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Phase Equilibria in Block Copolymer–Homopolymer Mixtures

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ABSTRACT: Phase equilibria in block copolymer (AB) + homopolymer (A) blends are considered theoretically in the strong segregation limit. The effect of homopolymer molecular weight is analyzed. In particular, the following are shown: (i) Long enough A-homopolymer chains ($N_h \gg N_{hc}$) are incompatible with stretched A-blocks so that homopolymer and block copolymer should be space separated in any morphology. (ii) Interaction between copolymer micelles in the region $N_h \gg N_{hc}$ crucially depends on homopolymer molecular weight. For $N_h < N_h^*$ interaction of copolymer micelles of any geometry is purely repulsive (here $N_h^* \gg N_{hc}$). On the other hand, micelles strongly attract each other (at not too short distances) if $N_h > N_h^*$. Separation of the system into two phases (block copolymer and homopolymer) is predicted as a result of this attraction. (iii) Addition of A-homopolymer to an AB-copolymer system with minor A-blocks results in a shifting of the regions of stability of the cylindrical and spherical morphologies toward more symmetric copolymers (smaller fraction of major B-blocks). In particular, the spherical morphology with matrix B-blocks could be the most favorable even if the volume fraction of the B-component is nearly 50%.

1. Introduction

Systems of block copolymers are of considerable interest in particular due to their remarkable structural and mechanical properties.[1] One of the most characteristic features of these systems is their ability to form spatially periodic microphase-separated structures.[2,3] The corresponding phase transitions for block copolymer (AB) + homopolymer (hA) mixtures have been extensively studied both experimentally[4–8] and theoretically.[9–14] Note, however, that most of the theoretical works have addressed the so-called weak segregation limit (slight inhomogeneity of distributions of A- and B-links) first considered by Leibler.[15] In the current paper I present a theory for micro/macroseparation in the opposite strong segregation limit (see, e.g., ref 3) which is sometimes closer to the experimental situation. Considerable attention is paid to the effect of homopolymer molecular weight. Critical micelle concentration for the system with shorter homopolymers in SSL was also considered theoretically by Leibler et al.[44]

The paper is organized as follows. In the next two sections extremely asymmetric block copolymers (with minor B-blocks) are considered. This case is important (although probably not realistic) since here it is possible to arrive at a detailed picture of phase transitions in a fairy analytical way (see section 3). After that, we turn to the more realistic case of not very asymmetric copolymers. The problem of interaction between two lamellar (cylindrical, spherical) copolymer micelles is analyzed in section 4. The phase behavior of the copolymer–homopolymer mixtures is considered in section 5, the last part of this section being devoted to copolymers with minor A-blocks (here somewhat unexpected morphological homopolymer-induced transitions are predicted).

2. Highly Asymmetric Block Copolymers: Interaction of Micelles

Let us consider a mixture of homopolymer (A) and block copolymer (AB). The free energy density of the homogeneous system is

$$F = (\phi/N)\ln(\phi/e) + ((1-\phi)/N_h)\ln((1-\phi)/e) + \chi f\phi(1-f\phi)$$

where $N = N_A + N_B$ is the total number of links per AB-copolymer, N_h is that per homopolymer chain, $\phi = \phi_c$ is the mean volume fraction of copolymers, χ is the Flory interaction parameter, and $f = N_B/N$ gives the copolymer composition. Here we assume that the volumes per A- and B-link are equal and are taken as a unit volume: $v_A = v_B = 1$; also kT is taken as an energetic unit. In addition, let us assume that $\chi N_B \gg 1$ (strong segregation limit) and that B-blocks are much shorter than A-blocks:[16]

$$f \ll (\chi N_B)^{-1} \ll 1 \qquad (2.1)$$

The chemical potential of block copolymer chains is

$$\mu = N[(1-\phi)(\partial F/\partial\phi) + F] \approx -(N/N_h) + \ln(\phi) + \chi N_B \qquad (2.2)$$

Here we take into account that $\phi \ll 1$ (see below).

As the concentration of copolymer chains, ϕ, increases, they will tend to aggregate and form spherical micelles,[13] consisting of a B-core (of radius R) and an A-shell (Figure 1). B-blocks in the core should be highly stretched since $\chi N_B \gg 1$. The same is true for the inner parts of the A-blocks in the shell (the coat).[17] The effective energy of a micelle is just the stretching energy of the B-blocks in the core plus that of the A-blocks in the coat plus the energy of the A–B interface. Under the restrictions mentioned above, the energy is nearly equal to that of a spherical micelle in the pure block copolymer melt[17] provided that homopolymers do not penetrate into the core or coat:

$$F_{sph}(Q) = Q\{1.74x^2/12 + 3\alpha^{0.5}/x + 0.5\ln(\alpha) + \ln(1/f)\} \qquad (2.3)$$

where

$$Q = (4\pi/3)R^3/N_B \qquad (2.4)$$

is the number of copolymer chains per micelle, $x \equiv R/(N_B^{0.5}a)$, and $\alpha = \chi N_B$. Here we assume that the A- and B-chains are characterized by the same statistical lengths: $b_A = b_B = 6^{0.5}a$ (so that, e.g., the mean square end-to-end distance of the whole block copolymer is $6Na^2$).

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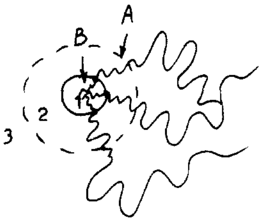

Figure 1. An isolated spherical micelle ($N_B \ll N_A$); region 1 is the core filled by stretched B-blocks, region 2 the coat of stretched A-blocks, and region 3 the corona region, where the volume fraction of A-blocks attached to the micelle, η, is small.

Minimization of $F_{\text{sph}}(Q)/Q$ over x gives

$$x = 2.18\alpha^{1/6}; \qquad R = xN_B^{1/2}a;$$
$$Q = (4\pi/3)(2.18^3)(\alpha N_B)^{1/2}a^3 \tag{2.5}$$

The characteristic energy of stretching per link in the core or coat is of order $\epsilon_1 \sim R^2/(N_B^2a^2) \sim \alpha^{1/3}/N_B$. Homopolymer chains will not penetrate into the core (or into the most stretched part of the shell) provided that $N_h\epsilon_1 \gg 1$, i.e.

$$N_h \gg Nf/\alpha^{1/3} \tag{2.6}$$

Note, however, that homopolymers do penetrate into the outer part of the shell (the corona), where the volume fraction of A-blocks, η, is small (see Figure 1 and compare with ref 17).

In what follows we will assume that homopolymer chains are long enough so that the condition (2.6) is fulfilled. Shorter homopolymer chains should be able to penetrate into the core of a micelle; short enough homopolymers will behave as a solvent. However, we are not going to consider these intermediate regimes here.

Depending on the homopolymer molecular weight, the A-blocks in the corona might be stretched or they might not be stretched. Let us *assume* that they are not stretched (so they are nearly Gaussian) and verify this assumption. As was shown in ref 17 for a pure block copolymer melt, the lion's share of the outer A-blocks should be just in the corona part of the shell (provided that condition 2.1 is fulfilled). The effect of homopolymers could result only in an increase of the fraction of A-blocks in the corona. Therefore the size of the corona should be of the order of the Gaussian size of the A-blocks, $R_{\text{corona}} \sim N_A^{0.5}a \gg R$. Thus, the copolymer volume fraction in the corona is

$$\eta \sim QN_A/R^3_{\text{corona}} \sim Q/(N^{0.5}a^3) \sim (\alpha f)^{0.5} \ll 1 \tag{2.7}$$

The energy needed to disturb appreciably the Gaussian conformations of the A-blocks (in the corona) is of the order of $1(kT)$ per block, so $F_{\text{deform}} \sim Q$ in total. The characteristic energy associated with the redistribution of homopolymer chains (their partial removal from the corona part of the micelle) is of the order

$$F_{\text{homo}} \sim R^3_{\text{corona}}\eta^2/N_h \sim Q\eta N/N_h$$

The corona parts of the A-blocks will be nearly Gaussian if $F_{\text{homo}} \ll F_{\text{deform}}$, i.e.

$$N_h \gg N(\alpha f)^{0.5} \tag{2.8}$$

Note that the condition (2.8) is stronger than (2.6); it will be assumed here and below until the end of section 3.

The thermodynamic potential of a Q-micelle is

$$\tilde{F}(Q) = F_{\text{sph}}(Q) - \mu Q \tag{2.9}$$

Formation of a micelle is favorable if $\tilde{F}(Q) < 0$. Using (2.3), this condition could be represented as $\mu > \mu_{\text{cmc}}$

$$\mu_{\text{cmc}} = \ln(1/f) + 0.5\ln(\alpha) + 2.06\alpha^{1/3} \tag{2.10}$$

Therefore the critical micelle concentration (cmc)

$$\phi_{\text{cmc}} = \exp(-\alpha + N/N_h + \mu_{\text{cmc}})$$

is exponentially small for large α. That is why we have assumed at the beginning of this section that $\phi \ll 1$ in the homogeneous state.

Now let us consider the interaction between two spherical micelles in an otherwise homogeneous system. Let r_{12} be the distance between the centers of the micelles. The most interesting range corresponds to $r_{12} \sim R_{\text{corona}}$ (see below; the interaction energy here is not small since Q is large). We have already shown that copolymer chains in the corona should be Gaussian (under the condition (2.8)). Note that exactly the same arguments could be applied to a pair of micelles with somewhat overlapping coronas. Therefore the distribution of copolymer links in the vicinity of the micelles is nearly the sum of the distributions for two virtually isolated micelles:

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \phi_0(\mathbf{r} - \mathbf{r}_{12}) \tag{2.11}$$

where $\phi_0(\mathbf{r})$ is the volume fraction of A-links attached to an isolated micelle at the distance r from its center. We could consider $\phi_0(r)$ as the volume concentration of links of Q Gaussian chains attached by their ends to the point $\mathbf{r} = 0$ since the core radius $R \ll R_{\text{corona}}$. Taking into account that $N_A \approx N$, we get for the Fourier image of $\phi_0(\mathbf{r})$

$$\phi_0(\mathbf{k}) = QN[1 - \exp(-u)]/u \tag{2.12}$$

where $u \equiv Nk^2a^2$.

Obviously, the homopolymer links in the vicinity of the micelles should be also redistributed in order to fit the incompressibility condition, $\phi_h = 1 - \phi(\mathbf{r})$. The energy of interaction of micelles is now mainly due to this inhomogeneity of homopolymer distribution. Note also that apart from the core–coat region (which could be neglected because its relative volume is very small) the inhomogeneity of distribution of homopolymer links is small since $\phi(\mathbf{r}) \sim \eta \ll 1$. Using the RPA method[18] and taking into account inhomogeneity as a perturbation we write the conformational free energy of homopolymer chains as (compare with ref 15)

$$F = F_0 + (^1/_2N_h)\int [f_D(k^2a^2N_h)]^{-1}|\Delta\phi_h(\mathbf{k})|^2\, d^3k/(2\pi)^3 \tag{2.13}$$

where F_0 is the free energy of the homogeneous state and $f_D(k^2a^2N_h)$ is the Debye scattering function for N_h-chains

$$f_D(u_h) = (2/u_h^2)(u_h - 1 + \exp(-u_h)) \tag{2.14}$$

Here $\Delta\phi_h(\mathbf{k})$ is the Fourier image of the function $\phi_h(\mathbf{r}) - 1 = -\phi(\mathbf{r})$.

Using eqs 2.11–2.14, we get the effective interaction energy of two micelles:

$$F_{\text{int}}(r) = 0.5Q^2N\int (1 - e^{-u})^2u^{-1}\left[1 - \frac{1 - \exp(-u_h)}{u_h}\right]^{-1} \times \exp(i\mathbf{qr})\, d^3q/(2\pi)^3 \tag{2.15}$$

where $u = q^2a^2N$, $u_h = q^2a^2N_h$, and $r \equiv r_{12}$. Note that eq 2.15 for $N_h = N$ coincides with that for the interaction energy of micelles in a pure block copolymer melt.[19] The plots of the reduced interaction energy vs reduced distance are shown in Figure 2 for $\beta \equiv N_h/N = 0, 1.5, 1.75, \infty$. The micelles always repel each other at short distances, the

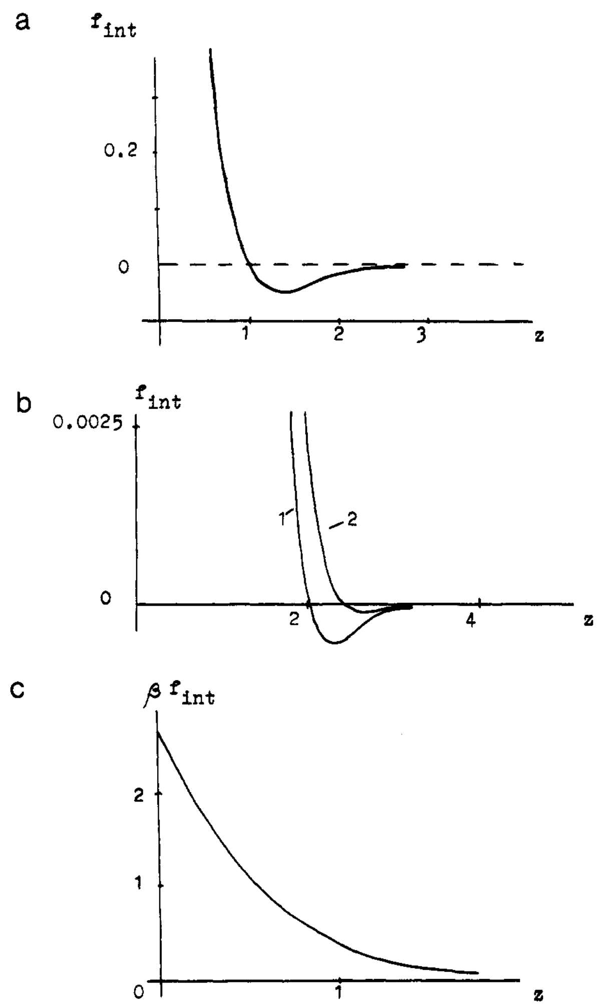

Figure 2. Dependence of the reduced energy of interactions between two spherical micelles, $f_{int} = 16\pi a^3 N^{0.5} F_{int}/Q^2$, on the reduced distance between their centers, $z = r/(2N^{0.5}a)$, for different homopolymer molecular weights: $\beta = N_h/N \to \infty$ (a); $\beta = 1.75$ (curve 1), $\beta = 1.5$ (curve 2) (b); $\lim_{\beta\to 0}(\beta f_{int})$ vs z (c).

asymptotic law for $r_{12} \ll R_{corona}$ being

$$F_{int}(r_{12}) = Q^2/(8\pi a^2 r_{12}) \qquad (2.16)$$

For long homopolymer chains ($N_h \gg N$) the function $F_{int}(r)$ reveals a pronounced minimum at $r^* \approx 2.7N^{0.5}a$. For $r > r^*$ micelles attract each other; the energy of attraction

$$|F_{int}(r^*)| = 0.066Q^2/(8\pi a^2 r^*) \approx 1.8\alpha f a^3 N^{0.5} \qquad (2.17)$$

is quite large for large N.

As homopolymer chains become shorter, the depth of the minimum decreases appreciably; it almost disappears at $N_h \approx 1.5N$ (see Figure 2b). So, for $N_h \lesssim N$ the interaction between micelles is purely repulsive.[20]

The physical meaning of this repulsion/attraction could be understood as follows: Let us consider two limits $N \gg N_h$ and $N \ll N_h$. In the first case the typical scale of interaction $\lambda \sim N^{1/2}a$ is much larger than the spatial homopolymer size $R_h \sim N_h^{1/2}a$. Therefore the free energy density, F_h, due to the slightly inhomogeneous homopolymer distribution, $\phi_h = \text{const} + \Delta\phi(\mathbf{r})$, must be proportional to $\Delta\phi^2$. In the middle region between two micelles, the total $\Delta\phi$ is the sum of two roughly equal contributions from the micelles: $\Delta\phi \approx 2\Delta\phi_1$, so that the free energy density $F_h \sim 4\Delta\phi_1^2$ is larger than the sum of the free energy densities corresponding to isolated (noninteresting) micelles, $F_h^{(0)} = 2\Delta\phi_1^2$. Thus the free energy of interaction is always positive.

On the other hand, for $N \ll N_h$ we have $\lambda \ll R_h$. Therefore now the free energy density should be proportional to the square of the gradient of $\Delta\phi$, $F_h \sim (\text{grad}\,(\Delta\phi))^2$ (see, e.g., ref 21). In the most important middle region the gradients due to both micelles, grad ($\Delta\phi_1$) and grad ($\Delta\phi_2$), almost compensate each other: grad ($\Delta\phi_1$) + grad ($\Delta\phi_2$) ≈ 0, so that the free energy of interaction is now negative, giving rise to attraction between the micelles.

The scheme used above could be easily generalized for an arbitrary number of micelles. The interaction energy in general is simply the sum of pair interactions (apart from some special cases of no importance). This is due to the "quadratic" structure of the general equation (2.13).

3. Micelle Ordering for the Highly Asymmetric Case

Let us consider the mixture AB + hA near the cmc. The thermodynamic potential of an isolated micelle could be rewritten as (see eq 2.9)

$$\tilde{F} = -Q^*\tau \qquad (3.1)$$

where $\tau \equiv \mu - \mu_{cmc}$ is assumed to be small ($\tau \ll 1$) and Q^* is the number of chains per critical micelle (at cmc) as given by eq 2.5. The concentration of micelles is determined by $\tilde{F}$ according to Gibbs statistics:

$$c \sim \exp(-\tilde{F}) \approx \exp(Q^*\tau) \qquad (3.2)$$

For negative τ the concentration is very small (if $|\tau| \gg 1/Q^*$); it increases sharply with τ since $Q^* \gg 1$. At some (large enough) concentration interaction between micelles will force a disorder–order transition, resulting in "freezing" of micelles in some superlattice.

Let us consider the corresponding transitions for the cases of long ($N_h \gg N$) and short ($N_h \ll N$) homopolymer chains.

Superlattice Formation for $N_h \gg N$. As was shown in the previous section, the interaction energy of micelles reveals a minimum at $r = r^*$. It seems natural to assume that at the ordering transition micelles should form a superlattice with a period (more precisely, the distance between nearest neighbors) d, equal to r^*. This is not the case, however. The most favorable period is much smaller than r^*. At first sight, that seems improbable since at distances $r < r^*$ micelles strongly repel each other (according to the $1/r$ "Coulomb" law). But note that the energy of repulsion at short distances is almost exactly compensated by the *attraction* between more distant micelles (that is, the $1/r$ law is effectively screened for zero wave vector, $\mathbf{k} = 0$). The unscreened part of the interaction energy is *negative*; its minimum (for a given mean concentration of micelles) corresponds to a body centered cubic (bcc) superstructure.[17] Now let us proceed in a quantitative way.

The interaction energy (2.13) for a 3d periodic structure could be rewritten as (the constant term F_0 is omitted)

$$F_{int} = (2VN_h)^{-1}\sum_{\mathbf{k}}[f_D(u_h)]^{-1}|\Delta\phi_h(\mathbf{k})|^2 \qquad (3.3)$$

where V is the total volume of the ordered phase, $u_h = k^2a^2N_h$, and the sum runs over all wave vectors $\mathbf{k}$ of the reciprocal lattice. Note that for all $\mathbf{k} \neq 0$ the parameter u_h is large, $u_h \gg 1$ since $N_h \gg N$ and $|\mathbf{k}| \gg 1/r^*$. Therefore using eq 2.14, we can simplify eq 3.3:

$$F_{int} = (4V)^{-1}\sum_{k>0}k^2a^2|\Delta\phi_h(\mathbf{k})|^2 + (2VN_h)^{-1}|\Delta\phi_h(0)|^2 \equiv F_{sh} + F_{id} \qquad (3.4)$$

The first term (F_{sh}) on the right-hand side of eq 3.4

corresponds to short-scale Coulomb interactions. Per micelle this term gives (see, e.g., ref 17)

$$\mathcal{F}_{\mathrm{sh}} = -0.23(Q^2/4a^2)c^{1/3} \qquad (3.5)$$

where $c = N/V$ is the concentration of micelles ($\mathbf{N}$ being the total number of micelles). The second term (F_{id}) is just the ideal gas free energy of homopolymers; per micelle it gives

$$\mathcal{F}_{\mathrm{id}} = (2N_{\mathrm{h}}\mathbf{N}V)^{-1}(\Delta\phi_{\mathrm{h}}(0))^2 = c(2N_{\mathrm{h}})^{-1}Q^2N^2 \qquad (3.6)$$

since $\Delta\phi_{\mathrm{h}}(\mathbf{k}=0) = V(\bar{\phi}_{\mathrm{h}} - 1) = -cVQN$.

Equation 3.6 is valid provided that $y \equiv cQN \ll 1$ (i.e., the mean volume fraction of block copolymer chains is small). It could be easily generalized for any cQN. The ideal gas free energy of homopolymer chains per unit volume is[22]

$$F_{\mathrm{id}}/V = \bar{\phi}_{\mathrm{h}} \ln(\bar{\phi}_{\mathrm{h}}) + 1 - \bar{\phi}_{\mathrm{h}} \qquad (3.7)$$

Therefore

$$\mathcal{F}_{\mathrm{id}} = (cN_{\mathrm{h}})^{-1}[(1-y)\ln(1-y) + y], \qquad y \equiv cQN \qquad (3.8)$$

Note that eq 3.5 is still valid in the region $cQN \sim 1$ (the effective role of homopolymer chains being played now by the parts of the A-blocks separated by many periods from the mother micelle they are attached to).

It remains to minimize the sum

$$\mathcal{F}_{\mathrm{int}} = \mathcal{F}_{\mathrm{sh}} + \mathcal{F}_{\mathrm{id}}$$

with respect to c. The effective free energy of the superstructure (i.e., the free energy of the *whole* system including the superstructure minus the free energy of the homogeneous system) is

$$F = \mathbf{N}(F_{\mathrm{int}} - Q\tau)$$

The ordered phase will appear just as F becomes negative, at

$$\tau_{\mathrm{c}} = \min F_{\mathrm{int}}/Q$$

In the region $1 \ll \beta \equiv N_{\mathrm{h}}/N \ll (\alpha f)^{-1/3}$ we get

$$\tau_{\mathrm{c}} = -0.75 \times 10^{-2}\beta^{0.5}Q/(N^{0.5}a^3) = -0.325(\beta\alpha f)^{0.5} \qquad (3.9)$$

Note that $|\tau_{\mathrm{c}}| \ll 1$ but $|\tau_{\mathrm{c}}|Q \gg 1$. Therefore the micelle concentration in the homogeneous phase (at $\tau = \tau_{\mathrm{c}}$) should be extremely small. Thus at $\tau = \tau_{\mathrm{c}}$ a sharp first-order transition from a very dilute gas of micelles (with $c \sim \exp(-Q^*|\tau_{\mathrm{c}}|)$ to a bcc superstructure occurs. The copolymer volume fraction in the gas phase is[23]

$$\phi_1 \approx \phi_{\mathrm{cmc}}(1 - |\tau_{\mathrm{c}}|) \approx \phi_{\mathrm{cmc}}$$

In the bcc phase the copolymer volume fraction is much larger:

$$\phi_2 \approx cQN = 0.32(\alpha\beta^3 f)^{1/2} \qquad (3.10)$$

but all the same $\phi_2 \ll 1$. For larger N_{h}, in the region $N_{\mathrm{h}} \gtrsim \tilde{N}_{\mathrm{h}} = N(\alpha f)^{-1/3}$, the homopolymer volume fraction in the ordered phase decreases appreciably: $\phi_{\mathrm{h}} = 1 - \phi_2 \rightarrow 0$ for $N_{\mathrm{h}} \gg \tilde{N}_{\mathrm{h}}$. The dependence of ϕ_{h} on $N_{\mathrm{h}}/\tilde{N}_{\mathrm{h}}$ is shown in Figure 3a; the function $\tau_{\mathrm{c}}/|\tau_{\mathrm{c}}(\tilde{N}_{\mathrm{h}})|$ vs $N_{\mathrm{h}}/\tilde{N}_{\mathrm{h}}$ is plotted in Figure 3b.

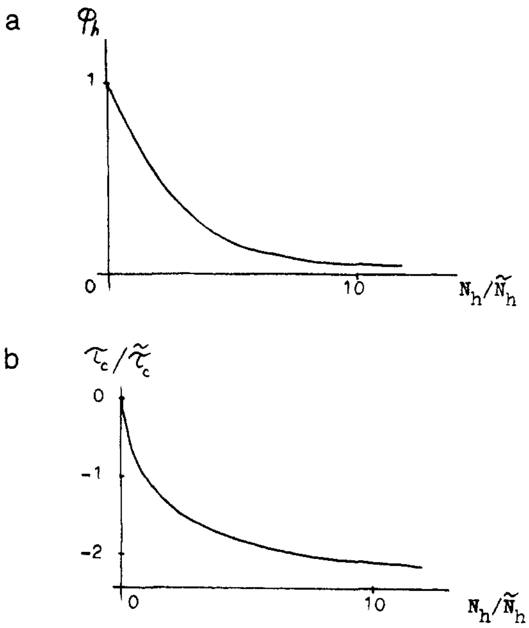

Figure 3. Dependence of the homopolymer volume fraction, ϕ_{h}, in the bcc superstructure of spherical domains (in equilibrium with the homopolymer phase) on the reduced homopolymer molecular weight, $N_{\mathrm{h}}/\tilde{N}_{\mathrm{h}}$ (a); dependence of the reduced chemical potential of copolymer chains at the transition point, $\tau_{\mathrm{c}}/\tilde{\tau}_{\mathrm{c}}$, on $N_{\mathrm{h}}/\tilde{N}_{\mathrm{h}}$, where $\tilde{\tau}_{\mathrm{c}} \equiv |\tau_{\mathrm{c}}(\tilde{N}_{\mathrm{h}})|$ (b).

Ordering of Micelles for $N_{\mathrm{h}} \ll N$. Now let us assume that homopolymer chains are much shorter than copolymers (however, the inequality (2.8) is still assumed). Equation 2.15 for the interaction energy in this region could be simplified as

$$F_{\mathrm{int}}(r) = (Q^2/(\pi a^3 N^{0.5}))z^{-1}[\psi(z/2^{0.5}) - \psi(z)] \qquad (3.11)$$

where $z = r/(2N^{0.5}a)$ and

$$\psi(z) = (0.25 + 0.5z^2)(1 - \mathrm{erf}(z)) - (z/(2\pi^{0.5}))\exp(-z^2) \qquad (3.12)$$

The interaction energy F_{int} is always positive. Thus the ordering transition should be expected for $\phi > \phi_{\mathrm{cmc}}$. In this regime the concentration of free copolymer chains (not connected to micelles) is almost fixed at ϕ_{cmc}, the concentration of micelles being[24]

$$c = (\phi - \phi_{\mathrm{cmc}})/(QN) \qquad (3.13)$$

As the concentration of micelles increases, the typical energy of interactions per micelle also increases; at some critical concentration c^* micelles will freeze into some superlattice. It was checked numerically that the most favorable structure of the ordered phase (near the transition point) is the face centered cubic (fcc) phase. Led d^* be the distance between the nearest neighbors in the ordered structure (at the transition point); then

$$c^* = 2^{0.5}/d^{*3} \qquad (3.14)$$

At the order–disorder transition the energy of interactions per micelle should be of order kT, i.e.

$$6F_{\mathrm{int}}(d^*) \sim 1 \qquad (3.15)$$

where 6 is one-half of the number of nearest neighbors in fcc. Using eqs 3.11, 3.14, and 3.15, we get

$$c^* \approx 0.18/(N^{1.5}a^3z^{*3}) \qquad (3.16)$$

where z^* is determined by the condition

$$z^{*4}\exp(z^{*2}/2) = 700a^3N^{0.5}(\alpha f/\beta) \gg 1 \qquad (3.17)$$

As the concentration of micelles, c, is further increased, the second first-order phase transition, fcc → bcc super-

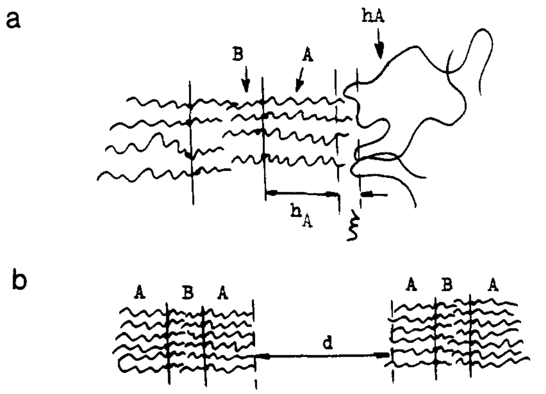

Figure 4. "Dry" lamellar micelle consisting of a B inner part (core) and a corona (of thickness h_A) filled by stretched A-blocks; homopolymer chains can only slightly penetrate into the corona, the interpenetration layer thickness, ξ, being much smaller than h_A (a). Two lamellae at the distance d (b).

structure, occurs at

$$c^{**} \approx 0.025/(N^{1.5}a^3) \tag{3.18}$$

for $c > c^{**}$, the bcc structure being always the most favorable.

4. Interaction of "Dry" Micelles

So far we have been considering micelles with a "dry" core filled by stretched B-blocks and a "wet" corona, where some parts of the A-blocks are not stretched. This situation corresponds to the regime $\alpha = \chi N_B \gg 1$, $\alpha f \ll 1$. Now we are going to consider another asymptotic limit of completely "stretched" micelles:

$$\alpha f \gg 1 \tag{4.1}$$

More precisely, we assume that α is a large parameter ($\alpha \gg 1$) and f is not very small.[25] We also assume that micelles are (almost) completely dry i.e., homopolymer chains cannot penetrate into the shell (corona) or the core of a micelle (Figure 4a). The corresponding condition is (the derivation being exactly the same as for eq 2.6)

$$N_h \equiv \beta N \gg N_{hc} = N/\alpha^{1/3} \tag{4.2}$$

Under these conditions ((4.1),(4.2)) the free energy of the micelle is virtually not influenced by the presence of homopolymer chains; so it should be the same as for the pure block copolymer melt.[17] Using this fact, the critical chemical potentials at the cmc were obtained in refs 26 and 27 for different micellar geometries (spheres, cylinders, and lamellae):

$$\mu_{\text{cmc}}^{\text{lam}} \approx 1.115(\chi N)^{1/3};\quad \mu_{\text{cmc}}^{\text{cyl}} \approx 1.19(\chi N f)^{1/3}(1.64 - \ln(f))^{1/3}$$

$$\mu_{\text{cmc}}^{\text{sph}} \approx 2.06(\chi N f)^{1/3}(1 - 0.57 f^{1/3})^{1/3} \tag{4.3}$$

The corresponding regimes of stability as obtained from eqs 4.3 are $f < 0.13$ (spheres), $0.13 < f < 0.28$ (cylinders), and $0.5 > f > 0.28$ (lamellae) (the case $f > 0.5$ will be considered in the next section).

Note that eq 4.3 for $\mu_{\text{cmc}}^{\text{lam}}$ is asymptotically exact. On the other hand, $\mu_{\text{cmc}}^{\text{cyl}}$ and $\mu_{\text{cmc}}^{\text{sph}}$ were obtained using the Alexander–de Gennes approximation for the micelles' shells (that is, it was assumed that all free ends of the A-blocks are attached to the outer surface of the shell; see ref 28 for more details). In order to estimate the ultimate error due to this approximation, I have calculated $\mu_{\text{cmc}}^{\text{cyl}}$ using (asymptotically) exact results for the energy of the cylindrical shell.[28] The recalculated (exact) boundary between the regions of stability of the lamellar and cylindrical structures, f_{lc}, is now

$$f_{\text{lc}} = 0.299$$

Thus it is only 5% larger than the approximate one ($f_{\text{lc}} = 0.283$).

Now let us consider interactions between two micelles and begin with the simplest lamellar case. The interaction of two lamellae in a mixture with very long homopolymer chains has already been considered.[27] For the case of arbitrary N_h (yet satisfying the condition (4.2)) the general scheme is exactly the same. I outline it here briefly. The characteristic scale of the interactions is determined by the thickness ξ of the interpenetration layer betwen the lamella (A-blocks) and the surrounding homopolymer (see Figure 4a). The free energy of this layer per unit area of the lamella is

$$\Delta F = \Delta F^{(h)} + \Delta F^{(c)} \tag{4.4}$$

where $\Delta F^{(h)}$ is the conformational free energy due to nonuniform homopolymer distribution and $\Delta F^{(c)}$ is the copolymer contribution. We represent $\Delta F^{(h)}$ as

$$\Delta F^{(h)} = (a^2/4)\int \frac{(\nabla\phi_h)^2}{\phi_h}\,dz + \int F_{id}(\phi_h)\,dz \tag{4.5}$$

where $\phi_h = \phi_h(z)$, the z-axis being normal to the lamella's surface. The first gradient term gives the short-scale contribution; the second (ideal gas) term is important for larger inhomogeneity scales

$$F_{id}(\phi_h) = (1/N_h)\phi_h \ln(\phi_h) \tag{4.6}$$

Equation 4.5 is asymptotically exact for characteristic inhomogeneity scales $\lambda \gg N_h^{0.5}a$ and $\lambda \ll N_h^{0.5}a$; in the general case, it presents a good enough approximation (see, e.g., ref 29).

The copolymer term, $\Delta F^{(c)}$, could also be represented as a sum of short-scale and long-scale contributions; for a surface (interpenetration) layer of an isolated micelle we get[27]

$$\Delta F^{(c)} = (a^2/4)\int \frac{(\nabla\phi_A)^2}{\phi_A}\,dz - \int_{z_1}^{\infty} U_A(z)[\phi_A(z) - \phi_A^{(\text{box})}(z)]\,dz \tag{4.7}$$

Here $\phi_A(z)$ is the copolymer volume concentration at the point z and $U_A(z)$ is the parabolic molecular field forcing the stretch of the A-blocks (in the shell of the lamella)[27,30]

$$U_A(z) = (\pi^2/16)(z - z_1)^2/(N_A^2 a^2) \tag{4.8}$$

where z_1 is the coordinate of the nearest B-core/A-shell interface (see Figure 4a). The second term on the right-hand side of eq 4.6 accounts for the additional energy of the elastic elongation of the A-blocks in comparison with its minimum value corresponding to a boxlike distribution of links:

$$\phi_A^{(\text{box})}(z) = H(z - z_1)\,H(z_1 + h_A - z)$$

where h_A is the thickness of the A-shell, and $H(\cdot)$ is the Heaviside function. Again eq 4.6 is asymptotically exact for large-scale and short-scale inhomogeneities ($\lambda \gg \xi$, $\lambda \ll \xi$).

Minimization of ΔF (eq 4.4) for an isolated lamella was performed using a trial function of the form[31]

$$\phi_A(z) = 0.5[1 - \tanh((z - z_1 - h_A)/\xi)]$$

For $N_h \to \infty$ the result is[27]

$$\xi^* = (48/\pi^4)^{1/3} a (a N_A^2/h_A)^{1/3} \qquad (4.9)$$

$$\Delta F^* = 0.75 a^2/\xi^* \qquad (4.10)$$

The result (4.9) is in agreement with that of ref 32. Note that under the conditions (4.1) the interpenetration layer is much thinner than the lamella itself

$$\xi^* \ll h_A \approx 2(3/\pi^2)(1-f) a N^{0.5} \alpha^{1/6}$$

(one can easily get the last equation from the results of ref 17).

Interaction between micelles can be considered in a similar way. The energy of interaction (per unit area) is

$$F_{\mathrm{int}}(d) = F(d) - F(\infty)$$

where

$$F(d) = \min_{\xi} \{2\Delta F^{(c)}(\xi) + \Delta F^{(h)}(\xi,d)\} \qquad (4.11)$$

Here d is the distance between the outer surfaces of the lamellae (see Figure 4b), ξ is now dependent on d, and $\Delta F^{(h)}(\xi,d)$ is given by eq 4.5 with

$$\phi_h(z) = 0.5[\tanh((z - z_1 - h_A)/\xi) + \tanh((d + z_1 + h_A - z)/\xi)] \qquad (4.12)$$

Plots of F_{int} vs d for different N_h are shown in Figure 5 using reduced variables. Note that for long homopolymer chains ($N_h > N_h^*$) the interaction is attractive at large distances; the critical number of links per homopolymer chain is

$$N_h^* \approx 2(\xi^*/a)^2 \approx 1.26(a N_A^2/h_A)^{2/3} \qquad (4.13)$$

For $N_h < N_h^*$ the interaction is always repulsive. These features qualitatively coincide with those obtained in section 3 for the interaction of spherical micelles. A weak attraction between two brushes due to partial penetration of long homopolymer chains into the middle region was also predicted in ref 45.

Note that for short homopolymer chains, $N_h \ll N_h^*$, the thickness of the interpenetration layer $\xi(N_h)$ is much larger than both ξ^* (corresponding to $N_h \to \infty$) and the Gaussian size of the h-chains, $a N_h^{0.5}$. Therefore the gradient terms in eqs 4.5 and 4.7 could be omitted (for $N_h \ll N_h^*$); also these equations become asymptotically exact. Moreover, the minimization of the interaction energy could be now performed analytically, the result being

$$F_{\mathrm{int}}(d) = F_{\mathrm{int}}(0)[1 - (d/d^*)^2 + 2(d/d^*)\ln(d/d^*)], \qquad d < d^* \qquad (4.14)$$

where

$$F_{\mathrm{int}}(0) = (8a^2/\pi^2) N_A^2/(h_A N_h^2)$$

$$d^* = (16/\pi^2)\, a^2 N_A^2/(h_A N_h) \approx 1.6\xi^*(N_h^*/N_h) \qquad (4.15)$$

Note that condition 2.6 is still assumed: eqs 4.14 and 4.15 are valid in the intermediate regime $N_h^* \gg N_h \gg N/\alpha^{1/3}$. The exact dependence (4.14) is compared with the approximate one obtained using trial functions (see eq 4.12) in Figure 5d.

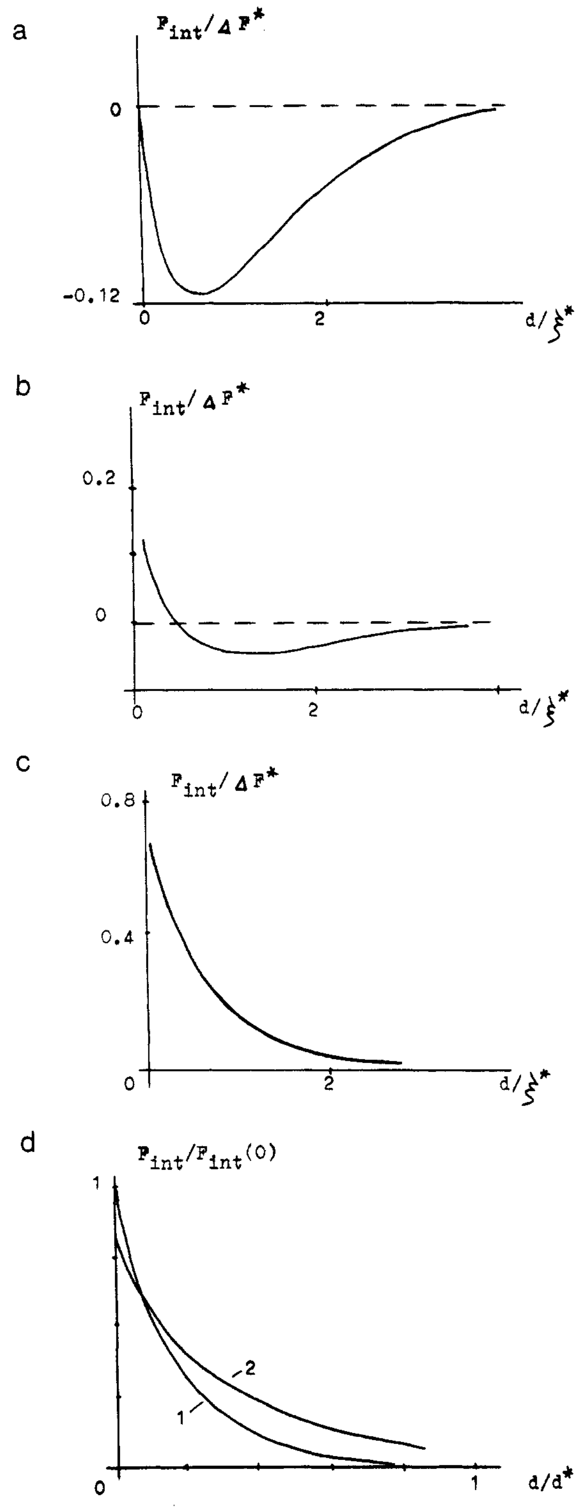

Figure 5. Dependence of the reduced interaction energy between two lamellar micelles, $F_{\mathrm{int}}/\Delta F^*$, on the reduced distance between them, d/ξ^*, for different molecular weights of homopolymer chains: $N_h/N_h^* = 1.54$ (a); $N_h/N_h^* = 1.23$ (b); $N_h/N_h^* = 0.82$ (c). Asymptotically exact (for $N_h \ll N_h^*$) plot of $F_{\mathrm{int}}/F_{\mathrm{int}}(0)$ vs d/d^*, curve 1; approximation obtained using trial functions (4.12), curve 2 (d).

The interaction energy between two spheres or cylinders could be reduced to that for the lamellar case using the Derjaguin approximation,[33] which is valid since the interpenetration layer thickness is much smaller than the micelle's diameter D. In all cases we have found attraction + short-scale repulsion for long homopolymer chains and pure repulsion for the short ones. The critical homopolymer molecular weight is always determined by eq 4.13; however, the shell thickness, h_A, depends on the micellar geometry. Substituting the particular expressions for h_A (which could be easily obtained from, e.g., the results of ref 17) into eq 4.13, we get

$$N_h{}^* = 1.03(1-f)^{2/3}N(\chi N)^{-1/9} \quad \text{for lamellar micelles} \tag{4.16a}$$

$$N_h{}^* = 0.68(1-f)^{4/3}N(\chi N)^{-1/9}f^{-1/9}(1-f^{0.5})^{-2/3} \times (1.645 - \ln(f))^{2/9} \quad \text{for cylindrical micelles} \tag{4.16b}$$

$$N_h{}^* = 0.66(1-f)^{4/3}N(\chi N)^{-1/9}f^{-2/9}(1-f^{1/3})^{-2/3} \times (1.74 - f^{1/3})^{2/9} \quad \text{for spherical micelles} \tag{4.16c}$$

5. Phase Diagram in the Strong Segregation Limit (SSL)

Minor B-Blocks. Using the results obtained in the previous section, we are in a position now to predict (at least qualitatively) the phase behavior of a copolymer–homopolymer mixture in the SSL (specified by condition 4.1). We will also use condition 4.2. Let us consider first the case of not very long homopolymer chains, $N_h < N_h{}^*$, i.e.

$$N(\chi N)^{-1/3} \ll N_h \lesssim N(\chi N)^{-1/9} \tag{5.1}$$

The critical micelle concentration (cmc) is determined now by eqs 4.3 and 2.2. Note that ϕ_{cmc} is exponentially small in the SSL. The volume fraction of micelles ϕ_{mic} is nearly equal to $\phi - \phi_{cmc}$ (since the micelles are *dry*), or $\phi_{mic} \approx \phi$ if we neglect ϕ_{cmc}. The micellar geometry is primarily determined by the composition of the copolymer chains, f (see section 4), and not by the total fraction of B-links, $f\phi$.

Note that *spherical* micelles are essentially hard spheres (since their interaction is purely repulsive within the range ξ, which is much shorter than the micelle's diameter). Thus we should expect an ordering (gas–crystal) transition (freezing of these spheres into a fcc superlattice) at $\phi \approx$ 0.5–0.55.[34] *Cylindrical* micelles are similar to long semirigid persistent macromolecules with diameter $D \sim aN^{0.5}(\chi N)^{1/6}$ and persistence length $l \sim a^4N^2\chi$.[35] Thus nematic ordering of these cylinders is expected at[38]

$$\phi \sim D/l \sim a^{-3}N^{-0.5}(\chi N)^{-5/6} \ll 1 \tag{5.2}$$

As block copolymer volume fraction is further increased, the cylinders should form a triangular superlattice. One should expect this transition at $\phi \sim 0.5$ (as for spheres; I am not aware of any detailed analytical theory or simulations concerning this type of transition). Translational ordering of lamellar micelles should also occur at $\phi \sim 0.5$.

Let us consider now the case of long homopolymer chains

$$N_h > N_h{}^* \sim N(\chi N)^{-1/9} \tag{5.3}$$

In this regime micelles attract each other and therefore they should readily separate and form a copolymer-rich superstructure, the copolymer volume fraction in another ("homopolymer") phase being extremely (exponentially) small (compare with section 3). The superstructure of the spherical (cylindrical) morphology is shown schematically in Figure 6. At equilibrium, copolymer domains should prefer to retain their symmetric spherical (cylindrical) shape, thus leaving gaps (interstitial regions) filled by homopolymer chains. The reason is that the energy of the copolymer–homopolymer interfaces (see Figure 6) is much lower than the energy of the additional elongation of the copolymer chains that should be produced to fill the gaps by the copolymer. The volume fraction of gaps in a closed-packed spherical superstructure is $\phi_{hs} = 1 - \pi(2^{0.5}/6) \approx 0.26$; in the hexagonal cylindrical superstructure $\phi_{hc} = 1 - (\pi/2)3^{0.5} \approx 0.09$. Obviously, the solubility of homopolymer in these (spherical, cylindrical) superstructures is limited by ϕ_{hs} and ϕ_{hc} correspondingly; moreover, the homopolymer is not soluable at all in the lamellar copolymer superstructure since there are no gaps in the lamellar case (more precisely, the homopolymer volume fraction in the lamellar phase should be exponentially small if conditions 4.1 and 4.2 are satisfied).

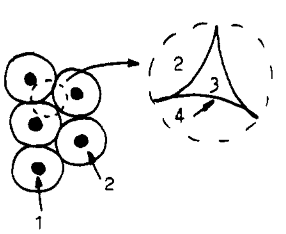

Figure 6. Spherical (cylindrical) micelles ordered in a close-packed superstructure: (1) B-core; (2) A-corona; (3) interstitial region filled by homopolymer chains; (4) interface between stretched A-blocks and A-homopolymers.

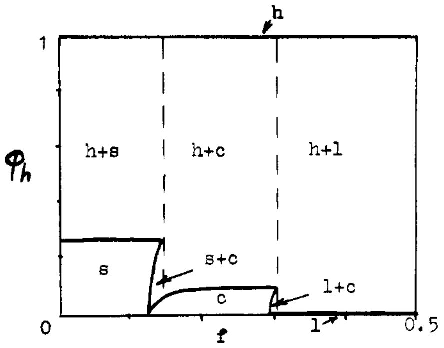

Figure 7. Phase diagram of the copolymer–homopolymer blend for the case of long homopolymer chains, $N_h > N_h{}^*$; l = lamellar phase, c = cylindrical phase, s = spherical phase, and h = homopolymer phase.

The phase diagram of the system (for $f < 0.5$) is shown schematically in Figure 7. Note that as homopolymer volume fraction increases (starting from zero), the phase equilibria between the cylindrical and lamellar morphologies shift to larger f. The same is true for the spherical–cylindrical transition. This is simply because for larger ϕ_h homopolymer is more effective in filling the gaps, thus decreasing the free energy of the cylindrical phase (but not the lamellar phase). For the spherical morphology the gaps are somewhat wider and so the effect of homopolymer is more pronounced than for the cylindrical case.

Major B-Blocks. For $f > 0.5$ (B-blocks longer than A-blocks) we should consider the possibility of inverse morphologies with homopolymer *inside* the cylindrical or spherical domains.[39] Again the energy of the interfaces between the A-blocks and A-homopolymers is much less important than the "elastic" energy of elongation of the blocks. To minimize this "elastic" energy, homopolymer chains should occupy the central regions of the spheres or cylinders (see Figure 8b). The free energies of the corresponding lamellar, cylindrical, and spherical structures were calculated following the approach of ref 17 (in particular, using the "spherical" approximation for the Wigner–Seitz cell and also assuming that the free ends of the B-blocks are localized at the outer surface of the cell). The particular expressions for the free energies are rather lengthy; we omit them here.

The calculated phase diagram in f (composition)–ϕ_h (homopolymer volume fraction) variables is shown in Figure 9. Note that addition of A-homopolymer increases the mean volume fraction of *minor* A-component. Therefore one might expect that homopolymer will induce a

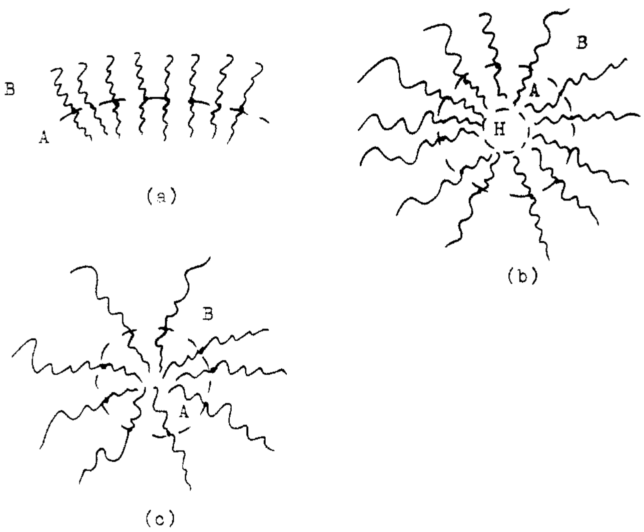

Figure 8. One half-lamellar copolymer sheet (a); the cylindrical (spherical) micelle with a hole (H) inside obtained as a result of bending of the sheet (the hole might be filled by homopolymer chains) (b); the pure copolymer micelle (without a hole) (c).

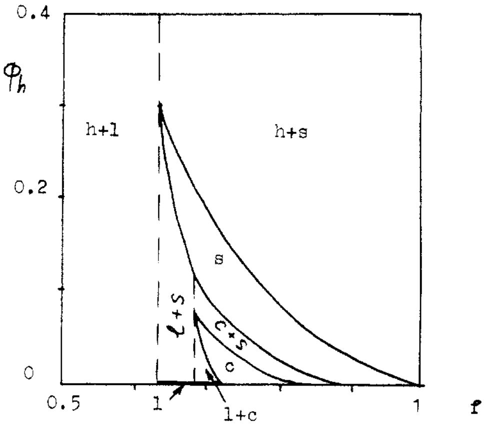

Figure 9. Phase diagram of the copolymer (AB)–homopolymer (A) system for the case $f > 0.5$ (major B-blocks). The phases are denoted as in Figure 7.

transition from spherical to cylindrical or from cylindrical to lamellar morphology. The phase diagram in Figure 9 shows, however, that the real situation is quite the opposite: the effect of homopolymer is revealed as a shift in the lamellar–cylindrical and cylindrical–spherical morphological transitions to *lower* values of f, corresponding to relatively longer A-blocks. Note also that for $f \lesssim 0.685$ the cylindrical morphology disappears altogether, but the spherical morphology still exists (in some range of ϕ_h) for $0.63 < f < 0.685$.

For example, for $f = 0.65$ pure block copolymer melt should have a lamellar structure; however, after addition of a small amount of homopolymer the system should readily separate into two macrophases (lamellar and spherical), the homopolymer being "captured" by the spherical phase (the concentration of homopolymer in the lamellar phase is extremely small). As ϕ_h increases, the relative volume of the spherical phase also increases (linearly in ϕ_h); at $\phi_h = 0.22$ the lamellar phase disappears. A one-phase region of spherical morphology corresponds to $0.22 \le \phi_h \le 0.27$; for $\phi_h > 0.27$ the system should again separate into two macrophases, one being pure homopolymer and the other microphase separated. For comparison, the following phase behavior is predicted for $f = 0.75$: $0 < \phi_h < 0.025$ corresponds to one macrophase with cylindrical morphology, $0.025 < \phi_h < 0.055$ corresponds to two macrophases (cylindrical and spherical), $0.055 < \phi_h < 0.13$ corresponds to one spherical macrophase, and $0.13 < \phi_h < 1$ again corresponds to two macrophases (spherical and pure homopolymer).

Now let us try to answer the question of why homopolymer stabilizes the cylindrical and particularly the spherical morphologies. Let us consider one half-lamellar sheet formed by not very asymmetric copolymer chains. If we bend the sheet in one (or two) direction(s), we will get eventually a cylinder (or sphere) with a hole inside (Figure 8a,b). For high enough bending curvature the hole should collapse to the central point so that we get a cylindrical (spherical) micelle similar to that in a pure block copolymer melt. Note that if we have a possibility to fill the hole (see Figure 8b) by A-homopolymer, then the surface energy of the hole would reduce appreciably and could be neglected. For this case it is natural to assume that (in some range of compositions) the curved sheet with a hole would be more favorable than the plain sheet or extremely curved sheet (see Figure 8c). In fact, using the results of ref 42, it is easy to prove that it is always the case for nearly symmetric block copolymers, bending in two directions (giving rise to the spherical morphology) being the most favorable. Therefore homopolymer being added to a microphase-separated block copolymer system could induce transitions from lamellar to cylindrical and spherical structures where homopolymer chains fill the central regions of the corresponding domains.

6. Discussion

In this paper we have shown that an AB-copolymer + A-homopolymer blend system in the strong segregation limit reveals complex phase behavior resulting from an interplay of possible macro- and microphase separations. This general result is in agreement with that obtained previously by Noolandi et al.[9–11] for the lamellar morphology in the weak segregation limit. Another general conclusion is that (at least for the case of A-blocks longer than B-blocks) an increase of homopolymer molecular weight, M_h, could induce macrophase separation of the system, one of the phases being almost pure homopolymer. In other words, the solubility of the homopolymer in a microphase-separated block copolymer structure drops sharply as M_h increases. This prediction is also in agreement with a previous result.[10]

The phase behavior of the blend in the strong segregation limit is primarily determined by the interaction of the copolymer micelles (of any geometry). We predict that this interaction is repulsive for shorter homopolymer chains, $N_h < N_h^*$, and attractive for $N_h > N_h^*$, where the critical number of links per homopolymer, N_h^*, depends on copolymer molecular weight, its composition, and also the χ-parameter (see eqs 4.16). The repulsive interaction between spherical micelles was also predicted by Leibler and Pincus.[13] Their results are not in disagreement with the present ones since at least numerical examples in ref 13 correspond to $N_h < N_h^*$. The same ($N_h < N_h^*$) is true for the PS·PI + hPS blends studied experimentally in ref 7 (apart from the only system with the largest homopolymer molecular weight, $M_h \approx 30 \times 10^3$). So it is not surprising that macroseparation of the blends (which is predicted in the region of attractive interaction of micelles) was not observed in ref 7.

On the other hand, the observed[7] morphological changes induced by an increase of the homopolymer volume fraction, ϕ_h (lamellar → OBDD → cylindrical → spherical structure), are in complete disagreement with the present theoretical results. Here we predict that (in real SSL) changes of ϕ_h do not induce and morphological transitions at all. A possible explanation of this disagreement is that the real systems studied experimentally were not in a completely equilibrium state since relaxation times of copolymer systems containing micelles should be extremely high.[27,43] Therefore the observed morphology should be controlled by dynamics, and thus formation of just spherical micelles is predicted even for nearly symmetric block copolymer provided that the mean copolymer volume fraction is small enough.[27]

We also predict that long enough homopolymer chains (see inequality (4.2)) which are dissolved in a cylindrical or spherical block copolymer structure should be separated from A-coronas of cylinders (or spheres) and fill the interstitial regions between them. This prediction is in agreement with SANS and SAXS observations for a PS-PB + hPS blend with a spherical morphology[8] (the idea of incompatibility between stretched PS blocks and unstretched PS homopolymers was also discussed in ref 5).

In the last part of the paper we have considered the phase behavior of AB + hA blend with A-blocks shorter than B-blocks. We have shown that an addition of homopolymer to the blend could induce lamellar → cylindrical → spherical morphological transitions. Note that from the purely geometrical point of view one should expect the opposite transitions (spherical → cylindrical → lamellar) since an increase of the homopolymer volume fraction results in a swelling of the inner parts (cores) of the domains. Thus these blends present another example where simple geometrical arguments (see, e.g., ref 7) are not valid.

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References and Notes

(1) Meier, D. J., Ed. *Block Copolymers: Science and Technology*; Harwood Academic Publishers: New York, 1983.
(2) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 267.
(3) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(4) Roe, R.-J.; Zin, W. C. *Macromolecules* **1984**, *17*, 189.
(5) Hashimoto, T.; Tanaka, H.; Hasegawa, H. *Macromolecules* **1990**, *23*, 4378.
(6) Tanaka, H.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1991**, *24*, 240.
(7) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *J. Chem. Phys.* **1991**, *95*, 9367.
(8) Berney, C. V.; Cheng, P.-L.; Cohen, R. E. *Macromolecules* **1988**, *21*, 2235.
(9) Hong, K. M.; Noolandi, J. *Macromolecules* **1983**, *16*, 1083.
(10) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 2486.
(11) Noolandi, J. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1147.
(12) Olvera de la Cruz, M.; Sanchez, I. C. *Macromolecules* **1987**, *20*, 440.
(13) Leibler, L.; Pincus, P. *Macromolecules* **1984**, *17*, 2922.
(14) Mayes, A. M.; Olvera de la Cruz, M. *Macromolecules* **1988**, *21*, 2543.
(15) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(16) The strong restriction $f \ll 1/(\chi N_B)$ will be adopted in the current and the next sections.
(17) Semenov, A. N. *Sov. Phys. JETP (Engl. Transl.)* **1985**, *61*, 733.
(18) De Gennes, P.-G. *J. Phys.* **1970**, *31*, 235.
(19) Semenov, A. N. *Macromolecules* **1989**, *22*, 2849.
(20) This type of interaction was predicted in ref 13.
(21) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(22) The term $1 - \bar{\phi}_h$ is included formally in order to satisfy the conditions $F_{id} = 0$ and $\partial F_{id}/\partial\bar{\phi}_h = 0$ for $\phi_h = 1$; thus contributions to the effective free energy from the disordered macrophase (where $\bar{\phi}_h \approx 1$) are avoided.
(23) The lion's share of ϕ_1 corresponds to free homopolymer chains (not attached to micelles).
(24) Note that the number of chains per micelle is still nearly constant in the region of interest since interactions give only a small correction to the self-energy of a micelle, F_{sph} (see eq 2.3).
(25) So, in the following f will be regarded as a numerical factor; thus the dependence on f will not be taken into account in the order-of-magnitude estimates.
(26) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(27) Semenov, A. N. *Macromolecules* **1992**, *25*, 4967.
(28) Ball, R. C.; Marko, J. F.; Milner, S. T.; Witten, T. A. *Macromolecules* **1991**, *24*, 693.
(29) Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L. *Macromolecules* **1990**, *23*, 132.
(30) Milner, S. T.; Wang, Z. G.; Witten, T. A. *Macromolecules* **1989**, *22*, 489.
(31) The incompressibility condition $\phi_h(z) = 1 - \phi_A(z)$ is also used.
(32) Witten, T. A.; Leibler, L.; Pincus, P. *Macromolecules* **1990**, *23*, 824.
(33) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: San Diego, CA, 1989.
(34) Hoover, W. G.; Ree, F. H. *J. Chem. Phys.* **1968**, *49*, 3609.
(35) Persistence length for a cylindrical micelle could be easily obtained using the approach outlined in refs 36 and 37.
(36) Milner, S. T.; Witten, T. A. *J. Phys.* **1988**, *49*, 1951.
(37) Fredrickson, G. H. *Macromolecules* **1991**, *24*, 3456.
(38) Khokhlov, A. R.; Semenov, A. N. *Physica A* **1981**, *108*, 645.
(39) Periodic bicontinuous double diamond (OBDD)[40,41] and similar structures that might be more favorable in some subregions[42] are not considered here.
(40) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, D. C.; Handlin, D. L., Jr.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197.
(41) Hasegawa, H.; Tanaka, H.; Yamasaki, K.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651.
(42) Ajdari, A.; Leibler, L. *Macromolecules* **1991**, *24*, 6803.
(43) Johner, A.; Joanny, J. F. *Macromolecules* **1990**, *24*, 5299.
(44) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(45) Gast, A. P.; Leibler, L. *Macromolecules* **1986**, *19*, 686.