

How ill-defined constituents produce well-defined nanoparticles: Effect of polymer dispersity on the uniformity of copolymeric micelles

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We investigate the effect of polymer length dispersity on the properties of self-assembled micelles in solution by self-consistent field calculations. Polydispersity stabilizes micelles by raising the free energy barriers of micelle formation and dissolution. Most importantly, it significantly reduces the size fluctuations of micelles: Block copolymers of moderate polydispersity form more uniform particles than their monodisperse counterparts. We attribute this to the fact that the packing of the solvophobic monomers in the core can be optimized if the constituent polymers have different length.

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I. INTRODUCTION

Polymeric nanoparticles are attracting considerable and growing interest because of their potential in materials science [1–3] and in nanomedicine, e.g., in targeted therapeutic or diagnostic systems [4,5]. One attractive way to fabricate such nanoparticles is to exploit the self-assembly of amphiphilic block copolymers in solution. Depending on the lengths and solubilities of the copolymer blocks, they can form a variety of interesting morphologies, such as vesicles, rods, and spherical micelles [6,7].

In the present paper, we consider the micelles, which have a core-shell structure with a solvophobic core and a solvophilic shell exposed to the solvent [8–10]. In principle, the core can be exploited to load the drug molecules, and efficient mechanisms can be devised to enhance bioavailability [11–13]. As long as the drug is stably encapsulated, it is believed that the distribution of drug-loaded polymeric micelles in the body is determined by the size and surface properties of polymeric micelles rather than the properties of the drug molecules [14–16]. Hence developing strategies to control the size distribution of polymeric micelles is important to improve the efficacy of targeted drug delivery techniques.

However, all synthetic polymers, including block copolymers, possess some inherent dispersity in the polymer length due to the nature of polymerization reaction [17–19]. Currently, it is not understood to which extent the polydispersity of block copolymers affects the dispersity of the formed micelles—especially since even monodisperse amphiphiles do not form monodisperse micelles [20]. Polydisperse poly-

mer systems contain individual polymers with shorter or longer blocks. This provides an entropic advantage in the self-assembly process, since long chains can fill the center of domains without having to stretch, whereas short chains adopt conformations near the interface [18,19]. Indeed, experiments on ABA triblock copolymer melts have indicated that polydispersity greatly enhances the stability of self-assembled lamellar structures [21]. Related observations have been made in theoretical studies of polymer brushes: They indicate that monodisperse brushes show multicritical behavior [22,23], which are associated with large anomalous chain fluctuations [24–26] that disappear in polydisperse brushes [22]. Hence it is not *a priori* clear whether polydispersity will enhance or reduce the size fluctuations of self-assembled micelles.

This question is addressed in the present paper. We use self-consistent field (SCF) theory to study the structures and free energy landscapes of micelles that assemble from polydisperse polymer solutions for varying polydispersity index (\bar{D}) close to the critical micelle concentration (CMC), i.e., the point where micelles just begin to form.

Studies of polydispersity effects on self-assembled nanostructures are still comparatively scarce (for reviews see Refs. [18,19]). Most studies have considered polydispersity effects on the self-organization in block copolymer melts [18,27–41]. Early theoretical studies [42,43] on micellar solutions have predicted that the CMC decreases with polydispersity [42] and that the polymers in the micelles are on average longer than in the surrounding solution. This was later confirmed by experiments [44,45]. The size of vesicles formed by amphiphilic diblock copolymers in solution was reported to decrease with increasing dispersity of the hydrophilic block [46–48]. In contrast, experimental studies on micelles made of amphiphilic triblocks with polydisperse inner (hydrophobic) block have shown that the micelle sizes may increase significantly with \bar{D} (at comparable average chain length) [49], in agreement with theoretical predictions [43], and that micelles may even become slightly oblate for high polydispersities [49]. The latter effect is however small (the aspect ratio is

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1:1.4), and since we focus on moderate polydispersities in the present work, we will assume that micelles are spherically symmetric.

II. MODEL AND METHOD

We study systems of polydisperse amphiphilic diblock copolymers with solvophobic blocks A (chain fraction f) and solvophilic blocks B [chain fraction $(1-f)$] immersed in a solvent S, in the grand canonical ensemble. Since every copolymer length N defines a separate species, we must introduce separate chemical potentials $\mu_P(N)$ for each. They are adjusted such that copolymers *in solution* are distributed according to a Schulz-Zimm distribution [50] $P_{SZ}(N)$ with average chain length $N_n = \sum_N N P_{SZ}(N)$ and polydispersity index $\mathcal{D} = \sum_N N^2 P(N) / N_n^2$. Note that the chain length distribution in the micelles may differ from $P_{SZ}(N)$.

Polymers are modeled as flexible Gaussian chains [51,52]. The segment interactions are characterized by Flory-Huggins parameters $\chi_{ij}N_n$ ($i, j = A, B, S$) and are chosen similar to previous work [53] as $\chi_{AB}N_n = 10.0$, $\chi_{AS}N_n = 17.4$, and $\chi_{BS}N_n = -0.5$. The system is compressible with compressibility (Helfand) parameter $\kappa_H N_n = 100$. The structure and the free energy of spherically symmetric micelles are calculated within the SCF theory [52,54,55]. The model equations, model parameters, and further details are given in the Supplemental Material [56]. The micelle free energy F_m is obtained from the free energy difference of a system containing a micelle and the corresponding (“bulk”) homogeneous system. The micelle radius is defined as the radius where the solvophobic density assumes the value $\Phi_A = 0.5$. In the following, spatial distances are reported in units of radius of gyration (\bar{R}_g) of ideal Gaussian chains with length N_n ($\bar{R}_g^2 = \frac{N_n b^2}{6}$), densities are made dimensionless by dividing them by the bulk segment density ρ_0 , and energies are given in units of $\bar{C} k_B T$, where $\bar{C} = \bar{R}_g^3 \rho_0 / N_n$ is the Ginzburg parameter which characterizes the strength of fluctuations in the system [52,57]. In the present paper, we consider block copolymers with A and B blocks of equal average molecular weight ($\langle f \rangle = 0.5$), as in the experimental system of Ref. [49].

III. RESULTS

A. Micelle structures and size distributions

We first consider copolymers with fixed block ratio $f = 0.5$. We compare systems with same average chain length in the bulk and same micelle free energy $F_m/k_B T \approx 0$ (where micelles just begin to form) but varying polydispersity index \mathcal{D} . To fix F_m , the bulk polymer volume fraction $\bar{\Phi}_p$ must be adjusted. We find that $\bar{\Phi}_p$ decreases significantly with \mathcal{D} (Fig. 1, inset), indicating that micelle formation sets in for smaller copolymer concentrations in polydisperse solutions. Moreover, the micelle size increases with \mathcal{D} (Fig. 1, left). The reason becomes clear when examining the chain length distribution in the micelles (Fig. 1, right). In polydisperse systems, it differs significantly from the chain length distribution in the bulk. The largest chains in solution aggregate first, presumably because they can form aggregates at lower cost of translational entropy, hence micelles become bigger. These

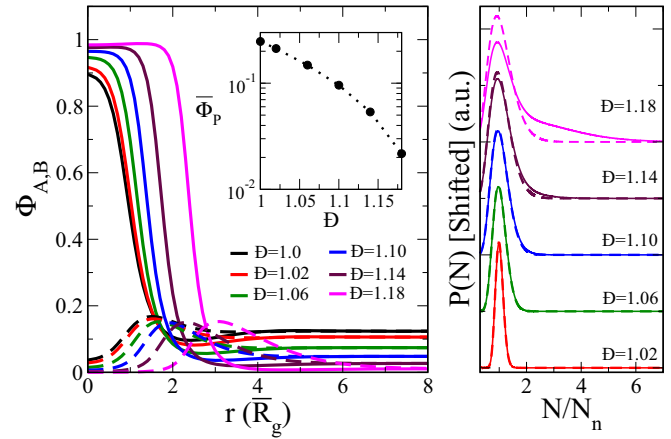


FIG. 1. Left: Spatial density profiles of solvophobic A segments (full lines) and solvophilic B segments (dashed lines) in micelles made of A:B copolymers with $f = 0.5$, $F_m/k_B T \approx 0$ for different bulk polydispersity indices \mathcal{D} as indicated. Inset shows the corresponding shift of the polymer volume fraction $\bar{\Phi}_p$ in the bulk. Right: Chain length distribution of copolymers in the bulk (dashed) and in the micelle (solid) for different values of \mathcal{D} . A constant offset has been added for better visibility.

effects are in agreement with earlier theoretical predictions [42,43] and experimental results [45,49]. Similar effects are observed for critical nuclei in polymer mixtures [58].

Next we study the size distribution of micelles. To this end, we determine the constrained free energy $F_m(R)$ for micelles of fixed radius R (see the Supplemental Material [56] for technical details). The probability for finding a micelle with size R is then proportional to $\exp(-F_m(R)/k_B T)$. The function $F_m(R)$ is shown in Fig. 2(left). It starts at $F_m(0) = 0$, then exhibits a maximum followed by a minimum. The minimum corresponds to the most probable micelle size R_{mp} and coincides with the solution of the unconstrained SCF equations discussed above (Fig. 1). Consistent with Fig. 1, it shifts to the right with increasing polymer polydispersity. The maximum correspond to an unstable micelle state: Micelles of this size may dissolve again. We will refer to it as critical micelle size R_{mc} . The height of the maximum gives the free energy barrier for micelle formation, and the free energy difference $\Delta F_m = F_m(R_{mc}) - F_m(R_{mp})$ gives the free energy barrier for micelle dissolution. According to Fig. 2, these barriers increase with increasing polydispersity. Hence polydispersity stabilizes micelles, suggesting that they might also have narrower size distributions.

The micelle size dispersity is characterized by the relative width of the size distribution, $\sigma_m = \sqrt{\langle R^2 \rangle / \langle R \rangle^2 - 1}$. To calculate σ_m , we fit the SCF results for $F_m(R)$ to a fourth order polynomial (see Fig. 2, left) and use that to determine the averages $\langle R^k \rangle = I_k / I_0$ with $I_k = \int_{R_{mc}}^{\infty} dR R^k e^{-F_m(R)/k_B T}$. In doing so, we must specify a value for the global prefactor \bar{C} in $F_m(R)$ (see Fig. 2, left). The Ginzburg \bar{C} is related to a complementary parameter called the invariant polymerization index (\bar{N}) as, $\bar{N} \propto \bar{C}^2$, where $\bar{N} = N_n \rho_0^2 b^6$. Typical values for \bar{N} in experimental systems are [59–62] $\bar{N} \simeq 200\text{--}20\,000$, which corresponds to $\bar{C} \simeq 1\text{--}10$. Figure 2 (right) shows our results for σ_m as a function of \mathcal{D} for three different choices

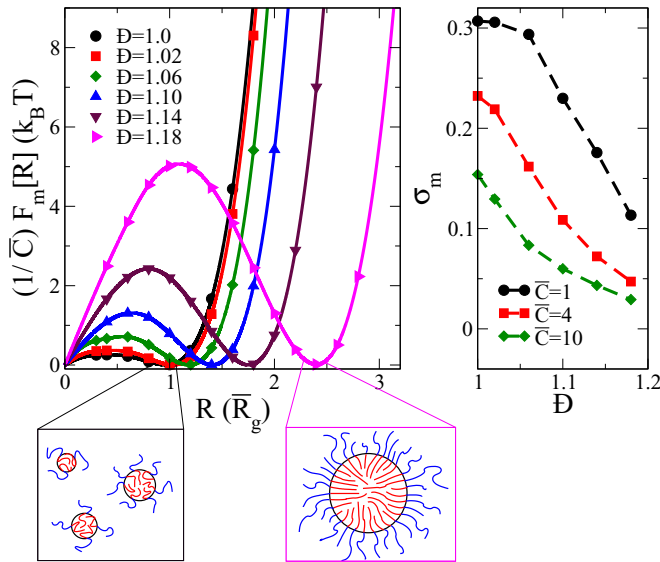


FIG. 2. Left: Micelle free energy as a function of micelle radius for the same systems as in Fig. 1. Symbols show SCF results, solid lines a fit to the polynomial $\sum_{n=1}^4 a_n x^n$. Right: Corresponding micelle size dispersity σ_m as a function of copolymer polydispersity index \bar{D} for different values of the scaling parameter \bar{C} . Cartoons illustrate the proposed stabilizing mechanism: Polydisperse solvophobic blocks can pack more efficiently in the core of the micelle.

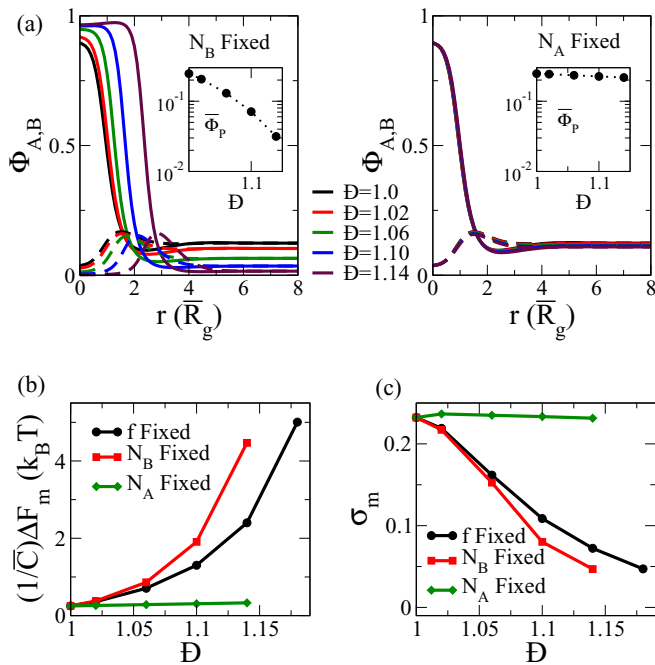


FIG. 3. (a) Density profiles of A and B segments (full/dashed lines) for micelles with micelle free energy $\Delta F_m = 0$ in systems where only the solvophobic (left) or solvophilic (right) chain block is polydisperse. The inset shows the corresponding bulk polymer volume fractions Φ_p . (b) Height ΔF_m of the free energy barrier for micelle dissolution. (c) Width σ_m of micelle size distribution at $\bar{C} = 4$ vs \bar{D} for all systems considered in the present work. Here \bar{D} refers to the dispersity in the corresponding polydisperse part of the chain (A or B or total).

$\bar{C} = 1, 4,$ and 10 . In all cases, the micelle size dispersity σ_m decreases with increasing polymer dispersity \bar{D} . Thus we find that polymer dispersity not only stabilizes micelles but also reduces their size dispersity. This is the main result of the present paper.

B. Other copolymer architectures

To further investigate this phenomenon, we study two other classes of systems where the copolymer blocks still have equal length on average ($\langle f \rangle = 0.5$) but are now varied independently: In the first system, this solvophobic block is polydisperse with $\langle N_A \rangle / N_n = 0.5$ and the length of the solvophilic block is kept fixed at $N_B / N_n = 0.5$. In the second system, the solvophobic block is fixed at $N_A / N_n = 0.5$ and the length of the solvophilic block fluctuates with $\langle N_B \rangle / N_n = 0.5$.

The main results of the SCF calculations are compiled in Fig. 3. If only the solvophobic block is polydisperse and the solvophilic block is kept monodisperse, the effect of polydispersity on the micelle size [Fig. 3(a), left], the chain length distribution (Fig. S2 in the Supplemental Material [56]), the height of the free energy barrier ΔF_m [Fig. 3(b)], and the micelle dispersity [Fig. 3(c)] is even stronger than before. In contrast, if the solvophobic block is monodisperse, polydispersity of the solvophilic block has almost no influence on the micelle size [Fig. 3(a), right] and the other micelle characteristics. Hence the micelle structure and size distribution in the solution is primarily determined by the dispersity of the solvophobic chain block. These results suggest that the main effect of polydispersity is to enhance the packing efficiency inside the hydrophobic core.

C. Free energy analysis

To test this hypothesis, we separate the different contributions to the micelle free energy according to $F_m = \Delta U + W_{\text{chem}} - T\Delta S$, where ΔU and ΔS are the interaction energy and entropy in the micelle relative to the bulk, and $W_{\text{chem}} = -\mu_s \Delta n_s - \sum_N \mu_p(N) \Delta n_p(N)$ refers to the chemical work required for bringing polymer into the system and moving solvent out (Δn_x is the excess number of molecules of type X in the micelle). Within the SCF framework, the contributions of polymers and solvent to the entropy and the chemical work can be calculated separately (see the Supplemental Material for technical details [56]). The results are shown in Fig. 4. The dominant terms are the polymer entropy and the chemical work associated with the polymers.

The polymer entropy decreases with increasing polydispersity \bar{D} . This supports the packing hypothesis: Well-packed polymers fluctuate less and explore fewer conformations, which reduces their entropy. Interestingly, micelle formation in polydisperse systems does not lead to a reduction of interaction energy U : Except in systems with fixed solvophobic block length, ΔU is positive. The picture changes in the canonical ensemble, where the number of polymers is fixed and one must consider the internal energy *per polymer segment*. This quantity is smaller in micelles than in the bulk (see Fig. 4, inset). Hence micelle formation is driven by a gain in energy per monomer but not necessarily by a gain in

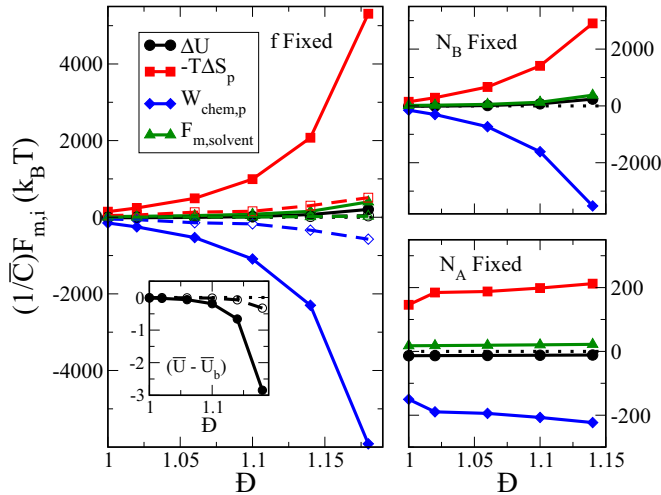


FIG. 4. Contributions to the micelle free energies from the interaction energy (black circles), the polymer entropy (red squares), the chemical work associated with the polymers (blue diamonds), and the sum of solvent entropy and solvent chemical work (green triangles) for the systems considered in this work. Full lines/full symbols refer to most probable micelles; dashed lines/open symbols refer to critical micelles. Inset shows the difference between the internal energy per polymer segment in the micelle system and in the bulk (in arbitrary units).

total energy in a grand canonical setup. The main negative contribution to F_m favoring micelle formation is the chemical work associated with the polymers. It becomes stronger with increasing \bar{D} . The chemical potential “pushes” polymers into the solution, and the system gains free energy if it can accommodate more polymers in the micelles. This again supports the packing hypothesis.

The proposed stabilizing mechanism is illustrated in Fig. 2 (cartoons). When forming spherical micelle cores from monodisperse solvophobic blocks, one necessarily creates frustration: Some blocks must stretch and some must compress to fill the space in the core. Therefore, the micelles offer little resistance to size variations. In contrast, polydisperse solvophobic blocks can optimize the packing inside the micelle and minimize the frustration, which makes them more stable.

IV. DISCUSSION

In summary, we have investigated the effect of polymer length dispersity on self-assembled micelles in solutions of amphiphilic diblock copolymers. Our main results can be summarized as follows: (i) Consistent with previous studies [42–45], we find that the chain composition in micelles differs from that in solution—chains are longer on average. The reason is that in polydisperse systems, long polymers can segregate from solution and gain energy by forming micelles at lower cost of translational entropy. As a consequence, the size of the micelles increases compared to monodisperse systems, in agreement with experimental data [49]. (ii) With increasing polydispersity, the free energy barrier for micelle

formation and dissolution increases, and (iii) the width of the size distribution of micelles decreases. Hence polymer polydispersity stabilizes micelles and reduces their size dispersity. A free energy analysis suggests that this phenomenon is driven by packing in the hydrophobic core, which is more efficient if the chains are polydisperse.

In the present work, we have considered a reference “bulk solution” where polymer segments are homogeneously distributed in the solution. In reality, the solvophobic blocks of individual chains may be collapsed [63,64]. This will affect the free energies of the reference state and the position of the CMC and also have an influence on the chain length distribution in the micelle. Unfortunately, studying these effects in a fully consistent manner is not possible in grand canonical SCF calculations, since the homogeneous bulk solution serves as outer boundary condition (see, e.g., Fig. 1). We plan to analyze this problem in more detail in the future.

We have considered moderate values of the polydispersity up to $\bar{D} \approx 1.2$. For larger values of the polydispersity, it was not possible to find a solution of the radial SCF equations, suggesting that spherical micelles may no longer be stable. Indeed, experiments suggest that large polydispersities may induce shape transitions and even morphological transitions [49]. This will be an interesting subject for future work.

We have considered systems close to the CMC, where micelles just begin to form, such that most copolymers are still in solution. Furthermore, we have assumed that micelles and micelle size distributions are fully equilibrated. This corresponds to an experimental situation where micelles are synthesized very slowly from a solution which does not change with time and provides an inexhaustible polymer reservoir. In reality, micelles consume polymers and the polymer composition changes during the process of micelle formation. Moreover, nanoparticles are not equilibrated. Their sizes, size distributions, and even morphologies depend on the parameters of the synthesis process [65–67]. Nevertheless, we believe that the insights from the present equilibrium considerations should also be relevant for real nonequilibrium processes and could provide useful guidance for experimental synthesis procedures. Roughly speaking, our study suggests that it may be easier to assemble well-defined polymeric nanoparticles with narrow size distribution from “bad” batches of polydisperse building blocks than from “good” batches of narrowly distributed building blocks, because the “bad” batches provide a range of different molecules which can be combined to optimize packing. This might be a general principle in solution self-assembly for nanoparticle synthesis.

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