I. Introduction

Diblock copolymers often form micelles in a selective solvent. The assembly of these macromolecules is very similar to the micellization of low molecular weight surfactants in water or oil solutions below the critical micellar concentration (cmc), only isolated chains are observed, while above this concentration almost all the chains belong to micelles. Single chains in solution adopt a tadpole morphology, with a collapsed headblock and a swollen tail. The collapsed heads are the driving force for micellization: they greatly reduce the number of monomers exposed to the poor solvent by sharing a common space with other collapsed blocks in the core of the micelle. The onset of micellization requires a large enough concentration to overcome the entropic effects that favor dispersion. For strongly selective solvents and large molecular weights of the block in a poor solvent, the critical micellar concentrations can be very low, and, in practice, micelles are observed at all concentrations. However, by reducing the solvent selectivity or the size of the collapsed block or by adding a second solvent which plasticizes the insoluble blocks, one can bring the critical micellar concentrations in the accessible experimental range. Of experimental interest are also the sizes and aggregation numbers of the micelles for which a number of theoretical predictions have been made. In the case where the molecules are very asymmetric, the number of molecules in the micelle is predicted to increase almost linearly with the number of monomers $N_A$ in the tadpole head and to decrease weakly with the number of monomers $N_B$ in the tadpole tail ($p = N_A^{0.5}/(\log N_B)^{0.5}$). This is generally observed in experiments and has even been quantitatively checked for a number of cases.

The size, aggregation number, critical micellar concentration, and other quantities which characterize a given micellar system can, in principle, be tuned by carefully tailoring the architecture and chemical nature of the macromolecules. In many experimental situations, this tuning is achieved by simply mixing molecules at different types. The mixing process is, however, not only a way to finely control the parameters of the system but may, in some cases, be necessary to introduce a new, specific property: fluorescence, detergency, etc.

The formation of mixed micelles of diblock copolymers from a bidisperse solution has been previously addressed by Shim et al. who considered the case where the copolymers have soluble blocks of the same chemical nature but different lengths and insoluble blocks of the same length but a different chemical nature. By varying the relevant parameters of the system (chain length, interaction between the chains in the core), these authors showed that it is possible to change the critical micellar concentration of the mixed micelles. They further showed that, depending on the concentration ratios of the two species in the solution, the mixed micelles can either form directly upon increasing the total concentration or be assembled in a two-stage process where micelles of one of the species are first created, and then polymers of the other species are progressively incorporated in the already formed micelles.

In this paper we present an extension of the study of ref 9 to the case where the soluble and the insoluble blocks of the two species have the same chemical nature but different chain lengths. More precisely, we consider A−B and C−D diblock copolymers, A being chemically identical to C and B chemically identical to D, but where all the chain lengths are different. By considering such mixtures, we hope not only to address on a more general basis the formation of mixed micelles but also to gain some insight into the behavior of mixtures of simple surfactants and diblock copolymers in the limit where the molecular weight of one of the copolymers is much smaller than the other one. Recent experimental results seem to show in certain conditions a bimodal distribution of the micellar sizes in mixtures of simple surfactants and triblock copolymers for which we give a qualitative explanation. Our study also provides a basis to understand polymers with a more complex architecture, such as polysoaps or multiblock copolymers.

The paper is organized as follows. In the next section we review the thermodynamics of the micellization of monodisperse solutions of diblock copolymers. In section III we present a model for the mixed micelles and analyze two limiting cases: the case where both coronas are much larger than the core sizes and the case where one of the coronas is much larger than the core size but the corona of the other species is much smaller than the core size. In the last section we summarize our...
main results and discuss experiments for which our approach is relevant.

II. Micellization in a Monodisperse Copolymer Solution

II.1. General Considerations. In this section we review the thermodynamics of micellization, which can first be described at a general, model-independent level, by recognizing that for large macromolecules aggregation sets in at low concentrations and that the aggregation numbers are large. Ignoring the interactions between micelles, it is then possible to write the free-energy density of the system as

\[ F = c_1 \log(c_1/e) + F_1 + \sum_{p=2}^{\infty} c_p \log(c_p/e) + F_p \]  

(1)

where \( F_p \) and \( c_p \) are respectively the free energy and concentration (number per unit volume) of micelles with \( p \) molecules. The free energies are measured in units where \( k_B T = 1 \). For clarity the energy has been split into the contributions of single chains \( p = 1 \) and of aggregates \( p \geq 2 \). The volume fraction of micelles with \( p \) molecules can be found by minimizing the free-energy density (1) with respect to \( c_p \), under the constraint of conservation of the total chain concentration \( \phi \)

\[ c_1 + \sum_{p=2}^{\infty} p c_p = \phi \]  

(2)

One finds

\[ c_1 = \exp(-F_1 + \mu); \quad c_p = \exp(-F_p + \mu p) \]  

(3)

where \( \mu \) is the chemical potential associated with the conservation of chain number. Equation 2 can then be rewritten as

\[ 1 + \sum_{p=2}^{\infty} p \exp(-\Omega_p) = \exp(F_1 + \log \phi - \mu) \]  

(4)

with the grand potential \( \Omega_p \) defined as \( \Omega_p = F_p - F_1 - \mu(p - 1) \). The typical variation of the grand potential of a spherical micelle is sketched in Figure 1. At low concentrations \( \Omega \) is everywhere larger than unity. This implies that the distribution \( c_p \) is strongly peaked around \( p = 1 \), and only single chains are present in the solution. The chemical potential can be written in this limit as

\[ \mu = F_1 + \log \phi \]  

(5)

When the chain volume fraction \( \phi \) is increased, the chemical potential increases and a minimum appears in \( \Omega_p \) at an aggregation number \( p = p_p \) larger than unity. Correspondingly, the distribution \( c_p \) develops a maximum around \( p_p \), indicating the presence of a finite concentration of micelles of aggregation number close to \( p \). In the following we show that, to a good approximation, the aggregation number and the critical micellar concentration can be determined from the two conditions:

\[ \Omega_p = \Omega_p/\phi = 0 \]  

(6)

Since the distribution is strongly peaked around \( p \), we can calculate the sum over the aggregation number in the conservation equation (2) using a steepest descent approximation and then solve for the two concentrations \( c_1 \) and \( c_p \). By defining the critical micellar concentration \( \phi_{cmc} \) as

\[ \phi_{cmc} = (p \Delta)^{1/(1-p)} \exp \left\{ - \frac{p F_1 - F_p}{p - 1} \right\} \]  

(7)

with \( \Delta^2 = 2\pi/\eta^2 F_1/p^2 |_{p=p_p} \), the concentrations of unimers and micelles are determined from

\[ \frac{c_1}{\phi_{cmc}} + \frac{c_p}{\phi_{cmc}} = \frac{\phi}{\phi_{cmc}} \]  

(8)

Well below the cmc almost no aggregate is formed and all the chains are isolated. Above the cmc almost all the chains belong to micelles:

\[ \begin{cases} \phi \ll \phi_{cmc} & c_1 \approx \phi; \\ \phi \approx \phi_{cmc} & c_1 \approx \phi_{cmc} \left[ \frac{\phi}{\phi_{cmc}} \right]^{1/p}; \quad c_2 \approx \phi/p \end{cases} \]  

(9)

Note that, due to the finite width in the micelle size distribution \( c_p \), the concentration of micelles with aggregation number close to \( p \) is \( c_p \Delta \) rather than \( c_p \), the value of the distribution at the peak. From eqs 9 and 3 we can now calculate the chemical potential below and above the cmc:

\[ \begin{cases} \phi \ll \phi_{cmc} & \mu = F_1 + \log \phi \\ \phi \gg \phi_{cmc} & \mu = F_1 + \frac{p-1}{p} \log \phi_{cmc} + \frac{1}{p} \log \phi \end{cases} \]  

(10)

The chemical potential at the cmc is given by \( \bar{\mu} = F_1 + \log \phi_{cmc} \) and coincides with the chemical potential at the cmc obtained from eq 6, up to a small correction of order \( \sim (\log \Delta_p)/p \). Above the cmc, the chemical potential (and
thus the aggregation number) varies slowly with the
concentration and can for practical purposes be consid-
ered as constant: $\mu (\phi \geq \phi_{mc}) = \mu (\phi_{mc})$.

II.2. Models for the Micellar Assembly. The
actual calculation of the chemical potential and ag-
gregation numbers from this description requires a
model for the micellar assembly, that allows the
determination of the free energies $F_p$. Hereafter, we
study asymmetric diblock copolymer chains, in the asymmetry
range $N_A < N_B^{2/3}$ ($N_A$ and $N_B$ being respectively the polymerization
indices of the collapsed and swollen blocks) where spherical micelles are formed. 11 Throughout the paper, we assume that the insoluble block of the copolymer is in so poor a solvent that it has a tendency to form molten regions where neither the solvent nor the other block penetrates. Micelle formation in a monodisperse copolymer solution has been studied in this limit in refs 4 and 5; we summarize here the essential results. Figure 1 depicts a representation of the structure of the micelle. The incompressibility of the core leads to a simple relationship between the number $p$ of chains in the micelle and the core radius: $R = (3pN_A/4\pi)^{1/3}b$, where $b$ is the size of one monomer. For simplicity we choose in the following a unit length where $b = 1$ and we assume that monomers A and B have equal sizes. The chains in the outer corona form a starlike object, a configuration first described by Daoud and Cotton. 12 In the corona the chains follow locally the statistics of a semiflexible polymer solution. They can thus be described by a local, position-dependent correlation length. Pictorially one associates a blob with the correlation length and describes the external shell as a succession of blobs of increasing size. At a
given distance $r$ from the center of the micelle (with $r > R$), there are $p$ blobs occupying a surface $4\pi r^2$. This gives a blob size which varies as $\xi(r) = r^{p-1/2}$. The external radius of the micelle $R + h$ can then be obtained by the conservation constraint $pN_A = 4\pi\int_0^{R+h} c(r) r^2 dr$, where the monomer concentration in the corona decays as $c(r) = p^{2/3} r^{2/3}$. When the corona is much larger than the core, this gives $R + h = N_b^{2/3} p^{1/3}$. The chains in the corona are thus extended by a factor $p^{2/3}$ with respect to their free radius in the solution. The free energy associated with these stretched configurations can be calculated by integrating the local free-energy density of an equivalent semiflexible solution $f_o = 4\pi k_N \gamma_k T B^{1/3} b^{1/3} + k_T r^{2/3} \log (1 + h/R)$. The other important contribution to the free energy of the micelle is the interfacial energy between the core and the solvent: $f_s = 4\pi R^2 \gamma = \gamma c N_A^{2/3} p^{2/3}$, where $\gamma$ is the relevant interfacial tension and $c$ is the numerical constant $c = (36\pi r)^{1/3}$. The potential $\Omega_p$ can now be written as

$$\Omega_p = f_o + f_s - \mu p$$

(11)

We show below that the contribution $-F_1 + \mu$ is
negligible.

In the case where the corona is much larger than the
core, the conditions (6) lead to the following values for the
aggregation number and the chemical potential

$$\mu = \frac{2(2c)^{1/6}}{A} N_A^{4/3} N_B^{2/3}$$

where $A = \log (1 + h/R)$ is in a first approximation taken
as a constant, evaluated at $p = p_c$.

When the corona is much smaller than the core
radius, the swollen tails form a planar grafted layer also

known as a brush, with grafting density $\sigma = \rho(4\pi R^2)$. The
osmotic contribution to the free energy can then be expanded in powers of $h/R$, leading to $f_c = p^{2/3} (h/R) [1 - \xi_1 h/R + \xi_2 (h/R)^2]$. The numerical constants are given by $\xi_1 = 5/6$ and $\xi_2 = 25/26$, and the brush thickness for a flat layer is $h_b \approx N_b^{2/3}$. Notice that the expansion coefficients for the mean-field version of a brush in a curved geometry have been previously calculated in refs 13 and 14. Our expansion, extracted from a scaling form for the free energy, gives obviously different coefficients but does preserve the correct scaling forms for a brush in good solvent.

In this limit the aggregation number and chemical
potential, calculated from (6) are given by

$$p = \left( \frac{6c}{5\xi N_B} \right)^{18/11} N_A^{2} \mu; \quad \bar{\mu} = 11 \left( \frac{c^{3/5} \xi}{6 N_B} \right)^{6/11}$$

(13)

where $\xi$ is another numerical factor; $\xi = 242/3 \pi^{4/3}$.

The leading neglected contribution to the potential
would introduce a relative correction of the order of $1/p$, negligible for typical aggregation numbers. We
have also neglected the stretching contribution from the
hydrophobic blocks in the core. In the asymmetry range
where the corona is much larger than the core, this
contribution, on the order of $R^2/N_A$, is negligible. For
$N_A^{1/3} < N_B < N_A^{1/2}$, the size of the corona is smaller than
the size of the core. In this range, it can also be checked that the elastic contribution is still much
smaller than the energy of the brush.

III. Mixed Micelles

In this section we consider mixtures of diblock copolymers
with different polymerization indices. For the sake of
simplicity, we study the formation of mixed micelles in
these mixtures in two different limits. First, we
consider diblock copolymers with large tails, in the
limit where the sizes of both tails are much larger
than the size of the core of the micelle. We refer to this
case as a copolymer mixture. Then we study mixtures
of diblock copolymers where the tails of one of the species
are much larger than the size of the core, the tail of the
other species being smaller than the size of the core.
Since we hope to mimic in this limit the behavior of
mixtures of macromolecular diblocks and small surfac-
tant molecules, we refer to this case as a copolymer–
surfactant mixture.

In both cases the formalism for studying mixed
micelization is a straightforward extension of that
presented in the previous section. There are now two
species in the solution, and we need, in general, to
describe the content of a micelle by the number of short
and long chains, respectively $p_s$ and $p_l$. The aggregation
number of the micelle is thus $p = p_s + p_l$, and the relative
composition of short chains in the micelle is $x_s = p_s/(p_s + p_l)$. There are also two chemical potentials
associated with the conservation of $p_s$ and $\phi_s$, the total
concentrations of chains of the two species. Within
the same approximations as above, we can write the free energy

$$\Omega_p = f_o (p_s, p_l) + f_s (p_s, p_l) - \mu_s p_s - \mu_l p_l$$

(14)

and derive the aggregation numbers and the chemical
potentials at the critical micellar concentration from the
conditions
\[
\Omega_f = \frac{\partial \Omega_p}{\partial \rho_s} = \frac{\partial \Omega_p}{\partial \rho_l} = 0
\] (15)

Note that there are four unknown quantities to be determined (two aggregation numbers and two chemical potentials) from three conditions. This implies that in a bidisperse copolymer solution the micellization process is described by a line \( \mu_s = \mu_s(\mu_l) \) in the \([\mu_s, \mu_l] \) phase diagram (or, equivalently, by a line \( \phi_s = \phi_s(\phi_l) \) in the \([\phi_s, \phi_l] \) phase diagram).

### III.1. Copolymer Mixtures

When the soluble blocks of both chains are larger than the core size of the micelle, one can easily describe the structure of the corona by a concentric two-shell picture, with radii \( R + h_l \) and \( R + h_s \) as shown on Figure 2a. The largest tails extend from the core to the micelle radius \( R + h_s \), whereas the smallest tail extends from the core to the radius of the first shell \( R + h_l \). The osmotic contribution of the corona is written as

\[
f_0 = (A - B)p_l^{2/3} + B(p_s + p_l)^{3/2}
\] (16)

with \( A = \log(1 + h/R) \) and \( B = \log(1 + h_s/R) \). The sizes of the coronas are given as above by \( h_s = N_{bg}^{1/4}p_l^{1/5} \) and \( h_l = N_{bg}^{1/4}(p_s + p_l)^{1/5} \) where \( N_{bg} \) and \( N_{bs} \) are the degrees of polymerization of the soluble blocks of the large and small copolymers, respectively. As before we consider in a first approximation \( A \) and \( B \) as constants, calculated from the aggregation numbers at the cmc.

The interfacial tension contribution reads

\[
f_s = c_l(N_p p_l + N_s p_s)^{2/3}
\] (17)

\( N_s \) and \( N_l \) being respectively the number of monomers of the collapsed blocks of the chains with the shortest and longest tails. For each of the copolymer species we define the reference aggregation numbers \( p_s^* \) and \( p_l^* \) and the reference chemical potentials \( \mu_s^* \) and \( \mu_l^* \) as the values obtained at the cmc for the pure solutions. They are obtained from eq 12 with \( A \) and \( N_s \) for the copolymers with the large tails and \( B \) and \( N_l \) for copolymers with the small tails.

The precise determination of the critical concentration for the formation of mixed micelles and of the aggregation numbers can only be achieved by a numerical solution of eq 15. However, a global picture can be drawn from the study of a few particular paths in the chemical potential (or concentration) phase diagram. Of special interest are the situation where micelles of the large copolymers are already formed in the solution, and one increases progressively the concentration of the small copolymers, or the situation where a few large copolymers are added to a solution of small copolymers.

#### III.1. Incorporation of Small Copolymers in a Large Copolymer Micelle

We first assume that micelles of the large copolymers have already formed in the solution. The chemical potential of the large copolymer is \( \mu_l^* \). We now add a small amount of short copolymers and study the conditions under which these molecules can form mixed micelles, by assembling into the micelles of the large diblock copolymer. If the small copolymer concentration is very low, no mixed micelles are formed; the critical micellar concentration is that of a pure large copolymer solution. Above a critical concentration of short chains or equivalently above a critical value \( \mu_s^* \) of the chemical potential of the short chains, the short copolymers are incorporated into the micelles.

Just above the threshold, \( \mu_s = \mu_s^* + \delta \mu_s \), we look for the cmc by expanding the equilibrium equations 15,

\[
p_l = p_l^* + \delta p_l, \quad p_s = \delta p_s, \quad \mu_l = \mu_l^* + \delta \mu_l.
\]

The zeroth-order term in the expansion gives the critical value of the chemical potential for mixed micelle formation

\[
\mu_s^* = \left( \frac{2}{3} \gamma \right)^{1/3} (AN_s)^{2/3} (b + n) = \left( \frac{3}{5} b + n \right) \mu_s^*. \tag{18}
\]

We have introduced here two parameters that characterize the asymmetry in molecular weights of the two copolymers: \( n = N_s/N_l \) is the ratio of the molecular weights of the insoluble parts and \( b = B/A \) is related to the difference in the heights of the corona and characterizes the asymmetry in the soluble blocks of the two copolymers. In the derivation of the free energy, we have implicitly assumed that \( b < 1 \); note also that, in principle, \( b \) varies with the aggregation numbers of the short and large blocks; this variation is very smooth, and \( b \) is considered here as a constant.

The critical chemical potential for mixed micelle formation is meaningful only if it is smaller than the chemical potential at the cmc of the pure short polymers. If it is larger than this cmc value, the short copolymer forms micelles before being incorporated into the large copolymer micelles. The chemical potential of the short copolymer then saturates at the cmc value, and no mixed micelles can form. This condition for the existence of mixed micelles reads

\[
\frac{3}{2} b + n < \frac{5}{2} (bn)^{2/5}
\] (19)

In particular, this criterion predicts that, for a given value of one of the asymmetry parameters \( n \) or \( b \), mixed micelles do not form if the other asymmetry parameter is too small. This reflects the fact that mixed micelles are not formed by surfactants with very different spontaneous curvature.

Just above the threshold, we obtain the cmc and the aggregation numbers at the cmc by a first-order expansion of the equilibrium equations (15)

\[
\delta p_s = \frac{50}{3D} p_l^* \delta \mu_s
\]

\[
\delta p_l = -\frac{10(9b - 4n)}{3D} \mu_s^* \delta \mu_s, \quad \delta \mu_l = 0 \tag{20}
\]

where \( D \) is a function of the asymmetry parameters \( n \).
and b

\[ D = 5b - 9b^2 + 8bn - 4n^2 \]  

(21)

Whenever \( D \) is positive, the aggregation number of the small copolymer \( p_s \) increases with the chemical potential or equivalently with the concentration and small copolymers are introduced progressively inside the mixed micelles. The aggregation number \( p_s \) decreases as small chains are incorporated when \( n < 9/4b \) and increases otherwise. Interestingly, the total aggregation number increases when \( n > 9/4b \) and \( n = 9/4b \). This leads to three distinct regions in the [\( b, n \)] diagram, separated by the two lines \( n = 9/4b - 5/4 \) and \( n = 9/4b \).

The change in the chemical potential of the large chains at the critical concentration for mixed-micelle formation \( \delta \mu_l \) vanishes at linear order in \( \delta p_s \). If the phase diagram of the mixture is represented in a plane \([\mu_l, \mu_s]\), the mixed micellization line has thus a vertical tangent at the point \([\mu_l^*, \mu_s^*]\). The chemical potential of the large copolymer on the micellization line then decreases as \( \mu_s \) increases.

In this case where \( D > 0 \), the typical variation of the grand-canonical free energy \( \Omega \) with the aggregation number \( p_s \) is shown in Figure 3a. The different curves correspond to different chemical potentials around the critical potential where mixed micelles are formed. The grand-canonical free energy has a single minimum at a finite value of \( p_s \). The value of \( p_s \) at the minimum increases when the chemical potential of the short copolymer increases. As for a monodisperse solution, the micelle size distribution given by eq 3 is proportional to \( \text{exp}(-\Omega) \). It only has one strong peak corresponding to mixed micelles.

In the opposite case where \( D < 0 \), the perturbation calculation for the cmc leads to a negative value of \( \delta p_s \) when the chemical potential of the short chains is increased above the critical value \( \mu_s^* \). This is clearly unphysical. The linearization around the pure large copolymer micelle is not possible in this case, and the short copolymers are incorporated discontinuously in the mixed micelles which always contain a finite number of short copolymer chains. Mixed micelles are formed in this case at a chemical potential smaller than \( \mu_s^* \).

We have numerically determined the solution of the equilibrium equations for the cmc in the case where \( D < 0 \). We start from a solution of large copolymers at the cmc and increase the chemical potential of the short chains. At a small value of the chemical potential \( \mu_s \), the short copolymers do not aggregate and the solution contains only micelles of the long copolymer chains. At a critical value \( \mu_s^* < \mu_s^* \) mixed micelles are formed which contain a finite number of short chains. If the chemical potential \( \mu_l \) of the large chains is smaller than the cmc value, mixed micelles are stable for a chemical potential of the short chains, \( \mu_s \), larger than \( \mu_s^* \). At the concentration where mixed micelles are first formed, the grand-canonical free energy shows a potential barrier between a state corresponding to mixed micelles and a state corresponding to pure large copolymer micelles (\( p_s = 0 \))—see Figure 3b. The micelle size distribution shows thus two peaks, one for mixed micelles and a second for pure large copolymer micelles. We show on Figure 4a an example of the micelle size distribution calculated numerically. The potential barrier is high in this case, and one expects a sharp distribution of micelle sizes around the peaks. At larger values of \( \mu_s \) along the mixed-micelle stability line, the peak corresponding to the monodisperse micelles disappears and the micelle size distribution shows only the mixed-micelle peak.

In this limit where \( D \) is negative, the formation of mixed micelles is only possible if the threshold chemical potential \( \mu_s^* \) is smaller than \( \mu_s^* \), the chemical potential at the cmc of the pure short copolymer. If one increases (say) \( n \) at constant \( b \), the smallest aggregation number of small chains in mixed micelles (for \( \mu_s = \mu_s^* \)) increases with \( n \) and the number of large chains decreases. Along a vertical line in the [\( b, n \)] diagram, the mixed micelles crossover smoothly to micelles of the short copolymer with \( p_s = 0 \). This condition corresponds to a boundary line in the [\( b, n \)] diagram, above which no mixed micelles can form. This boundary can be calculated by requesting the peak position of the size distribution for mixed micelles at \( \mu_s = \mu_s^* \) to coincide with the peak position of the size distribution for single short copolymer micelles (\( \mu_s = \mu_s^* \)). The linearization of eq 15 near \( p_s = 0 \), \( p_s = p_s^* \), \( \mu_s^* \), and \( \mu_s^* \) leads to a condition for the formation of mixed micelles.
The micelle population at these two intersecting points combines the features of both lines, namely, the existence of pure micelles of each species (for the conditions involving the chemical potentials), and a strong tendency for a degenerate distribution (on the line $D = 0$). This results in a "ridged" distribution, running across the $[p_s, p_l]$ plane; mixed micelles are therefore observed with a composition that continuously varies between the large ($p_l = 0$) and the small ($p_l = 0$) copolymer micelles.

The point $n = 1$, $b = 1$ on this diagram is a trivial point corresponding to a mixture of identical copolymers. It is interesting to notice that starting from this point we obtain very different behaviors when either $b$ or $n$ is varied. If the ratio of the molecular masses of the insoluble blocks of the copolymers $n$ is fixed to 1, when $b$ is decreased below 1, mixed micelles are formed and the small diblock copolymers are incorporated continuously into the micelles. When $b$ is fixed to 1, any small variation of $n$ to a lower value brings one into a region of the diagram where no mixed micelles are formed. It would be interesting to check whether this is a general feature for surfactants with identical head groups and different tails or whether it is very specific to our copolymer model that considers only the asymptotic limit of infinite molecular weights and thus neglects corrections to the free energy such as the free energy of mixing of the two surfactants in the micelle that could turn out to be important for small surfactants.

### III.1.b. Decoration of the Large Copolymers by Small Copolymers

We now consider a copolymer mixture where the concentration of the large copolymers is extremely small and discuss the decoration of the large copolymer by short copolymers that would aggregate around its collapsed insoluble block. The grand-canonical free energy of one large copolymer chain decorated with short copolymers is obtained directly from eqs 14, 16, and 17 with $p_l = 1$ and $\mu_l = 0$.

$$\Omega = B(p_s)^{32} + C_N^{2/3}(1 + np_s)^{2/3} - \mu_p s - np_s$$

When $n$ is varied, $n = N_s/N_l \ll 1$.

In this case we keep the reference terms in the energy, because the addition of one large diblock copolymer into the micelle might not be a small perturbation to the micelle shape. If the volume of the core is mainly occupied by the small diblocks ($np_s \gg 1$), this free energy is the same as the free energy that describes the micellization of a monodisperse solution of small diblock copolymers and no segregation of the small block is possible below the cmc. If $np_s < 1$, decoration occurs only above the cmc of the small diblock copolymer and is not relevant. If $np_s < 1$, the surface tension contribution to the free energy can be expanded

$$\Omega = B(p_s)^{32} + \frac{2}{3} C_N^{2/3}[np_s - \frac{6}{5}(np_s^2)]^2 - \mu_p s$$

The free energy has no minimum, and there is no decoration when $\mu_s < \mu_s^d$. The free energy has a minimum for a finite value $p_l = ((\mu_s - \mu_s^d)/B)^2$. Decoration actually occurs if the chemical potential threshold value is smaller than the cmc value $\mu_s^d$, i.e., when $N_s < N_{s,0}$ or $n < N_s^{-49}$. When this is the case, the number of small chains decorating a large chain increases from zero at $\mu_s^d$ and reaches its maximum value $p_s$ at the cmc of the short chains.
When the concentration of large chains is increased, if \( n < N_l^{1/4} \), one must keep in mind that the objects that aggregate to form the mixed micelles can be the decorated chains and not the isolated large chains. This does not change the critical chemical potentials for mixed-micelle formation but will slightly change the cmc for the large chains; in the following, we ignore this decoration effect. Therefore, a linearization scheme can also be carried out from the equilibrium equations to describe the incorporation of large diblock copolymer chains in micelles of small chains. The threshold corresponding to eq 18 is given now in the chemical potential representation by

\[
\mu_l^* = \frac{2}{5} \left( \frac{3}{5} + \frac{1}{n} \right) \left( \mu_s^* \right)^{25} \mu_l^0
\]

**III.1c. Critical Micellar Concentration of a Copolymer Mixture.** We have determined the phase diagram of the copolymer mixture by solving numerically the equilibrium equations (14). An example of the phase diagram in the chemical potential plane \([\mu_l, \mu_s]\)
short copolymers are incorporated continuously into the total concentration. We first discuss the case where the short chains are incorporated discontinuously (chains are incorporated discontinuously (the scenario is the same below the cmc). If the short chains are fixed at the cmc value, then the cmc, the chemical potential of the large chains increases; the concentration and the chemical potential of the large chains increase along the micellization line if \( x \) is kept constant. Provided that \( \mu_s^* \) is relevant.

If we start from a concentration of large chains larger than the cmc, the chemical potential of the large chains is fixed at the cmc value \( \mu_l^* \). When the short chains are incorporated continuously in the micelles (D > 0), the scenario is the same as below the cmc. If the short chains are incorporated discontinuously (D < 0), each mixed micelle contains a finite number of short chains and a small increase of the concentration above the value where mixed micelles appear cannot transform all the large-chain micelles into mixed micelles. There remains thus an excess of large-chain micelles in equilibrium with the mixed micelles.

(ii) The experiments are often performed by fixing the solution composition \( x = \phi_l/(\phi_l + \phi_s) \) and increasing the total concentration. We first discuss the case where the short copolymers are incorporated continuously into the micelles (D > 0). At low concentration, the path followed in the chemical potential \( [\mu_l, \mu_s] \) plane when increasing the concentration at fixed composition \( x \) is a straight line of slope 1. As the total concentration increases, both chemical potentials increase and the first micelles form in the solution. The composition \( x_m = p_r/(p_s + p_r) \) of the first micelles depends on the imposed concentration ratio and, in general, \( x_m \neq x \) (for example, if \( x_m < x \), there is an excess of small copolymer in the bulk). This excess of the free chains of one species changes the composition of the free chains in the bulk, which is the important parameter for the evolution of the composition of the mixed micelles. At higher concentration the chemical potential follows the micellization line until the micelle composition matches the imposed solution composition at high enough concentration. (The chemical potential of the small chains increases along the micellization line if \( x_m < x \) since the concentration of free chains increases.) The variation of the micelle composition at the cmc \( x_m \) with \( x \) is shown in Figure 7. Over a broad range of \( x \) the micelles form with a composition \( x_m \) virtually identical to the imposed composition \( x \); for these values of \( x \), the composition of the micelles remains approximately constant when the total concentration increases. A difference between \( x \) and \( x_m \) is, however, observed at small and large values of \( x \). For these compositions, the micelle composition increases with the polymer concentration from \( x_m \) when the micelles form to \( x \).

If \( x \) is very small, the chemical potential of the large chains reaches the cmc value \( \mu_l^* \) while the chemical
potential of the short chains is smaller than the value where mixed micelles are formed. This occurs when \( x < x^* = \phi^* (\phi^* + \phi_s^*) \) where \( \phi^* \) is the short-chain concentration when the chemical potential of the short chains is \( \mu_s^* \). Micelles containing only the large copolymer are then formed. As the concentration is increased further, more large-chain micelles are formed and the chemical potential of the large chains remains approximately constant at the cmc value; the concentration of the small chains increases and the chemical potential of the short chains increases until it reaches the critical value where mixed micelles are formed \( \mu_s^* \). The chemical potentials increase then up to the point where the fraction of short chains in the micelle is equal to \( x \). Note that a similar effect occurs in the vicinity of the cmc of the pure short copolymer micelles, but the corresponding composition \( x^* \) in Figure 7 is very close to 1 and is hardly visible.

We display also in Figure 7 a phase diagram showing the total concentration where mixed micelles appear \( (\phi = \phi^* + \phi_s^*) \) as a function of \( x \). Note that this cmc has a nonmonotonic variation with \( x \). Although the mixed micellization cannot in our case be described by the regular solution theory for mixed surfactants, the shape of the cmc in Figure 7 suggests a similarity with surfactant systems which fail in the class of positive \( \beta \).

In the surfactant theory mentioned above this parameter expresses the average interaction of the two different species in the micelle. A positive \( \beta \) in surfactant theory indicates effective repulsive interactions between the chains in the micelle. In our case they arise solely from the asymmetry of the different blocks, the two chemical species in the core or in the corona being identical.

The case \( D < 0 \), where the short chains are incorporated discontinuously into the mixed micelles, is more complex. For most values of the imposed solution composition \( x \), as the total concentration is increased, one reaches the critical line where mixed micelles are formed. At higher concentration, the chemical potentials change along the micellization line and the micelle composition changes. Different scenarios are possible depending on the value \( x_n^0 \) of the micelle composition on the micellization line at the chemical potential \( \mu_s^* \), which is the smallest composition that can be achieved in mixed micelles. If \( x_n^0 \) is smaller than \( x \), the behavior of the solution is similar to the \( D > 0 \) case. After the formation of the first micelles, the micelle composition changes and approaches the imposed solution composition \( x \). In the case where \( x_n^0 \) is larger than \( x \), there is always an excess of large copolymer chains in the solution as compared to the imposed composition, because even the mixed micelles with the smallest fraction of small copolymers have a small-chain fraction larger than that available from the bulk. At high enough concentration, the chemical potential of the large chains reaches the cmc value \( \mu_s^o \) at which the large chains also form micelles. There is then always coexistence between mixed micelles and large copolymer micelles.

### III.2. Copolymer–Surfactant Mixtures

In the limit where the small copolymer can be considered as a simple surfactant, the height of the small corona is smaller than the radius of the core of the mixed micelles and the small corona cannot be considered as a star polymer but must rather be considered as a flat (or slightly curved) grafted polymer layer. The equivalent grafting density is \( \sigma = (p_s + p_l)/(4\pi R^2) \), and the thickness of a flat grafted layer with this grafting density is

\[
\frac{h_0}{R} \simeq \frac{N_{s}(p_s + p_l)^{1/3}}{(N_{l}p_s + N_{l}p_l)^{5/9}}
\]

The actual size \( h_0 \) and the free energy of the curved inner corona can then be expanded in powers of \( h_0/R \) to account for the effect of curvature. The osmotic free energy can still be written in the form of eq 16, but \( B \) is no longer a constant and explicitly depends on the values of the aggregation numbers \( p_s \) and \( p_l \).

\[
B = \frac{h_0}{R} \left( 1 - \xi_1 \frac{h_0}{R} + \xi_2 \left( \frac{h_0}{R} \right)^2 \right)
\]

In order to investigate the formation of mixed micelles, as for the copolymer mixtures, we start from a solution of copolymers at the cmc \( (\mu_l = \mu_s^o) \) and increase the concentration or the chemical potential of the surfactant. There is here also a finite chemical potential threshold \( \mu_s^* \) above which the surfactant molecules are incorporated inside the large copolymer micelles. The threshold is obtained by linearizing the equilibrium equations around the point \( (\mu_s^o, \mu_s^* ) \) in the chemical potential phase diagram. The critical potential for the formation of mixed micelles is still given by eq 18 where \( B \) is calculated from eq 27 at the value \( H_0 \) of the grafted layer thickness which corresponds to \( p_s = 0 \) (this is the height of the small corona when the first surfactant molecule is incorporated inside the mixed micelle).

\[
H_0 \simeq \frac{N_{s}^s (p_s^{o})^{1/3}}{(N_{l}p_s^{l})^{5/9}}
\]

The change in the aggregation numbers \( \delta p_s \) and \( \delta p_l \) of the mixed micelle can also be determined when the chemical potential of the surfactant molecules is increased slightly above the critical value for mixed-micelle formation \( \mu_s = \mu_s^* + \delta \mu_s \).

\[
\delta p_s \simeq \frac{-p_o}{D \mu_l} \delta \mu_s
\]

\[
\delta p_l \simeq \frac{\left( H_0/AR \right) \left( \frac{1}{5} - \frac{3 \xi_2 H_0^2}{5 \left( R^2 \right)^{5/9}} \right) - \frac{4}{5} p_{o} \mu_l}{D \mu_s} \delta \mu_s
\]

where

\[
D = -36n^2 + 15 \frac{H_0}{AR} (7 - 4n) - \left( \frac{H_0^2}{AR} \right) (25 + (165 - 192n)A\xi_1) + \left( \frac{H_0^3}{AR} \right) (10A\xi_1 + (225 - 324n)A^2\xi_2)
\]

The results are qualitatively similar to those obtained for the copolymer mixtures, and one must distinguish two types of behaviors according to the sign of \( D \). The surfactant molecules are incorporated continuously into the large copolymer micelles when \( D \) is positive and discontinuously when \( D \) is negative; in this last case, the formation of mixed micelles occurs at a chemical potential smaller than \( \mu_s^* \). We display in Figure 8 a diagram showing the possibility of formation of mixed...
micelles as a function of the relative molecular weights of the copolymer and the surfactants. In order to characterize the asymmetry of the soluble block of the copolymer, we use here the variable \( H_0/R \) instead of \( b \) and with \( A \) fixed. We have explicitly checked that this diagram crosses over smoothly to the similar diagram for copolymer mixtures when \( B = 1 \)—see Figure 8.

When the surfactant molecules are incorporated discontinuously in the large copolymer micelles, the micelle size distribution is bimodal, with one peak corresponding to mixed micelles and one peak corresponding to a pure copolymer micelle. An example of the size distribution calculated numerically is shown in Figure 4b. For the chosen values of the parameters the potential barrier between the two peaks is less pronounced than that for the copolymer mixture, and we expect a broader distribution of the size of the micelles in this case. As in section III.1.b, one can also show that decoration of one large diblock head by small diblocks can always occur for large enough concentrations of the small diblock chains.

IV. Discussion

We have discussed in this paper the formation of mixed micelles in mixtures of long block copolymers or in mixtures of surfactant and long block copolymers. This has been done by extending the work of Shim et al.\(^9\) to diblock copolymers where both the soluble and insoluble sequences are chemically identical but have different molecular weights.

Our main result is the existence of two scenarios for the formation of mixed micelles. The choice of scenario is driven by the relative asymmetries of the copolymer blocks, measured by the quantity \( D \), which is positive for relatively small asymmetries and negative when the asymmetries are large. In the first scenario, when \( D \) is positive, the small copolymers are incorporated continuously into the micelles formed by the large copolymer and the micelle size distribution has a sharp peak corresponding to the mixed micelles. In the second scenario \( (D < 0) \) which is expected when the spontaneous curvatures of the two copolymers are very different, even at the cmc of the large copolymer chains, the mixed micelles contain a finite number of short copolymer chains. In this case the micelle size distribution is bimodal, with one peak corresponding to mixed micelles and one peak corresponding to pure large copolymer micelles. One also expects above the cmc of the large copolymer an equilibrium between mixed micelles and large copolymer micelles. In the case where \( D < 0 \), the formation of mixed micelles is thus very similar to a first-order transition.

Our study was motivated by the work of Hecht et al.,\(^10\) who have observed a bimodal micelle size distribution in a mixture of pluronic triblock copolymers and simple surfactants. Our results when \( D < 0 \) may provide a qualitative explanation of this experimental result. Although in these experiments the nature of the two hydrophobic moieties is different, the existence of a bimodal distribution suggests that they do not have large negative excess enthalpies of mixing. It can be checked that such a contribution of the form \(-\gamma (p_N s) - (p_N l)/(p_N s + p_N l)\) increases the region of the phase diagram (5) where mixed micelles are observed.

An important issue is then the generality of the result which is based theoretically on an expression for the free energy of the micelles where the molecular weight both of the hydrophilic group and of the hydrophobic core can be considered as extremely large. When this is not the case, several other contributions to the free energy of a micelle which are subdominant for copolymers are relevant. The entropy of mixing of the junction points on the surface of the core or the stretching of the tails inside the core could change somewhat our conclusions. For instance, the entropy contribution can broaden the border lines in the phase diagram (5). Another limitation of our study is the range of asymmetries which are accessible experimentally; we have assumed that the asymmetry parameters \( n \) and \( b \) can be varied without any limitations, but in certain cases this would lead to extremely large molecular weights. We are not aware of any other experiment than that of ref 10 on simple surfactants or on copolymer mixtures that would study quantitatively the micellar size distribution and would thus allow for confrontation with our predictions. Available self-consistent-field calculations on the specific case of polydisperse PEO–PPO–PEO triblock copolymers\(^16\) do not report the coexistence of micelles with...
different sizes, but this could be due either to the limited range of parameters explored or to the more continuous nature of the assumed polydispersity.

Another surprising result is the difference in the role of the asymmetry parameters \( b \) and \( n \). If the hydrophobic groups are identical \((n = 1)\), a slight difference in the hydrophilic blocks always leads to the formation of mixed micelles. This is not the case if the hydrophilic groups are identical \((b = 1)\), even a slight difference between the molecular weights of the hydrophobic blocks can lead to a situation where no mixed micelles are formed. This effect (which again could only be valid for asymptotically large molecular weights) may, however, be difficult to observe for two reasons. First, two micelle populations with the same hydrophilic blocks but slightly different hydrophobic blocks will be indistinguishable to most of the available techniques. Second, diblock copolymer solutions always have some polydispersity in both block lengths. One could, for instance, check that a system with fixed, monodisperse composition but presenting a total mass polydispersity would be represented by a line in the phase diagram which lays inside the region where mixed micelles are formed.

Acknowledgment. P.S. received support from the MRL program of the National Science Foundation under Award No. DMR-9123048. C.M.M. acknowledges the donors of the Petroleum Research Fund, administered by the ACS, for support of this research (Grant 29306-AC7). C.M.M. also acknowledges partial support by a NATO grant.

References and Notes

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