Single-chain scattering in heterogeneous block copolymers

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Diblock copolymers consisting of polystyrene (S) attached to a polybutadiene (B) block (which is either hydrogenous or perdeuterated) have been synthesized and blended in such a way that the microphase-separated S and B domains have equal scattering-length densities, thus eliminating the component of small-angle neutron scattering (SANS) due to the domain structure. Two samples were studied: one with small spherical polybutadiene microdomains whose size was in essential agreement with calculations assuming equilibrium, and a second one of larger molecular weight in which the sphere size, while larger, was considerably smaller than predicted from equilibrium theory. The SANS spectra of these samples were analysed to give the radii of gyration R_g and molecular weights M_w of the labelled polybutadiene blocks from plots of Γ^{-1} *versus* Q^2 and least-square fits to the single-chain scattering function proposed by Debye. Results for the first sample agreed with the molecular weight obtained from chromatography and u.v. absorption and with the R_g found in bulk polybutadiene of similar M_w. The SANS estimates of both M_w and R_g for the second sample were anomallously large; these deviations may be due to (a) non-Gaussian conformations of the polybutadiene chains imposed by the nonequilibrium state of the microdomain, or (b) clustering of the deuterated polybutadiene chains within the microdomain due to small isotopic differences in chemical potential, enhanced by the larger M_w. Observations on other systems suggest that the second effect is the dominant one.

Keywords Small-angle scattering; deuterated polymer chains; chain conformation; polybutadiene; heterogeneous block copolymers

INTRODUCTION

Small-angle neutron scattering (SANS) has recently gained wide popularity in the area of polymer physics, primarily due to the powerful deuterium substitution technique, which allows preferential labelling of individual components of a polymer system without significant chemical perturbation. In work described in previous[1-3] and forthcoming[4] reports from this laboratory we have utilized this contrast enhancement to increase the signal obtained from two-phase scattering in certain microphase-separated diblock copolymers of spherical morphology. This scattering, which includes Bragg, single-sphere and Porod scattering effects, enabled us to accurately determine several important structural parameters of the system, including average sphere size, the extent of sphere-size dispersion, the thickness of the interface, and the packing regime of the paracrystalline macrolattice. All of these results could in principle have been obtained from small-angle X-ray scattering (SAXS) experiments, although in practice the 30-metre SANS instrument at the National Center for Small-Angle Scattering Research, which was used in our experiments, gave better resolution in the low-Q region than any SAXS instrument available to us, and this resolution was essential in interpreting the Bragg scattering[1,3,4]. The primary consideration in selecting SANS for this overall study was the opportunity to examine the single-chain scattering behaviour of polymer blocks contained within the previously documented[1,4] microspherical domains. In the present paper we report on such studies carried out on polystyrene–polybutadiene diblock copolymers. The samples were prepared by blending a fully hydrogeneous block copolymer SB with an appropriate amount of another polymer SB_d, synthesized in the same way but using perdeuterated butadiene. The mole fraction of SB_d is chosen so that the scattering-length densities of the S and B/B_d phases are equalized. By this means, two-phase scattering is virtually eliminated and scattering from the labelled butadiene chains becomes the dominant effect. Since isotopic substitution has no perceptible effect on X-ray scattering, these experiments are possible only with SANS. The question they address is that of chain conformation in phase-separated microdomains.

Measurement of polymer single-chain dimensions by SANS originated less than a decade ago[5-7] and remains in a state of development. Brief reviews of the topic are included in refs. 8 and 9. Guinier and Fournet[10] have shown that scattering from any isotropic substance can be approximated in the low-Q region by an exponential in the radius of gyration R_g, giving:

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{d\Sigma}{d\Omega}(0)\exp(-R_g^2Q^2/3) \qquad (1)$$

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where $\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}$ is the coherent differential scattering cross section per unit volume of material and is proportional to the observed scattering intensity I. Q represents the momentum transfer, equal to $4\pi\lambda^{-1}\sin\theta$, where λ is the wavelength of the incident radiation and θ is half the scattering angle. Scattering from independent polymer chain coils which obey Gaussian statistics can be characterized by the Debye function[11],

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q) = \frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(0)\frac{2}{R_4^gQ^4}[R_g^2Q^2-1+\exp(-R_g^2Q^2)] \quad (2)$$

where R_g^2 is the mean-square radius of gyration of the coil. For $R_gQ<1$, equation 2 can be expanded to give:

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q) = \frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(0)\left[1-\frac{R_g^2Q^2}{3}+\frac{R_g^2Q^4}{12}-\ldots\right] \quad (3)$$

where (to the approximation of the first two terms) equation 3 is identical with the expansion of equation 1. To the extent that the higher-order terms can be neglected, equation 3 implies that the slope of a plot of $I(Q)^{-1}$ *versus* Q^2 will give R_g^2. Such plots, usually called Zimm plots, have been found to give reasonable values of R_n even when many of the plotted points lie outside the $R_gQ<1$ region[15,29]. More recently, workers with access to high-speed computing equipment have compared values of R_g obtained from Zimm plots with those obtained from weighted least-squares fits of the data to the complete Debye function (equation 2). Ballard and coworkers[12] report reasonable agreement for such a comparison, and Tangari *et al.*[13] find that Debye fitting gives R_g values 7–8% lower than those obtained from Zimm plots. Another question is whether the independent behaviour of the chains assumed in the derivation[11] is valid for bulk systems. Wignall *et al.*[14] have addressed this point, reporting a constant measured value of R_g for various concentrations up to 50 mole% deuterated polystyrene in hydrogenous polystyrene.

Scattering data extrapolated to $Q=0$ can be used to estimate the polymerization index and hence the molecular weight of labelled chains. For a single polymer species (designated P) where a fraction X has been labelled by substituting deuterium for hydrogen in the chain, the forward scattering for a system of statistically distributed molecules is related to the weight-averaged polymerization index:

$$N_w = \frac{1}{C_N}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(0) \quad (4)$$

where C_N is a neutron calibration constant given by:

$$C_N = (a_\mathrm{H}-a_\mathrm{D})^2N_0X(1-X) \quad (5)$$

Here N_0 is the number of monomers per unit volume, X is the mole fraction of labelled polymers and a_H and a_D are the coherent scattering amplitudes of a normal (hydrogenous) and labelled (deuterated) monomer unit. The weight-averaged molecular weight, M_w, may be calculated from the polymerization index N_w which is assumed to be independent of labelling in equations 4 and 5. In actual practice there is usually some mismatch in N_w between the labelled and unlabelled chains and small corrections for this effect were applied as described below.

SINGLE-CHAIN SCATTERING IN BLOCK COPOLYMERS

In the preceding discussion it has been assumed that the sample is homogeneous and that $\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q)$ can thus be represented by a single-chain correlation function. Obviously, phase-separated block copolymers are not consistent with this premise. These materials exhibit strong interference effects, attributable to both inter- and intraparticle scattering, the intensity of which is directly related to the contrast factor. These effects remain significant in fully hydrogenous samples. Therefore, extraction of a single-chain scattering function in these materials requires the subtraction of this structural scattering, or its elimination by appropriate deuterium labelling.

Richards and Thomason[15] have determined the single-chain dimensions of a perdeuterated polystyrene block contained in a diblock copolymer with *cis* 1,4 polyisoprene (sample DSI-1). In order to account for phase structure, these authors subtracted the scattered intensity obtained for an unlabelled sample from that obtained for a labelled (4% w/w) specimen. The resulting molecular weight obtained from a Zimm plot was reported to be in excellent agreement with that determined by gel permeation chromatography. These authors neglected the factor $(1-X)$ in equation 5, although in this case it represents only a minor correction.

Recently Jahshan and Summerfield[16] have derived an expression for the scattering from a two-phase polymer system in which one of the phases is composed of a mixture of labelled and unlabelled chains. For an incompressible blend of polymer species P and S, $\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q)$ is given by

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q,X) = X(1-X)(a_\mathrm{H}-a_\mathrm{D})^2N_wZ^2S_s(Q)$$

$$+\left(a_\mathrm{H}(1-X)+a_\mathrm{D}X-a_\mathrm{S}\frac{V_\mathrm{P}}{V_\mathrm{S}}\right)^2\frac{S_T(Q)}{V} \quad (6)$$

where

$$S_S(Q) = |\sum_j e^{iQ\cdot r}j|^2 \quad (7)$$

and

$$S_T(Q) = \langle|\sum_{M,j} e^{iQ\cdot(R_M+r_j)}|^2\rangle. \quad (8)$$

V is the total sample volume, V_p and V_S are the molar volumes of the P and S monomer species, R_M is the centre-of-mass position of the P species chains and r_j is the monomer position relative to the centre of mass of the chain. $S_S(Q)$ is the form factor of a P molecule. $S_T(Q)$ is proportional to the total scattering from a blend in which the P species is unlabelled ($X=0$) or fully labelled ($X=1$), and may be analysed to give information on the phase structure and the dimensions of the individual labelled chain. A similar treatment has been given independently by Koberstein[17].

Table 1 Molecular characterization of polystyrene homopolymer and diblock copolymers

Sample	$M_n^{S\,a}$	M_w^S/M_n^S	$M_n^{B\,b}$	M_w^{SB}/M_n^{SB}
S3	390	1.05	–	–
SB1	79	1.06	11	1.06
SB7	560	1.08	59	1.11
SB_d1	80	1.06	13	1.07
SB_d3	380	1.07	46	1.10

[a] Number-average molecular weight of the polystyrene fraction (kg mol^{-1}) obtained from high pressure size-exclusion chromatography (HPSEC) analysis[3]

[b] Number-average molecular weight of the polybutadiene fraction (kg mol^{-1}) obtained from M_n^S values and u.v. absorption data[3]

EXPERIMENTAL

Diblock copolymers were synthesized[1–4] under argon in benzene using n-butyllithium and a small amount of anisole as the initiation species. Styrene was polymerized first at 40°C; following removal of a small sample of the first block for g.p.c. analysis, butadiene was added to the reactor and the temperature was raised to 50°C. Living diblocks were terminated with methanol, dried in vacuum and stored at -20°C. Molecular characterization methods are described in detail elsewhere[1–4].

Examination of equation (6) reveals that determination of $S_S(Q)$ can be greatly simplified by choosing X so that the term multiplying $S_T(Q)$ becomes zero. This facilitates determining $S_S(Q)$ since it eliminates the need to independently determine $S_T(Q)$, which by definition[16,17] must derive from a structure identical to that in the blend; such perfect matching of structures in separate samples is experimentally difficult. Using coherent scattering lengths[9] for C, H and D of 0.665, -0.347 and 0.667 (all in units of 10^{-12} cm) and densities $\rho_S = 1.05$ and $\rho_B = 0.89$ g cm^{-3}, we calculate a value of $X = 0.16$ required to suppress the structural scattering in the polystyrene–polybutadiene systems considered here. Therefore samples in which 16% of the polybutadiene was of the perdeuterated form were film-cast from toluene (these samples are designated as $SB_d1/SB1$ and $SB_d3/SB7$). As documented in *Table 1*, the molecular characteristics of these paired polymers are very similar, particularly in the case of SB1 and SB_d1.

The scattering experiments were performed on the 30-metre SANS instrument[18] using neutrons of $\lambda = 4.75$ Å. Sample preparation, data treatment and corrections were carried out as previously reported[1,4]. SANS spectra were obtained for these samples at sample-to-detector distances of 2.74 m ($SB_d1/SB1$), 6 m ($SB_d3/SB7$) and 10 m ($SB_d3/SB7$). Spectra for sample S3 (a styrene homopolymer) were taken at all three distances to determine the incoherent scattering background. Pure diblock copolymer spectra were also obtained at a variety of detector distances as reported elsewhere[1–4].

While absolute intensity calibration is not required for determining R_g, it is necessary in order to calculate M_w using equation (4). Therefore background and detector-sensitivity corrected data were converted to an absolute differential scattering cross section per unit solid angle using neutron calibration constants determined from the scattering of vanadium, water and independently calibrated secondary standards[19].

Figure 1 shows the scattering patterns obtained from the hydrogenous diblock SB7, the deuterated diblock SB_d3, and blended sample $SB_d3/SB7$. The signal enhancement obtained by deuterating the B block is clearly apparent—SB_d3 scatters almost 30 times as strongly as SB7. Both unblended samples exhibit prominent peaks due to two-phase scattering, but in $SB_d3/SB7$ these features have been eliminated by the matching of scattering-length densities in the S and B/B_d blocks, thus providing experimental verification of the expression developed by Jahshan and Summerfield[16] and by Koberstein[17]. The smoothly-varying pattern that remains can be attributed to single-chain scattering from the labelled polybutadiene (equation (2)).

SANS data for the blended samples $SB_d1/SB1$ and $SB_d3/SB7$ have been corrected for incoherent scattering and recast in the form of Zimm plots (I^{-1} *versus* Q^2), which are given in *Figure 2*. Since the determination of M_w requires extrapolation to scattering intensity at zero angle, low-Q data have been used to derive the straight-line fits shown in the figures. The (Z-averaged) radii of gyration of the polybutadiene in SB_d1 and SB_d3 have been determined from the slopes of these fits, each value subject to ~15% error. Small polydispersity corrections[20] were applied to give weight-averaged radii, R_g^w, which are given in *Table 2*. M_w^B has been calculated by means of equations (4) and (5) using a density $\rho = 0.89$ g cm^{-3} and $X = 0.16$. The values quoted are equivalent to the molecular weights of unlabelled chains of the same polymerization index as the labelled chains and have been corrected for the slight mismatch in block lengths between the labelled and unlabelled chains using methods developed by Boué *et al.*[21] The molecular weights thus calculated are given in *Table 2*. These measurements are subject to ~15% error, primarily determined by the accuracy of the absolute

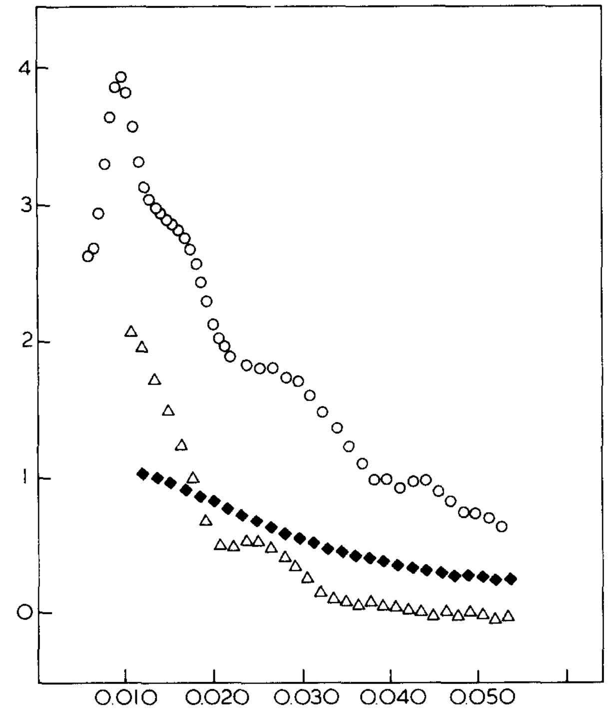

Figure 1 SANS data for (○) SB_d3, (◆) $SB_d3/SB7$, and (△) SB7. As predicted by Jahshan and Summerfield[16], a proper blend of diblock copolymers with hydrogenous and deuterated B blocks matches the scattering length densities of the two microphases and washes out the scattering due to two-phase structure

intensity calibration constant. Also included in *Table 2* are the values of M_w^B for the perdeuterated polybutadiene as measured by high-pressure size-exclusion chromatography (HPSEC) and u.v. absorption[3].

DISCUSSION

Unperturbed polymer chain dimensions (applicable to homopolymer systems) were long ago predicted[22] to follow the simple expression:

$$R_g/M_w^{1/2} = (K/\Phi)^{1/3} \qquad (9)$$

where K/Φ is constant for a given polymer at a fixed temperature. SANS measurements on bulk polystyrene have verified this behaviour[6,7] giving $(K/\Phi)_S{}^{1/3} = 0.27$ to 0.28 ($\text{Å}\,g^{-1/2}\,\text{mol}^{1/2}$). In the case of polybutadiene this parameter can be estimated[23] from intrinsic viscosity data obtained at theta conditions, giving $(K/\Phi)_B{}^{1/3} \simeq 0.37$ ($\text{Å}\,g^{-1/2}\,\text{mol}^{1/2}$). Predicted values of R_g for the polymers presently being considered have been calculated using the above constants and values of M_w^B from molecular characterization, and are listed in *Table 2*. Also included are results obtained by Richards and Thomason[15] on block polystyrene. The immediately apparent result is that labelled block chains in samples $SB_d1/SB1$ and DSI-1 assume conformations having radii of gyration equivalent to those of the corresponding homopolymers, while labelled chains in sample $SB_d3/SB7$ exhibit an apparently larger radius of gyration than would a homopolymer counterpart.

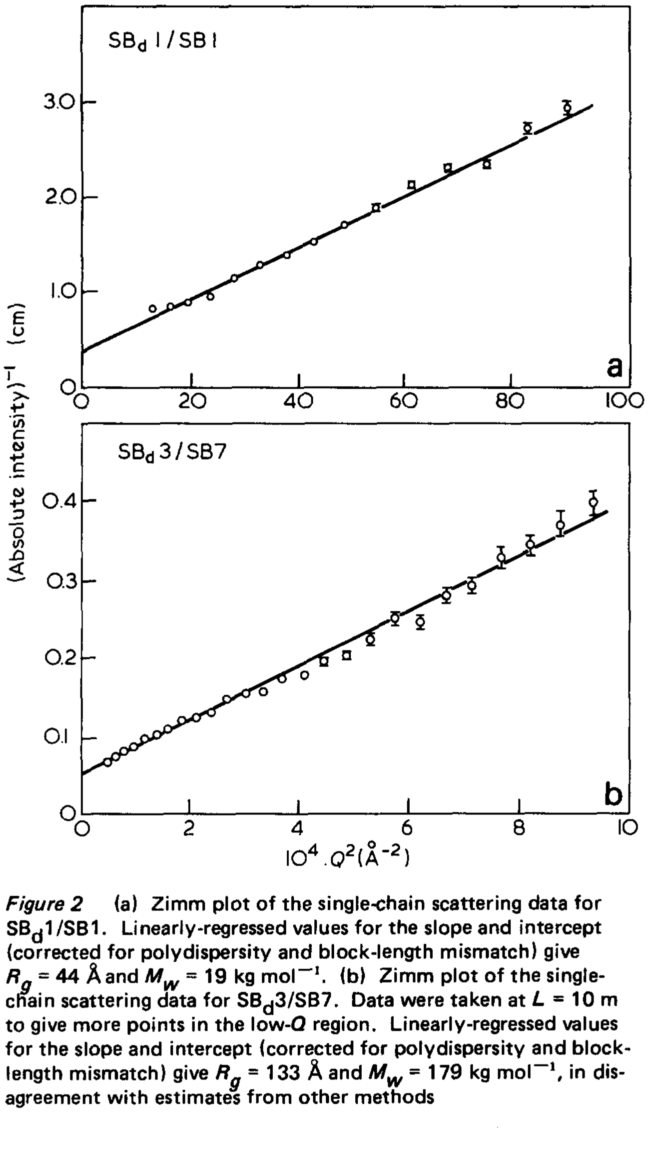

Figure 2 (a) Zimm plot of the single-chain scattering data for $SB_d1/SB1$. Linearly-regressed values for the slope and intercept (corrected for polydispersity and block-length mismatch) give $R_g = 44$ Å and $M_w = 19$ kg mol^{-1}. (b) Zimm plot of the single-chain scattering data for $SB_d3/SB7$. Data were taken at $L = 10$ m to give more points in the low-Q region. Linearly-regressed values for the slope and intercept (corrected for polydispersity and block-length mismatch) give $R_g = 133$ Å and $M_w = 179$ kg mol^{-1}, in disagreement with estimates from other methods

Due to instrumental limitations, most of our scattering data lie outside the $R_gQ < 1$ regime in which the approximation used in extracting R_g from the Zimm plot is valid. To check the reliability of these results, we have used a least-squares routine to fit the full Debye function (equation (2)) directly to the corrected data. The resulting curves are shown in *Figure 3* and the values of R_g^w obtained are listed in *Table 2*. The result for $SB_d1/SB1$ is in good agreement with both the value obtained from the Zimm plot and the homopolymer value calculated from constants quoted above. The result for $SB_d3/SB7$, however, is lower than the Zimm-plot value by about twice the average discrepancy found by Tangari *et al.*[13] (note that it is still about 35% higher than the homopolymer R_g). Inspection of *Figure 3b* shows that the least-squares fit has produced a curve which does not reproduce the data well at low Q; this failure (especially in combination with the other discrepancies) suggests that the assumption of independent chains used in deriving the Debye model is not valid for $SB_d3/SB7$.

The calculation of M_w from scattering data also involves the assumption that labelled polymer chains are randomly distributed within the sample. In practice it has been shown that this measurement is very sensitive to the degree of dispersion of single chains. Schelten *et al.*[24] demonstrated that in crystalline polyethylene both the apparent molecular weight and R_g correlated directly with the number of labelled chains diffracting cooperatively in a cluster. It is apparent from *Table 2* that a virtually statistical placement of labelled chains has

Table 2 Comparison of scattering results

	R_g^w (Å)			M_w^B (kg mol^{-1})		R_{sphere} (Å)	
Sample	Homopolymer value[b]	SANS (Zimm)	SANS (Debye)	Molecular characterization	SANS	Calculated[e]	Observed[f]
DSI–1[a]	40	40	–	21[c]	26	–	(130)
$SB_d1/SB1$	44	44	46	14[d]	19	131	119
$SB_d3/SB7$	86	133	114	51[d]	179	380	218

[a] Results of Richards and Thomason[15]
[b] Calculated from equation 9 and constants given in the text
[c] Molecular weight of the styrene block, determined[15] by g.p.c.
[d] Determined by HPSEC and u.v. absorption[3]
[e] Helfand and Wasserman[26]
[f] Mean radius of spherical microdomains, taken as the weighted average of SANS results for the pure components

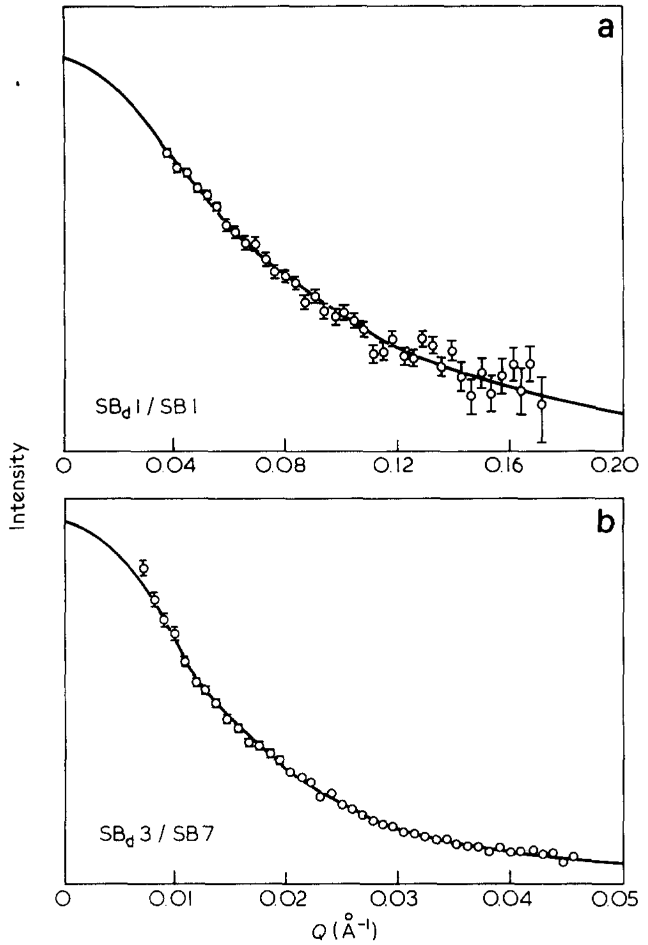

Figure 3 SANS data for SB$_d$1/SB1 plotted with a Debye function (equation 2) fit to the data with a least-squares routine. The value of R_g obtained was 46 Å. (b) SANS data for SB$_d$3/SB7 plotted with the best-fit Debye function (solid curve) for which the least-square routine gave R_g = 114 Å. Data at low Q descend more steeply than the calculated curve. This failure of a single Debye function to fit the data over the entire Q range is taken as an indication of nonstatistical chain placement in SB$_d$3/SB7

been achieved for sample SB$_d$1/SB1, as evidenced by the agreement of SANS and HPSEC molecular weights. For SB$_d$3/SB7, however, the scattering data overestimate M_w by a factor of 3.5, again indicating the nonrandom nature of chain placement in this sample.

Samples SB$_d$1 and SB1 are essentially in a state of phase equilibrium[1,4], i.e. the spherical domain radii and domain packing, as measured by SANS, are nearly equal to those predicted by Helfand and Wasserman[26] and Leibler[27] respectively. Reported polystyrene spherical domain dimensions are also consistently in agreement with equilibrium theory. The agreement between the R_g values in the equilibrium spheres and in the bulk homopolymers probably results from the correlation of two effects which operate to expand and collapse the chain dimensions respectively. Firstly, confining the chain to a domain tends to reduce the R_g of the molecule, as expanded configurations which would cross domain boundaries are excluded. Thus Wignall *et al.*[25] observed a smaller R_g than in the homopolymer for polyethylene molecules dispersed in polyethylene domains in an incompatible blend of polyethylene and polypropylene. In this case the reduction was not marked, as the domain dimensions were much larger than R_g. However, for sample SB$_d$1/SB1, the domain dimensions are of the same order as R_g and this effect should be more pronounced. A second effect tends to expand the chain, since placement of the block joint at the domain surface excludes configurations crossing the domain wall. These two opposing effects apparently cancel for sample SB$_d$1/SB1, giving an overall R_g similar to that of an equivalent homopolymer.

The marked discrepancy between SANS and HPSEC molecular weights for sample SB$_d$3/SB7 indicates that a statistical dispersion of labelled molecules was not achieved, and therefore the measured R_g cannot be interpreted as characteristic of an individual labelled chain. It seems unlikely that the cause of the nonrandom placement of labelled chains in SB$_d$3/SB7 should arise in the interfacial region between domains, as it is known[3] that the width of this region ($\Delta R \simeq 22$ Å is similar for both copolymer samples measured, and thus the fraction of the sphere contained in the interfacial region is actually smaller for sample SB$_d$3/SB7 than for SB$_d$1/SB1, where the placement was essentially statistical. Two important differences between samples SB$_d$1/SB1 and SB$_d$3/SB7 should be considered. Firstly, as reported in separate publications[3,4] the domains found in samples SB$_d$3 and SB7 are markedly smaller than is predicted from theory and exhibit no specific domain packing geometry. Using weighted pure-component SANS values, the domain size in sample SB$_d$3/SB7 is estimated to be $R = 218$ Å, as opposed to the predicted value of 380 Å at equilibrium. This represents a five-fold decrease in sphere volume from equilibrium. The development of smaller, non-equilibrium spheres in bulk is brought about by the presence of fewer chains per domain at the point of phase separation in solution[3,4,28]. This reduction in sphere size will increase the influence of the domain-boundary and joint-placement restrictions of polymer chain conformations. Secondly, the polybutadiene molecular weight in sample SB$_d$3 is 3.6 times that in sample SB$_d$1. The nonrandom distribution of labelled chains in sample SB$_d$3/SB7 may be related to either of these differences.

Segregation or 'clustering' of like species in blends of deuterated (PED) and hydrogenated (PEH) polyethylene has been shown to occur readily[29]. This is brought about by small thermodynamic differences between PED and PEH. While no such experimental data exist for polybutadiene, it would be expected that increasing molecular weight would increase the likelihood of segregation[30] (phase separation). This effect may be further enhanced by the nonequilibrium nature of the domains in sample SB$_d$3/SB7. Clearly, this aspect of the present study warrants further attention.

CONCLUSIONS

This single-chain scattering study has resulted in two significant findings. First, the theory developed by Jahshan and Summerfield[16] and Koberstein[17] concerning the scattering from two-phase systems has been verified, proving that structural scattering can be eliminated by properly labelling a given phase. Second, at equilibrium, block copolymer chains in spherical domains exhibit radii of gyration equal to the corresponding homopolymers. Under the nonequilibrium conditions which frequently occur in solvent-cast block copolymers of high molecular weight, the labelled molecules were found to be nonrandomly distributed in the polybutadiene domains as indicated by anomalous values of M_w and R_g.

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