(9) R. B. Blumstein and E. Stickles, *Mol. Cryst. Liq. Cryst., Lett.*, **82**, 151 (1982).
(10) J. Grebowicz and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, 21, 141 (1983).
(11) R. B. Blumstein, E. Stickles, and A. Blumstein, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 6, 205 (1982).
(12) H. Arnold, *J. Phys. Chem.*, **226**, 146 (1964).
(13) E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **36**, 193 (1976).
(14) G. Ronca and D. Y. Yoon, *J. Chem. Phys.*, **76**, 3295 (1982).
(15) P. J. Flory and R. S. Frost, *Macromolecules*, 11, 1126 (1978). P. J. Flory, *Ber. Bunsenges. Phys. Chem.*, **1981**, 885 (1977).

Phase Equilibria and Transition in Mixtures of a Homopolymer and a Block Copolymer. 1. Small-Angle X-ray Scattering Study

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ABSTRACT: The small-angle X-ray scattering technique is utilized to study the phase separation and phase transition occurring in mixtures of a styrene–butadiene diblock copolymer with a low molecular weight polystyrene. At low temperatures the scattering curve shows a main peak and a secondary peak, indicating the presence of well-developed microdomains. As the temperature is raised the peaks gradually lose intensity. The binodal and spinodal temperatures for the transition between the ordered structure at low temperature and the disordered, homogeneous structure at high temperature are determined and found to increase with increasing amount of added polystyrene. At low temperatures, with increasing amount of polystyrene, the main peak at first shifts toward lower angles, indicating an increased distance between microdomains. However, at concentrations beyond about 50% polystyrene, which evidently corresponds to the solubility limit of the latter in the microdomains, the peak position remains constant. The observed shift in the relative position of the secondary peak suggests that the morphology of the microdomains changes gradually from spherical to lamellar as the proportion of polystyrene is increased. With all the mixtures no evidence is found for an increase in the microdomain boundary thickness with increasing temperature.

I. Introduction

Block copolymers often attain geometrically regular arrangements of microdomains consisting of components segregated from eath other. On heating, such a block copolymer can sometimes be transformed into a homogeneous, disordered structure. The temperature of the transition depends on the degree of compatibility of the components forming the blocks and the lengths of the blocks. The presence of a diluent such as a common solvent or a compatible polymer also influences the transition temperature. In recent years a number of workers made theoretical and experimental studies that touch upon the transition phenomenon of block copolymer systems. To cite a few examples, Leibler[1] developed a theory that predicts the transition temperature. Chung and Gale[2] and Gouinlock and Porter[3] found a discontinuity, on changing the temperature, in the rheological properties of a styrene–butadiene triblock copolymer. We[4] made a detailed study of the effect of temperature on the small-angle X-ray scattering from styrene–butadiene diblock and triblock copolymers and obtained evidence of transition from a ordered, microdomain structure to a disordered, homogeneous structure.

In this work we extend the previous small-angle X-ray scattering study[4] to investigate mixtures of a styrene–butadiene diblock copolymer with various proportions of a low molecular weight polystyrene. We are interested in finding out how the addition of the homopolymer alters the structure of the microdomains and the temperature of transition to the disordered structure. We are also interested in determining the limit of solubility of the polystyrene in the microdomains of the block copolymer. In the companion paper,[5] we report on the results of cloud point measurements on the same mixture system and also on two other similar systems containing the styrene–butadiene block copolymer and either a polystyrene or a polybutadiene. Combining the results of the present small-angle X-ray scattering studies with those of the cloud point measurements, we have been able to construct phase diagrams[5] of such mixtures. They exhibit fascinating interplays of the phase separation behavior with the transition of the block copolymer between the ordered and disordered structures.

II. Experimental Section

A. Materials. The polystyrene homopolymer was purchased from Pressure Chemical Co., and its M_n (by vapor phase osmometry) and M_w (by viscometry) are 2200 and 2400, respectively, according to the information provided by the supplier. The styrene–butadiene diblock copolymer contains approximately 25% styrene and was kindly synthesized for our use by Dr. H. L. Hsieh of Phillips Petroleum Co. According to Dr. Hsieh, its M_n and M_w (by GPC) are 27 000 and 28 000, respectively, and the microstructure of the butadiene blocks (by IR) is 30% vinyl, 42% trans 1,4, and 28% cis 1,4. The styrene content was determined by the NMR technique in this laboratory[6] and found to be 27 ± 1%. This polymer was also characterized independently by Krause et al.[7] by NMR and GPC.

The polystyrene and the styrene–butadiene diblock copolymer are the same materials used in our previous study,[8] in which they were designated PS2 and B25/75, respectively.

B. Method. Small-angle X-ray scattering measurements were performed with a Kratky camera, which was modified[9] and fitted with a Tennelec one-dimensional position-sensitive detector. It was operated with Ni-filtered Cu radiation from a Philips XRG3100 generator operating at 45 kV and 35 mA. The intensity data, collected in a multichannel analyzer, were transferred to a PDP 11/23 laboratory computer, and the correction[9] for the nonuniformity of the detector efficiency along its window length was applied first before other corrections for background, slit smearing, etc. were made. The intensity data were scaled to the absolute unit by comparison with the scattering from a calibrated Lupolen sample[10] kindly supplied by Professor O. Kratky. The correction for the slit-smearing effect was performed by the desmearing algorithms of Glatter[11] and of Strobl.[12]

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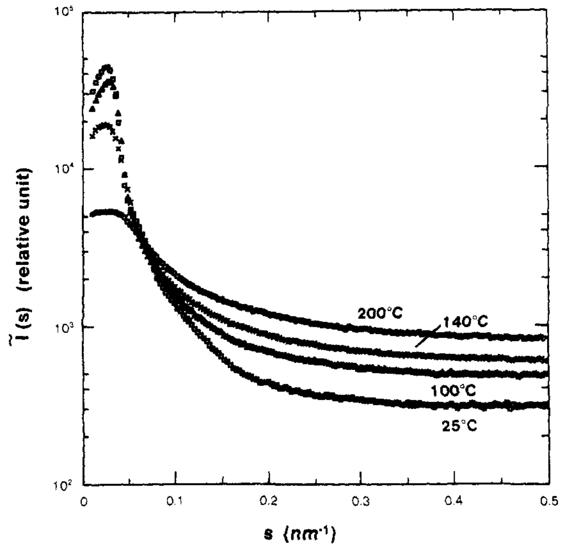

Figure 1. X-ray intensities (before correction for the slit-smearing effect), scattered from the mixture containing 30% polystyrene, plotted against the scattering angle s ($=(2 \sin \theta)/\lambda$), for the four temperatures of measurement indicated.

The sample was held in an aluminum sample holder, which was sealed vacuum tight with thin Kapton H films (a product of du Pont Co.) on both sides. A thermocouple placed close to the sample monitored the temperature, and the sample holder was heated with two cartridge heaters. Another thermocouple placed near the latter was used to control the temperature to within ±1 °C.

The mixtures of the polystyrene and the diblock copolymer were prepared by first dissolving them in toluene and then evaporating the solvent under vacuum at room temperature. The removal of solvent was considered complete when the sample ceased to form bubbles on subsequent heating to 150 °C under vacuum. Nine mixtures were prepared containing the following weight fractions of polystyrene: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, 0.65, and 0.80.

With each sample, the measurements were performed at various temperatures in the order 25, 50, 75, 100, 120, 140, 160, 180, 200, 180, 160, 140, 120, 100, 75, 50, 25, and 220 °C. After each step change in the temperature, a 20–30-min wait was allowed before a collection of the intensity data for 2000 s. The morphology change evidently followed the temperature change very quickly, and only a minor change in the scattered intensity was noticed during the 20–30-min wait period and no further change thereafter. The difference in the intensity data obtained at the same temperature on heating and cooling was within the experimental error, and no hysteresis effect could be detected. The average of the data obtained on heating and cooling is reported in this paper.

III. Results and Discussion

A. Scattering Curves. Figure 1 shows the intensity data (before correction for the slit-smearing effect) obtained with the mixture containing 30% polystyrene. For clarity, only the curves obtained at 25, 100, 140, and 200 °C are plotted. The low-angle peak diminishes rapidly with increasing temperature, indicating a progressive destruction of the ordered structure. The long tail at higher angles arises mostly from a thermal density fluctuation, which increases with increasing temperature. All the mixtures, as well as the diblock copolymer containing no polystyrene, give similar patterns of change in the scattered intensity with temperature. We believe our data represent an equilibrium behavior of the mixtures studied. This belief is based on the thermal reversibility and the rapidity of the change following a temperature change, observed both in this small-angle X-ray study and in the light scattering study reported separately,[5] and also on the fact that the component polymers involved are of relatively low molecular weight.

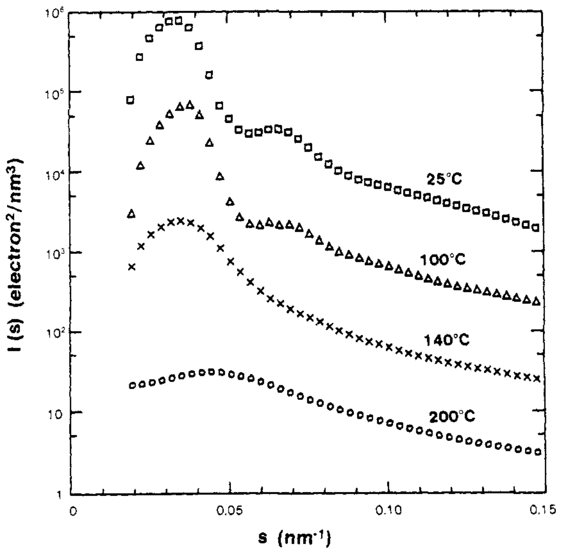

Figure 2. X-ray intensities, obtained from the mixture containing 30% polystyrene and corrected for the slit-smearing effect, plotted against the scattering angle s. The secondary peak disappears as the sample is heated above 100 °C, and even the main peak is reduced to a very weak, broad peak as the temperature is further raised. The plots for the data at 100, 140, and 200 °C are shifted downward successively by a factor of 10 for legibility.

In Figure 1 the curves obtained at different temperatures are all seen to cross approximately at a single scattering angle. All other samples show a similar behavior. Such results are reminiscent of the scattering curves obtained at different *times* during the spinodal decomposition of a binary metallic mixtures.[13,14] The reason our equilibrium data should resemble the kinetic data of mixtures undergoing a spinodal decomposition remains to be explained, although some plausible discussion was offered in the previous publication.[4]

In Figure 2 the intensity $I(s)$ corrected for slit smearing is plotted against s for the low-s region. ($s = (2 \sin \theta)/\lambda$, λ being the wavelength). At low temperatures, the presence of the secondary peak indicates that the microdomains are ordered fairly regularly. With an increase in the temperature, the secondary peak disappears and the intensity of the primary peak also diminishes, manifesting the disruption of the ordered structure. The remnant of the primary peak that persists to the highest temperature is due to the density inhomogeneity present[4] even in a thermodynamically homogeneous polymer liquid, stemming from the so-called "correlation hole" effect.[15]

B. Thermal Density Fluctuation. It is known that the scattered intensity at relatively high angles (see Figure 1) can be fitted empirically by[16-18]

$$\tilde{I}(s) = a + bs^n \tag{1}$$

where n is an even integer (4 or 6) or by[19,20]

$$\tilde{I}(s) = a \exp(bs^2) \tag{2}$$

In Figure 3, the logarithm of the intensity $\tilde{I}(s)$ obtained from the mixture containing 30% polystyrene is plotted against s^2, and the linear relation exhibited by the larger angle data indicates the validity of eq 2. The intensity $I(0)$, obtained by extrapolation of the linear region in Figure 3 to $s = 0$ (and corrected for slit smearing), represents the extent of the thermally induced density fluctuation present in homogeneous liquids and can be related to the isothermal compressibility κ_T of the liquid by

$$I(0) = kT\rho^2\kappa_T \tag{3}$$

where ρ is the electron density of the liquid and $I(0)$ is

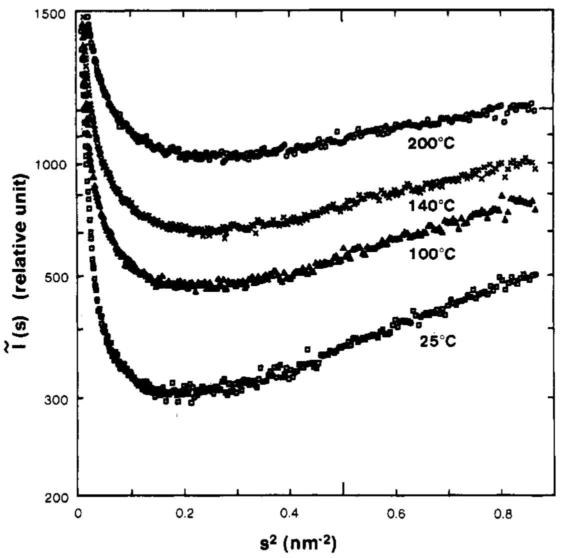

Figure 3. Slit-smeared intensities $\tilde{I}(s)$ obtained with the mixture containing 30% polystyrene plotted semilogarithmically against s^2 to illustrate that the tail of the scattering curves can be approximated well by $\exp(bs^2)$.

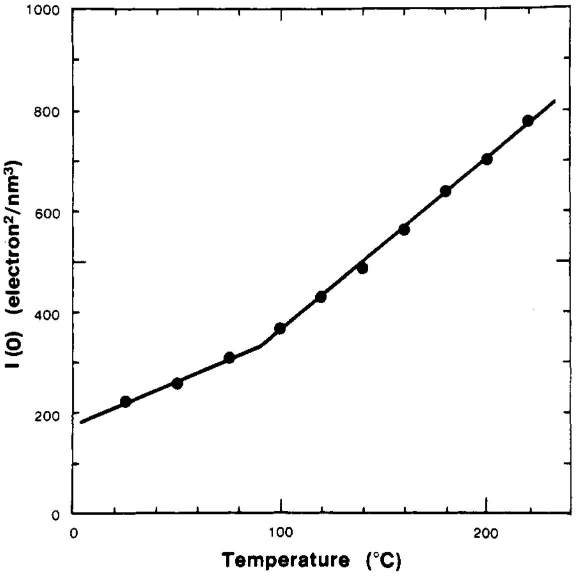

Figure 4. Intensity $I(0)$, obtained by extrapolating the tail of the observed intensity to $s = 0$, plotted against the temperature. There is a change in the slope at a temperature somewhat below 100 °C, which probably corresponds to the glass transition temperature of the styrene component. The data shown here were obtained with the mixture containing 30% polystyrene, but all other mixtures gave similar results as summarized in Table I.

expressed in electron units per unit volume. In Figure 4 the extrapolated $I(0)$ values, obtained for the mixture containing 30% polystyrene, are plotted against temperature. The break in the slope is believed to arise from the glass transition of polystyrene. Similar plots are obtained with all the other mixtures studied, and Table I gives the slopes below and above the break point and the temperature T_b of the break in the slope. The data for the pure polystyrene are quoted from our previous study.[20] The much larger temperature coefficients of $I(0)$ obtained in this work in comparison to the pure polystyrene data probably reflect the contribution of polybutadiene. The block copolymer containing no polystyrene or only 10% polystyrene shows the temperature T_b lower than that of other mixtures, suggesting[7] that the glass transition temperature of the styrene block in the block copolymer is lower than even that of the fairly low molecular weight (2400) polystyrene used in this study.

Table I
Temperature Coefficients of $I(0)$

wt fr of PS	temp (°C) of slope change, T_b	slope[a] below T_b	slope[a] above T_b
0	82	1.86	2.81
0.10	83	1.82	2.92
0.20	92	1.43	3.20
0.30	90	1.52	3.14
0.40	90	1.43	3.07
0.50	95	1.36	3.25
0.55	91	1.30	3.16
0.65	90	1.30	2.38
0.80	90	0.87	2.34
pure PS[b]	92	0.54	1.73

[a] In $e^2/(°C \cdot nm^3)$. [b] From ref 20.

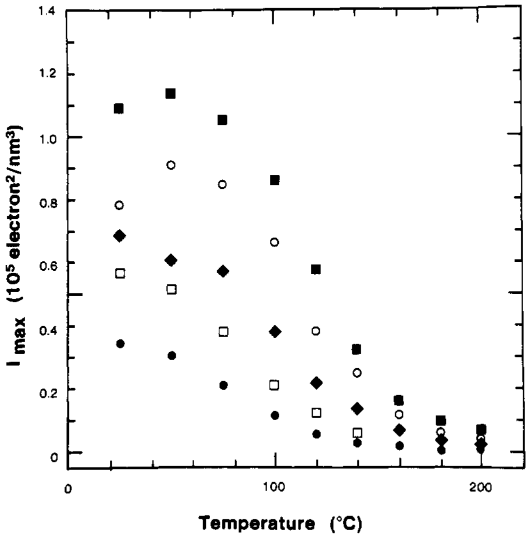

Figure 5. Intensity maximum of the main peak in the scattering curve plotted against temperature for the mixtures containing 40% polystyrene (filled squares), 30% polystyrene (open circles), 20% polystyrene (filled diamonds), 10% polystyrene (open squares), and 0% polystyrene (filled circles).

In all the scattered intensity data shown hereafter, the observed intensity has been "corrected for the background" by subtracting the contribution of the thermal density fluctuation as given by eq 2 (with the constants a and b evaluated from plots such as shown in Figure 3).

C. Thermal Transition Temperature. The change in the low-angle peak intensity with temperature indicates that the ordered microdomain structure, existing at low temperatures, gradually gives way to the disordered, homogeneous structure stable at high temperatures. Figure 5 shows the change with temperature in the peak intensity I_{max} obtained with the mixtures containing 0, 10, 20, 30, and 40% polystyrene. The peak height is seen to decrease over a broad temperature range from 50 to 200 °C. At any given temperature the peak intensity is higher for the mixture containing more polystyrene, and this aspect is discussed later in more detail.

Figure 6 shows the change with temperature in the angular position of the intensity peak for the mixtures containing 0, 10, 20, 30, and 40% polystyrene. At high temperatures the peak loses intensity and broadens appreciably, and as a result the peak angle determined is less precise. Even so, it appears that the peak shifts toward higher angles as the temperature is raised above 140 °C. Below this temperature the position of the peak remains

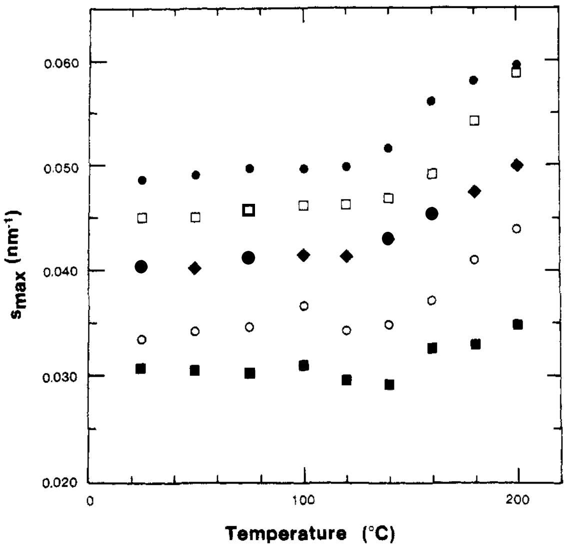

Figure 6. Angle s_{max} of the main peak plotted against temperature for the mixtures containing 40% polystyrene (filled squares), 30% polystyrene (open circles), 20% polystyrene (filled diamonds), 10% polystyrene (open squares), and 0% polystyrene (filled circles).

fairly constant, indicating that the type of structure present is probably unchanged. The mixtures containing 30 and 40% polystyrene, however, exhibit a momentary increase in the peak position at 100 °C. This effect, seen in Figure 6, is beyond the experimental error and is likely to be a reflection of some morphological change taking place at this temperature, possibly from a lamellar to a cylindrical or spherical microdomain structure.

Leibler, in his block copolymer theory,[1] predicts that the scattering of X-rays will persist even above the temperature of transition to a disordered structure, and the reciprocal of its intensity would be a linear function of the interaction parameter χ. Since for the styrene–butadiene pair χ is, to a good approximation,[8] proportional to $1/T$, the plot of $1/I_{max}$ against $1/T$ should then give a straight line. Similar plots have also been utilized[21-23] in the treatment of light scattering data from binary liquid mixtures near the phase separation temperature. Figure 7 gives the plot of $1/I_{max}$ against $1/T$, obtained with the mixture containing 30% polystyrene. Extrapolation of $1/I_{max}$ to zero gives the spinodal temperature T_S, and the point of deviation of the observed value from the straight line gives the binodal temperature T_B of microdomain formation. In Figure 8, the values of T_S and T_B so determined are plotted against the composition of the mixture.

It is seen that both the spinodal and binodal temperatures increase with increasing proportion of the added polystyrene. Beyond 30% polystyrene, the mixture becomes visibly cloudy in the temperature range of interest here, indicating an intervention of a macroscopic phase separation (see the details of cloud point measurements given in the companion paper[5]), and therefore the evaluation of the temperatures of transition by means of a plot similar to Figure 7 has not been attempted.

D. Low-Temperature Structure. Figure 2 shows that at low temperatures the scattering curves exhibit a main peak and a secondary peak, indicating that a fairly good ordering of segregated microdomains exists. The main peak position can be taken as a measure of the interdomain repeat distance. In Figure 9 the angle s_{max} of the main peak is plotted against the weight fraction of polystyrene. As the added polystyrene is solubilized in the styrene domains of the block copolymer, the interdomain distance becomes larger. Eventually, the solubility limit is reached, and the interdomain distance ceases to increase any further. Beyond this point the excess polystyrene separates out into a macroscopic phase consisting mostly of polystyrene with a small amount of dissolved block copolymer in it. In our light scattering study[5] the onset of turbidity at low temperatures was noted at around 46% polystyrene, giving a good agreement with the composition in Figure 9 at which the peak angle levels off.

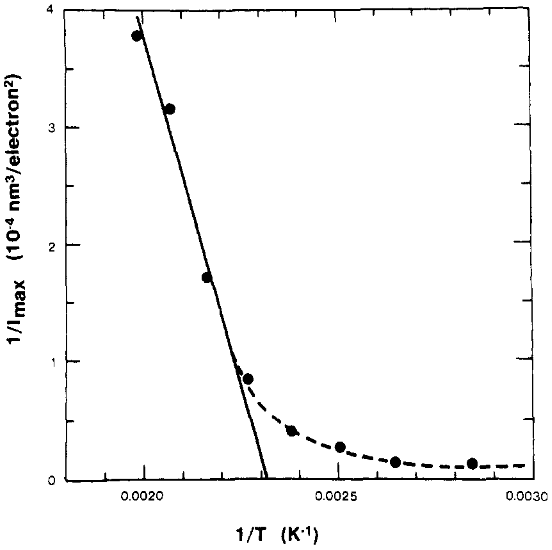

Figure 7. Reciprocal of the intensity I_{max} of the main peak plotted against the reciprocal of temperature T (K). A linear extrapolation of $1/I_{max}$ at high temperatures to zero gives the spinodal temperature, while the first deviation of the observed intensity (approximated by the broken curve) from the straight line gives the binodal temperature or the temperature of transition between the disordered, homogeneous structure and the ordered, microdomain structure. The plot gives the data obtained with the mixture containing 30% polystyrene.

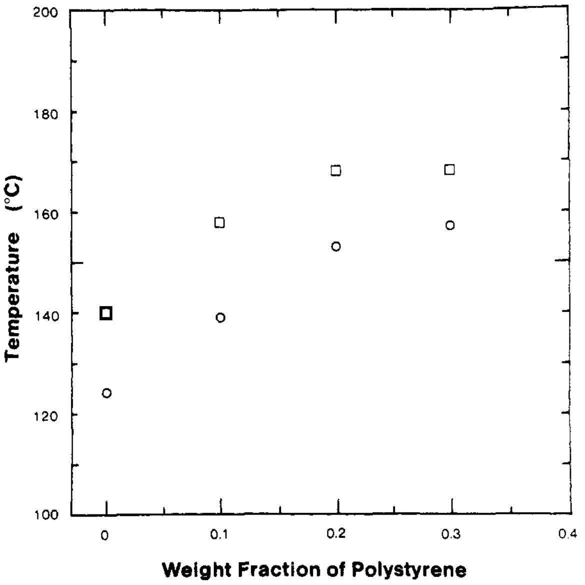

Figure 8. Spinodal temperatures (circles) and binodal temperatures (squares) obtained by the method illustrated in Figure 7 plotted against the composition of the mixture.

As the added polystyrene is solubilized into the styrene microdomains, the volume ratio of the styrene and butadiene microdomains becomes altered. This would then be reflected in the intensity of the scattered X-rays, since the scattering power of a sample is essentially proportional to $\phi(1 - \phi)$, where ϕ is the volume fraction of the styrene microdomains. A more accurate measure of the scattering

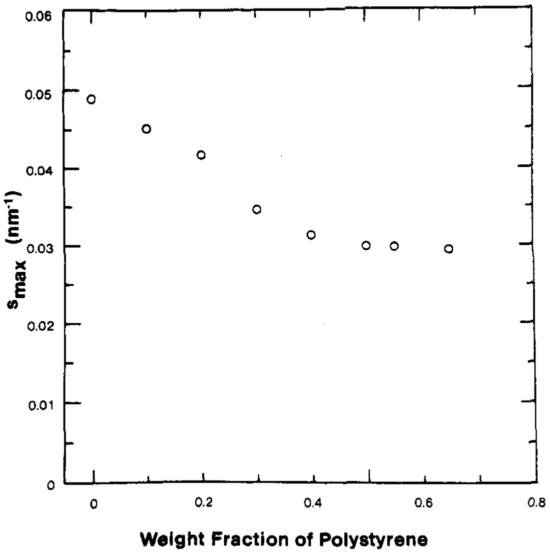

Figure 9. Angle s_{max} of the main peak (at 50 °C) plotted against the composition of the mixture. With increasing amount of polystyrene, the peak angle decreases, indicating an increase in the distance between microdomains. The solubility limit is reached at around 50% polystyrene and the peak angle then ceases to change on further addition of polystyrene.

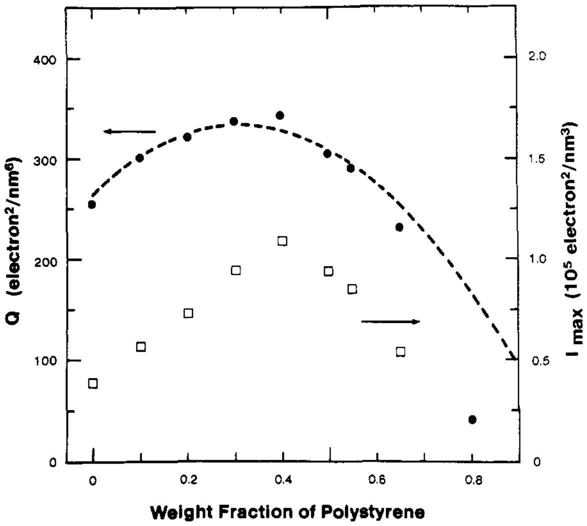

Figure 10. Filled circles show the values of the "invariant" Q evaluated from the scattered intensity obtained at 50 °C. The invariant of a two-phase system is proportional to $\phi(1 - \phi)$, where ϕ is the volume fraction of one of the phases. The broken curve gives the calculated values of $\phi(1 - \phi)$ multiplied by an arbitrary constant. The open squares give the peak intensity I_{max} (obtained at 25 °C) and show that its variation with the composition of the mixture follows a similar trend.

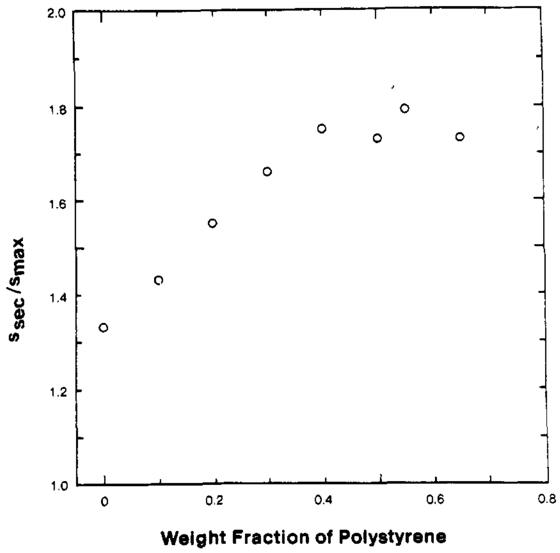

Figure 11. Ratio of the angle s_{sec} of the secondary peak to the angle s_{max} of the primary peak plotted against the composition of the mixture. For a body-centered cubic packing of spheres the ratio is expected to be 1.41, while for a lamellar morphology it should be equal to 2.0. The data thus suggest a gradual transformation of the structure from a spherical to a lamellar morphology.

power is given by the so-called "invariant" Q, which can be determined from the observed intensity by

$$Q = 4\pi \int_0^\infty s^2 I(s) \, \mathrm{d}s \qquad (4)$$

For an idealized two-phase system the invariant Q is rigorously related[24] to the volume fraction ϕ by

$$Q = (\Delta\rho)^2 \phi(1 - \phi) \qquad (5)$$

where $\Delta\rho$ is the electron density difference between the phases. In Figure 10 both the intensity I_{max} of the main peak and the invariant Q are plotted against the weight fraction of polystyrene. The broken curve drawn is to illustrate the variation in the product $\phi(1 - \phi)$, where ϕ includes the contributions from the styrene block in the copolymer and from the added polystyrene. To the right of the maximum in Figure 10, Q is seen to fall off more rapidly than the calculated $\phi(1 - \phi)$ values, and this is due to the fact that the polystyrene in excess of the solubility limit forms separate domains of sizes larger than can be detected by our X-ray measurement. The peak intensity I_{max} follows the same trend as exhibited by Q approximately but not precisely, because the peak intensity is sensitive also to the morphological details in addition to the volume fraction product $\phi(1 - \phi)$.

In Figure 11 the ratio of the angular position s_{sec} of the secondary peak to the position s_{max} of the main peak is plotted against the composition of the mixtures. (The values of the ratio are the averages of those observed at 25, 50, and 75 °C.) For a body-centered cubic packing of spheres, which is the morphology[25] most likely to be adopted by our block copolymer sample with no added polystyrene, the ratio s_{sec}/s_{max} should be equal to 1.41. For a hexagonal packing of cylinders, the ratio should be equal to 1.73 and for a lamellar packing the ratio should be equal to 2.00. The observed ratio shown in Figure 11 increases from about 1.33 to 1.8 with increasing amount of the added polystyrene, and this indicates probably that the morphology is gradually transformed from spherical to cylindrical and eventually to lamellar packing. There is, however, no evidence of sharp transition from one morphology to another. The failure to attain the precise crystallographic ratios mentioned above may also be taken as indicating that the packing is fairly imperfect and the sample may even contain patches of different morphologies.

E. Microdomain Boundary Thickness. The intensity of small-angle X-ray scattering from a sample of ideal two-phase structure, having sharp phase boundaries, decreases as s^{-4} at large s according to Porod.[24] When the boundary layer has a finite thickness, deviation of the intentisy from the inverse fourth power law results, and this suggests a possible method of determining the boundary thickness by analyzing the deviation of the observed data from Porod's law, as proposed initially by Ruland[26] and by Vonk.[27] Difficulties can arise in such an analysis because of the possible presence of other types of deviations from the ideal structure, because of the statistical errors present in the observed data, and because

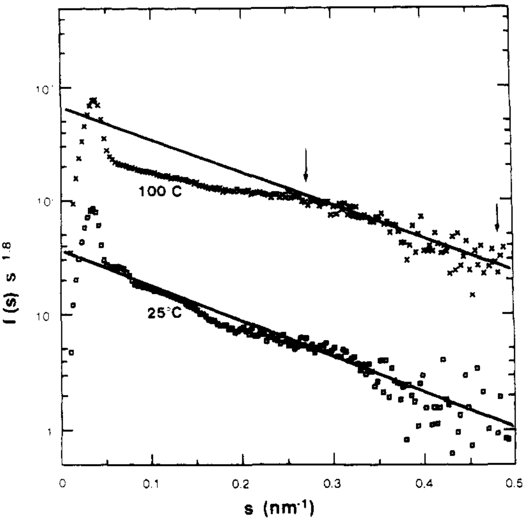

Figure 12. This plot has been constructed in order to evaluate the thickness of the microdomain boundaries according to the method suggested earlier.[28] The arrows indicate the angular range taken into consideration for the determination of the slope, from which the boundary thickness is evaluated. The plot for the data at 100 °C was shifted upward by a factor of 10 for legibility.

of the need, in most cases, of correcting, or allowing for, the slit-smearing effect present in the raw data initially obtained. In a previous publication[28] we reexamined the method of determining the boundary thickness, especially with regard to the error accruing in the values of the boundary layer thus determined. When an equilibrium condition prevails, the concentration profile across the boundary layer can be expressed as[29]

$$q(x) = \tanh\,(2x/t) \qquad (6)$$

where t is the effective thickness defined as the reciprocal of the density gradient at the center of the boundary layer. The value of t can then be determined[28] by constructing a plot of ln $[\tilde{I}(s)s^{1.8}]$ against s, where $\tilde{I}(s)$ is the slit-smeared intensity from which the "background" scattering has been subtracted. The slope of the linear portion of such a plot in the high-s region (so-called Porod region) then gives

$$t = -(\text{slope})(2/1.9\pi^2) \qquad (7)$$

In Figure 12, the scattered intensity $\tilde{I}(s)$ obtained with the mixture containing 30% polystyrene at 25 and 100 °C is plotted according to the procedure described above. The arrows denote the range of s in which the slope is evaluated. The thickness values t thus obtained are 7.6 and 7.0 Å at 25 and 100 °C, respectively. Similar results ranging from 5 to 9 Å were obtained with the pure block copolymer and the mixtures containing various proportions of the polystyrene.

These thickness values are much smaller than the values, around 20 Å, reported by other workers.[18,30-33] Since the block copolymer samples used in these different works are not identical and the methods of evaluation also differ in detail, it is difficult to find out the reason for the discrepancy. It rather suggests the need to examine the methods of determining the boundary thickness more critically through a cooperative effort among several laboratories.

None of the mixtures we studied shows any indication that the thickness becomes greater as the temperature is raised from 25 to 100 °C. Figures 1 and 5 show that the intensity of the main peak, on the other hand, decreases as the temperature is raised. The decrease in the peak intensity is most likely to occur from the decrease in the electron density contrast between the styrene and butadiene microdomains. On the basis of similar evidence obtained with the pure block copolymer, we concluded in our previous publication[4] that the transition from the ordered structure to a disordered, homogeneous structure proceeds through an intermediate structure, in which the styrene and butadiene blocks gradually dissolve into the microdomains of the opposite type without the domain boundaries, however, becoming appreciably more diffuse. The same conclusion appears to hold also in the case of mixtures containing various amounts of polystyrene as studied here.

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Registry No. Butadiene–styrene copolymer, 9003-55-8; polystyrene (homopolymer), 9003-53-6; polybutadiene (homopolymer), 9003-17-2.

References and Notes

(1) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(2) Chung, C. I.; Gale, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1149.
(3) Gouinlock, E. V.; Porter, R. S. *Polym. Eng. Sci.* **1977**, *17*, 534.
(4) Roe, R.-J.; Fishkis, M.; Chang, J. C. *Macromolecules* **1981**, *14*, 1091.
(5) Roe, R.-J.; Zin, W.-C *Macromolecules*, following paper in this issue.
(6) We thank D. Rigby for this measurement.
(7) Krause, S.; Lu, Z.-H.; Iskander, M. *Macromolecules* **1982**, *15*, 1076.
(8) Roe, R.-J.; Zin, W.-C. *Macromolecules* **1980**, *13*, 1221.
(9) Roe, R.-J.; Chang, J. C.; Fiskis, M.; Curro, J. J. *J. Appl. Crystallogr.* **1981**, *14*, 139.
(10) Kratky, O.; Pilz, I.; Schmitz, P. J. *J. Colloid Interface Sci.* **1966**, *21*, 24.
(11) Glatter, O. *J. Appl. Crystallogr.* **1974**, *7*, 147.
(12) Strobl, G. R. *Acta Crystallogr., Sect. A* **1970**, *A26*, 367.
(13) Agarwal, S.; Herman, H. *Scr. Met.* **1973**, *7*, 503.
(14) Gerald, V.; Kostorz, G. *J. Appl. Crystallogr.* **1978**, *11*, 376.
(15) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(16) Kortleve, G.; Tuynman, C. A. F.; Vonk, C. G. *J. Polym. Sci., Part A-2* **1972**, *10*, 123.
(17) Vonk, C. G. *J. Appl. Crystallogr.* **1973**, *6*, 81.
(18) Todo, A.; Hashimoto, T.; Kawai, H. *J. Appl. Crystallogr.* **1978**, *11*, 558.
(19) Rathje, J.; Ruland, W. *Colloid Polym. Sci.* **1976**, *254*, 358.
(20) Roe, R.-J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428.
(21) Derham, K.; Goldsborough, J.; Gordon, M. *Pure Appl. Chem.* **1974**, *38*, 97.
(22) Chu, B.; Schoenes, F. J.; Fisher, M. E. *Phys. Rev.* **1969**, *185*, 219.
(23) Scholte, Th. G. *J. Polym. Sci., Part A-2* **1971**, *9*, 1553.
(24) Porod, G. *Kolloid-Z.* **1951**, *124*, 83.
(25) Bates, F. S.; Cohen, R. E.; Berney, C. V. *Macromolecules* **1982**, *15*, 589.
(26) Ruland, W. *J. Appl. Crystallogr.* **1971**, *4*, 70.
(27) Vonk, C. G. *J. Appl. Crystallogr.* **1973**, *6*, 81.
(28) Roe, R.-J. *J. Appl. Crystallogr.* **1982**, *15*, 182.
(29) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258.
(30) Hashimoto, T.; Todo, A.; Itoi, H.; Kawai, H. *Macromolecules* **1977**, *10*, 377.
(31) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(32) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.
(33) Hashimoto, H.; Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1981**, *14*, 844.