Influence of Homopolymer on the Correlation Hole in a Homogeneous Diblock Copolymer

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ABSTRACT: A homogeneous, symmetric 1,4-polybutadiene–1,2-polybutadiene diblock copolymer containing a perdeuteriated 1,4-polybutadiene block has been mixed with equal molecular weight 1,2-polybutadiene homopolymer and examined by small-angle neutron scattering (SANS). The undiluted diblock copolymer exhibits a well-defined peak as measured by SANS which derives from the correlation hole effect. Addition of homopolymer initially shifts this peak to smaller scattering wavevectors and subsequently eliminates the correlation hole scattering. These results are in close agreement with the theoretically predicted scattering from homogeneous diblock copolymer–homopolymer mixtures, thus providing a method for determining the Flory–Huggins interaction parameter χ. The composition dependence of χ for the mixtures is found to be equivalent to that previously determined for undiluted diblock copolymer containing the same monomers.

Introduction

Over the last decade our knowledge of the thermodynamics of polymer–polymer mixing has advanced considerably. This progress has been particularly evident in the area of block copolymers and block copolymer–homopolymer mixtures. Perhaps the greatest gains can be found in our understanding of the phase transitions exhibited by these materials.

A survey of the literature indicates that Cohen and Ramos[1] were the first to document a macroscopic phase transition induced by the addition of homopolymer to a homogeneous diblock copolymer. Subsequently, Cohen and Wilfong,[2] Roe and Zin,[3] and Cohen and Torradas[4] observed the formation of micelles or microdomains upon the addition of homopolymer to various homogeneous diblock copolymers. These experimental findings have been paralleled by a number of theoretical developments.

Leibler[5] initiated the quantitative theoretical examination of the microphase separation transition (MST); previous theoretical research on block copolymers had focused on the strongly ordered region of the phase diagram. Using the random phase approximation (RPA) method, previously popularized by de Gennes[6] for dealing with homopolymer mixtures, Leibler derived the scattering structure factor for diblock copolymers in the homogeneous (disordered) state. This prediction is central to our understanding of the MST in that it provides a technique for extracting the thermodynamic segment–segment interaction parameter χ which forms the basis of most theories dealing with polymer–polymer phase behavior. Leibler[7] and co-workers,[8] and others,[9] have also developed theories for predicting the influence of a homopolymer on diblock copolymers near the MST, which seem to qualitatively account for the aforementioned experimental results.

In the last few years there has been a general confirmation of the predicted[10–12] correlation hole in homogeneous diblock copolymers and of the dependence of the small-angle scattering intensity on the product χN where N is the overall degree of polymerization. In a series of papers[11–14] we have reported both the rheological[14] and small-angle neutron scattering[11,12] behavior of a model set of 1,2-polybutadiene–1,4-polybutadiene diblock copolymers near the MST. Several questions have arisen as a result of the SANS study[12] on these polymers. While the scattering from the symmetric ($N_{1,2} = N_{1,4}$) diblock copolymers was found to be in relatively close agreement with the RPA prediction, that obtained from the assymetric samples ($N_{1,2} = 3N_{1,4}$) exhibited a significant amount of scattering in excess of the predicted correlation hole. We also found that the SANS-determined segment–segment interaction parameter depended strongly on composition.

Recently there have been at least three independent, but equivalent, derivations of the small-angle scattering structure factor for homogeneous mixtures of diblock copolymer and homopolymer.[15–17] However, to the best of our knowledge there are no reports of the evaluation of these predictions. As already mentioned, previous studies of block copolymer–homopolymer mixture have focused on systems that undergo a phase transition. In this paper we examine such mixtures under conditions which ensure homogeneity, making use of one of the symmetric homogeneous diblock copolymers studied previously.[12] This provides us with the opportunity to evaluate the homogeneous mixture prediction while concurrently comparing the SANS-determined χ parameter for such mixtures with that obtained from disordered diblock copolymers at the same composition.

Experimental Section

A series of mixtures was prepared from a 1,4-polybutadiene–1,2-polybutadiene diblock copolymer, previously denoted sample BB1,[12] and a 1,2-polybutadiene homopolymer. Both polymers were synthesized by the anionic polymerization technique by use of the previously described procedures.[13] The diblock copolymer consists of a perdeuteriated 1,4-polybutadiene block (53% trans, 36% cis, and 11% vinyl addition) and a normal (hydrogenated) 1,2-polybutadiene (>98% vinyl addition) block. In order to ensure thermodynamic equivalence between the 1,2 block of the diblock copolymer and the 1,2 homopolymer, the later was synthesized under the same conditions as the former. The overall number-average degree of polymerization N_N, polydispersisites N_W/N_N, and diblock copolymer composition $\Phi_{1,4} = N_{1,4}/(N_{1,4} + N_{1,2})$ have been determined by membrane osmometry, high-pressure size-exclusion chromatography (HPSEC), and infrared analysis as described elsewhere.[13] The characterization results are summarized as follows: diblock copolymer (sample BB1) $N_N = 470$, $N_W/N_N = 1.05$, $\Phi_{1,4} = 0.47$; homopolymer $N_N = 460$, $N_W/N_N = 1.04$. We estimate a possible error of approximately 5% and 0.02 in the determinations of N_N and N_W/N_N, respectively. Polymer segment volumes were determined to be $V_{1,4} = 1.00 \times 10^{-22}$ and $V_{1,2} = 1.01 \times 10^{-22}$ cm^3.[12]

Diblock copolymer–homopolymer mixtures were prepared by dissolution of each component in dry deoxygenated toluene, followed by solvent evaporation under inert gas conditions. Small-angle neutron scattering specimens were assembled by squeezing a polymer sample between $^1/_{16}$-in. quartz plates separated by a $^1/_{16}$-in. spacer. This procedure was conducted under vacuum in order to avoid the formation of bubbles and to minimize exposure to oxygen.

Small-angle neutron-scattering data were collected by using the 30-m SANS instrument at the National Center for Small Angle Scattering Research located at Oak Ridge National Laboratory, Oak Ridge, TN. This instrument was calibrated in units of reciprocal centimeters by using the absolute calibration methods described in a separate publication.[18] The presently reported data were collected at room temperature and reduced to the one-di-

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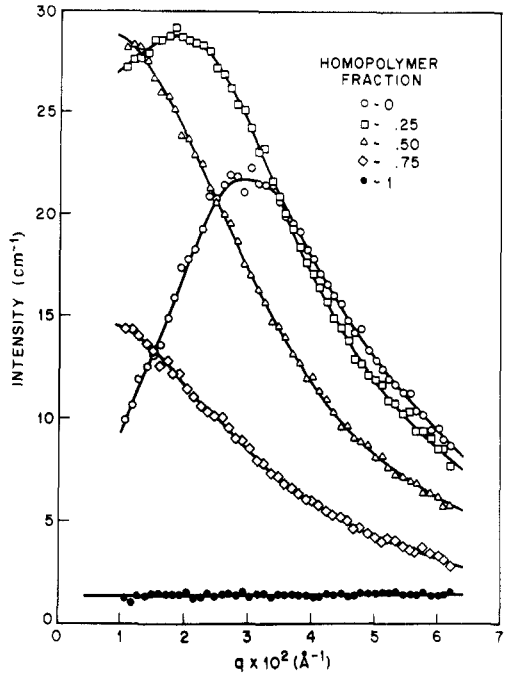

Figure 1. Small-angle neutron scattering from homogeneous mixtures of a perdeuterio-1,4-polybutadiene–1,2-polybutadiene diblock copolymer and 1,2-polybutadiene homopolymer. Open symbols represent coherent scattering while the closed circles correspond to the total scattering which is dominated by incoherent scattering events. The solid lines are guides for the eye.

mensional form of absolute intensity vs. scattering wavevector $q = 4\pi\lambda^{-1} \sin(\theta/2)$ as previously detailed.[12] The incoherent scattering contribution to the total scattering intensity was estimated as the linear combination of the angle-independent intensity obtained from perdeuteriated 1,4-polybutadiene[19] and normal 1,2-polybutadiene homopolymers. This was subtracted from the total intensity of the block copolymer and the mixtures. Although this method does not exactly account for the incoherent scattering intensities, the error involved (<20%) is insignificant in comparison with the coherent scattering intensities we will presently consider.

Results and Analysis

The coherent SANS results for the diblock copolymer and diblock copolymer–homopolymer mixtures containing 25, 50, and 75% by volume 1,2-polybutadiene homopolymer are collectively presented in Figure 1. Also shown in Figure 1 are the incoherent scattering data for the pure homopolymer. The flat featureless form of the homopolymer data demonstrates the absence of void scattering from these polymers over the range of reciprocal space presently under consideration. As indicated by the results depicted in Figure 1, the addition of equal molecular weight homopolymer to the symmetric diblock copolymer initially shifts the correlation hole toward zero angle and subsequently reduces the overall intensity. We will evaluate this behavior on the basis of the current theories regarding the homogeneous state of diblock copolymer–homopolymer mixtures.

In general, the absolute scattering intensity from a homogeneous (single phase or disordered) polymer melt containing two distinct monomers (repeat units) is given by the product of a contrast factor and a structure factor $S(q)$,

$$I(q) = V[(b_A/V_A) - (b_B/V_B)]^2 S(q) \quad (1)$$

where b and V_A refer to the scattering length and volume of monomer A, respectively. We have defined the reference volume to be $V = \Phi_A V_A + \Phi_B V_B$. Owing to the near equivalence of the repeat unit volumes under consideration, it is not necessary to correct the terms appearing in $S(q)$ for volume differences; the associated errors in interpreting $I(q)$ are less than 1%.

There have been at least three independent derivations of the structure factor for homogeneous diblock copolymer–homopolymer mixtures. Leibler and Benoit[15] have made use of the random phase approximation (RPA) method, previously popularized by de Gennes[6] and Leibler[5]; Benoit et al.[16] have extended a general "chain contact" technique to the bulk state, and recently de la Cruz and Sanchez[17] have determined the structure factor for such mixtures based on a path integral approach. All three derivations lead to the same structure factor, which is presented below.

For any combination of A–B diblock copolymer, A homopolymer and B homopolymer, the homogeneous state structure factor has the general form

$$S^{-1}(q) = F(N_{AB},N_A,N_B,\Phi_{AB},\Phi_A,f,a_A,a_B,q) - 2\chi_{AB} \quad (2)$$

where N_i, Φ_i, and a_i represent the weight-average degree of polymerization, volume fraction, and Gausian coil statistical length, respectively, of species i. f corresponds to the composition of the diblock copolymer which is given by the ratio of the number of A monomer units to the total number of monomer units per copolymer chain N_{AB}. χ_{AB} is the Flory–Huggins segment–segment interaction parameter, and $\Phi_{AB} + \Phi_A + \Phi_B = 1$ as a consequence of the incompressibility assumption. For the case of a binary mixture of monodisperse A–B diblock copolymer and A homopolymer ($\Phi_B = 0$),

$$F(N_{AB},N_A,\Phi_{AB},f,a_A,a_B,q) = \frac{(N_A/N_{AB})(1-\Phi_{AB})g(R_A) + \Phi_{AB}g_1(1)}{N_A\Phi_{AB}(1-\Phi_{AB})g_1(f)g_1(1-f) + N_{AB}\Phi_{AB}^2 G_{AB}}$$

$$G_{AB} = g_1(f)g_1(1-f) - \tfrac{1}{4}[g_1(1) - g_1(f) - g_1(1-f)]^2 \quad (3)$$

where

$$g_1(f) = 2[fR_{AB}^2q^2 + e^{-fR_{AB}^2q^2} - 1]/R_{AB}^4q^4 \quad (4)$$

in which R_{AB} is the overall radius of gyration of the diblock copolymer,

$$R_{AB}^2 = (N_{AB}/6)[fa_A^2 + (1-f)a_B^2] \quad (5)$$

and

$$g(x) = 2[x^2q^2 + e^{-x^2q^2} - 1]/x^4q^4 \quad (6)$$

where $R_A^2 = a_A^2N_A/6$ defines the radius of gyration of the homopolymer. In the limit $\Phi_{AB} = 1$, eq 3 reduces to the relationship given by Leibler[7] for undiluted homogeneous diblock copolymer, while the results derived by de Gennes[6] for homogeneous binary polymer mixtures is obtained for $f = 0$. Equations 4 and 6 apply to strictly monodisperse polymers. In order to account for the small degree of polydispersity characterizing the diblock copolymer and homopolymer, $g_1(x)$ and $g(x)$ have been calculated by using the previously described[12] polydispersity corrections, which are based on a Shultz–Zimm distribution of block and overall chain lengths.

In Figure 2 we present the theoretically calculated scattering curves for the diblock (Chart I). the three mixtures. With two exceptions, the parameters used in these calculations are based on molecular characterization (see Experimental Section) or independent estimation and where applicable are the same as were used previously for undiluted diblock copolymers of 1,4- and 1,2-polybutadiene:[12] $b_{1,4} = 6.659 \times 10^{-12}$ cm; $b_{1,2} = 0.413 \times 10^{-12}$ cm; $a_{1,4} = 6.7$ Å; $a_{1,2} = 5.9$ Å. Recently, we have determined the statistical lengths of these polymers directly by SANS and found them to be within experimental error of these

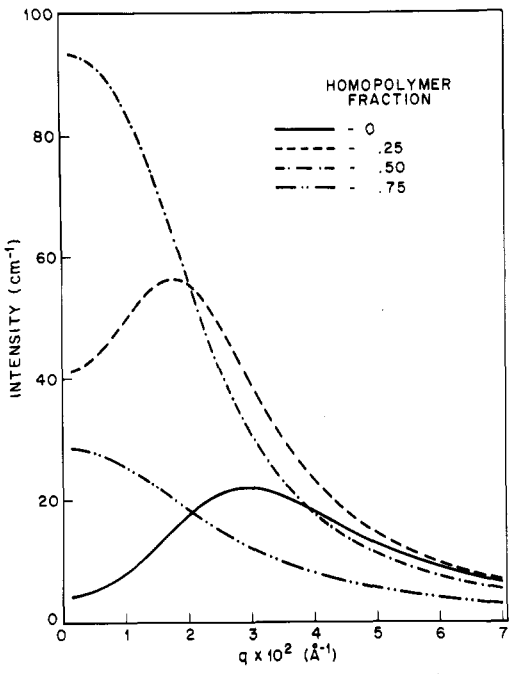

Figure 2. Predicted small-angle neutron scattering intensities for the diblock copolymer–homopolymer mixtures referred to in Figure 1. These calculated results are based on a single segment–segment interaction parameter $\chi_{1,4-1,2} = 0.0106$ and include small polydispersity corrections as described in the text.

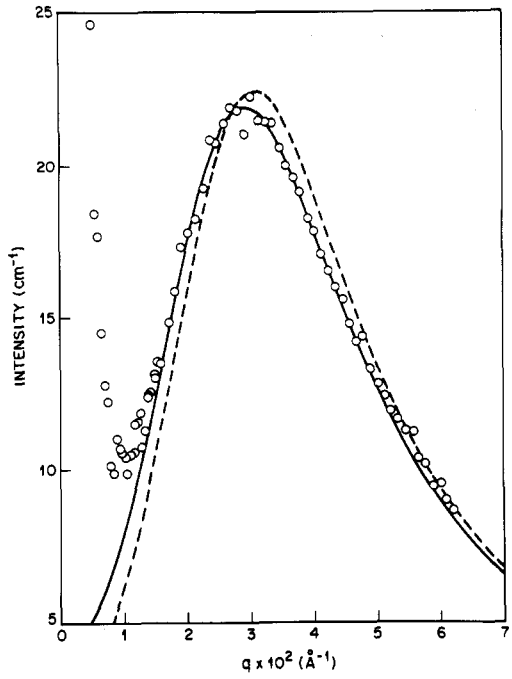

Figure 3. Coherent SANS results for the undiluted diblock copolymer. The dashed line represents the previously[12] reported theoretical prediction for the correlation hole based on $N_W/N_N = 1.05$ and $\chi_{1,4-1,2} = 0.0115$, while the solid curve corresponds to a best fit of the prediction to the data yielding $N_W/N_N = 1.075$ and $\chi_{1,4-1,2} = 0.0106$.

previously estimated values. We have determined the diblock copolymer polydispersity index, $N_W/N_N = 1.075$, and segment–segment interaction parameter, $\chi_{1,4-1,2} = 0.0106$, by fitting the predicted $\Phi_{AB} = 1$ scattering curve to the SANS results for the pure diblock copolymer (see below). The predicted scattering behavior illustrated in Figure 2 qualitatively resembles the experimental results of Figure 1. However, the predicted absolute scattering intensities are greatly overestimated for the mixtures. For example, at $q = 0.01$ Å^{-1} the predicted intensity for the 50% blend exceeds the measured value by about a factor of 3. As discussed below, these results can be understood on the basis of a composition-dependent segment–segment interaction parameter.

In our previous publication describing the SANS results from a series of homogeneous diblock copolymers, the RPA theory of Leibler was evaluated by using only $\chi_{1,4-1,2}$ as an adjustable parameter. The results of that analysis for sample BB1 are shown as a dashed line in Figure 3 along with the SANS data. For the present report we have reevaluated these data using *both* the polydispersity and $\chi_{1,4-1,2}$ as free parameters. As shown before,[12] varying χ produces a change in the predicted intensity without influencing the peak position. On the other hand, modifying the polydispersity index shifts the predicted peak position and modifies the intensity. In order to most quantitatively assess the SANS results from the mixtures, we have adjusted the polydispersity index for the diblock copolymer so as to bring the predicted peak position into agreement with the SANS data. Subsequently, the interaction parameter has been varied to obtain a best fit between theory and experiment. The results of this fitting procedure, given by the solid curve in Figure 3, are $N_W/N_N = 1.075$ and $\chi_{1,4-1,2} = 0.0106$. This SANS-determined polydispersity index is slightly higher than that estimated by high-pressure size-exclusion chromatography. It should be noted, however, that the neutron scattering experiment is sensitive to the distribution in block lengths while the HPSEC provides a measure of the overall diblock copolymer polydispersity. For example, a monodisperse (single overall chain length) diblock copolymer with a distribution in composition f would yield a polydispersity index of unity based on an HPSEC measurement, while an evaluation of the SANS intensities from such a specimen would lead to a value greater than unity. Therefore, we make use of the SANS-determined diblock copolymer polydispersity index in evaluating the scattering results from the mixtures.

Our analysis of the small-angle neutron scattering from the diblock copolymer–homopolymer mixtures is presented in Figures 4–6. In each case the curves have been calculated on the basis of polydispersity-corrected version of eq 3, with $\chi_{1,4-1,2}$ as an adjustable parameters; all other molecular parameters have been fixed at the previously specified values. The dashed curves in Figures 4–6 indicate the sensitivity of the theoretical predictions to variations in $\chi_{1,4-1,2}$, while the solid curves have been computed by using the quoted estimate for the segment–segment interaction parameter. A comparison of the interaction parameters obtained from the mixtures, long with the corresponding values determined previously[12] for undiluted diblock copolymers is presented as a function of the volume fraction of 1,4-polybutadiene in Figure 7. The errors in $\chi_{1,4-1,2}$ indicated by the vertical bars in Figure 7 represent an estimate of the combined effects of the uncertainties in the degrees of polymerization, statistical segment lengths, sample thicknesses, SANS intensity calibration, and overall fit between theory and SANS data.

Discussion and Conclusions

The small-angle neutron-scattering results presented in Figures 1 and 4–6 clearly indicate that the addition of homopolymer to a homogeneous diblock copolymer melt produces a predictable shift in the location of the correlation hole. As in the case of undiluted diblock copolymer, fitting the RPA[15] or other equivalent theories[16,17] to the SANS results from such mixtures provides a convenient method for determining the thermodynamic Flory–Huggins interaction parameter. An important conclusion of

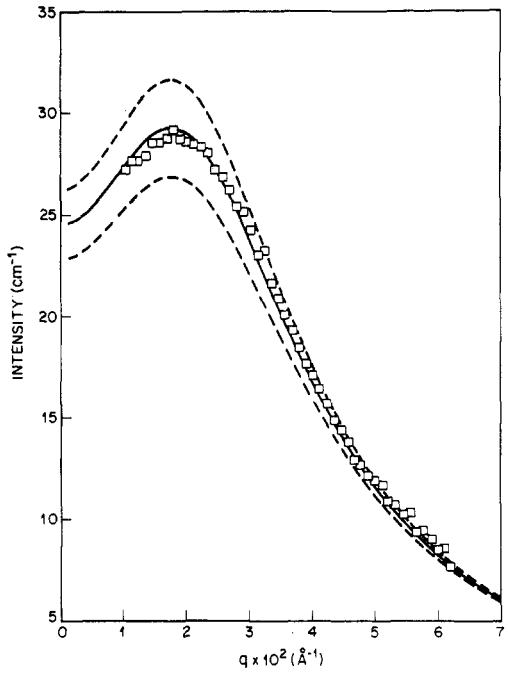

Figure 4. Coherent SANS results from the diblock copolymer–homopolymer mixture containing 75% by volume diblock copolymer. The curves have been calculated by using the predicted structure factor for different values of the segment–segment interaction parameter: solid and upper and lower dashed curves correspond to $\chi_{1,4\text{-}1,2}$ = 0.0074, 0.0080, and 0.0067.

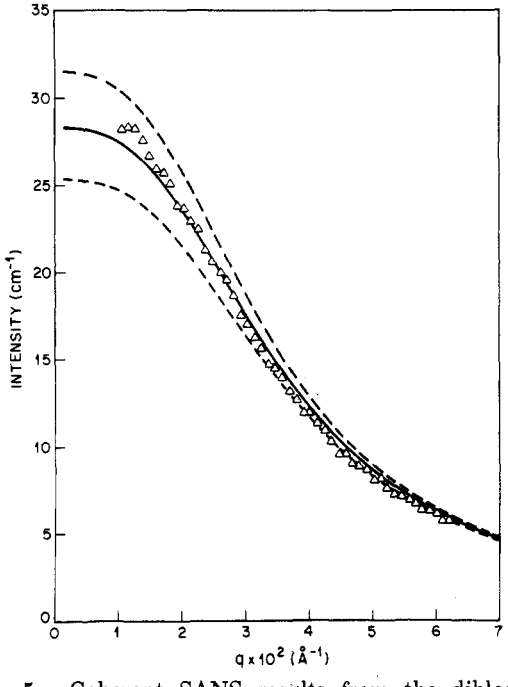

Figure 5. Coherent SANS results from the diblock copolymer–homopolymer mixture containing 50% by volume diblock copolymer. The curves have been calculated by using the predicted structure factor for different values of the segment–segment interaction parameter: solid and upper and lower dashed curves correspond to $\chi_{1,4\text{-}1,2}$ = 0.0058, 0.0065, and 0.0050.

this work is that the SANS-determined segment–segment interaction parameter obtained from a homogeneous diblock copolymer is equivalent to that extracted from a homogeneous diblock copolymer–homopolymer mixture, as illustrated in Figure 7.

A close examination of Figures 5 and 6 reveals that the predictions for the Φ_{AB} = 0.5 and 0.25 mixtures do not quantitatively account for the entire range of the SANS

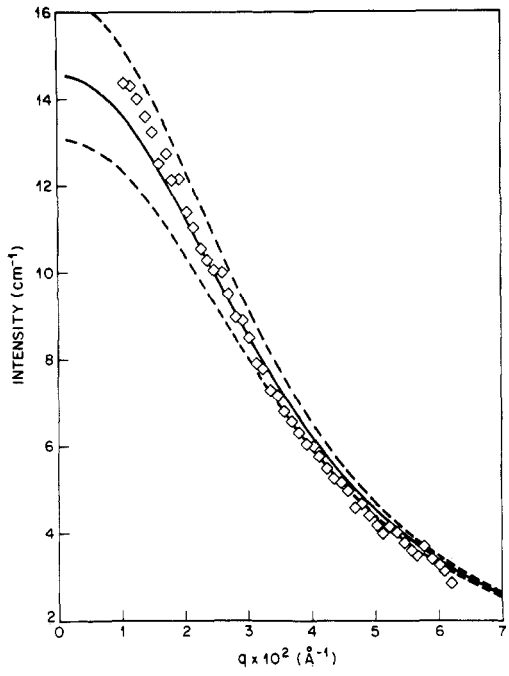

Figure 6. Coherent SANS results from the diblock copolymer–homopolymer mixture containing 25% by volume diblock copolymer. The curves have been calculated by using the predicted structure factor for different values of the segment–segment interaction parameter: solid and upper and lower dashed curves correspond to $\chi_{1,4\text{-}1,2}$ = 0.0040, 0.0055, and 0.0025.

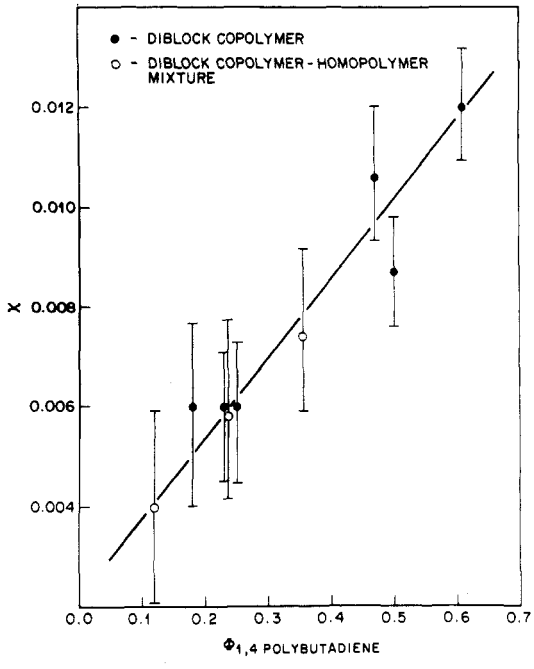

Figure 7. Comparison of the segment–segment interaction parameter for perdeuterio-1,4-polybutadiene and 1,2-polybutadiene obtained by small-angle neutron scattering from homogeneous diblock copolymers and diblock copolymer–homopolymer mixtures. The error bars reflect the combined estimated uncertainties in the degrees of polymerization, statistical segment lengths, sample thicknesses, SANS intensity calibration, and overall fit between theory and SANS data.

data. At the higher values of the scattering wavevector the calculated intensity tends to slightly overestimate the experimental results while at lower q the reverse is found. Such a discrepancy is not apparent in the results for the Φ_{AB} = 0.75 mixture (Figure 4). The undiluted diblock copolymers we have previously studied[12] exhibited a similar behavior at large q, for volume fractions of 1,4-poly-

butadiene near that of the 50% mixture. This observation may reflect on error in estimating the statistical segment lengths for these polymers. For large scattering wavevectors, $qRg \gg 1$, the intensity depends solely on the statistical segment lengths and composition. Thus, if the estimated statistical lengths were in slight error or if either or both were dependent on composition—as is the segment-segment interaction parameter—we would expect to observe a change in the agreement between theory and experiment with varying composition. However, it must be emphasized that this higher q disparity represents less than a 5% difference between the predicted and measured intensities, which is within the combined uncertainties in sample thickness and intensity calibration. Therefore, we can draw no firm conclusions regarding this point.

In our previous investigation of homogeneous diblock copolymer we also found a significant amount of scattering intensity at $q < q^*$ where q^* is the location of the scattering peak due to the correlation hole. This anomalous scattering was most evident in the highest molecular weight sample with a composition of 25% 1,4-polybutadiene (sample BB5). To a lesser extent such anomalous scattering is also apparent in the diblock copolymer presently under consideration (sample BB1) for $q < 0.01$ Å^{-1} as seen in Figure 3. One of the objectives of this study was to determine whether small amounts of homopolymer, always generated to some extent in block copolymer synthesis, could be responsible for this unexpected component of the SANS intensity. Clearly, the general agreement between the predicted and experimentally determined influence of homopolymer on the correlation hole rules out such a possibility. While there does appear to be some degree of spurious scattering present in the $\Phi_{AB} = 0.5$ and $\Phi_{AB} = 0.25$ mixtures (Figures 5 and 6) at low q, this is at least 2 orders of magnitude less than that found in diblock copolymer BB5. This spurious (excess) intensity seen at low q most likely has the same origins as that for the diblock copolymer (Figure 3), although we have no definitive explanation for such scattering in either the block copolymers or mixtures. Regardless of its origin, this minor unexplained feature does not significantly detract from the overall consistency we find between the predicted and observed SANS behavior for homogeneous diblock copolymer–homopolymer mixtures.

Summary

A set of binary homogeneous diblock copolymer–homopolymer mixtures has been examined by small-angle neutron scattering (SANS). The addition of equal molecular weight 1,2-polybutadiene homopolymer to a disordered ($\chi N = 5.2$), symmetric 1,4-polybutadiene–1,2-polybutadiene diblock copolymer produces a predictable[15,17] shift and subsequent disappearance of the correlation hole with increasing homopolymer concentration. The SANS intensity is sensitive to the magnitude of the Flory–Huggins parameter χ. Fitting the theoretical scattering function to the SANS data by adjustment of χ yields the same segment–segment interaction parameters that have previously been determined from undiluted diblock copolymers of similar composition. Increasing the volume fraction of 1,4-polybutadiene between 0.1 and 0.6 results in a 3-fold increase in the measured value of χ.

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Registry No. Polybutadiene, 9003-17-2; neutron, 12586-31-1.

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