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Nature of Disordered Micelles in Sphere-Forming Block Copolymer Melts

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ABSTRACT: Taking a nucleation perspective, we study the nature of the disordered micelles in highly asymmetric, sphere-forming diblock copolymer melts using the self-consistent-field theory. The micelles are shown to correspond to strong, activated, localized composition fluctuations in the disordered state due to finite molecular weights. By taking into account the translational entropy of the micelles, we obtain the concentration and the free energy of the disordered micelles. The critical micelle temperature (in terms of the familiar combination χN), operationally defined to correspond to the onset of sufficient number of micelles in the system, is identified by invoking a criterion involving the concentration of micelles. The disordered micelles are part of the disordered phase, and the only phase transition between the disordered state and the ordered phase is the order−disorder transition (ODT). However, there exists a sharply defined temperature (higher than the critical micelle temperature), which we term the micelle dissociation temperature, beyond which micelles with finite lifetimes become impossible. The range of χN for the disordered micelles to be observable shrinks as $N^{-1/2}$ with increasing degrees of polymerization N of the copolymers. In the infinite molecular weight limit, the window vanishes and the mean-field phase diagram calculated by Matsen and Bates is recovered. The disordered micelles, as a part of the disordered phase, contribute to the increased scattering intensity and the low-q shift of the structure factor in diblock copolymer melts near the ODT.

I. Introduction

Block copolymers exhibit rich microphase separation as a result of the chemical linkage between immiscible blocks. Depending on the chain architecture, the chain composition, and the degree of segregation measured by χN, where χ is the Flory−Huggins parameter and N is the degree of polymerization, a block copolymer melt can either be in a disordered state or take on different ordered structures including lamellar, cylinder, sphere, and more complex phases.[1] At the mean-field level, the phase behavior of block copolymers is well-described by the self-consistent-field theory (SCFT) developed by Matsen and co-workers.[2−4]

In recent years, the phase behavior near the order−disorder transition (ODT) in highly asymmetric, sphere-forming diblock copolymers has been reexamined both experimentally and theoretically. The state-of-the-art SCFT calculation by Matsen and Bates predicts the following sequence of phase transitions upon decreasing the temperature: disordered → close-packed spheres [including face-centered cubic (fcc) and hexagonally close-packed (hcp)] → body-centered cubic sphere (bcc).[3,4] [Close-packed spheres were first predicted by Semenov[5] using a strong segregation approximation.[6]] However, the close-packed sphere phases have never been observed experimentally. Instead, several groups reported that disordered micelles were observed near the ODT boundary in the asymmetric sphere-forming block copolymer melts.[7−16] Such disordered micelles were not considered in the SCFT calculations of Matsen and co-workers.

Schwab and Stühn first reported stable micelles of liquidlike order in block copolymer melts between a disordered state free of micelles at high temperatures and ordered bcc arrays of micelles at lower temperatures.[7,8] Han, Hashimoto, Kim, Sakurai, Lodge, and co-workers had similar experimental results from small-angle X-ray scattering or small-angle neutron scattering, rheology, and transmission electron microscopy.[9−14] Some authors found that the size and number of micelles increased monotonically with decreasing temperature. The volume fraction of micelles consequently increased, and at a critical volume fraction, ordering to bcc occurred.[7,8,14] However, there has been disagreement on the nature of the order−disorder transition (ODT) and whether the disordered micelles constitute a distinct, thermodynamically stable phase. Most of the authors agreed that the disordered micelles were thermodynamically stable in a narrow range of temperatures.[7−14] However, Register and co-workers suggested that the liquidlike spherical phase could result from a combination of kinetic trapping of long-relaxation-time, large-amplitude composition fluctuations due to high viscosity and the low thermodynamic driving force to form a bcc lattice.[15,16] These authors considered the equilibrium ODT to involve only one transition between two thermodynamic phases, the bcc phase and the disordered phase. On the other hand, Han, Hashimoto, Kim, Sakurai, and co-workers suggested a two-transition scenario: a lattice disordering transition (LDT) from bcc to disordered micelles and the disappearance of the micelles at what these authors termed the demicellization temperature (DMT).[9,12,13] While acknowledging that the second transition might not be a true

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thermodynamic transition, they nevertheless viewed the existence of disordered micelles as representing an essential difference between highly asymmetric, sphere-forming and less asymmetric block copolymers.

To address these issues, Dormidontova and Lodge[17] performed theoretical calculations by including disordered micelles. The D−L theory models the micelles and their interactions using Semenov's strong segregation theory.[5,6] By including the translational entropy of the disordered micelles and allowing equilibrium between micellized and unmicellized polymers, the D−L theory predicted the concentration of disordered micelles and a revised phase diagram that showed the ODT to be between bcc and the disordered micelle state. These authors concluded that the disordered micelles were part of the disordered phase, and their disappearance did not involve a thermodynamic phase transition. Indeed, in the D−L theory, the disordered micelles never quite disappear; only their number decreases rapidly beyond some "critical micelle temperature" (CMT).[17] An interesting question was raised as to the connection between disordered micelles and composition fluctuation. However, because of the use of the strong segregation theory and the presumed existence of micelles, the D−L theory is not suited to address this issue. In the words of the authors, "whether the disordered micelle regime should be viewed as another manifestation of strong composition fluctuations for asymmetric diblock copolymers, or not, remains an open question".

In this paper, we study the disordered micelles in sphere-forming diblock copolymer melts from a nucleation perspective, with a focus on the nature of the disordered micelles and their connection to composition fluctuations. Intuitively, disordered micelles form because they reduce the unfavorable contacts between immiscible monomers without sacrificing all the entropy of the disordered state.[17] Thus, the formation of disordered micelles shares the same physical origin as composition fluctuations, and there is reason to regard it as a type of composition fluctuation. The effects of composition fluctuations on microphase separation in block copolymers have been investigated by Fredrickson and Helfand[18] using a method developed by Brazovskii[19] based on a self-consistent Hartree approximation. However, the validity of the method is limited to symmetric, or moderately asymmetric, block copolymers. More importantly, the fluctuations considered in the F−H theory are soft and spatially extensive with characteristic length scales of the size of the polymer. In contrast, as we will demonstrate in this work, disordered micelles arise from strong, localized fluctuations through an activated process. Such activated composition fluctuations have not been considered in any previous fluctuation theories.[18,20−22] Our nucleation approach provides a natural framework for studying such activated processes.

The basic theoretical method we use is the self-consistent-field theory (SCFT). Whereas SCFT has usually been used to determine the equilibrium, bulk structures of microphase-separated block copolymers in either a reciprocal-space[2,3] or real-space[23] implementation, we have extended the SCFT to the study of local strong-fluctuation structures such as emulsion droplets and critical nuclei in macrophase separation.[24−26] Similar methods have been used to study micelles in small-molecule surfactant and block copolymer solutions by other groups.[27−29] Focusing on a single, isolated micelle, our method yields the structure and the excess free energy of formation of a micelle and its critical nucleus in a unified theoretical framework, which then provides the basis for further theoretical analysis of a collection of disordered micelles by the inclusion of translational entropy.

The main results of this paper are as follows. First, we show that the formation of a micelle is associated with strong, localized, activated composition fluctuation. We find that there exists a precisely defined value $(\chi N)_{\mathrm{MD}}$ for the dimensionless interaction parameter χN, below which micelles cannot exist as entities with finite lifetimes. We term the temperature corresponding to $(\chi N)_{\mathrm{MD}}$ the micelle dissociation temperature (MDT). Next, by including the translational entropy, we calculate the concentration of micelles below the MDT and show that a disordered micelle state with appreciable concentration of micelles can exist in a temperature window before the transition to periodically ordered body-centered-cubic (bcc) or face-centered-cubic (fcc) sphere phases. We find that this window shrinks with increasing degrees of polymerization, and for sufficiently long polymers, the disordered phase makes a direct transition to the periodically ordered sphere phase without an intervening disordered micelle state of appreciable concentration of micelles. The mean-field transition sequence dis ↔ fcc ↔ bcc predicted in refs 3 and 4 is recovered in the long chain limit. This result suggests that the existence of the disordered micelle state is a consequence of composition fluctuations due to finite molecular weight. Finally, we show that the presence of disordered micelles leads to enhanced scattering of the disordered phase and a shift of the scattering peak to smaller values of the wavenumber compared with the structure factor predicted by Leibler.

II. Model and Method

A. Self-Consistent-Field Theory. We consider an incompressible AB diblock copolymer melt, with an overall degree of polymerization N and A block composition $f = N_A/N$. The block copolymers are modeled as Gaussian chains, with the hard-core segmental repulsions accounted for by imposing local incompressibility. For simplicity both the A and B monomers are assumed to be of the same monomeric volume v and Kuhn length b. The self-consistent free energy for an arbitrary density profile of the A and B segments is given by[30]

$$\beta G[\phi_A,\phi_B,\omega_A,\omega_B,\xi] = \int \mathrm{d}r \left[\frac{\chi}{v}\,\phi_A(r)\,\phi_B(r) - \omega_A(r)\,\phi_A(r) - \omega_B(r)\,\phi_B(r)\right] - \frac{1}{Nv}\,Q[\omega_A,\omega_B] + \int \mathrm{d}r\;\xi(r)[\phi_A(r) + \phi_B(r) - 1] \quad (1)$$

where $\beta \equiv 1/(k_BT)$ and χ is the Flory−Huggins interaction parameter, ϕ_α (α = A, B) is the volume fraction of monomers of type α, ω_α is the molecular self-consistent-field conjugate to ϕ_α, and ξ is the effective pressure field to ensure the local incompressibility of the melt.

In eq 1, Q is the single chain partition function of an AB diblock copolymer chain in external fields ω_A and ω_B and can be calculated as

$$Q[\omega_A,\omega_B] = \int \mathrm{d}r\; q(r,N) \quad (2)$$

where the end-segment distribution function $q(r,N)$ is obtained from solving the modified diffusion equation

$$\left[\frac{\partial}{\partial\tau} - \frac{b^2}{6}\nabla_r^{\,2} + v\omega_{\mathrm{A}}(r)\right]q(r,\tau) = 0 \qquad 0 < \tau < fN$$

$$\left[\frac{\partial}{\partial\tau} - \frac{b^2}{6}\nabla_r^{\,2} + v\omega_{\mathrm{B}}(r)\right]q(r,\tau) = 0 \qquad fN < \tau < N \tag{3}$$

with the initial condition $q(r,0) = 1$. Because of the lack of inversion symmetry for the two blocks in the AB diblock copolymer, it is necessary to introduce a conjugate end-segment distribution function $q^{\ddagger}(r,\tau)$, which satisfies a similar modified diffusion equation to eq 3 with $\partial/\partial\tau$ multiplied by -1 and with the initial condition $q^{\ddagger}(r,N) = 1$.

The self-consistent-field equations are obtained by a variational extremization of the free energy with respect to ϕ_{A}, ϕ_{B}, ω_{A}, ω_{B}, and ξ, which yields

$$v\omega_{\mathrm{A}} = \chi\phi_{\mathrm{B}} + v\xi \tag{4}$$

$$v\omega_{\mathrm{B}} = \chi\phi_{\mathrm{A}} + v\xi \tag{5}$$

$$\phi_{\mathrm{A}} = \frac{1}{N}\int_0^{fN} \mathrm{d}\tau\, q(r,\tau)\, q^{\ddagger}(r,\tau) \tag{6}$$

$$\phi_{\mathrm{B}} = \frac{1}{N}\int_{fN}^{N} \mathrm{d}\tau\, q(r,\tau)\, q^{\ddagger}(r,\tau) \tag{7}$$

$$\phi_{\mathrm{A}} + \phi_{\mathrm{B}} = 1 \tag{8}$$

B. Method. In contrast to the treatment in ref 17 which presumes the existence of micelles, we consider the process of their formation as a result of localized, large-amplitude composition fluctuations. We focus on the regime where the concentration of micelles is not high enough for intermicelle interactions to be important; this allows us to focus on a single, isolated micelle. We use the order parameter, observational cell approach proposed by Kusaka et al.[31−33] for the study of nucleation in low-pressure gases. The basic idea is to focus on an appropriately chosen volume in a large system and ask what the free energy cost is for creating a specified type of fluctuation with its center-of-mass position fixed at the center of the volume. The type of fluctuation is described by an order parameter, and specifying the fluctuation corresponds to imposing a constraint on the order parameter.

An appropriate and convenient order parameter for describing the formation of a micelle is the material excess of the minor block (A block) that forms the core of the micelle, which is defined as $M^{\mathrm{ex}} \equiv 2\pi\int_0^{\infty} r^2\, \mathrm{d}r\, |\phi_{\mathrm{A}}(r) - f\,|$. This quantity measures the extent of local deviation from the uniform, disordered state;[34] the use of the spherical coordinates means that we will only consider micelles that on average are spherical.

The appropriate free energy for describing the formation of a micelle is the excess free energy with respect to the uniform disordered bulk phase. For the uniform disordered state, the self-consistent-field equations can be solved trivially, and its free energy density is simply

$$g^{(0)} = \chi f(1 - f) - \frac{1}{N} \tag{9}$$

The excess free energy is then obtained by subtracting this free energy ($G^{(0)} = g^{(0)}V$) from the free energy corresponding to a given material excess $G(M^{\mathrm{ex}})$

$$W = G(M^{\mathrm{ex}}) - G^{(0)} \tag{10}$$

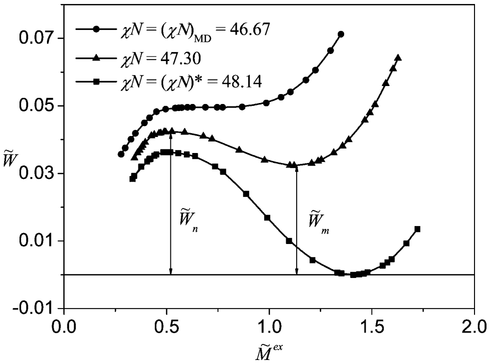

Figure 1. Excess free energy as a function of the material excess for micelle formation at three different values of χN for $f = 0.1$. The local minima correspond to the micelles, and the local maxima correspond to the critical nuclei. At $(\chi N)_{\mathrm{MD}} = 46.67$ the maximum and the minimum collapse into an inflection, and at $(\chi N)^* = 48.14$ the excess free energy of the micelle becomes zero.

where $G(M^{\mathrm{ex}})$ is obtained from solving the self-consistent equations (4)−(8) subject to a specified M^{ex} and substituting the solution to the free energy expression, eq 1. The constraint of fixing M^{ex} can be accomplished by fixing the value of the density profile at some radial distance as in ref 24 for the nucleation in A/B binary blend. The behavior of the excess free energy as a function of the material excess (the reaction coordinate) determines the state of the micelle, its free energy, the transition state (the critical nucleus), and the free energy barrier for the formation and dissociation of the micelle.

III. Results and Discussion

In this section, we present and discuss the main results of our work. As is typical in polymer blends or block copolymers, the interaction between the blocks is characterized by χN. To highlight the molecular weight scaling aspects of the properties, it is convenient to use dimensionless radial distance $\tilde{r} \equiv r/R_{\mathrm{g}}$, material excess $\tilde{M}^{\mathrm{ex}} \equiv M^{\mathrm{ex}}/R_{\mathrm{g}}^{\,3}$, and excess free energy $\tilde{W} \equiv \beta W/\bar{N}^{1/2}$, where $R_{\mathrm{g}} = 6^{-1/2}N^{1/2}b$ is the ideal radius of gyration of the diblock copolymer chain and $\bar{N} \equiv Nb^6/v^2$ is the scaled degree of polymerization that naturally emerges when studying fluctuation effects in polymer blends[35] and block copolymers.[18] Except for the phase diagram, all numerical examples will be given for $f = 0.1$. Changing f in this small f regime does not lead to qualitatively different behaviors. However, we find that for $f > \sim 0.22$ disordered micelles are preempted by the ordered phases.

A. Micelles as Strong Localized Activated Fluctuations. Just as micelle formation in small-molecule surfactant solutions and block copolymer solutions,[27−29] so the formation of a micelle in block copolymer melts is activated through localized composition fluctuations. Figure 1 shows the dimensionless excess free energy as a function of the dimensionless material excess for $f = 0.1$. Focusing for the moment on the middle curve, it is clear that the minimum at a finite $\tilde{M}^{\mathrm{ex}}$ corresponds to a micelle with free energy $\tilde{W}_{\mathrm{m}}$ (relative to the disordered, micelle-free state) and that its formation is an activated process that requires overcoming a free energy barrier $\tilde{W}_{\mathrm{n}}$. The dissociation of the micelle is also an activated process with a free energy barrier $\tilde{W}_{\mathrm{n}} - \tilde{W}_{\mathrm{m}}$; this free energy barrier determines the lifetime of the micelle.[36] Note that since $\tilde{W} = \beta W/\bar{N}^{1/2}$, the actual free energy of the micelle, the free energy barrier for its formation, and the free energy barrier for its dissociation will all be multiplied by $\bar{N}^{1/2}$. Thus, at a given χN, a micelle is more difficult to form and has a longer lifetime once it forms, and their concentration (determined by W_m) is smaller (for $W_m > 0$; see below), as the molecular weight increases. Qualitatively, in order for a micelle to be an entity with sufficiently long lifetime, we require that $W_n - W_m \gg kT$, whereas to have a sufficiently high concentration of micelles to be observable, we need $W_m \sim kT$. For a given molecular weight, these considerations yield a condition for the strength of the interaction χN in order to have experimentally observable concentration of micelles in the disordered state, as will be discussed in the next subsection.

Figure 1 identifies two special values of χN. The first marked by $(\chi N)_{MD}$ corresponds to the first appearance of the micelle as a local minimum in the free energy curve upon increasing the interaction or decreasing temperature in a normal system with UCST (upper critical solution temperature) behavior. (Henceforth, we will often refer to the increase/decrease in χN as a decrease/increase in the temperature.) For $f = 0.1$, this occurs at $(\chi N)_{MD} = 46.67$. We term the temperature corresponding to this value of χN the micelle dissociation temperature (MDT), since at this point the free energy barrier for the dissociation of the micelle vanishes. For temperatures above the MDT (i.e., $\chi N < (\chi N)_{MD}$), micellization is impossible, and therefore, the disordered state free of micelles is absolutely stable against composition fluctuations of any magnitudes.

The second special value denoted as $(\chi N)^*$ corresponds to the temperature at which $W_m = 0$. (This special χ is equivalent to χ_c defined in ref 5.) Beyond this point, the excess free energy of a single isolated micelle becomes negative, and thus thermodynamically, one expects that micelles will form in large numbers with high concentration. Our picture of noninteracting micelles no longer holds in this regime when considering the equilibrium properties of the system, although we may still use Figure 1 to investigate the initial stages in the nucleation of the micelles. As we will argue in the rest of this section, for $\chi N > (\chi N)^*$, the concentration of micelles will be sufficiently large to make them order into periodic structures; indeed, we find that $(\chi N)^*$ exceeds the value predicted by Matsen and Bates for the transition from the disordered phase to the fcc phase. Semenov argued similarly that at $(\chi N)^*$ the micelles will order into one of the periodic phases.[5] So the range for observing the disordered micelles will be limited to $(\chi N)_{MD} < \chi N < (\chi N)^*$. In the rest of this paper, we will limit our discussions to within this range.

The excess free energy of an isolated micelle, W_m, and the free energy barrier for its formation, W_n, corresponding respectively to the minimum and maximum of the free energy curve in Figure 1, are both decreasing functions of χN. Figure 2 shows this behavior for $f = 0.1$. In the case of macroscopic phase separation in a binary polymer blends, the free energy barrier for nucleation starts from zero at the spinodal and increases monotonically as χN decreases toward the binodal where it diverges.[24] The nucleation barrier for micellization also vanishes at the spinodal (for microphase separation); however, it never diverges but rather terminates with a finite value at $(\chi N)_{MD}$. The excess free energy of the micelle also increases upon decreasing χN. Thus, decreasing χN leads to a decrease both in the thermodynamic driving force for the formation of a micelle and in the rate of its formation. The difference between the free energy barrier for nucleation and the excess free energy of the micelle is the free energy barrier for the dissociation of the micelle, which determines the lifetime of the micelle. As can be seen from Figure 2, this free energy difference decreases as χN decreases and vanishes at $(\chi N)_{MD}$, the minimum and maximum of the excess free energy shown in Figure 1 merging at this temperature to become an inflection point.

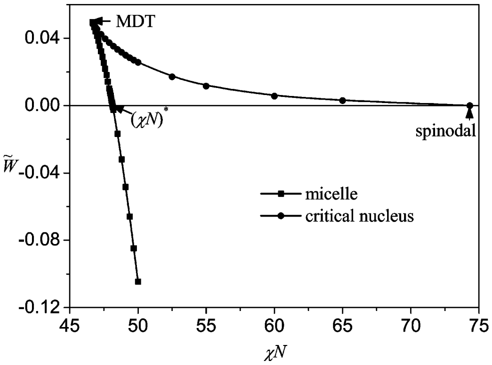

Figure 2. Excess free energy of the micelle and critical nucleus as a function of χN for $f = 0.1$.

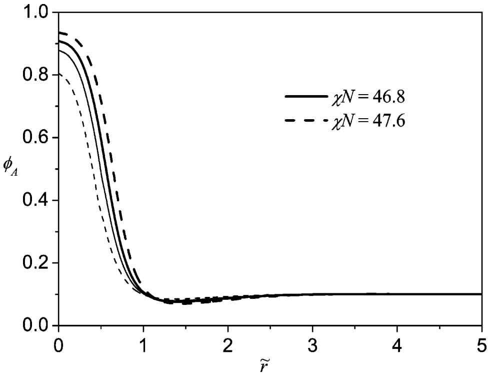

Figure 3. Representative density profiles of the micelle and critical nucleus at two different χN's for $f = 0.1$. The thick curves represent the profile for the micelles, and the corresponding thin curves represent the profile of the critical nuclei.

Both the micelle and its critical nucleus have core–corona structure. As shown in Figure 3 for $f = 0.1$, the A block density is greatly enriched in the core of both the micelle and its critical nucleus. Roughly the same amount of B block is enriched in the corona region because of chain connectivity. (However, there is small oscillation in the density profile that continues to larger distances than shown in the figure, which is indiscernible on the scale of the figure.) The density of the A block at the core center is very high (about 90% in volume fraction). On the other hand, significant concentration variation occurs throughout the micellar core and corona region, without a narrow interface. Thus, the strong segregation approximation used in refs 5 and 17 appears to be only partially justified. Comparing the two temperatures, we see that the micelle at the lower temperature (higher χN) has a higher concentration and larger amount of A monomer in the core and sharper core–corona "interface"; this is consistent with experimental observations.[7,13] In contrast, the critical nucleus exhibits the opposite temperature dependence: upon increasing χN, the concentration and amount of A monomers decrease in the core, and the interfacial region becomes more diffuse. Thus, as temperature increases from the

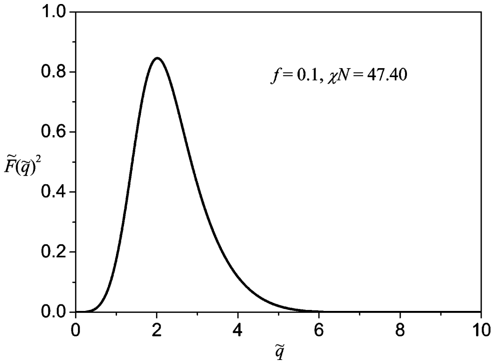

Figure 4. Dimensionless form factor square $\tilde{F}(\tilde{q})^2 \equiv [F(\tilde{q})/R_g^3]^2$ as a function of the dimensionless wavenumber $\tilde{q} \equiv qR_g$ for a single micelle at $f = 0.1$ and $\chi N = [(\chi N)_{\mathrm{MD}} + (\chi N)^*]/2 = 47.40$.

low-temperature side, the density profiles for the micelle and its critical nucleus approach each other and become identical at the MDT. Note that even at the MDT, the micelle still has a well-defined structure not much different from that for a micelle at lower temperatures. Indeed, in the range $(\chi N)_{\mathrm{MD}} < \chi N < (\chi N)^*$, even though the material excess (which gives a measure of the enrichment of the A monomers in the core and depletion in the corona) increases monotonically with χN by as much as 70%, if we define the size of the micelle by the outer boundary of the corona, the size is roughly $3.12R_g$ for $f = 0.1$, essentially constant in the entire range of $(\chi N)_{\mathrm{MD}} < \chi N < (\chi N)^*$.

Another way to characterize the structure of the micelle is to examine its form factor, $F(q)$, defined to be the Fourier transform of the micelle density profile $\phi_A(r) - f$. As we will show in section III.D, the form factor of the disordered micelles will be a significant contribution to the overall structure factor of the disordered state. Since the form factor appears squared in the structure factor (cf. eq 22 in section III.D), in Figure 4 we show the dimensionless $\tilde{F}(\tilde{q})^2 \equiv F(qR_g)^2/R_g^6$ for $f = 0.1$ at $\chi N = [(\chi N)_{\mathrm{MD}} + (\chi N)^*]/2 = 47.40$. The figure shows a strong peak at some characteristic wavenumber q_m, from which we can define the size (radius) of the micelle to be $R_m = 2\pi/q_m$. We will use R_m to denote the size of a micelle in the remainder of this paper. Like the radius defined using the density profile in real space, R_m changes little in the range $(\chi N)_{\mathrm{MD}} < \chi N < (\chi N)^*$, so for most purposes, we will use its value at $\chi N = [(\chi N)_{\mathrm{MD}} + (\chi N)^*]/2$.

B. Concentration of the Disordered Micelles and the Critical Micelle Temperature. In the previous subsection, we discussed the free energy and structure of a single, isolated micelle with a fixed center-of-mass position. That discussion led to the identification of two special values of χN: $(\chi N)_{\mathrm{MD}}$ corresponding to the maximum temperature (in a UCST system) for the existence of a micelle and $(\chi N)^*$ at which the excess free energy for creating a single, isolated micelle with its center-of-mass position fixed vanishes. In the range $(\chi N)_{\mathrm{MD}} < \chi N < (\chi N)^*$, the excess free energy of a micelle remains positive; this might seem to suggest that the formation of micelles is thermodynamically unfavorable. However, this is a consequence of neglecting the translational entropy of the micelles. We now include the translational entropy to determine the concentration of micelles and the system free energy.

Let n_m be the number of micelles in a system of total volume V_{tot}. If we neglect the size polydispersity of micelles and the interaction between micelles, the total excess grand potential $\beta G'$ due to the presence of micelles in a disordered state is simply

$$\beta G' = n_m \ln(n_m a^3/V_{\mathrm{tot}}) - n_m + n_m \beta W_m \tag{11}$$

where a is a reference length.[37] Note that the excess free energy W_m is used for the free energy of a micelle since it is formed in the reservoir of disordered diblock copolymers.

The equilibrium number of micelles is determined trivially by minimizing the total grand potential over the number of micelles, resulting in

$$n_m = \frac{V_{\mathrm{tot}}}{a^3} \exp(-\beta W_m) \tag{12}$$

This is in agreement with the result for the number of clusters in an attenuated gas obtained by Kusaka et al.[33] Substituting this result back into the excess grand potential in eq 11, we obtain

$$\beta G' = -n_m = -\frac{V_{\mathrm{tot}}}{a^3} \exp(-\beta W_m) \tag{13}$$

The excess grand potential density is then $\beta g' = -(1/a^3) \exp(-\beta W_m)$, which is, as expected, the negative of the osmotic pressure due to the micelles and therefore is always negative. Thus, although the excess free energy of a single micelle at a fixed position is positive, by taking into account the translational entropy, the state with disordered micelles is thermodynamically favored over the micelle-free disordered state when $\chi N > (\chi N)_{\mathrm{MD}}$.

Equations 11−13 involve an as-yet undefined reference length scale a. As explained in the footnote,[37] its determination involves the partition function of the micelle with all its degrees of freedom, including, for example, the shape fluctuation. Calculating this length scale requires going beyond the SCFT theory; we will not pursue such a task here. On physical ground, since both the size of the micelle and its shape fluctuation must scale as the radius of gyration R_g of the diblock copolymer, we take $a = R_g$. Then, the concentration of the micelles c_m is

$$c_m = \frac{1}{R_g^{\,3}} \exp(-\beta W_m) \tag{14}$$

and the grand potential density is

$$\beta g' = -c_m = -\frac{1}{R_g^{\,3}} \exp(-\beta W_m) \tag{15}$$

Equations 14 and 15 show that the excess free energy of a single micelle calculated in section III.A is of central importance in determining the state of disordered micelles. Since the excess free energy of a single micelle decreases with increasing χN, the concentration of micelles increases according to eq 14. This is in agreement with the experimental observations[7,8,14] and the predictions of the D−L theory.[17]

From eq 14, we can define a critical micelle temperature (CMT) corresponding to the temperature for the onset of detectable concentration of micelles. Unlike the micelle dissociation temperature (MDT), which has an unambiguous theoretical definition, the definition of the CMT requires an operational criterion. Here we choose

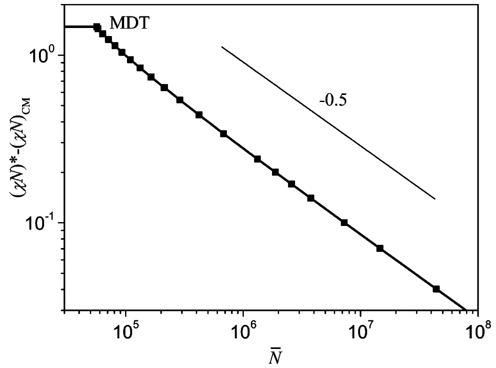

Figure 5. Dependence of the critical micelle temperature represented by $(\chi N)^* - (\chi N)_{CM}$ on the natural degree of polymerization $\bar{N}$ for $f = 0.1$.

a threshold value using the volume fraction occupied by the micelles. Defining the radius of a micelle R_m to be $R_m = 2\pi/q_m$ where q_m is the peak position of the form factor, the volume fraction of the micelles is then

$$\phi_m = \frac{4\pi}{3}\frac{{R_m}^3}{{R_g}^3}\exp(-\beta W_m) = 4.19{\tilde{R}_m}^{\ 3}\exp(-\bar{N}^{1/2}\tilde{W}_m) \tag{16}$$

where $\tilde{R}_m = R_m/R_g$ and $\bar{N} = Nb^6/v^2$ is the natural molecular weight that emerges in a theory that studies the fluctuation in block copolymer melts[18] and polymer blends.[35] As mentioned earlier, the radius of the micelle does not change much in the range $(\chi N)_{MD} < \chi N < (\chi N)^*$. Thus, in our numerics, we take R_m evaluated at $[(\chi N)_{MD} + (\chi N)^*]/2$. For example, at $f = 0.1$, the radius of the micelle $\tilde{R}_m$ is roughly 3.12, so the above equation reduces to $\phi_m = 127\exp(-\bar{N}^{1/2}\tilde{W}_m)$.

We define the critical micelle temperature to correspond to the value of χN when the volume fraction of the micelles reaches 0.001. (The precise value is inconsequential in all the important qualitative effects we consider here.) This sets the value of the excess free energy at the CMT to be

$$(\tilde{W}_m)_{CM} = \ln(4.19 \times 10^3{\tilde{R}_m}^{\ 3})\bar{N}^{-1/2} \tag{17}$$

which, together with Figure 2, determines the value of χN at the CMT, $(\chi N)_{CM}$. For $f = 0.1$, the above equation becomes $(\tilde{W}_m)_{CM} = 11.752\bar{N}^{-1/2}$.

C. Molecular Weight Effects. Equation 17 implies a molecular weight dependence for $(\chi N)_{CM}$. As shown in Figure 2, $\tilde{W}_m$ goes to zero linearly as χN approaches $(\chi N)^*$. Therefore, eq 17 implies that

$$(\chi N)^* - (\chi N)_{CM} \sim \bar{N}^{-1/2} \tag{18}$$

This scaling is seen clearly in Figure 5.

Thus, in contrast to $(\chi N)_{MD}$, $(\chi N)^*$, as well as the mean-field phase boundaries predicted in refs 3 and 4, all of which are independent of the molecular weight, $(\chi N)_{CM}$, the onset of observable concentration of micelles, does depend on the molecular weight. The longer the block copolymers are, the larger the value of χN needs to be to detect the micelles. In Figure 6, we show the location of $(\chi N)_{CM}$ for two molecular weights as well as $(\chi N)_{MD}$ and $(\chi N)^*$ on a phase diagram that has the mean-field dis−fcc and fcc−bcc phase boundaries predicted in refs 3 and 4. For the asymmetric block copolymers with $f < \sim 0.19$, $(\chi N)_{fcc-dis} < (\chi N)^* < (\chi N)_{bcc-fcc}$ and $(\chi N)_{MD} < (\chi N)_{fcc-dis}$. Therefore, the $(\chi N)_{CM}$, which is intermediate between the $(\chi N)^*$ and $(\chi N)_{MD}$, can be greater or less than $(\chi N)_{fcc-dis}$, depending on the molecular weight. For the two molecular weights shown in the figure, $(\chi N)_{CM}$ occurs before $(\chi N)_{fcc-dis}$, with $(\chi N)_{CM}$ for the larger molecular weight getting closer to $(\chi N)_{fcc-dis}$. In these cases, one should be able to observe an appreciable concentration of disordered micelles before they order. However, for very long polymer chains, eq 18 shows that $(\chi N)_{CM} \to (\chi N)^*$. For sufficiently long chains, $(\chi N)_{CM}$ can exceeds $(\chi N)_{dis-fcc}$; thus, the ordering transition into fcc can occur before the disordered micelles reach an appreciable concentration. This means that for very long polymers a direct transition will occur between the disordered, micelle-free state and the fcc phase without going through a state with a measurable concentration of micelles; the mean-field phase diagram predicted in refs 3 and 4 will be recovered in this long chain limit.

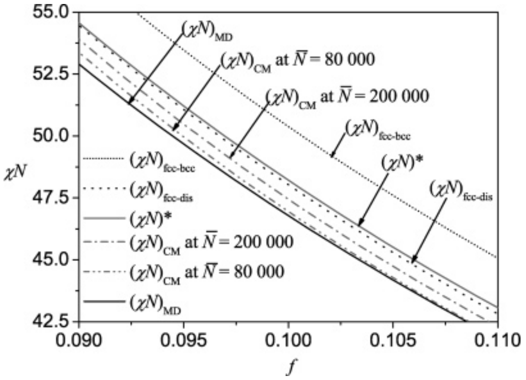

Figure 6. Location of $(\chi N)^*$, $(\chi N)_{MD}$, and $(\chi N)_{CM}$ on the mean-field phase diagram. Data for the fcc−dis and fcc−bcc phase boundaries are courtesy of M. W. Matsen.

The presence of disordered micelles leads to a decrease in the free energy of the disordered state, which alters the competition between the disordered state and the ordered states. A revised phase diagram will have to include the interaction between the micelles in the free energy of the disordered state in order to quantitatively compare the free energy of the different phases. Since our study ignores this interaction, such a task is beyond the scope of this work. Nevertheless, the information we have obtained allows us to draw some rather powerful qualitative conclusions about several different phase transition scenarios that reflect the molecular weight dependence.

We start with the excess free energy per chain of the disordered states with micelles obtained by multiplying the excess free energy density eq 15 by the volume per chain Nv; this gives

$$\beta f^{ex} = -6^{3/2}\bar{N}^{-1/2}\exp(-\bar{N}^{1/2}\tilde{W}_m) \tag{19}$$

Of particular interest is the value of this excess free energy at the CMT; it can be calculated using eq 17

$$\beta f_{CM}^{ex} = -\frac{3.51 \times 10^{-3}}{{\tilde{R}_m}^{\ 3}}\bar{N}^{-1/2} \tag{20}$$

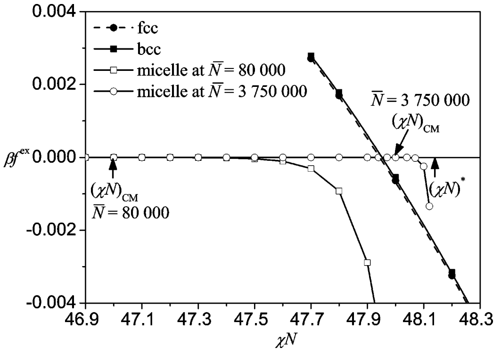

Figure 7. Comparison of the excess free energy per chain of the micelle at two molecular weights with that of the fcc and bcc phases for $f = 0.1$. The free energy of the fcc and bcc phases cross at ~50.46, which is beyond the scope of the figure. Data for the free energy of the fcc and bcc phases are courtesy of M. W. Matsen.

which become $\beta f_{\mathrm{CM}}^{\mathrm{ex}} = -1.16 \times 10^{-4}\bar{N}^{-1/2}$ at $f = 0.1$. If $f_{\mathrm{CM}}^{\mathrm{ex}} < \mathrm{Min}(f_{\mathrm{fcc}}^{\mathrm{ex}}, f_{\mathrm{bcc}}^{\mathrm{ex}})$, then we will observe the disordered micelle state with appreciable concentrations before the ordered phases. If the opposite is true, then one of the ordered phases will appear before the disordered micelles reach an appreciable concentration, and the disordered micelle state will be preempted by the ordering transition.

Figure 7 shows the comparison of the excess free energy per chain between the disordered micelles state and the bcc and fcc phases for block copolymers of $f = 0.1$ at two molecular weights. (The rightmost part of the free energy curve for the disordered micelles is meaningless because of the neglect of micelle–micelle interactions.) Since all excess free energies are defined relative to the micelle-free disordered state, its excess free energy is identically zero and is represented by the horizontal line. The free energy curves for the fcc and bcc cross at about $\chi N \approx 50.46$, which is beyond the frame of the figure to the lower right. For $\bar{N} = 80\,000$, $(\chi N)_{\mathrm{CM}}$ occurs well before $(\chi N)_{\mathrm{fcc-dis}}$, the crossing between the fcc and the disordered micelle free state, and the free energy of the disordered micelles at the CMT is lower than the free energy of the fcc. Therefore, we expect to observe the appearance of disordered micelles before any ordering transition takes place. However, these micelles will eventually become ordered, which means that, if the micelle–micelle interactions were properly accounted for, the free energy curve for the disordered micelles would eventually cross the free energy curves for the fcc and bcc. By eq 19, at a given χN, the shorter the polymer chain is, the more negative the excess free energy of the disordered micelles becomes, and hence the crossing will take place further to the lower right of the figure where the bcc already has a lower free energy than the fcc. Thus, the disordered micelles will make a direct transition to the bcc without going through the fcc for short to moderately long chains. This is consistent with the D–L prediction.[17] For $\bar{N} = 3\,750\,000$, on the other hand, the excess free energy of the disordered micelles at CMT is higher than the free energy of the fcc, and $(\chi N)_{\mathrm{CM}}$ sets in after the crossing between the free energy of the fcc with the micelle-free disordered state. In this case, the disordered phase will order into fcc without going through a state of appreciable concentration of micelles, with a further transition to the bcc at $(\chi N)_{\mathrm{fcc-bcc}} \approx 50.46$. Thus, the phase transition sequence dis ↔ fcc ↔ bcc predicted in refs 3 and 4 is recovered in the long chain limit. For some intermediate values of $\bar{N}$ it is possible for the crossing between the disordere micelle branch and the fcc branch to take place before fcc crosses bcc. In this case, we have a transition from the disordered micelles to fcc followed by fcc to bcc. Therefore, depending on the molecular weight, we predict the following phase transition scenarios:

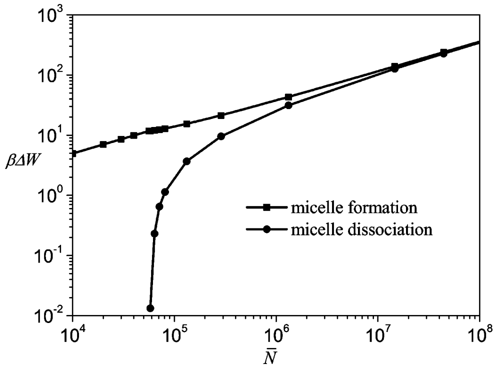

Figure 8. Actual free energy barriers for micelle formation and dissociation at the CMT as a function of $\bar{N}$ for $f = 0.1$.

disordered micelles ↔ bcc
for short to moderately long chains;

disordered micelles ↔ fcc ↔ bcc
for long chains;

micelle-free disordered state ↔ fcc ↔ bcc
for extremely long chains

We close this discussion of the molecular weight effects by returning to the nature of the disordered micelle state. As the molecular weight decreases from infinity, $(\chi N)_{\mathrm{CM}}$ decreases from $(\chi N)^*$ according to eq 18. However, this decrease is cut off at $(\chi N)_{\mathrm{MD}}$ (cf. Figure 5), below which the existence of the micelle is impossible. For $f = 0.1$, $(\chi N)_{\mathrm{CM}} = (\chi N)_{\mathrm{MD}}$ at $\bar{N} \approx 56\,000$. This means that for $\bar{N} \le 56\,000$, as soon as χN exceeds $(\chi N)_{\mathrm{MD}}$, the free energy of the micelle will be low enough to result in a concentration of micelles $\phi_{\mathrm{m}} > 0.001$. In this case, the CMT becomes equivalent to the MDT, and we expect a sharp increase in the number of micelles as χN increases past $(\chi N)_{\mathrm{MD}}$, which may give the *appearance* of a phase transition.

Further insights into the molecular weight dependence on the state of the disordered micelles can be obtained by considering the kinetics of the formation and dissociation of the micelles. Because the free energy shown in Figure 1 is scaled by $\bar{N}^{1/2}$, the actual free energy of the micelle, the free energy barrier for its formation and the free energy barrier for its dissociation will all be multiplied by this factor. Therefore, for a given χN in the range $(\chi N)_{\mathrm{MD}} < \chi N < (\chi N)^*$, a micelle is more difficult to form both thermodynamically (cf. eq 16) and kinetically, the longer the polymer chain is, but once formed, a micelle will also have a longer lifetime. Of particular interest are the free energy barriers for the formation and dissociation at the CMT. Figure 8 shows these free energy barriers at the CMT as a function of the natural degree of polymerization $\bar{N}$ for $f = 0.1$. Because $(\chi N)_{\mathrm{CM}} \rightarrow (\chi N)^*$ in the large $\bar{N}$ limit, and $(\chi N)^*$ is defined to be when the excess free energy of a micelle is zero (and hence the free energy barriers for the formation and dissociation of a micelle are equal; see Figure 1), the free energy barriers for the micelle formation and dissociation approach each other in the large $\bar{N}$ limit. As $\bar{N}$ decreases, $(\chi N)_{\mathrm{CM}}$ decreases toward $(\chi N)_{\mathrm{MD}}$. Thus, the free energy barrier for micelle dissociation drops precipitously at $\bar{N} \approx 56\,000$ where $(\chi N)_{\mathrm{CM}} \approx (\chi N)_{\mathrm{MD}}$. If we take $10kT$ as the smallest free energy barrier for the dissociation of a micelle to make it an entity with still a well-defined lifetime, then for $f = 0.1$, at the CMT, this requires $\bar{N} > 3 \times 10^5$. Since the range of $\bar{N}$ used in the experiments are typically $\leq 10^5$, the lifetime of the disordered micelles should be rather short at the CMT. So, for short block copolymers, although the number of micelles increases rapidly as χN exceeds $(\chi N)_{\mathrm{CM}}$, the free energy barrier for their dissociation is actually quite low, making them essentially dynamic entities with short lifetimes. In this sense, the appearance of micelles as CMT is approached can be considered a manifestation of enhanced composition fluctuations.

D. Contribution by the Micelles to the Structure Factor of the Disordered Phase. As large, localized composition fluctuations, the disordered micelles contribute to the total scattering function (structure factor) of the disordered phase, leading to deviation from the RPA structure factor predicted by Leibler.[38] The deviation from the Leibler structure factor near the ODT for symmetric or nearly symmetric block copolymers is well-known. Whereas the Leibler theory predicts a peak position q^* of the structure factor that is independent of χN, experimentally it was found that the peak shifts toward low q values as the ODT is approached, with a larger shift and over a broader range of χN for lower molecular weight polymers.[39] Theoretically, the shift has been explained as due to chain stretching from its ideal Gaussian conformation implicit in the RPA theory of Leibler.[20] Computer simulation indeed revealed significant increase in the end-to-end distance of the diblock copolymer chains in the disordered state as χN increases toward the ODT.[40]

In this subsection, we show that the presence of disordered micelles provides an alternative mechanism for the low-q shift of the structure factor for highly asymmetric diblock copolymers. In a complete theory, one must include the liquidlike structure of the micelles due to the interaction between the micelles. Indeed, the Percus−Yevick equation was used to fit the experimental scattering function in ref 7. Here we focus on the effects due to the form factor of the micelle. Neglecting the intermicelle correlation, we can write the overall structure factor of the disordered state as a weighted sum of the Leibler structure factor of the micelle-free disordered state and the form factor of the micelles

$$S_{\mathrm{tot}}(q) = n_{\mathrm{m}} |\Psi_{\mathrm{m}}(q)|^2 + \langle \Psi'(q)\, \Psi'(-q) \rangle \qquad (21)$$

where n_{m} is the number of micelles, Ψ_{m} is the mean-field order parameter profile of a single micelle, and Ψ' is the fluctuating part of the order parameter in regions where there are no micelles.

We can rewrite eq 21 as

$$S_{\mathrm{tot}}(q) = n_{\mathrm{m}} R_{\mathrm{g}}{}^{6} \tilde{F}(\tilde{q})^2 + vNV'_{\mathrm{tot}} \tilde{S}(\tilde{q}) \qquad (22)$$

where $\tilde{F}(\tilde{q})$ is the dimensionless Fourier transform of the micelle density profile $\phi_{\mathrm{A}}(r) - f$ (see Figure 4), V'_{tot} is the volume taken by the unmicellized chains, and $\tilde{S}(\tilde{q})$ is the structure factor given in the Leibler theory.[38] Now dividing both sides of eq 22 by $vV_{\mathrm{tot}}N$, we get a normalized total structure factor

$$\tilde{S}_{\mathrm{tot}}(\tilde{q}) = \frac{3\bar{N}^{1/2} \tilde{q}_{\mathrm{m}}{}^{3}}{32\sqrt{6}^{3} \pi^4} \phi_{\mathrm{m}} \tilde{F}(\tilde{q})^2 + (1 - \phi_{\mathrm{m}}) \tilde{S}(\tilde{q}) \qquad (23)$$

where ϕ_{m} is the volume fraction of the micelles given by eq 16. In Figure 9 we show the structure factor calculated using eq 23 for $\bar{N} = 80\,000$ at $f = 0.1$ and $\chi N = 47.40$ $(= [(\chi N)_{\mathrm{MD}} + (\chi N)^*]/2)$ and compare it with that of the micelle-free disordered state predicted by the Leibler theory. The volume fraction of the disordered micelles at this condition is 0.047. As shown in the figure, because of the existence of the disordered micelles, the peak position of the structure factor q^* shifts to a lower value compared to the Leibler structure factor, and the scattering intensity is enhanced. This latter aspect is to be contrasted with symmetric diblock copolymers near the ODT. There, the scattering intensity is reduced from that predicted by Leibler, caused by the renormalization due to large fluctuations near a mean-field spinodal.[18] In our case, the system is far from the spinodal of the disordered phase; the increased scattering intensity is caused by the formation of thermally activated, localized structures (micelles). Nevertheless, in both cases, the deviations from the Leibler mean-field structure factor are manifestation of fluctuation effects due to finite molecular weights.

Equation 23 can be used to study the change of the structure factor as a function of χN and N. Since the main effect upon changing the temperature in the range $(\chi N)_{\mathrm{MD}} < \chi N < (\chi N)^*$ is the change in the number of micelles, we ignore the weak temperature dependence in $\tilde{q}_{\mathrm{m}}$ and take it to be a fixed value evaluated at $\chi N = [(\chi N)_{\mathrm{MD}} + (\chi N)^*]/2$. If we further ignore the temperature dependence in $\tilde{F}(\tilde{q})$ which is also fairly weak, the main temperature and molecular weight dependence in the structure factor is through the volume fraction of the micelles.[14] Additional molecular weight dependence enters in the weighting between the two terms in eq 23. Because of the strong exponential dependence eq 16, at a given χN, the micelle contribution to the structure factor decreases as the molecular weight increases; at a given $\bar{N}$, the micelle contribution decreases as χN decreases. (Equation 23 assumes $\chi N > (\chi N)_{\mathrm{MD}}$; for $\chi N < (\chi N)_{\mathrm{MD}}$, ϕ_{m} should be set to zero.) In Figure 10 we show the dependence of the peak value $\tilde{q}^*$ of the structure factor as a function of χN for several values of $\bar{N}$. In all cases significant decrease of $\tilde{q}^*$ occurs approximately at the CMT for the corresponding $\bar{N}$. For $\bar{N} \to \infty$, there are no disordered micelles, and deviation from the Leibler structure factor vanishes. The decrease of $\tilde{q}^*$ with increasing χN is consistent with the experimental finding in refs 7, 9, 12, and 13; the predicted molecular weight dependence remains to be tested.

IV. Conclusion

In this work, the nature of disordered micelles near the ODT in asymmetric sphere-forming diblock copolymer melts is examined from a nucleation perspective using the self-consistent-field theory. In contrast to earlier work which presumed the existence of micelles, we follow the free energy change as a function of the reaction coordinate (the material excess) as a single micelle emerges from the uniform disordered state. Thus, we are able to address both the (quasi-equilibrium) kinetics of the micelle formation and dissociation and the connection of micelle formation to composition fluctuation.

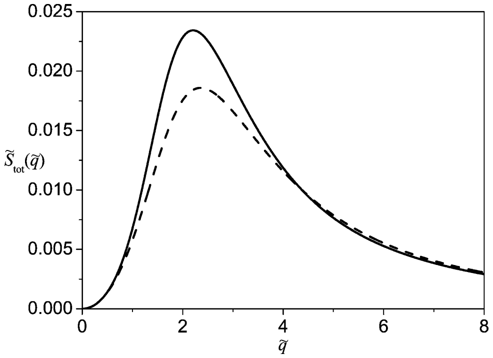

Figure 9. Total structure factor for $f = 0.1$ at $\chi N = 47.43$ and $\bar{N} = 80\,000$ (solid line) compared with the Leibler structure factor (dashed line). At the specified conditions, the volume fraction of the micelles is $\phi_m = 0.047$.

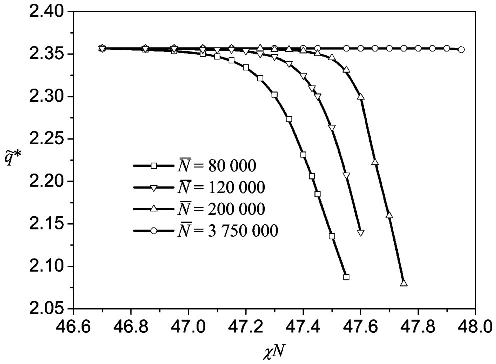

Figure 10. Shift in dimensionless peak position $\tilde{q}^*$ ($\tilde{q} \equiv qR_g$) of the structure factor as a function of χN for $f = 0.1$ at several $\bar{N}$'s.

The most important result of this work is that the disordered micelles are strong, localized composition fluctuations formed through nucleation. The micelles correspond to the local minimum of the free energy along the material excess coordinate. There exist two well-defined temperatures given in terms of the dimensionless interaction parameter χN: $(\chi N)_{MD}$ corresponds to the temperature (termed the micelle dissociation temperature, MDT), beyond which micelles cannot exist with finite lifetimes (i.e., the free energy barrier for micelle dissociation vanishes), and $(\chi N)^*$ corresponds to the temperature where the excess free energy of forming a micelle is zero, or equivalently, the free energy barriers for the formation and dissociation are equal. Both $(\chi N)_{MD}$ and $(\chi N)^*$ are independent of molecular weights at a given block composition.

By including the translational entropy of the micelles, we can determine the concentration of the disordered micelles. At a given χN in the range $(\chi N)_{MD} < \chi N < (\chi N)^*$, the concentration of micelles decreases exponentially with molecular weight. From the temperature dependence (i.e., the χN dependence) of the micelle concentration, a critical micelle temperature ($(\chi N)_{CM}$) can be defined by invoking some threshold value for the concentration of micelles. Physically speaking, the critical micelle temperature corresponds to the χN at which the excess free energy of a micelle relative to the uniform disordered state becomes of order kT. Unlike $(\chi N)_{MD}$, which has a precisely defined value below which the free energy barrier for micelle dissociation vanishes, $(\chi N)_{CM}$ can only be defined in an operational manner. More importantly, $(\chi N)_{CM}$ depends on the molecular weight and is bracketed by $(\chi N)_{MD}$ on the low molecular weight end and by $(\chi N)^*$ on the high molecular weight end.

Below the micelle dissociation temperature, the presence of disordered micelles leads to a decrease of the free energy of the disordered phase by an amount proportional to the osmotic pressure of the micelles. Since the concentration of micelles depends strongly on the molecular weight, the competition between the disordered micelle state and the ordered fcc and bcc states—whose free energy is independent of molecular weight—leads to phase transition scenarios that depend on the molecular weights. For short to moderately long polymers, we predict that a direct transition between the disordered micelle state and the bcc phase preempts the disordered to fcc and fcc to bcc transitions, in agreement with the experimental observations[7−16] and the D−L prediction.[17] For long polymers, there can be an ODT between the disordered micelles and the fcc, followed by the fcc to bcc transition. Finally, for very long polymers, the ODT is that between the micelle-free disordered phase and the fcc phase without the intervening disordered micelles; the disordered to fcc to bcc transition sequence predicted by Matsen and Bates is recovered. In the infinite chain length limit, the SCFT mean-field phase diagram of refs 3 and 4 becomes exact.

Finally, we show that the presence of disordered micelles leads to enhanced scattering in the disordered phase and a low-q shift in the peak of the structure factor compared to the RPA structure factor obtained by Leibler. The deviation is more significant for lower molecular weight polymers. In the infinite chain length limit, the structure factor reduces to that predicted by Leibler.

That the effects of disordered micelles disappear in the infinitely long chain limit and that mean-field predictions, such as on the phase diagram and structure factor, become exact in this limit, should not come as a surprise. The dependence of fluctuation effects on molecular weights was first elucidated by de Gennes,[41] who showed that deviation from mean-field behavior of the phase diagram in a binary polymer blend is limited to a narrow region that shrinks with increasing molecular weight and vanishes in the infinite molecular weight limit. Similar arguments were invoked by Binder in the study of nucleation in binary polymer blends.[42] Fredrickson and Helfand[18] explicitly worked out the finite molecular weight correction in the structure and thermodynamics for diblock copolymers and showed similarly that the fluctuation effects vanish in the infinite chain limit. Thus, our results are consistent with our general understanding of the molecular weight effects on fluctuation. However, quantitatively, as shown in refs 18 and 35, extremely long polymers are required to reach this long chain limit. The experimentally accessible molecular weights are usually far from this limit, and therefore fluctuation effects are almost always relevant.

We conclude this paper with a discussion of the concept of the demicellization temperature (DMT) and the two-transition scenario for the ODT advocated by Han, Hashimoto, Kim, Sakurai, and co-workers.[9,12,13] We agree with Dormidontova and Lodge[17] that, strictly speaking, there is only one thermodynamic transition between the disordered phase and an ordered phase and that disordered micelles are part of the disordered phase. However, as we have shown, there exists a distinct temperature (the micelle dissociation temperature, MDT) beyond which micelles with finite lifetimes are impossible. In essence, $(\chi N)_{\mathrm{MD}}$ acts as a spinodal for the micelles and in principle can be determined by measuring the kinetics of the micelle dissociation in a temperature jump experiment. Thus, if we interpret the DMT to mean the same as our MDT, the concept is a valid one from the mean-field, kinetic point of view. Thermodynamically, we have argued in section III.C that for sufficiently low molecular weights ($\bar{N} \leq 56\,000$ for $f = 0.1$) the CMT coincides with the MDT and that the appearance or disappearance of micelles can happen in a relatively sharp manner, making it to appear like a phase transition. A key point in the view of the authors of refs 9, 12, and 13 is that the existence of disordered micelles in the highly asymmetric, sphere-forming block copolymers reflects an essential difference from the more symmetric block copolymers. Insofar as the micelles represent strong, localized composition fluctuations with well-defined shape and domain structure that correspond to local free energy minima − which are different from the nebulous and ephemeral composition fluctuations near the ODT for more symmetric block copolymers—this distinction appears to be valid. For example, we find that for $f > \sim 0.22$ $(\chi N)_{\mathrm{MD}}$ is higher than the χN required for the ordering into both fcc and bcc phases, so disordered micelles can only exist as part of the disordered phase for $f < \sim 0.22$. Thus, the nature of composition fluctuation in the disordered phase in highly asymmetric block copolymers may indeed be quite different from that in the more symmetric ones. An interesting question is whether in the more symmetric block copolymers, localized, activated, large-amplitude fluctuations can be manifested in aggregates of other well-defined shapes and structures. This possibility remains to be explored.

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(34) The deviation of the density of the minor block from its value in the uniform, disordered state is an oscillatory function and includes both excess and depletion in equal amount; the use of the absolute value in the definition of the material excess counts both contributions. Thus, 2π instead of 4π is used to correct for this double counting. However, this is purely a matter of convention; a material excess with the factor of 4π would have been an equally valid definition of the order parameter.
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(36) This statement implicitly assumes that the pathway for the formation and dissociation of a micelle is properly described by the “reaction coordinate” of Figure 1. We believe this assumption to be physically reasonable; however, its rigorous justification would require analyzing the actual kinetics of the formation and dissociation of a micelle, which is beyond the scope of this work.
(37) The appearance of the volume scale a^3 can be equivalently understood by the following consideration. Let the partition function of disordered phase of n unassociated diblock copolymers be $\Omega(n)$ in a system of volume V_{tot} and the partition function of the same system but having one micelle of m diblock copolymers be $V_{\mathrm{tot}}\Omega'(m, n - m)$, where the factor V_{tot} results from integrating the center-of-mass position of the micelle, then equilibrium number of micelles can be obtained as the ratio $V\Omega'/\Omega$; see ref 33. This ratio defines both the excess free energy W_{m} of the micelle and the volume scale a^3 through $V\Omega'/\Omega = (V/a^3)\exp(-\beta W_{\mathrm{m}})$. We thank Prof. David Morse for a helpful discussion on this point.
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