associated with the low M component of the blends. Anionically polymerized PS of the type used in this study has an n-butyl end group due to the n-butyl lithium initiator used in the polymerization. The other chain end is formed by capping the propagating anion with hydrogen ion and is chemically similar to the interior chain segments. The χ values for the blends of high and low molecular weight PS can be crudely calculated from the relation

$$\chi = \frac{V_m(\delta_{\text{high}} - \delta_{\text{low}})^2}{RT} \tag{10}$$

where V_m is the segmental molar volume and δ is the solubility parameter. The solubility parameter of the low M component differs from the high M component due to the presence of the chain end:

$$\delta_{\text{low}} = \frac{\delta_e + N\delta_s}{N+1} \tag{11}$$

where N is the number of styrene segments in the oligomer (equal to the degree of polymerization), and δ_s and δ_e are the solubility parameters for the styrene segments and the butyl end group, respectively. The chain end in the high M component has a negligible contribution and is not considered in the calculation. Taking $\delta_{\text{high}} = \delta_s$ and inserting equation (11) into equation (10) yields

$$\chi = \frac{V_m(\delta_s - \delta_e)^2}{RT(N+1)^2} \tag{12}$$

N is calculated from $N = (M - 57)/104$ where 57 is the molecular weight of the end group and 104 is the molecular weight of a polystyrene repeat unit. A plot of χ *versus* N is shown in *Figure 4* for the blends containing

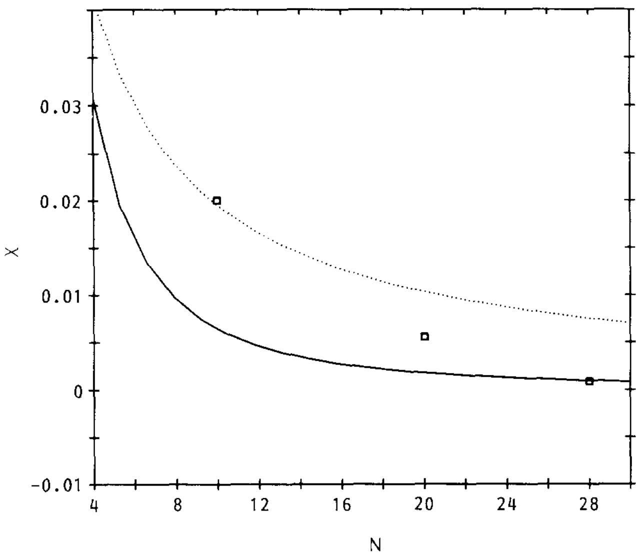

Figure 4 Interaction parameter plotted as a function of N, the number of styrene segments in the low M component for blends containing 30% high M component. ———, Calculated from equation (12); ·····, from equation (13)

30% high M. The solid line in *Figure 4* was calculated from equation (12) using the following parameters: $\delta_S = \delta_{PS} = 9.1$ (cal cm^{-3})$^{1/2}$ (Reference 23), $\delta_e = 6.8$ (cal cm^{-3})$^{1/2}$ as calculated for the n-butyl group from the method of group molar contributions[24], and $V_m = V_{PS} = 98.5$ cm^3 mol^{-1}. Following the work of Kramer and Sillescu[25], we take T to be the measured T_g of the blend, assuming that the sample falls out of equilibrium at this temperature during cooling. For the 70/30 blends, T_g ranges from 306 K for the 1050/D blend to 349 K for the 2950/D blend. It can be seen that equation (12) predicts the measured value of χ accurately for the 2950/D blend, but underestimates χ for the lower molecular weights. The molar average approach to calculating δ_{low} does not require that the butyl group be at the chain end, and this effect may contribute to the differences between the experimental data and equation (12) at the lower molecular weights. We note that a result identical to equation (12) is obtained by treating the oligomer as a copolymer and using the binary interaction model of Paul and Barlow[26] to calculate χ between this copolymer and a PS homopolymer. Corrections to this simple approach that account for the non-random nature of the copolymer are possible[27] but were not attempted because of the additional unknown parameters introduced. The dotted line in *Figure 4* is calculated from

$$\chi = \chi_0 \phi_e \phi_s \qquad (13)$$

where χ_0 is given by $V_m(\delta_s - \delta_e)^2/RT$, and ϕ_s and ϕ_e are the volume fractions of styrene and butyl groups, respectively, in the overall blend. It is seen that this type of averaging apparently provides an upper bound to the data, with good agreement with experiment at low molecular weight. We present this as an empirical observation without theoretical justification. Equation (13) also introduces a dependence of χ on the blend composition; for a given N, $\phi_e = \phi_{low}/(N+1)$ and $\phi_s \approx 1$ so that χ is proportional to ϕ_{low}. This is a stronger dependence than that observed in *Figure 3*. Finally, we note that the experimental points in *Figure 4* extrapolate to $\chi = 0$ at an N value corresponding approximately to $M = 3300$ for the low molecular weight component, whereas the calculated curves properly extrapolate to zero at infinite molecular weight. Because of the large uncertainties in measuring small values of χ in these blends by SANS, great confidence is not placed upon the extrapolated behaviour of the data. However, the magnitude and molecular weight dependence of χ is suggestive of an effect due to the chain ends.

Statistical segment length

The effects of blend composition and molecular weight on the average statistical segment length a_{av} are shown in *Figure 5*. Values in the range of 6.5–7.2 Å were obtained for the 2950/D and 2150/D blends, with no significant trend observed with blend composition. These values are comparable to the literature values for PS which range from 6.7 to 7.0 Å (References 20 and 28), indicating essentially ideal chain dimensions in these blends. The values of a_{av} for the 1050/D blends are less than the literature values and drop significantly with increasing amounts of the high M component, reaching a value of 4.4 Å for the 50/50 blend.

Although a_{av} represents an average statistical segment length for the blend, the observed changes in a_{av} can be associated primarily with a decrease in R_g for the high M component. The structure factor of the low M component certainly contributes to the magnitude of the observed scattering but the angular dependence, from which the chain dimensions are derived, is dominated by the high M component. This is because the functions describing the individual structure factors in equation (5) decrease more rapidly with q for larger scattering objects, regardless of the shape of the scatterer. For the 1050/D blends, R_g of the high M component is about ten times that of the low M component. For example, $S(q)$ decreases from 0.736 at $q = 0.01$ to 0.031 at $q = 0.08$ for the high M component, whereas $S(q)$ decreases from 0.997 to 0.817 over the same q range for the low M component. In cases where there is less of a mismatch in molecular weight, $S_H(q)$ and $S_D(q)$ would have more similar angular dependences and with increasing ϕ_D, the angular dependence of the H chains would contribute

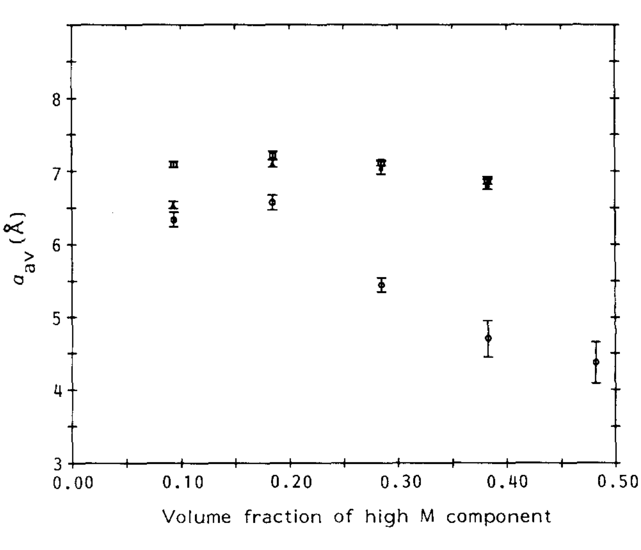

Figure 5 Compositional dependence of the average statistical segment length, plotted as a function of the volume fraction of the high M component. Error bars represent the standard error from the RPA fits. ○, 1050/D blends; ▲, 2150/D blends; □, 2950/D blends

more to the overall angular dependence, according to equation (5). For the widely bimodal blends considered here, this weighting effect is not significant. In terms of the blend scattering, these factors combine to make the low M component of the blend contribute mostly to the background 'solvent' scattering. In addition, the relative insensitivity of $S(q)$ to shape for small sizes makes the assumption of Gaussian chain statistics, required by the RPA, less critical for the low M component. Because of the statistical inability to determine the component a values individually, we will retain the definition of a_{av} as an average quantity with the knowledge that changes in a_{av} are due primarily to changes in a of the high M component.

The dramatic difference between the 1050/D blend system and the other two blends is ascribed to its proximity to phase separation: $\chi \approx \chi_s/3$. With the blends so close to their spinodal decomposition points, the unfavourable interactions caused by the end group effects discussed above could result in a contraction of the high M chains. A value of $a = 7$ Å corresponds to $R_g = 90$ Å, whereas $a = 4.4$ Å corresponds to $R_g = 57$ Å. This interpretation is supported by the essentially ideal dimensions observed at all compositions for the 2150/D and 2950/D blends. These blends are further from their spinodal points, with $\chi \approx \chi_s/7$ and $\chi \approx \chi_s/42$, respectively.

Weighted subtraction

The method of Warner *et al.*[17] expressed by equation (8) was used to provide an independent check on the accuracy of the data analysis. Scattering data were collected from the 1050/D (70/30) binary blend and a 1050/D/H (70/15/15) ternary blend, where H represents the high molecular weight hydrogenous sample described in *Table 1*. Equation (8) was written for the ternary blend in terms of a labelled fraction c_t and for the binary blend in terms of a labelled fraction c_b. After background correction, the scattering from the binary blend was multiplied by the factor α and subtracted from the ternary blend scattering, where α is given by

$$\alpha = \frac{[c_t b_D + (1 - c_t) b_H - b_H]^2}{[c_b b_D + (1 - c_b) b_H - b_H]^2} \qquad (14)$$

For the two blends considered here, $c_t = 0.5$, $c_b = 1$ and $\alpha = 0.25$. The effect of the weighted subtraction was to eliminate the first term in equation (8), leaving the net scattering described by

$$\frac{d\Sigma}{d\Omega}(\text{net}) = 0.25(b_D - b_H)^2 N_A \phi_A v_A^{-1} S_A(q) \qquad (15)$$

where $S_A(q)$ is given by equation (6). As discussed above, the subtraction isolates the single-chain scattering of the labelled component A (the high M component of the blend). The net scattering curve is shown in *Figure 6* after the weighted subtraction. Analysis according to equation (15) yielded $R_g = 76$ Å ($a = 5.9$ Å). This value is in reasonable agreement with the value of 5.5 Å determined from the non-linear fit to the RPA. The agreement between the two approaches gives evidence that the reduced chain dimensions obtained from the RPA analysis of the 1050/D blends are not an artefact of the RPA analysis associated with the weighting of the component scattering functions discussed above. Our supposition that the reduced dimensions are associated with the high M component of the blends is supported by the weighted subtraction method, which gives size information on this component alone. The available data do not allow us to obtain R_g directly for the low M component of the blend. It is certainly of interest to check the validity of the assumption of random coil statistics for this component, particularly for the 1050/D blends in which the low M component has of the order of 20 carbon–carbon bonds. Miller and Cooper[29] measured the dimensions of a poly(oxytetramethylene) oligomer of $M_n = 1000$ in the bulk state by SANS and found it to obey random coil statistics even at this short a chain length.

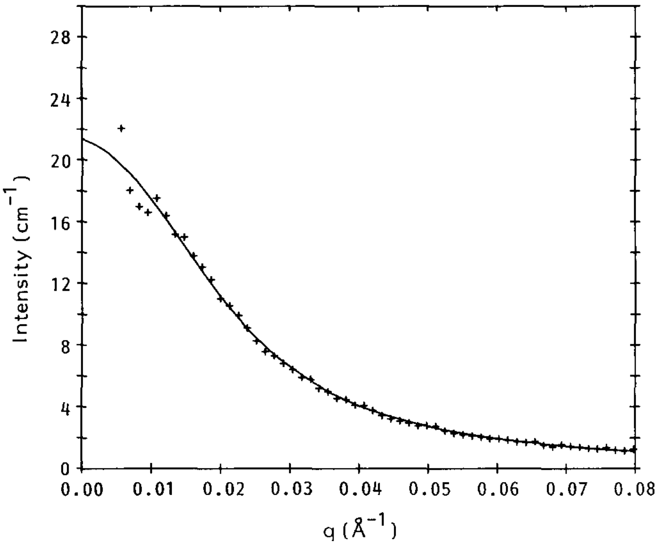

Figure 6 Scattering curve resulting from a weighted subtraction of the 70L/30D binary blend scattering from the 70L/15H/15D ternary blend scattering. ———, Fit to equation (15)

The intercept at $q = 0$ in *Figure 6* allows the degree of polymerization N_A to be calculated from equation (15). The value obtained was about 25% lower than the g.p.c.-derived value. As pointed out by Warner *et al.*[17], at least part of this discrepancy can be attributed to increased uncertainties in absolute intensity caused by doing two separate incoherent background corrections before the weighted subtraction. However, as in any single-chain scattering analysis, the accuracy of the absolute intensity scale does not affect the size information obtained from the angular dependence.

SUMMARY

The results of the SANS analysis based on the random phase approximation indicate that significant non-ideal mixing can exist in single-phase blends of polymers and oligomers that are essentially identical chemically. The source of the non-ideal mixing in the polystyrene system studied here was the *n*-butyl chain end resulting from the initiator used in the polymerization. The magnitude of the measured interaction parameter was comparable to that calculated from a simple solubility parameter approach accounting for the fraction of the chain that was due to the initiator. The dependence of the interaction parameter on the molecular weight of the low M component was also consistent with a chain end effect. The dimensions of the high molecular weight component ($M = 110000$) were essentially ideal for blends having low M components of $M = 2150$ and 2950, whereas a significant reduction in chain dimensions was seen in a blend having a low M component of $M = 1050$. This was related to the proximity of the blend to its spinodal decomposition point. The measured chain dimensions were confirmed for a representative blend sample by an independent SANS technique.

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