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Surface Micellar Nanopattern Formation of Adsorbed Diblock Copolymer Systems

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ABSTRACT: In this paper, we investigate theoretically the structure of an ultrathin layer of diblock copolymers. It is assumed that one of the blocks is strongly adsorbed on a planar surface while the nonadsorbed block aggregates with the formation of surface micelles. We adopt a simple model in which the adsorbed blocks of the copolymers are assumed to form a two-dimensional melt while the surface micelles of the second blocks are approximated by parts of a sphere. The equilibrium structure of the micelles, which is governed by the interplay of the surface energy which favours the aggregation process and the energy of stretching of the adsorbed blocks is analyzed. It is shown that the number of the chains in one micelle, the radius and the height of the micelles scale with the length N_B of a nonadsorbed block as $N_B^{1/2}$.

1. Introduction

Surface modification by polymers and formation of patterned polymer layers is a subject of recent intensive experimental and theoretical studies due to their fundamental importance and broad technological applications. One example of such systems are grafted homopolymer layers immersed in a poor solvent.[1−6] The polymers tend to phase separate, but since their ends are bound to the surface, only microphase separation can take place with polymer-rich and polymer-poor regions on the surface if the grafting density is rather low. The formation of laterally inhomogeneous structures on the surface was predicted theoretically[1,2] and observed in computer simulations[3−5] as well as in experiments,[6] and the parameters of the structure as functions of polymer length, grafting density, and solvent quality were investigated.

More complex surface structures can be formed in the case of grafted block copolymers due to different interaction energies between different monomer units and solvent molecules.[7,8] In the case of linear A−B diblock copolymers grafted by one end onto a planar surface it was demonstrated that novel types of pinned micelles, like “onions” and “garlics”, can be formed, depending on the interaction parameters of the components.[8] Layers of Y-shaped A−B copolymers grafted to the surface by the junction points of the blocks can self-assemble into a checkerboard pattern with alternating A and B micellar domains.[7]

Highly ordered multilayers of microdomains are observed also for thin films of diblock copolymers.[9−11,15] Laterally ordered microdomains appear on the surface in the process of adsorption of diblock copolymers from a selective solvent onto a flat solid substrate.[11−15] Due to the selectivity of the solvent, spherical micelles consisting of a core of the insoluble block surrounded by a highly stretched corona of the soluble block appear. Thorough experimental investigations strongly indicate that the domain structure of the films is formed due to the adsorption of the whole micelles from the solution.[11] Depending on the polarity of the substrate, the micelles can directly adsorb onto the surface or their adsorption can be preceded by the adsorption of free chains from the solution, and then micelles are deposited as a second layer on a brush formed by free copolymer chains[12,13] The aggregation number of the adsorbed micelles and their size are shown to correspond to those of micelles in the bulk.[11] It should be mentioned that this surface structure—a hexagonally ordered array of micelles—does not correspond to thermodynamical equilibrium but is obtained by rapid solvent evaporation. Annealing leads to disappearing of the ordered structures which transform into lamellae parallel to the adsorbing surface.[13]

Recently a new way to generate equilibrium surface patterns by means of self-assembly has been reported.[16,17] Heterogeneous, highly ordered structures have been observed in ultrathin films of polystyrene (PS)-block-poly(2-vinyl-pyridine) (P2VP) copolymers which were cast from a nonselective solvent onto a mica surface. It has been found that polar P2VP blocks are strongly adsorbed forming an ultrathin layer on the surface while hydrophobic PS blocks dewet from the PV2P layer and form a kind of surface micelle to minimize the number of unfavorable contacts with polar blocks and the air. For this laterally ordered equilibrium microdomain structure to occur, it is essential that the film thickness is much smaller than the thickness of a complete lamella.

A similar periodic surface micelle structure was observed in a system of diblock copolymers with one hydrophobic block and one polyelectrolyte or polar block adsorbed at the air/water interface.[18] It seems that self-assembly of diblock copolymers into ordered structures in two dimensions is a quite general phenomenon.

In this paper, we describe theoretically the observed micellar structure in the thin layer of adsorbed block copolymers and reveal the main physical factors leading to microphase separation in this system. We investigate the dependence of the parameters of the surface micelles on the block length and the chemical nature of mono-

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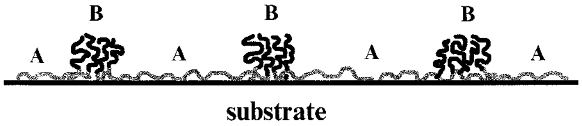

Figure 1. Schematic representation of the layer of adsorbed A−B copolymers.

meric units. In the next section, we describe the model and consider the free energy of the system under consideration. Then we present the results of our calculations followed by their discussion.

2. The Model and the Free Energy of the System

We consider a dry film of A−B block copolymers. A and B chains are assumed to be flexible and contain $N_A \gg 1$ and $N_B \gg 1$ monomer units, respectively. Let a be the size of a monomer unit and let us assume that it is the only microscopic length parameter for A and B chains.

In spite of the fact that pure A and pure B domains may be glassy at room temperature (as in the example of P2VP−PS block copolymers mentioned above), we will consider thermodynamic equilibrium. We assume that the structure corresponding to the equilibrium has been formed in the course of the drying of the film (i.e., elimination of plasticizer).

According to the experimental observations, the degree of adsorption of P2VP blocks on the hydrophilic substrate is rather high so that most of the monomeric units of these blocks are in direct contact with the surface (in the terminology of ref 19 they form “trains”) and the fraction of loops escaping from the surface is very small. For example, X-ray photoelectron spectroscopy shows that every second to third pyridine group is in direct chemical contact with the mica substrate.[17] This fact allows us to use a simplified model of the system. Namely, we suppose that all the monomeric units of A blocks directly lay on the surface, i.e., we consider the A chains as two-dimensional coils. The volume fraction of A monomeric units on the plane is $\Phi = 1$, which corresponds to the case of a two-dimensional melt. On the other hand, B chains occupy the 3D space above the surface. One can say that they are grafted to the surface and form a kind of a brush. The length of the A chains defines the grafting density of B chains, i.e., the larger N_A is, the smaller is the grafting density.

Obviously for nonattractive B units, junction points are distributed homogeneously on the surface. In the case of strong attraction between B units not only monomeric units of single chains will attract each other but also B chains tend to assemble and to form aggregates above the surface. If the adsorbed A chains are longer than B chains, i.e., $N_A > N_B$, one can expect that these aggregates would be B chain surface micelles as it has been observed experimentally in ref 16 (see Figure 1).

We consider the strong segregation limit,[20,21] when B blocks are extremely incompatible with A blocks and the air and investigate the morphology of the B layer and the parameters of the micellar structure which is formed by B chains on the surface.

One should mention that in contrast to the case of an ordinary brush the grafting points or junction points of the two blocks are also mobile, due to the mobility of A blocks on the surface. As will be shown below, this additional degree of freedom together with the strong adsorption of one of the blocks influences the structure of the surface micelles which appears to be strongly different from that of pinned micelles formed by grafted homopolymers in poor solvent and grafted block copolymers.

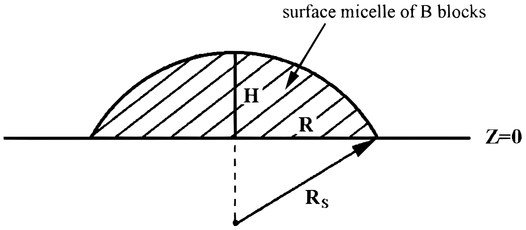

Figure 2. Schematic representation of a surface micelle formed by diblock copolymers on the adsorbing surface $Z = 0$. The micelle is described as part of a sphere with radius R_s. We denote as H and R the height of the micelle and its radius at the surface $Z = 0$, respectively.

We suppose for simplicity that the form of a single micelle can be represented by a part of a sphere as shown in Figure 2. Let us denote the radius of this sphere as R_s and the height and the radius of the micelle (in the plane $Z = 0$) as H and R, respectively. These three parameters are connected through the geometrical relation $R^2 = 2R_sH - H^2$. We assume that the B segments are strongly incompatible with air, so that monomeric units of B blocks are densely packed in micelles and their volume fraction in the aggregates is equal to unity. Thus, the volume of a micelle, V, can be estimated simply as $V = QN_Ba^3$, where Q is the average number of B blocks in one micelle (the aggregation number). On the other hand, the volume V can be expressed in terms of the micelle radius, R, and its height, H: $V = \pi H(H^2 + 3R^2)/6$. Thus, the micellar structure can be well described by two independent parameters. Let us choose for this purpose the radius of a micelle, R, and the micelle height, H.

To determine these parameters let us consider the free energy of a micelle. It can be written as a sum of three terms

$$F = F_{surf} + F_{el}^{A} + F_{el}^{B} \tag{1}$$

where F_{surf} is the surface free energy of the micelle, F_{el}^{A} and F_{el}^{B} are the elastic free energies of A and B blocks.

The surface free energy of the micelle, F_{surf}, has a simple form

$$F_{surf} = \gamma_1 S_1 + \gamma_2 S_2 + \gamma_3 S_3 \tag{2}$$

where the first and the second terms are the free energies of the polymer B/air and polymer A/air interfaces and the last term describes the interfacial free energy of the polymer A/polymer B boundary. The parameters γ_1, γ_2, and γ_3 are the corresponding surface tension coefficients, S_1 is the surface area of the outer part of the micelle (part of sphere)—$S_1 = \pi(R^2 + H^2)$—S_3 is the surface area under the micelle—$S_3 = \pi R^2$—while S_2 is the surface area of the polymer A/air interface: $S_2 = N_AQa^2 - \pi R^2$.

The next term in eq 1, F_{el}^{A}, is the free energy of stretching of A blocks laying on the surface. To calculate this contribution to the free energy we have to know the distribution of junction points on the plane under the micelle (see Figure 3a). Due to the attraction of B blocks, A chains form a kind of a two-dimensional micelle on the surface (it can be also viewed as a two-dimensional star) as is schematically shown in Figure

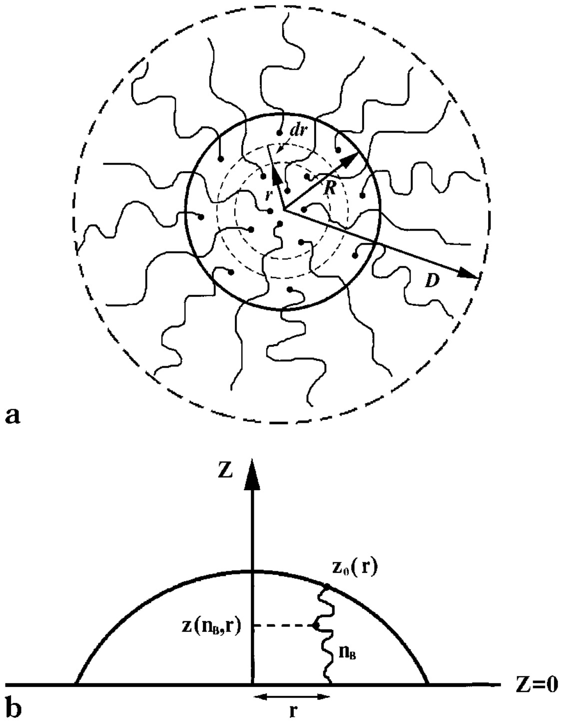

Figure 3. (a) Schematic representation of the adsorbed A blocks in the surface micelle (top view). We denoted as “core” region the circle of the radius R where the junction points of the blocks are located, and as “corona” region the ring $R < r < D$ where A blocks are in contact with the air. (b) Schematic representation of the assumed trajectories of B blocks in the surface micelle.

3a. The core of the micelle is the circular region of radius R where all the A–B junction points are located. The region $r > R$, where A segments are exposed to the air, form the corona of this micelle. One can assume that A chains of the neighboring micelles do not penetrate each other in the scaling sense (arguments in favor of this assumption are given in ref 20). Thus, the outer radius of the corona, D, can be estimated from the space-filling arguments: the surface area per one micelle in the melt is QN_Aa^2, on the other hand it should be on the order of πD^2. Hence, for the radius of the corona, we obtain the scaling estimation $D \sim \sqrt{QN_Aa^2/\pi}$.

Let us denote by $\sigma(r)$ the two-dimensional radial distribution of the junction points on the plane $Z = 0$, where r is the distance from the center of the micelle (see Figure 3a), then $\sigma(r)\,\mathrm{d}r$ is the number of junction points in the ring of radius r of width $\mathrm{d}r$. Then, the grafting density of B chains in the surface micelle, i.e., the surface area per one B chain, is $2\pi r/\sigma$. We suppose that B chains are stretched and form a kind of a brush (Figure 3b). Let us therefore denote as $z_0(r)$ the height of the chains in the brush at the distance r from the center of the micelle (Figure 3b), then, from space-filling conditions, the volume occupied by the chains in the surface micelle at the distance r from the center is

$$2\pi r z_0(r)/\sigma(r) = N_B a^3 \tag{3}$$

Thus, for the radial distribution of the junction points in the core region, i.e., for $r \le R$ we obtain

$$\sigma(\mathrm{r}) = \frac{2\pi \mathrm{r}}{N_B a^3} z_0(r) = \frac{2\pi r}{N_B a^3}\left(\sqrt{R_s^{\,2} - r^2} + H - R_s\right) \tag{4}$$

The total number of chains in the micelle is expressed through $\sigma(r)$ simply as

$$Q = \int_0^R \sigma(r')\,\mathrm{d}r' \tag{5}$$

The A chains are radially stretched. As usual, let us characterize each chain by the contour $\mathbf{r}(n_A)$, where n_A is the number of monomer units of the chain up to the distance r from the center of the micelle. The number of chains with one end point within a circle of radius r is

$$\begin{cases} q(r) = \int_0^r \sigma(r')\,\mathrm{d}r', & r \le R \\ q(r) = Q, & r > R \end{cases} \tag{6}$$

From the space-filling conditions we have

$$\begin{cases} 2\pi r\,\mathrm{d}r = \mathrm{d}n_A a^2 \int_0^r \sigma(r')\,\mathrm{d}r', & r \le R \\ 2\pi r\,\mathrm{d}r = \mathrm{d}n_A a^2 Q, & r > R \end{cases} \tag{7}$$

and, hence, the local elongation of the chains is

$$\begin{cases} \dfrac{\mathrm{d}r}{\mathrm{d}n_A} = \dfrac{a^2}{2\pi r}\displaystyle\int_0^r \sigma(r')\,\mathrm{d}r', & r \le R \\ \dfrac{\mathrm{d}r}{\mathrm{d}n_A} = \dfrac{Qa^2}{2\pi r}, & r > R \end{cases} \tag{8}$$

The free energy of A chains is, therefore,

$$F_{el}^{A} = kT\int_0^D q(r)\left(\frac{\mathrm{d}r}{\mathrm{d}n_A}\right)\frac{\mathrm{d}r}{a^2} \tag{9}$$

In this expression we put D as the upper limit of the integration supposing that all the A chains end approximately at the distance D from the center of the 2D micelle. Of course, in reality the A chain ends are distributed somehow in the layer $[D - \delta D, D]$, and hence the different chains have different local elongations in this layer. However the corresponding contribution is small (chain ends are practically not stretched), and we can use the circle approximation for the Wigner–Seitz cell[20] in our scaling analysis.

The free energy F_{el}^{A} can be represented as a sum of two terms:

$$F_{el}^{A} = (F_{el}^{A})_{in} + (F_{el}^{A})_{out} \tag{10}$$

$$(F_{el}^{A})_{in} = kT\int_0^R q(r)\left(\frac{\mathrm{d}r}{\mathrm{d}n_A}\right)\frac{\mathrm{d}r}{a^2} \tag{11}$$

$$(F_{el}^{A})_{out} = kT\int_R^D q(r)\left(\frac{\mathrm{d}r}{\mathrm{d}n_A}\right)\frac{\mathrm{d}r}{a^2} \tag{12}$$

Here the first term, $(F_{el}^{A})_{in}$, describes the free energy of stretching of A blocks in the core region, i.e., for $r \le R$, while the second term, $(F_{el}^{A})_{out}$, is connected with the chain stretching in the region outside the micelle, i.e., for $r > R$, where A chains are exposed to air.

Substituting here eqs 6, 8, and 4, we obtain

$$(F_{\mathrm{el}}^{\mathrm{A}})_{\mathrm{in}} = \frac{3}{16}kTQ\frac{H^3}{N_{\mathrm{B}}a^3}K(R/H) \tag{13}$$

$$(F_{\mathrm{el}}^{\mathrm{A}})_{\mathrm{out}} = kT\frac{Q^2}{2\pi}\ln(D/R) \tag{14}$$

The expression for the function $K(z)$ is given in the Appendix.

One should mention that the expression for $(F_{\mathrm{el}}^{\mathrm{A}})_{\mathrm{out}}$ has the same form as the one for a two-dimensional star of Q arms if R is the radius of the star core and D is the distance at which the ends of star arms are located.[22]

Let us now calculate the free energy of stretching of B chains in the micelle, $F_{\mathrm{el}}^{\mathrm{B}}$, which can be performed in the same way as for the A chains. Let us consider the chains which start at the distance r from the center of the micelle. Let us denote the average spatial position of B monomer units of these chains separated by n_{B} units from the A−B junction points by $z(n_{\mathrm{B}}, r)$ (see Figure 3b). Then, from the space-filling arguments applied for the chain segment of n_{B} monomer units, we find that the local elongation of B chains is

$$\frac{\mathrm{d}z(n_{\mathrm{B}}, r)}{\mathrm{d}n_{\mathrm{B}}} = \frac{\sigma}{2\pi r}a^3 \tag{15}$$

Therefore, the free energy of stretching of B chains can be written as

$$F_{\mathrm{el}}^{\mathrm{B}} = \frac{kT}{a^2}\int_0^R \mathrm{d}r\,\sigma(r)\int_0^{N_{\mathrm{B}}}\left[\frac{\mathrm{d}z(n_{\mathrm{B}}, r)}{\mathrm{d}n_{\mathrm{B}}}\right]^2 \mathrm{d}n_{\mathrm{B}} \tag{16}$$

Substituting here expression 15, we obtain after intergation

$$\frac{F_{\mathrm{el}}^{\mathrm{B}}}{kT} = \frac{\pi}{4}\frac{H^3}{a^5\,N_{\mathrm{B}}^{\,2}}\left(R^2 + \frac{3}{5}H^2\right) \tag{17}$$

Thus, eqs 1, 2, 10, 13, 14, and 17 define completely the free energy of the surface micelle.

One can show that the contribution to the free energy from the stretching of B blocks in the surface micelle, $F_{\mathrm{el}}^{\mathrm{B}}$, eq 17, is always negligible in comparison with the energy of stretching of A blocks on the surface, $F_{\mathrm{el}}^{\mathrm{A}}$. Indeed,

$$\frac{F_{\mathrm{el}}^{\mathrm{B}}}{F_{\mathrm{el}}^{\mathrm{A}}} \sim \begin{cases} \dfrac{a}{H}, & H \geq R \\ \dfrac{aH}{R^2}, & H \ll R \end{cases} \tag{18}$$

and this ratio is much less than unity for all values of R/H, i.e., $F_{\mathrm{el}}^{\mathrm{B}} \ll F_{\mathrm{el}}^{\mathrm{A}}$. Thus, the total free energy of the micelle is defined only by two factors, the free energy of the interfaces, F_{surf}, and $F_{\mathrm{el}}^{\mathrm{A}}$. The aggregation process is favored by the gain in the surface free energy but is opposed by the stretching of the A blocks on the surface. It is the interplay of these two factors that defines the equilibrium structure of the micelle.

It is convenient to express the total free energy per chain of a micelle as a function of the renormalized height of the micelle

$$h = H/(a\bar{\gamma}_1^{\,1/4}N_{\mathrm{B}}^{\,1/2}) \tag{19}$$

where $\bar{\gamma}_1 = \gamma_1 a^2/kT$, and where $z = R/H$ is the ratio of the radius of the micelle R to its height H. The free energy per chain in these variables has the following form:

$$\frac{F}{k_{\mathrm{B}}TQN_{\mathrm{B}}^{\,1/2}\gamma_1^{\,3/4}} = \frac{6}{h}\frac{1 + z^2(1+\delta)}{1+3z^2} + \frac{3}{64}h^3K(z) + \\ \frac{h^3}{24}(1+3z^2)\ln\left[\frac{t^{1/4}}{2}h\left(1 + \frac{1}{3z^2}\right)\right] \tag{20}$$

The function $K(z)$ is presented in the Appendix. The parameter $\delta = (\gamma_3 - \gamma_2)/\gamma_1$ describes the relationship between surface tension coefficients, i.e., the degree of incompatibility of various components of the system. The dependence on the length of the blocks, N_{A} and N_{B}, appears in the free energy through the dimensionless parameter $t = \bar{\gamma}_1 N_{\mathrm{A}}^4/N_{\mathrm{B}}^2$.

3. Results and Discussion

To obtain the equilibrium values of the parameters describing the micellar structure we have to minimize the free energy per block with respect to the two variables z and h. One can see from expression 20 that, apart from the logarithmic factors, the equilibrium values of h and z, obtained by minimizing the free energy, depend only on the single parameter δ. Thus, taking into account the combination, eq 19, we may conclude that the number of blocks in the micelle as well as the height and the radius of the micelle scale with the length of B blocks as $N_{\mathrm{B}}^{1/2}$. It means that the conformation of B blocks in the surface aggregates is nearly Gaussian.

This result seems to be in agreement with the experimental observations: the estimations of the height of PS clusters by atomic force microscopy shows that PS chains in micelles remain practically unperturbed.[16,17] On the other hand, this conclusion differs essentially from that found for the usual case of three-dimensional micelles in block-copolymer melts. In this case, it is known[20,21] that the radius of the micelles in the bulk scale like $R \sim N_{\mathrm{B}}^{2/3}$, and hence the blocks forming the core of the micelles are rather stretched. In the case under consideration, due to additional degrees of freedom, the chains can arrange in such a way that they minimize the energy of stretching of B blocks.

The decrease of the dimensions of the micelle on the surface in comparison with micelles in the bulk is connected with the strong stretching of the adsorbed chains. In fact, the average distance $2D$ between neighboring aggregates (which is connected with the size of adsorbed A blocks in the system under consideration) is $D \sim N_{\mathrm{A}}^{1/2}N_{\mathrm{B}}^{1/4}$ while for a spherical micelle in the bulk (in the case $N_{\mathrm{A}} \gg N_{\mathrm{B}}$) this distance is $D^{\mathrm{sp}} \sim (N_{\mathrm{A}}N_{\mathrm{B}})^{1/3}$, and hence, the stretching for the latter case is smaller. Thus, to compensate for the gain in the surface free energy of the micelle on the surface, one needs a smaller number of chains Q than for the micelle in the bulk, and therefore the core size of the surface

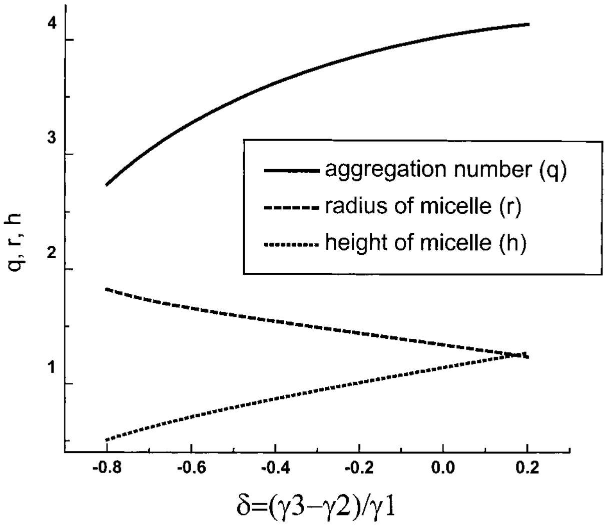

Figure 4. Dependencies of the renormalized aggregation number of the micelle q, its radius, $\bar{r}$, and height, h, on the parameter $\delta = (\gamma_3 - \gamma_2)/\gamma_1$ at $t = 1000$.

micelle $R \sim (QN_B)^{1/3}$ is also smaller. The dependences of D on N_A and N_B is in agreement with experimental results.[16,17] A detailed comparison will be given elsewhere.

As already mentioned in the introduction, surface micelles can also be formed in grafted layers of homopolymers in poor solvents at low grafting densities.[1-6] Since the chains in this case are irreversibly grafted to the surface and cannot move freely on the surface contrary to the case of adsorbed block copolymers, these micelles minimize the surface energy of the collapsed globules at the expense of chain stretching energy; i.e., the chains in micelles are very stretched. The aggregation number of these micelles, their radius and the periodicity of the micellar structure depend on the grafting density ρ and on the chains length N as $N^{4/5}(\rho a^2)^{3/5}$, $aN^{3/5}(\rho a^2)^{1/5}$, and $aN^{2/5}(\rho a^2)^{-1/5}$, respectively.[1] This behavior is fundamentally different from that of the system under consideration. In our case, the grafting density is defined by the length of the adsorbed block, $\rho = 1/(N_A a^2)$ but the aggregation number and the radius of the micelles practically (apart from a logarithmic factor) do not depend on ρ. The number of chains in the micelle formed by adsorbed symmetrical diblock copolymers with $N_A = N_B = N$ is $Q \sim N^{1/2}$ while for layers of grafted chains with grafting density $\rho a^2 \sim N^{-1}$ the aggregation number of micelles would be $\sim N^{1/5}$ which is much less than for the former case.

The minimization of the free energy in eq 20 leads to a system of two equations which was solved numerically. The results are presented in Figure 4. Here we plot as a function of δ the renormalized aggregation number of the micelle, $q = Q/(N_B^{1/2}\bar{\gamma}_1^{3/4})$, its radius, $\bar{r} = R/(aN_B^{1/2}\bar{\gamma}_1^{1/4})$, and the height, $h = H/(aN_B^{1/2}\bar{\gamma}_1^{1/4})$, at fixed value of $t = 1000$, i.e., at a fixed length of the blocks.

It is worth noting that according to Young's law the parameter δ defines the contact angle θ of the spherical cap of B chains with the surface, i.e. $\cos\theta = (\gamma_2 - \gamma_3)/\gamma_1 = -\delta$. It has been mentioned above that in the experimental situation[16,17] the adsorbed A blocks are chains of P2VP while the surface micelles are formed by PS. The surface tension coefficient of P2VP with the air is higher than that of P2VP with PS; this means that $\gamma_2 > \gamma_3$ and hence the value of δ is negative. Therefore the contact angle is $\theta < 90°$ and PS clusters partially wet the surface covered by P2VP blocks.

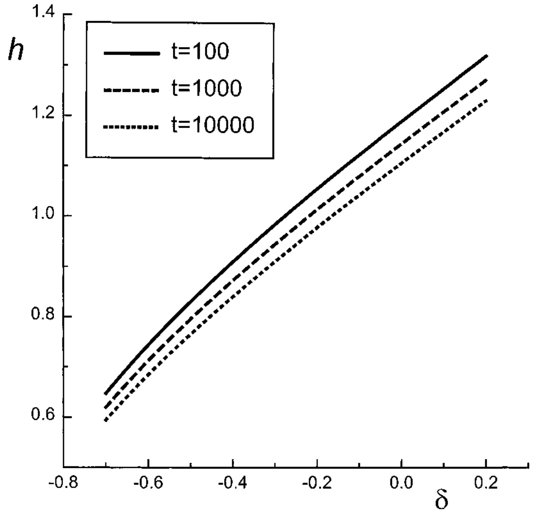

Figure 5. Renormalized height of the micelle h, as function of δ for various values of t.

Figure 4 shows that the increase of δ leads to a change in the form of the micelle: the height of the micelle grows while its radius decreases; i.e, the value of θ increases. At $\delta = 0$ (that means that $\gamma_2 = \gamma_3$) the values of R and H are practically equal, so that the form of the micelle is close to a half-sphere in accordance with Young's law. Simultaneously, with the increase of δ the aggregation number of the micelle, q, also increases slightly since in the case of larger aggregates the total number of contacts between A and B monomeric units decreases. This tendency is prevented by the stretching of A blocks in larger aggregates; therefore different micelles do not coalesce.

At $\delta = 0$, i.e., when the compatibility of A blocks with the air is the same as with B blocks the parameters of the micelles depends on the value of $\bar{\gamma}_1$ which describes the surface energy of the B chains/air interface. One can see from the expression for the free energy, eq 20, and eq 19 that micelle parameters depend on $\bar{\gamma}_1$ as $H \sim R \sim \bar{\gamma}_1^{1/4}$, $Q \sim \bar{\gamma}_1^{3/4}$. It means that the volume of the micelle, i.e., its aggregation number, grows with the increase of $\bar{\gamma}_1$ since the system tends to minimize its surface free energy by increasing the number of chains in one micelle. At the same time the form of micelles does not change in this case; $H \sim R \sim \bar{\gamma}_1^{1/4}$.

In Figure 5 we present the dependence of h on δ for different values of the parameter $t = \bar{\gamma}_1 N_A^4/N_B^2$. One can see that these curves lay very close to each other in a wide range of t. Therefore, we can indeed neglect the weak logarithmic dependence of the micellar structure on t.

One should mention that our results can be extended to the case that the compatibility of B monomer units with the air is improved. This is achieved using the blob concept.[23,24] Let us suppose for simplicity that $\gamma_1 = \gamma_3 = \gamma$. The surface micelle can be viewed as a spherical cap densely filled by thermal blobs. The size of the blob is $\xi \sim a/\tau$, where τ is the relative temperature deviation from the θ conditions for B monomer units, $\tau = (\theta - T)/T$. Inside each blob the polymer conformation is ideal and the number of monomer units in the blob is $n \sim \xi^2 \sim 1/\tau^2$. Thus, the number of blobs in one B chain is equal to $N_B\tau^2$. The surface tension γ at the polymer B/air and polymer B/polymer A interfaces can be estimated as γ

$\sim kT/\xi^2$. The B polymer chains can be considered as chains of blobs and the results for this case can be obtained by the substitutions $N_B \rightarrow N_B\tau^2$ and $a \rightarrow a\tau$.

When the length of the adsorbed blocks is much larger than that of nonadsorbed blocks, at some small value of the ratio N_B/N_A the concentration of the blocks on the surface is very small and it may become more favorable for B chains to form single globules rather than aggregate into micelles. One can estimate the critical value of N_B/N_A from the following simple scaling arguments. If the chains do not aggregate, the main contributions to the free energy of the system, F_I, are the energies of the independent translational motion of the chains on the plane $Z = 0$, F_0, and the surface free energies, F_{surf}, of individual globules. The first contribution has a simple form

$$F_0 = kTn \ln(n/S) \qquad (21)$$

where n is the number of chains in the system and S is the surface area of the system. Since $S = nN_Aa^2$ we obtain

$$F_0 = kTn \ln(1/N_Aa^2) \qquad (22)$$

For simplicity, let us assume that $\gamma_2 = \gamma_3$ and let us consider the globules to be semispheres of radius $N_B^{1/3}a$. Then the surface free energy can be estimated as follows:

$$F_{surf} \sim nN_B^{2/3}\gamma_1 a^2 \qquad (23)$$

In the case that B chains do not aggregate, we obtain for the free energy per chain

$$\frac{F_I}{kTn} \sim \ln(1/N_Aa^2) + N_B^{2/3}\bar{\gamma}_1 \qquad (24)$$

To find out whether micelles are formed in a system or not we have to compare the free energy F_I with the free energy of a chain in the micellar aggregates, eq 20.

Let us consider the case of $\delta = 0$, i.e., $z \approx 1$; we find that the minimum of free energy in (20) is reached at $h \sim 1/(\ln t)^{1/4}$, $t = \bar{\gamma}_1 N_A^4/N_B^2 \gg 1$ and the free energy has the following form

$$\frac{F}{kTQ} \sim (N_B)^{1/2}\bar{\gamma}_1^{3/4}(\ln t)^{1/4} \qquad (25)$$

To estimate the critical value $(N_A)_c$, such that for $N_A > (N_A)_c$ a single B globule is formed, we have also to take into account the energy $kTQ \ln(Q/R^2)$ of the translational motion of the chains in the micelles. Finally, for an estimation of $(N_A)_c$ we have

$$\ln(1/N_A) + N_B^{2/3}\bar{\gamma}_1 \sim (N_B)^{1/2}\bar{\gamma}_1^{3/4}(\ln t)^{1/4} + \ln(\bar{\gamma}_1^{1/4}/N_B^{1/2}) \qquad (26)$$

or

$$(N_A)_c \sim N_B^{1/2}/\bar{\gamma}_1^{1/4} \exp(\bar{\gamma}_1 N_B^{2/3}) \qquad (27)$$

Thus, the critical value $(N_A)_c$ of the length of A blocks, above which single B globules are formed, grows exponentially with the increasing length of B blocks and with the incompatibility of B blocks with the air, i.e., the surface tension coefficient γ_1.

The other limit for micelle formation is realized when the radius of the micelles becomes comparable with the distance between micelles (it takes place when the length of the adsorbed blocks is smaller than the length of non-adsorbed blocks). In this case the micellar structure may become unfavourable and might be transformed into lamellar structures of patches of B blocks. This situation will be described in a forthcoming publication.

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Appendix

The function $K(z)$ in the expression for the free energy of stretching of A blocks under the micelle (see eq 13) is expressed as follows:

$$K(z) = \frac{(1 + z^2)^6}{1 + 3z^2}(I(y) - I(0)) \qquad (28)$$

Here the function $I(z)$ is

$$I(y) = \frac{8}{9}\ln(1 + \sqrt{1 - y^2}) - \frac{2}{3}y^2 + \frac{y^4}{3} - \frac{2}{27}y^6 - \frac{8}{27}(1 - y^2)^{3/2} - \frac{8}{9}\sqrt{1 - y^2} + l\left(l\frac{y^4}{4} + \frac{2}{3}y^2 + \frac{4}{15}(1 - y^2)^{5/2}\right)$$

where $y = 2z/(1 + z^2)$ and $l = (1 - z^2)/(1 + z^2)$.

The asymptotic behavior of the function $K(z)$ is as follows

$$K(z) = \begin{cases} \frac{22}{9}z^2, & z \gg 1 \\ 16z^4, & z \ll 1 \end{cases} \qquad (29)$$

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