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The Order−Disorder Transition and the Disordered Micelle Regime in Sphere-Forming Block Copolymer Melts

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ABSTRACT: The order−disorder transition in a melt of asymmetric micelle-forming diblock copolymers is studied analytically in the strong segregation limit. In contrast to previous calculations by Semenov and by self-consistent mean-field theory, both the translational entropy of the micelles in a disordered micelle regime and the intermicelle free energy are taken into account. This enables us to locate the order−disorder transition, ODT, where the long-range order (or lattice) of micelles disappears. In agreement with some experimental observations, the ODT occurs between body-centered-cubic spheres and disordered micelles. A face-centered-cubic sphere phase remains thermodynamically unstable, as it is superseded by the disordered micelle regime due to the gain in the translational entropy of micelles. The ODT is accompanied by a decrease in the micelle volume fraction and, more importantly, in the number density of micelles. The aggregation number and the average distance between micelles also change at the ODT, but only slightly. At higher temperatures the number of micelles decreases, but some small fraction of micelles may persist to very high temperatures. A "critical micelle temperature" (cmt) may be estimated, which separates the disordered micelle regime (with a finite micelle concentration) from a disordered melt (with exponentially small micelle fraction), but it is not a true phase transition. Thus, the disordered micelle regime is part of the disordered phase. The composition dependence of the ODT is also analyzed. We compare the predictions of this model with experimental data for poly(styrene-*b*-isoprene) diblock copolymers, with encouraging agreement.

Introduction

The structural and dynamic properties of block copolymer melts in the vicinity of the order−disorder transition (ODT) have been the subject of extensive investigation in recent years. Experiments, computer simulations, and theoretical developments have uncovered a very rich phenomenology, and as a consequence our understanding of this class of materials has advanced markedly.[1,2] However, fundamental issues remain unresolved, and many of these concern highly asymmetric copolymers, which at low temperature order as spherical micelles on a cubic lattice. Aspects of this problem have been examined experimentally by many groups.[3−17] Comparisons among these results reveal possible discrepancies. For example, it is not yet clear how many distinct equilibrium phases exist. Some authors consider two (i.e., an ordered body-centered-cubic (bcc) array of spheres and a disordered state, possibly with significant concentration fluctuations[9,10]) and others three (a liquidlike arrangement of distinct spherical micelles at temperatures intermediate between bcc spheres and the fully disordered melt[12−14,16,17]). In the first picture, schematically shown in Figure 1, there would only be one thermodynamic phase transition, the ODT. In the second picture, there could be two transitions: one between bcc and disordered micelles and another between micelles and complete disorder.

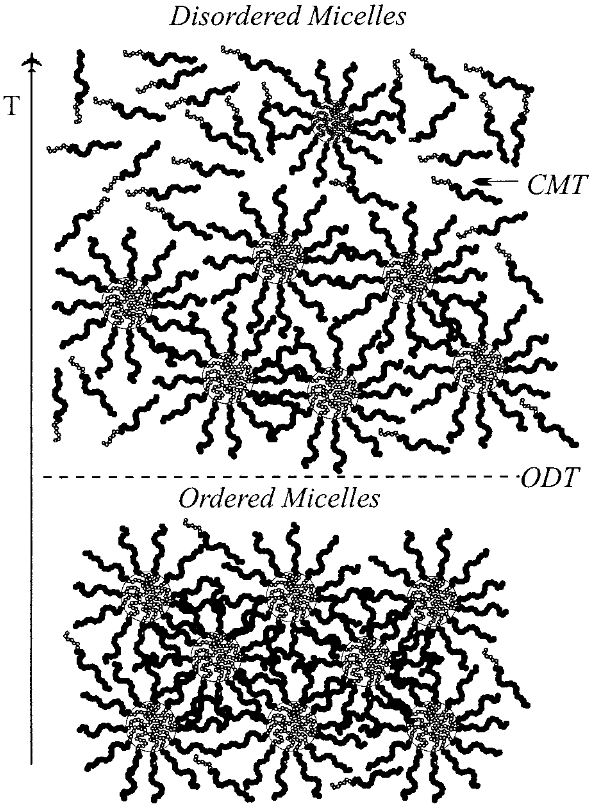

Figure 1. Schematic illustration of the ordered state, the disordered micelle regime, and the associated transition.

The large body of experimental data reporting a direct transition from bcc to a disordered state (with or without micelles) conflicts with detailed theoretical predictions, where the formation of close-packed structures (cps) was expected as an intermediate state between bcc and the

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disordered melt.[18-20] To our knowledge, formation of cps has not been reported in asymmetric diblock copolymer melts. Inspection of the theoretical models applied so far, however, shows that in fact a disordered, liquidlike micelle state has not been considered in the calculations, as the free energy of an ordered state has been compared (either directly or indirectly) with the free energy of the "fully" disordered state (free of micelles). Hence, the formation of a stable disordered micelle regime, as apparently observed experimentally, has been overlooked theoretically. We address this problem in the present contribution.

In the main thrust of this paper we explore further implications of Semenov's strong-segregation theory for asymmetric copolymers.[18,19] This model considers the ordering of an assembly of micelles and thus incorporates the possibility of three distinct phases. However, we extend this theory in order to examine the nature of the two possible transitions in more detail and the dependence of the ODT and the characteristics of the polymer system near the ODT on molecular parameters. These predictions are compared with some of the experimental results. We also attempt to reconcile the "two phases, one transition" and the "three phases, two transitions" pictures. From our calculations the ODT remains the only thermodynamic phase transition between an ordered (bcc) arrangement of micelles and a disordered micelle regime. The disordered micelles progressively decrease in concentration with increasing temperature, and a critical micelle temperature (cmt) can be estimated, but there is no further phase transition. Therefore, we conclude that there are strictly only two phases (bcc and disordered) and one phase transition (the ODT) but that the disordered phase may be viewed as comprising two *regimes*—one with a liquidlike arrangement of micelles near the ODT, separated by the cmt from one with a negligible fraction of micelles at higher temperatures. Prior to describing our model, we begin by summarizing previous theoretical approaches, and especially that of Semenov.[18,19]

Theoretical Background

Traditionally, the order–disorder transition (ODT) has been associated with the weak segregation limit (WSL), where the blocks are only slightly incompatible and the chains remain Gaussian, but more recently it has become apparent that much of the phase diagram near the ODT falls into an intermediate segregation regime. Leibler[21] first applied the random phase approximation (RPA) to AB diblocks in the WSL, and later this approach was extended in many different ways by other researchers.[22-26] Important improvements to the RPA approach were made by Fredrickson and Helfand (FH),[23] Olvera de la Cruz and Mayes,[24,25] and Barrat and Fredrickson,[26] who considered fluctuation corrections using a self-consistent Hartree approximation.[27] They found the ODT to be first order for all compositions including $f = 0.5$. Moreover, the ODT occurs at lower temperatures; the fluctuations stabilize the disordered state. The magnitude of this shift decreases with increasing block asymmetry, f, and chain length, N, tending to the Leibler result for infinite chain length (or strongly asymmetric diblocks).

An alternative approach to the Leibler mean-field theory has been considered by Schweizer and coworkers.[28,29] They performed numerical and analytical calculations on the basis of PRISM theory, emphasizing compositionally symmetric melts. Good agreement was found between the predictions of both the PRISM and FH models and experimental data for symmetric diblocks. For the only asymmetric case considered ($f = 0.77$) the predictions of PRISM model seem to be more consistent with experiment than the FH model. A key distinction is that the physical origins of the fluctuations differ: those in FH as well as in the Barrat–Fredrickson and Olvera de la Cruz models come from intramolecular entropy, whereas those of the PRISM model are enthalpic in nature. The FH results coincide with Leibler's in the limit $N \to \infty$, whereas the PRISM results recover Leibler's results in the limit $T \to \infty$, when the interactions are switched off.

In the ordered state, self-consistent mean-field (SCMF) calculations provide a smooth transition from the weak to strong segregation regime.[20,30,31] The phase map obtained recovers the results of the WSL at small χN near the critical point (where χ is the A/B interaction parameter) and converges to Helfand's strong segregation results at very low temperatures.[32-34] With respect to compositionally asymmetric copolymers an important finding is that the region of stability for hex and bcc phases increases dramatically in comparison with Leibler's diagram, even near the critical point. The reason for this becomes evident when the calculated concentration profiles are compared near the corresponding ODT.[31] For slightly asymmetric copolymers with small $(\chi N)_{\mathrm{ODT}}$ the concentration profile is a smooth sinusoid-like function, whereas for strongly asymmetric copolymers with much larger $(\chi N)_{\mathrm{ODT}}$ the profile has a rather sharp interface, adopting the shape typical of the SSL. Hence, the failure of the WSL approach to predict the ODT correctly for asymmetric copolymers has a very natural reason: the transition occurs essentially in the SSL. Consequently, a strong segregation approach may be more appropriate for studying very asymmetric copolymers.

Another important SCMF result for asymmetric copolymers is that a very narrow region of closed-packed spheres (cps) (i.e., face-centered cubic, fcc, or hexagonally close-packed, hcp) is found near the ODT.[20,30] At this point it is worthwhile to emphasize that the calculated boundary between disordered and ordered states depends on the definition of the disordered state. In all the models discussed above the disordered state is treated as a state where both blocks are nearly homogeneously mixed, and the corresponding free energy is simply the interaction free energy (in units of kT):

$$F_{\mathrm{dis}} = F_{\mathrm{un}}^{\mathrm{int}} = \chi N n f(1 - f) \tag{1}$$

where n is the number of chains; the superscript "int" denotes the interaction energy, and the subscript "un" refers to unimers. However, for strongly asymmetric diblock copolymers, formation of stable micelles even in the disordered state is possible. Such a disordered state can be viewed as a mixture of at least two components, micelles (neglecting any polydispersity in micelle size/aggregation number) and unimers (although from the point of view of the phase rule, it is still a one-component, one-phase state). Consequently, in addition to the interaction free energy, the translational entropy, F_{trans}, together with the free energy of micelles, F_{mic}, should be taken into account.

$$F_{\mathrm{dis}}^{\mathrm{mic}} = F_{\mathrm{trans}} + n_{\mathrm{un}} F_{\mathrm{un}}^{\mathrm{int}} + n_{\mathrm{mic}} F_{\mathrm{mic}} \qquad (2)$$

Here n_{un} and n_{mic} are the number of unimers and micelles, respectively, and the interaction energy is incorporated into $F_{\mathrm{un}}^{\mathrm{int}}$ and F_{mic}. It is evident that the location of the ODT will depend on the form of the free energy taken for the disordered state. Since in some vicinity of the ODT the free energy of disordered micelles, eq 2, may well be lower than that of unimers, eq 1, the former should be used for the comparison with the free energy of an ordered state. Hence, conclusions about the stability of the cps phase are under question until the disordered micelle regime is taken into consideration.

It has been suggested that cps stability arises from the significant number of unimers present in the melt near (but below) the ODT, which act in the similar way as homopolymers (of the same chemical nature as a corona-forming block) to promote formation of cps.[20,30] However, there is an essential difference between unimers and homopolymers. For instance, long homopolymer chains can screen long-range interactions between micelles, leading to enhancement of attractions between micelles at shorter distances (and hence a tendency toward cps formation, possibly as a coexisting phase at macrophase separation).[35,36] In the absence of homopolymers, a sufficiently large distance between micelles for attractive forces to come into play (for cps formation) can only be achieved at the expense of unimer expulsion, i.e., when the fraction of micelles is small. In this case, however, the translational entropy of the micelles can be considerable, and the disordered micelle regime can supersede cps. In the present paper we will attempt to analyze this problem employing the strong segregation limit formalism developed by Semenov,[18,19] who also anticipated stabilization of a cps phase near the ODT but did not examine the disordered micelle regime.

Semenov's Model. We begin with a brief description and analysis of the strong segregation formalism developed by Semenov,[18,19] following the previous results of Helfand and Wasserman.[32−34] By minimizing the micelle free energy (containing the elastic free energy of block extension and the surface free energy) with respect to the micelle core radius R, the equilibrium radius of the micelle was found to be $R = 2.18 x_c^{1/6} R_A$, where $R_A = N_A^{1/2} l_A / 6^{1/2}$ is the radius of gyration of the core-forming block. Here $x_c = \chi_c N_A$ is the threshold when formation of a single micelle becomes thermodynamically possible, i.e., when the free energy per micelle becomes negative:

$$x_c = \log\left(\frac{x_c^{1/2}}{f}\right) - 2.06 x_c^{1/3} \qquad (3)$$

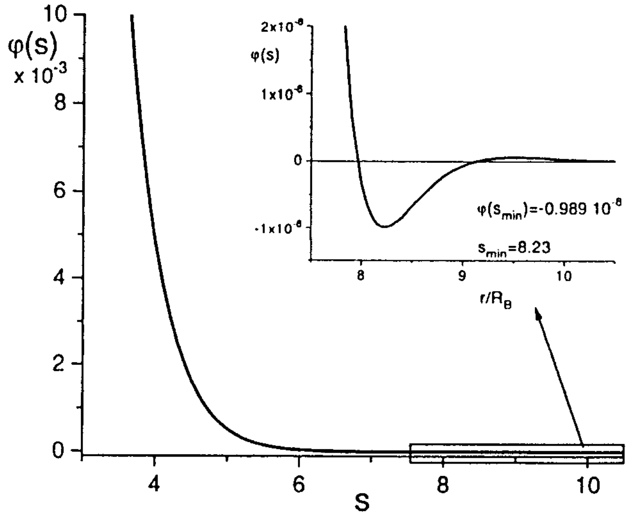

Figure 2. Reduced micelle interaction potential $\varphi(s)$ (eq 6) as a function of reduced distance between micelles $s = r/R_B$, where $R_B = N_B^{1/2} l_B / 6^{1/2}$.

When there are multiple micelles in the system, they interact with each other. The interaction between two micelles separated by the center-to-center distance r can be described by the binary interaction potential (in units of kT), which was obtained using the RPA result for the density correlation function of the A block:[18,19]

$$U_{\mathrm{int}} = \frac{1}{8\pi} \frac{N_B Q^2 \nu}{R_B^{\ 3}} \varphi(r/R_B) \qquad (4)$$

where R_B is the radius of gyration for the B block, ν is the volume per monomer unit, and

$$\varphi(s) = 4\pi \int d^3q \, \frac{1}{(2\pi)^3} \exp(iqs) \frac{(1 - \exp(-q^2))^2}{q^2 - (1 - \exp(-q^2))} \qquad (5)$$

$$= 1/s \qquad s \ll 1$$

$$= 0.5\pi^{-1/2} \exp(-s^2/4) - \frac{15.56}{s} \exp(-2.218 s) \sin(1.682 s + 0.273) \qquad s \gg 1 \quad (6)$$

At short distances, when the distance between micelles is less than or comparable to the size of micelle corona ($s \ll 1$), there is a strong repulsion between micelle coronas:

$$U_{\mathrm{int}} = \frac{6}{8\pi} \frac{\nu}{l_B^{\ 2}} \frac{Q^2}{r} \qquad (7)$$

This expression for the interaction potential can be also obtained in a different way, using the electrostatic analogy (where the local chain extension is considered as an analogue of the intensity of an electric field, while the core of the micelle is analogous to a charged sphere with the aggregation number Q playing the role of the total charge[19]).

At very large distances the micelles do not feel each other so the potential tends to zero, as can be seen from Figure 2 where $\varphi(s)$ described by eq 6 is shown. At intermediate distances both repulsion and attraction were found to be possible as $\varphi(s)$ exhibits damped oscillations. The contribution of the second term (responsible for oscillations) in eq 6 becomes noticeable only when $s = 8$. The absolute minimum $\varphi_{\mathrm{min}} = -0.989 \times 10^{-8}$ corresponds to $s_{\mathrm{min}} = 8.23$.[18]

Considering the case $U_{\mathrm{int}} \gg 1$, Semenov concluded that the most stable micelle structure at the ODT should satisfy two conditions: (i) the average distance between micelles must be $r_{\mathrm{min}} = s_{\mathrm{min}} R_B$, i.e., corresponding to the minimum of the interaction free energy, and (ii) the number of nearest neighbors should be maximal since there is attraction between micelles at $r = r_{\mathrm{min}}$. The ordering transition was defined from the balance of interaction free energy and free energy per micelle:

$$F_{\mathrm{mic}} = -6U_{\mathrm{int}} \tag{8}$$

We note that the translational entropy of the micelles was neglected as a small factor compared to $U_{\mathrm{int}} \gg 1$. The resulting stable phase at the ODT (as defined from eq 8) turned out to be fcc. With an increase of χ (decrease of an averaged $\langle r\rangle$) a series of transitions fcc → hcp → fcc → hcp → fcc → hcp → bcc were predicted.

When the more realistic case for polymer systems, $U_{\mathrm{int}} \ll 1$, was considered, the ODT was estimated from equating the interaction free energy to kT:

$$6U_{\mathrm{int}} = 1 \tag{9}$$

When χ_{ODT} and the corresponding r were defined in this way, the scheme of phase transitions for $U_{\mathrm{int}} \gg 1$ was employed (as a function of $s = \langle r\rangle/R_{\mathrm{B}}$). Thus, for poly(styrene-*b*-isoprene) (SI) copolymers with $f \approx 0.1$, the average distance between micelles at the ODT was found to correspond to $s = 4.3-5.2$, and the following sequence of transitions (upon cooling) was predicted: dis → fcc → hcp → bcc.[18]

We note that the approach presented above appears inconsistent in some points. The two conditions by which the most stable phase was selected for fixed χ (or $\langle r\rangle$) correspond to the situation when there is a net attraction between micelles. However, the average distance between the micelles at the ODT for the case relevant to polymer systems, $U_{\mathrm{int}} \ll 1$, is considerably smaller than r_{min} (i.e., $s_{\mathrm{min}} = 8.23$). As noted above, for SI diblocks s was estimated to be 4.3−5.2 at the ODT, and hence the interaction between micelles should not be attractive; but, then the condition for selecting the most stable phase is no longer appropriate as micelles will seek the most spacious arrangement with a smaller number of nearest neighbors. Disordered micelles can be a suitable candidate for such arrangement. The other inconsistency is the neglect of the translational entropy of the micelles. For the case $U_{\mathrm{int}} \gg 1$ this is correct, but for polymer systems with $U_{\mathrm{int}} \ll 1$ it is not justified. As a result, it is not obvious whether the sequence of phase transformations obtained for $U_{\mathrm{int}} \gg 1$ can be applied to the case $U_{\mathrm{int}} \ll 1$, as a liquidlike arrangement of micelles was in fact a priori excluded from the competition for the most stable phase (even though a dilute gas of micelles was taken as the high-temperature state).

Model

On the basis of the omission of a disordered micelle regime in these theoretical considerations and experimental observations of such a phase, it is evident that further attempts to understand the ODT for sphere-forming block copolymers are required. In the following we present a model for the thermodynamic behavior of an asymmetric copolymer upon heating from the bcc phase. After developing the free energy expressions for the various possible states, we examine the ODT (and the cmt). We then briefly compare these predictions with experimental results in the literature for styrene−isoprene diblocks.

To analyze the ODT (which is equivalent to the term “lattice disordering transition” used by some authors[6,12,13]) for strongly asymmetric diblock copolymer melts, we extend Semenov’s approach described above, but with particular attention to the disordered micelle phase. We assume that each polymer chain contains N monomer units, of which N_{A} monomers of type A can lie in the micellar core (i.e., $f = N_{\mathrm{A}}/N < 0.5$). In this framework the monomer units of both types occupy the same volume v, whereas the statistical segment length can be different, $l_{\mathrm{A}} \neq l_{\mathrm{B}}$ (i.e., conformational asymmetry is included). Also, we assume that the aggregation number of micelles Q corresponds to the equilibrium aggregation number, and any polydispersity of the micelle size distribution will be neglected. Some polydispersity in Q would presumably be present experimentally, but in the context of an approximate model it is a complication that can be neglected.

A. Ordered Micelles. The free energy per chain (in units of kT) of the mixture of ordered micelles can be written in the following form (cf. ref 19):

$$F_{\mathrm{ord}} = (1-y)\ln(1-y) + y + yF_{\mathrm{mic}} + Cy\frac{U_{\mathrm{int}}}{Q} + (1-y)F_{\mathrm{un}} \tag{10}$$

where $y = n_{\mathrm{mic}}Q/n$ is the fraction of polymer chains associated into micelles (i.e., the volume fraction of micelles $y = n_{\mathrm{mic}}QNv/V$, where n_{mic} and n are the total number of micelles and the total number of chains in the system, respectively, and V is the volume of the system). The first two terms on the right-hand side of eq 10 correspond to the translational entropy of unimers, the next term to the free energy of the micelles, the fourth term to the intermicelle interactions, and the last term to the unimer interaction free energy. $2C$ is the number of nearest-neighbor micelles in an ordered structure: i.e., $C = 6$ for close-packed structures, $C = 4$ for bcc, and $C = 3$ for simple cubic (sc).

The free energy per chain of a polymer micelle with an aggregation number Q (core radius R) can be written in the following form (cf. ref 19)

$$F_{\mathrm{mic}} = F_{\mathrm{el}} + F_{\mathrm{surf}} \tag{11}$$

where

$$F_{\mathrm{el}} = \frac{1}{2}\frac{R^2}{Nfl_{\mathrm{B}}^{\,2}}\left[1 + \frac{3\pi^2}{40}\left(\frac{l_{\mathrm{B}}}{l_{\mathrm{A}}}\right)^2\right] \tag{12}$$

is the elastic free energy of block extension in both core and corona regions. F_{surf} is the free energy describing interactions at the core/corona interface:

$$F_{\mathrm{surf}} = \frac{3f\langle l\rangle(N\alpha)^{1/2}}{R} + \ln\left[\frac{\alpha^{1/2}l_{\mathrm{A}}}{3\pi f^{1/2}\bar{l}\sqrt{6}}\right] \tag{13}$$

where $\alpha \equiv \chi N$ and

$$\langle l\rangle = \frac{1}{\sqrt{6}}\left[\frac{l_{\mathrm{A}} + l_{\mathrm{B}}}{2} + \frac{1}{6}\frac{(l_{\mathrm{A}} - l_{\mathrm{B}})^2}{l_{\mathrm{A}} + l_{\mathrm{B}}}\right] \tag{14}$$

$$\bar{l} = \frac{1}{\sqrt{6}}\left[\frac{l_{\mathrm{A}}^{\,2} + l_{\mathrm{B}}^{\,2}}{2}\right]^{1/2} \tag{15}$$

The two terms in the expression for F_{surf} correspond to the main contribution from the surface tension and the correction for the “smoothness” of the interface, respectively. Here we have used the results of Helfand and Sapse for the surface tension coefficient calculated for blends of conformationally asymmetric polymers,[37] whereas the correction for the connectivity of the blocks was incorporated in a similar way to Semenov.[19]

For the interaction free energy of two micelles separated by a distance r, we will employ Semenov's results (eqs 4−6 for the case $s \gg 1$) as we are mainly interested in the conditions close to the ODT (and cmt) when the average distance between micelles exceeds the corona size. Because for all realistic conditions the ODT occurs when the intermicellar distance is well below $r_{\min}$ (and hence $s < 8$), we will omit the second term in eq 6 as negligibly small. (Note that accounting for the second term would not change the final results but makes the calculations somewhat more complicated.) We note that the interaction energy decreases exponentially with increasing intermicellar distance. As a result, the contributions from next-nearest neighbors are negligible and can be omitted (unless the difference between free energies of some phases, such as fcc and hcp, is extremely small).[18,19] In what follows we will consider mainly binary interactions between nearest-neighbor micelles. This is certainly a simplification (which can be overcome using, e.g., perturbation theory[38]); however, taking into account the above and the fact that even the main contribution of the interaction free energy is not so large near the ODT (and becomes negligible near the cmt) compared with other terms of the free energy, it is likely that the corrections would only have a small impact on the absolute value of the ODT and other quantitative results. Because of the scaling nature of the approach, we consider our main goal to be qualitative, rather than quantitative, predictions.

Thus, the specificity of different ordered structures is accounted in the interaction free energy via (i) the coefficient C preceding the interaction free energy in eq 10 and the number of nearest neighbors in an ordered micelle lattice and (ii) the nearest-neighbor distance, $r_{\rm nn}$, which is used for r in $U_{\rm int}(r)$. The values of coefficient C referred above and $r_{\rm nn}$ can be obtained from simple geometrical considerations:

$$\begin{aligned} r_{\rm nn} &= b_{\rm sc} && \text{sc} \\ &= \frac{\sqrt{3}}{2} b_{\rm bcc} && \text{bcc} \\ &= 2^{-1/2} b_{\rm fcc} && \text{fcc} \end{aligned} \qquad (16)$$

where b_i is the size of the corresponding lattice i = sc, bcc, fcc. The size of a lattice is connected with the number density of micelles through $n_{\rm mic}/V$ as $b = (V/n_{\rm mic})^{1/3}$. We note that for homogeneously distributed micelles the average distance between them can be defined as $\langle r \rangle = (V/n_{\rm mic})^{1/3}$. The number density of micelles in turn is related to the micelle volume fraction, y, as $n_{\rm mic}/V = y/(QNv)$. Taking into account that there is one micelle per cell of sc, two micelles per cell of bcc, and four micelles per cell of fcc, we find

$$\begin{aligned} r_{\rm nn} &= \left(\frac{QNv}{y}\right)^{1/3} && \text{sc} \\ &= \frac{\sqrt{3}}{2^{2/3}}\left(\frac{QNv}{y}\right)^{1/3} && \text{bcc} \\ &= 2^{1/6}\left(\frac{QNv}{y}\right)^{1/3} && \text{fcc} \end{aligned} \qquad (17)$$

For the same number density of micelles, $n_{\rm mic}/V$, fcc has relatively larger distances separating nearest neighbors compared with sc and bcc, but it has also the maximum number of nearest neighbors. The sc structure has the minimal number of nearest neighbors but the smallest distance separating nearest neighbors. Comparing interaction free energies, one finds that sc is practically never favored. Both fcc and bcc are very close in interaction free energy, with bcc preferred at intermediate to small $\langle r \rangle$ and with fcc favored at large $\langle r \rangle$, i.e., in the vicinity of the ODT. However, the question of which phase is thermodynamically the most favorable just above and just below the ODT remains open, because the disordered micelle regime has also to be taken into account.

The last term in the equation for the free energy (eq 10) is the unimer interaction free energy. When the volume fraction of unimers, $(1 - y)$, tends to unity, the free energy of unimers is the usual Flory−Huggins interaction free energy, i.e., $F_{\rm un} = \chi f(1 - f)$. In a well-ordered state $y \approx 1$ (i.e., well below the ODT) the free energy of a unimer is defined by surface interactions as the A-block collapses, forming a "micelle" with aggregation number equal to 1. So, the free energy of a unimer in this state would be defined by

$$F_{\rm sur} = 4\pi R_{\rm un}^{\;2}\sigma_0 = (4\pi)^{1/3}3^{2/3}N^{1/6}\alpha^{1/2}f^{\,2/3}\langle l\rangle v^{-1/3} \qquad (18)$$

where $\sigma_0 = \langle l\rangle\chi^{1/2}/v$ is the surface tension coefficient and $R_{\rm un} = (3Nfv/4\pi)^{1/3}$ is the radius of collapsed A-block of unimer.

In the intermediate temperatures range both volume and surface interactions (as well as block stretching/collapse) give contributions to the unimer free energy. To account for these different contributions correctly is a complicated task; so far no clear analytical expression has been obtained.[39] Also, there is not much experimental information concerning changes in unimer conformation upon temperature decrease across the ODT. So below we will use the following approximate form for $F_{\rm un}$, which at least provides the correct limits at high and low temperature:

$$F_{\rm un} = \alpha f(1 - f)\frac{\chi_{\rm cmt}}{\chi} + (4\pi)^{1/3}3^{2/3}N^{1/6}\alpha^{1/2}f^{\,2/3}\langle l\rangle v^{-1/3}\left(1 - \frac{\chi_{\rm cmt}}{\chi}\right) \qquad (19)$$

This expression for $F_{\rm un}$ is an attempt to modify the Flory−Huggins form of the interaction free energy to reflect the fact that the unimer conformation starts to deviate from Gaussian near the ODT. In the Appendix we consider another form for $F_{\rm un}$ and will compare it with the present expression in the vicinity of cmt and ODT. We show that both variants lead to qualitatively similar results, and even the quantitative differences in micellar characteristics at the ODT are minor.

The free energy per chain in the ordered state (eq 10) can be considered as a function of two variables: the micelle core radius, R (or aggregation number Q), and the micelle volume fraction, y (or averaged intermicelle distance $\langle r\rangle = (QNv/y)^{1/3}$). Their equilibrium values are obtained by minimizing the free energy. Minimization of eq 10 with respect to R yields

$$\frac{R}{Nfl_{\rm B}}S - 3\,\frac{f\langle l\rangle(N\alpha)^{1/2}}{R^2} + C\,\frac{\partial}{\partial R}\left(\frac{U_{\rm int}}{Q}\right) = 0 \qquad (20)$$

In general, the contribution from the interaction free energy is relatively small, so it makes only a small correction to the well-known results for the radius of micelle and aggregation number (calculated neglecting the last term in eq 20), $R_{\mathrm{m}} = (3\langle l\rangle)^{1/3}\alpha^{1/6}(fl_{\mathrm{B}})^{2/3}N^{1/2}/S^{1/3}$ where $S = 1 + 3\pi^2 l_{\mathrm{B}}^2/(40 l_{\mathrm{A}}^2)$. However, since we wish to locate the ODT and even relatively small contributions can be of importance, we will retain the whole equation for R (eq 20), and the micelle radius (and average aggregation number Q) will be weakly dependent on micelle fraction y.

Minimization of eq 10 with respect to y leads to

$$-\ln(1-y) + F_{\mathrm{mic}} + C\frac{U_{\mathrm{int}}}{Q} + Cy\frac{\partial}{\partial y}\left(\frac{U_{\mathrm{int}}}{Q}\right) - F_{\mathrm{un}} = 0 \tag{21}$$

Upon solving eqs 20 and 21 numerically, we obtain the equilibrium values y_0 and $R_0(Q_0)$. The average distance between micelles can be estimated as $\langle r\rangle = (Q_0 Nv/y_0)^{1/3}$. Using the values of y_0 and Q_0 obtained, the equilibrium free energy (per chain) for ordered micelles can be calculated

$$F_{\mathrm{ord}}^{\mathrm{eq}} = y_0 + F_{\mathrm{mic}} + C\frac{U_{\mathrm{int}}}{Q_0} + Cy(1-y)\frac{\partial}{\partial y}\left(\frac{U_{\mathrm{int}}}{Q}\right) \tag{22}$$

B. Disordered Micelles. The free energy per chain (in units of kT) of the mixture of disordered micelles can be written in a similar form as for the ordered micelles

$$F_{\mathrm{dis}} = \frac{y}{Q}\ln\frac{y}{e} + (1-y)\ln(1-y) + y + yF_{\mathrm{mic}} + C_1 y\frac{U_{\mathrm{int}}^{\mathrm{dis}}}{Q} + (1-y)F_{\mathrm{un}} \tag{23}$$

except for the translational entropy of micelles in the disordered state (the first term in eq 24), an ideal-gas term,[18,35] and the intermicelle interaction term, which is somewhat different from U_{int} for ordered micelles. $2C_1$ is the number of nearest neighbors for the disordered micelle regime, i.e., $C_1 = 6$.

The free energy of intermicelle interaction for disordered micelles can be estimated in the following way. For any two micelles separated by the distance r the expression for U_{int} (eqs 4–6) can be applied. Although there is some average separation $\langle r\rangle$, in the disordered regime micelles can occupy random positions, so that the distance between nearest neighbors varies from point to point. The probability to find two micelles separated by the distance r, $P(r)$, can be a complicated function based on the form of intermicelle interaction potential. However, because the intermicellar potential (described by eqs 4–6) has relatively sharp walls for small micelle separations, $P(r)$ is maximal for r corresponding to intermicellar distances near the average. For simplicity, we will assume that the probability to find two nearest-neighbor micelles separated by any distance r inside the interval $[\langle r\rangle - \Delta, \langle r\rangle + \Delta]$ is the same:

$$\begin{aligned} P(r) &= \frac{1}{2\Delta} \qquad \langle r\rangle - \Delta \le r \le \langle r\rangle + \Delta \\ &= 0 \qquad \text{otherwise} \end{aligned} \tag{24}$$

When $\Delta \to 0$ (corresponding to the situation when the distance between nearest neighbors is fixed at the averaged distance, as is the case for large micelle fractions $y \to 1$), $P(r)$ becomes a delta function, and the interaction free energy is defined by eqs 4–6 with $r = \langle r\rangle$. The smaller the number of micelles, the larger the range of accessible distances between nearest neighbors, Δ. Taking into account that the minimal distance between nearest neighbors is $2D$, with D being the radius of a "collapsed" micelle: $D \cong (3QNv/4\pi)^{1/3}$, Δ can be estimated as

$$\Delta \cong \langle r\rangle - 2D \tag{25}$$

Thus, the averaged interaction potential can be defined as, e.g.,

$$\begin{aligned} U_{\mathrm{int}}^{\mathrm{dis}} &= \int U_{\mathrm{int}}(r)P(r)\,\mathrm{d}r \\ &= \frac{Q^2 N_{\mathrm{B}} v}{32\pi R_{\mathrm{B}}^2\Delta}\left[\mathrm{erf}\left(\frac{\langle r\rangle + \Delta}{2R_{\mathrm{B}}}\right) - \mathrm{erf}\left(\frac{\langle r\rangle - \Delta}{2R_{\mathrm{B}}}\right)\right] \end{aligned} \tag{26}$$

where we used eqs 4–6 for $U_{\mathrm{int}}(r)$ (keeping only the first term in eq 6, similar to ordered micelles case) and eq 24 for $P(r)$. It is worth noting that the largest contribution to $U_{\mathrm{int}}^{\mathrm{dis}}$ is associated with $U_{\mathrm{int}}(\langle r\rangle - \Delta)$, with $\langle r\rangle - \Delta$ being the minimal distance between micelles. Because of the repulsive nature of the interactions $U_{\mathrm{int}}^{\mathrm{dis}}$ is larger than U_{int} for ordered micelles with the same $\langle r\rangle$. The difference between the interaction free energies becomes especially pronounced as Δ increases, i.e., near the cmt, and it is practically negligible when the micelle fraction is large. Accordingly, the choice of Δ and the form of $P(r)$ are of some importance for the ODT, although it represents only a correction to the main contribution associated with $U_{\mathrm{int}}(\langle r\rangle)$. It is worth noting that $U_{\mathrm{int}}^{\mathrm{dis}}$ is a complicated function of y via $\langle r\rangle$ $(= (QNv/y)^{1/3})$ and Δ.

Minimization of the free energy (per chain) for the disordered micelles, eq 23, with respect to R and y leads to

$$\frac{R}{Nfl_{\mathrm{B}}}S - 3\frac{f\langle l\rangle(N\alpha)^{1/2}}{R^2} - \frac{9}{4\pi}\frac{Nvf}{R^4}(\ln y - 1) + C_1\frac{\partial}{\partial R}\left(\frac{U_{\mathrm{int}}}{Q}\right) = 0 \tag{27}$$

$$\frac{1}{Q}\ln y - \ln(1-y) + F_{\mathrm{mic}} + C_1\frac{U_{\mathrm{int}}^{\mathrm{dis}}}{Q} + C_1 y\frac{\partial}{\partial y}\left(\frac{U_{\mathrm{int}}^{\mathrm{dis}}}{Q}\right) - F_{\mathrm{un}} = 0 \tag{28}$$

Numerical solution of this set of equations determines the equilibrium fraction of micelles in the disordered state y_{d} and the equilibrium micelle core radius R_{d} (aggregation number Q_{d}). The average distance between micelles $\langle r\rangle$ is defined by $\langle r\rangle = (Q_{\mathrm{d}}Nv/y_{\mathrm{d}})^{1/3}$. The equilibrium free energy (per chain) for disordered micelles is

$$F_{\mathrm{dis}}^{\mathrm{eq}} = \frac{1}{Q_{\mathrm{d}}}\ln y_{\mathrm{d}} - \frac{y_{\mathrm{d}}}{Q_{\mathrm{d}}} + y_{\mathrm{d}} + F_{\mathrm{mic}} + C_1\frac{U_{\mathrm{int}}^{\mathrm{dis}}}{Q_{\mathrm{d}}} + C_1 y(1-y)\frac{\partial}{\partial y}\left(\frac{U_{\mathrm{int}}^{\mathrm{dis}}}{Q_{\mathrm{d}}}\right) \tag{29}$$

C. ODT and cmt. At low temperature comparison of the free energies of bcc, fcc, sc, and disordered micelle

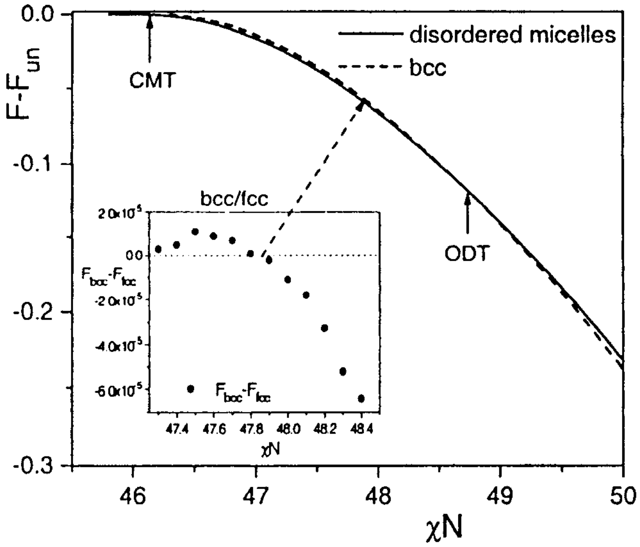

Figure 3. Free energy per chain of the bcc and disordered micelle states with respect to the free energy per chain of the disordered melt at the same temperature vs χN, for a melt of diblock copolymers with $N = 1000$, $f = 0.1$, $l_A = 0.68$ nm, $l_B = 0.7263$ nm, and $v = 0.165$ nm^3. The cmt is taken as the region where the free energy of disordered micelles approaches that for the unimer melt (see also Figure 9), whereas the ODT is the point where the free energy of the disordered micelles becomes equal to that of the ordered (bcc) phase. The insert illustrates the χN dependence of the difference between fcc and bcc free energies (per chain), thereby defining the hypothetical transition point between the phases, which occurs at smaller χN than the ODT.

phases confirms the thermodynamic preference for the bcc micelle structure, with a negligibly small fraction of unimers present. The advantage of bcc over fcc is dictated by the smaller number of nearest neighbors allowing the most spacious arrangements of micelles. With an increase of temperature, the repulsive interactions between monomers becomes less strong and the tendency toward formation of well-ordered micelles with sharp interfaces decreases. The fraction of micelles decreases as well. The preference of bcc over fcc and disordered micelles decreases, and at some point it completely disappears. Our calculations show that first the transition from bcc into the disordered micelle regime, the ODT, occurs at the temperature satisfying the condition

$$F_{\mathrm{dis}}^{\mathrm{eq}} = F_{\mathrm{ord}}^{\mathrm{eq}} \tag{30}$$

For the case illustrated in Figure 3, where the various free energies are compared for a diblock with $N = 1000$ and $f = 0.1$, the ODT corresponds to $\chi N_{\mathrm{ODT}} \approx 48.7$. The driving force for the transition is the gain in translational entropy of the micelles in the disordered state, even though the intermicellar interaction free energy is higher.

Further temperature increase, accompanied by a decrease in micelle fraction, leads to a loss of the preference of bcc among the ordered structures as well, and the fcc phase takes over ($\chi N_{\mathrm{fcc/bcc}} \approx 47.83$ for the case illustrated in Figure 3, see insert picture). At such micelle concentrations the advantage of having larger distances between nearest-neighbor micelles becomes preferable over having a smaller number of nearest neighbors. The preference for fcc over bcc is fairly small. The free energy of the disordered micelles remains lower than that of either fcc or bcc, and the difference in the free energy between disordered and ordered micelle phases only increases, as the micelle fraction decreases with an increase of temperature; the gain in translational entropy of disordered micelles becomes more pronounced compared to the loss in intermicelle interaction free energy.

At even higher temperature formation of micelles becomes less favorable thermodynamically, and their fraction decreases considerably. In the limit $y \to 0$, the interaction free energy between micelles becomes totally negligible and free energy of an ordered phase (eq 22) tends (taking into account eq 21) to the unimer free energy in Flory–Huggins form. As to the disordered micelle phase, an analysis of eq 28 in the limit $y \to 0$ shows that there is a solution of the equation, defining the equilibrium fraction of micelles:

$$y_{\mathrm{d}}^{0} \cong \exp[-Q(F_{\mathrm{un}} - F_{\mathrm{mic}})] \tag{31}$$

The fraction of micelles in this limit is exponentially small; however, it is not zero. Substitution of y_{d}^{0} into eq 29 gives

$$F_{\mathrm{dis}}^{\mathrm{eq}}|_{y\to 0} \cong F_{\mathrm{un}} - \frac{y_{\mathrm{d}}^{0}}{Q_{\mathrm{d}}^{0}} \tag{32}$$

where Q_{d}^{0} is the solution of eq 27 for y_{d}^{0} defined by eq 31. Thus, the free energy of the disordered micelles also approaches the Flory–Huggins free energy in the limit $y \to 0$, but from the negative side. Therefore, it is thermodynamically favorable to have even an exponentially small fraction of micelles, due to the gain in translational entropy. Near the ODT the fraction of micelles is still considerable, but it decreases greatly with temperature increase. The region (above the ODT) where the rate of the decrease in micelle volume fraction (or number density of micelles) changes with increasing temperature could be assigned as the critical micelle temperature, cmt, in analogy with block copolymer or surfactant solutions. However, as will be discussed below, the thermodynamic state above and below this point is essentially the same, so the cmt is not a phase transition (in contrast to the ODT). The ODT and cmt are separated by a significant temperature interval (which is about 3 on the χN scale for the case illustrated in Figure 3).

The dependence of χN at the transition on f for both the ODT and the estimated cmt is presented in Figure 4. The (hypothetical) fcc/bcc transition is also indicated on the diagram. For the whole range of compositions considered the sequence of transitions remains similar to that described above, even though the fcc/bcc transition point becomes closer to the ODT (but still above on the temperature scale) for less asymmetric samples.

A comparison of SCMF calculations for the cps/bcc transition[20,30] with our results in Figure 5 shows a very good quantitative agreement. We note that the predicted cps/bcc transition,[20,30] which can be directly compared with our fcc/bcc transition, is always above (on the temperature scale) the ODT between bcc and the disordered micelle regime predicted by our model. Thus, fcc, predicted by SCMF calculations (neglecting disordered micelles) to be thermodynamically the most stable phase in the vicinity of cmt, turns out to be only metastable when disordered micelles are taken into account. The prediction that disordered micelles are

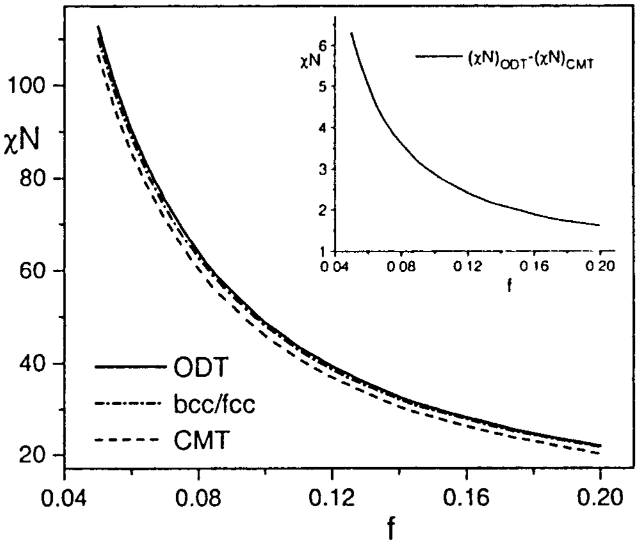

Figure 4. Composition dependence of the ODT, cmt, and fcc/bcc transition for a melt of diblock copolymers with $N = 1000$, $l_A = 0.68$ nm, $l_B = 0.7263$ nm, and $v = 0.165$ nm^3. The fcc/bcc transition is shown for comparison only, as the fcc phase remains metastable. The insert shows the concentration dependence of the width of the region between the ODT and cmt, i.e., where disordered micelles are favored. All the transitions are relatively insensitive to N, except for very short chains.

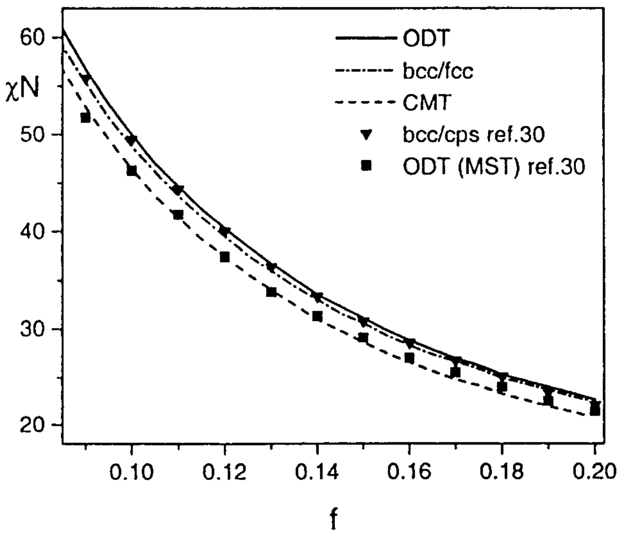

Figure 5. Composition dependence of the cmt and the fcc/bcc transition for a melt of diblock copolymers with $N = 1000$, $l_A = l_B = 0.68$ nm, and $v = 0.165$ nm^3 in comparison with SCMF calculations.[20,30] The ODT (or MST) obtained in refs 20 and 30 represents the transition point between cps and disordered unimers.

thermodynamically preferable in this region is consistent with experimental observations of the liquidlike order of micelles emerging from bcc phase upon the temperature increase above the ODT and the absence of an fcc phase. Our cmt can be compared with the ODT predicted by SCMF,[20,30] since the point where the free energy of an ordered micelle state approaches the Flory–Huggins free energy (i.e., $y_0 \rightarrow 0$) in the latter is very close to the location of the cmt in our model. However, it is important to emphasize that these two transitions are very different in character.

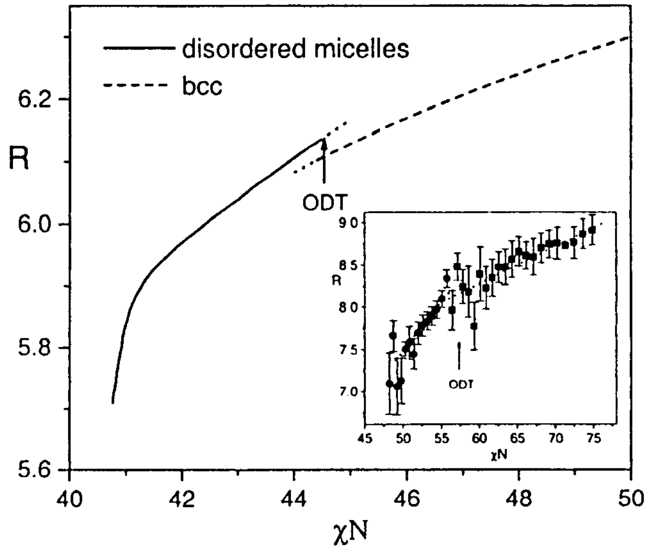

Figure 6. χN dependence of the micelle core radius, R, in the bcc and disordered micelle states for $f = 0.11$, $N = 500$, $l_A = 0.68$ nm, $l_B = 0.7263$ nm, and $v = 0.165$ nm^3 in comparison with experimental results from ref 17 (insert).

The interval between the ODT and the cmt, i.e., the region where the disordered micelle regime should be observed, increases for polymers with more asymmetric compositions, as shown in Figure 4. The reason for this effect is the following. The ODT occurs when the gain in translational entropy of the micelles exceeds the loss in energy of intermicelle interaction. The latter depends on the composition, f, via the micelle aggregation number Q and the average intermicelle distance $\langle r \rangle$: as f increases, the larger the contribution of intermicellar interactions becomes and hence the larger the translational entropy of micelles (i.e., the smaller number of micelles) needed for the ODT to occur. As a result, for diblock copolymers with large f the ODT occurs at a relatively small number density of micelles, i.e., closer to the cmt, whereas for micelles with smaller f the ODT lies well below the cmt in temperature.

Now we consider the changes in the main characteristics of the micelles (i.e., aggregation number, intermicelle distance, and fraction of micelles) that accompany the ODT. With a decrease in χN (temperature increase) the average micelle core radius (and aggregation number) decreases smoothly but slowly for both disordered and ordered (bcc) micelle states (Figure 6). Only as the cmt is approached does the decrease in R for the disordered micelles become more significant. At the ODT there is a small increase in the average aggregation number, as the transition from bcc to disordered micelles occurs. We note that the amplitude of the jump is only about 1.5% of the aggregation number, which corresponds to an even smaller change in the radius of the core. Accordingly, such a small change is hard to detect experimentally, even though this trend has been reported in some papers.[12,17] Experimental data for the core radius for PS–PI micelles with $f = 0.11$ and $N = 500$ from ref 17 are shown in the insert as a function of χN. Originally the data were obtained as a function of temperature, so we used the $\chi(T)$ dependence reported in the paper ($\chi N = 0.004 + 43/T$) to convert the temperature to χN to compare with the predictions of our model. Although the calculations made with parameters corresponding to the experimental sample does not provide a good quantitative fit for the data, the qualitative similarity is encouraging.

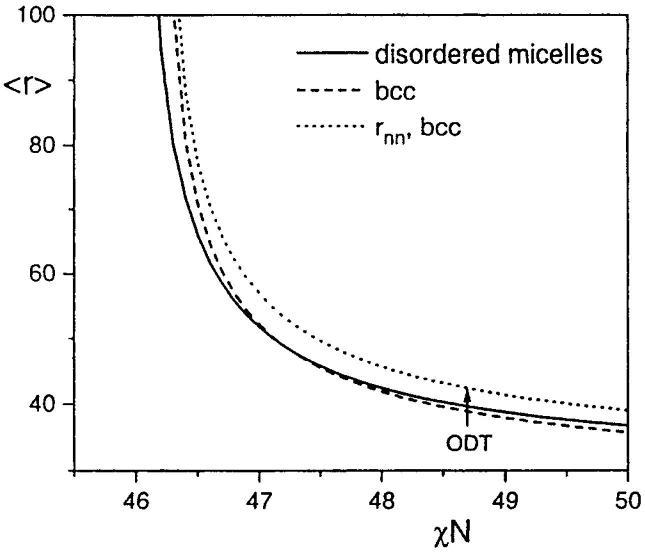

Figure 7. χN dependence of the average intermicelle distance, $\langle r\rangle$, in the bcc and disordered micelle states for the same diblock copolymer melt as in Figure 3. The distance between nearest-neighbor micelles in the bcc state is also shown for comparison.

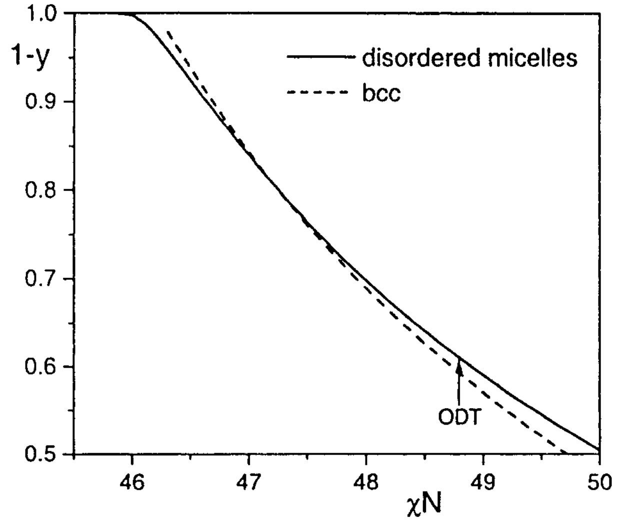

Figure 8. χN dependence of the free unimer volume fraction, $1 - y$, in the bcc and disordered micelle states for the same diblock copolymer melt as in Figure 3.

Although the aggregation number decreases only slightly with decreasing χN, the average distance between micelles increases more strongly for both ordered (bcc) and disordered micelles, as shown in Figure 7 (for $N = 1000$ and $f = 0.1$). At the ODT $\langle r\rangle$ increases by about 2% as the transition from bcc to the disordered micelles occurs. (We note that $\langle r\rangle_{\mathrm{bcc}} = b/2^{1/3}$ for bcc phase, where b is the cell size, whereas the nearest-neighbor distance is $r_{\mathrm{nn}} = b\sqrt{3}/2$ and is larger than $\langle r\rangle$ for the disordered micelle regime at the ODT.) Thus, at the ODT the average micelle aggregation number increases only slightly, whereas the average intermicelle distance undergoes a larger increase. This may occur only if the unimer volume fraction increases, which indeed takes place at the ODT (Figure 8). Once again, the jump in the volume fraction is not so large, about 2.5–3% of the average value. For the case considered the transition occurs at $y = 0.4$ in the bcc phase. With further decrease of χN the volume fraction of unimers increases, tending toward unity in the vicinity of the cmt.

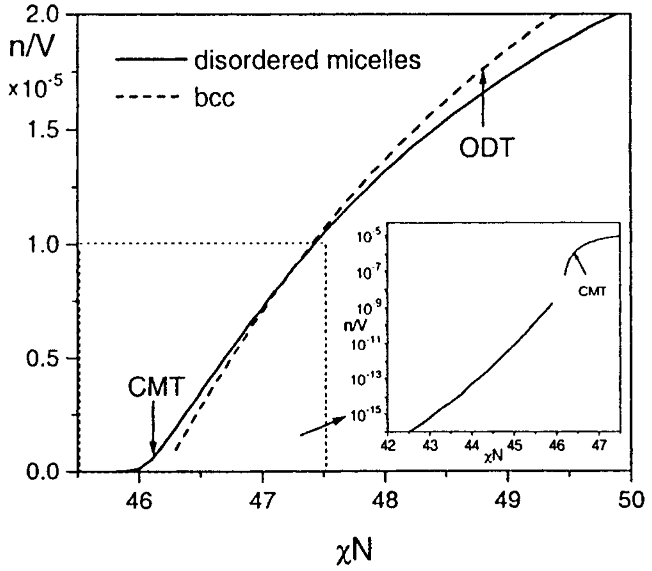

Figure 9. χN dependence of the average number density of micelles, n/V, in the bcc and disordered micelle states for the same diblock copolymer melt as in Figure 3. The number density of micelles below the cmt is calculated using eq 31 and shown on a logarithmic scale in the insert.

The increase in aggregation number at the ODT accompanied by an increase in unimer volume fraction implies that at the transition point the number of micelles decreases. Indeed, the decrease in the number density of micelles at ODT is evident from Figure 9. The decrease is about 5–6% of the average value. This jump in the number of micelles is the most distinctive feature of the transition, but unfortunately this is not a value that can be measured in a straightforward way. The decrease in micelle number density ensures larger intermicelle distances, thereby decreasing the micelle interaction free energy and increasing the translational entropy. With an increase of temperature across the ODT some fraction of micelles simply dissociate into unimers. The reverse transition, from a disordered into an ordered bcc micelle phase, is more hindered kinetically: the number of micelles should increase by redistribution of chains between micelles and free unimers (which may involve the process of micelle fission), and then they should arrange themselves onto the lattice. Both of these processes should be rather slow, so it is not surprising that experimentally the disorder → order transition takes much more time than the reverse.

Near the cmt the number of micelles approaches a relatively small value, and more importantly, the rate of decrease changes. In the insert we use a logarithmic scale to show the change in micelle number density around the cmt and much below it. For the region below the cmt we used eq 31 for the micelle volume fraction. As is evident from the insert, the cmt is not a phase transition because the phase below and above are identical to each other in all but the number of micelles (and possibly their aggregation number). The micelle fraction in this region is rather small and varying continuously, and its experimental estimation therefore involves considerable uncertainty. Furthermore, any distribution in micelle size was neglected in our model but should exist in reality and therefore make the changes in number density of micelles even more smooth. Therefore, it is difficult to suggest an accurate experimental criterion to locate the cmt.

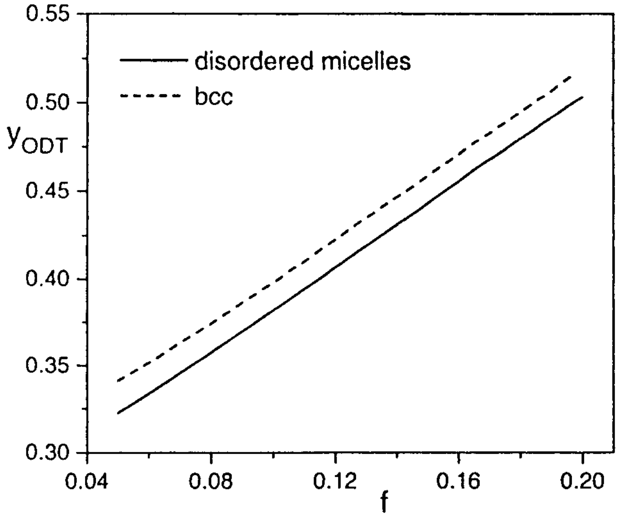

Figure 10. Composition dependence of the micelle volume fraction, y, in the bcc and disordered micelle states at the ODT for a melt of diblock copolymers with $N = 1000$, $l_A = 0.68$ nm, $l_B = 0.7263$ nm, and $v = 0.165$ nm^3.

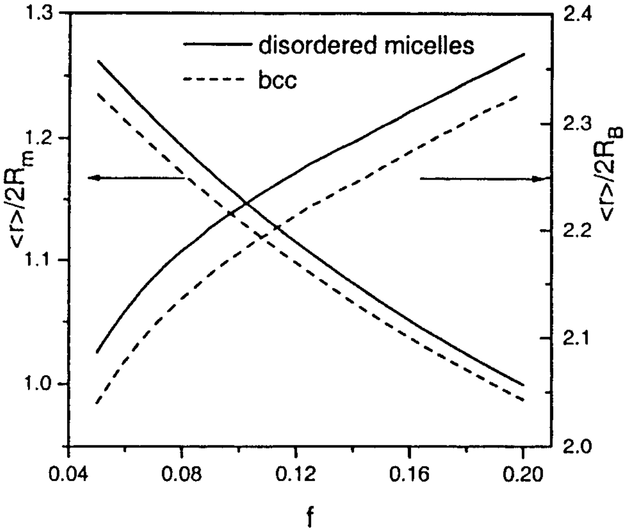

Figure 11. Composition dependence of the average intermicelle distance with respect to the micelle radius and the corona block radius of gyration in the bcc and disordered micelle states at the ODT, for a melt of diblock copolymers with $N = 1000$, $l_A = 0.68$ nm, $l_B = 0.7263$ nm, and $v = 0.165$ nm^3.

If we compare the micelle volume fractions for the bcc and disordered micelle phases at the ODT for diblock copolymers of different composition, we find that the jump in the micelle volume fraction at the transition remains nearly the same, whereas the absolute value of y changes linearly with composition (Figure 10). The increase of y with composition implies that micelles cannot be considered strictly as hard spheres, which are known to order at a volume fraction of ca. 0.49. The analysis of other micelle characteristics shows that, with the increase of f, the number density of micelles decreases, whereas the average separation increases, leveling off for $f \gtrsim 0.12$. Comparing the average distance between micelles, $\langle r\rangle$, with a micelle diameter $2R_m$ ($R_m = R + R_B$, where R_B is the radius of gyration of B-block), one finds that $\langle r\rangle/2R_m$ decreases from about 1.25 at $f = 0.05$ to 1 at $f = 0.2$ (Figure 11). Hence, for a diblock with composition close to 0.2 the ODT occurs at $y = 0.5$ when micelle coronas (more precisely their fraction characterized by R_B) are about touching each other. This is close to a hard-sphere model scenario of the ODT.

For strongly asymmetric diblocks, the situation is different. The ODT occurs at a smaller micelle fraction, when the surfaces of micelle cores are separated by a distance exceeding $2R_B$ (but less than twice end-to-end distance for the B-block). For diblocks of strongly asymmetric composition the aggregation number per micelle is smaller, whereas the number of micelles is larger, than in diblocks with larger f. One might expect that having a smaller aggregation number the interaction energy between micelles would be also smaller, but the large number of micelles implies that they are separated by smaller distances (in units of R_B), which exponentially increases the interaction free energy (eqs 4–6). Hence, the disordering transition, when micelles lose in interaction free energy but gain in translational entropy, can occur only when the distance between micelles becomes considerable (to decrease the interaction free energy) and their number reasonably small (to increase the translational entropy) (Figure 11).

Comparison with Experiments

Although the approach presented here is designed to emphasize qualitative features, we now attempt to test its ability to predict the ODT in a systematic way by comparing our results with available experimental data. The polymer system studied in most detail is polystyrene/polyisoprene (SI) diblock copolymers in the melt.[9,10,13,15–17,40] The experimental data cover a range of chain length and composition. We have chosen to take the styrene monomer volume as the reference and normalized the monomer and block length for PI correspondingly. Consequently, the f and N values may differ from the original reports, where often a common reference for the two blocks was not selected. Given N and f, we can predict χ_{ODT}. However, it is not so straightforward to convert this to the measured quantity, the ODT temperature. One route would be to use the relations between χ and T obtained experimentally, which generally follow

$$\chi = A + \frac{B}{T} \tag{33}$$

However, the coefficients A and B for SI systems from different sources are not always in close agreement, due inter alia to different reference volumes and different methods of determination. Furthermore, the values for A and B obtained for the diblocks of nearly symmetric composition often differ from those for asymmetric diblocks. Consequently, we take a somewhat different approach. In Figure 12 we plot χ_{ODT} calculated theoretically (from eqs 22, 29, and 30) vs $1/T_{ODT}$ determined experimentally. The various data points collapse rather well to single curve, with the exception of two samples; the reason for this discrepancy is not readily apparent. For several of the samples in Figure 12 the ODT temperatures are given rather large error bars, which correspond to the width of the transitions reported by the authors. By fitting the data for SI diblock copolymers in Figure 12 to a straight line (excluding the two outliers), we obtain a relation between χ and T:

$$\chi = -0.0372 + \frac{37.85}{T} \tag{34}$$

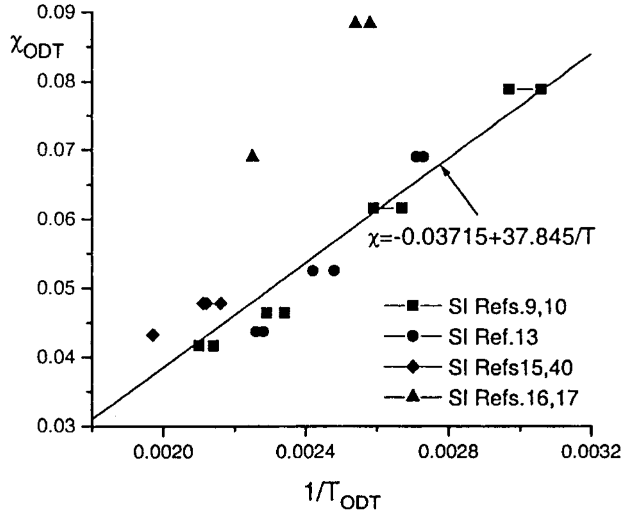

Figure 12. Theoretically calculated χ_{ODT} for PS–PI diblock copolymers (listed in Table 1) vs inverse T_{ODT} reported experimentally. The least-squares fit is shown as a straight line: $\chi = -0.03715 + 37.845/T$. The error bars correspond to the temperature range of the experimental transition.

Table 1. Comparison of the ODT Temperature Measured Experimentally and Calculated Theoretically for Sphere-Forming PS–PI Diblock Copolymers

sample	ref	f	N	T_{ODT}, °C (expt)	T_{ODT}, °C (calcd)
D48	9, 10	0.1164	524	54–64	53.3
D62	9, 10	0.1147	680	102–113	110.4
D78	9, 10	0.12	851	154–163	180
D90	9, 10	0.11585	984	195–204	207
SI-7/29	13	0.17	388	93–96	83
SI-10/53	13	0.142	617	130–140	149
SI-12/83	13	0.115	945	165–170	195
SI-10/50	15	0.148	648	198–202	172.5
SI-10/50	40	0.1475	651	190	172.5
SI-11/52	40	0.155	680	235	198
D65	16, 17	0.1	708	172	83.5
D46	16, 17	0.11	500	114–120	28.5

This dependence is gratifyingly close to that obtained by Lodge et al.[41] for nearly symmetric SI diblocks in melts and in neutral solvents: $\chi = -0.0228 + 33/T$ and that reported by Register et al. $\chi = -0.058 + 48.9/T$.[9,10] Although not shown, data for SIS triblocks also fall close to the same line. The ODT temperatures calculated based on χ_{ODT} from eq 34 are presented in Table 1 together with the experimental data. As one can see, there is a good agreement in most cases.

Discussion

In this section we return briefly to the question posed in the Introduction, namely, for sphere-forming block copolymers are there two (bcc and disordered) or three (bcc, disordered micelles, disordered chains) equilibrium phases? Should we think in terms of one phase transition, the ODT, or two, the ODT and the cmt? Experimentally, it is apparent that the concept of a disordered micelle regime is consistent with the results.[13,14,16,17] Theoretically, our calculations confirm that this state becomes thermodynamically favorable at the order–disorder transition and remains stable (i.e., thermodynamically preferable to the bcc, fcc, or sc) over some temperature range above the ODT. The cmt is more subtle. The disordered phase near the ODT has a significant volume fraction of micelles, which decreases smoothly with increasing temperature until the cmt is reached. Although it is possible in theory to define the cmt where, for example, there is a distinct change with increasing temperature in the *rate* of decrease in the micelle number density (or volume fraction), the cmt is definitely *not* a phase transition because the states below and above the cmt are essentially the same: a disordered state with a larger or smaller micelle fraction. Consequently, we conclude that there is only one phase transition, the ODT, which separates the ordered (bcc) and disordered phases.

This interpretation differs in some points from the scenario described by some other authors. For example, Han, Hashimoto, and Kim (HHK)[12–14] advocate distinguishing the ODT for sphere-forming copolymers from that for more-symmetric polymers. To emphasize the distinction, they term the transition from bcc to disordered micelles the lattice disordering transition (LDT or LDOT), and the disappearance of the micelles occurs at the demicellization temperature (DMT). In this view, the existence of the disordered micelle regime represents an essential difference between sphere-forming and more symmetric block copolymers. However, we are not persuaded by this argument for the following reasons. Whatever the copolymer composition, there is only one thermodynamic phase transition, the ODT; it always takes place between an ordered state and a disordered state, it is always first-order, and in careful measurements it exhibits similar small-angle scattering and rheological signatures. Therefore, we see no essential difference between the lattice disordering transition and the ODT. If one were to take the view that the disordered micelle regime was actually part of the *ordered* state (which would contradict, however, the accepted definition of an ordered state), then this transition would have to be considered as an order–order transition (and distinguishing it from the ODT would then be appropriate). This would lead to the conceptual difficulty of making the critical micelle temperature (called DMT by HHK) equivalent to the ODT, which is completely inconsistent with the requirement that the ODT be a true thermodynamic phase transition. Within the disordered state, more symmetric diblocks exhibit a broad mean-field/non-mean-field crossover, with substantial composition fluctuations as the ODT is approached; this crossover, however, like the cmt is not a phase transition. The existence of disordered micelles arises for the same reason as fluctuations, namely to reduce A/B contacts without sacrificing all the entropy of a disordered state. It remains an interesting question whether there is any deep distinction for asymmetric copolymers between fluctuations and disordered micelles, but they are clearly both part of the disordered phase. As a strong segregation theory, our approach is not really suitable for addressing this issue.

Conclusions

We have considered the order–disorder transition in micelle-forming asymmetric diblock copolymers, employing a mean-field theory in the strong segregation regime. The principal new feature is the prediction of a stable disordered micelle regime at temperatures just above the ODT. The primary origin of this behavior is enhanced translational entropy of the micelles relative to the bcc lattice. This regime has been observed in several experimental studies. Furthermore, inclusion of a disordered micelle regime in the free energy competition removes any region of stability of fcc or close-packed spheres. This resolves a persistent discrepancy between previous SCMF theory and experiment, where cps have not been observed for a block copolymer melt.

The order–disorder transition (ODT) between the bcc and disordered micelle regime is located in terms of the usual variables: chain composition, f, and the degree of segregation, χN. The results for the bcc/fcc transition are consistent with previous SCMF calculations, but the ODT occurs at lower temperature and the fcc phase is not stable. An accurate description of the changes in unimer conformation with temperature will be essential for locating the ODT precisely. However, the sequence of transitions, and the qualitative changes in micelle characteristics accompanying the ODT, are independent of the exact form of the unimer free energy. We also tested the ability of the model to predict the ODT in a systematic way, by comparing our results with experimental data for SI diblock copolymers. Most of the data form a common line and can be characterized by a single $\chi(T)$ dependence. Even the absolute value of the ODT temperatures predicted by our model is in reasonable agreement with experimental observations.

Examining the ODT in more detail, we find that increasing temperature brings about a gradual decrease in the number of micelles, accompanied by an even slower decrease in the aggregation number. When the number of micelles becomes smaller (and the average distance between them larger) than some critical value, the ODT occurs. On the basis of our calculations, we would expect a minor increase in the micelle aggregation number, a somewhat larger increase in the average intermicelle distance and in the number of free unimers at the ODT, and an even larger decrease in the number density of micelles. The reverse, ordering process as temperature decreases involves the redistribution of unimers among micelles, leading to an increase in the number of micelles. It is natural to expect this process to exhibit slower kinetics, which is a common experimental observation.

Above the ODT the number density of micelles decreases steadily. Over some region which we term the critical micelle temperature (cmt), the rate of decrease changes, and then the free energy of the disordered micelle regime (with very low micelle concentration) is only slightly lower than the Flory–Huggins free energy for a homogeneous melt. The cmt is not a phase transition, and the disordered micelle regime is part of the disordered phase. It should be noted that at higher temperatures the interactions between blocks becomes less repulsive, and micelles can be difficult to distinguish experimentally from random fluctuations of concentration. Thus, 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.

Appendix

With decreasing temperature across the cmt and ODT not only the number but also the average conformation of the unimers changes. For example, it has been reported that the A-block of the unimer starts to collapse, whereas B-block either does not change its conformation appreciably or stretches slightly.[26,39,42] As a result, the unimer assumes a ball-and-chain-like conformation. These conformational changes are accompanied by changes in the net interaction between A and B monomers. To account correctly for the unimer interaction free energy is a complicated task, due to the interplay of chain stretching, volume and surface interactions, etc. As no clear analytical expression has been obtained for the free energy of a unimer, one has to resort to approximations. One of them was described in the main part of the text; another variant is considered below.

At the cmt, when the fraction of micelles is very small, the unimer interaction free energy can be described by the Flory–Huggins free energy. With further temperature decrease the volume containing the A-block, V_0, will decrease as the block assumes more compact conformation $V_A = \lambda V_0$ with $\lambda \lesssim 1$. The free energy describing the binary and ternary interactions between monomers and the elastic free energy for the A-block can be written in the following form (by analogy with Flory's theory for the coil–globule transition applied to the A-block)

$$F_{\mathrm{un}} = \alpha f\left(1 - \frac{f}{\lambda}\right) + \omega f^{3}\left(\frac{1}{\lambda^{2}} - 1\right) + \frac{3}{2}(\lambda^{2/3} + \lambda^{-2/3} - 2) \tag{A1}$$

When $\lambda \to 1$, F_{un} coincides with the Flory–Huggins free energy. Minimizing the free energy with respect to λ, we find

$$\alpha\frac{f^{2}}{\lambda^{2}} - 2\omega\frac{f^{3}}{\lambda^{3}} + \lambda^{-1/3} - \lambda^{-5/3} = 0 \tag{A2}$$

At the initial condition, when the A-block conformation is Gaussian, i.e., close to the cmt, $\lambda = 1$, and we get $\omega = \alpha_{\mathrm{cmt}}/2f$. At lower temperatures, when $\lambda < 1$, the main contributions in eq A2 are the first two terms, so that λ can be estimated as

$$\lambda \cong \frac{2\omega f}{\alpha} = \frac{\alpha_{\mathrm{cmt}}}{\alpha} \tag{A3}$$

Using eq A3, the unimer free energy eq A1 can be rewritten in the following form

$$F_{\mathrm{un}} = \alpha f\left(1 - \frac{f}{\lambda}\right) + \frac{1}{2}\alpha_{\mathrm{cmt}} f^{2}\left(\frac{1}{\lambda^{2}} - 1\right) + \frac{3}{2}(\lambda^{2/3} + \lambda^{-2/3} - 2) \tag{A4}$$

We note that this form of the unimer free energy is appropriate not too far away from the cmt, being a minor correction to the Flory–Huggins free energy that neglects the surface interactions. Using this form of the free energy for the calculations described in the main part, we find that the ODT occurs at $\chi N = 56.3$, which is somewhat higher than the results obtained using eq 19 ($\chi N = 48.7$). The fcc/bcc transition occurs also at a higher χN, $(\chi N)_{\mathrm{bcc/fcc}} = 53.3$, than that obtained using eq 19 ($\chi N = 47.83$). Correspondingly the difference (in χN values) between fcc/bcc transition and ODT and between cmt and ODT increases. In general, the weaker the unimer conformational change with temperature, the lower the ODT temperature and the broader the ODT–cmt gap. Despite these quantitative differences, the main qualitative result concerning the sequence of transitions occurring upon temperature decrease remains the same. Moreover, the amplitude of changes occurring at the ODT, and even the absolute value of the volume fraction and intermicelle distance at the transition, are nearly the same. Hence, it appears that regardless of the exact form of the unimer interaction free energy, the main qualitative results and even some quantitative ones remain unchanged.

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