Macromolecules 1991, *24*, 6803–6805

Bending Moduli and Stability of Copolymer Bilayers

Amphiphilic molecules in solution spontaneously assemble and exhibit a rich variety of structures including small aggregates such as spherical and wormlike micelles, bicontinuous disordered spongelike phases, and lyotropic liquid-crystalline phases (e.g., lamellar, hexagonal, cubic).[1] In this paper we consider the polymeric analogue of such systems: solutions of diblock copolymers A–B, i.e., chains containing a sequence of N_A monomers A chemically linked to a sequence of N_B monomers B, mixed with a homopolymer B. Indeed, many structures similar to those found in small surfactant systems have already been reported.[2,3] From a theoretical point of view, macromolecular systems are of particular interest, since at the molecular level configurational entropic effects control self-assembling of chains and make possible a statistical description, with no need for a detailed model of microscopic interactions.[4] It is then possible to evaluate phenomenological parameters such as bending moduli or spontaneous radii of curvature of monolayers, which are basic ingredients of theories of surfactant phase behavior.[4–8]

The formation of copolymer micelles diluted at a homopolymer matrix seems to be rather successfully described by theoretical models. It is much more difficult to predict nonspherical shapes and the onset of ordered mesophases in terms of the molecular parameters such as copolymer and homopolymer polymerization indexes, copolymer composition $f = N_A/(N_A + N_B)$, and Flory parameter χ characterizing effective interactions between unlike monomers. Here, we will deal with the strong segregation limit where the A/B interfaces are narrow, and we focus on the case of relatively long homopolymers B, which are thus excluded from both inner (A) and outer (B) parts of the aggregates.

The situation seems to be clear when the copolymer is asymmetric with a small A block ($f < 0.5$). The organization is controlled by the competition between the tendency to decrease the interfacial area of A–B contacts and the necessity to keep the overall density constant in the aggregate, which implies stretching of the chains. As a result the A/B interfaces tend to curve so that the short A block is located on the inside. Hence, as the copolymer symmetry increases, one expects less curved shapes to occur, namely, cylindrical aggregates and eventually bilayers (lamellarlike aggregates) for nearly symmetric copolymers.[9]

An interesting question arises as to what happens when the A block is longer than the B one ($f > 0.5$). In this case, the system is "frustrated" as decreasing A/B contacts by formation of copolymer aggregates with A cores implies "unnatural" curvature of A/B interfaces and thus high deformation energy penalties. In a small range of copolymer asymmetry, $f \gtrsim 0.5$, this frustration is limited and should lead to aggregation in flat bilayers.[6] However, we find that, for intermediate asymmetry, i.e., for compositions f larger than a critical value f^*, saddle-splay deformation of the lamellas becomes energetically favorable. This indicates that for carefully chosen copolymer architecture interesting swollen bicontinuous phases may occur. These phases may be analogous to so-called "plumber's nightmare" cubic phases observed in classical surfactant systems.[1,10–12]

Let us briefly describe the formation of aggregates made of a bilayer (e.g., vesicles, cigars, tubules, lamellas, ...). In such structures the B blocks are in contact with the B homopolymers and protect the A blocks from an unfavorable environment. Consider an aggregate of a given shape and size. We call Q_1 and Q_2 the number of copolymer chains on the two sides of the bilayer. The free energy of the aggregate $F(Q_1,Q_2)$ can be written as a sum of two main contributions: A/B interfacial energy and chain deformation energy. Moreover, it is useful to consider the grand potential of the aggregate, $\Omega = F - \mu(Q_1 + Q_2)$, with μ being the chemical potential of the chains dispersed in the homopolymer. The grand potential Ω becomes a function of μ only, as we impose the equilibrium of the chains of the two sides of the bilayer with the dispersed ones:

$$\partial\Omega/\partial Q_1 = \partial\Omega/\partial Q_2 = 0 \qquad (1)$$

When the copolymer is added progressively to the homopolymer, the chemical potential rises. Our aggregate will form when μ reaches the critical value μ_c defined by $\Omega(\mu_c) = 0$. It is then clear that the kind of aggregate that appears first is the one for which μ_c has the lowest value. It is also the most stable one in the sense that it allows the smallest free energy per chain. A similar procedure has been used to predict the ranges of asymmetry f for which spherical and cylindrical micelles are obtained (such aggregates are not made of a bilayer and there is only one parameter Q).[6,9,13]

The critical value μ_0 at which flat bilayers appear can be evaluated with an Alexander–de Gennes type description of the deformation energy and appears to be independent of f[6,8]

$$\mu_0 \simeq (3^{4/3}/2)(\Gamma^2 N)^{1/3} \qquad (2)$$

where Γ is the A/B interfacial tension. For the sake of simplicity we take both the statistical length and the monomer size to be equal to 1 and write all energies in kT units. In the more elaborated self-consistent model of Semenov,[14] one gets a slightly modified prefactor $3\pi^{2/3}/2^{5/3}$ rather than $3^{4/3}/2$.

It is interesting to note that when an aggregate appears, the free energy of any of its chains is μ_c. Then, a simple ad absurdum argument allows us to show that vesicles or tubules built out of a bilayer are unstable, i.e., that flat lamellas always form at lower chemical potential than vesicles and tubules. Suppose, for a moment, that a vesicle appears at $\mu_c < \mu_0$, for example, in the case of $f > 0.5$. Then, the free energy of each of the chains in the vesicle would be equal to μ_c and thus smaller than μ_0. Consider now the outer surface of the vesicle. It is curved the wrong way from the point of view of the chain asymmetry. This implies that the free energy per copolymer chain in the outer layer is lower than that in a hypothetical flat bilayer structure which would have the same surface density of joints at the A/B interface. Indeed, in the latter structure the interfacial energy would be the same, but the chains would be less deformed. Since the energies per copolymer in the outer and inner layers of the vesicle are both equal to μ_c, we conclude that the hypothetical flat bilayer with surface density equal to that of the outer layer of the vesicle would form at a chemical potential μ smaller than μ_c and thus smaller than μ_0. This is in contradiction with the definition of μ_0. Thus, a vesicle cannot appear below μ_0.

The above argument can of course be extended to the case of $f < 0.5$ by considering the chains of the inner monolayer rather than the outer one. Moreover, it holds for any bilayer shape such that at one of its points the two principal curvatures are of the same sign. However, it must be stressed that we did take into account neither the translational entropy of the aggregates nor the energy losses

0024-9297/91/2224-6803$02.50/0

at the boundaries of lamellas. These effects may be responsible for the formation of very large vesicles, but with no preferential size.

It is anyway necessary to consider other shapes, such as, for example, those obtained by saddle-splay deformation of flat lamellas. Locally, for a general deformation characterized by principal curvatures c_1 and c_2, the grand potential per unit surface (of the monolayer/monolayer contact area) can be written

$$\omega = \phi(\sigma_1,\sigma_2,c_1,c_2) - (\sigma_1 + \sigma_2)\mu \tag{3}$$

where σ_1 and σ_2 are the surface densities of the chains of the two sides and ϕ includes A/B interfacial tension and deformation energy. Using the equivalent of eq 1 allows us to write

$$\omega = \omega(c_1,c_2,\mu) = \omega(0,0,\mu) + \frac{1}{2}K(\mu)\,(c_1 + c_2)^2 + \bar{K}(\mu)\,c_1c_2 \tag{4}$$

where K and $\bar{K}$ are, respectively, the mean and Gaussian bending moduli. They can be most easily calculated by considering separately the cases of a large sphere and a large cylinder.

In these two cases we calculate the deformation energy using the approximation that in the brushes all chains end on the surface. Then we take into account the nonuniformity of the deformation by writing for a chain[6,14]

$$f = \frac{3}{2}\int\left(\frac{\mathrm{d}r}{\mathrm{d}n}\right)^2 \mathrm{d}n \tag{5}$$

together with the incompressibility condition

$$S_\mathrm{d}\,\mathrm{d}r = Q_i\,\mathrm{d}n \tag{6}$$

where Q_i is the number of copolymer chains on the ith side, and S_d is $4\pi r^2$ for a sphere and $2\pi rh$ for a cylinder of length h. This allows us to calculate K and $\bar{K}$ for any value of μ.

To discuss the stability of flat lamellas, it is useful to consider that the chemical potential μ is at the critical value μ_0 and examine whether, for some given deformation, the free energy per chain can be inferior to μ_0. If such is the case, then the deformed aggregate will form before flat lamellas. The stability of flat lamellas depends therefore on the sign of the bending moduli for $\mu = \mu_0$:

$$K(\mu_0) = (8/3^{5/3})f(1-f)N^{4/3}\Gamma^{5/3} \tag{7}$$

$$\bar{K}(\mu_0) = (2/3^{5/3})(3f^2 - 1)N^{4/3}\Gamma_{5/3} \tag{8}$$

Equation 7 shows that K is always positive, which is consistent with our proof of the nonstability of large vesicles. More interestingly, eq 8 shows that, for $f > f^* = 3^{-1/2} \simeq 0.58$, $\bar{K}$ is positive, i.e., flat lamellas are unstable with respect to saddle-splay deformation. Here is an important difference with the case of monolayers, for which the saddle-splay (Gaussian) bending modulus is always negative and favors principal curvatures of the same sign.[7]

The above calculation can be modified to include a distribution of chain ends as in ref 7. One gets

$$K(\mu_0) = 3(2/\pi^4)^{1/3}f(1-f)N^{4/3}\Gamma^{5/3} \tag{9}$$

$$\bar{K}(\mu_0) = (1/5)(2/\pi^4)^{1/3}(18f^2 - 3f - 4)N^{4/3}\Gamma^{5/3} \tag{10}$$

The picture is the same apart from modification of the numerical factors and a slight shift of f^* to a smaller value $f^* \simeq 0.56$.

It is easy to see qualitatively why such an instability with respect to a saddle-splay deformation occurs for asymmetric chains. Indeed, we already remarked that for $f > 0.5$ monolayers prefer to curve so that the shorter B blocks are at the inner (convex) side. In a bilayer this preference can be partially satisfied in a saddle-splay deformation: monolayers are curved favorably in one plane and unfavorably in the perpendicular one. The overall gain may come from the fact that the favorable curvature can be larger than the unfavorable one. For large asymmetry, flat lamellas are therefore unstable. However, for small asymmetry, saddle-splay deformation imposes an overall deformation of chains which cannot be compensated by the curvature gain. This is why the threshold value f^* is larger than 0.5.

A quantitative evaluation of the threshold can be done along the lines proposed for small surfactants using the concept of bending moduli and spontaneous curvature of the monolayers.[15,16] For a saddle-splay deformation with zero mean curvature ($c_1 = -c_2 = c$) the two monolayers are equivalent and in particular the interfacial density $\sigma_1 = \sigma_2 = \sigma$. Then, the energy variation due to this deformation with respect to a flat bilayer is

$$\Delta\omega \simeq -2c^2(2\sigma c_0\kappa_\mathrm{m}N + \bar{\kappa}_\mathrm{m}) \tag{11}$$

with c_0, κ_m, and $\bar{\kappa}_\mathrm{m}$ being, respectively, spontaneous curvature and bending moduli of the monolayer. Since the saddle-splay modulus of a monolayer is always negative, the deformation becomes favorable ($\Delta\omega < 0$) only when c_0, which is proportional to the asymmetry $f - 0.5$ of the chains, is large enough. By putting the values calculated in the different models of copolymer monolayers, one recovers indeed the values of the threshold f^* quoted above.

In conclusion, we argued that, for very symmetric copolymer chains dissolved in a long homopolymer, flat bilayers should be the most stable form of aggregation. For more asymmetric chains with $f > f^*$ we expect a phase behavior similar to that proposed for small surfactants.[1,17] In particular, periodic "plumber's nightmare" bicontinuous phases may appear for composition of copolymer f larger but close to $f^* \simeq 0.56$. At equilibrium, these phases are more likely to be observed than, for example, disordered spongelike phases because of the high values of bending moduli K and $\bar{K}$.[18] The copolymer compositions for which such an ordered bicontinuous phase might be formed should be limited, since for more asymmetric chains a demixing to an almost pure copolymer phase (with favorably curved structures) should occur. Indeed, for very asymmetric chains, the chemical potential at which demixing is expected for chains with composition f is close to the value of the critical chemical potential of aggregation of chains of composition $1 - f$, which is smaller than μ_0.

The consideration presented here can be extended to take into account an asymmetry of rigidity between A and B blocks. It is also interesting to discuss the case of solutions in a selective solvent or in a shorter homopolymer. In these situations the copolymer concentration should become a relevant control parameter, and it should be easier to observe these intriguing swollen bicontinuous phases.[19]

Acknowledgment. We are deeply indebted to J. Prost for his interest in this project and enlightening suggestions. We thank G. H. Fredrickson, A. C. Maggs, C. Ligoure, G. Porte, P. Pincus, T. A. Witten, and S. A. Safran for interesting discussions. We are grateful to ATOCHEM for financial support.

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Received July 30, 1991
Revised Manuscript Received September 25, 1991