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Small-Angle X-ray Scattering Study of Micelle Formation in Mixtures of Butadiene Homopolymer and Styrene–Butadiene Block Copolymer

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ABSTRACT: The small-angle X-ray scattering technique is utilized to study the formation of micelles in mixtures containing polybutadiene homopolymer ($M_n = 2350$) with much smaller amounts (0.5–8 wt %) of styrene–butadiene diblock copolymer ($M_n = 25\,000$, 52.2 wt % styrene). The following quantities, characterizing the structure of the micelle core consisting of styrene blocks swollen with polybutadiene, have been evaluated as a function of temperature and the copolymer concentration: the radius of gyration of the core, the degree of swelling of the core, the number of block copolymer molecules forming a micelle, and the volume of a core. In addition, the critical micelle concentration (i.e., the minimum copolymer concentration necessary for micelle formation) and the number density of micelles as a function of the concenration were also determined. The degree of swelling of micelle cores by polybutadiene increases steadily with increasing temperature. The micelle core size is fairly independent of the concentration and, as the temperature is raised, at first remains unchanged but then increases rapidly before it finally dissolves completely. The temperature of dissolution increases with concentration of the copolymer. The micelle core volumes, determined by two independent methods (one by the Guinier analysis and the other from the ratio $I(0)/Q$), agree well with each other.

I. Introduction

In a recent series of papers we reported on the study of thermodynamic behavior of polymer systems containing block copolymers. In particular, we investigated,[1] by means of the small-angle X-ray scattering technique, the thermal transition occurring in diblock and triblock copolymers from an ordered microdomain structure to a disordered homogeneous structure. We further investigated,[2,3] by means of small-angle X-ray scattering and turbidity measurements, mixtures of a diblock copolymer with a homopolymer with regard to the solubility of the homopolymer and the effect of the homopolymer concentration on the thermal transition of the block copolymer. In the present work we continue our effort to understand the phase transition and phase separation behaviors of block copolymer systems. In contrast to previous systems studied, we now take up mixtures in which the block copolymer is present as a minority component. Specifically, we investigate mixtures containing a small concentration (up to 8%) of a styrene–butadiene diblock copolymer (50%–50%) dispersed in a low molecular weight polybutadiene. At high temperature and at low concentration the block copolymer is molecularly dissolved. As the temperature is lowered below a certain temperature (which depends on the concentration) block copolymer molecules aggregate into micelles. In this work we utilize the small-angle X-ray scattering technique and determine the critical micelle concentration as a function of temperature and the size and degree of swelling of the micelles as a function of temperature and concentration.

The formation of block copolymer micelles in solutions of selective solvents, i.e., small-molecule solvents which are good for one of the blocks but poor for the other, has been studied by others by small-angle X-ray scattering[7] as well as by light scattering[8–12] and by sedimentation velocity measurements.[7,10,13] In comparison to these, the mixture of a block copolymer with a homopolymer offers advantages both experimentally and theoretically. Interpretation of small-angle scattering data is more straightforward in the system containing a homopolymer, since it has a two-phase structure (that is, has only two regions of differing electron density) whereas the system containing a solvent has a three-phase structure. Theoretical interpretation is simpler in the system containing a homopolymer because the homopolymer shares the same repeat unit with one of the blocks and thus only a single polymer–polymer interaction parameter is required to characterize the thermodynamic behavior of the mixture. The value of the interaction parameter between the styrene and butadiene units has previously been determined[14] from a

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detailed study of the phase separation behavior of mixtures containing styrene and butadiene homopolymers and random copolymers. Moreover, mixtures containing only polymers instead of a polymer and a small-molecule solvent are inherently more readily amenable to theoretical treatments. For polymer–polymer mixtures the excluded volume effect does not arise[15] and also the equation-of-state contribution to the free energy of mixing is quite small[14] and can often be neglected. As a consequence the Flory–Huggins free energy of mixing, originally developed for treatment of polymer solutions, in fact turns out to be a much better approximation for discussion of polymer mixtures. The recent theories[4–6] on block copolymer micelle formation, based among others on the Flory–Huggins free energy of mixing, should therefore be tested more appropriately with results obtained with systems involving polymeric rather than small-molecule solvents.

There is a further practical motivation for studying the mixture of block copolymers with homopolymers. The possible utility of adding a small amount of a block copolymer to a homopolymer as an impact modifier or to a polymer mixture as a compatibilizer has been widely recognized. Efficient utilization of block copolymers in such applications calls for a better understanding of the thermodynamics governing the miscibility behavior of block copolymers and homopolymers.

II. Experimental Section

Materials. The polybutadiene (CDS-B-3) was obtained from the Goodyear Chemical Co. According to the manufacturer, its number-average molecular weight (by VPO) is 2350, and its M_w/M_n ratio (by GPC) is 1.13. The microstructure is stated to be 53% trans 1,4, 41% cis 1,4, and 6% vinyl 1,2.

The styrene–butadiene diblock copolymer was kindly synthesized for our use by Dr. H. L. Hsieh of Philips Petroleum Co. The data supplied by Dr. Hsieh read that it has $M_n = 25\,000$ (by GPC), $M_w/M_n = 1.04$ (by GPC), and 50% styrene by weight, and the microstructure of the butadiene block is 45% trans 1,4, 24% cis 1,4, and 31% vinyl 1,2. The styrene content was determined also in this laboratory, by the NMR technique described by Senn,[16] and was found to be 52.2 ± 1%. This polymer has also been characterized independently by Krause et al.[17]

Method. Weighed amounts of the polybutadiene (viscous liquid) and the solid copolymer were placed in a glass tube fitted with a magnetically activated stirrer. The components were then heated under vacuum to 200 °C to remove volatile fractions from the polybutadiene and to facilitate mechanical mixing. The resulting mixture was optically clear at 200 °C but developed a characteristic blue translucence on cooling to room temperature. The temperature at which this translucence first developed was observed to decrease with decreasing copolymer concentration. The liquid-like mixture was transferred to an aluminum scattering cell which was sealed vacuum tight with windows of Kapton H film (a product of du Pont Co.). Heat was supplied to the sample by cartridge heaters placed in contact with the cell. The sample temperature was monitored by a thermocouple mounted in the aluminum cell next to the sample compartment, while a second thermocouple nearer the heater served to control the temperature.

Mixtures containing 0.5, 1.0, 2.0, 4.0, 6.0, and 8.0% (by weight) of block copolymer were studied. In most cases, scattering measurements were made at intervals of 10 °C between 30 °C and the temperature at which the micellar scattering disappeared (70–120 °C, depending on the concentration). In selected cases, measurements were also made on the homogeneous mixture, after the disappearance of micelles, up to a temperature of 160 °C. The time for each measurement was adjusted between 1 and 4 h, according to the copolymer concentration and temperature, so that the points within the Guinier region would have a statistical error of less than 1% after background subtraction.

The reproducibility of measurements made on increasing and decreasing the temperature was found to be good at the lower temperatures. At temperatures close to the dissolution temperature of the micelles, however, agreement between measurements made on heating and on cooling was sometimes less satisfactory. This was thought to arise not from any nonequilibrium effect but from the fact that in this region the number and size of micelles present in the mixure were more sensitive to small differences in temperature. To eliminate possible artifacts caused by drifts in the instrument during the course of the study, the samples of different concentrations were studied in the order 2%, 4%, 8%, 1%, 0.5%, and 6%.

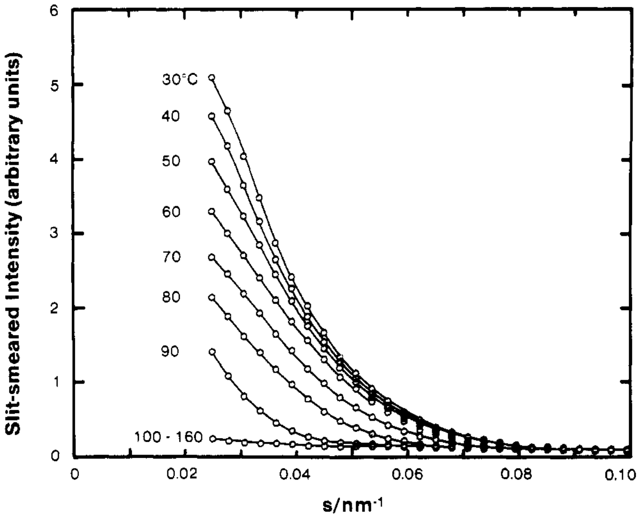

Figure 1. Scattered X-ray intensity obtained with the mixture containing 4% copolymer. The corrections for the nonuniformity of the detector sensitivity and for the background have already been made but the effect of slit-length smearing has not been corrected for.

The small-angle X-ray instrumentation consists of a Kratky camera with an 80-μm entrance slit, and a Tennelec one-dimensional position-sensitive detector mounted at a distance 50 cm from the sample position. The details of this arrangement have been described elsewhere.[18] The data collected in a multichannel analyzer were transferred to a PDP 11/23 laboratory computer, where a correction was made for the nonuniformity of the detector efficiency along its length, followed by reduction to absolute units by comparison with the scattering from a calibrated Lupolen standard[19] kindly furnished by Prof. O. Kratky.

The intensity obtained with pure polybutadiene was subtracted from all the data obtained with copolymer mixtures as a background correction. Since the X-ray beam path length through the sample was not always identical (due to thermal expansion of the sample and the flexible nature of the Kapton window), some minor scaling adjustment had to be made to the polybutadiene intensity so that after its subtraction the intensity would fall to zero at s ($=2 \sin \theta/\lambda$) between 0.25 and 0.35 nm^{-1}. Figure 1 illustrates the scattering curves, slit-smeared intensity $\tilde{I}(s)$, thus obtained after the background correction. The sharp peak at very small angles, characteristic of the micellar scattering, gradually disappeares as the temperature is raised. Even at 100 °C and above, however, there still remains weak, broad scattering extending to $s \simeq 0.3$ nm^{-1}. The intensity of this broad scattering does not change with temperature (between 100 and 160 °C for the 4% solution illustrated in Figure 1), but is approximately proportional to the concentration of the copolymer in the mixture. The same broad scattering is also present, superposed on the micellar scattering, in all the scattering curves obtained at lower temperatures, as can be seen in Figure 1. Although the source of this broad scattering is not clearly understood, it evidently is not associated with the presence of micelles. For the purpose of evaluating the "invariant" Q

$$Q = 4\pi \int_0^\infty I(s)\, s^2\, ds \tag{1}$$

$$= 2\pi \int_0^\infty \tilde{I}(s) s\, ds \tag{2}$$

the contribution of this broad scattering (as represented by the high-temperature data) was therefore subtracted from $\tilde{I}(s)$ before the integration was performed.

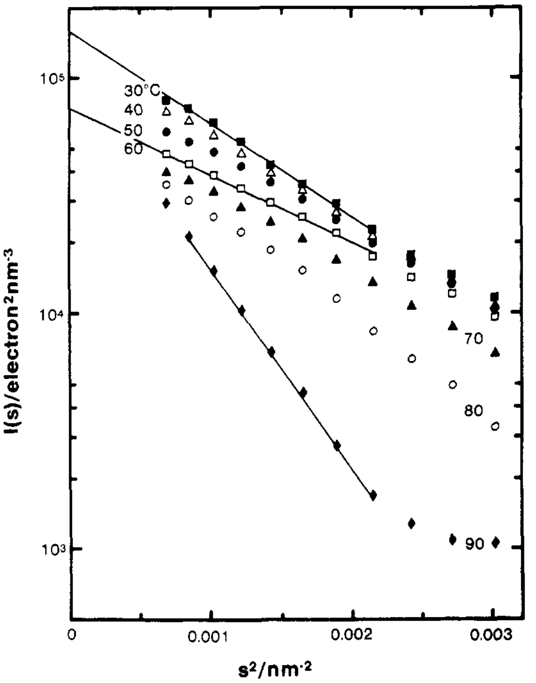

Figure 2. Guinier plot of the data obtained with the mixture containing 4% copolymer. The intensity $I(s)$ was corrected for the slit-length smearing effect by the method of Strobl.[20]

For the evaluation of the radius of gyration R by means of the Guinier law

$$I(s) = I(0)\exp(-4\pi^2 R^2 s^2/3) \qquad (3)$$

the correction for the slit-length smearing was first applied by the Strobl[20] method. Figure 2 shows the plot of log $I(s)$ against s^2 for the set of data obtained with the 4% mixture. The radius of gyration R' obtained from the slope of such a plot still contains the effect of slit-width smearing. The correction for this effect can be made and the correct radius of gyration R obtained by the relation

$$R = R'[1 + (2/3)\pi^2 R'^2/p^2] \qquad (4)$$

where p represents the spread of the slit-width weighting function $W(s)$

$$W(s) = W_0 \exp(-p^2 s^2) \qquad (5)$$

In our instrument p^2 was determined to be 50 000 nm^2 and the correction given by eq 4 then amounts to about 0.8%.

III. Analysis of X-ray Data

Before presenting the results, we here summarize the methods employed for the analysis of the X-ray data. For the kind of system under study, there are four types of information that can be derived directly from the data. They are (1) the radius of gyration, (2) the extrapolated intensity $I(0)$ in absolute units, (3) the invariant Q, and (4) the specific phase boundary area.

For a dilute suspension of identical particles, the intensity $I(s)$ at small angles follows the Guinier law given by eq 3. The proportionality constant $I(0)$, which is the intensity extrapolated to angle zero, is given by

$$I(0) = N(\Delta n)^2 \qquad (6)$$

where N is the number of particles per unit volume of the sample and Δn is the number of excess electrons per particle, that is, the difference between the actual number of electrons contained within each particle and the number of electrons contained in an equal volume of the surrounding medium. (Here and in subsequent discussions, $I(s)$ is understood to be given in electron units per unit volume).

When the particles are not identical, the radius of gyration obtained from the Guinier law is a z-average R_z defined by

$$R_z^2 = \sum N_i(\Delta n_i)^2 R_i^2 / \sum N_i(\Delta n_i)^2 \qquad (7)$$

which agrees with the more customary definition of the z-average $X_z = \sum N_i M_i^2 X_i / \sum N_i M_i^2$ if the electron density within the particles is uniform. Similarly for particles differing in size but having the same constant density, $I(0)$ is given by

$$I(0) = N(\Delta\rho)^2 V_n V_w \qquad (8)$$

where $\Delta\rho$ is the electron density difference between the particle and the surrounding medium and V_n and V_w are the number-average and weight-average volumes of the particles, respectively.

The invariant Q, which can be evaluated by eq 1 or 2 from the observed intensity, is equal to the mean square fluctuation in electron density in the sample. For an ideal two-phase system having sharp phase boundaries and constant densities within the phases, one has

$$Q = (\Delta\rho)^2 \phi_1 \phi_2 \qquad (9)$$

where ϕ_1 and ϕ_2 are the volume fractions of the two phases. For the present context of a particulate system $\phi_1 = NV_n$, and therefore

$$Q = (\Delta\rho)^2 NV_n(1 - NV_n) \qquad (10)$$

Combined with eq 8, it gives

$$I(0)/Q = V_w/(1 - NV_n) \qquad (11)$$

Equation 11 and the Guinier analysis amount to two independent methods of determining the particle size.

There is potentially a third method for the particle size determination. This relies on the analysis of the intensity at relatively large angle s—the so-called Porod region. In this region the intensity of scattering from an ideal two-phase system is expected to follow the Porod law:

$$I(s) = (1/8\pi^3)S(\Delta\rho)^2/s^4 \qquad (12)$$

where S is the phase boundary area per unit volume. For particles of known shape and number density, the particle size can then be calculated from the knowledge of S. In the present work involving fairly low concentrations of block copolymers the intensity in the Porod region was, however, found to be too weak and too imprecise to warrant the Porod law analysis.

We assume the micelles in our system to consist of a core formed from the styrene block of the copolymer and the surrounding shell formed from the butadiene block. (The overall shape of the micelle is most likely to be spherical, but the following analysis does not require the assumption of spherical shape.) The core may or may not contain dissolved polybutadiene, depending on the temperature. The shell is certainly highly swollen with polybutadiene and would be indistinguishable from the bulk polybutadiene in its electron density. Thus, the scattering of X-rays arises solely from the micelle cores. If the volume fraction of styrene in the core is equal to η, the net difference $\Delta\rho$ in the electron density between the core and the surrounding medium is given by

$$\Delta\rho = \eta\Delta\rho_{SB} \qquad (13)$$

where $\Delta\rho_{SB}$ is the electron density difference between pure polystyrene and polybutadiene. (Here it is assumed that there is no volume change on mixing and that the effect of the small concentration of dissolved copolymer present in the bulk phase can be neglected.) Thus once the electron density contrast $\Delta\rho$ is determined from the X-ray data, the degree of swelling of the micelle core can be evaluated.

Equations 8 and 10 show that $\Delta\rho$ can be obtained from either $I(0)$ or Q once the micelle volume V and its number density N are known. The method of determining V from the ratio $I(0)/Q$ was outlined above. N is then obtained by dividing with V the total amount of styrene component available for micelle formation. Not all the block copolymer present in the mixture is available for micelle formation, since some of the block copolymers remain molecularly dissolved in the bulk polybutadiene phase. In order to evaluate N, V, and η with a due allowance given for the amount of dissolved block copolymer, we make the following analysis of the mass balance. Let ϕ be the concentration (volume fraction) of the total styrene units in the mixture. ϕ consists of two components:

$$\phi = \phi_m + \phi_s \qquad (14)$$

where ϕ_m represents the amount of styrene in micelles and ϕ_s that dissolved in the polybutadiene phase. Clearly, we have

$$\phi_m = NV_n\eta \qquad (15)$$

and

$$\phi_s = \phi_c(1 - NV_nf) \qquad (16)$$

where ϕ_c is the critical micelle concentration (i.e., the concentration of styrene in the polybutadiene phase, expressed in terms of the volume fraction of styrene) and f is the ratio of the volume of the whole micelle (including the surrounding shell of butadiene blocks as well as the core) to the micelle core. In writing (16), we assume that the volume occupied by the micelle shell is excluded to the styrene blocks dissolved in the polybutadiene phase. The critical micelle concentration ϕ_c can be determined from the data on the dependence of $I(0)$ on ϕ by extrapolating to $I(0) \rightarrow 0$. Precise information on f is not available, but for the fairly low critical micelle concentrations encountered in our system, the values of N and η deduced are affected only marginally by the uncertainty in f. We assume that the thickness of the shell is comparable to the radius of the core (since the lengths of the butadiene and styrene blocks are about the same) and therefore equate f to 2.[3]

Combining eq 8, 10, and 13–16, one can write down the following set of three equations

$$I(0) = (\Delta\rho_{SB})^2\eta^2NV_nV_w \qquad (17)$$

$$Q = (\Delta\rho_{SB})^2\eta^2NV_n(1 - NV_n) \qquad (18)$$

$$\phi = NV_n\eta + \phi_c(1 - NV_nf) \qquad (19)$$

which can then be solved simultaneously for the three unknowns N, η, and V_n (on the approximation that $V_n \sim V_w$).

IV. Results

The radius of gyration R_z, evaluated from the Guinier analysis as described in the Experimental Section, is plotted against temperature in Figure 3. The estimated error of the individual points is indicated by an error bar for the data of the 4% mixture. The errors for the other mixtures are also comparable but are not shown in the figures to avoid cluttering. At low temperature R_z is fairly independent of the concentration. Although one can discern a tendency for R_z at low temperature to increase very slightly with increasing concentration (especially for 6 and 8% solutions), it is barely beyond the experimental error. At all concentrations the effect of raising temperature is at first to reduce R_z slightly but then to increase it rapidly at higher temperatures. This rapid increase in micelle size is associated with the swelling of the micelle core with polybutadiene and the eventual dissolution of the micelles, and more will be discussed about this later. The onset of the rapid increase in R_z occurs at higher temperatures as the concentration of copolymer in the mixture increases.

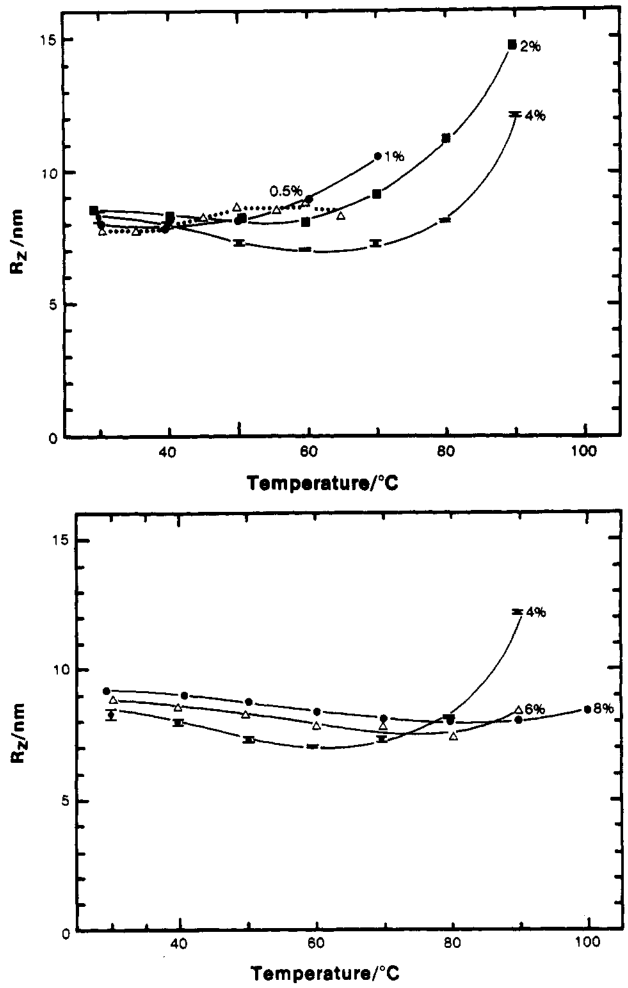

Figure 3. Radius of gyration R_z obtained from the Guinier analysis. The estimated errors are indicated for the 4% mixture. The errors for other mixtures are comparable.

Figure 4 shows the $I(0)$ values plotted against temperature for all the mixtures (except for the 6% solution to avoid cluttering the figure). The $I(0)$ values were evaluated by extrapolating $I(s)$ toward $s^2 \rightarrow 0$ in the Guinier plot. For each mixture the value of $I(0)$ at first decreases only moderately with temperature but then falls rapidly within a narrow temperature range of 10–20 °C, indicating sudden dissolution of micelles with increasing temperature. The temperature of dissolution increases with increasing concentration of copolymer in the mixture and parallels the similar trend noted in Figure 3 with respect to the temperature of rapid increase in R_z.

When, at any given temperature, the value of $I(0)$ is plotted against the concentration, a fairly good straight line is obtained. On extrapolating it until $I(0)$ equals zero, we obtain the criical micelle concentration, that is, the minimum concentration necessary for the formation of micelles at the temperature. Figure 5 shows the critical micelle concentration (given as wt % of the copolymer) thus obtained against the temperature. It is seen that its temperature dependence is very moderate at low temperatures.

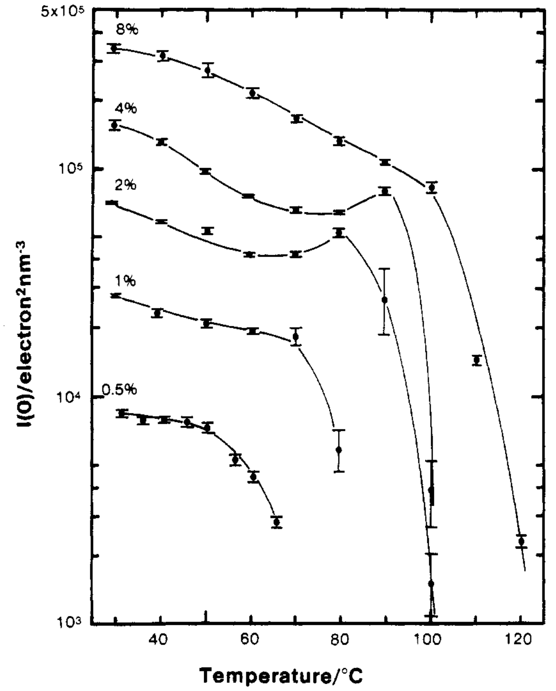

Figure 4. Extrapolated intensity $I(0)$ plotted against temperature. The data for 6% mixture are omitted for clarity. The values of $I(0)$ were obtained by linear extrapolation toward $s^2 \to 0$ in the Guinier plot.

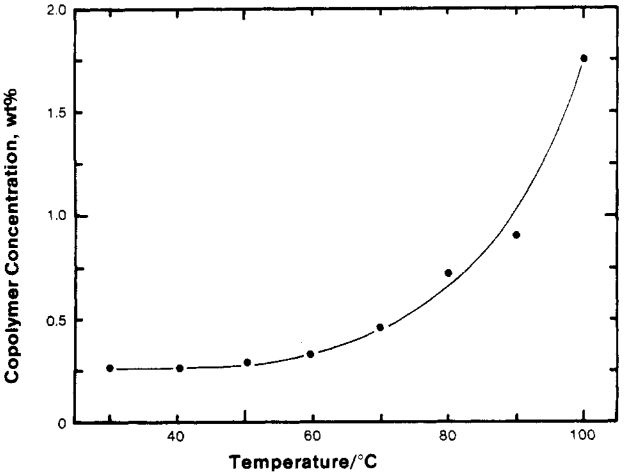

Figure 5. Critical micelle concentration plotted against temperature. The critical micelle concentration was determined by plotting the $I(0)$ values in Figure 4 against concentration at a given temperature and extrapolating linearly toward $I(0) \to 0$.

The values of the invariant Q, evaluated in the manner described in the Experimental Section, are plotted in Figure 6 against temperature for all the concentrations studied. Unlike $I(0)$, the invariant is seen to exhibit a steady decline with increasing temperature. For each concentration, the temperature at which Q extrapolates to zero compares well with the temperature at which the $I(0)$ value similarly extrapolates to zero. When the values of Q are plotted against concentration at a given temperature, a good straight line is again obtained. The critical micelle concentration evaluated from such a plot of Q against concentration agrees well with that given in Figure 5 (with the exception that at 100 °C a higher concentration of about 3% is obtained instead of 1.75% given in Figure 5).

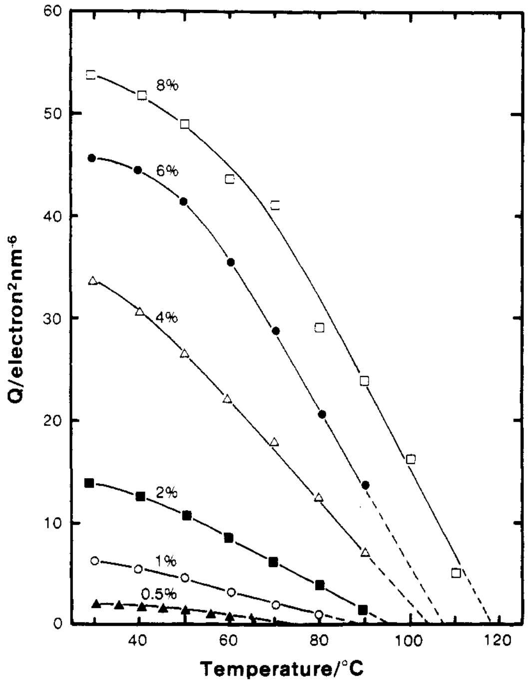

Figure 6. Invariant Q, evaluated according to eq 1, for all the mixtures studied.

Making use of the data presented in Figures 4–6, we are now ready to solve the set of simultaneous equations (17)–(19) to obtain the number density N of micelles, the volume V of a micelle core, and the volume fraction η of styrene in the core. The electron density difference $\Delta\rho_{SB}$ between pure polystyrene and polybutadiene, required as a function of temperature for this purpose, is calculated from the specific volume[21] of polybutadiene $v = 1.0968 + 8.24 \times 10^{-4}t$ and the specific volume[22] (above T_g) of polystyrene $v = 0.9217 + 5.412 \times 10^{-4}t + 1.687 \times 10^{-7}t^2$. The temperature coefficient of the specific volume of polystyrene undergoes a discontinuous change at T_g, and as a result the specific volume below T_g depends on the precise location of T_g. The T_g of polystyrene of molecular weight 12 500 is about 85 °C.[17,22] However, the T_g of styrene microdomains in a block copolymer is known[17] to be lower in general than the T_g of polystyrene of the same chain length by about 20 °C. Krause et al.[17] determined the T_g of the block copolymer used in this work to be 67 °C by DSC and 62 °C by the refractive index measurements. The T_g of the micelle core in our samples will be lowered still further to an extent depending on the degree of swelling by polybutadiene which, as will be shown shortly, is appreciable in many cases. We therefore assume that the T_g of the core is equal to 45 °C and calculate the specific volume of polystyrene below T_g by $v = 0.9369 + 2.006 \times 10^{-4}t + 2.470 \times 10^{-7}t^2$ (the second and third terms of this expression being taken from the data by Richardson and Savill[22]). Once the degree of swelling is obtained on this assumption, it is then possible to make a better estimate of T_g which will lead to a further refinement in the calculated values of N, η, and V. But the correction resulting from such an iteration turns out to be small, and the results shown in Figures 7–10 are all based on the T_g of 45 °C.

Figure 7 shows the volume fraction η of styrene in micelle cores plotted against temperature for three concentrations, 1, 4, and 8%. Other concentrations give similar results but are omitted from Figure 7 for clarity. The estimated errors for the points in Figure 7 are such that at low temperatures the difference among mixtures of different concentrations is probably not significant. At all concentrations there is clearly a tendency for the degree of swelling to increase steadily as the temperature is increased. Figure 8 gives the number of block copolymer

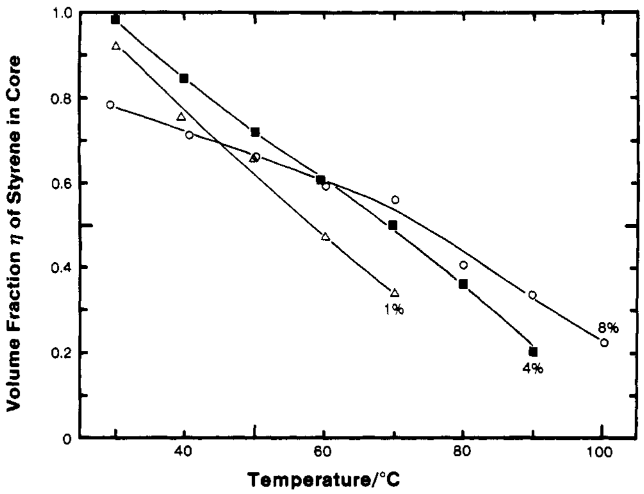

Figure 7. Volume fraction η of styrene in the micelle core. This shows that the degree of swelling of the micelle core increases appreciably with increasing temperature.

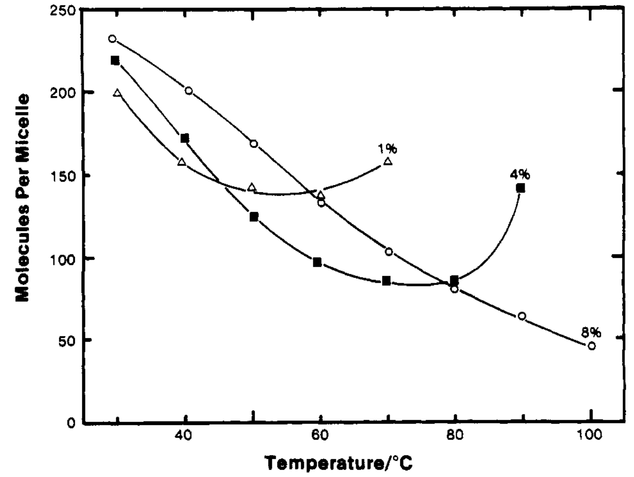

Figure 8. Number of block copolymer molecules aggregating to form a micelle.

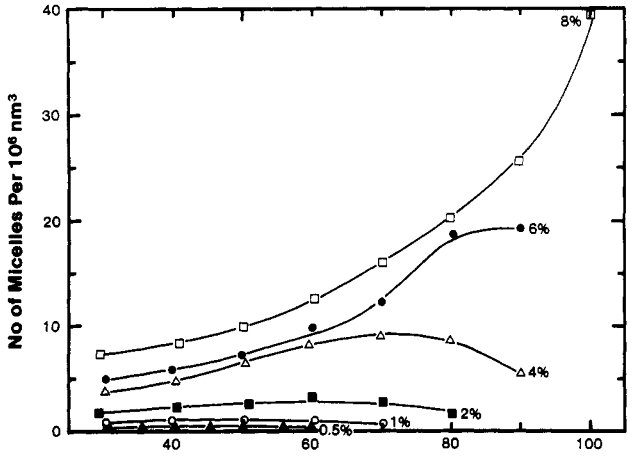

Figure 9. Number density N of micelles. The ordinate scale shows the number of micelles present in (100 nm)^3 of the mixture.

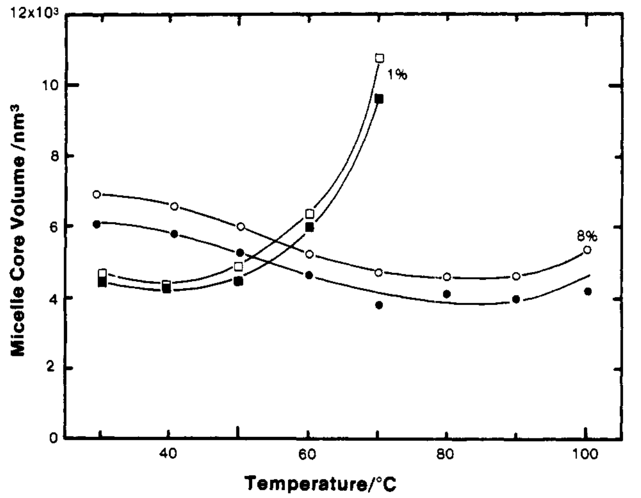

Figure 10. Comparison of volume of a micelle core evaluated by two independent methods. The open symbols represent the z-average volumes V_z calculated from the radius of gyration, and the solid symbols represent the weight-average volume V_w obtained from $I(0)/Q$ (or more precisely, from the solution of eq 17–19).

molecules participating in a micelle. At room temperature about 200 molecules aggregate to form a micelle, but with increasing temperature the number decreases appreciably as the micelles become more swollen with polybutadiene. It is interesting to recall that, as shown in Figure 3, the size of the micelles essentially remains unchanged until the dissolution temperature is approached. The rapid increase in the micelle size just below the dissolution temperature then forces the number of molecules per micelle to increase likewise. The upturn in Figure 8 exhibited by 1% and 4% mixtures is believed to be real and well outside the experimental error. Figure 9 shows the number density N of micelles as a function of temperature for the mixtures of different concentrations. At low concentrations the number density is insensitive to the change in temperature. At higher concentrations the temperature range for micelle stability increases, and the number density then exhibits fairly large variations with temperature reflecting the changes in the size and the degree of swelling of the micelles.

As stated earlier, the size of the micelles can be determined by two independent methods, the radius of gyration R_z from the Guinier analysis and the weight-average volume V per micelle from the ratio $I(0)/Q$ (or from the simultaneous solution of eq 17–19). When the particles are spherical and of uniform density within the particle, then the radius of the sphere is given by $(5/3)^{1/2}R_z$. In Figure 10 the z-average volume V_z per micelle, calculated from the radius of gyration, and the weight-average volume V_w, calculated from the ratio $I(0)/Q$, are compared. It shows an excellent agreement between the two sets of values, thus indicating that the micelles are indeed spherical. V_z is slightly larger than V_w in all cases and this can probably be attributed to the polydispersity in the size of micelles. The fairly small number of molecules involved in a micelle gives rise to a thermodynamic fluctuation in the size of micelles even under equilibrium conditions. Leibler et al.[6] estimate that for a system comparable to ours the fluctuation would be about 5%. Scattering from strictly monodisperse spheres is expected to exhibit several sharp minima at regular angular intervals, and the absence of such minima in our observed $I(s)$ curves also suggests some degree of polydispersity in the micelle size.

V. Discussion

Let us recapitulate some of the qualitative features revealed by the results presented in Figures 3–10. When the amount of the copolymer is below the critical micelle concentration, it remains molecularly dissolved in the polybutadiene. As the concentration is increased, the copolymer in excess of the critical micelle concentration aggregates into micelles. At low temperatures, the size of the micelles is fairly independent of the concentration; more micelles are formed when more copolymer is added. Around room temperature, in our system, the micelle core consists of mostly pure styrene blocks with very little imbibed polybutadiene. With increasing temperature the degree of swelling of the core with polybutadiene increases steadily until at a certain temperature the micelles dissolve completely. The dissolution temperature increases with increasing concentration. At a relatively narrow temperature interval below the dissolution point, the swollen micelles also become enlarged markedly. At lower temperatures below the onset of such enlargement, the micelle size remains fairly constant even when the degree of swelling is changing appreciably with temperature.

With the mixture containing 8% copolymer reliable evaluation of the micelle size could not be obtained above 100 °C (either through the Guinier analysis or from the $I(0)/Q$ ratio) because the scattered X-ray intensity became too weak. Thus, although 4% and 6% mixtures clearly showed a tendency for the micelle to increase in size at temperatures just below the dissolution temperature (see Figure 3b), a similar tendency could not be confirmed with the 8% mixture. Indeed, with the latter the number density of micelles is so high, especially at higher temperatures (see Figure 9), that the micelles are very likely to be impinging on each other and may even be on the verge of forming a superlattice of microdomains—the kind of structure usually found with bulk block copolymers. The possible transition between these two types of structures, that is, one containing randomly spaced micelles and another consisting of ordered arrays of microdomains, is a subject of interest. We plan to make a more detailed study of this aspect shortly by extending the measurements to higher concentrations.

A crude estimate of the concentration at which the impingement among micelles becomes important can be obtained as follows. The radius r of the micelle core can be estimated by $(5/3)^{1/2}R_z$ from the knowledge of R_z. We next assume that the thickness t of the micelle shell consisting of butadiene blocks is comparable to the unperturbed end-to-end distance of a polybutadiene chain of the same length. For polybutadiene of molecular weight 12 500 the latter is about 10 nm. The volume fraction x of the mixture which is actually occupied by micelle cores and shells (assuming no overlap of neighboring shells) is given by

$$x = (4/3)\pi(r + t)^3N$$

For example, for $R_z = 8$ nm and $N =$ ca. 10^{-5} nm^{-3} (the data for 6% mixture at 70 °C), x is equal to 0.35. When spheres are tightly packed in a simple cubic lattice, the fraction of volume occupied by the spheres is equal to 0.52; when packed in a body-centered cubic lattice, the fraction is 0.68; and in a face-centered cubic lattice, it is 0.74. Thus, when x is less than about 0.50, as in the above example cited, micelles may maintain still enough distance between each other to enable them to move around. When the number density N exceeds ca. 2×10^{-5} nm^{-3}, as is found to occur at 80 °C or above for 8% mixture (see Figure 9), the volume fraction x approaches unity, and a considerable interpenetration of shells of neighboring micelles has to occur. The shape of the X-ray scattering curve suggests, however, that even for the 8% mixture above 80 °C ordering of micelles into a superlattice has not yet developed, and the locations of the micelle cores may still be regarded fairly random in space.

The unperturbed root-mean-square end-to-end distance of polystyrene of molecular weigh 12 500 is equal to 7.3 nm. Its fully extended chain length is 30.5 nm. The radius r of the micelle core of R_z equal to 9 nm is 11.6 nm. This means that the styrene blocks of the copolymer must be moderately stretched if a uniform density of styrene is to be maintained within the core. It is conceivable that, when the core becomes very highly swollen with polybutadiene, a nonuniform distribution of styrene monomers within the core might eventually develop. More polybutadiene might concentrate toward the center of the core if the entropy loss associated with the chain stretching becomes so severe as to be greater than the entropy loss from a nonuniform distribution of styrene monomers. If this happens, the radius of gyration would become larger than $(3/5)^{1/2}r$ and approach r as the nonuniformity becomes more severe. The good agreement, shown in Figure 10, between the core volumes calculated from R_z and from $I(0)/Q$, however, suggests that in our mixtures the distribution of styrene monomers remains uniform in the core under all conditions studied.

In this work we have been able to obtain rather detailed information on the structure of block copolymer micelles as a function of temperature and concentration. The data we present should offer an excellent opportunity for testing theories of micelle formation. Two such theories have recently[4-6] been advanced. Two factors, however, prevented us from making detailed comparison of our data with these theories at this time. First, quantitative predictions from these theories can be obtained only through a rather involved numerical computation, especially in the case of the theory by Hong and Noolandi.[4,5] Second, some of the simplifying assumptions made in these theories may not be appropriate for our system. Thus, Hong and Noolandi[5] assume that a negligible amount of block copolymer remains molecularly dissolved in the continuous solvent (or homopolymer) phase. Leibler[6] et al. do not allow for the possibility that the micelle core becomes swollen with homopolymer.

We have nevertheless made some limited amount of computation according to the theory by Leibler et al. For this purpose the number of segments (N in the theory[6]) per copolymer molecule was assumed to be 240 and the length a of a segment to be 0.71 nm. The interaction parameter between styrene and butadiene was taken from our previously published data.[14] With these values of the parameters the theory predicts the micelle core radius to be about 10.5 nm and the number of copolymer molecules per micelle to be about 120 at room temperature. The predicted core radius is in excellent agreement with our results given in Figure 3. The predicted number of molecules per micelle is about half the experimental value. (There is a degree of latitude in choosing the length a of a segment and the number N of such segments to represent a real copolymer molecule. The values predicted by the theory depend somewhat on these choices made. The apparent inconsistency shown by the good agreement in one respect—radius—and a less satisfactory agreement in another—molecules per micelle—is also a consequence of the difficulty in making the most rational assignment to a and N.) The predicted value of the radius decreases with temperature much more rapidly than our experimental results indicate. This discrepancy may arise from the swelling of micelle cores which the theory did not allow. Modification of the theory to incorporate this feature should be fairly straightforward, and then a much more detailed comparison with our data would become possible.

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mation prior to publication.

Registry No. (Butadiene) (homopolymer), 9003-17-2; (butadiene)·(styrene) (copolymer), 9003-55-8.

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Expansion Factor of a Part of a Polymer Chain in a Good Solvent Measured by Small-Angle Neutron Scattering

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ABSTRACT: The radii of gyration of deuterium-labeled sections of polystyrenes with narrow molecular weight distributions were determined in a good solvent (carbon disulfide) by small-angle neutron scattering (SANS). The expansion factors of the labeled sections were calculated from the measured radii of gyration using unperturbed dimensions estimated from literature radius of gyration–molecular weight relationships for polystyrenes. The expansion factors of the labeled sections are smaller than those of the whole chains but are larger than that of a whole chain with the same molecular weight as the labeled section. Both results are reasonable in comparison with a Monte Carlo calculation in the literature and also with the perturbation theory.

Introduction

It is well-known that the mean square radius of gyration of nonionic polymers in good solvents $\langle s^2 \rangle$ is proportional to the $(1 + \epsilon)$th power of the molecular weight, $M^{1+\epsilon}$, where ϵ is about 0.2. This implies that the conformation of the polymer coils does not follow Gaussian statistics. In their calculation of the scattering factor $P(\theta)$, Peterlin[2] et al.[3,4] took into account this non-Gaussian distribution of segments by assuming that the mean square distance between the ith and jth segments $\langle r_{ij}^2 \rangle$ is proportional to $|i - j|^{1+\epsilon}$, as in the mean square radius of gyration–molecular weight relationship for whole molecules.

Experimental determinations of $P(\theta)$ by light scattering, however, showed that $P(\theta)$ does not agree with the function of Peterlin et al. but is better approximated by the Debye function based on the Gaussian distribution of segments, if the scattering angles are low enough.[5] To understand the conformation of polymers in good solvents more clearly, therefore, it is desirable to determine the expansion factors for portions of polymer chains relative to those of the entire chain.[6-9]

In the present work, we determined the radii of gyration of deuterated sections of polystyrenes by small-angle neutron scattering, using block copolymers of ordinary and deuterated polystyrenes having narrow molecular weight distributions both in each block and in the whole molecule.[10] The samples were prepared carefully, as previously described, in view of the fact that scattering from block copolymers is very sensitive to heterogeneities in both molecular weight and composition.

Experimental Section

Materials. A deuterated styrene homopolymer and partially labeled polystyrenes used as samples in this work were prepared by a sequential monomer addition method in anionic polymerization. The polymerization was carried out in benzene with *sec*-butyllithium. Sample TUN-01 is a homopolymer of d styrene, TUN-14 is a diblock copolymer of d and h styrenes, and TUN-15 is a triblock copolymer of h, d, and h styrenes. The polymers obtained were purified by fractional precipitation. Their number- and weight-average molecular weights were determined by membrane osmometry and light scattering. The contents of d styrene in the two block copolymers were determined by pyrolysis–gas chromatography.[11] The molecular weights of the deuterated sections were calculated from the total molecular weights and the d styrene content of the purified samples. Molecular characteristics of the samples are listed in Table I.

Spectrograde CS$_2$ was used as a good solvent for polystyrenes without further purification. Since the scattering length of CS$_2$ is nearly equal to that of ordinary polystyrene, the observed coherent scattering is due to the deuterated portions of the samples.

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