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Micelles of Coil−Comb Block Copolymers in Selective Solvents: Competition of Length Scales

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ABSTRACT: We study micelles formed by the coil−comb block copolymer, A-*b*-(A-*g*-B), in a B-selective solvent, S. The equilibrium distribution of micelles is obtained according to the thermodynamics of noninteracting micellar solutions, with the free energy of a single isolated micelle calculated using the self-consistent-field theory. Depending on the lengths of the various blocks and the balance of interactions, two types of micelles of different sizes and structures can be observed. This is a manifestation of the competition between two micellar assemblies of the coil−comb block copolymer at different length scales.

Microphase separation in immiscible block copolymer melts leads to periodic structures with long-range order.[1,2] Dilution with solvents or homopolymers may destroy the long-range order of microphase-separated morphologies and result in locally assembled structures such as spherical and wormlike micelles.[3−7] A microscopic length scale on the order of the end-to-end distance can be identified in both the microphase-ordered morphologies and the locally assembled structures. The length scale depends primarily on the interplay between the energetic benefit of having less interfacial area and the entropic cost due to the chain stretching.[8] For block copolymers with a simple architecture such as a linear diblock copolymer, A-*b*-B, only one length scale prevails—that associated with the periodicity of the ordered domains or the size of the assembled aggregates.

It is possible to have more than one prevailing length scales in block copolymers with more complex architectures, e.g., comblike block copolymers.[9−14] Theoretical studies revealed that the coil−comb block copolymer, A-*b*-(A-*g*-B), can phase separate both inside the comb block, A-*g*-B, and between the coil block and the comb block in some region of the parameter space, and the competition between the two length scales may lead to hierarchical structures.[11−13] Recently, Bao and co-workers reported bimodally distributed micelles in an *n*-heptane solution of polystryrene-*b*-(polystyrene-*g*-polyisoprene), and the authors suggested that the bimodal distribution is the result of micellar assembly at two competing length scales.[14] Similar bimodal distributions of micelles have been observed in *ternary* solutions of two diblock copolymers of the same chemical blocks but different block lengths, which is the result of competition between the two block copolymers.[15,16] Different from ternary mixed diblock copolymer solutions, in the coil−comb block copolymer solutions, the putative coexisting micelles should result from *competing conformations*.

In this paper, we investigate micellar assembly of coil−comb block copolymer, A-*b*-(A-*g*-B), in a B-selective homopolymer solvent, S. The architecture of the coil−comb block copolymer is sketched in Figure 1A. The coil block and the backbone of the comb block are of type A, and the side chains of the comb block are of type B. The side chains are distributed evenly on the backbone of the comb block. The length of the coil block is N_{A1}, and the comb block can be viewed as a string of n T-shaped "mini" copolymers, each of which has N_B B segments connected to the middle of a chain of N_{A2} A segments. Then, $N = N_{A1} + n(N_{A2} + N_B)$ is the total degree of polymerization of the coil−comb block copolymer. Solvent S is treated as a homopolymer of chain length N_S. In this paper, we only consider $N/N_S \gg 1$ and take N_S as the reference. In the presentation of results, we take $N_S = 1$ and $\rho b^3 = 1$, where the inverse monomer volume, ρ, and Kuhn length, b, are assumed to be the same for all species. The interaction parameters χ_{AB}, χ_{AS}, and χ_{BS} are chosen to reflect the usual features of micellar solutions: A and B are immiscible and S prefers B to A. As suggested by Bao and co-workers,[14] the coil−comb block copolymer can assemble in two ways, leading to two types of micelles of different sizes, whose structures are illustrated in Figure 1B.[17] In micelles of type I, the coil block and the backbone of the comb block form the core and the side chains of the comb block form the corona. In micelles of type II, the coil block forms the core and the whole comb block forms the corona.

We consider a closed solution of the coil−comb block copolymer of the afore-described architecture in a selective solvent. Because of the immiscibility between the two blocks and the selectivity of the solvent, the block copolymer molecules self-assemble into micelles of different association number, m, which has number density, C_m. The Helmholtz free energy density of the micellar solution can be written as

$$\mathscr{F}/V = k_B T \sum_{m=1}^{\infty} C_m [\ln(C_m \Lambda^{3mN}/Z'_m) - 1] \qquad (1)$$

where Λ is the thermal de Broglie length for a monomer, N the total degree of polymerization, and Z'_m the configurational part of the partition function of a micelle of m copolymers, excluding the degree of freedom associated with the center of mass of the micelle. In eq 1, Z'_1 is taken to be the configurational partition

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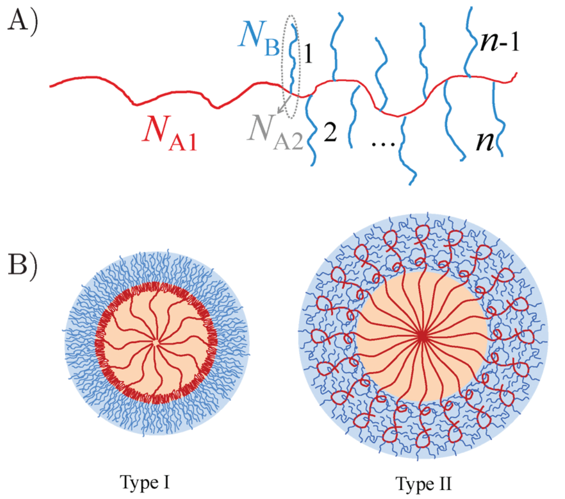

Type I

Type II

Figure 1. (A) Schematic picture of the coil−comb block copolymer, $A_{N_{A1}}$-*b*-$(A_{N_{A2}}$-*g*-$B_{N_B})_n$. (B) Models of two types of micelle assembly of the coil−comb block copolymer.

function of a single copolymer, which is taken to be a special micelle of association number $m = 1$. This is because for the interaction parameters we consider, a single copolymer takes a partially collapsed conformation instead of an ideal one since the former has a lower free energy. We have also ignored the interaction between micelles assuming the solution to be ideal. Minimization of the free energy density in eq 1 with respect to C_m at a fixed total mass concentration $\sum_{m=1}^{\infty} C_m m$ leads to

$$k_B T \ln(C_m \Lambda^{3mN}/Z_m') - m\mu' = 0 \qquad (2)$$

with μ' the Lagrangian multiplier ensuring the mass conservation constraint. Equation 2 means the chemical potential of the copolymer is equal for all micelle species, and it is the condition of chemical equilibrium.[18−23] Taking the special case of $m = 1$ to express the chemical potential in terms of the concentration of the free polymers, and using the result back in eq 2 for general m, we obtain the equilibrium distribution of micelles as

$$C_m = (C_1)^m \frac{Z_m'}{(Z_1')^m} \qquad (3)$$

Note that the thermal de Broglie length does not appear in the micellar distribution; this is to be expected as our treatment is in the realm of classical statistical mechanics, and therefore the momentum and position degrees of freedom are completely decoupled.

The ratio of the two restricted partition functions in eq 3 suggests a free energy difference between a micelle of m copolymers and m free copolymers. However, the ratio has dimensions of $C_m/(C_1)^m$. We account for the dimensions by introducing a volume scale a_m and write eq 3 as

$$C_m a_m = (C_1 a_1)^m \exp\left(-\frac{\Delta F_m}{k_B T}\right) \qquad (4)$$

with the definition $\Delta F_m \equiv F_m - mF_1$. ΔF_m can be considered the standard free energy of formation of a micelle of association number m from m free chains. a_m cannot be determined in a mean field theory (it arises from evaluation of the full partition function of a micelle which includes fluctuation in the physical dimension and shape of the micelle); for simplicity, we take it to be the volume of a single micelle, and thus $C_m a_m$ is the volume fraction of micelles.

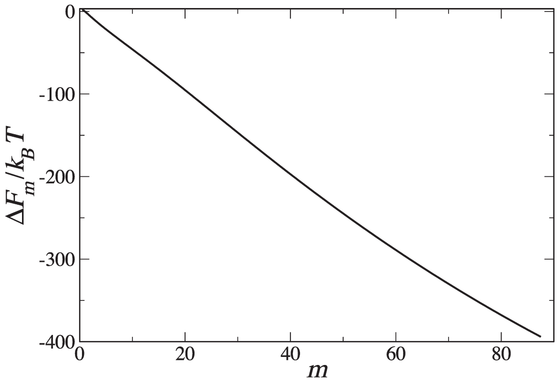

Figure 2. Standard free energy of formation ΔF_m of the micelle as a function of its association number, m. The coil−comb block copolymer has $n = 13$, $N_{A1} = 60$, $N_B = 8$, and $N_{A2} = 6$. The interaction parameters are $\chi_{AS}/k_B T = 2$, $\chi_{BS}/k_B T = 0.3$, and $\chi_{AB}/k_B T = 0.125$.

The free energy of a single isolated micelle, F_m, is the key property to determining the equilibrium distribution. In this work, the free energy of a single micelle and its density profile are calculated numerically using self-consistent-field theory (SCFT),[24] without any preassumption of micelle structure, other than spherical symmetry. The formulation of SCFT and related numerical details can be found in refs 7, 25, and 26. The calculation is performed in the canonical ensemble, with the micelle situated at the center of the calculation box. Because of the relatively large interaction strength and the low concentration of unassociated copolymers, essentially all the copolymer molecules are incorporated into the micelle; the number of unassociated copolymers in the box is negligible. This claim is substantiated by the density profiles shown in Figure 4: beyond some distance from the micellar core, the concentration of copolymers is practically zero. We calculate F_m of a single micelle as a function of its association number, m. The property of direct relevance to micelle formation is ΔF_m defined below eq 4; its behavior is shown in Figure 2. While ΔF_m is monotonically decreasing, the free energy per chain, $\Delta F_m/m$, is nonmonotonic and exhibits a minimum or more. In the early consideration by de Gennes and others, the minimum of $\Delta F_m/m$ is considered to correspond to the micelle.[27,28] This is valid only if the minimum is deep and occurs at a large association number when the translational entropy of the micelles can be neglected. In general, however, the thermodynamics of micelle formation is governed by eq 4.

We can absorb the factor $(C_1 a_1)^m$ into the work for micelle formation that includes the translational entropy of the unassociated single chains by defining the free energy

$$\Delta G_m = \Delta F_m - m\mu \qquad (5)$$

with the chemical potential $\mu \equiv k_B T \ln(C_1 a_1)$. If ΔG_m exhibits two minima, the equilibrium micelles have a bimodal distribution, and if ΔG_m has only one minimum, the equilibrium distribution of micelles exhibits a single peak. (To have a physical $C_m a_m$ and stay in dilute limit, i.e., $C_m a_m \ll 1$, requires $\Delta G_m/k_B T \gg 0$. However, given the uncertainty in a_m and the scaling with the solvent molecular weight N_S, we also present data with $C_m a_m$ up to 1.)

ΔG_m can be viewed as the work required to generate a single isolated micelle of association number m at the fixed chemical potential of the unassociated polymers, μ, and the minimum of ΔG_m is regarded as the stable/metastable micelle in the reservoir of the unassociated polymers.[29−34] For block copolymers with simple architectures, such as diblock copolymer, there is only one minimum in $\Delta F_m/m$. In that case, depending on the value of μ, the

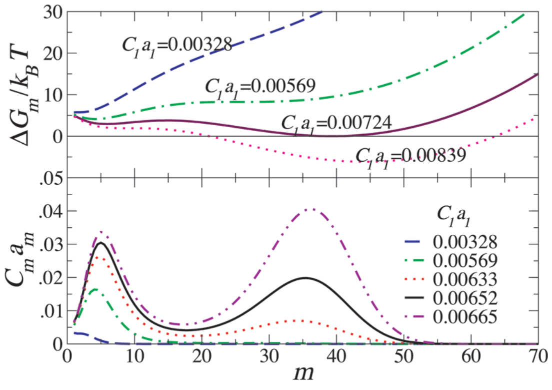

Figure 3. (A) Work of micelle formation as a function of the association number at several characteristic values of C_1a_1. (B) Typical equilibrium distributions of micelles at different C_1a_1s specified in the legend. The parameters of block copolymer are the same as in Figure 2.

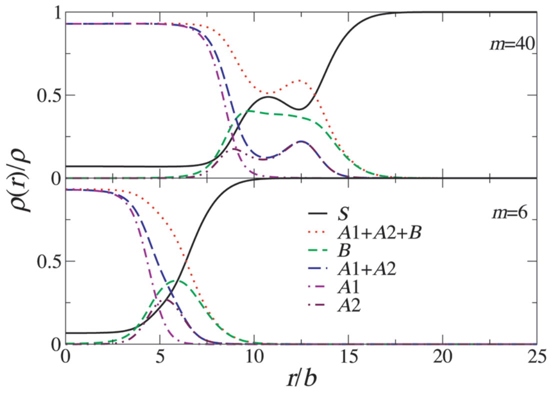

Figure 4. Typical density profiles for micelles with different values of association number, m, corresponding to the minima of work for micelle formation at $(C_1a_1)_{c2}$ shown in Figure 3.

following behavior is expected of ΔG_m: when μ is very negative corresponding to very low concentration of copolymers, ΔG_m is a monotonically increasing function of m, indicating that aggregation of block copolymer chains is unfavorable; as μ increases, a minimum of ΔG_m appears, corresponding to the formation of stable or metastable micelles of finite size. Increasing μ, the free energy of micelle decreases and its association number increases. The condition where the micelle first appears is identified as the micelle dissociation condition, μ_d, and that with minimum at $\Delta G_m = 0$ is the "critical" micelle condition (cmc), μ_c.[34]

Micelle assembly in the coil−comb block copolymer solution is richer and delicately depends on the block lengths and interaction parameters. The behavior of linear diblock copolymer solutions is recovered in the limit of small number of side chains, which will be discussed later. The most interesting feature for our purpose is that, with some parameters, ΔG_m exhibits two minima, indicating the existence of bimodal distribution of micelles. (However, this does not necessarily require that $\Delta F_m/m$ possess two minima.) Here we take the coil−comb block copolymer with $n = 13$ as an example, and Figure 3A presents ΔG_m as a function of m at different values of C_1a_1 (or μ). Below $(C_1a_1)_{d1}$, the association of block copolymer chains is unfavorable, and above it, the first minimum appears and micelles become metastable or stable. Above $(C_1a_1)_{d2}$, the second minimum appears, signaling another kind of self-assembly, and a maximum separates the two minima. We label the association number at the minima by m_1 and m_2, respectively. Increasing C_1a_1, the minima shift to larger values of association number. At a high value, $(C_1a_1)_a$, the first minimum and the maximum collapse into an inflection. In principle, for each micelle we can identify a "critical" micelle condition, i.e., $(C_1a_1)_{c1}$ and $(C_1a_1)_{c2}$. However, under some conditions, like the example shown in Figure 3, the first minimum disappears before its value reaches zero, and in this case, we cannot locate $(C_1a_1)_{c1}$. As the association number changes with the concentration, in comparing micelles of different parameters, we need to choose some special concentration. In the following we compare micelles of different parameters at their own $(C_1a_1)_{c2}$ if micelles of type II exist and otherwise at their $(C_1a_1)_{c1}$. The difference of free energy at the two minima, $\Delta G_m{}^* = \Delta G_{m1} - \Delta G_{m2}$, reflects their relative concentration. $\Delta G_m{}^* = 0$ gives the coexistence of two types of micelles in the mean-field limit. We point out that with other parameters it is possible to have $(C_1a_1)_{d2} < (C_1a_1)_{d1}$; i.e., when increasing the amount of block copolymer, the micelle of type II first becomes stable/metastable, followed by that of type I.

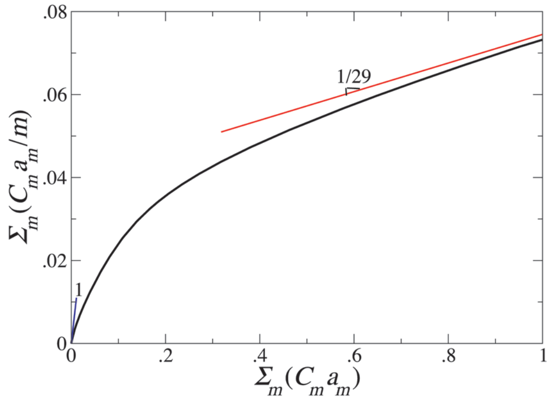

Figure 5. Osmotic pressure of micelle solutions as a function of volume fraction of block copolymer. The parameters are the same as in Figure 2.

Figure 3B gives the equilibrium distribution of micelle at different values of C_1a_1 (note that the concentrations used in this figure are not all identical to those in Figure 3A). At a small value of $C_1a_1 \leq (C_1a_1)_{d1} = 0.00328$, single unassociated chains (partially collapsed) have the largest population, and additional association is not favored. When $(C_1a_1)_{d1} < C_1a_1 \leq (C_1a_1)_{d2} = 0.00569$, micelles of type I are dominant, and the distribution shows just one peak. At $C_1a_1 > (C_1a_1)_{d2}$, e.g., 0.006 33 and 0.006 52, a peak of micelles of type II appears and becomes dominant when increasing C_1a_1. Increasing C_1a_1, the population of all micelles increases according to $C_ma_m \propto (C_1a_1)^m$, and the concentration of the larger micelles increases faster. m_1 and m_2 also slightly increases with C_1a_1. At a high value of C_1a_1, i.e., $C_1a_1 > (C_1a_1)_a$, the peak of micelles of type I vanishes and micelle of type II dominates.

To get structural information about the two types of micelles, we examine their density profiles. Figure 4 shows typical density profiles of the two types of micelles, corresponding to the first and second minimum of ΔG_m at $(C_1a_1)_{c2}$, respectively, in Figure 3A. Both types of micelles exhibit core−corona structures. When m is small, e.g. $m_1 = 6$, besides the coil block, part of the backbone of the comb block also goes in the core together with some side chains. Clearly, with an increase in the association number, more and more comb blocks are expelled out of the core into the corona. When m is large, e.g. $m_2 = 40$, most of the backbone of the comb block stays in the corona, and the core mainly consists of the coil block. These results are consistent with the schematic models of micelle assembly shown in Figure 1, which can be viewed as two limiting cases of our results.

One way to characterize the formation of micelles is by examining the behavior of the osmotic pressure, with the critical micelle concentration identified as corresponding to a sharp turn in the slope. Figure 5 presents the osmotic pressure of the copolymers, $\Pi/k_BT = \sum_m C_m$, calculated as $\sum_m(C_ma_m/m)$, as a function of the total concentration of copolymers, $\sum_m(C_ma_m)$.

(Note that by our choice of a_m as the volume of a micelle of aggregation number m, the factor a_m/m is simply the monomer volume. So the ordinate in Figure 5 is a dimensionless osmotic pressure scaled by k_BT and by the volume of a copolymer.) The slope starts at unity for very low concentration when nearly all the copolymers exist as unassociated (but partially collapsed) species and eventually asymptotes to 1/29, i.e., the inverse of the association number of the larger micelles. But the slope change is quite gradual with no obvious sharp turns. Furthermore, there are not clear signatures in the osmotic pressure data as the population of micelles shifts from the smaller one to the larger one. This behavior is related to the fact that the peaks of the micellar size distribution are rather broad and overlap each other. Thus, for the system with this set of parameters, there does not seem to be a clearly defined cmc. Although we have not exhaustively explored the full parameter space, we have tried several different sets of parameters, with similar conclusions. It will be interesting to see whether this behavior will be observed in experiments.

The competition between the two types of micelle assembly depends on the lengths of the blocks in the copolymer and the interactions among blocks and solvent. In the following, we investigate effect of changing one parameter at a time while keeping the other parameters as specified in Figure 2. As explained earlier, the comparison for different parameters is made at the special concentration, $(C_1a_1)_{c2}$ where $\Delta G_{m2} = 0$ if micelles of type II exist and otherwise at their $(C_1a_1)_{c1}$ where $\Delta G_{m1} = 0$. In order not to have an excessive number of figures, we discuss the effects mostly in words, resorting to figures only for those effects that are most nonobvious.

We start with the effects of the number of side chains n. The coil–comb block copolymers with a small number of side chains, i.e. $n \leq 8$, behave like linear diblock copolymers, and only micelles of type I form, where most of backbone of comb block stays in the core. For block copolymers with $n \geq 12$, micelles of type II with most of the comb block in the corona can coexist with micelles of type I. Both types of micelles tend to have small association numbers with an increase in n, and when $n \simeq 20$, the micelle of type I consists essential of a single copolymer molecule. The decrease in the association number for large n can be rationalized from packing considerations. For block copolymers with $8 < n < 12$, only one micelle forms and its association number *increases* with n. From its density profile (not shown), we see that it has a structure intermediate between type I and type II micelles. In this case, the increase in the association number with n can be ascribed to the transition from micelles of type I to those of type II.

The core of micelle of type II consists mainly of the coil block, and therefore, its association number increases with the length of coil block, N_{A1}. The dependence of the association number of micelle of type I on N_{A1} is much weaker than that of m_2. Increasing N_{A1}, it first increases and then decreases. Such a delicate behavior can be ascribed to the fact that the core of micelle of type I is formed by both the coil block and the backbone of comb block. Moreover, decreasing N_{A1} favors micelles of type I over those of type II, and when $N_{A1} \leq 40$, the peak of micelles of type II disappears. This is consistent with the logic that in the uniformly grafted comb copolymer only micelles of type I exist.

For micelles of type I, the backbone of comb block stays in the core; therefore, the association number increases monotonically with N_{A2}. While for micelles of type II, the backbone of the comb block goes to the corona, and therefore increasing N_{A2} has two effects: on the one hand, due to the strong immiscibility between solvent and backbone, increasing N_{A2} will make the corona compact, which increases m_2; on the other hand, a larger value of N_{A2} makes the comb block bulkier, which prefers smaller micelles. Thus, m_2 first increases and then decreases with N_{A2}. This effect is shown in Figure 6: the aggregation number for type II micelle at the minimum shifts rightward for the first 4 values of N_{A2} and then back when increasing N_{A2} from 4 to 5. It can also be seen that, increasing N_{A2}, the relative ratio of micelle of type I increases. Micelles of type II become unstable at a large value of N_{A2} while micelles of type I become unstable at a small value of N_{A2}. For both types of micelles, side chains are the main component of the corona. So increasing the length of side chains, N_B, the association numbers of both types of micelles, m_1 and m_2, decrease monotonically, and the decrease in m_1 is slower than that in m_2. At the same time, the relative weight of micelle of type I in the distribution increases. Coexistence of two types of micelles is only possible for intermediate values of N_B. If N_B is small, the peak of micelles of type I vanishes, and if N_B is large, micelles of type II become unstable.

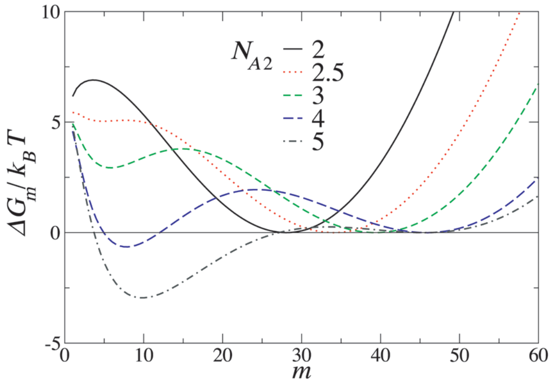

Figure 6. Work of micelle formation as a function of the association number for the coil–comb block copolymer with different lengths of the backbone the comb block N_{A2}. The values N_{A2} are indicated in the figure, and the other parameters are the same as in Figure 2.

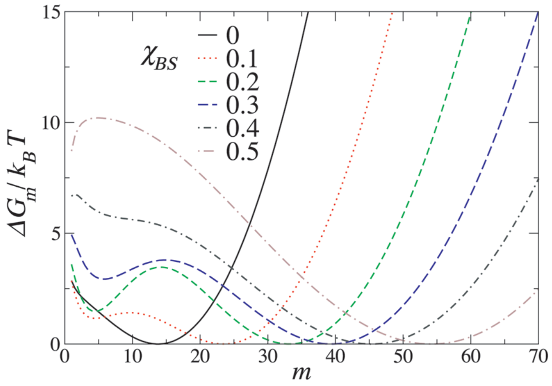

Figure 7. Work of micelle formation as a function of the association number for the coil–comb block copolymer with different values of χ_{BS} indicated in the figure. The other parameters are the same as in Figure 2.

We now discuss the effects of the interactions between segments A, B, and S on micelle assembly. Increasing χ_{AS} or χ_{BS}, both m_1 and m_2 increase monotonically. A large value of χ_{AS} means a large interfacial tension between the core and the solvent, which prefers larger micelles. An increase in χ_{BS} makes the side chains compact, which also results in large micelles. Moreover, a large χ_{AS} prefers the backbone of the comb block staying in the core to mixing with side chains in the corona. Therefore, increasing χ_{AS}, the relative ratio of micelles of type I increases, and the peak of micelles of type II disappears at a large value of χ_{AS} and that of micelles of type I vanishes at a small value of χ_{AS}. The effects of χ_{BS} are more subtle. As shown in Figure 7, the relative ratio of micelles of type I increases with decreasing χ_{BS}. Decreasing χ_{BS} makes the solvent better for the B segments, effectively increasing their excluded volume repulsion. Too good a solvent for the B monomers decreases the size of the type II micelles so much that the two free energy minima collapse into one. On the other hand, making the solvent a poor solvent for B tends to favor very large micelles. The distribution peak of micelles of type I disappears both below $\chi_{BS} = 0$ and above $\chi_{BS} = 0.5$.

Finally, we briefly comment on the effect of N_S, which is taken as the reference chain length. The work of formation defined in eq 5 has a multiplicative factor of $N_S^{-1/2}$, which means when increasing N_S, $C_m a_m$ decreases if ΔG_m is positive. In the limit of infinitely long solvent chains, $\Delta G_m = 0$ signals a sharp transition to the appearance of micelles.

In conclusion, we have theoretically investigated the competition between two types of micelle assembly at different length scales of the coil–comb block copolymer in selective solvent, which can lead to a bimodal distribution of micelles. Our results are consistent with the experimental results in the recent work by Bao and co-workers[14] and lend theoretical support to their conjectured model for the two types of micelles but at the same time provide many additional insights that are not accessible or not addressed in the experiments. We find that the assembly of the two types of micelles and their thermodynamics depend in nontrivial ways on the chain architecture and interactions. It would be helpful if further experiments can verify some of the predictions of our work. It would also be interesting to study similar competitions that may also occur in ABC triblock copolymer where the competition can be adjusted by the interaction.[35]

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