(26) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 258.
(27) Richards, R. W., private communication. Richards, R. W.; Thomason, J. L. *Macromolecules* **1983**, *16*, 982.
(28) Bates, F. S., private communication.
(29) Pedemonte, E.; Turturro, A.; Bianchi, V.; Devetta, P. *Polymer* **1973**, *14*, 145.
(30) Douy, A.; Gallot, B. *Makromol. Chem.* **1981**, *182*, 265.
(31) Richards, R. W.; Thomason, J. L. *Polymer* **1981**, *22*, 581.
(32) Bates, F. S.; Cohen, R. E.; Berney, C. V. *Macromolecules* **1982**, *15*, 589.
(33) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1967.
(34) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca (NY) and London, 1979.
(35) Vonk, C. G. *J. Appl. Crystallogr.* **1973**, *6*, 81.
(36) LeGrand, D. G. *J. Polym. Sci., Part B* **1970**, *8*, 195.
(37) Kim, H. *Macromolecules* **1972**, *5*, 594.
(38) Hashimoto, T.; Nagatoshi, K.; Todo, A.; Hasegawa, H.; Kawai, H. *Macromolecules* **1974**, *7*, 364.
(39) Bonart, R.; Müller, E. H. *J. Macromol. Sci., Phys.* **1974**, *B10* (1), 177.
(40) Hashimoto, T.; Todo, A.; Itoi, H.; Kawai, H. *Macromolecules* **1977**, *10*, 377.
(41) Todo, A.; Uno, H.; Miyoshi, K.; Hashimoto, T.; Kawai, H. *Polym. Eng. Sci.* **1977**, *17*, 587.
(42) Koberstein, J. T.; Morra, B.; Stein, R. S. *J. Appl. Crystallogr.* **1980**, *13*, 34.
(43) Campos-Lopez, E.; McIntyre, D.; Fetters, L. J. *Macromolecules* **1973**, *6*, 415.
(44) Roe, R.-J. *J. Appl. Crystallogr.* **1982**, *15*, 182.

Theory of Block Copolymer Micelles in Solution

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ABSTRACT: A simple model of AB diblock copolymer micelles in solution is presented. A spherical shape is assumed, with a completely uniform inner core formed from the insoluble B blocks and a uniform outer shell composed of the soluble A blocks. The interaction parameters, as well as the molecular weight, composition, and overall volume fraction of the copolymers, are assumed to be given. All energetic and entropic contributions to the free energy can be written down simply, with the exception of the interfacial tension γ of the asymmetric interphase. An approximation for γ is developed, and the free energy is minimized to obtain the equilibrium size of the micelle. Good agreement with the small-angle X-ray scattering data on the polystyrene/polybutadiene/*n*-heptane system is obtained. Numerical results, as well as scaling arguments, indicate that the size of the micelle, even for different block copolymer compositions, is characterized by power law functions of the total molecular weight of the block copolymer.

1. Introduction

Although there is a vast experimental literature on diblock copolymer micelles in selective solvents (ref 1–5 and numerous references contained therein), little theoretical work has been done to predict their structural properties from equilibrium statistical mechanics. In particular, given the overall volume fraction of block copolymer in solution, as well as its molecular weight and chemical composition, one would like to know the sizes of the insoluble core and the soluble outer shell, the degrees of swelling of the two blocks, and the number of polymer chains per micelle. These predictions can then be checked against the results of small-angle X-ray scattering experiments.

In this paper, we present a simple model from which these quantities can be calculated in a straightforward way. We note, however, that we consider only lyophilic systems. Although micellar solutions obtained with amphiphilic block copolymers in the presence of water, oil, and alcohol have been intensively studied recently,[6–10] the corresponding theoretical treatment involves more parameters and will not be discussed here. For the present work, the only complication that arises is the determination of the interfacial tension between the soluble and insoluble blocks of the micelle. We deal with this problem by referring to a general (mean field) expression for the interfacial tension γ of an asymmetric interphase derived earlier[11] using the functional integral formalism. For the present situation, we develop an approximation for γ that involves only χ parameters and the (bulk) volume fractions of polymers away from the interphase. The derivation is given in the Appendix.

In section 2, we describe the micelle model in detail. The contributions to the free energy come from polymer–polymer and polymer–solvent interactions, the combinatorial entropy of the solvent molecules, the entropy loss from localization of block copolymer joints at the interphase, the entropy loss from the stretching of the blocks, and the loss of entropy from the turning back of polymers at the interphase. We assume uniform polymer density profiles in both the soluble and insoluble parts of the micelle, and consequently no integrals over the free energy density remain in the final expressions.

The comparison of experiment and theory is discussed in section 3, with the results summarized in Table I. For definiteness, we have chosen a particular set of experiments carried out by Plestil and Baldrian.[2] Section 4 contains the conclusions, with emphasis on the theoretically predicted power law dependencies of the micelle size parameters on molecular weight. Similar results for the power laws only have been obtained earlier by de Gennes,[12] whose work, however, does not allow a prediction of the various size parameters.

2. Description of Micelle Model

As described in one of our earlier publications,[13] we assume a spherical model for the micelle, shown in Figure 1, that is made up of three uniform regions. In the presence of a poor solvent for the B block of the copolymer, the center core, labeled as region 1, is composed of a concentrated solution of B chains. The outer shell (region 2) is formed from a less concentrated solution of A blocks of the copolymer. Hence, the solvent–polymer interaction parameter for the A block (χ_{AS}) is assumed to be much smaller than that for the B block (χ_{BS}). The outside of the micelle, region 3, is composed of pure solvent. The radius l_B, and the thickness of the shell, l_A, are the average

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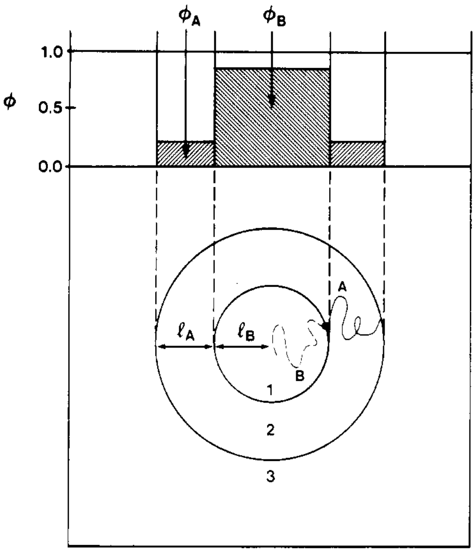

Figure 1. Cross section of spherical micelle composed of AB diblock copolymers, showing uniform core formed from the B blocks and uniform outer shell formed from the A blocks. The narrow asymmetric interphase between regions 1 and 2 is not shown. The upper panel shows the results of the calculations for the volume fractions of the components in the three regions for the polystyrene/polybutadiene/*n*-heptane system, with the interaction parameters given in section 3.

end-to-end distances of the B and A blocks, respectively, and are determined by minimization of the total free energy. The radius of the unit cell, which encloses the entire micelle, as well as some pure solvent, is denoted by R and is determined by the same procedure.

The central core and the outer shell of the micelle are separated by a narrow interphase region, whose width is discussed later. The overall volume fraction of the copolymer is φ_C^0, and in the present case since we have only a two-component system, the overall volume fraction of solvent is $\varphi_S^0 = 1 - \varphi_C^0$. These quantities are determined by the experimental conditions. Other quantities to be determined by the calculation are the fractions of solvent (by volume) in regions 1, 2, and 3, denoted by F_1^S, F_2^S, and F_3^S, respectively, and the fractions of the total volume of the three regions, denoted by G_1^υ, G_2^υ, and G_3^υ. The degrees of polymerization of the copolymer blocks are given by Z_A and Z_B, with $Z_C = Z_A + Z_B$. The reduced molecular volumes with respect to the solvent are $r_A = Z_A\rho_{0S}/\rho_{0A}$ and $r_B = Z_B\rho_{0S}/\rho_{0B}$, with $r_C = r_A + r_B$, $f_A = r_A/r_C$, and $f_B = r_B/r_C$, where $\rho_{0\kappa}$ is the molar density of the pure component κ.

Since the volume fractions of the different components must sum to unity for each of the three regions, we have the relations:

$$\begin{aligned} 1 &= f_B(\varphi_C^0/G_1^\upsilon) + (F_1^S/G_1^\upsilon)\varphi_S^0 \\ 1 &= f_A(\varphi_C^0/G_2^\upsilon) + (F_2^S/G_2^\upsilon)\varphi_S^0 \qquad (2\text{-}1) \\ 1 &= (F_3^S/G_3^\upsilon)\varphi_S^0 \end{aligned}$$

In addition, the G_i^υ's sum to unity and are given in terms of the length parameters as

$$\begin{aligned} G_1^\upsilon &= (l_B/R)^3 \\ G_2^\upsilon &= \left(\frac{l_A + l_B}{R}\right)^3 - \left(\frac{l_B}{R}\right)^3 \qquad (2\text{-}2) \\ G_3^\upsilon &= 1 - \left(\frac{l_A + l_B}{R}\right)^3 \end{aligned}$$

Clearly, if the lengths are known, the G's and F's can be determined from eq 2-1 and 2-2.

At this point, we are ready to consider the form of the free energy per unit volume of the micelle, which we write relative to the corresponding free energy of the homogeneous random state:

$$\Delta g = \frac{G_{\text{micelle}} - G_{\text{random}}}{\rho_{0S} V k_B T} \qquad (2\text{-}3)$$

where V is the volume and ρ_{0S} is the reference density. For the block copolymer concentrations we will be dealing with, this quantity will be negative and we will not be concerned with the much smaller value of the critical micelle volume fraction.[13] Instead we will minimize Δg with respect to variations in the length parameters l_A, l_B, and R for given block copolymer molecular weight, composition, and overall concentration. Now the polymer interaction energy contribution to Δg (exclusive of the interfacial tension, which we discuss later) is given by recalling that the volume fraction of block A in region 2 is $\varphi_A = f_A(\varphi_C^0/G_2^\upsilon)$ while that of the solvent is $F_2^S(\varphi_S^0/G_2^\upsilon)$, with similar expressions for region 1.

$$\begin{aligned} \Delta g_{\text{int}} = {} & -\chi_{AB} f_A f_B (\varphi_C^0)^2 + \chi_{AS} f_A \varphi_C^0 \varphi_S^0 F_2^S/G_2^\upsilon - \\ & \chi_{AS} f_A \varphi_C^0 \varphi_S^0 + \chi_{BS} f_B \varphi_C^0 \varphi_S^0 F_1^S/G_1^\upsilon - \chi_{BS} f_B \varphi_C^0 \varphi_S^0 \qquad (2\text{-}4) \end{aligned}$$

Note that the AB polymer interaction term for the ordered state vanishes in this expression, since we include the interfacial tension term separately, and one $(1/G)$ factor is missing from each of the two positive terms because we are calculating the free energy per unit volume.

The contribution to Δg from the combinatorial entropy of the solvent molecules involves terms like $(\varphi_S^0 F_1^S/G_1^\upsilon) \ln (\varphi_S^0 F_1^S/G_1^\upsilon)$, and the total contribution per unit volume with respect to the homogeneous state becomes

$$\begin{aligned} \Delta g_S = \varphi_S^0\{ & F_1^S \ln (F_1^S/G_1^\upsilon) + F_2^S \ln (F_2^S/G_2^\upsilon) + \\ & F_3^S \ln (F_3^S/G_3^\upsilon)\} \qquad (2\text{-}5) \end{aligned}$$

As in our earlier paper,[13] we lump the decrease in entropy of the block copolymers from that of the random state into three terms, the first arising from the localization of joints:

$$g_J = -(\varphi_C^0/r_C) \ln (3 l_B^2 d_I/R^3) \qquad (2\text{-}6)$$

where d_I is the width of the interphase. Another contribution, the so-called "elastic energy", accounts for the decrease in entropy arising from a stretching or compression of the copolymer chains along the radial direction and is given by the Flory expression[14]

$$g_{\text{el}} = (\varphi_C^0/r_C)\frac{1}{2}\left(\alpha_A^2 + \alpha_B^2 + \frac{2}{\alpha_A} + \frac{2}{\alpha_B} - 6\right) \qquad (2\text{-}7)$$

where

$$\alpha_A = \left(\frac{3}{Z_A}\right)^{1/2}\frac{l_A}{b_A} \qquad \alpha_B = \left(\frac{3}{Z_B}\right)^{1/2}\frac{l_B}{b_B} \qquad (2\text{-}8)$$

and b_A and b_B are the Kuhn lengths for the copolymer.

The last of the three terms is the interfacial tension, g_I, which is partly due to the interaction of the A and B blocks but also includes the change in the copolymer entropy arising from the turning back of the A and B chains at the interphase and confinement in their respective regions. Although there are actually two interphases in the micelle, between regions 1 and 2 and between regions 2 and 3 we neglect the second one because the outer block is soluble and we write

$$g_I = (\gamma_{12}/\rho_{0S} k_B T)(3 l_B^2/R^3) \qquad (2\text{-}9)$$

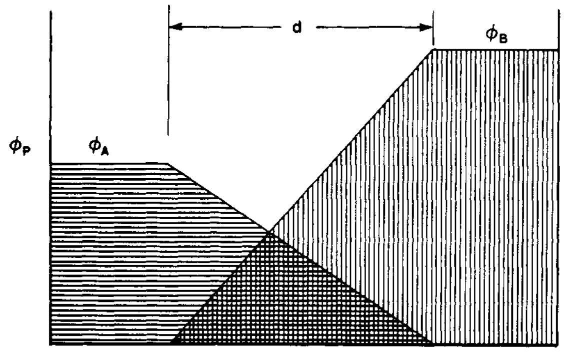

Figure 2. Linear density profile approximation used to obtain eq 2-10 and 2-11 for interfacial tension and width of an asymmetric interphase.

where ρ_{0S} is the reference density. In order to proceed at this point in the spirit of the rest of the calculation, we need a simple but reasonably accurate approximation for γ. This is developed in the Appendix, using the linear density profiles shown in Figure 2.

The expression for γ_{12} is finally given by

$$\gamma_{12}/\rho_{0S}k_BT = [\tfrac{1}{3}(\varphi_A + \varphi_B)\Delta f_{12}]^{1/2} \tag{2-10}$$

and the width of the interphase between regions 1 and 2 is given by

$$d_I = [(\varphi_A + \varphi_B)/12\Delta f_{12}]^{1/2} \tag{2-11}$$

In the above expression, $\varphi_A = f_A(\varphi_C^0/G_2^v)$ is the volume fraction of polymer A in region 2, $\varphi_B = f_B(\varphi_C^0/G_1^v)$ is the volume fraction of polymer B in region 1, and as explained in the Appendix

$$\Delta f_{12} = f\left(\frac{\varphi_A}{2}, \frac{\varphi_B}{2}\right) - \frac{1}{2}[f(\varphi_A,0) + f(0,\varphi_B)] \tag{2-12}$$

where

$$f(\varphi_A,\varphi_B) = \chi_{AB}\varphi_A\varphi_B + \chi_{AS}\varphi_A\varphi_S + \chi_{BS}\varphi_B\varphi_S + \varphi_S \ln \varphi_S \tag{2-13}$$

and $\varphi_A + \varphi_B + \varphi_S = 1$. The agreement of these simple expressions with more detailed numerical calculations is remarkably good, as shown in Figure 3. In deriving these results, we have assumed that the molecular weights of the two homopolymers are infinite. This is a good approximation since it is known that the interfacial tension is insensitive to the degree of polymerization at the large values corresponding to micelle formation.[15]

The sum of all the contributions to Δg is then

$$\Delta g = \Delta g_{\text{int}} + \Delta g_S + g_J + g_I + g_{\text{el}} \tag{2-14}$$

and in the present case is a function of the three length parameters l_A, l_B, and R. Unfortunately, in spite of all the simplifications, this function still must be minimized with respect to the parameters by a numerical method. The results are discussed in the next section, where comparison with experimental data is made for some specific cases.

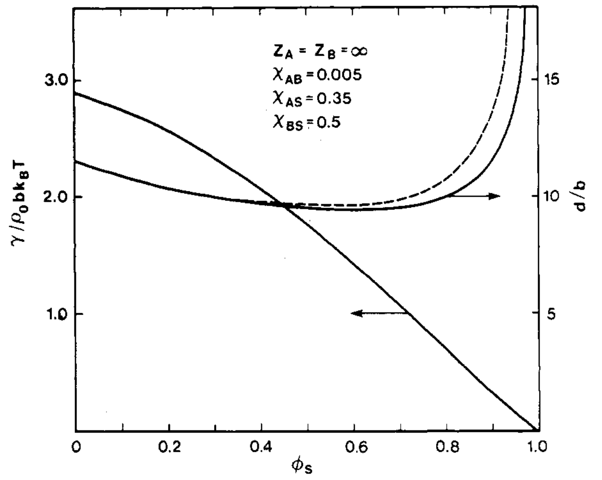

Figure 3. Solid lines show calculated interfacial tension γ (in reduced units) and interfacial width d (in units of the Kuhn length b) as a function of total solvent volume fraction, obtained from the approximate formulas, eq 2-10 and 2-11. The interaction parameters are $\chi_{AS} = 0.35$, $\chi_{BS} = 0.5$, and $\chi_{AB} = 0.005$. The broken line shows the results of d obtained from a numerical solution of the modified diffusion equation.[15] The corresponding values of γ are indistinguishable from the solid line.

3. Comparison with Experimental Results

In this section, we compare the predictions of our theory to the small-angle X-ray scattering data of Plestil and Baldrian[2] on styrene/butadiene block copolymer micelles in n-heptane. For these experiments, the number-average molecular weight of the copolymer was $M_n = 64\,700$, with 24% polystyrene content by weight, giving Z_A(PBD) = 911 and Z_B(PS) = 149. The monomer densities of the pure materials at room temperature, in mol cm^{-3} are $\rho_{0A} = 0.0176$,[16] $\rho_{0B} = 0.0103$,[17] and $\rho_{0S} = 0.00684$.[2] The overall volume fraction of copolymer, φ_C^0, varied from 0.005 to 0.4 and both the experimental and theoretical results were insensitive to changes in φ_C^0 in this range. The Kuhn lengths of the polybutadiene and polystyrene are $b_A = 6.8$ Å and $b_B = 7.1$ Å, respectively.[16] The determination of the χ parameters is less certain, but recent experiments give[18]

$$\chi_{AB} = -0.169 + 123/T \tag{3-1}$$

and the interaction parameter for polystyrene/n-heptane has been estimated to be[19]

$$\chi_{BS} = -1.12 + 901/T \tag{3-2}$$

The temperature dependence of the polybutadiene/n-heptane χ parameter apparently is not available in the literature, so we treat χ_{AS} as a temperature-independent constant determined from the calculation. A fit to the Plestil and Baldrian data[2] gives $\chi_{AS} = 0.53$, which is reasonable since it is close to the values for polyisoprene/n-heptane, which range from 0.49 to 0.51.[20] The results of the calculation are shown in Table I. Some of the quantities of interest are R_B, the radius of gyration of the polystyrene core

$$R_B^2 = \tfrac{3}{5}l_B^2 \tag{3-3}$$

and R_M, the radius of gyration of the whole micelle[2]

$$R_M^2 = \frac{3}{5}\,\frac{a_Ar_A(l_M^5 - l_B^5)/(l_M^3 - l_B^3) + a_Br_Bl_B^2}{a_Ar_A + a_Br_B} \tag{3-4}$$

where $r_P = (\rho_{0S}Z_P)/\rho_{0P}$, $l_M = l_A + l_B$, and a_A and a_B represent the "excess" electrons of the polybutadiene and polystyrene, respectively. The number of polymer chains per micelle, N_M, is given by

$$N_M = \frac{\rho_{0S}}{r_C}\varphi_C^0\frac{4\pi}{3}R^3 \tag{3-5}$$

From Table I, it is evident that the agreement between theory and experiment is very good, except for the calculated values of N_M, which do not decrease as fast as the experimental values. The reason for this may be our neglect of the temperature dependence of χ_{AS}. However, we felt it was not particularly illuminating to introduce yet another parameter into the model. Clearly, the size

Table I
Comparison of Experimental[a] and Theoretical Results for Parameters Characterizing Polystyrene/Polybutadiene Micelles in *n*-Heptane[b]

	18 °C		25 °C		35 °C		50 °C	
	exptl	theor	exptl	theor	exptl	theor	exptl	theor
a_A	0.1127		0.1145		0.1173		0.1218	
a_B	0.1878		0.1879		0.1876		0.1892	
R_B, Å	86	81	82	80	77	79	71	77
R_M, Å	202	202	199	200	195	197	182	193
N_M	190	187	175	179	137	168	100	152
φ_A^{-1}	5.06	6.80	5.35	6.87	6.16	6.96	8.40	7.12
φ_B^{-1}	1.27	1.07	1.19	1.08	1.25	1.09	1.29	1.11
α_A		1.66		1.64		1.61		1.57
α_B		2.09		2.07		2.03		1.98
d_I, Å		7.4		7.7		8.2		8.9

[a] Reference 2. [b] A refers to polybutadiene (PBD) and B to polystyrene (PS). a_P (P = A, B) refers to the number of "excess" electrons of the P block of the copolymer. R_B and R_M are the radii of gyration of the PS core and the whole micelle, respectively, in angstroms. N_M is the number of polymer chains per micelle, and φ_P^{-1} is the degree of swelling of the P block of the copolymer. α_P is the stretching ratio of block P of the copolymer as defined in the text. d_I is the width of the interphase between the soluble and insoluble parts of the micelle in angstroms.

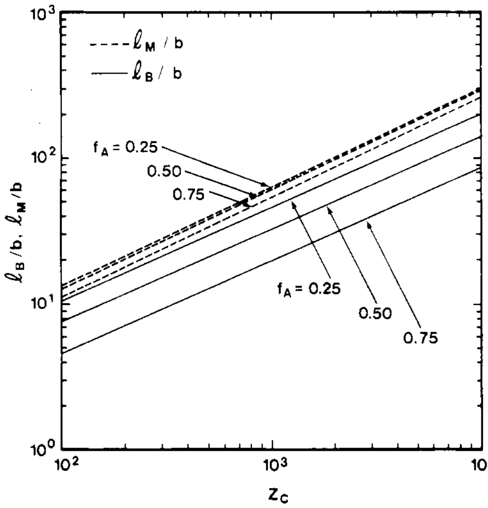

Figure 4. Radius of micelle (l_M) and central core (l_B) as a function of total copolymer molecular weight for varying copolymer compositions, $f_A = Z_A/Z_C$. The exponent for the micelle radius is 0.68 and for the core is 0.64. In these plots the χ parameters for the polystyrene/polybutadiene/*n*-heptane system were used (section 3). In addition, we have put $b_A = b_B = b$, and $\rho_{0_\kappa} = \rho_0$ for all components.

of the micelle as the temperature is raised is primarily determined by two conflicting trends. The decrease of χ_{AB} will lead to less segregation of the chains and favors shrinkage. However, the decrease of χ_{BS} and in particular, χ_{AS}, lead to an expansion of the micelle due to additional swelling, especially the outer shell, as the quality of the solvent improves. The fact that we obtain the overall trends correctly from this simple model is encouraging.

Several other points are worth mentioning. First, the interphase between regions 1 and 2 turns out to be narrow (in the range of 7–9 Å) as expected. However, because the A block is soluble, the outer shell does not have a narrow interphase between the polymer and the solvent. This points to an obvious way to improve the model, which is to remove the constant-density profile constraint in the outer shell (as well as the core) and to do a fully self-consistent calculation. However, we believe this is not justified at the present stage, and we maintain the uniform-shell model.

Second, plots of the calculated overall size of the micelle (l_M/b) as well as of the central core (l_B/b) as a function of the total block copolymer molecular weight (Z_C) show a power law dependence even for different copolymer compositions, as indicated in Figure 4. The degree of association, or number of polymer chains per micelle (N_M), also shows a power law dependence on Z_C, as seen in Figure 5.

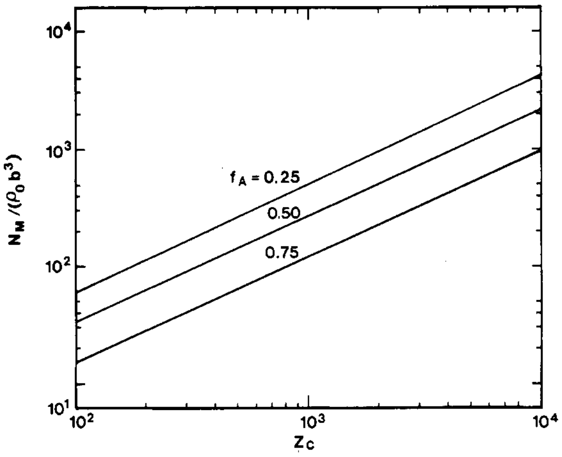

Figure 5. Degree of association or number of polymer chains per micelle as a function of total copolymer molecular weight for varying copolymer compositions, $f_A = Z_A/Z_C$. The exponent in this case is close to 0.9. The other parameters are the same as for Figure 4.

The scaling arguments for obtaining these power laws are very simple. Retaining only the main contributions to the free energy, we have

$$\Delta g \simeq \frac{\gamma}{\rho_0 k_B T}\frac{3 l_B^2}{R^3} + \frac{\varphi_C^0}{Z_C}\frac{1}{2}\alpha_B^2 \tag{3-6}$$

where α_B^2 is given by eq 2-8. Since the swelling ratios φ_A^{-1} and φ_B^{-1} do not change with block copolymer molecular weight, we also have $l_A \propto l_B$, and for this reason, we have not explicitly included the α_A^2 term in eq 3-6. (Actually φ_A^{-1} changes by a factor of 2 when the molecular weight changes by 2 decades, but we ignore this effect.) Now conservation of the volume occupied by the polymer requires

$$f_B \varphi_C^0 (4/3)\pi R^3 = \varphi_B (4/3)\pi l_B^3 \tag{3-7}$$

so that R scales with molecular weight in the same way as l_B. Using this relation, we rewrite eq 3-6 to give

$$\Delta g = \frac{\gamma}{\rho_0 k_B T}\frac{3 f_B \varphi_C^0}{\varphi_B}\frac{1}{l_B} + \frac{3}{2}\frac{\varphi_C^0}{f_B Z_C^2 b^2} l_B^2 \tag{3-8}$$

and minimizing this expression with respect to l_B gives

$$l_{\mathrm{B}}^3 = \frac{1}{\varphi_{\mathrm{B}}} f_{\mathrm{B}}^2 Z_{\mathrm{C}}^2 b^2 \frac{\gamma}{\rho_0 k_{\mathrm{B}} T} \tag{3-9}$$

The swelling ratio of the B blocks in the core of the micelle turns out to be almost unity; i.e., $\varphi_{\mathrm{B}}^{-1} \simeq 1$. According to this result, the size of the core and the overall size of the micelle scale as $Z_{\mathrm{C}}^{2/3}$, in close agreement with the results obtained from the more detailed calculations shown in Figure 4. The number of chains per micelle is obtained from eq 3-5:

$$\begin{aligned} N_{\mathrm{M}} &= \rho_0 \frac{\varphi_{\mathrm{B}}(4/3)\pi l_{\mathrm{B}}^3}{f_{\mathrm{B}} Z_{\mathrm{C}}} \\ &= \frac{4}{3}\pi f_{\mathrm{B}} Z_{\mathrm{C}} b^2 \frac{\gamma}{k_{\mathrm{B}} T} \end{aligned} \tag{3-10}$$

and the numerical results (Figure 5) are again in good agreement with the scaling prediction. To summarize these results, for a constant copolymer volume fraction, increasing Z_{C} increases $N_{\mathrm{M}} \propto Z_{\mathrm{C}}$, which means there are fewer micelles of larger size, $l \propto Z_{\mathrm{C}}^{2/3}$, in unit cells of larger volume, $R \propto Z_{\mathrm{C}}^{2/3}$.

To our knowledge, the scaling results were first obtained by Inoue et al.,[21] using the free energy per unit volume, although a slight oversight led to the wrong exponent. Later the correct exponents were calculated by de Gennes[12] on a free energy per chain basis.

4. Conclusions

We have presented a simple model of diblock copolymer micelles in a solvent that is good for one of the blocks and poor for the other. The assumption of uniform-density profiles for both the core of the micelle and the outer shell makes it possible to write down the free energy with respect to the homogeneous state in an elementary way. An approximation for the interfacial tension γ of an asymmetric interphase (assuming infinite molecular weight) had to be developed, however, by using the balance between the energy of interaction at the interphase and the conformational entropy in order to determine the equilibrium density profiles. The approximate expression for γ agrees very well with the more detailed calculations based on the numerical solution of the mean field diffusion equations for the polymer distribution functions. The agreement between theory and experiment is remarkably good for the polystyrene/polybutadiene/*n*-heptane system studied by Plestil and Baldrian,[2] to the extent of correctly predicting the changes with temperature of the radii of gyration, the degrees of swelling of the two blocks, and the degree of association of the micelle. The theoretical model is generally expected to be useful for interpreting small-angle X-ray scattering experiments on diblock copolymer micelles in solution. In particular, the predicted power law dependencies of the micelle size parameters on copolymer molecular weight are worth investigating experimentally. With regard to this point, it is probably important to obtain more accurate measurements of the radius of gyration of the core, R_{B}, rather than R_{M}, the radius of gyration of the whole micelle, since R_{B} is directly proportional to l_{B} and does not depend on the excess electron parameters a_{A} and a_{B} that appear in the expression for R_{M}. Finally, it would be interesting to experimentally subject the micelles to a rapid change in temperature and to measure the relaxation time to the equilibrium size as a function of molecular weight. The observations could be compared to the dynamic response predicted by reptation theory.[22,23]

Acknowledgment. We thank Dr. Giuseppa DiPaola-Baranyi for discussions concerning the polystyrene/*n*-heptane χ parameter. We are also grateful to Dr. L. Leibler for making us aware of ref 12.

Appendix

In this Appendix, we derive expressions for the interfacial tension and interfacial thickness for two homopolymers A and B of infinite molecular weight in the presence of an asymmetric solvent S. From ref 11, neglecting nonlocal effects, the interfacial tension γ is given by

$$\gamma/\rho_0 k_{\mathrm{B}} T = \int \mathrm{d}x \, [\Delta f(x) - \sum_{\mathrm{P}} \varphi_{\mathrm{P}}(x)\omega_{\mathrm{P}}(x)] \tag{A-1}$$

where ρ_0 is some reference density, x is the distance from the interface, $\Delta f(x)$ is the inhomogeneous free energy density (which vanishes in the bulk), $\varphi_{\mathrm{P}}(x)$ is the local volume fraction of polymer P, and $\omega_{\mathrm{P}}(x)$ is the mean field acting on polymer P. Note that the index P refers only to polymers A and B. The inhomogeneous free energy density is given explicitly by

$$\Delta f(x) = f[\varphi_{\mathrm{A}}(x), \varphi_{\mathrm{B}}(x)] - \sum_{\kappa} \varphi_{\kappa}(x)\mu_{\kappa} \tag{A-2}$$

where μ_{κ} is the chemical potential and κ now runs over all components A, B, and S. In terms of χ parameters, we have

$$f(\varphi_{\mathrm{A}}, \varphi_{\mathrm{B}}) = \tfrac{1}{2}\sum_{\kappa,\kappa'} \chi_{\kappa\kappa'} \varphi_{\kappa} \varphi_{\kappa'} + \varphi_{\mathrm{S}} \ln \varphi_{\mathrm{S}} \tag{A-3}$$

and of course

$$\varphi_{\mathrm{S}} = 1 - (\varphi_{\mathrm{A}} + \varphi_{\mathrm{B}}) \tag{A-4}$$

The effective potential $\omega_{\mathrm{P}}(x)$ is related to the polymer density $\varphi_{\mathrm{P}}(x)$ via the equations[11,24]

$$\varphi_{\mathrm{P}}(x) = [q_{\mathrm{P}}(x)]^2 \tag{A-5}$$

$$b^2 q_{\mathrm{P}}''(x) - \omega_{\mathrm{P}}(x) q_{\mathrm{P}}(x) = 0 \tag{A-6}$$

which have the above simple form only for polymers of infinite molecular weight. Here, for simplicity, we have taken the reduced Kuhn lengths of the polymers to be the same; i.e., $b_{\mathrm{A}} = b_{\mathrm{B}} = b$. In addition, the relevant boundary conditions are $\varphi_{\mathrm{A}}(-\infty) = \varphi_{\mathrm{B}}(\infty) = 0$.

Eliminating ω_{P} in terms of φ_{P} in eq A-1, we obtain

$$\gamma/\rho_0 k_{\mathrm{B}} T = \int \mathrm{d}x \left[\Delta f(x) + \frac{b^2}{24} \sum_{\mathrm{P}} \frac{[\varphi_{\mathrm{P}}'(x)]^2}{\varphi_{\mathrm{P}}(x)} \right] \tag{A-7}$$

and it is this expression that we now approximate in order to obtain a simple, manageable result for the interfacial tension. Since the integrand vanishes except near the interface ($x \simeq 0$), we put

$$\varphi_{\kappa}(0) \simeq \tfrac{1}{2}[\varphi_{\kappa}(\infty) + \varphi_{\kappa}(-\infty)] \tag{A-8}$$

$$\varphi_{\mathrm{A}}'(0) \simeq \frac{\varphi_{\mathrm{A}}(\infty)}{d} \equiv \frac{\varphi_{\mathrm{A}}^{b}}{d} \tag{A-9}$$

$$\varphi_{\mathrm{B}}'(0) \simeq -\frac{\varphi_{\mathrm{B}}(-\infty)}{d} \equiv -\frac{\varphi_{\mathrm{B}}^{b}}{d} \tag{A-10}$$

where d is the interfacial thickness, at present undetermined. Substituting these approximations in eq A-7, we get

$$\gamma/\rho_0 k_{\mathrm{B}} T \simeq \mathrm{d}\Delta f(0) + \frac{b^2}{12d} \sum_{\mathrm{P}} \varphi_{\mathrm{P}}^{b} \tag{A-11}$$

and minimizing γ with respect to d, we obtain the actual width of the interface:

$$d_I/b = [\sum_P \varphi_P{}^b/12\Delta f(0)]^{1/2} \qquad \text{(A-12)}$$

and

$$\gamma/\rho_0 b k_B T = b\sum_P \varphi_P{}^b/6d_I \qquad \text{(A-13)}$$

For our applications in this paper, it is convenient to express the chemical potential in terms of the asymptotic volume fractions $\varphi_P{}^b$. By noting that for a homogeneous system

$$f = \sum_\kappa \varphi_\kappa \mu_\kappa \qquad \text{(A-14)}$$

we see from eq A-2 and A-8 that

$$\Delta f(0) = f|_{x=0} - \tfrac{1}{2}(f|_{x=\infty} + f|_{x=-\infty}) = f\left(\frac{\varphi_A{}^b}{2}, \frac{\varphi_B{}^b}{2}\right) - \frac{1}{2}[f(\varphi_A{}^b,0) + f(0,\varphi_B{}^b)] \qquad \text{(A-15)}$$

The results obtained by using eq A-12, A-13, and A-15 agree very well with the more elaborate calculations of our earlier work,[15] as shown in Figure 3. Furthermore, for the case of a nonselective solvent ($\chi_{AS} = \chi_{BS}$), we have

$$\varphi_A{}^b = \varphi_B{}^b = 1 - \varphi_S \qquad \text{(A-16)}$$

and hence eq A-12 and A-13 reduce to

$$d_I/b = (2/3\chi_{AB})^{1/2}(1 - \varphi_S)^{-1/2} \qquad \text{(A-17)}$$

$$\gamma/\rho_0 b k_B T = (\chi_{AB}/6)^{1/2}(1 - \varphi_S)^{3/2} \qquad \text{(A-18)}$$

These results have been derived and used earlier.[15,24]

Registry No. Styrene/butadiene copolymer, 9003-55-8.

References and Notes

(1) Price, C.; Wood, D. *Eur. Polym. J.* **1973**, *9*, 827.
(2) Plestil, J.; Baldrian, J. *Makromol. Chem.* **1975**, *176*, 1009.
(3) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976**, *6*, 201.
(4) Kotaka, T.; Tanaka, T.; Hattori, M.; Inagaki, H. *Macromolecules* **1978**, *11*, 138.
(5) Stacy, C. J.; Kraus, G. *Polym. Eng. Sci.* **1977**, *17*, 627.
(6) Candau, F.; Guenet, J.-M.; Boutillier, J.; Picot, C. *Polymer* **1979**, *20*, 1227.
(7) Maire, P.; Duplessix, R.; Gallot, Y.; Picot, C. *Macromolecules* **1979**, *12*, 1180.
(8) Marie, P.; Gallot, Y. *Makromol. Chem.* **1979**, *180*, 1611.
(9) Selb, J.; Gallot, Y. *Makromol. Chem.* **1980**, *181*, 809.
(10) Selb, J.; Gallot, Y. *Makromol. Chem.* **1980**, *181*, 2605.
(11) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 727. (A similar approach to the interfacial energy of surfaces with adsorbed polymers has been developed by: Klein, J.; Pincus, P. *Macromolecules* **1982**, *15*, 1129.)
(12) de Gennes, P.-G. "Solid State Physics"; Academic Press: New York, 1978; Suppl. 14, p 1.
(13) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482.
(14) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(15) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 736.
(16) Brandrup, J.; Immergut, E. G., Eds. "Polymer Handbook"; Interscience: New York, 1966.
(17) Höcker, H.; Blake, G. J.; Flory P. J. *Trans. Faraday Soc.* **1971**, *67*, 2252.
(18) Roe, R.-J.; Zin, W. C. *Macromolecules* **1980**, *13*, 1221.
(19) Dr. Giuseppa DiPaola-Baranyi, Xerox Research Centre of Canada, private communication.
(20) Orwoll, R. A. *Rubber Chem. Technol.* **1977**, *50*, 451.
(21) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. "Block Copolymers"; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970.
(22) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(23) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(24) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.

Effect of Molecular Weight on Polymer Blend Phase Separation Kinetics

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ABSTRACT: The technique of excimer fluorescence has been used to study the effect of molecular weight on the kinetics of phase separation in polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends. From the fluorescence results, which have been analyzed by assuming that demixing occurs by spinodal decomposition, the growth rate of the dominant concentration fluctuation has been determined for 10% and 50% PS blends with PS molecular weights of 100 000 and 1 800 000. At both compositions, the unstable growth rate was found to decrease with increasing PS molecular weight. The observed effect was weaker than expected, presumably due to the polydispersity of the PVME.

Introduction

de Gennes[1] and Pincus[2] have used scaling techniques recently to extend Cahn's theory of spinodal decomposition[3] to polymer blends in the melt. Specifically, their analyses were developed for the case in which both components have the same molecular weight and are above the critical entanglement length. They found two important changes must be made in the theory. First, the dominant term resulting from concentration gradients in the free energy expression is entropic rather than enthalpic. Second, the Onsager coefficient is a function of wavenumber for a given Fourier component of composition because the frictional coefficient describing chain motion in an entangled network depends on the distance scale over which diffusion takes place.

Pincus has shown that the growth rate of the concentration fluctuation which controls the kinetics during the early stages of decomposition is proportional to the melt reptation diffusion coefficient.[2] Thus, provided the thermodynamic driving force for phase separation is kept relatively constant, the kinetics of the early stages of the process should depend strongly on molecular weight. The

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