Surface Micelles Formation by Adsorption of Block Copolymers

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ABSTRACT: We discuss the adsorption of asymmetric diblock copolymers from a selective solvent onto an adsorbing surface, in the case when the block interacting unfavorably with the solvent only partially wets the surface. We calculate the wetting angle of an adsorbed droplet of copolymers, and we show that it differs only slightly from the contact angle given by the Young law. The main prediction of the model concerns the existence of a critical surface micellar concentration (csmc) different from the bulk one (cmc). When the contact angle, which characterizes the interfacial interactions between the copolymer, adsorbing surface, and solvent, is lower than some universal value $\theta_0^c \simeq 51°$, surface micelles appear at a lower copolymer concentration than bulk ones. The size distribution of these surface micelles is also studied.

I. Introduction

Recently, a considerable effort has been devoted to the study of the adsorption of block copolymers[1–8] and end-functionalized chains[9–12] from solution. In a selective solvent, block copolymers adsorb in a conformation such that the block interacting unfavorably with the solvent adsorbs in a molten state to the surface, while the solvated block extends away from the surface, forming a grafted layer. When the density of grafted chains is large enough to allow overlap, the chains are stretched and the layer thickness is several times thicker than the radius of gyration. Such layers are often called "brushes". Note that the same thermodynamic factors driving the adsorption cause block copolymers to aggregate into structures such as micelles in a solution.

Previous studies[1] focused on the wetting case, when A-blocks occupy all the available surface, leading to a homogeneous adsorbed layer. Tassin et al.[3] have investigated the kinetics of adsorption of polystyrene–poly(2-vinylpyridine) diblock copolymers on silver substrates. They conjectured that, at short times, copolymer micelles adsorb on the surface and create regions with a high polymer density leading to an inhomogeneous adsorbed layer. On the other hand, Johner and Joanny[7] argued that, for copolymers in a selective solvent, the potential barrier for direct adsorption of micelles is extremely high and only nonassociated chains can adsorb to the wall. Then the question arises as to how the surface coverage may be so inhomogeneous. It has been argued that a possible mechanism of inhomogeneous grafting is related to the roughness of the surface.[13] It has been shown that, in contrast with the adsorption of homopolymers, which tends to smooth the defects of the surface, the terminal anchoring of chains or the adsorption of asymmetric block copolymers should amplify the effect of surface roughness and result in an important inhomogeneous surface coverage. However, this decoration effect of rough surfaces by chain grafting cannot explain an eventual inhomogeneity of grafted layers on a liquid interface for which the curvature of the defects is of the order of the capillarity length, and thus much too high to expect any effects on the chain grafting.

In this paper we propose another possible explanation based on the existence of surface micelles (Figure 1) at equilibrium with copolymers in solution. Indeed, in the case when the A-blocks only partially wet the surface, one expects the formation of droplets of copolymers on the surface rather than a homogeneous film.

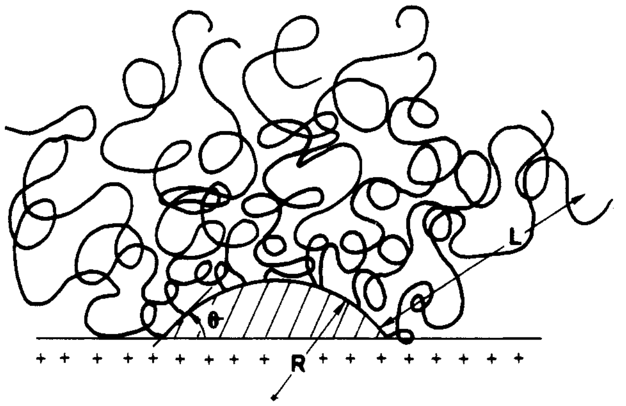

Figure 1. Schematic representation of a surface micelle of A–B diblock copolymers. The A-blocks, in a molten state, are adsorbed on the surface, forming a cap of sphere characterized by its wetting angle θ and its radius of curvature R. The B-blocks are swollen and stretched and form a corona of thickness L.

The paper is organized as follows: in section II we present a simple model of a surface micelle whose shape is supposed to be a spherical cap. We calculate the free energy of a droplet of Q chains as a function of Q and the contact angle θ. We show, in particular, that the conformational energy of the stretched blocks depends only weakly on the contact angle θ. This allows us to calculate its equilibrium value as a perturbation of the Young angle θ_0. The conformational energy turns out to be maximum for $\theta = 90°$. Hence, quite surprisingly, the presence of corona chains is favorable to the wetting for small contact angles ($\theta < 90°$) and unfavorable to the wetting for the big ones ($\theta > 90°$). We also take into account the line tension of the droplet, which should be of some relevance because of the mesoscopic size of the droplet. Section III is devoted to the discussion of the equilibrium of a surface micelle in contact with a solution of copolymers. We calculate the grand canonical free energy, and we evaluate more particularly the chemical potential as well as the aggregation number corresponding to the surface critical micellar concentration. We show the existence of a universal value of the Young angle θ_0^c, below which surface micelles appear at lower concentration than bulk ones. Finally we discuss the size distribution of surface micelles and optimum conditions under which they can be detected.

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II. Free Energy of a Droplet and Contact Angle

We consider a solution of diblock copolymers A–B. We denote by N_A and N_B, respectively, the polymerization index of the A- and B-blocks. For simplicity, we assume that the solvent is highly selective, good for the nonadsorbing block B and poor for the adsorbing block A, so that the B-blocks are swollen and the A-blocks are in the molten state. The parameter $\beta = N_B^{3/5}/N_A^{1/3}$,[1] characterizing the asymmetry of the chains, is supposed to be very large, so that only the B-blocks contribute to the deformation energy. A droplet, of spherical cap shape, formed by Q chains adsorbed on the surface (the wall) is characterized by the radius R, the thickness of the corona L, and the wetting angle θ (Figure 1). The incompressibility condition for the molten core relating θ and R reads

$$V = QN_A a^3 = (\pi/3)R^3(1 - \cos\theta)^2(2 + \cos\theta) \qquad (1)$$

The free energy of a surface micelle is the sum of three contributions:

$$F = F_C + F_S + F_L \qquad (2)$$

Here, within a Flory-type approximation, F_C is the deformation and excluded volume energy of the corona shell, F_S represents the interfacial energy, and F_L is the energy related to the line tension.

$$\frac{F_C}{QkT} = \frac{3L^2}{2N_B a^2} + \frac{vQN_B^{\,2}}{V(L)} \qquad (3)$$

The first term is the elastic deformation of the B-blocks, and the second one comes from excluded-volume interactions; v denotes the excluded volume and $V(L)$ is the volume of the corona. Note that, in the limit of asymmetric diblocks ($\beta \gg 1$), we can neglect the eventual contribution of the deformation energy due to the A-blocks. $V(L)$, L, R, and θ are related through the following equation: $V(L) = \pi[(2/3)L^3 + (2 - \cos\theta)L^2R + 2(1 - \cos\theta)R^2L]$. In order to obtain this equation, we only impose that the B-blocks are grafted on the spherical cap constituted by the melt core of A-blocks and that they cannot go across the wall. The surface energy includes the contribution from A–solvent and A–wall interfaces:

$$F_S = 2\pi(1 - \cos\theta)R^2\gamma + (\gamma_{WA} - \gamma_{WS})\pi(R\sin\theta)^2 \qquad (4)$$

The reference here is the wall in contact with pure solvent; γ, γ_{WA}, and γ_{WS}, denote the interfacial tension between, respectively, the A–solvent, wall–A, and wall–solvent. Note that only the core contributes to the interfacial energy because B-blocks are swollen by the solvent, so their contribution to the interfacial energy can be neglected.

The last contribution comes from the line tension τ: $F_L = 2\pi R(\sin\theta)\tau$. On dimensional grounds $\tau \propto \gamma a$, and thus the line tension introduces only small corrections when $R \gg a$.

The corona thickness is obtained by minimization of F with respect to L, keeping Q and θ constant:

$$L = \frac{N_B^{\,3}a^2vQ}{3V(L)^2}\left.\frac{\partial V}{\partial L}\right|_{\theta,Q} \qquad (5)$$

We consider two limiting regimes. In the first one, $L \gg R$, the curvature effects are important, whereas in the second one, $L \ll R$, they are negligible. In the first regime, one gets: $L = L^* - l$ with $L^* = (3/2\pi)^{1/5}(a^2v)^{1/5}Q^{1/5}N_B^{3/5}$ and $l = (2/5)(2 - \cos\theta)R$. Note that $l \ll L^*$ and L^* does not depend on θ. Putting the expression for L in (3), the corona energy reads

$$\frac{F_C}{QkT} = \left(\frac{3}{2}\frac{L^{*2}}{N_B a^2} + \frac{3v}{2\pi}\frac{QN_B^{\,2}}{L^{*3}}\right) + \left(\frac{3L^{*2}}{N_B a^2} + \frac{9v}{8\pi}\frac{QN_B^{\,2}}{L^{*3}}\right)\frac{l}{L^*} \qquad (6)$$

The first regime is valid when $(1 - \cos\theta)^2(2 + \cos\theta) \gg (Q^{2/5}/\beta^3)$. The second one corresponds to the opposite limit. In fact, because of the high asymmetry of the copolymers ($\beta \gg 1$), only the first regime seems to be realistic. The second one should be relevant only when $\beta \simeq 1$ or $\theta \simeq 0$. When $\beta \simeq 1$, the chains are symmetric or slightly asymmetric and the shape of surface micelles should be cylindrical or lamellar, whereas when $\theta \simeq 0$, long-range interactions such as van der Waals forces cannot be neglected. Thus, in the following we restrict our attention to the first regime.

The value of the wetting angle is given by minimization of the total free energy with respect to θ:

$$\partial F/\partial\theta = 0 \qquad (7)$$

In view of (6), the corona energy depends weakly on the wetting angle θ, because the first term in (6) is independent of θ, whereas the remaining terms bring only small corrections. Thus the wetting angle θ is only slightly different from the Young angle θ_0 of a droplet of A-polymers, which is given by minimization of the surface energy F_S with respect to the core volume and equals $\cos\theta_0 = (\gamma_{WS} - \gamma_{WA})/\gamma$. θ_0 measures the spreading power of A-monomers on the wall in contact with the solvent. The wetting angle of a Q-surface micelle is given by minimization of the total free energy with respect to the core volume. It can be written as $\theta = \theta_0 + \delta\theta$ with $|\delta\theta/\theta_0| \ll 1$, because, as seen above, the angular dependence of the free energy arises essentially from the surface contribution, so that we can expand the left side of (7) in Taylor series around $\theta = \theta_0$ and, remaining that $\partial F_S/\partial\theta|_{\theta=\theta_0} = 0$ by definition of the Young angle, we get

$$\delta\theta = -\left.\frac{\partial(F_L + F_S)/\partial\theta}{\partial^2F_S/\partial\theta^2}\right|_{\theta=\theta_0} \qquad (8)$$

with

$$\frac{1}{kT}\frac{\partial F_C}{\partial\theta} = 3(3/2\pi)^{8/15}Q^{8/15}N_B^{\,-2/5}N_A^{\,1/3}(v/a^3)^{1/5} \times \sin\theta\cos\theta(1 - \cos\theta)^{-5/3}(2 + \cos\theta)^{-4/3} \qquad (9a)$$

$$\frac{\partial F_L}{\partial\theta} = -2\pi(3/\pi)^{1/3}Q^{1/3}N_A^{\,1/3}\tau a(1 - \cos\theta)^{-1/3}(2 + \cos\theta)^{-4/3} \qquad (9b)$$

$$\left.\frac{\partial^2F_S}{\partial\theta^2}\right|_{\theta=\theta_0} = 2(3/\pi)^{2/3}Q^{2/3}N_A^{\,2/3}\gamma a^2(1 - \cos\theta_0)^{-4/3} \times (2 + \cos\theta_0)^{-5/3}\sin^2\theta_0 \qquad (9c)$$

By considering (9a), it appears that the corona energy reaches its maximum for $\theta = \pi/2$. This result has a simple interpretation. It is the consequence of a noteworthy geometrical property of a spherical cap of constant volume. One can show easily that the curved surface of an incompressible spherical cap (the melt core of A-blocks in this case) is minimal for a hemisphere ($\theta = \pi/2$). As a consequence, the B-blocks, which are "grafted" on this curved surface, reach their maximum of stretching for the same value $\theta = \pi/2$. This simple geometric property has an important consequence. The corona energy will have opposite effects in two different cases: if $\theta_0 > \pi/2$, the corona effect will increase the wetting angle of the micelle ($\theta > \theta_0$) in order to decrease the corona energy. In this case the corona effect is unfavorable to the wetting. On the contrary, when $\theta_0 < \pi/2$, for the same reason it will decrease the wetting angle ($\theta < \theta_0$), and in this case the corona effect is favorable to the wetting. It should also be noticed that the line energy decreases when θ increases, meaning, as expected, that the line tension always opposes wetting.

For example, using the set of parameters a = 5 Å; v = 8 Å^3; N_A = 20; N_B = 1000; γ = 20 dyn cm^{-1}; $\tau \simeq \gamma a = 10^{-6}$ dyn, we can evaluate $\delta\theta$ for two different surfaces corresponding to two different Young angles (θ_{01} = 30° and θ_{02} = 120°, respectively). In both cases $\beta = 23.2 \gg 1$; thus, for reasonable values of Q, both situations correspond to the first regime. One obtains by putting these values in (8 and 9) the following: $\delta\theta_1$ = −0.2° and $\delta\theta_2$ = +2.4° for Q = 10; $\delta\theta_1$ = −0.04° and $\delta\theta_2$ = +1.1° for Q = 100; $\delta\theta_1$ = +0.02° and $\delta\theta_2$ = −0.5° for Q = 1000. One can remark that $\partial^2 F_S/\partial\theta^2 \propto Q^{2/3}$ whereas $\partial F_C/\partial\theta \propto Q^{8/15}$ and $\partial F_L/\partial\theta \propto Q^{1/3}$; thus, the deviation from the Young's angle decreases when the aggregation number increases. Note also that, for small Q, the line contribution seems to dominate the corona one, canceling the geometric effect that we have discussed above.

III. Critical Surface Micellar Concentration and Size Distribution

In this section we shall consider the thermodynamic equilibrium of a surface micelle with a reservoir of chains in solution, assuming that the aggregates formed by the adsorbed copolymers on the wall have a bimodal distribution: single chains and monodisperse spherical cap shape surface micelles. The critical surface micelle concentration is a sharp transition if we neglect the surface micelles translational entropy on the wall. We shall then discuss the surface micelle size distribution and, in particular, check the validity of the bimodal approximation. We then shall compare these results with the "classical" ones concerning the formation of spherical micelles of the same block copolymer in the selective solvent. Actually, we use a similar approach as for the treatment of bulk micellar formation of diblocks, which has been extensively studied.[15-19] Thus we just give the results for the bulk micellar formation; the same model will be developed for surface micellar formation.

The ability of diblock copolymers to self-assemble into micelles, even in very dilute solution, has been established over 2 decades. At extremely low concentration only individual chains are found in solution. As the concentration increases, it reaches the cmc, where spherical micelles form. The optimum aggregation number Q^* for bulk micelles is given by minimization of the free energy per chain in the micelle F'/Q with

$$F'/Q = (5/2)(3/4\pi)^{2/5}(v/a^3)^{2/5}{N_B}^{1/5}Q^{2/5}kT + (9\pi/16)^{2/3}\gamma a^2 {N_A}^{2/3}Q^{-1/3} \quad (10)$$

F' is the sum of two contributions: the first one is the corona energy calculated with the simple Flory model that we used for surface micelles, and the second one is the surface energy between the molten core of A-blocks and the corona of swollen B-blocks. Q^* is given by the requirement $\partial(F'/Q)/\partial Q = 0$. One gets

$$Q^* = 2^{-8/11}(\pi/3)(\gamma a^2/kT)^{15/11}(a^3/v)^{6/11}{N_B}^{-3/11}{N_A}^{10/11} \quad (11)$$

Using a blob model, Halperin[19] obtains with equivalent arguments $Q^* \simeq {N_A}^{4/5}$. The chemical potential of a chain at the cmc can be evaluated by $\mu_{cmc} = \partial F'/\partial Q|_{Q=Q^*}$, which gives

$$\mu_{cmc}/kT = (11/2)2^{-12/11}(\gamma a^2/kT)^{6/11} \times (v/a^3)^{2/11}{N_B}^{1/11}{N_A}^{4/11} \quad (12)$$

Below the cmc, if the concentration of free chains is ϕ_1, in a dilute solution the chemical potential of the free chains is

$$\mu_1 = kT \log \phi_1 + 4\pi\gamma a^2 {N_A}^{2/3} \quad (13)$$

The dominant contribution to the free energy of a collapsed chain is the surface energy between the solvent and the molten A globule. One can show, using a classical pseudo-phase-equilibrium model[15,17] that the distribution of bulk micelles is peaked around the optimum aggregation number Q^*. Above the cmc, the fraction of free chains in solution remains roughly constant, whereas the fraction of chains self-associated in Q-mers increases. The chemical potential increases much more slowly above the cmc than below, because the entropy of mixing Q-mers is approximately Q times weaker than the entropy of mixing free chains. Indeed, above the cmc the chemical potential reads[16,17]

$$\mu_{ext} = \mu_{cmc} + \frac{kT}{Q^*}\log\left(\frac{\phi}{(2\pi)^{1/2}Q^*\,\delta Q}\right) \quad (14)$$

where δQ is the root-mean-square average spread of the distribution (when the distribution is approximated by a Gaussian function with average $\bar{Q} \simeq Q^*$), and ϕ is the total concentration of chains. One gets

$$\delta Q = [\partial^2(F'/Q)/\partial Q^2|_{Q=Q^*}]^{1/2}{Q^*}^{-1/2} \simeq {N_A}^{-7/11}{N_B}^{1/11} \quad (15)$$

Let us consider a surface micelle in contact with a reservoir of chains in solution, which imposes the chemical potential of chains μ_{ext}. The equilibrium values of Q and θ may be obtained by minimizing with respect to Q and θ the grand canonical free energy of the micelle Ω

$$\Omega = F - \mu_{ext}Q + V(L)\Pi_{ext} \quad (16)$$

where Π_{ext} denotes the osmotic pressure acting on the micelle. The equilibrium condition reads

$$\begin{cases}\partial\Omega/\partial\theta = 0 \\ \partial\Omega/\partial Q = 0\end{cases} \quad (17)$$

In a micelle the B-blocks are stretched and overlap strongly; thus, the concentration is much higher than the overlap threshold c^*, so that we can neglect the osmotic term in the grand canonical free energy.[1]

The first equation in (17) was solved in the previous section. It gives the wetting angle of the surface micelle as a correction of the Young angle θ_0. For high enough chemical potential μ_{ext}, $\Omega(Q)$ has a minimum corresponding to a stable micelle. The surface critical micellar concentration is thus given by

$$\begin{cases}\partial\Omega/\partial Q = 0 \\ \Omega = 0\end{cases} \quad (18)$$

As shown above, because the corona energy is roughly independent of the wetting angle, this one differs only slightly from the Young angle θ_0. That allows us to make the approximation $\theta = \theta_0$ in order to calculate the optimum aggregation number $Q^*(\theta_0)$ and the critical surface micellar chemical potential $\mu_{csmc}(\theta_0)$. Equation 15 is equivalent to the requirement $\partial(F/Q)/\partial Q = 0$, leading to

$$Q^*(\theta_0) = 2^{14/11}f(\theta_0)^{15/11}Q^* \quad (19)$$

where

$$f(\theta_0) = \frac{2 - \cos\theta_0(1 + \cos\theta_0)}{(2 + \cos\theta_0)^{2/3}(1 - \cos\theta_0)^{1/3}}$$

f is an increasing function of θ_0. It varies between $f(0) = 0$ and $f(\pi) = 2^{2/3}$. Obviously the micelle exists only for $Q^*(\theta_0) > 1$. This condition imposes from (16) $\theta_0 > \theta_0^{\min}$, where $\theta_0^{\min}$ is defined by the condition $f(\theta_0^{\min}) > 2^{-14/11}Q^{*-11/15}$. Below this value, that is, for sufficiently good wetting, one could expect adsorption of isolated chains at low concentration in solution and formation of a homogeneous adsorbed layer at higher concentration.

We can now calculate the chemical potential at the critical surface micellar concentration (csmc): $\mu_{\mathrm{csmc}}(\theta_0) = \partial F/\partial Q|_{Q=Q^*(\theta_0)}$, leading to

$$\mu_{\mathrm{csmc}}(\theta_0) = 2^{10/11} f(\theta_0)^{6/11} \mu_{\mathrm{cmc}} \tag{20}$$

From (20), we can define a critical angle θ_0^{c} by the requirement $\mu_{\mathrm{csmc}}(\theta_0^{\mathrm{c}}) = \mu_{\mathrm{cmc}}$. It is important to remark that θ_0^{c} has a universal value and depends only on the model that is used to calculate the corona energy of a micelle: in the Flory model $\theta_0^{\mathrm{c}} \simeq 51°$. When $\theta_0 < \theta_0^{\mathrm{c}}$, $\mu_{\mathrm{csmc}}(\theta_0)$ is less than μ_{cmc}. In this case from (13) and (20) we can evaluate the polymer concentrations at the cmc and csmc, respectively:

$$\phi_{\mathrm{cmc}} \simeq \exp(-4\pi(\gamma a^2/kT)N_{\mathrm{A}}^{2/3} + \mu_{\mathrm{cmc}})$$

$$\phi_{\mathrm{csmc}}(\theta_0) = \phi_{\mathrm{cmc}} \exp(\mu_{\mathrm{csmc}}(\theta_0) - \mu_{\mathrm{cmc}}) \tag{21}$$

Clearly, surface micelles appear at lower concentration than bulk ones, and because of their exponential dependence on the chemical potential, the csmc can be much less than the cmc. One can interpret this preferential surface micellization tendency of the block copolymer within the framework of the free energy contributions. For micelle formation to occur, the net free energy of micellization per chain must be negative. The corona free energy contribution is positive, because the B-block has to stretch if chains self-associate. The contribution of the entropy of mixing is positive too because the entropy of mixing decreases with increasing aggregation number. On the contrary, the interfacial free energy contribution is negative, because the aggregation of A-blocks diminishes the contacts between A monomers and solvent, which are unfavorable. Thus, one can understand clearly that, for high enough concentration, chains will prefer to self-associate in micelles (bulk or surface ones) than to stay isolated. By comparison of (4) and the second term in the right-hand side of (10), it appears clearly that, for the same aggregation number Q, the interfacial energy of a surface micelle is less than the interfacial energy of a bulk one (they are equal for $\theta_0 = \pi$). On the other hand, the corona energy of a surface micelle is bigger than the corona energy of the same micelle in the bulk: actually, because the corona energy of a surface micelle is in first approximation, independent of the wetting angle, such a micelle can be viewed as hemispherical, and, obviously, the corona energy of a Q hemispherical micelle is half the corona energy of a $2Q$ spherical one. More concisely, corona energy favors bulk micelle formation, whereas interfacial energy favors surface micelle formation. These opposite effects cancel for $\theta_0 = \theta_0^{\mathrm{c}}$. It means that for $\theta_0 < \theta_0^{\mathrm{c}}$, the spreading power of A-blocks is big enough to favor surface micelle formation. Thus, as seen above, csmc is less than cmc. For the same reasons, $Q^*(\theta_0)$ is less than Q^*. Therefore, when $\theta_0 < \theta_0^{\mathrm{c}}$, one expects for $\phi_{\mathrm{csmc}} < \phi < \phi_{\mathrm{cmc}}$ the coexistence of free chains in solution, free adsorbed chains, and aggregated adsorbed chains.

In the opposite case, that is, for $\theta_0 > \theta_0^{\mathrm{c}}$, $\mu_{\mathrm{csmc}}(\theta_0)$ is higher than μ_{cmc}. Thus, bulk micelles appear at lower polymer concentration than surface ones, and from (14) and (20) the polymer concentration at the csmc is

$$\phi_{\mathrm{csmc}}(\theta_0) = (2\pi)^{1/2} Q^* \delta Q \exp(Q^*/kT(\mu_{\mathrm{csmc}}(\theta_0) - \mu_{\mathrm{cmc}})) \tag{22}$$

Note the presence of the factor Q in the exponential in (22). This means that ϕ_{csmc} is much higher than ϕ_{cmc}, so that, in most practical cases, one never reaches ϕ_{csmc}. In this way, if $\theta_0 > \theta_0^{\mathrm{c}}$, the spreading power is not big enough to favor surface micelles formation. Indeed, above the cmc, as seen previously, the external chemical potential increases much more slowly with the polymer concentration than below. Thus it can happen that μ_{ext} never reaches the value μ_{csmc} necessary for the formation of surface micelles.

Let us discuss briefly the validity of the bimodal approximation, which has been implicitly used to describe the surface micelle formation. We now suppose that $\theta_0 < \theta_0^{\mathrm{c}}$ ($\phi_{\mathrm{csmc}} < \phi_{\mathrm{cmc}}$) and that the surface micelles appear for $\phi > \phi_{\mathrm{csmc}}$. On the surface coexist isolated adsorbed chains and aggregates of several sizes. Each aggregate is characterized by its number of aggregation Q and its wetting angle $\theta(Q)$. As seen in the previous section, $\theta(Q)$ depends only slightly on Q; therefore, we assume $\theta(Q) \simeq \theta_0$. Following classical treatments,[17] we begin with the condition of chemical equilibrium between Q-adsorbed-mers

$$\mu_Q(\theta_0) = \mu_1 = \mu_{\mathrm{ext}} \tag{23}$$

for all Q. μ_Q is the full chemical potential of a single chain in a Q-surface micelle, and μ_1 is the chemical potential of an isolated adsorbed chain. If one defines σ_Q to be the surface density of adsorbed chains in Q aggregates, (23) gives

$$\mu_{\mathrm{ext}} = \mu_Q{}^0 + \frac{kT}{Q}\ln(\sigma/Q) = \mu_0{}^1 + kT\ln\sigma_1 \tag{24}$$

where $\mu_Q{}^0 = \partial F/\partial Q|_{\theta=\theta_0}$ and $\mu_0{}^1$ are, respectively, the standard energy of an adsorbed chain in a Q aggregate and the standard energy of an isolated adsorbed chain. Rewriting (23), we get the law of mass action:

$$\sigma_Q = Q\exp\left\{\frac{\mu_{\mathrm{ext}} - \mu_Q{}^0}{kT}Q\right\} \tag{25}$$

Equation 25 shows that values of Q for which $\mu_{\mathrm{ext}} > \mu_Q{}^0$ dominates the distribution. That is, for small μ_{ext} one sees only isolated adsorbed chains in equilibrium with free chains in solution. If one increases the concentration (increasing μ_{ext}) at a special concentration (corresponding to csmc), a second free energy minimum can compete with the minimum that describes isolated adsorbed chains. If the distribution of Q-surface micelles can be approximated by a Gaussian function centered upon $Q^*(\theta_0)$ that corresponds to the minimum of $\mu_Q{}^0$, one gets

$$\sigma_Q \simeq \exp(-|Q - \bar{Q}|^2/2\delta Q^2(\theta_0)) \tag{26}$$

where $\bar{Q} = \sum_{Q>1} Q\sigma_Q / \sum_{Q>1}\sigma_Q$ is the mean aggregation number (note that in this approximation $\bar{Q} \simeq Q^*$) and $\delta Q(\theta_0)$ denotes now the root-mean-square average of the surface micelles distribution:

$$\delta Q(\theta_0) = Q^*(\theta_0)^{-1/2}(\partial^2\mu_Q{}^0/\partial Q^2)^{1/2}|_{Q=Q^*(\theta_0)} \tag{27}$$

From (1)–(3), (4), and (6), $\mu_Q{}^0 \simeq (v/a^3)^{2/5} Q^{2/5} N_{\mathrm{B}}{}^{1/5}$, and thus, using (19), one obtains

$$\frac{\delta Q(\theta_0)}{Q^*(\theta_0)} \simeq f(\theta_0)^{-21/22}(\gamma a^2)^{-21/22}(v/a^3)^{2/11}N_B^{\ 1/11}N_A^{\ -7/11} \qquad (28)$$

The bimodal approximation gives a rather good description of surface micelle formation as long as $\delta Q(\theta_0)/Q^*(\theta_0) \ll 1$. The function f, defined by (19) vanishes for $\theta_0 = 0$, so that there is a value of the wetting angle θ_0^{d} below which the bimodal approximation is not correct. θ_0^{d} may be defined by the requirement $\delta Q(\theta_0^{\mathrm{d}})/Q^*(\theta_0^{\mathrm{d}}) = 1$. This result means that, in contrast to the case of bulk micelles for which the size distribution is essentially monodisperse, one has to distinguish between two different cases for surface micelles: when the spreading power of A-blocks on the surface is strong ($\theta_0 \ll \theta_0^{\mathrm{d}}$), surface micelles of small size form with a large-size distribution. In the opposite case ($\theta_0 \gg \theta_0^{\mathrm{d}}$), that is, for a spreading power of A-blocks weak enough, the distribution size of surface micelles is rather similar to that of bulk ones: they are very monodisperse, with a high aggregation number of about $Q^*(\theta_0)$.

It should be noticed that we did not take into account the interactions between surface micelles, which start to play an important role at high surface coverage and may lead to the formation of ordered structures: two-dimensional macrocrystals. The surface coverage for the same polymer concentration is higher when the spreading power is stronger; therefore, it may be that the approximation, which consists in neglecting interactions between surface micelles, is not realistic. Thus, our brief analysis of size distribution should be carefully considered, in particular, in the case of high spreading power.

IV. Conclusion

In this paper, we have developed a theoretical model describing the adsorption of asymmetric diblock copolymers from a selective solvent onto a surface, in the case when the short block wets only partially the surface. We have shown that droplets of copolymers can form on the adsorbing surface, leading to a nonhomogeneous adsorbed layer. This effect can, in principle, be experimentally observable. The free energy of a single droplet has been calculated, as well as its contact angle, which turns out to differ only slightly from the well-known Young angle. The conformational effects of the chains in the droplet play a minor role for the wetting angle; they favor the wetting when the Young angle is less than 90° and oppose it when it is higher.

The main result of this model concerns the existence of a critical surface micellar concentration (csmc) different from the bulk one (cmc), which has been exhaustively studied: when the Young angle, which characterizes the interfacial interactions between copolymer, adsorbing surface, and solvent, is less than a universal value $\theta_0^{\mathrm{c}} \simeq 51°$, surface micelles appear at a lower concentration of copolymers in the solution than do bulk ones; in the opposite case the csmc is higher than the cmc, and thus, when the csmc is too high, surface micelles cannot be observed. Finally we predict that, in the existence domain of surface micelles, we can distinguish between two regions: in the first one, surface micelles are small and very polydisperse, whereas in the second one, they are very monodisperse and their aggregation number is large.

We have restricted our study to the case of the adsorption from a solvent, but it could be easily extended to the adsorption from a melt constituted from homopolymers and copolymers, and as in the solvent case, one expects in the melt case the existence of a csmc different from that of the cmc.

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