Phase behaviors of bidisperse nanoparticle/block copolymer mixtures in dilute solutions

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Abstract

The complex microstructures of bidisperse nanoparticles/diblock copolymer mixtures in dilute solutions have been investigated by a theoretical approach which combines the self-consistent field theory (SCFT) and the density functional theory (DFT). Special attention is paid to the role played by the block ratio and the interaction parameters between each component in the mixture. It is shown that the conformational entropy of the polymer chains, the block ratio of the diblock copolymer, the chemical difference between two kinds of particles and the steric packing effect of the particles play important roles in determining the morphologies of the systems. It is found that with the increase of the block ratio, the mixture undergoes a morphological transition from compound micelles to spherelike micelles. The increase of chemical difference between the two kinds of particles can promote the formation of “a jujube set in a cake”. When the selectivity of the particles is changed, another type of micelle emerges. Specifically, in the case where the particles are nonselective to the A- and B-blocks, ordered structures from the phase separation between the two types of particles emerge inside the micelles formed by the amphiphilic diblock copolymers in solutions.

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1. Introduction

The self-assembly of amphiphilic block copolymers in dilute solutions has attracted tremendous academic and industrial interests in recent years [1–16]. The mixture can self-assemble into complex microstructures such as rod-like micelles, spherical micelles and vesicles etc. These morphologies can serve as templates for the spatial organization of nanoparticles. The encapsulation of inorganic and biochemical nanoparticles by amphiphilic block copolymers in solutions can have potential applications in nanoelectronics and drug delivery and release [7,17–32]. This has triggered intense experimental research interests in the self-assembly of amphiphilic block copolymer/nanoparticle mixture in selective solvents [33–37].

Taton et al. [38–40] reported the self-assembly of amphiphilic poly(styrene-b-acrylic acid)/nanoparticle mixture in dilute solutions which shows that the nanoparticles have a great influence on the supramolecular structures of block copolymers and leads to the morphological transition of the parent block copolymer. Lin et al. [41] prepared a new type of hybrid polymeric micelles for drug delivery applications with the self-organization of PLGA-B-PPO-B-PLGA (PLGA: poly(l-glutamic acid); PPO: poly(propylene oxide)), PEG-B-PPO (PEG: polyethylene glycol) and drugs in water. During the self-assembly, the hydrophobic PPO block of both block copolymers forms aggregates encapsulating the drugs within the core, while the hydrophilic PLGA block and PEG block forms the corona. In an acidic condition (The environment around tumor cells is acidic), the structure of PLGA block changes, leading to the microphase separation between PLGA and PEG blocks in micelle coronas and the formation of PEG channels which connect the inner core and the outer milieu. These PEG channels can accelerate the diffusion of drugs from micelles. Compared to the large amount of experimental works, there are very few theoretical studies in this area. Lin et al. [42] applied the SCFT/DFT approach developed by Balazs et al. [43,44] to study the self-assembly behaviors of amphiphilic block copolymer/nanoparticle mixture in dilute solutions. Different morphologies, such as vesicles, circletlike micelles, rod-like micelles, and compound micelles are observed in the simulation. It was found that the aggregate morphologies can be tuned by the particle volume fraction and the particle size. In their studies, the particles are assumed to be monodisperse, and the effect of particle size distribution on the self-assembly behavior is not considered. In experiments, synthesizing nanoparticles monodisperse in size is a very difficult task. Thus, it is more realistic to assume nanoparticles to be polydisperse in size in theories and simulations. Furthermore, it is of special interest to study the self-assembly of nanoparticle/diblock
copolymers in dilute solutions in which nanoparticles with different chemical natures are involved. Such a scenario has relevance to the drug delivery system in which nanoparticles with different biomedical functionalities due to different chemical natures of the particles are presented.

Real-space self-consistent field method (SCFT) has been widely used for studying the self-assembly and morphologies of polymeric systems [43–48]. This method has the advantage of requiring no prior knowledge of the equilibrium structure of the system. In this paper, we apply the combined “SCFT/DFT” model developed by Balazs et al. [43,44] to investigate the phase behaviors of bidisperse hard sphere/diblock copolymer mixture in dilute solutions. The polymer part is dealt with by the SCFT, while the particle part is treated with the DFT. As will be shown later in this paper, rich phase behaviors are discovered which result from the delicate interplay of conformation entropy of polymers, the block ratio, the differences between two kinds of particles, and the steric repulsive interaction between particles. In the simulations, the interaction parameters between different components are chosen to mimic the different nature of components in the system. These interaction parameters are in the range commonly used in SCFT simulations which can qualitatively, and even quantitatively in some cases, describe experimental results. Although our simulation work in this paper may not exactly correspond to realistic experiments, it can provide guidance to experimental design and help in interpreting experimental results. The simulation results in this paper are expected to have implications on the drug delivery system which consists of drug nanoparticles with different sizes and different biomedical functionalities due to the differences in chemical nature. The rest of the paper is organized as follows. In Section 2, the “SCFT/DFT” model for the bidisperse hard sphere/diblock copolymer mixture in dilute solutions is briefly outlined and the governing equations are presented. In Section 3, complex morphologies of the system are discovered from the simulations by changing the block ratio and interaction parameters between each component.

\[
\frac{NF}{\rho_0 K_\text{B} T V} = - \sum_{i=1,2} \frac{\phi_i}{\alpha_i} \ln \left( \frac{Q_{\text{D}} \alpha_i}{V \phi_D} \right) - \phi_D \ln \left( \frac{Q_{\text{D}}}{V \phi_D} \right) - \phi_S \ln \left( \frac{Q_S}{V \phi_S} \right) + \frac{1}{V} \int d\mathbf{r} \left[ \frac{1}{2} \sum_{\mu \neq v} \chi_{\mu \nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \right]
\]

where \( K_\text{B} \) is the Boltzmann constant and \( T \) is the absolute temperature; \( \chi_{\mu \nu} \) characterize the Flory-Huggins interaction parameter between species \( \mu \) and \( \nu \); \( \phi_{\mu}(\mathbf{r}) \) expresses the local volume fraction of each constituent of the mixture; \( \rho_{\mu}(\mathbf{r}) \) is the center distribution of particles of type \( \mu \) and particles \( \nu \), respectively, \( \xi(\mathbf{r}) \) is the Lagrange multiplier which enforces the incompressibility condition of the system. The volume ratio of the particles \( \rho_1 \) and particles \( \rho_2 \) to a copolymer is given by

\[
\alpha_i = \frac{V_{\mu \nu} \rho_0}{N} = \frac{4\pi}{3} \left( \frac{R_{\mu}}{R_0} \right)^3 N^{1/2}
\]

Fig. 1. Density distributions of particles in a bidisperse hard sphere/diblock copolymer solution with a block ratio \( f = 0.76 \) and the particle volume fractions \( \phi_{P_1} - \phi_{P_2} = 0.01 \). (a) Density distribution of particles \( P_1 \), (b) Density distribution of particles \( P_2 \). Light regions indicate high concentrations of particles and dark regions mark lower concentrations of particles.
where $N = a^6 r_0^2 N$ is the polymerization index, $R_0 = aN^{1/2}$ is the root-mean-square end-to-end distance of the copolymer chain. In Eq. (1) the last term containing $\Psi$ represents the steric repulsive interaction between particles in the density functional theory (DFT) [49]. It is a function of the number fraction of the various particle species and the weighted densities [50]. The number fractions in terms of the overall volume fractions are obtained as

\[ x_i = \frac{a_i}{a \sum_j a_j} \]  

(In this work, we let $i$ and $j$ be different particle species)

and the weighted densities have the following mathematical expression:

In Eq. (3), $V_{(R_i + R_j)}$ denotes the volume of a sphere of radius $R_i + R_j$, $p_i(\vec{r})$ denotes the particle center distributions. $Q_D$ is the partition function of one copolymer chain, $Q_N$ is the partition function of a single particle $i$, $Q_S$ is the partition function of the solvent, and they are given by

\[ Q_D = \int d \vec{r}_q \rho_q(\vec{r}, \vec{s}) \]  

\[ Q_N = \int d \vec{r}_p \exp(-W_P(\vec{r})) \]  

\[ Q_S = \int d \vec{r}_s \exp\left(-\frac{W_S(\vec{r})}{N}\right) \]  

Minimizing the free energy in Eq. (1) with respect to the local volume fractions and their conjugate fields as well as the Lagrange multiplier, the following self-consistent equations describing the equilibrium morphologies of the system can be obtained:

\[ W_A(\vec{r}) = \chi_{AB}N\phi_B + \chi_{AP1}N\phi_{P1} + \chi_{AP2}N\phi_{P2} + \chi_{AS}N\phi_S + \xi(\vec{r}) \]  

\[ W_B(\vec{r}) = \chi_{AB}N\phi_A + \chi_{BP1}N\phi_{P1} + \chi_{BP2}N\phi_{P2} + \chi_{BS}N\phi_S + \xi(\vec{r}) \]  

\[ W_S(\vec{r}) = \chi_{AS}N\phi_A + \chi_{BS}N\phi_B + \chi_{PS1}N\phi_{P1} + \chi_{PS2}N\phi_{P2} + \xi(\vec{r}) \]
In Eqs. (4), (12) and (13), \(q(r,s)\) and \(q^+(r,s)\) are the probabilities of finding the segment \(s\) at the position \(r\) with either end of the diblock copolymer chain free, and they satisfy the following modified diffusion equations

\[
W_{P1}(\mathbf{r}) = \Psi(\mathbf{r}, \{\mathbf{x}_j\}) + \frac{\alpha_{p1}}{v_{R1} + v_{R2}} \int |\mathbf{r}| < R_{P1} \mathbf{d} \mathbf{r} \left[ \chi_{BP1}N_{\Phi_B}(\mathbf{r} + \mathbf{r}) + \chi_{BP2}N_{\Phi_B}(\mathbf{r} + \mathbf{r}) + \chi_{BP3}N_{\Phi_B}(\mathbf{r} + \mathbf{r}) \right]
\]

\[
+ \frac{\alpha_{p1}}{v_{R1} + v_{R2}} \int |\mathbf{r}| < R_{P1} + R_{P2} \mathbf{d} \mathbf{r} [\rho_{P1}(\mathbf{r} + \mathbf{r})] \Psi(\mathbf{r}, \{\mathbf{x}_j\})
\]

\[
+ \frac{\alpha_{p2}}{v_{R1} + v_{R2}} \int |\mathbf{r}| < R_{P1} + R_{P2} \mathbf{d} \mathbf{r} [\rho_{P2}(\mathbf{r} + \mathbf{r})] \Psi(\mathbf{r}, \{\mathbf{x}_j\})
\]

\[
W_{P2}(\mathbf{r}) = \Psi(\mathbf{r}, \{\mathbf{x}_j\}) + \frac{\alpha_{p2}}{v_{R2} + v_{R3}} \int |\mathbf{r}| < R_{P2} \mathbf{d} \mathbf{r} \left[ \chi_{BP1}N_{\Phi_B}(\mathbf{r} + \mathbf{r}) + \chi_{BP2}N_{\Phi_B}(\mathbf{r} + \mathbf{r}) + \chi_{BP3}N_{\Phi_B}(\mathbf{r} + \mathbf{r}) \right]
\]

\[
+ \frac{\alpha_{p1}}{v_{R1} + v_{R2}} \int |\mathbf{r}| < R_{P1} + R_{P2} \mathbf{d} \mathbf{r} [\rho_{P1}(\mathbf{r} + \mathbf{r})] \Psi(\mathbf{r}, \{\mathbf{x}_j\})
\]

\[
+ \frac{\alpha_{p2}}{v_{R2} + v_{R3}} \int |\mathbf{r}| < R_{P2} + R_{P2} \mathbf{d} \mathbf{r} [\rho_{P2}(\mathbf{r} + \mathbf{r})] \Psi(\mathbf{r}, \{\mathbf{x}_j\})
\]

\[
\frac{\partial q(r,s)}{\partial t} = \nabla^2 q(r,s) - W(r)q(r,s)
\]
\[
\frac{\partial q^+(\vec{r},s)}{\partial s} = - \nabla^2 q^+(\vec{r},s) + W(\vec{r})q^+(\vec{r},s)
\]  
(19)

where \( W(\vec{r}) = W_A(\vec{r}) \) when \( 0 \leq s \leq f \), and \( W(\vec{r}) = W_B(\vec{r}) \) when \( f < s \leq 1 \), with the initial conditions of \( q(\vec{r},0) = 1 \) and \( q^+(\vec{r},1) = 1 \), respectively.

The above self-consistent field equations (Eqs. (7)–(17)) are numerically solved in the real-space, and it is assumed that the equilibrium is reached when the relative change in the free energy between two consecutive iteration steps is smaller than \( 10^{-6} \) (namely \( \Delta F < 10^{-6} \)). So we take the equilibrium phase to be the structure which has the lowest free energy. In the simulations, the sizes of the computational domain are \( L_x = L_z = 20R_0 \) with periodic boundary conditions. It is noted that the resulting aggregate morphologies depend on the amplitude of the initial density fluctuations. The different initial density fluctuations result in different microstructures. So we use the same initial density fluctuation amplitude in all the simulations. Also, the simulations are repeated 8–16 times for different initial random states and different random numbers to ensure that the phenomena are not accidental.

3. Results and discussion

In this paper, we consider a dilute solution with 10% of the solute, namely \( \phi_D + \phi_{P_1} + \phi_{P_2} = 0.1 \) (here \( \phi_D = 8\% \)). Block B is assumed to be hydrophobic, and the interaction parameter between \( B \) and the solvent is set as \( \chi_{BS}N = 43.0 \). Block A is assumed to be hydrophilic compared to block \( B \), and \( \chi_{A}N \) is fixed at 21.0. As we are interested in studying the phase behaviors of bidisperse hard sphere/diblock copolymer mixtures in dilute solutions, so we set one group of spheres with a radius \( R_{P_1} = 0.4R_0 \), the other with \( R_{P_2} = 0.2R_0 \), and we assume all the particles are attractive with block \( A \) (\( \chi_{AP_1}N = \chi_{AP_2}N = 0.0 \), \( \chi_{BP_1}N = \chi_{BP_2}N = 23.0 \)). Furthermore, the chain length of the diblock copolymer is set to be 25, while other parameters are taken as \( \chi_{AB}N = 23.0 \), \( \chi_{P_1}N = \chi_{P_2}N = 23.0 \) and

![Fig. 6. Density distribution of particles P1 is shown in the left column, and that of particles P2 is shown in the right column with the increase of the interaction between two kinds of particles: (a–b) \( \chi_{P_1}N = 5.0 \), (c–d) \( \chi_{P_1}N = 8.0 \), (e–f) \( \chi_{P_1}N = 10.0 \). Light regions indicate high concentrations of one species and dark regions mark low concentrations of one species.](image-url)
$\chi_{P1P2N} = 0.0$. These interaction parameters are similar to those used by Lin et al. [42] and Balazs et al. [43,44].

First the self-assembly of the bidisperse hard sphere/diblock copolymer solution are studied by choosing the block composition $f = 0.76$, with $\phi_{P1} = \phi_{P2} = 0.01$. The equilibrium morphology of such a system is displayed in Fig. 1, where light regions indicate high concentrations of one species and dark regions mark low concentrations of one species. As can be seen from Fig. 1, both spherical micelles and compound micelles emerge from the solution. Nearly all the particles aggregate in shell $A$, but the larger particles $P_1$ are surrounded by the smaller particles $P_2$ (the density profiles of copolymer are not shown here).

In order to get more detailed morphological information about the aggregates, the density distributions of various constituents except the solvent S of the spherical micelle of Fig. 1 are shown in Fig. 2.

From Fig. 2, it can be seen that the profile of $\phi_A(r)$ shows a convex shape located in the center of the spherical micelle, while the profile of $\phi_B(r)$ shows two protrusions near the interface making it a spherical shell of the micelle. Particles $P_2$ concentrate near the center of block $A$. However, particles $P_2$ are distributed in both the inside and outside of particles $P_1$, and to some degree into the $B$-block region of $B$-domain, making it another shell of particles $P_1$. Clearly, we observe here the segregation of particles based on size, which is also observed in the morphological study of nanocomposites composed of bidisperse hard spheres and diblock copolymers [50]. As elucidated by Balazs et al., such segregation of particles is entropic in nature, due to the confinement within the diblock matrix. As the smaller particles are pushed into the block $B$ domain, there is an enthalpic penalty due to the unfavorable interaction between particles and the block $B$. However, this is more than compensated by the steric contribution to the free energy due to the excluded volume interaction between the particles, and the translational entropy of the small particles. The self-assembly process is vividly illustrated in the schematic representations shown in Fig. 3.

It is very interesting to find that changing the block ratio from $f = 0.76$ to $f = 0.8$ while keeping all other parameters unchanged, a different morphology emerges, as illustrated in Fig. 4. The compound micelles in the solution at $f = 0.76$ all transform into a single class of spherelike micelles at $f = 0.8$. And the density distributions of various constituents except the solvent S of the spherelike micelle of Fig. 4 are shown in Fig. 5. Obviously, the profile of each constituent changes greatly, both $A$ and $B$ monomers are quite uniformly distributed inside the micelles, showing much reduced degree of phase separation between the two blocks compared to that shown in Fig. 2. Moreover, different from the distribution in Fig. 1, plenty of the smaller particles $P_2$ are expelled to the $B$ domain and are quite uniformly distributed in $B$ domain. As the block ratio increases, the length of the hydrophobic $B$-block gets shorter. Thus, the enthalpic penalty due to the presence of the smaller particles in $B$ domain gets smaller. Eventually, at $f = 0.8$, the steric effect due to the excluded volume interaction between particles and the translational entropic effect due to the presence of the smaller particles in $B$ domain dominate over the unfavorable enthalpic effect, leading to the uniform distribution of the smaller particles in $B$ domain.

Next we investigate the phase behaviors of the system in which the two kinds of particles are different in chemical nature. The simulation shows that the equilibrium morphology of such a system changes with the increase in the interaction parameter $\chi_{P1P2N}$ between two kinds of particles, as shown in Fig. 6 where all the other parameters are the same as in Fig. 4. The values $\phi_{P1P2N}$ fall in a similar range as the other interaction parameters such as $\chi_{ABN}$. These values may not correspond to real experimental ones.

**Fig. 7.** Density distributions of various constituents except solvent S of the system along the intersecting line through the center of a compound micelle corresponding to Fig. 6 are displayed. The solid line, dashed line and dot line, represent the situation that $\chi_{P1P2N}$ is 5.0, 8.0 and 10.0, respectively.

**Fig. 8.** (a) the translational entropy per particle $P_1$, (b) the translational entropy per particle $P_2$, with the increase in interactions between two kinds of particles.
kinds of particles, as like “a jujube set in a cake”. This phenomenon has become apparent as $\chi_{P1P2}N$ reaches 10.0. The density distributions of various constituents except solvent $S$ in the micelle with different chemical nature between two kinds of particles are illustrated in Fig. 7. As shown in Fig. 7, the hydrophobic block $B$ is certainly centralized in the inside of the cluster due to its strong repulsion to the solvent. Moreover, the density profile of the hydrophilic $A$ exhibits a high plateau in the central region of the cluster, similar to the case shown in Fig. 5. With the enhancement of the chemical differences between two kinds of particles, the density of particles $P_1$ near the interface becomes much higher, and its width also increases. Also with the increase of the repulsion between the two kinds of particles, the density of the smaller particles inside the interfacial region gradually decreases, showing the stronger segregation between the two kinds of particles in the interfacial region.

With the increase of the repulsive interaction between the two types of particles, the degree of phase separation between them gets strong, and the density of the larger particles gets enhanced in the periphery of the micelles. Also the width of the large particle rich domain increases slightly with the increase of the repulsive interaction between the large and small particles. Because the total volume fraction of the larger particles is fixed, to maintain the mass conservation, a higher density and slightly larger width of the large particle rich domains result in the breakup the circular domain, thus particles $P_1$ assemble into a mosaic of super micro-domain structure. Compared to the circular domain of the large particles in the absence of repulsive interaction between the two types of particles, the confinement in the isolated smaller domains rich in particles $P_2$, the translational degree of freedom of the particles $P_1$ is reduced. The translational entropies of the two types of particles are calculated from the following equation [14,47,51] and displayed against the interaction parameter $\chi_{P1P2}N$ in Fig. 8.

$$\frac{S_{P1}}{nk_b} = \frac{4\pi r_p^3}{V_0} \frac{1}{\phi_1} \ln \left( \frac{Q_{P1}\phi_1}{V\phi_n} \right)$$  \hspace{1cm} (20)

As expected, with the increase of the interaction parameter $\chi_{P1P2}N$, the translational entropy of the larger particles decrease. On the other hand, due to the increase in the accessible space by the smaller particles from the breakup of the circular domain rich in $P_1$, the translational entropy of the smaller particles increases.

Now we turn our attention to another situation, that is, the two kinds of particles differ in chemical nature such that the larger particles $P_1$ are preferentially wetted by block $A$ and the smaller particles $P_2$ are selective to block $B$. It is thus assumed that $\chi_{AP1}N = \chi_{BP2}N = 0.0$, $\chi_{AP2}N = \chi_{BP1}N = 23.0$ with other parameters the same as in Fig. 1. The resulting equilibrium morphology is shown in Fig. 9, from which it can be clearly seen that the two kinds of particles are fully segregated into the respectively selective block domains. The density distributions of various constituents except the solvent $S$ are shown in Fig. 10 corresponding to the spherical micelle in Fig. 9. As expected, the two kinds of particles completely phase separate due to the reinforcing enthalpic repulsion between them.

So far, the particles are assumed to be selective to the diblock copolymer chains. We have observed the entropically generated separation of particles based on size when all the particles are selective to $A$-block. Now we investigate the phase behaviors of the system of bidisperse nanoparticle/diblock copolymer in a solution in which all the particles are nonselective to the diblock copolymer chains. The equilibrium morphologies of such a system at different $\chi_{P1P2}N$ are displayed in Fig. 11. Because the nanoparticles are hydrophobic, the nanoparticles are encapsulated inside the micelles formed by the amphiphilic diblock copolymer chains. At $\chi_{P1P2}N = 0$, it can be seen from (a–b) of Fig. 11, the larger particles form isolated circular domains, while the smaller particles show a certain degree of entropically generated separation based on size from the larger particles, although the phase separation is not very strong. We can use the symbol $S_{i,m}$ to characterize the circular morphology of the larger particles inside the micelles, where $i$ (0 or 1) denotes the number of circles composed of the larger particles in

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**Fig. 9.** Density distributions of particles in a binary hard sphere/diblock copolymer solution. (a) The density distribution of particles $P_1$, (b) The density distribution of particles $P_2$. Light regions indicate high concentrations of a species and dark regions mark low concentrations of a species.

**Fig. 10.** Density distributions of various constituents except the solvent $S$ of the system along the intercepting line through the center of spherical micelle in Fig. 8. The solid line represents the $A$-block distribution, the dashed line denotes $B$-block distribution, the dot-dashed line shows the distribution of particles $P_1$, and dotted line expresses the distribution of particles $P_2$. 

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the center of the micelle, and $j$ stands for the number of circles between the center and the periphery of the micelles. Thus the morphology of the larger particles shown in (a) of Fig. 11 can be labeled as $S_{1-e}^{1,7}$, $S_{0-e}^{1,4}$, $S_{0-e}^{1,5}$. As the repulsive interaction between the two kinds of particles increases, the phase separation between the larger and the smaller particles gets stronger, and the smaller particles form the continuous phase inside the micelles within which the circular domains of the larger particles are embedded, as shown in (d) and (f) of Fig. 11. It can be also observed that, as $\chi_{P1P2}N$ increases, the morphology of the larger particles changes slightly. The $S_{1-e}$ phase of the larger particles inside one micelle shown in (a) of Fig 11 transforms into the $S_{1-e}^{1,6}$ phase shown in (c) and (d) of Fig 11.

4. Conclusions

To conclude, we have applied the combined self-consistent field theory (SCFT) and the density functional theory (DFT) to investigate the aggregation behavior of bidisperse hard sphere/diblock copolymer mixture in dilute solutions. The morphologies of the formed aggregates depend on the block ratio and the interaction parameters between each component, etc. We have observed the entropically generated separation of particles based on size when all the particles are selective to one block of the diblock copolymers. As the block ratio increases, the mixture can experience a transition from compound micelles to spherelike micelles. It is observed that the increase of chemical difference between the two particles can promote the formation of “a jujube set in a cake” under the competition between the enthalpic and entropic effects, where the circular domain rich in the larger particles breaks up into isolated smaller domains. If the two kinds of particles are nonselective to both blocks of the diblock copolymers, the competitions among the steric repulsive interactions and the enthalpic interactions between the two types of particles lead to the formation of ordered structures inside the micelles formed by the amphiphilic diblock copolymers.

In this paper, it is demonstrated that the particle size distribution and the enthalpic/entropic interactions between the particles offer opportunity to finely tune the morphologies of the hard
sphere/block copolymer mixture in solutions. The results provide new ways to stabilize and fabricate the complex microstructures of bidisperse hard sphere/diblock copolymer mixture in dilute solutions. The self-assembly of bidisperse hard sphere/diblock copolymer mixture in dilute solutions is expected to have implications in the formation of medical “functional units” which are composed of two kinds of drug particles dispersed in an amphiphilic system.

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