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A Model of Micellization for Block Copolymers in Solutions

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ABSTRACT: Block copolymers are generally polydisperse, and the molecular weight distribution of a block copolymer has a profound effect on its micellization behavior in solution. When the block copolymer concentration is lower than the mixed critical micelle concentration [cmc(mix)], the insoluble block is assumed to adopt a spherical collapsed conformation. This leads to the proposal that the association energy of the collapsed spheres can be described by the Hamaker equation, i.e., that the interaction energy is proportional to the radius of the spheres. From this model, a relationship between the cmc of each component and the length of the insoluble block can be obtained. This relationship is used in combination with a treatment of mixed micellization to account for the dependence of the cmc(mix) on the insoluble chain length and on its polydispersity, and satisfactory results are obtained for the poly(styrene-*b*-isoprene)/*n*-hexadecane and poly(styrene-*b*-sodium acrylate)/water systems. From this model, the single chain fraction of the block copolymer can be calculated as a function of the total block copolymer concentration. The molecular weight distributions of the single chain and the micellar fractions can also be obtained. The cmc(mix) was found to decrease as the polydispersity index increases. The single chain fraction and molecular weight distributions of the single chain and the micellar fractions are found to be influenced by the dependence of the cmc of each component on the insoluble chain length.

Introduction

The micellization process of block copolymers in solvents selectively poor for one of the blocks[1-7] is generally considered to resemble that of low molecular weight amphiphilic molecules in aqueous or organic media.[8-13] In very dilute solutions, block copolymers exist as single chains. When the concentration of the block copolymer reaches a critical value, the so-called critical micelle concentration (cmc), block copolymer molecules begin to associate to form micelles, with the insoluble block in the core and the soluble block pointing outward. The critical micelle concentrations of block copolymers are normally much lower than those of low molecular weight surfactants and are thus quite difficult to determine experimentally. Only in recent years has significant progress been made in applying some sensitive experimental techniques such as light scattering[14-16] and fluorescence probes[17-19] to the measurements of cmc's. Size-exclusion chromatography (SEC) was also used to determine the single chain and micellar fractions at different insoluble and soluble block lengths.[20,21] A number of theoretical treatments on block copolymer micelles have appeared,[22-35] and some of them address the phenomenon of the critical micelle concentration.[23,26,30,34,35] In spite of this extensive effort, several problems still remain to be addressed theoretically, especially when one considers the block copolymer micelles in comparison with their low molecular weight counterparts:

1. Block copolymers are not monodisperse; even at a polydispersity index of 1.03, the best achieved by use of anionic polymerization techniques, the distributions of the polymers are still very broad compared to those of monodisperse low molecular weight surfactants. Figure 1 shows the molecular weight distributions of a series of polymers of different polydispersities; Gaussian distributions are assumed in this example. For a polymer with an average chain length of 100 repeat units and a polydispersity index of 1.03, there are only 2.3% of the polymer molecules with exactly 100 repeat units. Among the other 97.7% of the polymer molecules, 1.95% and 1.18% have 90 and 80 repeat units, respectively. It is obvious that in block copolymer solutions we are always dealing with mixed micelles consisting of block copolymers with different chain lengths. In the theoretical treatments,[22-35] block copolymers are generally assumed to be monodisperse.

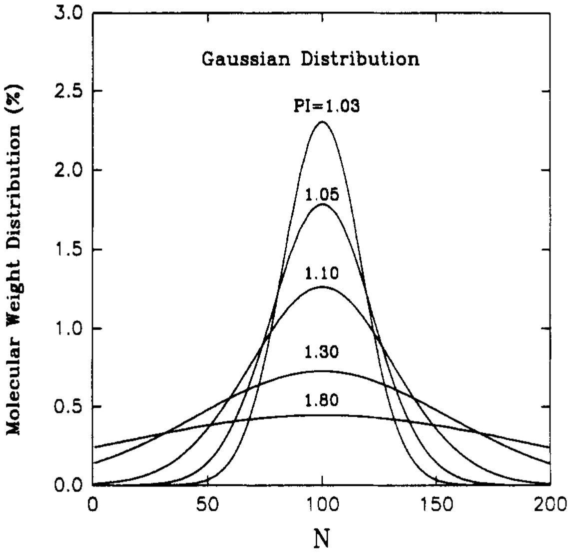

Figure 1. Illustrative molecular weight distributions (Gaussian function) of polymers with an average chain length of 100 repeat units and polydispersities of 1.03, 1.05, 1.10, 1.30, and 1.80.

2. For most low molecular weight surfactants in aqueous medium, the free energy of micellization ($\Delta G^\circ = RT \ln$ cmc) is proportional to the length of the alkyl chain.[8-12] However, the free energy of micellization of a block copolymer is normally not proportional to the length of the insoluble block.[15-19] Experimentally, weak dependencies have been found, but no theoretical treatment accounts quantitatively for this behavior.

3. It is known that when the concentration of the polymer is lower than the critical micelle concentration (cmc), the insoluble block of the single chain polymer

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collapses to form the so-called monomolecular micelles.[36,37] The associations of these collapsed single chains to form micelles should be quite different from those of uncollapsed low molecular weight surfactant molecules.

4. In a number of block copolymer systems, it has been found that both the molar mass and the hydrodynamic radius of micelles are larger near the critical micelle concentration.[7,38–40] Intrinsic excimer fluorescence of poly(styrene-*b*-ethylene/propylene) in *n*-alkanes indicates that the micellar cores near the cmc are highly swollen by the solvent; as the polymer concentration increases, solvent molecules are increasingly driven out of the micellar cores, resulting in a shrinkage of the cores.[40]

The effect of molecular weight distribution on the single chain and micellar fractions, as obtained from size-exclusion chromatography for block ionomer micelles, was addressed previously in an approximate manner by Desjardins and Eisenberg[20] and by Zhong et al.[21] It was assumed that block copolymers with insoluble blocks longer than a critical length are located in the micellar phase, while those with insoluble blocks shorter than the critical length exist as single chains. This simple model accounted for the size-exclusion chromatography results of poly(styrene-*b*-sodium acrylate) block ionomers in tetrahydrofuran (THF).[21] However, in that model, the possible partitioning of block copolymers of the same length between the micellar phase and the solution phase was not taken into consideration.

The preceding paper[19] reported the most recent results of critical micelle concentration data of block polyelectrolytes obtained in this laboratory. For poly(styrene-*b*-sodium acrylate) with short styrene blocks and long sodium acrylate blocks (block polyelectrolytes) in water, the critical micelle concentrations at different styrene block lengths were obtained from fluorescence techniques. In the block polyelectrolyte micellar systems, the free energy of transfer of a block copolymer molecule from the solution phase to the micellar phase was found to be a nonlinear function of the number of repeat units in the insoluble block.

In the present paper, a more general model is proposed for the micellization of block copolymers in solutions, and the above four questions will be addressed. Poly(styrene-*b*-isoprene)/*n*-hexadecane[15] and poly(styrene-*b*-sodium acrylate)/water[19] systems will be treated, and the model will be used to account for the dependence of the mixed critical micelle concentration on the number of the repeat units in the insoluble block. The single chain concentration of the block polymers as a function of the total concentration and the molecular weight distributions of the single chain and the micellar fractions will be calculated. A subsequent publication will address micellization of block ionomers composed of short ionic and long nonionic blocks.

Mixed Micellization

For low molecular weight surfactants, a number of models for mixed micellization have been developed for multicomponent systems;[41–52] most of these are based on the pseudo-phase-separation approach.[41–50] The composition of a mixed micelle of nonionic surfactants with polydisperse ethylene oxide chains was also treated theoretically by Warr et al.[46] In that paper, the polydispersity of the soluble block was considered since the insoluble block was the monodisperse alkyl chain. The effect of the polydispersity of the soluble block on the micellization behavior is generally much smaller than that of the polydispersity of the insoluble block. The paper by Warr et al.[46] predicts that the dependence of the mixed cmc of polydisperse nonionic surfactants on the average ethoxyl chain length is approximately the same as that of the cmc of monodisperse nonionic surfactant on the ethoxyl chain length. The mixed micelle model developed by Holland and Rubingh[47,50] for low molecular weight surfactants provides a relatively straightforward approach to systems containing a large number of different components. This model appears to be the most suitable one to be extended to polydisperse block copolymer systems. In the present paper, the model of Holland and Rubingh[47,50] will be used to account for the polydispersity effect of the insoluble blocks on the micellization process of block copolymers in solutions.

In a micellar solution of monodisperse block copolymer, the chemical potential of the polymer in the micellar phase $\mu_i°(\text{mic})$ is equal to that of the polymer in the single chain form, according to the pseudo-phase-separation model.

$$\mu_i°(\text{mic}) = \mu_i° + RT \ln C_i \qquad (1)$$

where C_i is the critical micelle concentration of the monodisperse polymer and $\mu_i°$ is the standard chemical potential for the polymer in solution. In this case, the activity coefficient of the single chain is assumed to be unity. When the polymer is in a mixture with other polymers or the polymer is a component of a polydisperse system, its chemical potential in the solvent phase is given by

$$\mu_i = \mu_i° + RT \ln C_i^{\text{s}} \qquad (2)$$

where C_i^{s} is the concentration of the polymer in the solvent phase (single chain). On the other hand, the chemical potential of the polymer in the mixed micellar phase is given by

$$\mu_i(\text{mic}) = \mu_i°(\text{mic}) + RT \ln f_i x_i \qquad (3)$$

In eq 3, x_i is the mole fraction of the polymer in the micellar phase and f_i is the activity coefficient. At equilibrium, the chemical potentials of the polymer in the solvent phase and the micellar phase should be equal, $\mu_i(\text{mic}) = \mu_i$, and from eqs 1–3 we have

$$C_i^{\text{s}} = f_i x_i C_i \qquad (4)$$

In a multicomponent system, mixed micelles are assumed to form at a critical concentration, the so-called mixed critical micelle concentration or cmc(mix). At the cmc(mix), the concentration of a component in the single chain form is given by

$$C_i^{\text{s}} = \alpha_i \text{cmc(mix)} \qquad (5)$$

where α_i is the total mole fraction of the component in the block polymer mixture. In combination with $\sum_i^n x_i = 1$ and eq 4, we have

$$\text{cmc(mix)} = \{\sum_i^n (\alpha_i/f_i C_i)\}^{-1} \qquad (6)$$

The molecular weight distribution of polymers prepared by anionic polymerization techniques can be described by either Poisson or Gaussian distribution functions. For block copolymers, the situation becomes more complicated since either block consists of a distribution of different lengths.[53,54] However, it is known that the cmc(mix) is mainly determined by the length of the insoluble block when the length of the soluble block reaches a certain value.[19] In the present paper, only the effect of the insoluble block length is considered, and the distribution in the soluble block is assumed to have little effect on the cmc(mix). If a Gaussian distribution is assumed for the insoluble block, the mole fraction of the ith component is given by

$$\alpha_i = (2\pi)^{-1/2}\sigma^{-1}\exp[-(N_i - \bar{N})^2/2\sigma^2] \qquad (7)$$

where $\sigma = \overline{\mathrm{DP}}_n(\overline{\mathrm{DP}}_w/\overline{\mathrm{DP}}_n - 1)^{1/2} = \overline{\mathrm{DP}}_n(\mathrm{PI} - 1)^{1/2}$ and $\bar{N} = \overline{\mathrm{DP}}_n$. $\overline{\mathrm{DP}}_w$, $\overline{\mathrm{DP}}_n$, and PI denote the weight- and number-average degrees of polymerization and the polydispersity index, respectively.

According to mass balance, the mole fraction of the ith component in the micellar phase is related to its mole fraction in the mixture, α_i, its single chain concentration C_i^s, the total concentration of the mixture, C, and the total single chain concentration S ($S = \sum_i^n C_i^s$)

$$x_i = (\alpha_i C - C_i^s)/(C - S) \qquad (8)$$

Substituting C_i^s in the numerator from eq 4 and combining with $\sum_i^n x_i = 1$ yields a simple relationship:

$$\sum_i^n \frac{\alpha_i C}{C + f_i C_i - S} = 1 \qquad (9)$$

It has been found that, for nonionic surfactants and for surfactants with the same sign of charge, the mixing is almost ideal,[43,52] i.e., $f_i = 1$. This should also apply to the present cases of block copolymers mixtures. If the critical micelle concentration, C_i, and mole fraction of each polymer, α_i, in the mixture are known, S can be obtained from eq 9 as a function of total concentration C. Once S is known, the single chain concentration of the ith component, C_i^s, and its mole fraction in the micelle, x_i, can be calculated by use of the following equations.

$$C_i^s = \frac{\alpha_i f_i C_i C}{C + f_i C_i - S} \qquad (10)$$

$$x_i = \frac{\alpha_i C}{C + f_i C_i - S} \qquad (11)$$

In a block copolymer system, if the molecular weight distribution and the critical micelle concentration of each component are known, the mixed cmc, the total and individual single chain concentrations, and the mole fraction of each component in the micellar phase can be calculated using eqs 6 and 9–11, respectively. On the other hand, we could also use the mixed cmc determined experimentally to obtain the relationship between the cmc of an individual component (C_i) and the insoluble block length, as will be discussed below.

Micellization Process of Block Copolymers

According to eq 1, the free energy of micellization for a monodisperse block copolymer is given by

$$\Delta G_i^\circ(\mathrm{mic}) = \mu_i^\circ(\mathrm{mic}) - \mu_i^\circ = RT \ln C_i \qquad (12)$$

For a homologous series of low molecular weight surfactants, the free energy of micellization is proportional to the number of methylene groups. The relationship between the critical micelle concentration, C_i, and the number of methylene groups, N_i, generally obeys the equation[8-12]

$$\log C_i = a'N_i + b' \qquad (13)$$

where a' and b' are constants. However, for most block copolymer systems, the relationship between the cmc and the number of the repeat units in the insoluble block deviates significantly from the above equation.[18,19] The collapse of polymers in poor solvents has been a subject of investigations for many years.[55-68] At temperatures well below the Θ temperature, coil-to-globule transitions occur in highly dilute polymer solutions before interchain aggregation takes place.[61] In block copolymer solutions, it has also been suggested that the insoluble block might collapse even when the polymers are in the single chain state.[36,37]

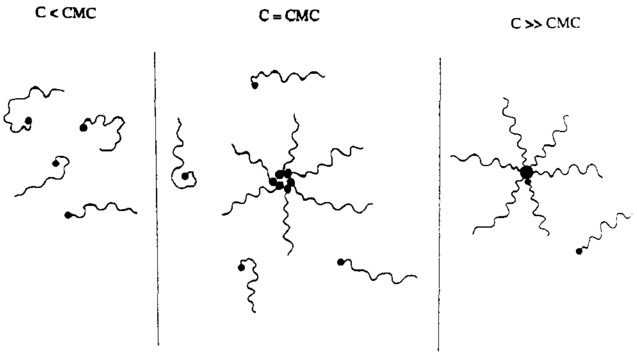

Figure 2. Schematic representation of the micellization process.

The states of a block copolymer with one collapsed block at concentrations below the cmc, equal to the cmc, and above the cmc are represented schematically in Figure 2. At concentrations below the cmc, all the block copolymers are in the single chain form. At the cmc, the collapsed blocks begin to associate to form loose aggregates. In this stage the insoluble blocks remain in their individual collapsed states in order to maintain an equilibrium with the single chains. A significant amount of solvent is trapped in the micellar cores, and the sizes of the micelles are larger than those in the later stage ($C \gg$ cmc). This model is in agreement with the observations of the larger and solvent-swollen micelles near the cmc.[38-40] Bednar et al. also pointed out in their study of micellization kinetics of block copolymers that in the dissociation process the first step is a rapid influx of solvent molecules into the micellar core and the second step is a separation of copolymer molecules.[69] As the concentration of the block copolymer increases, the equilibrium shifts in favor of the micellar form. The insoluble blocks in the micellar cores rearrange to find their low-energy conformation, and the solvent molecules are gradually driven out of the micellar cores. At higher polymer concentrations, large collapsed micellar cores consisting of many insoluble blocks are present together with a few "buds" (individual collapsed insoluble blocks) on their surfaces, as indicated by Halperin and Alexander,[29] to maintain the micelle–single chain equilibrium. When the block copolymer reaches a much higher concentration region where the intermicellar interactions become important, the micelle–single chain equilibrium is perturbed due to the formation of long-range superstructures.[39,70] However, the high concentration region is beyond the scope of the present paper.

The driving force for the micellization of block copolymers is generally considered to be due to van der Waals interactions.[14] For the association of two spherical colloidal particles with the same size, the free energy of interaction could be accounted for by use of the Hamaker equation[71]

$$\Delta G^{\mathrm{att}} = -A_{\mathrm{H}}R/12H \qquad (14)$$

where A_{H} is the Hamaker constant, which is dependent on the material, as well as on solvent and temperature,[72] R is the radius of the colloidal spheres, and H is the distance between the surfaces of the two particles. Equation 14 is valid only when the spheres are very close ($H/R \ll 1$). If more than two colloidal particles are associated, the total interaction energy should also be proportional to R, the radius of the colloidal particles, according to eq 14. It is obvious that, if the aggregation number is large enough, or is infinitely large as defined in the pseudo-phase-

Table I. Block Copolymer Systems Used and the Least-Squares Fitting Results[a]

block copolymer	M_w	N_{PS}	PI_{PS}	cmc(mix)	a	b	χ^2
PS-*b*-PI	24 600	67	1.08[b]	2.67×10^{-4} (40 °C)[15]	−1.65	3.55	0.03
PS-*b*-PI	46 600	83	1.09	1.15×10^{-4} (40 °C)[15]			
PS-*b*-PI	26 800	125	1.10	4.90×10^{-6} (40 °C)[15]			
PS-*b*-PI	54 228	122	1.06	8.08×10^{-6} (40 °C)[15]			
PS-*b*-PANa	[c]	6	1.18	1.6×10^{-5}	−0.68	−4.02	0.49
PS-*b*-PANa		11	1.13	1.6×10^{-6}			
PS-*b*-PANa		14	1.16	1.6×10^{-6}			
PS-*b*-PANa		23	1.14	5.0×10^{-7}			
PS-*b*-PANa		28	1.09	1.0×10^{-6}			
PS-*b*-PANa		40	1.13	2.5×10^{-7}			
PS-*b*-PANa		86	1.09	1.3×10^{-7}			
PS-*b*-PANa		110	1.08	5.6×10^{-8}			

[a] The values of a and b can be determined with relatively good accuracy. The χ^2 values are very sensitive to the variations in a. For instance, in the PS-*b*-PANa system, near the minimum changes in a and b by 0.1 lead to variations in χ^2 by ca. 0.1 and ca. 0.01, respectively. The errors of a and b are estimated to be ca. 15% when the errors of the cmc values are within 50%. [b] The polydispersity indexes of the polystyrene blocks are assumed to the same as those of the block copolymers. [c] The cmc(mix) values are obtained from the extrapolation at 1000 units of PANa from the plots of cmc(mix) as a function of PANa repeat units.[19] The cmc(mix) values were determined at room temperature.[19]

separation model, the free energy of transfer of a polymer from the single chain state to the micellar state is independent of the aggregation number since the insoluble block interacts only with those in its close proximity. Thus, for the association of a monodisperse block copolymer at the cmc, the free energy of micellization should be proportional to the radius of the collapsed insoluble blocks instead of to the number of repeat units in the insoluble block. Since the effect of the soluble block length to the cmc(mix) is relatively small compared to that of the insoluble block length, in the case where the soluble block length is kept almost constant, the contribution from the soluble block to the total free energy of micellization can also be assumed to be a constant. In the cases where the soluble block is nonionic, the contribution from the soluble block includes a negative enthalpic term ($\Delta H°$) and a positive entropic term ($-T\Delta S°$) due to the losses of translational and rotational freedom. Thus, the total free energy of micellization for a block copolymer with a collapsed insoluble block can be written as

$$\Delta G_i°(\text{mic})/2.303RT = \log C_i = a''R_i + b'' \qquad (15)$$

where a'' and b'' are constants. Since the volume of a highly collapsed single chain is proportional to N_i, the number of repeat units in the insoluble block, the radius of the sphere is related linearly to $N_i^{1/3}$. It is also known that in the poor solvent region the radius of a flexible chain is given by[61]

$$R_i \sim N_i^{1/3}|\tau^{-1/3}| \qquad (16)$$

where $\tau = (T - \Theta)/\Theta$; Θ is the theta temperature. Therefore, at a constant temperature the relationship between cmc and the number of repeat units in the insoluble block can be expressed as

$$\log C_i = aN_i^{1/3} + b \qquad (17)$$

When N_i is very small, it is difficult for the polymer (oligomer) to adopt the collapsed conformation; equation 17 is valid only when N_i is longer than the minimum chain length for the polymer to collapse. This minimum length is obviously dependent on the polymer, the solvent, and the temperature. We are not aware of any study on conformations of oligomers in poor solvents. It is also anticipated that in the case of long insoluble blocks, although most of the units would collapse in poor solvents, some of the units near the diblock junction most likely exist in an extended form. These effects on the critical micelle concentration will be discussed later. By substituting C_i into eq 6 and assuming activity coefficient f_i = 1, we have

$$\text{cmc(mix)} = \{\sum_i^n(\alpha_i/\exp_{10}(aN_i^{1/3} + b))\}^{-1} \qquad (18)$$

The values of a and b in eq 18 can be calculated from a least-squares fitting procedure once cmc(mix) is determined as a function of the average number of repeat units in the insoluble block. On the other hand, if at a particular concentration the single chain fractions of a number of block copolymers with different insoluble block lengths are known, as determined from SEC,[20,21] a and b values can be obtained by substituting eq 17 into eq 9. When the relationship between C_i and N_i is known, S, C_i^s, and x_i at higher block copolymer concentrations can be further calculated using eqs 9–11, respectively. At higher polymer concentrations, the insoluble blocks may rearrange in the micellar cores to form more compact ones through interpenetration, as illustrated schematically in Figure 2. The free energy of micellization or the relationship between C_i and N_i at these concentrations may not be exactly the same as that at the cmc(mix). However, in the present study this difference is assumed to be very small in the concentration range investigated and is not taken into consideration in the calculations.

In the following sections, two block copolymer micellar systems, poly(styrene-*b*-isoprene)/*n*-hexadecane and poly(styrene-*b*-sodium acrylate)/H_2O, will be subjected to the above theoretical treatments. a and b values in eq 17 will be determined in these systems by minimization of χ^2, which is defined as

$$\chi^2 = \sum(\log \text{cmc(mix)}_{\text{expt}} - \log \text{cmc(mix)}_{\text{cal}})^2 \qquad (19)$$

Poly(styrene-*b*-isoprene)/*n*-Hexadecane System[15]

The compositions, polydispersity indexes, and mixed cmc's of four poly(styrene-*b*-isoprene) block copolymers in *n*-hexadecane are given in Table I, together with values of a and b and χ^2 obtained by fitting eq 18 to the experimental data. In these calculations, the polydispersity indexes of the insoluble blocks are assumed to be the same as those of the whole block copolymers. In principle, if polydispersity indexes of the whole block copolymer and of one of the blocks were known, the polydispersity index of the other block could also be calculated.[53,54] However, in this case, only the polydispersity indexes of the whole block copolymers were given. Also, in the calculations, the effect of a soluble block (polyisoprene) on the cmc(mix) is assumed to be constant regardless of the length. The plot of experimental and theoretical cmc(mix) vs number of polystyrene repeat units is shown in

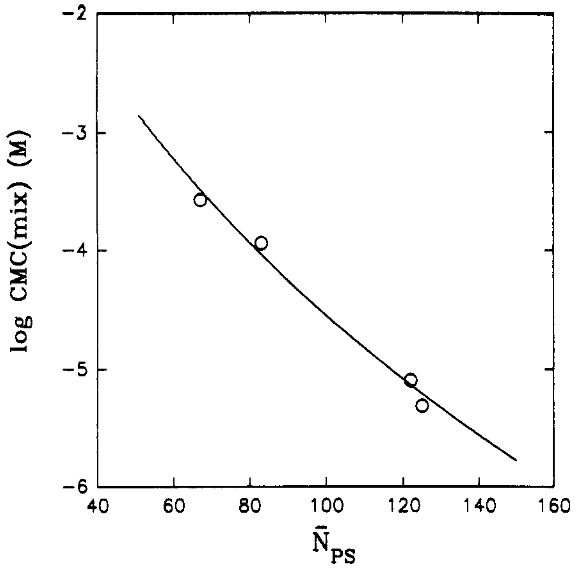

Figure 3. Theoretical and experimental values[15] of log cmc(mix) as a function of the insoluble polystyrene block length for poly(styrene-*b*-isoprene) in *n*-hexadecane. The theoretical curve was generated using a polydispersity index of 1.08 for all the samples.

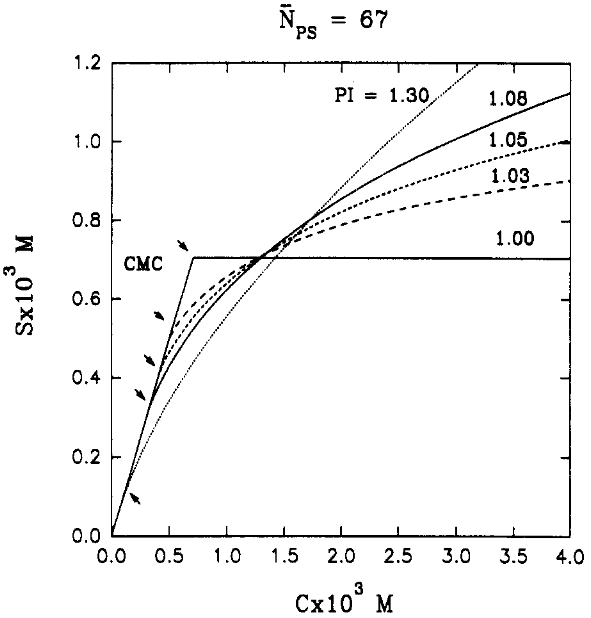

Figure 4. Single chain concentrations as a function of the total block copolymer concentration at different polydispersity indexes in the poly(styrene-*b*-isoprene)/*n*-hexadecane system.

Figure 3. In the fitting procedure, polydispersity indexes corresponding to the polymers were used to obtain one set of a and b values. In Figure 3, the theoretical curve is generated by use of a polydispersity index of 1.08 for all the samples. Figure 3 shows an excellent fit between the calculated and experimental values, indicating that eq 18 provides a satisfactory account for the dependence of cmc(mix) on the number of repeat units of polystyrene.

Figure 4 illustrates the effect of polydispersity on the relationship between the total single chain concentration S and the total block copolymer concentration for poly(styrene-*b*-isoprene) with an average of 67 styrene units. The values of S were obtained from eq 9. When the total block copolymer concentrations are below the cmc or the cmc(mix), all the polymers are in the single chain form and the total concentration of the single chains equals that of the block copolymer. For a monodisperse block copolymer (PI = 1.00), the total single chain concentration remains constant after the polymer concentration reaches the cmc. However, for polydisperse block copolymers, the single chain concentrations continue to increase above the cmc(mix), and with increasing polydispersity indexes, more pronounced increases in the single chain concentrations are observed. The values of cmc(mix) for polydisperse polymers are substantially lower than the cmc for the monodisperse polymer, even at a polydispersity index of 1.03, the best ever produced by the anionic polymerization technique. This is clearly due to the fact that contributions to the cmc(mix) from the block copolymers with a polystyrene chain longer than 67 repeat units are significantly larger than those from the block copolymer with a polystyrene chain equal to 67 repeat units, as is also indicated in eq 18. The higher the polydispersity index, the lower the cmc(mix). It is thus not surprising that one obtains different cmc(mix) values for block copolymers with very similar soluble and insoluble lengths but slightly different polydispersity indexes.

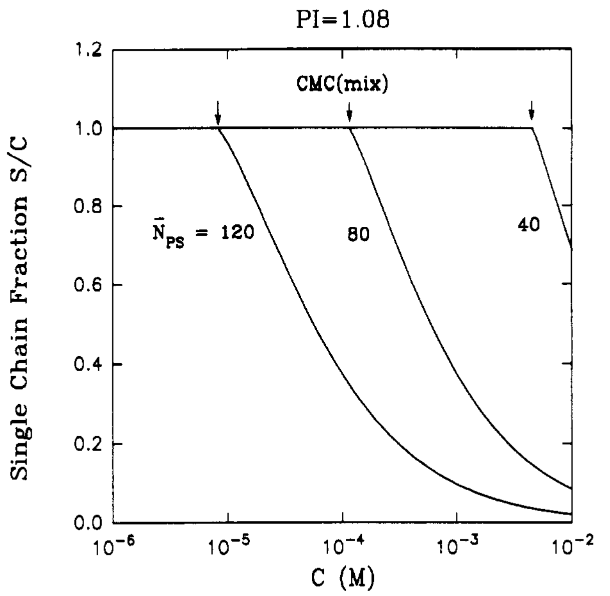

Figure 5. Single chain fractions as a function of the total block copolymer concentration for poly(styrene-*b*-isoprene) with an average of 120, 80, and 40 styrene repeat units and polydispersity indexes of 1.08 in *n*-hexadecane.

It is of interest to note from Figure 4 that the discontinuities in the total single chain concentrations at the cmc(mix) are not very clear for polydisperse block copolymers, especially for block copolymers with polydispersity indexes higher than 1.05. Thus, techniques that monitor the concentrations of the single chain, such as surface tension and conductivity, are not suitable for the determination of cmc(mix) of block copolymers. However, techniques which are sensitive to the presence of micelles, such as fluorescence probes and light scattering, should be more suitable for cmc(mix) measurements.

The single chain fractions of three poly(styrene-*b*-isoprene) copolymers with an average of 40, 80, and 120 styrene units at different total concentrations are given in Figure 5. In these cases, a polydispersity index of 1.08 is assumed for all three polymers. As shown in Figure 5, the single chain fractions equal 1 up to the cmc(mix) and begin to decrease above that point. For the block copolymer with an average of 120 styrene units, the single chain fraction decreases to approximately 10% when the total polymer concentration becomes about 2 orders of magnitude higher than the cmc(mix). It is also obvious that the decrease in the single chain fraction with total concentration is faster for block copolymers with shorter polystyrene chain lengths.

The single chain concentrations of an individual component in a polydisperse block copolymer can also be calculated using eq 10. For a block copolymer with an

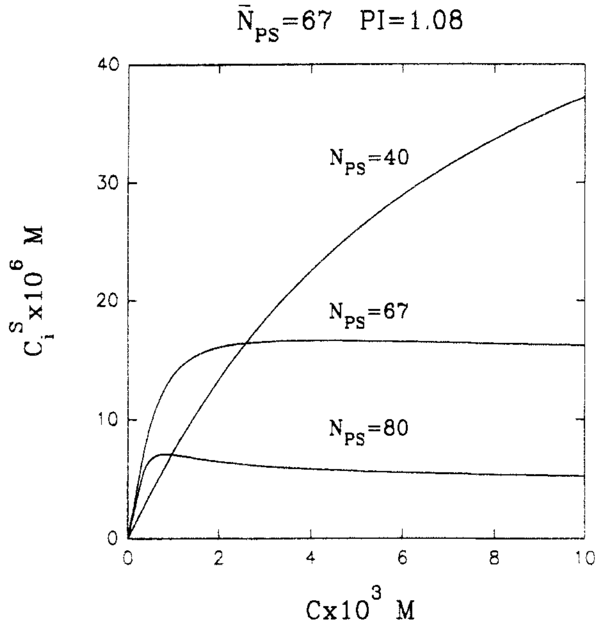

Figure 6. Single chain concentrations of individual components with 40, 67, and 80 styrene repeat units as a function of the total block copolymer concentration for poly(styrene-*b*-isoprene) with an average of 67 styrene repeat units and a polydispersity index of 1.08 in *n*-hexadecane.

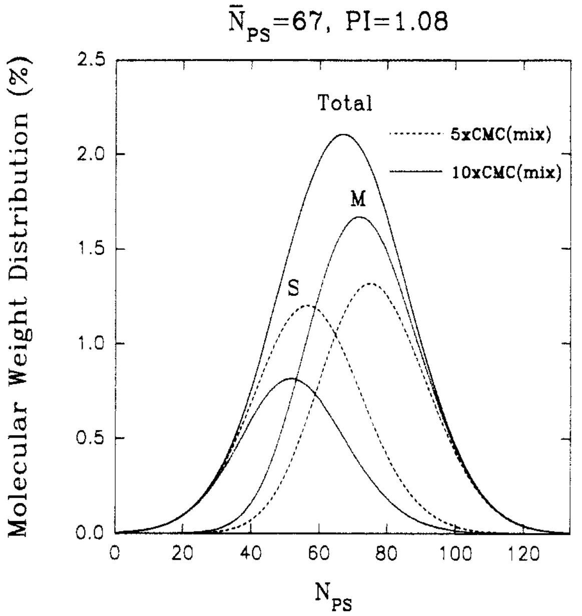

Figure 7. Molecular weight distribution of the single chain and the micellar fraction for a poly(styrene-*b*-isoprene) with an average of 67 styrene repeat units and a polydispersity index of 1.08 at 5 and 10 times the cmc(mix).

average of 67 styrene units and a polydispersity index of 1.08, single chain concentrations for components with 40, 67, and 80 styrene units are presented in Figure 6 as a function of the total polymer concentration. For the block copolymer with 40 styrene units, the single chain concentration increases gradually over the entire concentration range. No discontinuity is observed at the cmc(mix) for the block copolymers with 40 and 67 styrene units, which is not surprising since, at a polydispersity index of 1.08, the change at the cmc(mix) is very small in the plot of total single chain concentration vs total concentration (Figure 4). While the single chain concentrations of the components with short insoluble blocks continue to increase after the cmc(mix), the single chain concentrations of the components with longer insoluble blocks decrease with the total concentration after the cmc(mix). This can be understood on the basis of the equilibrium between single chains and micelles. At the cmc(mix), the micelles mainly consist of block copolymers with long insoluble blocks; i.e., the fractions of polymers with longer insoluble blocks in the micelles (x_i) are higher at the cmc(mix). As the concentration is increased, more copolymer molecules with shorter insoluble blocks incorporate to the micellar phase. Thus, the x_i values of the copolymer molecules with longer insoluble blocks decrease at higher concentrations. According to eq 4, the single chain concentrations of these components should also decrease at higher total block polymer concentrations.

If the single chain concentrations of all the components in the polydisperse copolymer system are calculated, one can obtain the molecular weight distributions of the copolymers in the single chain and the micellar states. Figure 7 shows the molecular weight distributions of the single chain and the micellar fractions of a polydisperse poly(styrene-*b*-isoprene) with an average of 67 styrene units and a polydispersity index of 1.08 at concentrations of 5 and 10 times the cmc(mix). The theoretical value of the cmc(mix) for this system is 3.24×10^{-4} M. As shown in Figure 7, at a concentration of 5 times the cmc(mix), most of the copolymers with insoluble blocks longer than 90 styrene units and shorter than 40 styrene units mainly reside in the micellar and solvent phases, respectively. At a concentration of 10 times the cmc(mix), concentrations of copolymers with 30–100 styrene units shift in favor of the micellar phase, while most of the copolymers with styrene chains shorter than 30 styrene units still remain in the solvent phase.

Poly(styrene-*b*-sodium acrylate)/H_2O[19]

It has been shown in the preceding paper that the cmc(mix) of the block polyelectrolyte poly(styrene-*b*-sodium acrylate) depends significantly on the length of the insoluble polystyrene block. A description of the samples and the fluorescence technique used to determine the cmc's can be found in that paper. Here only the results of poly(styrene-*b*-sodium acrylate) with an average of 1000 sodium acrylate units but different numbers of styrene units will be treated (Table I). Similar to the previous case, the polydispersity of the soluble block is assumed to have little effect on the cmc. The effect of the soluble polyelectrolyte block on the cmc(mix) has been shown, in the preceding paper, to be much smaller than that of the insoluble polystyrene block.

Experimental cmc(mix) values, fitted using eq 18, are shown in Figure 8 together with the fits as a function of the insoluble polystyrene chain length. The theoretical curve was generated using a polydispersity of 1.10. The relationship between the cmc of the block polyelectrolyte and the chain length of the insoluble block was found to be $\log C_i = -0.68N_i^{1/3} - 4.02$. This relationship is valid only when the insoluble block is in the collapsed form, i.e., when N_i is larger than a certain value. For the case of block polyelectrolytes in water, it was also suggested that $\log C_i$ should be proportional to $N_i^{2/3}$.[35] However, if this relationship is used, the value of χ^2 is much higher ($\chi^2 = 0.78$ for $\log C_i = aN_i^{2/3} + b$ vs $\chi^2 = 0.49$ for $\log C_i = aN_i^{1/3} + b$).

The negative value of the *b* term (−4.02) may be due to the styrene units near the diblock junction; these units may exist in an extended form. In the case of poly(styrene-*b*-isoprene)/*n*-hexadecane described earlier, the contribution of some extended styrene units near the diblock junction may not have such a significant effect on the cmc. In the block polyelectrolyte/water case, the interactions between styrene and water are much stronger than those between styrene and *n*-hexadecane and the presence

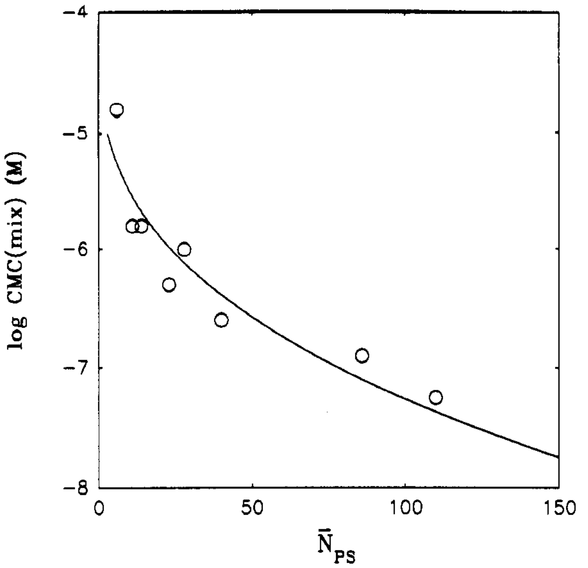

Figure 8. Theoretical and experimental values of log cmc(mix) as a function of polystyrene block length for block polyelectrolytes poly(styrene-*b*-sodium acrylate) in water.[19] The experimental values are given for the block polyelectrolytes with an average of 1000 sodium acrylate repeat units.[19] The theoretical curve was generated using a polydispersity index of 1.10 for the polystyrene block.

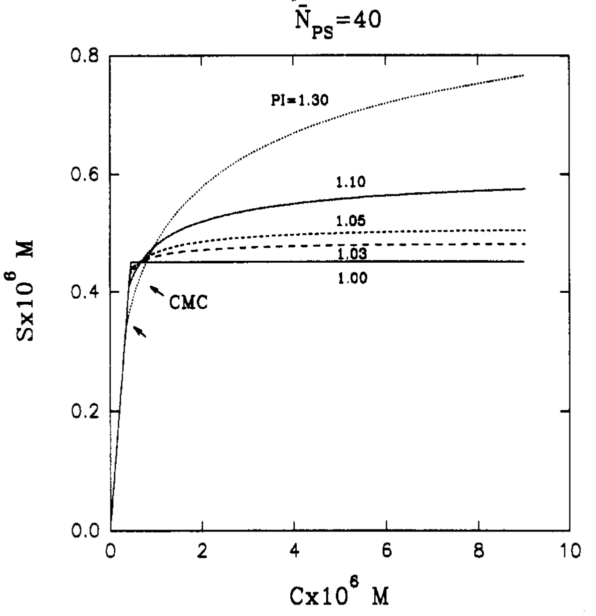

Figure 9. Single chain concentrations as a function of the total block copolymer concentration at different polydispersities for poly(styrene-*b*-sodium acrylate) with an average of 40 styrene repeat units in water.

of a few styrene units in the extended form may lead to a substantial decrease in the cmc. The effect of the insoluble block may be considered as the sum of two contributions. One is due to the interactions between the collapsed styrene block, which can be described by use of the Hamaker equation (eq 14), and the other is the interaction involving the extended styrene units near the diblock junction. Detailed investigations on the conformation of the styrene block are clearly needed in the future.

The effect of polydispersity on the relationship between the total single chain concentration and the total block copolymer concentration is shown in Figure 9 for poly(styrene-*b*-sodium acrylate) with an average of 40 styrene units. It is clear that the effect of polydispersity on the single chain fraction is much smaller in this case compared to the poly(styrene-*b*-isoprene)/*n*-hexadecane system (Figure 4). This is due to the fact that the dependence of the cmc on the insoluble block length is weaker in the poly(styrene-*b*-sodium acrylate)/water systems ($a = -0.68$). The molecular weight distributions of the single chain and the micellar fractions at total block polymer concentrations of 5 and 10 times the cmc(mix) are given in Figure 10. In the calculations for this figure, the theoretical cmc(mix) value of 4.10×10^{-7} M was used. The molecular weights of single chain and micellar regions overlap extensively, which is also due to the weaker dependence of the cmc on the insoluble block length.

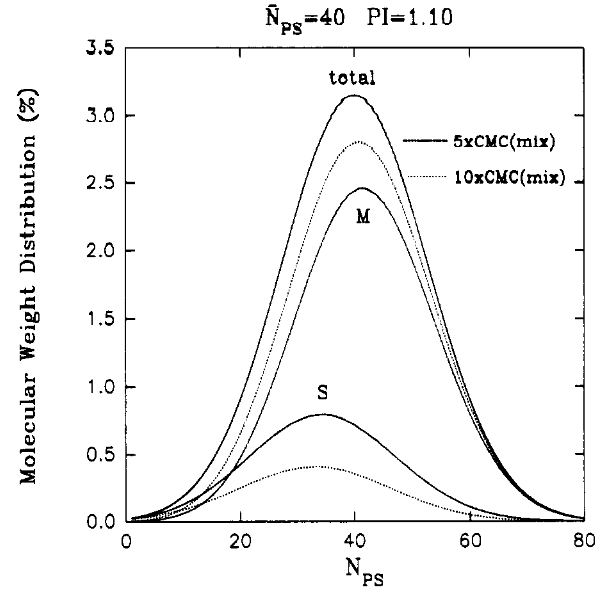

Figure 10. Molecular weight distributions of the single chain and the micellar fractions for poly(styrene-*b*-sodium acrylate) with an average of 40 styrene repeat units and a polydispersity index of 1.10 in water at 5 and 10 times the cmc(mix).

It should be noted that the present approach can in principle be applied to poly(styrene-*b*-ethylene/propylene)/*n*-decane,[16] poly(styrene-*b*-ethylene/propylene)/*n*-octane,[73] poly(styrene-*b*-ethylene/propylene)/5-methylhexane-2-one,[73] and triblock poly(oxyethylene-*b*-oxybutylene-*b*-oxyethylene)/water[74] systems for which cmc(mix) data are available. The studies of micellar systems of block ionomer poly(styrene-*b*-sodium acrylate) in nonaqueous media are in progress in this laboratory.

Conclusions

It is proposed that the association of the block copolymers in solvents selectively poor for one of the blocks is driven by the van de Waals interactions between collapsed insoluble blocks and that the interaction energy can be described by the Hamaker equation. Thus, for a monodisperse block copolymer, the relationship between the critical micelle concentration and the number of repeat units in the insoluble block N_i is given by $\log C_i = aN_i^{1/3} + b$. By use of this relationship, the effect of polydispersity on the micellization process of block copolymers can be accounted for using a thermodynamic treatment analogous to that of Holland and Rubingh,[47] proposed for low molecular weight surfactants. Satisfactory results were obtained from the fitting of the present model to the dependence of cmc(mix) on the insoluble block length obtained experimentally for poly(styrene-*b*-isoprene)/*n*-hexadecane as well as poly(styrene-*b*-sodium acrylate)/water systems.

The cmc(mix) for a polydisperse block copolymer is dependent on the polydispersity index; the higher the polydispersity index, the lower the cmc(mix). The total single chain concentration of a polydisperse block copolymer increases with increasing total polymer concentration. The discontinuity of the single chain concentration at the cmc(mix) is less significant at higher polydispersity. The weaker the dependence of the cmc on the insoluble block length, as expressed by the value of a, the smaller the effect of polydispersity of on the cmc(mix). In a block copolymer system, the single chain concentration of a component increases with increasing total concentration for components with insoluble block lengths shorter than the average but decreases with increasing total concentration for those with insoluble block lengths longer than the average. The molecular weight distributions of the single chain and micellar fractions can also be calculated by use of the present model. The single chain and micellar fractions overlap extensively with respect to the molecular weight of the insoluble block for systems studied here. It is anticipated that, for some block copolymer systems in which a small change in the insoluble block length leads to a large change in the cmc, as might be the case in block ionomers,[20] the molecular weight of the single chain and micellar fraction would be very different. In such a special case, the critical micelle length concept[21] can be applied.

If the molecular weight distribution of the insoluble block is very narrow or if the cmc is only weakly dependent on the number of repeat units in the insoluble block, eq 17 can be applied directly to cmc(mix); i.e., the log cmc(mix) values obtained experimentally should be proportional to $N^{1/3}$, where N is the number repeat units in the insoluble block. Finally, mixtures of two or more polydisperse block copolymers can also be treated with the present model simply by using α_i as the mole fraction of the ith component in the mixture.

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References and Notes

(1) Brown, R. A.; Masters, A. J.; Price, C.; Yuan, X. F. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: Toronto, 1989; Vol. 2, p 155.
(2) Price, C. In *Development in Block Copolymers*; Goodman, I., Ed.; Elsevier Applied Science: London, U.K., 1982; Vol. 1, Chapter 2.
(3) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
(4) Riess, G.; Hurtrez, G.; Bahadur, P. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley & Sons: New York, 1985; Vol. 2, p 324.
(5) Selb, J.; Gallot, Y. In *Development in Block Copolymers*; Goodman, I., Ed.; Elsevier Applied Science: London, U.K., 1985; Vol. 2, Chapter 2.
(6) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976**, *6*, 201.
(7) Tuzar, Z. *Macromol. Rep.* **1992**, *A29* (Suppl. 2), 173.
(8) Lindman, B.; Wennerstrom, H. *Top. Curr. Chem.* **1980**, *87*, 1.
(9) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989.
(10) Fendler, J. H. *Membrane Mimetic Chemistry*; John Wiley & Sons: New York, 1982.
(11) Mayers, D. *Surfactant Science and Technology*; VCH Publishers, Inc.: New York, 1988,
(12) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; John Wiley & Sons: New York, 1980.
(13) Tadros, T., Ed. *Surfactants*; Plenum: New York, 1984.
(14) Price, C. *Pure Appl. Chem.* **1983**, *55*, 1563.
(15) Price, C.; Chan, E. K. M.; Stubbersfield, R. B. *Eur. Polym. J.* **1987**, *23*, 649.
(16) Price, C.; Stubbersfield, R. B.; El-Kafrawy, S.; Kendall, K. D. *Br. Polym. J.* **1989**, *21*, 391.
(17) Zhao, C. L.; Winnik, M. A.; Riess, G.; Croucher, M. D. *Langmuir* **1990**, *6*, 514.
(18) Wilhelm, M.; Zhao, C. L.; Wang, Y.; Xu, R.; Winnik, M. A. *Macromolecules* **1991**, *24*, 1033.
(19) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules*, preceding paper in this issue.
(20) Desjardins, A.; Eisenberg, A. *Macromolecules* **1991**, *24*, 5779.
(21) Zhong, X. F.; Varshney, S. K.; Eisenberg, A. *Macromolecules* **1992**, *25*, 7160.
(22) de Gennes, P.-G. In *Solid State Physics*; Leibert, L., Ed.; Academic Press: New York, 1978; Supplement 4.
(23) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482.
(24) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443.
(25) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.
(26) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(27) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(28) Halperin, A. *Macromolecules* **1989**, *22*, 3806.
(29) Halperin, A.; Alexander, S. *Macromolecules* **1989**, *22*, 2403.
(30) Yuan, X. F.; Masters, A. J.; Price, C. *Macromolecules* **1992**, *25*, 6876.
(31) Bug, A. L. R.; Gates, M. E.; Safran, S. A.; Witten, T. A. *J. Chem. Phys.* **1987**, *87*, 1824.
(32) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(33) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(34) Nagarajan, R.; Ganesh, K. *J. Phys. Chem.* **1989**, *90*, 5843.
(35) Marko, J. F.; Rabin, Y. *Macromolecules* **1992**, *25*, 1503.
(36) Sadron, C. *Pure Appl. Chem.* **1962**, *4*, 347.
(37) Selb, J.; Gallot, Y. In *Polymeric Amines and Ammonium Salts*; Goethals, E. J., Ed.; Pergamon Press: New York, 1980; p 205.
(38) Tuzar, Z.; Stepanek, P.; Konak, C.; Kratochvil, P. *J. Colloid Interface Sci.* **1985**, *105*, 372.
(39) Yeung, A. S.; Frank, C. W. *Polymer* **1990**, *31*, 2089.
(40) Yeung, A. S.; Frank, C. W. *Polymer* **1990**, *31*, 2101.
(41) Lange, H. *Kolloid Z.* **1953**, *131*, 96.
(42) Shinoda, K. *J. Phys. Chem.* **1954**, *58*, 541.
(43) Lange, H.; Beck, K. H. *Kolloid Z. Z. Polym.* **1973**, *251*, 424.
(44) Clint, J. *J. Chem. Soc.* **1975**, *71*, 1327.
(45) Harusawa, F.; Tanaka, M. *J. Phys. Chem.* **1981**, *85*, 882.
(46) Warr, G. G.; Grieser, F.; Healy, T. W. *J. Phys. Chem.* **1983**, *87*, 1220.
(47) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984.
(48) Osborne-Lee, I. W.; Schechter, R. S.; Wade, W. H.; Barakat, Y. *J. Colloid Interface Sci.* **1985**, *108*, 60.
(49) Nguyen, C. M.; Rathman, J. F.; Scamehorn, J. F. *J. Colloid Interface Sci.* **1986**, *112*, 438.
(50) Holland, P. M. *Adv. Colloid Interface Sci.* **1986**, *26*, 111.
(51) Kamrath, R. F.; Franses, E. I. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 230.
(52) Nagarajan, R. *Langmuir* **1985**, *1*, 331.
(53) Omoto, M.; Tanaka, T.; Kadokura, S.; Inagaki, H. *Polymer* **1979**, *20*, 129.
(54) Tanaka, K.; Omoto, M.; Donkai, N.; Inagaki, H. *J. Macromol. Sci., Phys.* **1980**, *B17*, 211.
(55) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1975**, *37*, 973.
(56) Slagowski, E.; Tsai, B.; McIntyre, D. *Macromolecules* **1976**, *9*, 687.
(57) Nierlich, M.; Cotton, J. P.; Farnoux, B. *J. Chem. Phys.* **1978**, *69*, 1379.
(58) Post, C. B.; Zimm, B. H. *Biopolymers* **1979**, *18*, 1487.
(59) Sanchez, I. C. *Macromolecules* **1979**, *12*, 980.
(60) Bauer, D. R.; Ullman, R. *Macromolecules* **1980**, *13*, 392.
(61) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 433.
(62) Swislow, G.; Sun, S. T.; Nishio, I.; Tanaka, T. *Phys. Rev. Lett.* **1980**, *44*, 796.
(63) Di Marzio, E. A. *Macromolecules* **1981**, *14*, 969.
(64) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(65) Park, I. H.; Wang, Q.-W.; Chu, B. *Macromolecules* **1987**, *20*, 1965.
(66) Birshtein, T M.; Pryamitsyn, V. A. *Macromolecules* **1991**, *24*, 1554.
(67) Grosberg, A. Yu.; Kuznetsov, D. V. *Macromolecules* **1992**, *25*, 1970.
(68) Park, I. H.; Kim, J.-H.; Chang, T. *Macromolecules* **1992**, *25*, 7300.
(69) Bednar, B.; Edwards, K.; Almgren, M.; Tormod, S.; Tuzar, Z. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 785.
(70) Hashimoto, T.; Shibayama, M.; Kawai, H.; Watanabe, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 361.
(71) Hamaker, H. C. *Physica* **1937**, *4*, 1058.
(72) Visser, J. In *Surface and Colloid Science*; Matijevic, E., Ed.; Wiley-Interscience: New York, 1971; Vol. 8, p 3.
(73) Quintana, J. R.; Villacampa, M.; Salazar, R.; Katime, I. A. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2739.
(74) Nicholas, C. V.; Luo, Y.-Z.; Deng, N.-J.; Attwood, D.; Collett, J. H.; Price, C.; Booth, C. *Polymer* **1993**, *34*, 138.