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Block Copolymers at Interfaces. 1. Micelle Formation

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ABSTRACT: We apply the theory of Leibler et al. (*J. Chem. Phys.* **1983**, *79*, 3550) to describe the micellization of diblock copolymers in solutions. First, we consider the formation of spherical micelles and find that the critical micelle concentration and aggregation number increase as the copolymer–solvent compatibility increases, as the B block becomes smaller relative to the A block, and as the size of the solvent decreases. We also show how the radius of the micelle increases as the B blocks and solvent become less compatible. We discuss some limiting cases and give approximations for the model in the limit of small critical micelle concentration. We then consider the formation of lamellar micelles and predict regimes where lamellar micellization precludes that for spheres. Lamellar micelles are favored when the B and A blocks are equal in length and the solvent size is large.

I. Introduction

The behavior of amphiphilic diblock copolymers at interfaces plays an important role in homogenization of polymer blends,[1] detergency or surfactancy, and stabilization of colloidal particles.[2] Stabilization of colloidal particles is realized by adsorption of diblock copolymers onto their surfaces. The block interacting unfavorably with the solvent adsorbs onto the surface of a particle while the solvated block extends into the solution and forms a steric layer thus imparting stability. This adsorption process is complicated by the tendency of amphiphilic block copolymers to form micelles if the concentration of the solution exceeds the critical micelle concentration, cmc. The critical micelle concentration is defined as the concentration below which virtually no micelles exist and above which all additional copolymer goes into the micellar phase.[3] Since the critical micelle concentration often occurs at very low concentrations, a model of the adsorption process must include a description of micellization. The goal of this work is to address this problem by first describing the micellization process in this paper, and then, in the following paper, extending our analysis to block copolymer adsorption.

Theoretical models have been developed employing the mean-field theory to describe cmc and size of micelles.[4–6] We follow the development of Leibler et al.[4] who present a theory for micelle formation for a mixture of diblock copolymer and homopolymers. They considered copolymers of equal block lengths with a homopolymer of degree of polymerization typically one-fifth the polymerization index of the copolymer. Roe[7] shows a reasonable comparison between the results of this theory and the experimental results of Rigby and Roe.[8,9]

The purpose of this paper is to qualitatively describe micelle formation in block copolymers with much smaller insoluble head groups and in solutions of smaller solvent molecules than those treated previously.[4–6] One motivation for focusing our attention on these systems arises from the observation that colloidal stability is improved by maximizing the number of chains on the surface.[2] We expect the surface density of adsorbed block copolymers to increase with decreasing anchoring unit size, hence we focus our attention on systems with small head groups. Another motivation for studying small head groups arises from the many studies of surfactant systems typically having very small polar head groups. Generally systems of practical importance contain a solvent whose molecular size is much smaller than the copolymer molecules', and thus we also investigate this small-solvent regime.

We briefly present the model of Leibler et al.[4] and define the important parameters of this study, the ratio of block lengths, the relative solvent size, and the solvent compatibility. We then describe results of numerical calculations showing several important trends. We demonstrate that the critical micelle concentration increases as the relative length of the less soluble block decreases, as the size of the solvent decreases, and as the solubility of the head group increases. We note an interesting result that the radius of the micelle increases when the solubility of the head group decreases even though the number of chains per micelle decreases.

We present some useful asymptotic results showing the regimes where polydispersity becomes important, invalidating the assumptions of monodisperse spherical micelles, and where the cmc, chains per micelle, and micelle size can be predicted from simple expressions. We also describe

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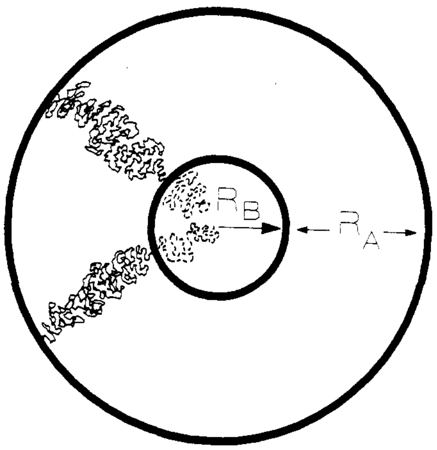

Figure 1. Schematic of the micellar system. Each micelle of radius R consists of p chains. The micelle core of radius R_B is a melt of B chains while the corona, having thickness $R_A = R - R_B$, contains solvent molecules and the A blocks of the copolymer chains at volume fraction ϕ_0. The region outside of the micelles contains isolated A–B diblock-copolymers and solvent molecules S.

the formation of a lamellar micelle, and in section IV we present regions where lamellar micelles are preferred over spherical micelles. In these domains, of near equal block lengths and large solvent molecules, the formation of nonspherical micelles have been neglected in the past[4] and must be considered to more completely describe micellization.

II. Micellization Model

We describe a system of diblock copolymer chains of N_A segments of species A linked to N_B segments of species B immersed in a solvent S of N_S segments. We assume that all species A, B, and S have the same segment length, a, and that the total volume of our system is Ωa^3. We consider a range of block lengths, with $\alpha = N_B/N_A$ from 0.1 to 1, at fixed total degree of polymerization $N = N_A + N_B = N_A(1 + \alpha)$. We also study the effect of the solvent size on micellization through variation of the ratio of the total degree of polymerization to the solvent size, $\beta = N/N_S$. As in Leibler et al.,[4] the polymers form spherical micelles of p chains of radius $R = R_A + R_B$, where R_B is the radius of the core of B blocks and R_A is the corona thickness. We assume the core to be essentially a melt of B chains while the corona contains A chains at a volume fraction ϕ_0 with solvent S. A schematic of the system is shown is Figure 1.

Flory's dimensionless interaction parameter χ_{BS} describes the interactions between the solvent S and the B monomers. For simplicity, we assume athermal interactions between A segments and solvent, i.e., $\chi_{AS} = 0$. The parameter χ_{BS} determines the effective interaction energy per B segment, and thus $\chi_{BS}N_B$ represents the total effective interaction per chain since the A chain is in an athermal environment. As noted by Leibler et al.,[4] $\chi_{BS}N_B$ is a measure of the degree of incompatibility of the system.

First we write the energy of a single micelle as given by Leibler et al.[4] as

$$\mathcal{F} = 4\pi R_B^2\gamma + \mathcal{F}_d + \mathcal{F}_m \tag{1}$$

The first term is the interfacial energy for a copolymer with comonomers of equal density, statistical segment length, and compressibility where $\gamma = (kT/a^2)(\chi_{BS}/6)^{1/2}$.[10] While this expression for γ was derived for an interface between pure homopolymers, we note in the Appendix that the decrease in γ due to the presence of small solvent molecules will be a small contribution to the free energy. The second contribution arises from the elastic deformation of the p copolymer chains in the micelle[11,12]

$$\mathcal{F}_d = \tfrac{3}{2}kTp\left(\frac{R_B^2}{N_Ba^2} + \frac{N_Ba^2}{R_B^2} + \frac{R_A^2}{N_Aa^2} + \frac{N_Aa^2}{R_A^2} - 4\right) \tag{2}$$

where k is the Boltzmann constant and T is the temperature. The last term, $\mathcal{F}_m$,

$$\mathcal{F}_m = \frac{\beta pkT}{(1+\alpha)}\frac{(1-\phi_0)}{\phi_0}\ln(1-\phi_0) + pkT\chi_{AS}N_A(1-\phi_0) \tag{3}$$

accounts for the free energy of mixing of solvent molecules with the A monomers in the corona.

Expressions for the radii in terms of p and ϕ_0 are obtained from the incompressibility conditions

$$\tfrac{4}{3}\pi R_B^3 = p\alpha N_A a^3 \tag{4}$$

and

$$\tfrac{4}{3}\pi\phi_0(R^3 - R_B^3) = pN_Aa^3 \tag{5}$$

Collecting the above terms, the energy per chain of a single micelle with $\chi_{AS} = 0$ is

$$\frac{f}{kT} = \frac{\mathcal{F}}{pkT} = 4\pi\left(\frac{3N_B}{4\pi}\right)^{2/3}\left(\frac{\chi_{BS}}{6}\right)^{1/2}p^{-1/3} + \frac{3}{2}\left[\left(\frac{3p}{4\pi N_A^{1/2}}\right)^{2/3}\left(\frac{1}{\alpha^{1/3}} + \left(\left(\frac{1+\alpha\phi_0}{\phi_0}\right)^{1/3} - \alpha^{1/3}\right)^2\right) + \left(\frac{4\pi N_A^{1/2}}{3p}\right)^{2/3}\left(\alpha^{1/3} + \left(\left(\frac{1+\alpha\phi_0}{\phi_0}\right)^{1/3} - \alpha^{1/3}\right)^{-2}\right)\right] + \frac{\beta}{1+\alpha}\frac{1-\phi_0}{\phi_0}\ln(1-\phi_0) \tag{6}$$

Minimization of f with respect to the number of chains per micelle, p, and the concentration of A chains in the corona, ϕ_0, yields equilibrium values of these variables for an isolated single micelle. These values provide initial estimates for the complete system when $\alpha,\beta \sim \mathcal{O}(1)$ and at low cmc values.

As Leibler et al.[4] note, a critical micelle concentration cannot be predicted by calculating the energy of the micelle alone; the model must include the equilibrium between the finite concentration of single chains remaining and the micelles. The total free energy of the system now includes the energy of the micelles, f, plus two additional contributions

$$\frac{F_T}{kT} = \frac{\Omega\phi\zeta}{N}\frac{f}{kT} + \frac{F_{mix}}{kT} - \frac{S_m}{k} \tag{7}$$

where ζ is the fraction of the copolymer chains existing in micelles and $\Omega\phi\zeta/N$ is the total number of chains participating in micelles. The free energy of mixing of the individual diblock copolymers with solvent molecules is given by

$$\frac{F_{mix}}{kT} = \frac{\Omega(1-\phi_m)}{N}\left[\phi_1\ln\phi_1 + \beta(1-\phi_1)\ln(1-\phi_1) + \frac{\chi_{BS}N\alpha\phi_1}{1+\alpha}\left(1 - \frac{\alpha\phi_1}{1+\alpha}\right)\right] \tag{8}$$

where ϕ_1 is the volume fraction of copolymers outside of

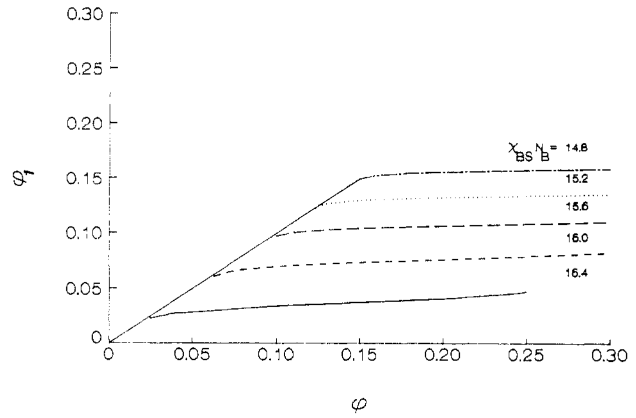

Figure 2. Free copolymer concentration as a function of the overall copolymer concentration for incompatibility degree $\chi_{BS}N_B$ = 14.8, 15.2, 15.6, 16.0, and 16.4 for $\alpha = 0.1$, $\beta = 50$, and $N = 200$.

the micelles and ϕ_m is the volume fraction of micelles in the system. The expressions for ϕ_1 and ϕ_m are

$$\phi_1 = \phi(1 - \zeta)/(1 - \phi_m)$$

and

$$\phi_m = \phi\zeta\xi$$

where

$$\xi = \frac{1 + \alpha\phi_0}{(1 + \alpha)\phi_0}$$

The last term in eq 7 is the free energy contribution arising from the translational entropy of the gas of micelles:

$$\frac{S_m}{k} = \frac{-\Omega\phi_0(1 + \alpha)}{pN(1 + \alpha\phi_0)}[\phi_m \ln \phi_m + (1 - \phi_m) \ln (1 - \phi_m)] \quad (9)$$

We minimize the total free energy, F_T, with respect to p, ϕ_0, and ϕ_1 to yield three coupled, nonlinear equations determining the equilibrium aggregation number, p, corona concentration, ϕ_0, and free copolymer concentration, ϕ_1. We choose to minimize eq 7 with respect to ϕ_1 rather than ζ for algebraic convenience.

III. Results and Discussion

In this section we describe the results of calculations probing the effects of polymer incompatibility, block length, and solvent size on the micellization process. We then define limits of validity of such a model and discuss some simple asymptotic results.

A. Incompatibility. The phenomenon of micellization is best illustrated in a plot of the free copolymer concentration as a function of the overall copolymer concentration as shown in Figure 2 for various degrees of incompatibility. Up to a certain concentration, the concentration of copolymer molecules existing as free chains is equal to that of the total. Above this concentration, little additional copolymer contributes to the free copolymer concentration, and the curve levels off. The concentration where this sharp transition occurs is denoted as the critical micelle concentration, the concentration below which virtually no micelles exist and above which almost all additional copolymer goes into the micellar phase. We define the cmc as the point where extrapolations from the two linear regimes intersect.

The free copolymer concentration is calculated for various B–S interactions. As expected, the critical micelle concentration is lower when the solvent-B chain interaction is less favorable, i.e., as $\chi_{BS}N_B$ increases. Also, at the highest degree of incompatibility the free copolymer concentration continues to increase slowly above cmc due to

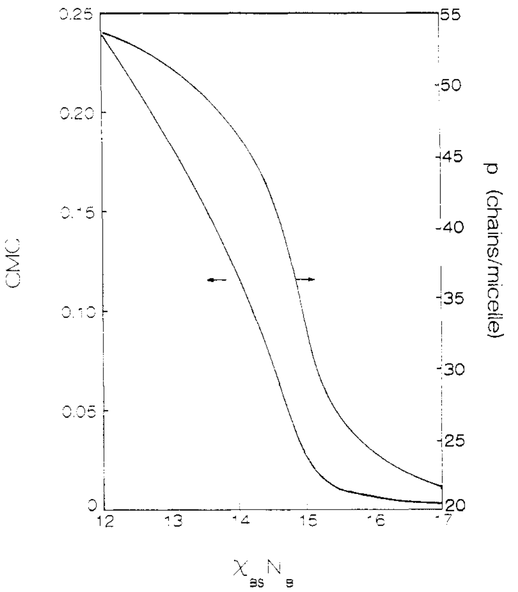

Figure 3. Critical micelle concentration and number of chains per micelle, p, as a function of the degree of incompatibility, $\chi_{BS}N_B$, for $\alpha = N_B/N_A = 0.1$, $\beta = N/N_S = 50$, and $N = 200$.

a balance between the entropy of the free copolymer solution and the stretching energy of the extended A blocks as described below.

Since we consider athermal interactions for the A chain, $\chi_{BS}N_B$ is a measure of the interaction of a chain with the solvent and thus a gauge of the incompatibility of the system.[4,11] Figure 3 demonstrates how the cmc and p vary with the degree of incompatibility. As the copolymer chains become more compatible with the solvent, the concentration required to form micelles rises. The critical micelle concentration represents the background concentration of free chains in equilibrium with the micelles. The system can respond to the background polymer concentration in two ways. One response to increasing the cmc is to form micelles with more chains, i.e., increase p, thereby creating a higher density micellar phase to equilibrate with the higher concentration in the background solution. We observe that p generally follows cmc as illustrated in Figure 3. The second response to a high cmc is to compress the corona as discussed below.

Assuming a segment length of 7 Å, the radius of the core R_B, the corona thickness R_A, and the total radius of the micelle R were calculated as functions of the degree of incompatibility $\chi_{BS}N_B$ and are shown in Figure 4. The core radius decreases slightly with $\chi_{BS}N_B$ as expected due to the fact that p decreases, thus requiring fewer chains to be packed in the core. Also, we note that the B chains of the core are always slightly stretched beyond their random-coil configuration. A more interesting result is found in the behavior of the corona thickness, R_A, and therefore R, with $\chi_{BS}N_B$. We find that the corona thickness increases as the incompatibility increases. The reason for this trend can be explained as follows. First consider the region of small $\chi_{BS}N_B$, where the cmc is high and p is large. The concentration of free chains ϕ_1 is approximately equal to the cmc since above the cmc nearly all additional copolymer goes into micelles. Therefore for small $\chi_{BS}N_B$, we have a phase of concentrated, free copolymer chains, phase I, in equilibrium with a micellar phase, phase II, as shown in Figure 5. At equilibrium, the osmotic pressure and chemical potential of each species in both phases I and II must be equal. To accommodate this, the chains in the micelle's corona must be concentrated, thus compressing the A chains. Increasing the incompatibility by increasing

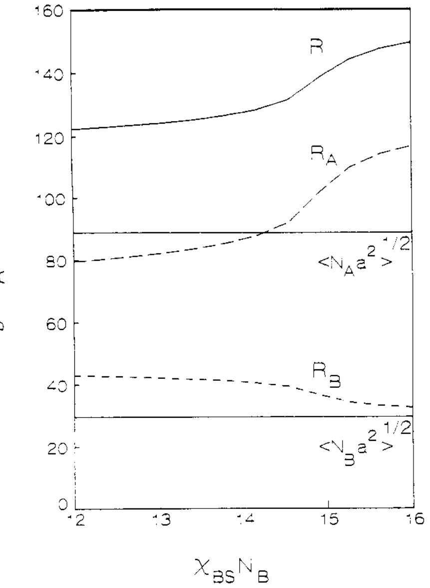

Figure 4. Radius of the core R_B, corona thickness R_A, and overall micelle radius R as a function of the degree of incompatibility $\chi_{BS}N_B$ for the same conditions as in Figure 3, assuming a monomer size a = 7 Å. The horizontal lines are the random coil size for the core and corona blocks, given for comparison.

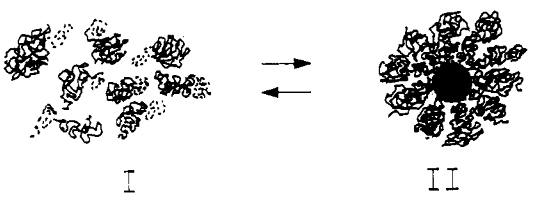

Figure 5. Illustration of the effect of the degree of incompatibility $\chi_{BS}N_B$ on the corona thickness R_A and overall radius R. The osmotic pressure of each species in the corona must equal its osmotic pressure in the free phase I. The A chains of the corona compress or extend to accommodate this condition. For small $\chi_{BS}N_B$ the background phase of free chains is concentrated, and so the A chains of the corona create a concentrated region by compressing. As $\chi_{BS}N_B$ increases, the concentration of free copolymer chains lowers, and the A chains of the corona must dilute by extending beyond their random coil configuration.

$\chi_{BS}N_B$ effectively dilutes the background phase I by lowering the cmc and thus dilutes the micellar phase II. This swells the corona and causes the thickness R_A to increase as in Figure 4. At small $\chi_{BS}N_B$, R_A is compressed from the random coil configuration, but at a $\chi_{BS}N_B$ of about 14.6 the A chains become extended beyond their random coil configuration. We also note that except at very high degree of incompatibility ($\chi_{BS}N_B \geq 16$), R remains fairly constant as the overall copolymer concentration ϕ is changed, illustrating the constancy of the background copolymer concentration above the cmc.

B. Block Length and Solvent Size. The critical micelle concentration as a function of $\alpha = N_B/N_A$ is shown in Figure 6. These curves demonstrate that as the B block becomes larger relative to the A block, the copolymer molecules become less compatible with the solvent and consequently the critical micelle concentration decreases. This trend is consistent with the incompatibility arguments in the preceding section where here we are changing N_B with χ_{BS} constant. Results are presented for different values of χ_{BS} indicating the increased tendency to form micelles as the solubility decreases.

Decreasing the size of the solvent has an interesting effect on the micellization. Figure 7 shows that as the size of the solvent decreases, increasing β, the critical micelle concentration increases. This trend reflects the enhanced solubility of the copolymer molecules in smaller solvents where micelles will only form at high concentrations. We also show the number of chains per micelle, p, in Figure 7 where again p follows the same trend as the cmc.

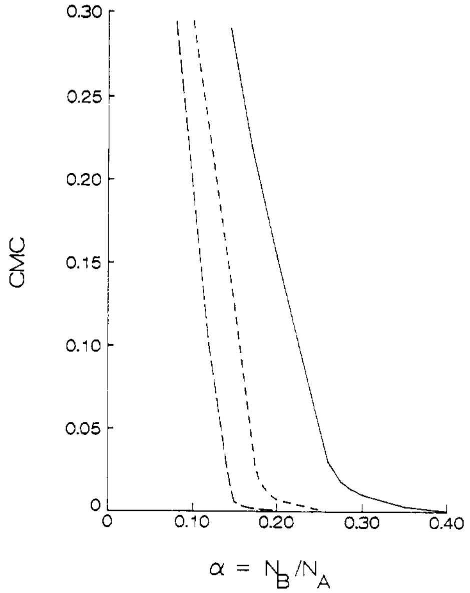

Figure 6. Critical micelle concentration as a function of $\alpha = N_B/N_A$ for β = 50 and N = 200. χ_{BS} = 0.5 (—); 0.6 (- - -); 0.7 (– – –).

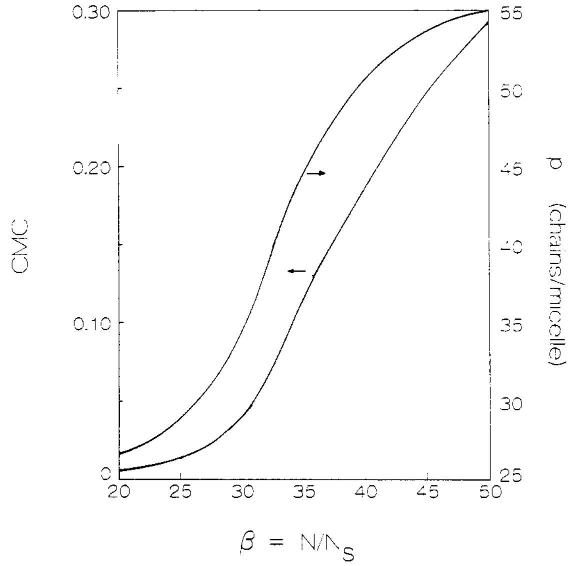

Figure 7. Critical micelle concentration and number of chains per micelle, p, versus $\beta = N/N_S$ for α = 0.1, $\chi_{BS}N_B$ = 12.0, and N = 200.

In conclusion, we find that the ratio of the B to A chain lengths, the size of the solvent, and the degree of incompatibility have a profound effect on the critical micelle concentration and the size of the micelles formed. The critical micelle concentration is found to increase as the length of the B block relative to the A block decreases, as the size of the solvent decreases, and as the degree of incompatibility decreases. The number of chains per micelle increases with increasing cmc, and increasing the degree of incompatibility increases the micelle radius by swelling the corona.

C. Asymptotic Behavior. In the limit of a monomeric solvent, $\beta \rightarrow N$, a high degree of incompatibility is required to form micelles. This was observed in Figure 7 where at fixed χ_{BS}, the cmc increases with β. A physical restriction that the cmc remains in a relatively dilute solution ($\leq$0.2) requires that the incompatibility increases to offset the

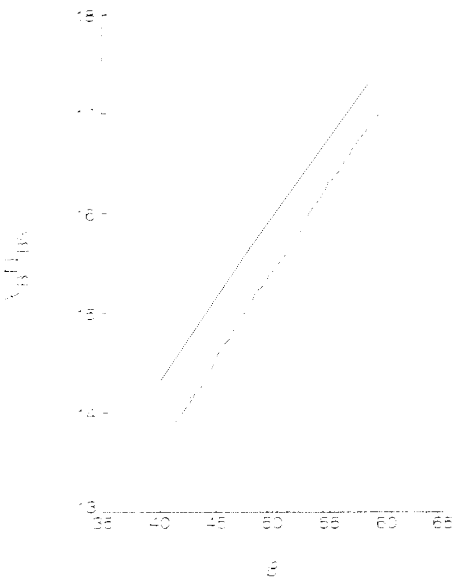

Figure 8. Degree of incompatibility, $\chi_{BS}N_B$, as a function of $\beta = N/N_S$ necessary to maintain a constant value of the cmc for $\alpha = 0.1$ and $N = 200$. The slopes of the lines for cmc = 0.0045 (—) and 0.012 (- - -) are 0.156 and 0.173, respectively, in good agreement with those predicted from the asymptotic analysis presented in section III.C.

enhanced solubility in small solvents. We can quantify this regime by examining the asymptotic behavior of the free polymer concentration as β and $\chi_{BS}N_B$ increase. The free energy minimization with respect to ϕ_1 yields an estimate for the critical micelle concentration as $\phi_1 \to 0$ as[4]

$$\phi_1 \cong \exp\left(\frac{f}{kT} + \beta - \chi_{BS}N_B\right) \tag{10}$$

Thus for $\phi_1 \to 0$ to apply, $\chi_{BS}N_B$ must be much greater than $f/kT + \beta$. Here the leading order terms in the energy per chain in an isolated micelle

$$\frac{f}{kT} \cong (6\pi^2 N_B)^{1/6}(\chi_{BS}N_B)^{1/2}p^{-1/3} + \frac{\beta}{1+\alpha}\,\frac{1-\phi_0}{\phi_0}\ln(1-\phi_0) \tag{11}$$

clearly require $\chi_{BS}N_B$ to increase as β increases. To first order this relationship will be linear with slope $\sim(1 + (1-\phi_0)\ln(1-\phi_0)/(1+\alpha)\phi_0)$ as shown in a plot of the $\chi_{BS}N_B$ necessary to maintain a constant cmc as β increases in Figure 8. For example, the relationship above predicts slopes of 0.143 and 0.161 for constant cmc values of 0.0045 and 0.012, respectively, in good agreement with the actual slopes of 0.156 and 0.173.

Another difficulty arising for large incompatibilities and small solvents is the insensitivity of the free energy surface to the number of chains in the micelle p. This is evident in the curvature of the surface at the minimum,

$$(\partial^2 F_T/\partial p^2)_{p_{\min}} = C_1 p^{-7/3} - C_2 p^{-4/3} + C_3 p^{-8/3} + \frac{2}{p^3}\left[\ln\phi_m + \frac{1-\phi_m}{\phi_m}\ln(1-\phi_m)\right] \tag{12}$$

which goes rapidly to zero as p increases, thus invalidating the assumption of monodisperse micelles in the large β and large p regime. In the limit of small micelles (where ϕ_1, p, and ϕ_0 are all decreasing), p and ϕ_0 become insensitive to the choice of ϕ_1 requiring calculation of p and ϕ_0 from the minimization of the single-micelle equation (6). In this limit ϕ_1 can be estimated from eq 10. This is physically reasonable; as the background free polymer concentration becomes very small, the micelle properties approach those of the single micelle.

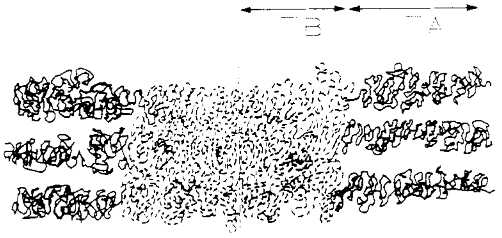

Figure 9. Schematic of the lamellar micelle model. A melt of B chains forms a planar layer of thickness L_B while the A chains form a layer of thickness L_A at a volume fraction ϕ_A with the solvent. The region outside the lamellar micelle contains isolated A–B copolymers and solvent S.

IV. Lamellar Micelle Model

In order to develop our model of polymer adsorption into steric layers, we investigate the formation of lamellar or surface micelles. In ref 13 we describe the use of such a model to describe block-copolymer adsorption onto solid surfaces having attractive interfacial energies. Here we describe the lamellar model in the absence of any polymer–surface attraction corresponding to the formation of lamellar micelles. We show regimes where the block copolymers form lamellar domains at a lower free energy than the spherical micelles. In these cases the alternate geometries of lamellae and cylinders must be considered to show a complete picture of polymer micellization.

We describe lamellar micelles in a similar way to the spherical micelles. The copolymers, having the same molecular parameters as in section II, form a planar layer consisting of a melt of B chains of thickness L_B surrounded by a layer of A chains and solvent of thickness L_A and volume fraction ϕ_A as illustrated in Figure 9. We introduce a dimensionless surface density, σ, such that the surface area per chain equals a^2/σ. Again Flory's dimensionless interaction parameter describes the interactions between the solvent and B segments and is the driving force for the micellization. Again we take the A chains to be in an athermal solvent, $\chi_{AS} = 0$.

The energy per chain in the lamellar micelle is given by

$$f_{\mathrm{lam}} = f_{\mathrm{def}} + f_{\mathrm{mix}} + f_{\mathrm{int}} \tag{13}$$

where

$$f_{\mathrm{def}} = \frac{3}{2}kT\left(\frac{L_A^2}{N_A a^2} + \frac{N_A a^2}{L_A^2} + \frac{L_B^2}{N_B a^2} + \frac{N_B a^2}{L_B^2} - 4\right) \tag{14}$$

$$f_{\mathrm{mix}} = \frac{kT\beta(1-\phi_A)}{(1+\alpha)\,\phi_A}\ln(1-\phi_A) + kT\chi_{AS}N_A(1-\phi_A) \tag{15}$$

and

$$f_{\mathrm{int}} = \frac{kT}{\sigma}\left(\frac{\chi_{BS}N_B}{6}\right)^{1/2} \tag{16}$$

Here the deformation, mixing, and interfacial contributions to the free energy are written in the same form as eq 1–3 of section II. The incompressibility conditions relating L_A and L_B to σ and ϕ_A are

$$L_A = Na\sigma/(1+\alpha)\phi_A \tag{17}$$

and

$$L_B = Na\sigma\alpha/(1+\alpha) \tag{18}$$

As before we must include the contributions to the free energy due to chains not participating in micelles. In this model we consider only single chains in equilibrium with the lamellae; i.e., we do not allow the coexistence of spherical micelles and lamellae. Thus by introducing the fraction of chains in a lamellae ζ_l, we can again write the overall energy as

$$F_T = \Omega kT\left[\frac{\phi\,\zeta_l}{N}\frac{f_{\mathrm{lam}}}{kT} + \frac{F_{\mathrm{mix}}}{\Omega kT}\right] \qquad (19)$$

where F_{mix} is analogous to the mixing energy from eq 8 with the volume fractions ϕ_1 and ϕ_M replaced by ϕ_{1l} and ϕ_L, respectively, with

$$\phi_{1l} = \frac{\phi(1-\zeta_l)}{1-\phi_L}$$

$$\phi_L = \phi\,\zeta_l\xi_l$$

and

$$\xi_l = \frac{1+\alpha\phi_A}{(1+\alpha)\phi_A}$$

Now ϕ_{1l} is the volume fraction of single copolymer chains outside the lamellae, and ϕ_L is the total volume fraction of lamellae.

Minimization of F_T with respect to σ, ϕ_A, and ϕ_{1l} allows us to calculate equilibrium surface areas per chain, layer concentrations and thicknesses, and critical micelle concentrations. This calculation results in regimes where lamellar micelles form at concentrations below the critical micelle concentration found for spherical micelles. The lower free energy of the lamellae in these cases precludes the formation of spherical micelles. The regime where this occurs is indicated in Figure 10a, illustrating the significant effect of solvent size and block length on micellization. We see from Figure 10a that lamellar micelles are favored when the A and B blocks are equal in length and the solvent size is large. Upon lowering the solvent size, the swelling of the A chains will make a curved surface favorable, resulting in spherical micelles. As the size of the B block decreases, decreasing α, the chains pack more closely, and again the repulsion of the A chains will bend the surface to form spherical micelles. Intermediate to these two configurations may be a cylindrical micelle as noted for block copolymer microphase separation.[14] Figure 10b illustrates the effect of incompatibility on the lamellae–sphere boundary. The results show that for high $\chi_{BS}N_B$ the lamellar phase becomes more stable as is the case for a block–copolymer melt.[14] However, it appears from these figures that for a given degree of incompatibility, there is a critical block length ratio below which only spherical micelles will form regardless of solvent size, as seen for $N_S \rightarrow \infty$.

The addition of a surface energy for the anchoring blocks in eq 13 will allow prediction of the adsorption isotherms and surface density for adsorption onto solid substrates to be presented in ref 13.

V. Conclusions

In conclusion, we have presented results for micellization of diblock copolymers for various degrees of incompatibility and a range of A–B block length ratios and solvent sizes. We find that for a given degree of incompatibility, $\chi_{BS}N_B$, spherical micelles are favored when the insoluble B block is smaller than the A block and when the solvent size becomes small with respect to the polymer. In these cases, the critical micelle concentration and aggregation number increase as the degree of incompatibility decreases, as the length of the B block becomes smaller, and as the solvent size decreases. Also as the incompatibility decreases, the radius of the spherical micelle increases due to swelling of the corona. Polydispersity effects are important when the solvent becomes very small and the aggregation number large, restricting the application of a model assuming monodisperse micelles. In the limit of small aggregation numbers, the micelle properties become independent of the free copolymer concentration and can be determined from consideration of a single micelle alone. A simple expression for the cmc is given in this limit. We also show that lamellar micelle formation is favored by equal B and A block lengths and a large solvent size.

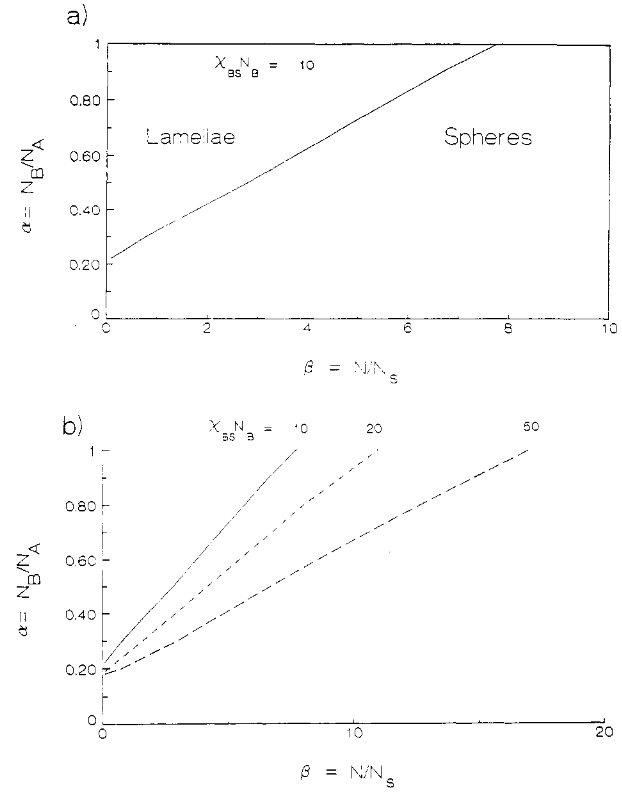

Figure 10. Lamellar and spherical micellar regions for α and β. (a) Illustration of the lamellar region on the left of curve and spherical region to the right for $\chi_{BS}N_B = 10.0$. (b) Boundaries for formation of lamellae for $\chi_{BS}N_B$ = 10, 20, and 50.

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Appendix

In the free energy expression in eq 1, we apply an expression for the interfacial tension between two homopolymers to a micellar interface between a core of pure polymer and a corona of polymer and solvent. In so doing we neglect the translational entropy of the solvent at the interface. A small solvent will preferentially adsorb to an interface,[6,15,16] increasing the thickness of the interfacial region and lowering the interfacial tension.[17,18] This drop in interfacial energy will favor micelle formation causing the cmc to decrease. We will show in this Appendix that the overestimation of the cmc from the interfacial energy expression will be small due to the dominance of the mixing energy in eq 19.

To evaluate the magnitude of the interfacial energy change in the presence of small solvents, we model the interface as a region where the A chain profile decays from its concentration in the corona, ϕ_0, to a surface density $\sigma = p(R_B/a)/4\pi$ at a point one segment length from the interface at $r = a$. Continuing with the mean-field model, we write the A chain concentration profile as[19]

$$\phi_A(r) = \sigma(r/a) \tag{A.1}$$

and the interfacial thickness as

$$d_I/a = \phi_0(36\pi N_B/p)^{1/3} \tag{A.2}$$

The Flory–Huggins mixing energy per chain in this region is then

$$\frac{f_{m,i}}{kT} = \frac{2\pi\phi_0 \ln (\phi_0/2)}{3pN_S}\left[\left(\left(\left(\frac{3N_Bp}{4\pi}\right)^{1/3} + \phi_0\left(\frac{36\pi N_B^2}{p}\right)^{1/3}\right)\right)^3 - \frac{3N_Bp}{4\pi}\right] \tag{A.3}$$

Evaluating this contribution to the micelle free energy shows that its magnitude is small, e.g., for $\chi_{BS}N_B = 16.73$, $f_{m,i}/kT = -0.57$, while the total micelle energy is $f/kT = -38.6$. Only at very small values of $\chi_{BS}N_B$ does the interfacial energy contribution grow to 10% of the total. In this limit of nearly soluble B blocks, the interface becomes more diffuse and a more detailed approach is warranted.

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Block Copolymers at Interfaces. 2. Surface Adsorption

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ABSTRACT: We present a theory for adsorption of diblock copolymers onto surfaces. We find that a critical adsorption concentration exists, analogous to the critical micelle concentration in micellization. This critical adsorption concentration decreases as the surface attraction increases, as the copolymer–solvent compatibility decreases, as the more soluble A block length decreases, and as the size of the solvent increases. The thickness of the adsorbed layer increases as the length of the A block increases, as the surface attraction for the anchoring B block increases, and as the solvent becomes smaller. We present a number of useful scaling relationships for layer thicknesses and surface densities as functions of block lengths of both the copolymer and the solvent. We are able to predict regions where only adsorption or only micellization are expected to occur.

I. Introduction

The behavior of amphiphilic diblock copolymers at interfaces plays an important role in the stabilization of colloidal particles in inks, paints, coatings, pharmaceuticals, and magnetic storage materials.[1] Stabilization of colloidal particles is realized by adsorption of diblock copolymers onto their surfaces. The block interacting unfavorably with the solvent adsorbs onto the surface of a particle while the solvated block extends into the solution and forms a steric layer thus imparting stability. This adsorption process is complicated by the tendency of amphiphilic block copolymers to form micelles if the concentration of the solution exceeds the critical micelle concentration. In the previous paper we investigated this micellization process in diblock copolymers as a function of the relative lengths of the blocks, the size of the solvent, and the solubility of the head group.[2] Here we extend the analysis to block copolymer adsorption.

Several reviews and monographs discuss homopolymer adsorption.[3-6] In general, homopolymers adsorb at several points along the chain in conformations having loops, trains, and tails.[7] Due to their amphiphilic nature, block copolymers adsorb in a very different fashion. Experiments have shown that diblock copolymers adsorb with one compact, tightly bound block and one extended, swollen block stretching away from the surface,[8] prompting researchers to model them as terminally anchored homopolymers. Previous investigators have studied the conformations of polymer layers where the polymers are attached to a surface by one end at a fixed surface density.[9,10] In this study, we allow the chains to reach the surface density and conformation determined by equilibration with the solution of block copolymers.

This paper concentrates on adsorption of block copolymers with small insoluble anchoring blocks in solutions of small solvent molecules. One motivation for focusing our attention on these systems arises from the observation that colloidal stability is improved by maximizing the number of chains on the surface.[1] We expect the surface density of adsorbed block copolymers to increase with

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