Self-Assembly in Mixtures of Diblock Copolymers

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ABSTRACT: A self-consistent field model is used to study the effect of mixing on self-assembled diblock copolymer monolayers and bilayers, in the strong segregation limit. The mixtures contain chains of identical chemistry but different molecular weights or asymmetries. The interactions between such chains are shown to be attractive, so that segregation is unfavorable. The equilibrium curvature and surface density of the monolayer vary nonlinearly with mixture composition, due to interactions between the components. In bilayers, the spontaneous curvature energy promotes demixing, i.e., nonuniform distribution of the components between the two monolayers composing the bilayer. While a homogeneously mixed system adopts a lamellar configuration, in the demixed bilayer equilibrium vesicles are favorable. The stability boundaries of the lamellar, vesicular, and saddle-shaped phases are calculated as a function of chain characteristics and mixture composition.

(I) Introduction

The amphiphilic nature of block copolymers is manifested in self-assembly phenomena, either in bulk or in the presence of selective media. The inherent incompatibility between most long-chain polymers induces microphase separation between the blocks, thereby forming an interface between the different components. Aggregates are characterized by interfacial properties: the surface density (number of chains per area) and the geometry and magnitude of the interface curvature. Of special technological interest are self-assembled copolymer monolayers as stabilizers of homopolymer blends[1,2] and equilibrium vesicles for encapsulation.[3-5] Successful utilization of these materials necessitates, therefore, accurate control of interfacial properties.

Monodisperse diblock copolymer monolayers and bilayers have been widely investigated.[1-9] Theoretical models[6-9] predict that the surface density decreases with overall chain molecular weight (so that the number of aggregates per unit volume should increase) while the interfacial curvature increases with the molecular weight ratio of the two blocks. Manipulation of domain properties is, therefore, possible through adjustments in the overall chain molecular weight or asymmetry. However, this method of control requires synthesis of various copolymer chains, which is a complicated and expensive process, and is therefore impractical.

Mixing copolymers could provide a way of tailoring microdomain properties through simple composition variations; new structures may thus be obtained by changing the system composition, rather than through synthesis of new copolymers. Moreover, the phase diagrams of mixed surfactants have been shown to be distinctly different from those of single component systems;[10] while single surfactants are not known to form thermodynamically stable vesicles, an equilibrium vesicle phase spontaneously appears in mixtures of oppositely charged surfactants.[10]

The appearance of equilibrium vesicles in mixtures is explained by the relationship between monolayer composition (molar fraction of each surfactant) and spontaneous curvature.[11-13] In single component or homogeneously mixed bilayers, the compositions of the two monolayers constituting the bilayer, and hence, their spontaneous curvatures, are identical. The bilayer adopts a flat configuration where both monolayers are equally frustrated with respect to their preferred curvature. Demixing can relieve this frustration by modifying the spontaneous curvature[14,15] of each monolayer, so that a curved bilayer becomes energetically favorable. Such phenomena are likely to occur also in mixtures of diblock copolymers. Unfortunately, the analysis of surfactant interfaces is based on a delicate balance between phenomenological parameters (namely, the spontaneous curvature and bending moduli) which are difficult to estimate directly. Mixed copolymer interfaces, on the other hand, can be quantitatively characterized.[16-18]

In this paper we investigate the effect of mixing on the properties of self-assembled diblock copolymer monolayers and bilayers. Since the strong incompatibility between most long-chain polymers[1] usually leads to complete segregation, we investigate mixtures of copolymers with identical chemistries, but of different molecular weights, or asymmetries (ratio of the two blocks molecular weight). Such mixtures are supposed to have no inherent chemical tendency to segregate.[17] We use the analogy between block copolymer interfaces in the strong segregation limit and polymeric "brushes",[16-18] i.e., chains that are irreversibly anchored by one end to an impenetrable surface, to calculate the properties of the mixed diblock interface. The outline of the paper is as follows: In section II the properties of mixed copolymer monolayers are calculated as a function of mixture composition and component structure. We find that there are specific interactions between chains of different asymmetries or overall molecular weights. These interactions are always attractive. As a result, the properties of the monolayer cannot be inferred from simple mixing rules. In section III we consider mixed bilayers and investigate the equilibrium phases. The attractive interactions between the two components favor homogeneous mixing, and thus, flat bilayers. However, the energetic penalty due to the spontaneous curvature overcomes this mixing energy when the molecular weight difference between the two chains increases, thus inducing formation of equilibrium vesicles. The paper is concluded with a discussion in section IV.

(II) Mixed Monolayers

Polydisperse brushes, i.e., polymer chains grafted by one end to an impenetrable surface, have been studied using a self-consistent field model by Milner and Witten[17]

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and Birshtein et al.[18] The free energy, per chain, of a brush in the melt state grafted onto surfaces of low curvature[14–18] is given by

$$F = \boldsymbol{F}_0 + \frac{1}{2}\mathbf{K}\{c_1 + c_2 - 2c_0\}^2 + \bar{\mathbf{K}}c_1c_2 \equiv \sigma^2\mathrm{f} + \frac{1}{2}\sigma^3 k(c_1 + c_2) + \sigma^4\{\kappa(c_1 + c_2)^2 + \bar{\kappa}c_1c_2\} \quad (1)$$

where **K** and $\bar{\mathbf{K}}$ are, respectively, the mean and Gaussian moduli (per chain), c_0 is the spontaneous curvature,[14,15] and c_1 and c_2 are the dimensionless local curvatures. σ is the dimensionless surface density. All length scales are normalized by the size of a segment, a. The first term, σ^2f, defines the energy of the flat brush and accounts for chain stretching and excluded volume interactions. The second term is proportional to the spontaneous curvature of the brush, c_0; when k is equal to zero, the minimal energy state is that of a flat layer, while a finite value of k indicates an energetic minimum at a finite curvature. The third term accounts for the brush bending stiffness. κ and $\bar{\kappa}$ are proportional, respectively, to the mean (**K**) and Gaussian ($\bar{\mathbf{K}}$) bending moduli. For a mixed brush containing a fraction ϕ of longer chains of molecular weight N_L and a fraction $(1 - \phi)$ of shorter chains of molecular weight N_s (namely, a bimodal brush)[16–18]

$$\mathrm{f}(\phi,\alpha) = \frac{\pi^2}{24}N_s(1 + \alpha\phi^3) \quad (2)$$

$$k(\phi,\alpha) = \frac{\pi^2 N_s^{\,2}}{32}\left\{(1 + \alpha\phi^3)(1 + \alpha\phi) - \frac{1}{2}\alpha(1 - \phi^2)^2 \ln\left[\frac{1 + \phi}{1 - \phi}\right]\right\} \quad (3)$$

$$\kappa(\phi,\alpha) = \frac{\pi^2 N_s^{\,3}}{32}\left\{1 + \alpha\phi^3(1 + \alpha\phi)^2 + \alpha(1 - \phi^2)^2 \times \ln\left[\frac{1 + \phi}{1 - \phi}\right]\left(-(1 + \alpha\phi) + \frac{1}{4}(\alpha + \phi)\ln\left[\frac{1 + \phi}{1 - \phi}\right]\right)\right\} \quad (4)$$

$$\bar{\kappa}(\phi,\alpha) = -\frac{\pi^2 N_s^{\,2}}{60}\{1 - 2\alpha^2 + 5\alpha\phi^2(\alpha + \phi) + \alpha\phi^5(\alpha^2 - 2) + 2\alpha^2(1 - \phi^2)^{5/2}(1 + \phi)^{5/2}\} \quad (5)$$

α is a measure of the molecular weight difference between the two chains, defined as $(N_L - N_s)/N_s$. All energies are given in units of kT, where k is the Boltzmann constant and T the temperature.

Consider now a mixture of two A–B diblock copolymers, with different overall molecular weights and/or asymmetries (ratio of A to B block), in a blend of highly incompatible A and B homopolymers. The solubility of high molecular weight, moderately asymmetric copolymers in either homopolymer is exceedingly low.[1,6,7,9] We can therefore assume that all copolymer chains are localized at the AB interface. In strongly segregated systems such as these, the probability of A to B crossover is negligible. The copolymer junction points are thus confined to a narrow interfacial region, and the two blocks form brush-like regions on either side of the interface[1] (Figure 1). However, in these self-assembled systems the surface density is determined by thermodynamic equilibrium, not fixed a priori as in the grafted brush. For simplicity, we limit our discussion to systems where the molecular weight of the A and B homopolymers is higher than that of any block, and homopolymer interpenetration into the copolymer monolayer is negligible. Solvent-swollen, mixed interfaces may be analyzed in a similar manner, and the results will be qualitatively unchanged (although, due to the different dependence of system parameters on surface density, the phase boundaries will, of course, shift).[6,7,9,16,17]

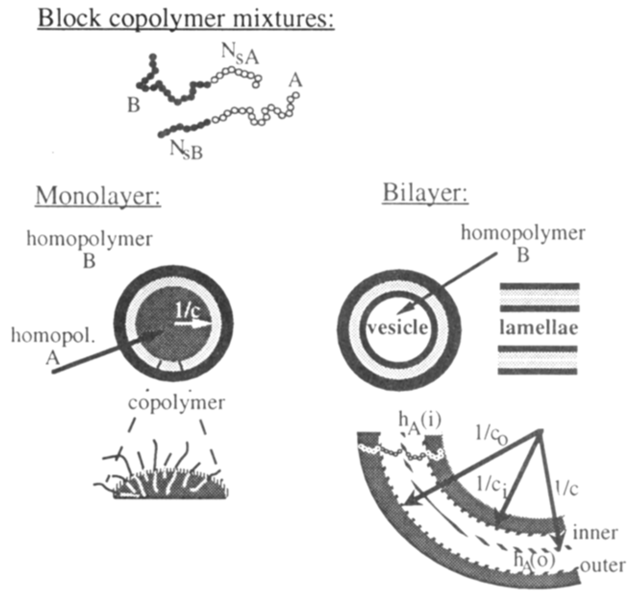

Figure 1. Mixed diblock copolymer monolayer and bilayer. The mixture contains two A–B diblock copolymers of different molecular weights and/or asymmetries. $N_{s,A}$ ($N_{s,B}$) is the molecular weight of the shorter A (B) block. The monolayer curvature is defined at the copolymer junction points, which are restricted to an interfacial region, much narrower than the chain dimension. The bilayer is composed of two, inner and outer, monolayers which are inversely curved. The curvature of the bilayer is defined at the boundary between the two monolayers.

The free energy of a self-assembled diblock copolymer interface can be written as the sum of the mixed A and B brush energies defined in eq 1. We take the center of curvature at the AB interface, so that the curvatures of the B block brush have signs opposite to those of the A brush), with an added contribution for the interfacial energy[19]

$$F_M = F_A(c_1,c_2) + F_B(-c_1,-c_2) + \gamma/\sigma \equiv \sigma^2(\mathrm{f}_A + \mathrm{f}_B) + \frac{1}{2}\sigma^3(c_1 + c_2)(k_A - k_B) + \sigma^4[(c_1 + c_2)^2(\kappa_A + \kappa_B) + c_1c_2(\bar{\kappa}_A + \bar{\kappa}_B)] + \gamma/\sigma \quad (6)$$

where γ is the dimensionless AB surface tension, in units of kT. f_J, k_J, κ_J, and $\bar{\kappa}_J$ are as defined in eqs 2–5 for $N_s = N_{sJ}$, $\alpha = \alpha_J$, and $\phi = \phi_J$ (J = A, B). Note that, since ϕ_J denotes the fraction of *longer* J blocks in the J brush, two scenarios are possible: one, where the same chain contains both the longer A block and the longer B block, so that $\phi_A = \phi_B$. In the other case, one chain contains the longer A block, while the other contains the longer B block, so that $\phi_A = 1 - \phi_B$.

Assuming that all copolymer chains are localized at the interface, ϕ_J is controlled by the experimentally imposed composition of the mixture. However, both the surface density and the interface curvature are free to vary and are determined by minimization of the self-assembled interface energy, F_M. The equilibrium surface density is set, to first order, by a balance between the interfacial energy (which decreases linearly with σ) and the flat layer energy (which increases with σ). The equilibrium interface curvature is a result of the balance between the spontaneous curvature and the bending stiffness. For a spherically deformed interface (where $c_1 = c_2 = c$) we find, at equilibrium

$$\sigma^* = \sigma_0\left\{1 + \frac{\delta k^2}{4\kappa f}\right\} \qquad (7.A)$$

$$c^* = -\frac{\delta k}{2\kappa\sigma_0}\left\{1 - \frac{\delta k^2}{4\kappa f}\right\} \qquad (7.B)$$

$$F^*_M = 3\sigma_0^2 f\left\{1 - \frac{\delta k^2}{12f\kappa} + \frac{\delta k^4}{16f^2\kappa^2}\right\} \qquad (7.C)$$

where $f = f_A + f_B$ and σ_0 is equal to $\{\gamma/2f\}^{1/3}$. The spontaneous curvature contribution of the A/B interface is proportional to $\delta k = (k_A - k_B)$, and the overall bending stiffness is given by $\kappa = (2\kappa_A + \bar{\kappa}_A) + (2\kappa_B + \bar{\kappa}_B)$. Note that, since the equilibrium interface curvature is proportional to δk a flat lamellar monolayer is stable only when $\delta k = 0$, in which case $\sigma = \sigma_0$.

For purposes of illustration, we examine three representative mixtures: (i) The molecular weight of one block is equal in both chains, so that $\alpha_A = 0$. (ii) The two chains have the same overall molecular weight but different asymmetries, so that ($N_{sA} = N_{sB}\alpha_B/\alpha_A$) and $\phi_A = 1 - \phi_B$. (iii) The two chains have the same asymmetry (N_A/N_B) but different overall molecular weights, so that $\alpha_A = \alpha_B$ and $\phi_A = \phi_B$.

We first examine the free energy of the mixed interface as a function of composition. F^*_M is shown, in Figure 2, to be a simple concave function of the solution composition, with no inflection points for all three cases. We find that this is the case for many sets of parameters. A mixed interface is, therefore, preferable to a segregated one, indicating thereby an effective attraction between the two components. Since F^*_M does not include an entropic mixing term,[20] this attraction is solely due to chain–chain interactions; the shorter blocks are nearly unperturbed by incorporation of some longer chains into the monolayer. However, the stretching energy of the longer chains is significantly reduced by the presence of shorter chains, since they act at "spacers" (see Figure 1). The interactions between long and short blocks are thus attractive.

The surface density is directly related to the total surface area in the system; for a given copolymer concentration, the overall interface area is inversely proportional to σ. Thus, σ defines the emulsification efficiency of the copolymer. The effects of mixing on the equilibrium surface density in cases i and iii are similar (Figure 2). The addition of a small fraction of longer chains ($\phi \ll 1$) does not perturb the shorter-chain monolayer and, hence, does not change the surface density significantly. However, the addition of a small fraction of shorter chains ($\phi \sim 1$) to the longer-chain monolayer relaxes the stretching energy and allows dense packing of chains at the interface. In case ii, where the two chains have the same overall molecular weight but different asymmetries, the effect of mixing on the surface density is nonmonotonic and σ^* obtains a maximum at a finite composition.

The size of microemulsion droplets in the system is inversely proportional to the equilibrium curvature. The interface curvature in case i follows the same trends as the surface density; it is nearly constant in the limit of a small fraction of longer chains, $\phi \ll 1$, and varies linearly with concentration when $\phi \approx 1$. In case iii, where the two chains have the same asymmetry but different molecular weights, interface curvature is unaffected by the addition of a small fraction of either short or long chains. Note that although the asymmetries of the chains are the same, the equilibrium curvatures of the purely long and purely short monolayers are not identical. This is due to the nonlinear dependence of k on N_s. In case ii, however, we find that mixing a low fraction of chains of low spontaneous curvature with chains of high spontaneous curvature *increases* the curvature of the mixed monolayer ($\phi \ll 1$), while mixing a small fraction of chains of high δk with chains of lower asymmetry *decreases* the monolayer curvature.[21] An experiment where the size of equilibrium droplets is measured, as a function of the composition of the copolymer mixture, should be able to examine these predictions.

The free energy of a cylindrical monolayer can be calculated by minimization of eq 6 where $c_1 = c$ and $c_2 = 0$. We find that the expressions for the equilibrium curvature and surface density are given by eqs 7.A and 7.B, when replacing δk by $\delta k/2$ and κ by ($\kappa_A + \kappa_B$). As in single component monolayers,[6,7,9] if there are no constraints on the volume of the microemulsion phase, the free energy of noninteracting spherical monolayers is always lower than that of cylindrical ones. Equilibrium cylinders are therefore unlikely to form in dilute copolymer solutions.

(III) Mixed Bilayers

In a single selective solvent, such as a B homopolymer, copolymers of high asymmetry assemble into micelles, while those of moderate asymmetry form bilayers.[1,3,4] The bilayer is composed of two adjacent monolayers, defined as "inner" and "outer" (see Figure 1). The A block in both monolayers faces the interior, thereby minimizing unfavorable interactions with the B solvent, while the B block forms the bilayer exterior (corona). The bilayer energy, per chain, is written as

$$F_B = x_i F_i + x_o F_o \qquad (8)$$

where x defines the fraction of chains in a monolayer, and the substript i (o) refers to the inner (outer) monolayer. F_j is the free energy of a chain in monolayer j, as given by eq (6). In a spherically deformed bilayer, the fraction of chains in each monolayer is given by

$$x_j = \frac{\sigma_j/c_j^2}{\sigma_i/c_i^2 + \sigma_o c_o^2} \qquad (9)$$

c_j is the curvature, and σ_j the surface density, of monolayer j. These quantities are defined at the A/B interface of each monolayer. The curvatures of the two monolayers are related to the midpoint bilayer curvature, c (see Figure 1), through simple geometry. Since the thickness of the A core region of monolayer j, h_{Aj}, is equal (to zeroth order in curvature) to $\sigma_j N_{s,A}(1 + \alpha_A)$

$$c_i = -c\{1 + ch_{i,A}\} \approx -c\{1 + c\sigma_i N_{sA}(1 + \alpha_A)\} \qquad (10.A)$$

$$c_o = c\{1 - ch_{o,A}\} \approx c\{1 - c\sigma_i N_{sA}(1 + \alpha_A)\} \qquad (10.B)$$

to leading order in c.

The composition of the bilayer is determined by the overall solution composition, assuming low copolymer solubility in the B homopolymer. However, the distribution of the two types of chains between the monolayers may not be equal.[11,12] The overall bilayer composition is conserved by the simple constraints

$$\psi_A = \phi_{i,A}x_i + \phi_{o,A}x_o \qquad (11.A)$$

$$\psi_B = \phi_{i,B}x_i + \phi_{o,B}x_o \qquad (11.B)$$

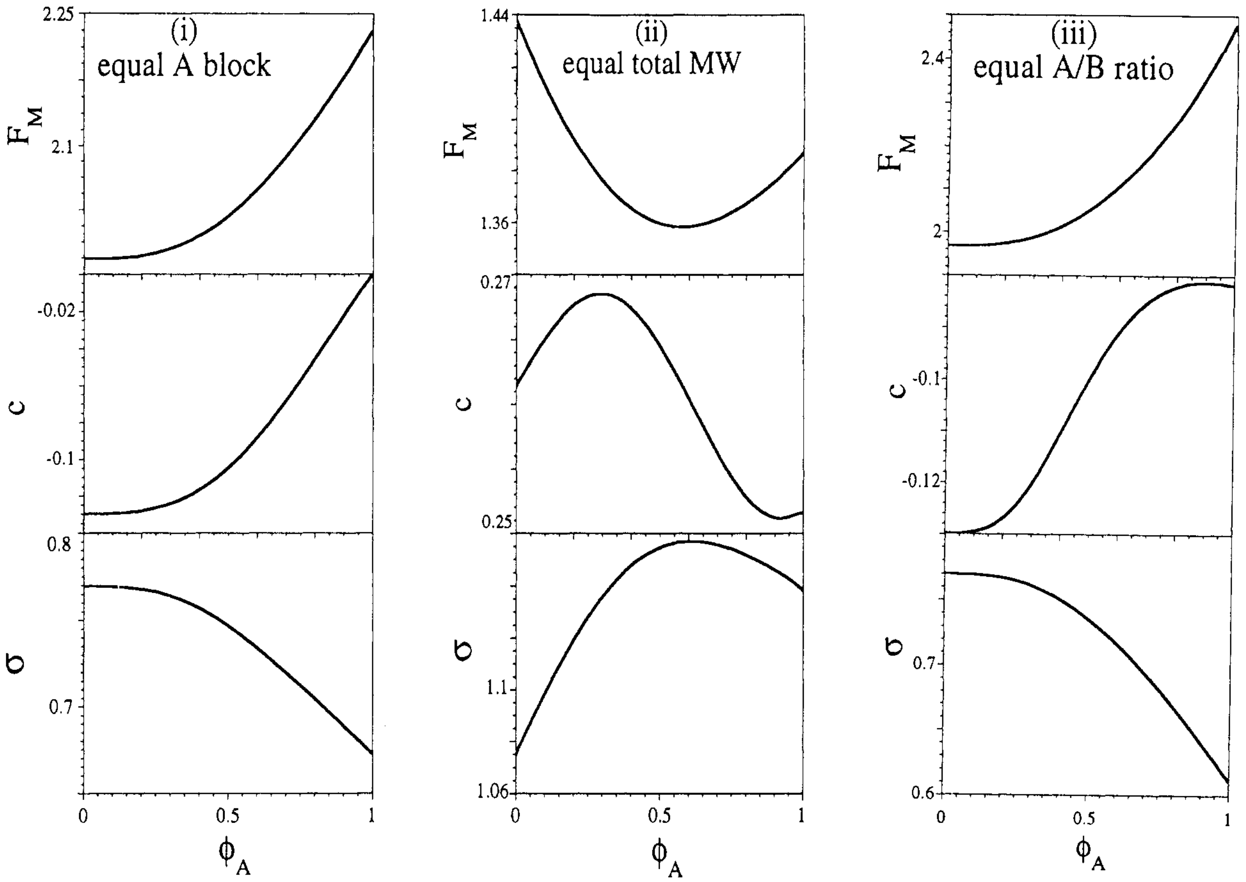

Figure 2. Equilibrium monolayer free energy, F_M^* (in units of $\gamma^{2/3}N_{s,B}^{1/3}$), the equilibrium curvature, c^* (in units of $\gamma^{-1/3}N_{s,B}^{-2/3}$), and the surface density, σ^* (in units of $\gamma^{1/3}N_{s,B}^{-1/3}$), for the three cases. (i) One block is monodisperse; the molecular weight of the A block is equal in both chains so that $\alpha_A = 0$; $\alpha_B = 1$, $N_{s,A} = 2N_{s,B}$, $\phi = \phi_B$. (ii) Both chains have the same overall molecular weight (but different asymmetries): $\alpha_A = 1$, $\alpha_B = 0.15$, $N_{s,A} = N_{s,B}\alpha_B/\alpha_A$, $\phi = \phi_A = 1 - \phi_B$. (iii) The two chains have the same asymmetry (N_A/N_B) but different overall molecular weights: $\alpha_A = \alpha_B = 1$, $N_{sA} = 2N_{s,B}$, $\phi = \phi_A = \phi_B$.

where ψ_J is the overall (average) bilayer fraction of the longer J chains, and $\phi_{j,J}$ is the fraction of longer J chains in monolayer j. We define the composition difference between the monolayers as $\Delta_J \equiv \{\phi_{o,J} - \phi_{i,J}\}/2$, and assume that $|\Delta_J| \ll \psi_J$. This assumption will be shown, presently, to be consistent with the low curvature expansion used to obtain the free energy expression of eq 1.

For simplicity, we discuss only binary copolymer mixtures of type i, where both chains have the same A block molecular weight and differ by the length of the B block. Since the A bruch is monodisperse, $\alpha_A = 0$ or, equivalently, $\psi_A = 0$. The bilayer composition is thus defined by the overall fraction of chains containing the longer B blocks, $\psi_B \equiv \psi$, and by the distribution of those chains between the two monolayers, $\Delta_B \equiv \Delta$. For added notational simplicity, we define $N_{s,B} \equiv N_s$ and $N_{s,A} \equiv \epsilon N_s$.

Three self-adjusting quantities determine the structure of a bilayer with a given curvature: the surface density of the inner and outer monolayers, σ_i and σ_o, and the composition difference between the monolayers, as defined through Δ. The equilibrium bilayer properties are calculated by minimization of the bilayer free energy with respect to these parameters, under the constraint of eq 11.B. We find

$$\sigma_i^* = \sigma_0\left\{1 - c\sigma_0\frac{4\delta k\, f + f'\Delta^*/\sigma_0 c}{3f}\right\} \qquad (12.A)$$

$$\sigma_o^* = \sigma_0\left\{1 + c\sigma_0\frac{4\delta k\, f + f'\Delta^*/\sigma_0 c}{3f}\right\} \qquad (12.B)$$

$$\Delta^* = 2c\sigma_0\left\{\frac{ff'\delta k - 3f^2\delta k'}{3ff'' - 2f'^2}\right\} \qquad (12.C)$$

where f, σ_0, and δk are defined under eq 7 and evaluated at ψ, the average bilayer composition. The derivatives, $f' \equiv \partial f/\partial\psi$, $f'' \equiv \partial^2 f/\partial\psi^2$, and $\delta k' \equiv \partial\delta k/\partial\psi$, are also evaluated at $\phi = \psi$. Since Δ^* is linearly proportional to the bilayer curvature, assuming that either Δ or c is small is, indeed, equivalent. The free energy of the equilibrium bilayer is

$$F_B = 3\sigma_0^2\{1 + A_2 c^2 N_{sB}^2\sigma_0^2\} \qquad (13)$$

We see that the linear term in the curvature expansion vanishes. The sign and magnitude of the c^2 coefficient, A_2, determine therefore the equilibrium bilayer properties:[22] When A_2 is positive, the free energy of the bilayer increases with curvature, and flat (lamellar) bilayers are thus the equilibrium structure. However, when A_2 is negative, the free energy of the bilayer decreases with curvature; the lamellar bilayers are unstable, and equilibrium vesicles will form. A_2 is given by

$$A_2 = \left\{\frac{\Delta}{c\sigma_0}\right\}^2\left\{\frac{3ff'' - 2f'^2}{18f^2}\right\} + \frac{\kappa}{3} - \frac{2\delta k}{3}\left\{\epsilon + \frac{8\delta k}{3} + \left(\frac{\Delta}{c\sigma_0}\right)\left[\frac{f'}{3f} - \frac{\delta k'}{\delta k}\right]\right\} \qquad (14)$$

The first term describes the energetic penalty for demixing in the flat bilayer and is therefore always positive. The second contribution, which is also always positive, arises from the bilayer bending stiffness. The last term accounts

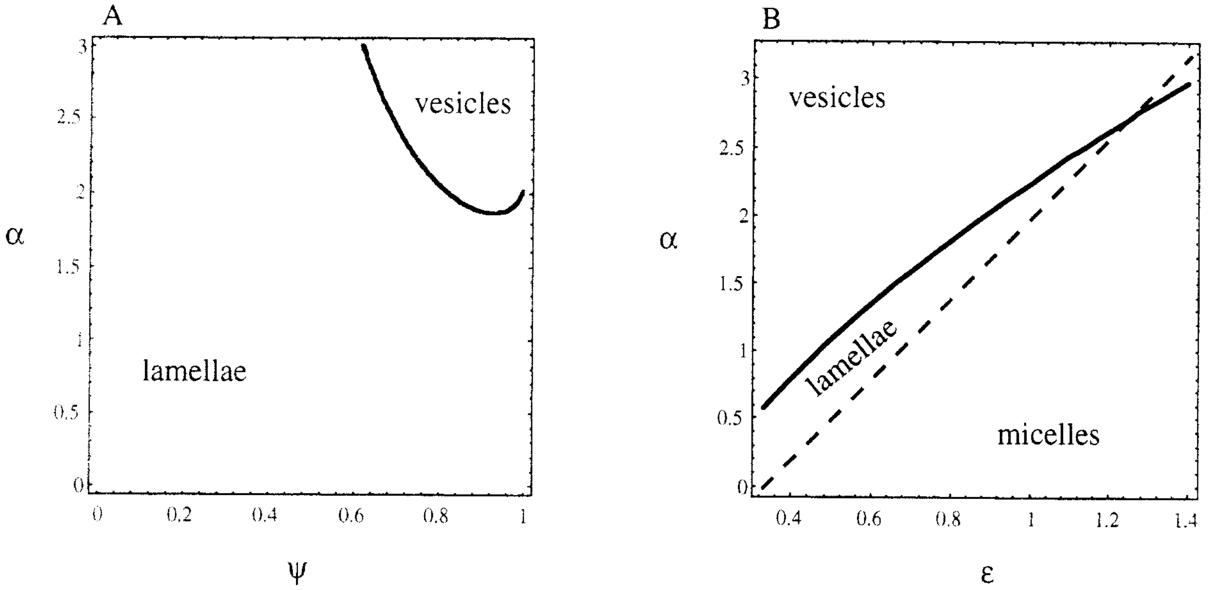

Figure 3. Vesicle phase boundary for mixtures of type i, where $\alpha_A = 0$. The solid line denotes a transition from flat lamellar structures to equilibrium, spherical vesicles. (A) Fixed short chain asymmetry: $\epsilon \equiv N_{sA}/N_{s,B} = 1$, i.e., symmetric short chains. (B) Fixed composition: $\psi = 0.8$. The dashed line denotes the approximate transition boundary between flat lamellae and cylindrical micelles for the longer chains (i.e., $\epsilon/\{1 + \alpha\} = {}^1/_3$). $\bar{K}$ is negative for all the values of (α, ϵ, ψ). Saddle-type deformations are, therefore, unfavorable.

for the copolymer spontaneous curvature and can be either positive or negative: when this curvature energy is positive, the bilayer favors lamellae. However, a negative sign indicates a tendency of the bilayer to demix and thus bend. Vesicles are obtained when this effect is strong enough to overcome the bending stiffness and mixing contributions. The equilibrium vesicle curvature, however, cannot be determined without an expansion of the bilayer energy to fourth order in curvature, which is beyond the scope of this paper.

In the limit of low ψ, where the overall fraction of longer chains in the mixture is small (i.e., chains with a longer B block), the surface density and composition difference have the simplified forms

$$\sigma_j^* = \sigma_0\left\{1 \pm 3cN_{sB}\sigma_0\left(\epsilon - 1 - \frac{2\alpha\psi^3}{3(\epsilon + 1)}\right)\right\} \qquad (15.A)$$

$$\Delta^* = \psi c N_{s,B}\sigma_0(\epsilon + 1) \qquad (15.B)$$

$$A_2 = \frac{1}{30}\left\{11\epsilon^2 + 19\epsilon - 4 - \alpha\psi^3\frac{11\epsilon^2 + 19\epsilon + 16}{1 + \epsilon}\right\} \qquad (15.C)$$

σ_0 is evaluated at $\psi = 0$. For monodisperse bilayers of chains with asymmetry ratio $\epsilon \equiv N_A/N_{s,B}(\psi{=}0)$ we see that A_2 becomes negative for $\epsilon \lesssim 0.19$; namely, monodisperse chains may form vesicles if the asymmetry is high enough. This is in exact agreement with the predictions of Ajdari and Leibler[3] and Wang.[4] However, such asymmetric chains are expected to form micelles rather than bilayers.[24,25] The addition of longer chains decreases A_2 for any ϵ and α. A monodisperse monolayer of low asymmetry chains, that favors lamellar structure, may therefore be destabilized by mixing with longer chains, although the effect of mixing in this limit is relatively weak, due to the ψ^3 dependence.

In the opposite limit, where the mixture contains only a small fraction of shorter chains, we find

$$\sigma_j^* = \sigma_0\left\{1 \pm \frac{cN_{sB}\sigma_0}{(1 + \epsilon)}\right\}\left\{\epsilon^2 - \alpha - 1 - \alpha(1 - \psi)\left(\ln\left[\frac{1 - \psi}{2}\right] - 1\right)\right\} \qquad (16.A)$$

$$\Delta^* = \frac{cN_{sB}\sigma_0(\epsilon + \alpha + 1)}{(1 + \epsilon)}\left\{1 - (1 - \psi)\left(\epsilon^2 + 2\alpha\epsilon + \epsilon + \ln\left[\frac{1 - \psi}{2}\right]\right)\right\} \qquad (16.B)$$

$$A_2 = \left\{-4(1 + \alpha)^2 + 15\epsilon(1 + 2\epsilon) + 11\epsilon(\epsilon^2 - \epsilon + \alpha) + 60\alpha\epsilon(1 - \Psi)\ln\left[\frac{1 - \Psi}{2}\right]\right\}\Big/\{30(1 + \epsilon)\} \qquad (16.C)$$

σ_0 is evaluated at $\psi = 1$. We see that the addition of a small fraction of shorter chains to a monolayer of longer chains significantly decreases the value of A_2, thereby destabilizing the flat bilayers and leading to the formation of equilibrium vesicles.[23]

The stability limits of the vesicle phase, which are given by $A_2 = 0$, are shown in Figure 3. Since we consider only vesicles vs flat bilayers, systems where micelles or saddle-type deformations may form have to be excluded. The parameter which determines the structure is the chain asymmetry, namely, the ratio of core to corona block molecular weight. In our case, this ratio is given by ϵ for the short chains and $\epsilon/(1 + \alpha)$ for the long chains. It has been shown[24,25] that micelles are preferable to lamellae if the asymmetry ratio is smaller than approximately 1/3 (note that the asymmetry ratio below which monodisperse copolymer bilayers form vesicles[4] is about 0.19. Competition between vesicles and micellar structures is, therefore, probable in monodisperse systems). Saddles are predicted to form[3] when the asymmetry ratio is larger than approximately 7/5. Our discussion excludes, therefore, chains that exceed these boundaries.

We see that one component, stable lamellar bilayers, can be destabilized by mixing. Vesicles are more easily obtained (i.e., at lower α values) in mixtures where the fraction of shorter chains is relatively small. The phase boundaries correspond to the trends shown in eqs 15.C and 16.C. In bilayers containing a small fraction of longer chains, vesicles are stable only when $\alpha \sim 1/\psi^3$, namely, a very high value since $\psi \ll 1$. However, in the opposite limit, vesicle stability is obtained when $\alpha \sim (1 - \psi)$, which can be moderate (of order 2-4).

The properties of a cylindrical bilayer can be calculated in a manner similar to that of the spherical system. We find that the equilibrium composition difference between the cylinder inner and outer layers is half that of an equivalent sphere, namely, $\phi_0 - \phi_i = \Delta^*$ (eq 12.C). The surface density of the inner and outer monolayers can be described by eqs 12.A and 12.B, respectively, by replacing δk with $\delta k/4$ and Δ^* with $\Delta^*/4$. Once the expressions for the free energy of a cylindrical and a spherical bilayer are known, eq 1 can be used to evaluate the Gaussian (saddle splay) modulus, $\bar{\mathbf{K}}$:

$$\bar{\mathbf{K}} = \sigma_0^{\,4}\left\{\epsilon\delta k + (\bar{\kappa}_A + \bar{\kappa}_B) - 76\frac{\delta k^2}{f}\right\} + 4\Delta^*\sigma_0^{\,3}\left\{\frac{f'\delta k}{f} - \frac{3}{4}\delta k'\right\} + 21\Delta^{*2}\sigma_0^{\,2}\left\{\frac{f'^2}{f} - \frac{3}{2}f''\right\} \quad (17)$$

We find that $\bar{\mathbf{K}}$ is always negative in the regions where vesicles are favorable, thereby excluding possible competition between equilibrium vesicles (uniform curvature) and saddles.

Reversing the bilayer, so that the outer B block is monodisperse while the A blocks in the core are mixed (i.e. $\alpha_B = 0$ and $\alpha_A \neq 0$), leads to formation of equilibrium vesicles only when ψ is small and α_A is very large (of order 20). Although copolymers with such a high molecular weight difference between the two blocks are not impossible to make, their significance for practical applications is doubtful.

(IV) Discussion

The properties of self-assembled, mixed copolymer monolayers and bilayers have been investigated, using an analytical self-consistent field model. We find that there are specific interactions between copolymer chains of different molecular weights or asymmetries. Thus, the properties of the copolymer system cannot be predicted from simple mixing rules applicable to ideal (noninteracting) mixtures.

The interactions between chains of different asymmetries or molecular weights are always found to be attractive. This attraction is due to a relaxation in the stretching energy of the longer blocks upon mixing with shorter blocks. The surface density of the mixture is therefore higher than that expected from linear averaging of the pure component monolayers. Cantor[26] calculated the properties of mixed, symmetric surfactant monolayers (corresponding to our case iii when $N_{s,A} = N_{s,B}$) using a molecular model where the surfactant chains are placed on a lattice and excluded volume interactions are accounted for through a mean field approximation. The same trends were obtained, i.e., nonlinear variation of the surface density with composition, a significant increase of σ with the addition of a small fraction of shorter chains ($\phi \rightarrow 1$), and only a small variation when $\phi \rightarrow 0$. The nonideality of the mixtures is especially pronounced when the effect of mixing on the equilibrium interface curvature is examined. Since the radius of a polymeric microemulsion droplet (coexisting with the two bulk homopolymer phases) is inversely proportional to the interface curvature, it should be possible to verify these predictions experimentally.

Equilibrium curvature in monodisperse copolymer bilayers is stabilized by adjustments in the surface density of the two constituent monolayers. However, such vesicles are predicted to form only when the chains are highly asymmetric,[4] a regime in which micelles are likely to be more stable than bilayers.[24,25] On the other hand, curvature in a mixed bilayer can be obtained through compositional differences between the two monolayers. In previous publications, we show that even if the differences in curvature and surface density between the two monolayers are neglected, equilibrium vesicles could form if the molecular weight difference between the two chains is of order $\alpha \approx 6$. In the present, more detailed analysis, we find that accounting for the adjustments in σ_{in}, σ_{out}, c_{in}, and c_{out} enables formation of equilibrium vesicles in mixtures where the molecular weight difference is much smaller ($\alpha \approx 2$). These α values are still large enough to exclude the possibility of typical polydispersity destabilizing lamellae but, on the other hand, not so high as to be prohibitive from an experimental point of view. Also, the asymmetry of both components in the equilibrium vesicle "window" is low, so that micellar structures are excluded. An experiment where the equilibrium structures formed by a mixture of such copolymers as a function of the mixture composition would be able to examine these predictions.

We also find a comparatively large window where $\bar{\mathbf{K}}$ of the mixed bilayer is positive, namely, where saddle-shaped deformations are stable. There is no overlap in the stability diagram between this region and the equilibrium vesicle phase. Saddle-shaped interfaces may be associated with spongelike structures. A transition, induced by changes in the mixture composition, from lamellae to an equilibrium sponge phase would therefore indicate a change in the sign of $\bar{\mathbf{K}}$.

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References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 31.

(2) See, for example: Park, D. W.; Roe, R. J. *Macromolecules* **1991**, *24*, 5324. Russell; et al. *Macromolecules* **1991**, *24*, 1575. Braun; et al. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 55.

(3) Ajdari, A.; Leibler, L. *Macromolecules* **1991**, *24*, 6803.

(4) Wang, Z. G. *Macromolecules* **1992**, *25*, 3702.

(5) Dan, N.; Safran, S. A. *Euphys. Lett.* **1993**, *9*, 975.

(6) Wang, Z. G.; Safran, S. A. *J. Chem. Phys.* **1991**, *94*, 679.

(7) Wang, Z. G.; Safran, S. A. *J. Phys. Fr.* **1990**, *51*, 185.

(8) Cantor, R. *Macromolecules* **1981**, *14*, 1186.

(9) Dan, N.; Tirrell, M. *Macromolecules* **1993**, *26*, 637.

(10) Kaler, E. W.; Herrington, K. L.; Miller, D. D.; Zasadzinski, J. A. *NATO ASI Ser. C* **1991**, *369*, 571.

(11) Safran, S. A.; Pincus, P.; Andelman, D. *Science* **1990**, *248*, 354.

(12) Safran, S. A.; MacKintosh, F. C.; Pincus, P.; Andelman, D. *Prog. Colloid Polym. Sci.* **1991**, *84*, 3.

(13) Lin, T.-L. *J. Colloid Interface Sci.* **1992**, *154*, 444.

(14) Helfrich, W. *Z. Naturforch.* **1973**, *28A*, 693; *J. Phys.* (*Paris*) **1986**, *47*, 321.

(15) Safran, S. A. *Statistical Thermodynamics of Surfaces, Interfaces and Membranes*; Addison-Wesley: Reading, MA, 1994.

(16) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1989**, *22*, 853.

(17) Milner, S. T.; Witten, T. A. *J. Phys. Fr.* **1988**, *49*, 1951. There are misprints in eqs 32 and 37 of this paper. The correct forms correspond to our eqs 3–5 (S. Milner, private communication).

(18) Birshtein, T. M.; Liatskaya, Yu. V.; Zhulina, E. B. *Polymer* **1990**, *31*, 2185.

(19) We need not consider competition with micelles, as microemulsion droplets in mixtures containing an excess of both solvents are always more stable than micelles; in microemulsions, interface curvature is dictated by the spontaneous curvature alone. In micelles, however, the space-filling requirements constrain the AB interface curvature, thereby increasing the micelle free energy.

(20) The entropy of mixing scales as kT per molecule, i.e., per chain. However, the free energy of strongly stretched chains scales as kT per segment. The mixing entropy is therefore negligible.

(21) In the special case where both copolymers are symmetrical, $\delta k = 0$. The interface is then flat for all ϕ, and the surface density scales as $\{N_s(1 + \alpha\phi^3)\}^{-1/3}$.

(22) The self-consistent field model coefficients for the third- and fourth-order terms of the Helfrich expansion (eq 1) have not been calculated. However, we have used a Flory type mean field model to estimate these coefficients. We found that the regions where A_2 became negative largely overlapped in both models. The mean field equilibrium bilayer free energy did not contain a third-order curvature term, and the coefficient of the fourth-order term was positive throughout the region of interest.

(23) There are some anomalies in this limit; when $\psi \equiv 1$, namely, when the monolayer contains only longer chains, Δ^* is not zero. Also, $A_2 \neq 0$ for $\psi = 1$ and $\epsilon/(1 + \alpha) \approx 0.19$. These deviations are due to the inability of our present model to constrain the monolayer composition so that ψ_j would not exceed unity. A consistent solution will require calculation of the equilibrium bilayer curvature. However, these deviations should be significant only when $(1 - \psi) \ll 1$.

(24) Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers-1*; Goodman, I., Ed.; Applied Sciences: New York, 1982.

(25) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733.

(26) Cantor, R. S. *J. Chem. Phys.* **1993**, *99*, 7124.