Application of the Random Phase Approximation to Styrene–Isoprene Diblock Copolymers in Solution

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ABSTRACT: The essential aspects of the random-phase approximation applied to homogenous melts of diblock copolymers are reviewed. Small-angle neutron scattering has been used to examine cyclohexane solutions of deuteriostyrene–isoprene linear block copolymers with a range of concentrations and over a range of temperatures (294–413 K). The data were analyzed by nonlinear least-squares fitting of the random-phase approximation expression to the scattering profiles. For copolymers with spherical styrene domains in the microphase-separated state the resultant variation of the interaction parameter with temperature was in good agreement with that obtained by other methods. For a system that produces cylindrical domains on microphase separation, anisotropic scattering was observed and the temperature dependence of the interaction parameter was found to differ depending on which detection plane was used. However, this had little influence on the phase diagram constructed using these interaction parameter equations and interpolated spinodal temperatures.

Introduction

Due to the molecular connectivity between constituent block in block copolymers, macroscopic phase separation of the chemically distinct components is prevented. Microphase separation takes place in the solid state, leading to domains of regular morphology with colloidal dimensions being dispersed throughout the matrix formed by the constituent present in excess.

The domains are arranged with considerable long-range order, and the nature and types of ordering depends on the domain morphology (spherical, cylindrical, or lamellar). The structure of such block copolymers (mainly styrene–diene types) has been extensively investigated over a number of years using small-angle X-ray scattering (SAXS),[1] transmission electron microscopy,[2,3] and small-angle neutron scattering (SANS).[4] Equilibrium statistical thermodynamic descriptions of this state have been provided by the work of Meier[5] and Helfand,[6] while the macrolattice formed has been described by paracrystalline modifications[7,8] of simple crystalline lattices.

Following the application of the random-phase approximation (RPA) by de Gennes to homogeneous homopolymer mixtures,[9] Leibler[10] used this technique to describe homogeneous melts of linear diblock copolymers. By this method it is possible to predict the nature of the phase transition to the ordered state and moreover the morphology of that ordered state depending on the composition of the copolymer. This has been extended to other copolymer types (grafts, stars, etc.) by Olvera de la Cruz and Sanchez,[11] and detailed calculations for linear block copolymers and their mixtures with homopolymer have been provided by Mori et al.[12] Apart from the composition, the other parameter that completely describes the equilibrium thermodynamic state of the block copolymers is χN, the product of the Flory–Huggins interaction parameter, χ, and the total degree of polymerization of the block copolymer, N. In particular, these theories provide expressions for the scattering law of the copolymers in the homogeneous melt. Improvements to the original Leibler theory have been recently presented by Ohta and Kawasaki[13] and Fredrickson and Helfand.[14] Extensions have been made by Benoit et al.[24] and Fredrickson and Leibler.[25]

In sufficiently concentrated solutions, the ordered microphase-separated structures persist over a reasonable temperature range. Where the solvent is thermodynamically good for both blocks, the concentration of copolymer needed to observe ordered states is relatively high, but if the solvent is selective for only one component, the concentration is considerably reduced. Typically, in such solvents, ordered phases may be observed for copolymer volume fractions greater than 0.1. Hashimoto and co-workers[15-18] have thoroughly investigated the concentration and temperature dependence of the interdomain distance and domain size of styrene–isoprene diblock copolymers in a variety of solvents. Similar to the undiluted block copolymers, the solutions transform to a homogeneous disordered state on heating above a microphase-separation temperature (T_{MST}). We discuss here the application of Leibler's RPA theory to concentrated solutions of two styrene–isoprene linear diblock copolymers. The aims of this work were the following: to evaluate the scope of SANS for such studies; to investigate the applicability of the RPA to such solutions; to evaluate χ for the copolymers.

Theoretical Background

The phase state of a polymer system may be described by an order parameter, $\psi(\mathbf{r})$, defined by

$$\psi(\mathbf{r}) = \langle (1-x)\rho_{\mathrm{A}}(\mathbf{r}) - x\rho_{\mathrm{B}}(\mathbf{r}) \rangle \tag{1}$$

$$\psi(\mathbf{r}) = \langle \rho_{\mathrm{A}}(\mathbf{r}) - x \rangle \tag{2}$$

where $\rho_i(\mathbf{r})$ is the local number density of monomer species i divided by the average density of all monomer units.

In the single-phase state $\psi(\mathbf{r}) = 0$, and the Fourier transform of the density–density correlation function written in terms of $\psi(\mathbf{r})$ describes the scattering law for the polymer systems; i.e.

$$S(Q) \propto \langle |\psi(Q)|^2 \rangle \tag{3}$$

with the scattering vector, Q, $=(4\pi/\lambda)\sin\theta$ for radiation

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wavelength and scattering angle 2θ.

This equation was solved by Leibler[10] using RPA theory to predict the response of the homogeneous system to external perturbations. The general equation obtained was

$$S(Q) \propto [(U(Q)/W(Q)) - 2\chi]^{-1} \tag{4}$$

where $U(Q)$ is the sum of Fourier transforms of the different density–density correlation functions in the system and $W(Q)$ is the determinant of these same terms. Equation 4 was solved for homopolymers by de Gennes and the detailed equation for diblock copolymers obtained by Leibler[10] is

$$S(Q) \propto N/(F(u) - 2\chi N) \tag{5}$$

where

$$N = N_{\mathrm{A}} + N_{\mathrm{B}} \qquad \text{for a diblock copolymer}$$

$$F(u) = g_{\mathrm{D}}(i,u)/(g_{\mathrm{D}}(x,u) - g_{\mathrm{D}}(1-x) - {}^{1}/_{4}[g_{\mathrm{D}}(1,u) - g_{\mathrm{D}}(x,u) - g_{\mathrm{D}}(1-x,u)]^{2}) \tag{6}$$

with

$$g_{\mathrm{D}}(x,u) = (2/u^{2})\,(xu + \exp(-ux) - 1) \tag{7}$$

Equation 5 predicts a radically different scattering law for symmetric block copolymers compared to that for an equivalent mixture of homopolymers. In particular, the scattering law obtained for block copolymers has a maximum at a finite value of Q.

In both cases, the scattering law is strongly dependent on the value of χN. As χN increases, the magnitude of $S(Q)$ increases rapidly, becoming divergent when the spinodal point is passed. This behavior can be used to characterize the spinodal value $(\chi N)_{\mathrm{s}}$ at the scattering vector where the intensity is a maximum, $Q_{\max}$, and then at the spinodal point $I(Q_{\max})^{-1} = 0$; hence for a diblock copolymer

$$F(u) = 2(\chi N)_{\mathrm{s}} \tag{8}$$

For a linear diblock copolymer, at the critical point of the phase diagram

$$(\chi N)_{\mathrm{s}} = 10.495 \tag{9}$$

From the value of $Q_{\max}$, the radius of gyration of the block copolymer can be calculated since

$$R_{\mathrm{g}} \simeq 2/Q_{\max} \tag{10}$$

and it should be noted that $Q_{\max}$ does not alter as χN increases.

As originally set out by Leibler,[10] the RPA theory pertains to a weak segregation limit; i.e., the order parameter, $\psi(r)$, changes smoothly over one wavelength of the concentration fluctuations and there are no sharp interfaces between the two components. The theory has little similarity with the strong segregation theories of Helfand[6] and Ohta and Kawasaki.[13] Leibler's theory apportions the significant effects in the homogeneous melts to the concentration fluctuations with wave vectors $=Q_{\max}$. However, he points out that contributions from fluctuations with different wave vectors can seriously modify the nature of the phase transition. Such corrections have been described by Fredickson and Helfand.[14] They lead to a modified scattering law and moreover the expression for $(\chi N)_{\mathrm{c}}$ is modified to

$$(\chi N)_{\mathrm{c}} = 10.495 + 41.022N^{-1/3} \tag{11}$$

For the systems for which we present results here, namely styrene–isoprene diblock copolymers in cyclohexane solution, we retain the original Leibler theory, since the presence of solvent will lead to a smooth variation in monomer density over a concentration fluctuation wavelength; i.e., weak segregation prevails.

Table I
Composition, Number Average Molecular Weight, and Polydispersity of Diblock Copolymer

specimen	weight fraction of deuteriostyrene	M_{n}, 10^{3} g mol^{-1}	$M_{\mathrm{w}}/M_{\mathrm{n}}$
S	0.189	82.34	1.05
C	0.380	82.30	1.03

Table II
Scattering Length Density of Components of Block Copolymer Solutions

component	ρ, 10^{10} cm^{-2}
deuteriostyrene	6.09
isoprene	0.29
deuteriocyclohexane	7.48
cyclohexane	−0.33

Experimental Section

Copolymers. Linear diblock copolymers of deuteriostyrene (DS) and isoprene (I) were prepared by anionic polymerization under high vacuum. Both monomers were purified by prolonged stirring over calcium hydride and repeated freeze–thaw cycles. Shortly before use, each monomer was prepolymerized to remove the last traces of polar impurities, and the desired amount immediately distilled into the reaction flask. Polymerization of the DS was initiated by injecting a known quantity of *n*-butyllithium; after 4 h the required quantity of I was added and the reaction left overnight. Benzene was used as the solvent, and all polymerizations were carried out at ambient temperature. Degassed methanol was injected to terminte the polymerization and the polymer isolated by pouring the solution into a cooled, well-stirred large volume of methanol containing a trace of hydrochloric acid. The copolymers were dried under vacuum and stored in the refrigerator until required.

Compositional analysis was performed by UV spectrometry using the wavelengths 262 and 268 nm. Molecular weights were determined by osmometry while size-exclusion chromatography was used to ascertain the molecular weight distribution. Table I shows the composition and molecular weights of the copolymers used.

Small-Angle Neutron Scattering (SANS). For SANS experiments, solutions of each of the copolymers were made in cyclohexane. The range of concentrations was from 14% to 77% for copolymer S and from 51% to 71% for copolymer C. Each solution was prepared by weighing the block copolymers into a quartz cell with a 1-mm path length, the required volume of cyclohexane was added, and the contents of the cell were degassed. The quartz cell was then flame sealed and placed in an oven at 353 K for 3 weeks. Periodically the cells were agitated to encourage mixing.

Table II shows the scattering length densities of deuteriostyrene, hydrogeneous isoprene, deuteriocyclohexane, and hydrogeneous cyclohexane.

The noteworthy point is that the scattering length density for isoprene lies between that of the two isotopes of cyclohexane. Consequently, the cyclohexane used to dissolve the copolymers was a mixture of the two isotropes such that the volume fraction of the deuteriocyclohexane was 0.08. The mixture has the same scattering length density as polyisoprene, and hence no scattering contrast was developed between the polyisoprene blocks and the solvents. Consequently, all the excess scattering above the background was due to the polydeuteriostyrene blocks alone.

SANS data (scattered intensity as a function of scattering vector Q) were obtained using the D11 small-angle diffractometer at the Institut Laue-Langevin, France. A neutron wavelength of 10 Å was used. The quartz cells containing the solutions were placed in a massive brass jacket, which was thermostated by the circulation of oil from an external bath through

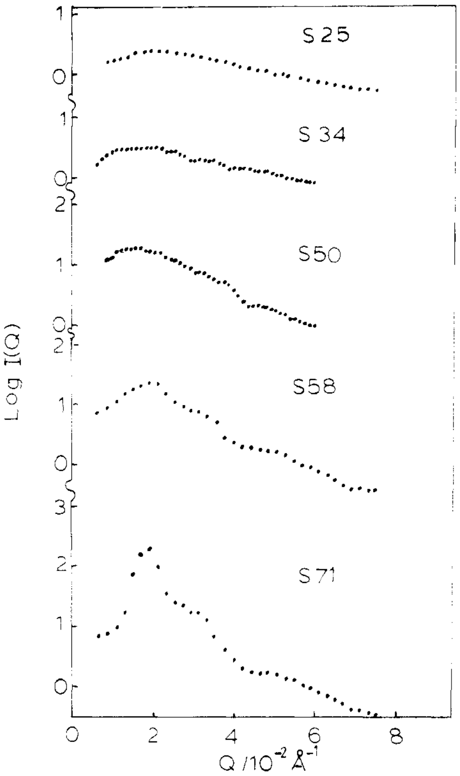

Figure 1. Dependence of small-angle neutron-scattering intensity on solution concentration for copolymer S at 300 K.

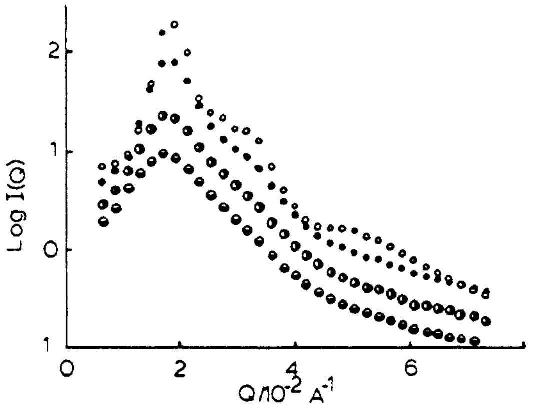

Figure 2. Influence of temperature on scattering intensity for copolymer solution S71: ○, 295 K; ●, 347 K; ◐, 373 K; ⊖, 416 K.

the block. A thermocouple was located close to the position of the quartz cell to monitor the temperature. At each temperature studied, the solution (a volume of ca. 0.1 mL) was equilibrated for at least 20 min before collecting data. A temperature range from ca. 294 K to ca. 413 K was used.

Results and Discussion

Figure 1 shows the dependence of the scattered intensity on block copolymer concentration for copolymer S at temperatures ca. 303 K. At low concentrations only one broad maximum is evident in the scattering; microphase-separated structures appear to be formed at a concentration of 50%. Higher order maxima appear, and the most intense peak at the lowest Q value increases in amplitude and becomes narrower. The temperatures dependence of the scattered intensity for S71 (copolymer S at 71% concentration) is shown in Figure 2 for selected temperatures. As the temperature increases the broad maximum centered at $Q \simeq 0.05$ Å^{-1} disappears first followed by the maxima centered on $Q \simeq 0.03$ Å^{-1}.

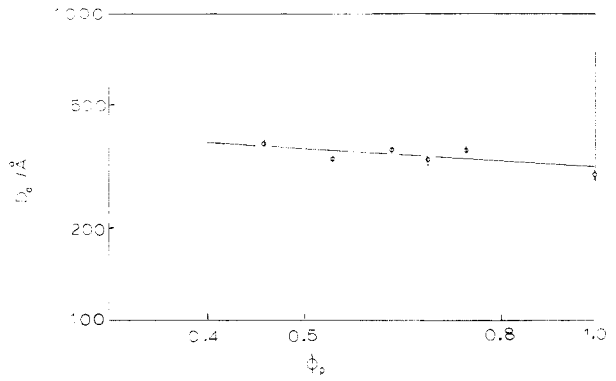

Figure 3. Double-logarithmic plot of nearest-neighbor separation as a function of copolymer S volume fraction in cyclohexane solution at 300 K.

The intensity of the whole scattering profile decreases with increasing temperature, and the width of the remaining broad maximum increases at the same time. The composition of copolymer S is such that one would expect spherical domains of polydeuteriostyrene. A cubic organization of such domains is usually observed in the solid state; however, an insufficient number of scattering maxima are observed to determine the exact nature of the cubic structure. Nonetheless, we are able to make some comparisons with the highly detailed study of Hashimoto on concentrated solutions of styrene–butadiene block copolymers in a selective solvent.[15] The Bragg spacing, D ($\equiv 2\pi/Q_{\max}$), was evaluated by small-angle X-ray scattering in the microphase-separated phase and its dependence on copolymer volume fraction, φ_p, given by

$$D \propto \varphi_p^{-0.14}$$

For copolymer S, D evaluated from SANS data for the cyclohexane solutions is given as a function of φ_p in the double logarithmic plot of Figure 3. A linear least-squares fit to this data gives

$$D = 313\varphi_p^{-0.19}$$

in reasonable agreement with the equation above. However, unlike Hashimoto et al., we do not observe any dependence of the position of maximum intensity on temperature apart from an abrupt displacement to lower Q when the system passes through the order–disorder temperature (T_{MST}) into a molecularly homogeneous phase. There is then no further change in $Q_{\max}$ on increasing the temperature still further.

Block copolymers with cylindrical domains are ordered to a much higher degree than those with spherical domains. This is reflected in our data, of which two scattering profiles are shown in Figure 4 for C71 (71% solution of copolymer C). At the lowest temperature of 295 K, several maxima are observed in the diffraction profile; the arrows on Figure 4 indicate where maxima should be observed in the Q range covered for a hexagonally close-packed array of cylinders. These coincide well with the peaks in the diffraction profile although, due to the geometrical limitations of the detector, they are not particularly well resolved. At the higher temperatures, the diffraction profile decomposes to one broad peak of lower intensity, which is shifted to a somewhat higher value of Q. The data are shown in Figure 4 for the equatorial scattering from the specimen. An isointensity contour plot (Figure 5) (essentially a "map" of the scattered intensity) shows that the scattering from copolymer C is anisotropic, being more intense in the equatorial plane and having the lowest scattering intensity in the meridional

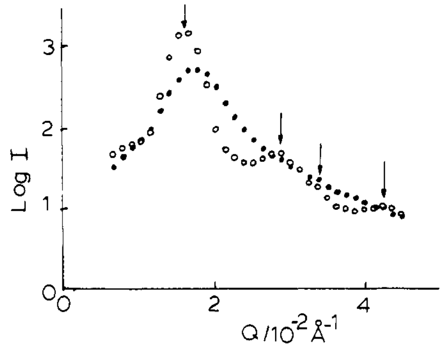

Figure 4. Equatorial scattered neutron intensity for copolymer C71 in cyclohexane solution. Arrows mark expected positions of Bragg maxima for hexagonally close-packed cylinders: ○, 295 K; ●, 359 K.

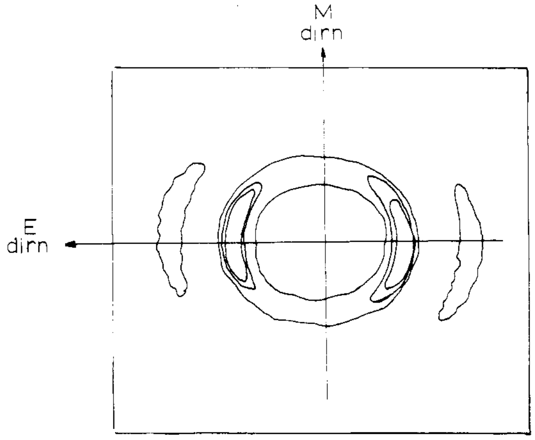

Figure 5. Isointensity contour map of small-angle neutron scattering from solution C71 at 295 K.

plane. This indicates that there is a preferential orientation of the cylindrical polystyrene domains in the scattering cell; the contour plot indicates that the axis of the cylinders is preferentially aligned vertical to the incident neutron beam. Notwithstanding this orientation, both meridional and equatorial scattering showed the same features as in Figure 4, with only the amplitudes of the maxima in the meridional scattering being somewhat reduced.

Evaluation of Order–Disorder Temperature. The expression for the scattered intensity for a diblock copolymer derived from the random-phase approximation (eq 5) may be written as

$$1/I(Q) = (F(u)/N) - 2\chi \tag{12}$$

The most general representation of χ is

$$\chi = A + B/T \tag{13}$$

Hence, eq 12 above should be linear in $1/T$ for diblock copolymers in the *homogeneous disordered* state.

In the ordered microphase-separated state, the temperature dependence of $1/I(Q)$ should be sensibly invariant. In this state there will be no further increase in the number of scattering particles as the temperature decreases; hence, the scattered intensity will not increase markedly. There will be some osmotic deswelling of the individual blocks due to the decrease in temperature, and this will increase the monomer number density slightly; however, the concomitant increase in scattering intensity will be very small compared to the large increase in intensity due to formation of a microphase-separated system. For solutions S15, S25, and S34 only one broad maximum was observed over the temperature range studied and no transition to an ordered state was noted; hence, we conclude that over these temperatures (295–354 K) the copolymers are in the homogeneous disordered state. Figure 6 shows a plot of the reciprocal scattered intensity at Q_{max} as a function of reciprocal temperature for the remaining solutions of copolymer S. Table III gives the order–disorder temperatures as a function of copolymer concentration evaluated from these plots. For solution S77, no order–disorder temperature was observed in the temperature range investigated.

The scattering from copolymer C solutions was investigated in both the meridional (M) and equatorial (E) planes. Figure 7 shows the reciprocal intensities at Q_{max} as a function of reciprocal temperature in both planes for three solutions. The features of the two sets of data are identical for both concentrations, with only the magnitude of $1/I$ differing. Similar behavior was observed for the other solutions of copolymer C. The order–dis-

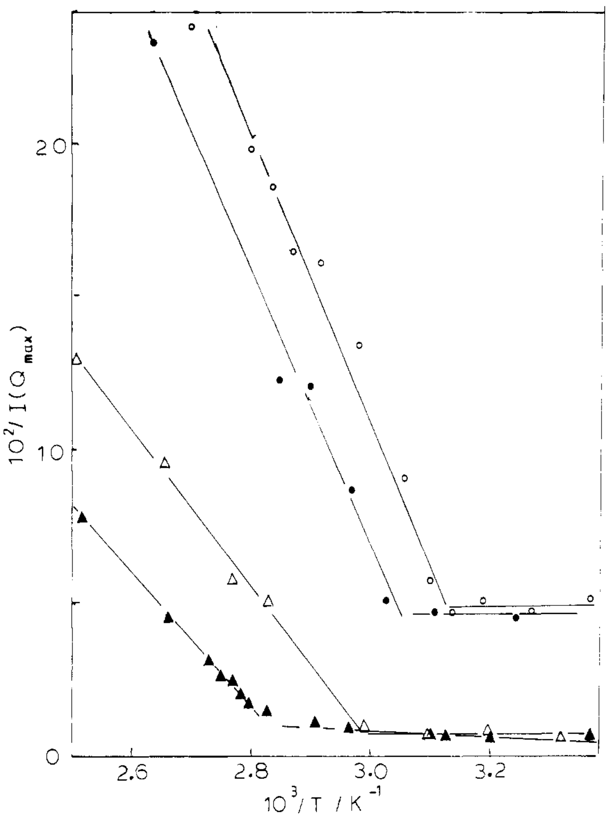

Figure 6. Reciprocal intensity at Q_{max} as a function of reciprocal temperature for copolymer S: ○, S50; ●, S58; △, S66; ▲, S71.

Table III
Order–Disorder Temperatures (T_{MST}) for Block Copolymer Solutions

vol fraction	MST,[a] K
Copolymer S	
0.454	319.5
0.535	327.9
0.603	334.4
0.671	352.1
Copolymer C	
0.452	335.0 ± 1
0.509	336.7 ± 1
0.550	341.0 ± 1
0.613	353.0 ± 1
0.666	366.0 ± 1

[a] Mean value obtained from M and E scattering for copolymer C only.

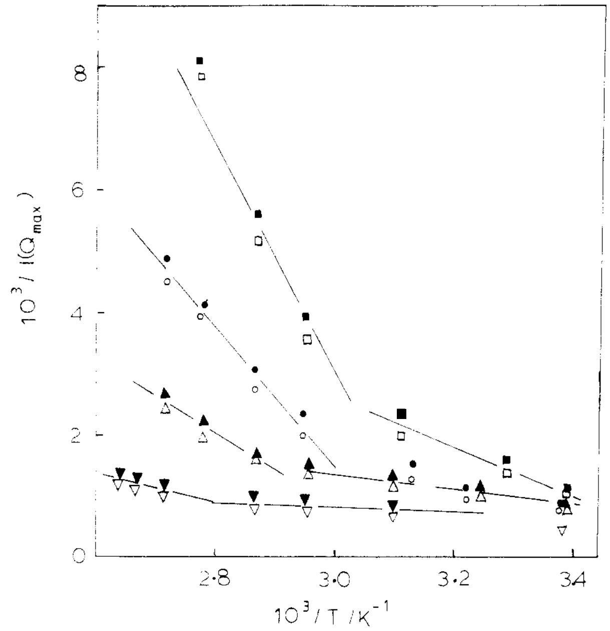

Figure 7. Reciprocal intensity at Q_{max} as a function of reciprocal temperature for copolymer C: □, C51; ○, C56; △, C66; ▽, C71. Open for equatorial scattering; filled for meridional scattering.

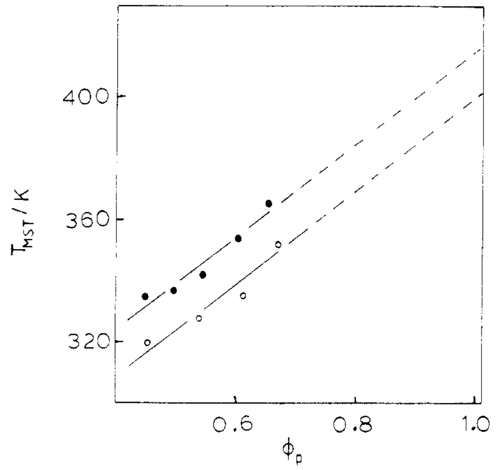

Figure 8. Order–disorder temperature as a function of copolymer volume fraction: ○, copolymer S; ●, copolymer C.

order temperature (T_{MST}) evaluated from either M or E scattering data was the same to within ±1°.

The variation of the order–disorder temperatures with volume fraction of copolymer is shown in Figure 8, and over the concentration range investigated, this is essentially linear. Extrapolation of the line drawn through these data suggests that for bulk copolymer S and C the order–disorder temperatures are 400 and 415 K, respectively. However, the extrapolation involved is very long, and as the copolymer concentration approaches the bulk value, the linear dependence on concentration of the order–disorder temperature may no longer be valid.

Evaluation of the Polymer–Polymer Interaction Parameter. Values of the polymer–polymer interaction parameter were obtained by nonlinear least-squares fitting of eq 5 (using eq 6 and 7) to the scattering profiles obtained for copolymers in the homogeneous disordered state. For this purpose both experimental data and theoretical curves were normalized to their respective maximum intensities. Adjustable parameters in the fitting were R_g and the interaction parameter χ.[20] The criterion of "goodness of fit" was that the difference between the reduced χ-square statistical parameter for successive fits be 0.001 or less.

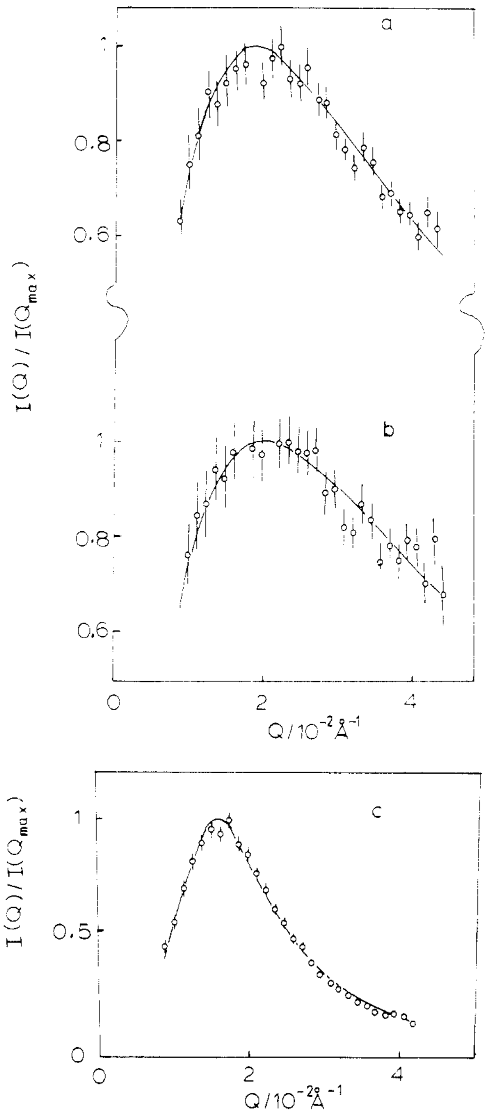

Figure 9. Fit of random-phase approximation (solid line) to scattered intensity for copolymer S in disordered homogeneous phase: (a) S50 at 352 K; (b) S50 at 360 K; (c) S71 at 370 K.

Typical examples of these fits are shown in Figure 9 for copolymer S solutions. For the lower concentration solutions, the error bars on the points reflect the lower signal to noise ratio compared to the higher concentration solutions. A note of caution is appropriate here. For the S copolymer solutions, it is also possible to fit the random-phase approximation expressions to the data for systems *within* the ordered phase; Figure 10 shows one such example. This probably reflects the relatively high fraction of imperfectly ordered polystyrene domains within the system leading to broad Bragg maxima in the scattering profile. In the solid state of block copolymers with spherical domains this has lead to the uncertainty in assigning the exact type of cubic structure attained. Consequently, it is of importance that the order–disorder temperature be known so that the RPA equations may be applied to the correct temperature range. However, this transition temperature also becomes apparent in the values of χ obtained by the fitting procedure.

Because of the presence of solvent in the systems examined here, the interaction parameter is not that pertaining to the two bulk components of the block copolymer. It is an effective interaction parameter, χ_{eff}, which is the

Table IV
Value of A and B in the Equation $\chi_{eff} = A + B/T$ for Solutions of Copolymer S

solution	φ_p	A	B, K
S14	0.12	−0.128	35.15
S25	0.204	−0.057	10.57
S34	0.288	−0.066	19.09
S50	0.455	−0.149	49.94
S58	0.537	−0.119	45.49
S66	0.603	−0.046	22.06
S71	0.671	−0.068	29.92

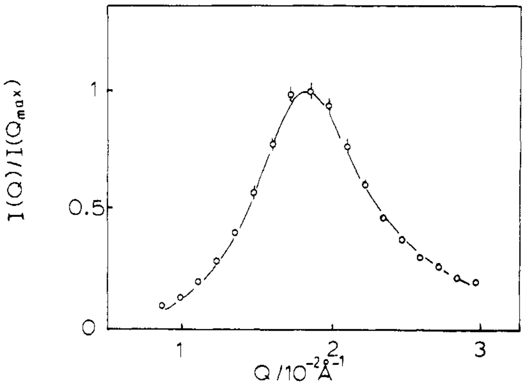

Figure 10. Example of fitting random-phase approximation (solid line) to scattering from S71 in the ordered region.

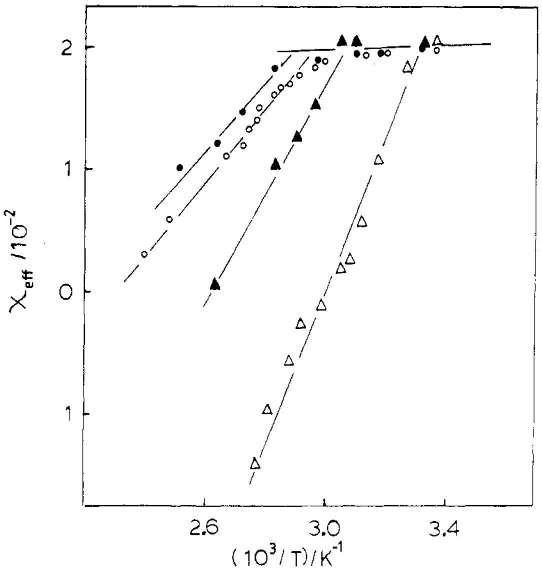

Figure 11. χ_{eff} as a function of reciprocal temperature for copolymer S solutions: △, S50; ▲, S58; ●, S71; ○, S66.

bulk interaction parameter, χ_{bulk}, mediated by the solvent. Table IV gives the values A and B in eq 20 obtained by a linear least-squares fit to the values of χ_{eff} obtained in the disordered region. Figure 11 shows the values of χ_{eff} obtained and the least-squares line through the values pertaining to the disordered region. The ordered region is readily apparent even though good fits to the Leibler[10] equation could be obtained in some cases as remarked earlier. From a mean-field approximation we can write[21]

$$\chi_{eff} = \chi_{bulk}\varphi_p \tag{14}$$

However, this does not allow the possibility of *negative* χ_{eff} values. We allow for this possibility by an empirical method. Equation 14 above is rewritten as

$$\chi_{eff} = \chi_{bulk} - C\varphi_s\chi_{bulk} \tag{15}$$

where C is an arbitrary factor that is dependent on temperature and φ_s is the volume fraction of cyclohexane. For each copolymer solution, values of χ_{eff} have been calculated for selected temperatures in the disordered region using the values of A and B obtained above. Plotting these values as a function of φ_s (Figure 12) for each temperature enables the evaluation of χ_{bulk} (from the intercept) and of C at each temperature (from the slope). With the extrapolated values of χ_{bulk} plotted as a function of reciprocal temperature in Figure 13 for copolymer S, the regression line through the points is described by the equation

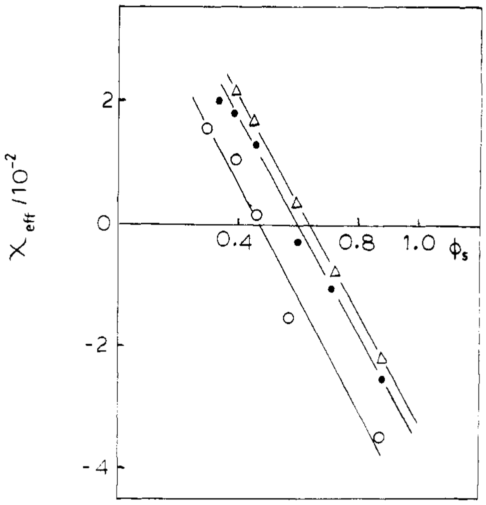

Figure 12. χ_{eff} as a function of volume fraction of cyclohexane for copolymer S solutions at selected temperatures: solid line, linear least-squares fit; ○, 376 K; ●, 354 K; △, 313 K.

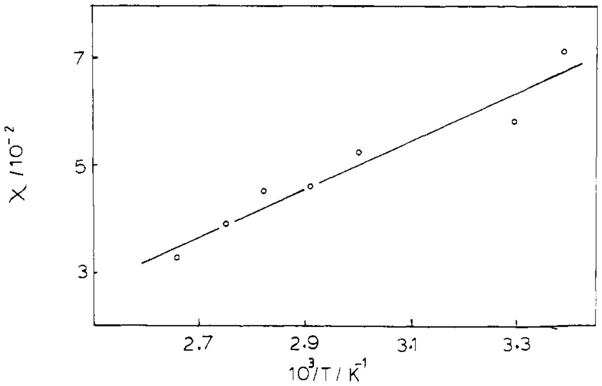

Figure 13. χ_{bulk} extrapolated from Figure 16 as a function of T^{-1}: solid line, linear least-squares fit.

$$\chi_{bulk} = -7.77 \times 10^{-2} + 42.18/T \quad (T \text{ in K}) \tag{16}$$

The empirical factor C in eq 15 is linear in temperature and has the form of

$$C = -1.29 + 8.71 \times 10^{-3}T \tag{17}$$

For copolymer C, the method of analysis used above is complicated by the anisotropic scattering, although this appears to have little influence on the MST. Consequently, the nonlinear least-squares fitting of the random-phase approximation equations to the scattering profiles to obtain χ_{eff} was applied to both M and E plane scattering. Examples of the fits obtained are shown in Figure 14. The dependence of χ_{eff} on $1/T$ for copolymer C solutions was qualitatively similar to that for copolymer S (Figure 11); i.e., in the high-temperature homogeneous phase there was a strong dependence of χ_{eff} on $1/T$. In the microphase-separated region the dependence on $1/T$ was essentially negligible; this was the case

Table V
Values of A and B in the Equation $\chi_{eff} = A + B/T$ for Solutions of Copolymer C

		E plane		M plane	
solution	φ_p	A, 10^{-3}	B, K	A, 10^{-3}	B, K
C51	0.452	1.44	3.13	1.83	2.94
C56	0.509	4.55	2.18	5.06	1.95
C60	0.550	7.77	1.13	6.13	1.68
C66	0.613	9.22	0.65	8.00	1.04
C71	0.666	8.70	0.88	8.77	0.81

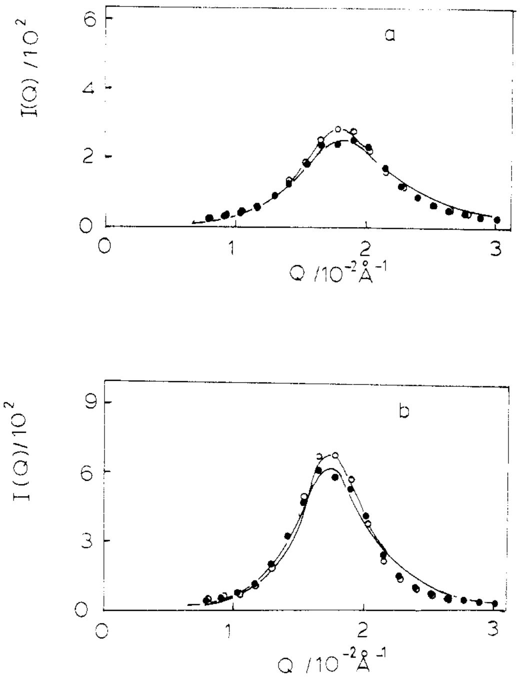

Figure 14. Typical fits of the random-phase equation to scattered intensity for copolymer C solutions in the disordered region: (a) C51; (b) C66; open points, equatorial scattering; filled points, meridional scattering; solid line, fit to data.

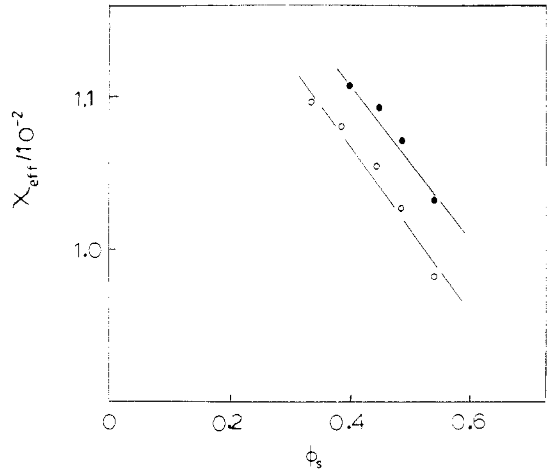

Figure 15. χ_{eff} as a function of cyclohexane volume fraction for copolymer C solutions: ○, T = 373 K, from meridional scattering data; ●, T = 353 K, from equatorial scattering data.

for χ_{eff} obtained from fitting to either E or M plane scattering data. From linear least-squares fits to χ_{eff} values in the disordered region, the parameters A and B in Table V were obtained. From these parameters values of χ_{eff} in the homogeneous disordered region were calculated (temperatures of 343–378 K were used for this purpose) and plotted as a function of φ_s for each temperature; Figure 15 shows typical examples and the least-squares lines through the data points. From the least-squares fits, the values of χ_{bulk} (intercept at φ_s = 0) and the empirical parameter, C (slope/intercept), in eq 15 was obtained as a function of temperature. From these values, the temperature dependences given below were obtained for χ_{bulk} and C.

equatorial plane scattering

$$\chi_{bulk} = 7.04 \times 10^{-3} + 2.30/T \tag{18}$$

$$C = 0.23 + 5.8 \times 10^{-4}T \tag{19}$$

meridional plane scattering

$$\chi_{bulk} = 0.32 \times 10^{-3} + 4.17/T \tag{20}$$

$$C = 0.97 - 14.2 \times 10^{-4}/T \tag{21}$$

The expressions for χ_{bulk} for copolymer C are quite different depending on which scattering orientation one uses. Clearly, this is due to anisometric scattering units whose memory persists, albeit slightly, into the homogeneous region. The only source for this preferential orientation is some interaction with the quartz walls of the cell acting as sites for domain formation in the microphase-separated state. However, the nature of these sites is unknown, and moreover such an interaction would be expected to encourage *lamellar* domain formation on the assumption that *all* of the quartz cell wall would be effective in this way.

Comparison with Other Data. Values of χ_{bulk} and its temperature dependence for other styrene–diene block copolymers and blends are scarce. Hashimoto et al.[22] have produced a relation for χ_{bulk} for a SI diblock copolymer of very low molecular weight using small-angle X-ray scattering. It is very similar in form, and magnitude of components, to eq 16 above. Similarly, Helfand[6] quotes a relation provided by Rounds and McIntyre, which also has the same form as eq 16. Hence, the very different relations obtained for copolymer C (eqs 18 and 20), together with the experimentally observed anisotropic scattering for this copolymer, could be cause for some concern. Perhaps the best way of ascertaining the validity of all of these relations is to construct the phase diagram of the SI diblock copolymer, i.e., a plot of $(\chi N)_s$ as a function of x, the fraction of styrene monomers in the copolymer. To do this, values of the spinodal temperature are required. These have been estimated from the plots of $I(Q_{max})^{-1}$ as a function of T^{-1}, by extrapolating the line through the strongly temperature-dependent data points to the T^{-1} axis (i.e., to the point where $I(Q_{max})^{-1}$ = 0; eq 8) for each concentration of copolymer used. These data points were subsequently used to obtain the spinodal temperature, T_s, for the bulk copolymers using the same procedure as in Figure 7 for the MST. By these means, we obtain spinodal temperatures of 355 and 397 K for bulk C and S copolymers. A value for T_s for the copolymer studied by Hashimoto et al.[22] was extracted from their data. Values of χ_{bulk} at the spinodal temperature were then calculated using the appropriate relations (eqs 16, 18, and 20 and that obtained by Hashimoto), and we note here that, although eqs 18 and 20 appear to be radically different, the values of χ_{bulk} calculated from each differ by very little. Values of $(\chi N)_s$ so obtained are plotted in Figure 16 as a function of x, and on the basis that the phase diagram is symmetrical about x, the right-hand half has been drawn as a dashed line. Exact agreement with the theoretical phase diagram is not obtained, but the general form is retained.

Conclusions

The application of the random-phase approximation theory to concentrated solutions of block copolymers has

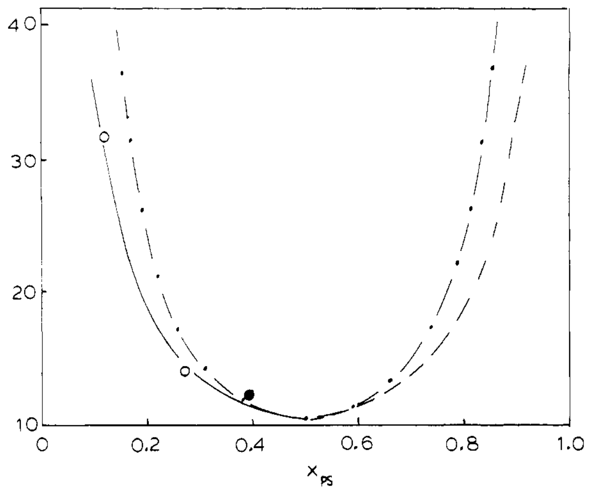

Figure 16. Phase diagram obtained from interpolated spinodal temperatures and calculated values of χ_B: ○, data obtained in this work; ●, calculated from Hashimoto et al.;[22] – · –, theoretical curve.

been demonstrated. In the homogeneous, disordered state the small-angle neutron-scattering profile has one broad maximum, which is describable by the original theory due to Leibler. Values of the effective interaction parameter have been evaluated by nonlinear least-squares fitting of the random-phase approximation expression to the scattering data. The variation of the effective interaction parameter with temperature indicates clearly the order–disorder temperature. Values for the interaction parameter between the bulk polystyrene–polyisoprene components of the block copolymers were obtained by a semiempirical extrapolation process. The temperature dependence of these interaction parameters is qualitatively similar to those obtained by others and gives fair agreement with the theoretical phase diagram calculated from the random-phase approximation expression.

An unsolved aspect is the occurrence of anisotropic scattering in the microphase-separated region for the copolymer with cylindrical styrene domains. This persists, albeit weakly, into the homogeneous phase, and therefore there is a possibility that a *metastable* state has been observed. Against this possibility, however, is the fact that the specimens were in the disordered region for many hours (>12). While data were collected over a range of temperatures, Pakula et al.[23] studied the reversal to randomly arranged cylindrical domains on high-temperature annealing of uniaxially oriented styrene–butadiene–styrene triblock copolymers. For specimens annealed for 30 min above the order–disorder temperature, a random orientation of cylindrical domains was obtained after cooling. Essentially, this is the process that copolymer C has undergone in our experiments; nonetheless, residual anisotropy is evident, and hence some other source for this behavior must be present.

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(19) To distinguish between simple cubic, body-centered cubic, and face-centered cubic arrangement, 7 orders of Bragg maxima are needed. On the basis of compositional analysis and volume fraction analysis, Richards and Thomason (*Macromolecules*, **1983**, *16*, 982) suggested a face-centered cubic analysis. However, Bates, Berney, and Cohen (*Macromolecules* **1983**, *16*, 1101) propose a body-centered cubic lattice from their SANS data.
(20) The critical fitting parameter, which governs the full-width of half-height of the fitted curve, is actually the product of $N\chi$. For our data, N was fixed at the value obtained from the known copolymer molecular weight and composition.
(21) As the polymer concentration increases, the screening length decreases, and at $\varphi_p = 1$, the screening length is that of a segment and excluded-volume effects disappear; hence, $\chi_{eff} = \chi_{bulk}$. See ref 9.
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Registry No. (S)(I) (block copolymer), 105729-79-1; neutron, 12586-31-1.