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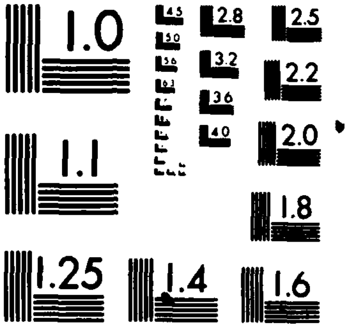

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by

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Calculations utilizing a scattering formalism due to deGennes are compared with previously-reported SANS data from two polystyrene-polybutadiene samples which have been blended with similar diblocks in which the B segment is deuterated. The present conclusion is that both the lower- and higher- molecular-weight samples exhibit scattering in excess of that predicted, presumably due to clustering of the labelled chains or some other chain-length dependent phenomenon.

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INTRODUCTION

Bates and coworkers recently reported a study[1] of polybutadiene chain characteristics in samples of polystyrene-polybutadiene block copolymers SB. In these samples, spherical microdomains of polybutadiene are formed when the material is cast from solution. A diblock in which the polybutadiene segment was completely deuterated (SB_d) was blended with a normal (hydrogenous) diblock of similar molecular weight. The B_d/B ratio was chosen so that the neutron scattering-length density of the B domains was matched with that of the S matrix; thus, when small-angle neutron scattering (SANS) spectra of these samples were acquired, structural scattering from the quasicrystalline lattice of microdomains was eliminated, leaving scattering from the labeled B_d chains (confined within the spherical B regions) as the dominant mechanism. The SANS data were used to derive an apparent weight-average polymerization index N_w and a radius of gyration R_g for each of two samples, one of relatively low molecular weight ($SB_d1/SB1$) and one of relatively high molecular weight ($SB_d3/SB7$). The results were compared with values of N_w obtained from more direct techniques[2] (gel permeation chromatography and UV absorption) and values of R_g appropriate for bulk polybutadiene of given N_w. For $SB_d1/SB1$, the SANS value for N_w was found to be within 40 per cent of the GPC/UV value, a result which was taken to indicate substantial agreement. For the higher molecular-weight sample, $SB_d3/SB7$, N_w from the SANS analysis was nearly 4 times that from the conventional characterization. This increase (reflecting an increased level of scattering) was attributed[1] to "clustering" (isotopic phase separation) of the labeled B_d chains within the polybutadiene microdomains.

Since the appearance of the above report, Bates and coworkers have published a number of illuminating studies of the nonideal behavior of mixtures of hydrogenous and deuterated polymers[3-5]. These studies have demonstrated the usefulness of the mean-field random-phase formalism due to de Gennes[6] in describing the SANS results from isotopic mixtures of polymers. This treatment predicts increased scattering due to random fluctuations in isotopic composition even in the absence of isotopic phase separation. One is then moved to ask whether the mean-field formalism will account for the increased scattering from the SB_d/SB samples previously studied. This communication reports calculations carried out in order to answer this question.

EXPERIMENTAL

The SANS data used in this reconsideration are the the same as those previously reported[1]. They were acquired on the 30-m instrument at the National Center for Small-Angle Scattering Research at the Oak Ridge National Laboratory. Since the scattering patterns were isotropic, results were radially averaged and converted to absolute intensities (cm^{-1}) via calibration of the instrument by secondary standards[7]. The incoherent scattering correction I_{inc} was determined by running a sample of polystyrene and fitting the results to an equation linear in Q (Q is the momentum transfer, equal to $4\pi\lambda^{-1} \sin \theta$, where λ, the neutron wavelength, is 4.75 Å, and θ is half the scattering angle).

CALCULATIONS

In the original study[1], the observed intensities were reduced to coherent scattering intensities by subtracting the incoherent contribution:

$$I_{coh}(Q) = I_{obs}(Q) - I_{inc}(Q) \tag{1}$$

The resulting coherent intensities were used to determine the parameters I_0 and R_g in a Debye function fit to the data by means of a least-squares routine.

$$I_{coh}(Q) = I_0[2R_g^{-4}Q^{-4}(R_g^2Q^2 - 1 + e^{-R_g^2Q^2})] = I_0D \tag{2}$$

I_0, the coherent scattering intensity at Q = 0, is related to N_w as follows:

$$I_0 = \frac{(a_H - a_D)^2}{v_{seg}} X(1 - X)\phi_B N_w \tag{3}$$

where a_H and a_D are the coherent scattering amplitudes of the normal and deuterated repeat units, v_{seg} the volume of a segment of the polymer chain, X the volume fraction of labeled chains in the B domains, and ϕ_B the volume fraction of B domains in the SB sample. For polybutadiene, $a_H = 0.412 \times 10^{-12}$ cm, $a_D = 6.662 \times 10^{-12}$ cm and $v_{seg} = 1.009 \times 10^{-22}$ cm^3. The samples studied here have X = 0.16, and $\phi_B = 0.1414$ (SB$_d$1/SB1) or 0.113 (SB$_d$3/SB7).

De Gennes[6] presents the results of his mean-field calculation in terms of the inverse of a correlation function S(Q):

$$S^{-1}(Q) = [N_1XD_1(R_{g1}, Q)]^{-1} + [N_2(1 - X)D_2(R_{g2}, Q)]^{-1} - 2\chi \tag{4}$$

Here N_1, R_{g1} and N_2, R_{g2} are the weight-average polymerization indices and radii of gyration of the labeled and normal polymers, and D_1, D_2 are Debye functions without the I_0 as indicated in Equation 2. The Flory parameter χ characterizes the interaction between repeat units of labeled and unlabeled chains; its value for polybutadiene at 296 K has been reported[2] to be 8.7×10^{-4}. Coherent scattering intensity $I_{coh}(Q)$ in our SB samples is simply related to S(Q):

$$I_{coh}(Q) = \frac{(a_H - a_D)^2}{v_{seg}} \phi_B S(Q) \tag{5}$$

For $\chi = 0$ and $N_1 = N_2$, $R_{g1} = R_{g2}$, Equation 5 can be shown to be equivalent to the single-Debye model specified by Equations 2 and 3.

Results for the lower molecular-weight sample, $SB_d1/SB1$, are shown in Figure 1a. As indicated in the original study[1], a single Debye function with *the fitted SANS parameters (N_w = 351, R_g = 46 Å) reproduces the observed* scattering almost exactly. A calculation based on Equations 4 and 5 with GPC/UV parameters (N_1, N_2 = 257, 216; R_{g1}, R_{g2} = 43.6, 40.0 Å) and $\chi = 8.7 \times 10^{-4}$ gives results for which the coherent component at low Q is smaller than the observed values by a factor of about 0.75.

Results for the higher molecular-weight sample, $SB_d3/SB7$, are shown in Figure 1b. As before, a single Debye function with fitted parameters (N_w = 3309, R_g = 114 Å) goes through most of the data points, but now the mean-field calculation with GPC/UV parameters (N_1, N_2 = 935, 1170; R_{g1}, R_{g2} = 83.2, 93.1 Å; $\chi = 8.7 \times 10^{-4}$) gives coherent intensities at low Q which are too small by a factor of 0.38.

CONCLUSIONS

In our earlier report[1] we concluded that the discrepancy for SB$_d$1/SB1 could be explained by uncertainty in our knowledge of the chain length of the polybutadiene block, while the discrepancy for SB$_d$3/SB7 was clearly outside these limits. Since then we have acquired more confidence in the accuracy of our molecular weight measurements (partly due to close agreement between the calculated and observed positions of major structural features in the SANS spectra of unblended SB$_d$1 and SB1), and our present feeling is that SB$_d$1/SB1 exhibits extra scattering, although clearly less of it than SB$_d$3/SB7.

In addition, de Gennes' formulation[6] of the expected scattering in terms of the Flory parameter χ provides a new way of approaching the problem. One can force agreement at low Q by manipulating χ rather than N_1: one finds that the required χ for SB$_d$1/SB1 is 0.0043 (5 times the reported value[3]) and for SB$_d$3/SB7 it is 0.0027 (3 times the reported value). From this point of view, SB$_d$1/SB1 is more anomalous than SB$_d$3/SB7, although in the case of SB$_d$1/SB1, the apparent anomaly is accentuated by the short chain length (the ratio of $\chi^* N_1$ for the two samples, where χ^* takes on the forced values quoted above, is about the same as the ratio of the discrepancy factors for coherent scattering at low Q quoted in the previous section). Thus we conclude that clustering of labeled chains (or some other chain-length-related mechanism) is operating to produce enhanced neutron scattering in both SB$_d$1/SB1 and SB$_d$3/SB7.

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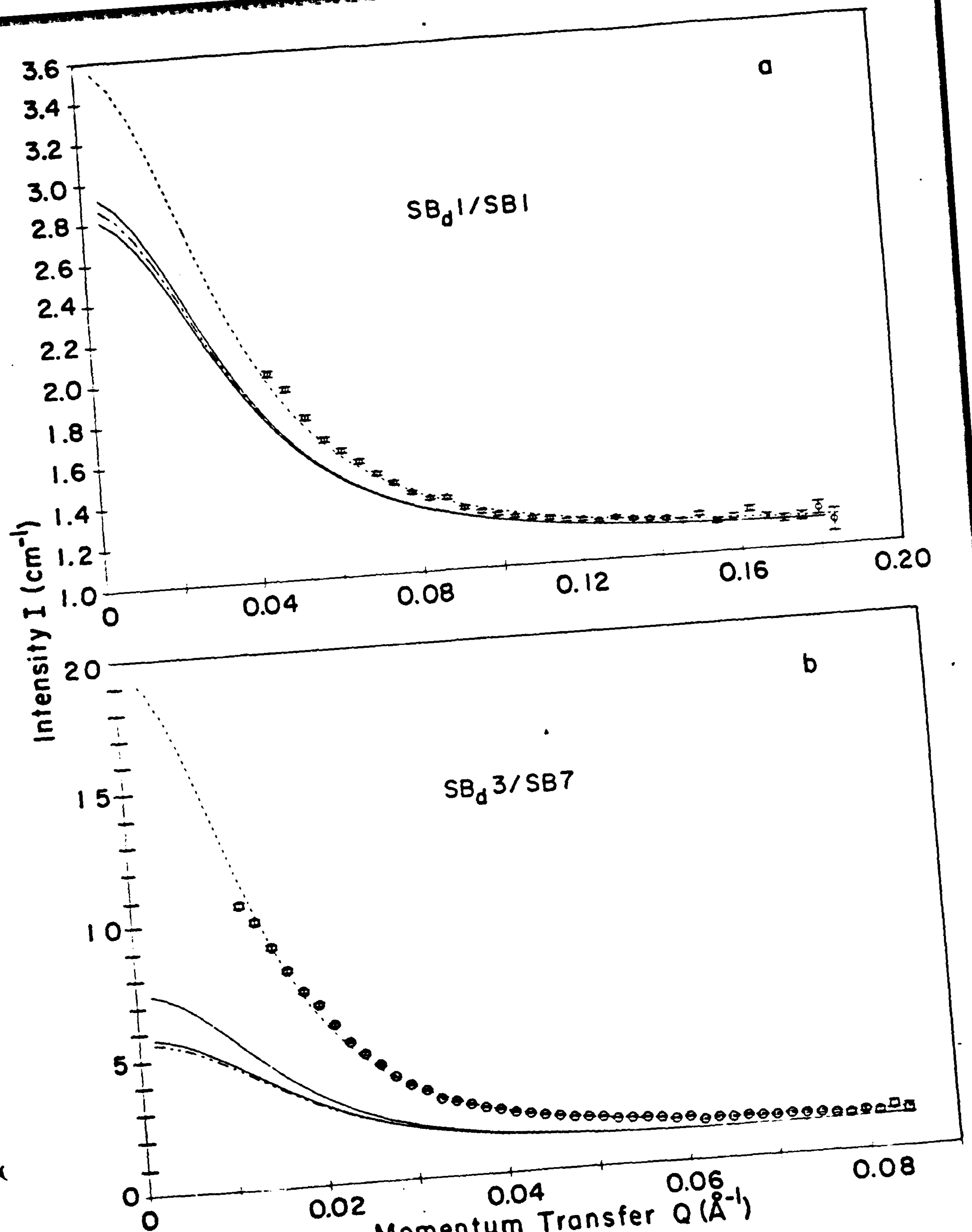
CAPTION FOR THE FIGURE

Fig. 1 (a) SANS data for $SB_d1/SB1$ with calculated curves. Dashed line (---) is the Debye curve fitted to the SANS data ($N_w = 351$, $R_g = 46$ Å); the full curves below the dashed curve represent mean-field calculations (see text) using GPC/UV parameters for N_1, N_2, R_{g1} and R_{g2}. The upper full curve was calculated with $\chi = 8.7 \times 10^{-4}$, the lower full curve with $\chi = 0$, simply to show the effect of varying χ. A calculation (____ .. ____ ..) using a single Debye function with GPC/UV parameters for the labeled chains ($N_w = 257$, $R_g = 43.6$ Å) lies between the mean-field curves. (b) SANS data for $SB_d3/SB7$ with calculated curves (note that both ordinate and abscissa scales are different). Dashed line (---) is the Debye curve fitted to the SANS data ($N_w = 3309$, $R_g = 114$ Å). The full curves are again mean-field calculations using GPC/UV parameters and values for χ of 8.7×10^{-4} and 0. This time the Debye curve using GPC/UV parameters ($N_w = 935$, $R_g = 83.2$ Å) (____ .. ____ ..) is below the zero-χ mean-field curve. In all cases above, the incoherent scattering has been added to the calculated curves to facilitate direct comparison with the experimental data.



a
SB$_d$1/SB1
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
0.04
0.08
0.12
0.16
0.20
Intensity I (cm^{-1})
b
SB$_d$3/SB7
20
15
10
5
0
0
0.02
0.04
0.06
0.08
Momentum Transfer Q (Å^{-1})

Figure 1

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