

## SIMULATION STUDY OF CO-ASSEMBLY OF ABC TRIBLOCK COPOLYMER/NANOPARTICLE INTO MULTICOMPARTMENT HYBRIDS IN SELECTIVE SOLVENT\*

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**Abstract** Co-assembly of ABC linear triblock copolymer/nanoparticle into bump-surface multicompartment hybrids in selective solvent was studied through self-consistent field theory (SCFT) simulation. Results from three-dimensional SCFT simulation showed that the hybrid morphology depended on the length and number of grafted chains, whereas the number and shape of bumps relied on nanoparticle size. Moreover, the simulation results showed that the length and number of grafted chains had equivalent effect on hybrid morphology. Calculated results indicated that entropy was a more important factor than enthalpy in the co-assembly.

**Keywords:** Co-assembly; Triblock copolymer; Nanoparticle; Multicompartment hybrid; Self-consistent field theory.

### INTRODUCTION

Amphiphilic block copolymers have attracted considerable attention for many researchers due to their self-assembly capability in selective solvent. Amphiphilic block copolymers can self-assemble into various ordered structures such as spherical, rod-like, ring-shaped micelles<sup>[1–4]</sup>, which are believed to have extensive potential applications in microelectronics<sup>[5, 6]</sup>, bioreactors<sup>[7]</sup>, microcapsules<sup>[8]</sup>, nanotemplates<sup>[9]</sup>, drug delivery and targeting release<sup>[10–12]</sup>, and so on.

Moreover, amphiphilic block copolymer/nanoparticle can form various hybrids *via* co-assembly in selective solvent. Nanoparticles can impart unique functionalities to the hybrid materials, whereas flexible polymers provide morphology controllability and processability. Hybrid aggregates possess desirable properties in electrical, optical, magnetic, thermal, or mechanical applications<sup>[13–16]</sup>. The hybrid morphology and the location of nanoparticles are important for realizing the full potential of polymer/nanoparticle hybrid materials.

Various nanoparticles have been successfully incorporated into spherical micelles, rod-like micelles, films, vesicles, tubes, and the like<sup>[17–21]</sup>. Multicompartment micelles have recently become the subject of considerable attention for their subdivided solvophobic cores, which can perform distinct functions<sup>[22–25]</sup>. However, studies on the incorporation of nanoparticles into multicompartment micelles are rarely reported. In addition, the incorporation of nanoparticles into polymer aggregates is generally associated with a change in interactive enthalpy, a change in polymer conformational entropy and a gain in particle translational entropy<sup>[26–28]</sup>. Fundamental questions concerning the role of enthalpy and entropy remain unanswered. Aiming to these

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questions, the effect of nanoparticle size as well as the length and number of grafted copolymer chains on the morphologies of multicompartment micelles was studied through SCFT simulation.

### THEORETICAL MODEL

In this study, the amphiphilic ABC triblock copolymers, nanoparticles grafted by short homopolymer A and selective solvent S are dissolved in volume  $V$ . Each triblock copolymer consists of  $N$  segments, including a hydrophobic block A with  $N_A$  segments, a hydrophobic block B with  $N_B$  segments and a hydrophilic block C with  $N_C$  segments, *i.e.*,  $N = N_A + N_B + N_C$ . The length fraction of block A, B and C in one triblock copolymer chain is  $f_A = N_A/N$ ,  $f_B = N_B/N$  and  $f_C = 1 - f_A - f_B$ . For the grafted nanoparticles, each particle consists of  $\sigma$  short homopolymer A with  $N_G = \beta N$  segments, where  $\beta$  is the chain length ratio of the grafted homopolymer to the triblock copolymer. The volume ratio of particle P to a triblock copolymer chain is defined by  $\alpha = 4\pi R_p^3 / (3N)$ , where  $R_p$  is the radius of the particle. The volume fractions of triblock copolymers and grafted nanoparticles are  $f_T$  and  $f_G$ , respectively. As a result, the volume fraction of solvent is  $f_s = 1 - f_T - f_G$ .

In the SCFT, we consider a single polymer chain placed in a set of effective chemical potential fields  $\omega_I(\vec{r})$  ( $I = A, B, C, P$  and S) provided by all other components. These chemical potential fields are conjugated to corresponding segment density fields  $\phi_I(\vec{r})$ . In the canonical ensemble, the dimensionless free energy of the system is given by

$$F = -f_T \ln\left(\frac{Q_T}{Vf_T}\right) - \frac{f_G}{(\alpha + \sigma\beta)} \ln\left(\frac{Q_G}{Vf_G}\right) - Nf_s \ln\left(\frac{Q_s}{Vf_s}\right) + \frac{1}{V} \int d\vec{r} \left[ \sum_{I \neq J} \chi_{IJ} N \phi_I(\vec{r}) \phi_J(\vec{r}) - \sum_I \omega_I(\vec{r}) \phi_I(\vec{r}) - \eta(\vec{r}) (1 - \sum_I \phi_I(\vec{r})) \right] \quad (1)$$

Where  $\chi_{IJ}$  is the Flory-Huggins interaction parameter between components  $I$  and  $J$ .  $\eta(\vec{r})$  is the Lagrange multiplier arising from the incompressibility condition.  $Q_T$ ,  $Q_G$  and  $Q_s$  are the partition function of a single polymer chain, a polymer-grafted nanoparticle and a solvent, respectively.

For a single polymer chain,  $Q_T = \int d\vec{r} q_T(\vec{r}, 1)$ , where  $q_T(\vec{r}, s)$  is the end-segment distribution function that gives the probability of finding segment  $s$  at position  $\vec{r}$ . The single polymer chain is parameterized with the variable  $s$ , which increases from 0 to 1. With the use of flexible Gaussian model, the end-segment distribution function  $q_T(\vec{r}, s)$  satisfies the modified diffusion equation

$$\frac{\partial q_T(\vec{r}, s)}{\partial s} = \nabla^2 q_T(\vec{r}, s) - \omega_I(\vec{r}, s) q_T(\vec{r}, s) \quad (2)$$

Where  $\omega_I(\vec{r}, s)$  is  $\omega_A(\vec{r}, s)$  when  $0 < s < f_A$ ,  $\omega_B(\vec{r}, s)$  when  $f_A < s < f_A + f_B$ , and  $\omega_C(\vec{r}, s)$  when  $f_A + f_B < s < 1$ . The initial condition is  $q_T(\vec{r}, 0) = 1$ . Because the two ends of ABC triblock copolymer are different, a second end-segment distribution function  $q_T^+(\vec{r}, s)$  is needed, which also satisfies Eq. (2).

For the grafted chain on the nanoparticle, the end-segment distribution function  $q_G(\vec{r}, s)$  satisfies

$$\frac{\partial q_G(\vec{r}, s)}{\partial s} = \beta \nabla^2 q_G(\vec{r}, s) - \beta \omega_A(\vec{r}, s) q_G(\vec{r}, s) \quad (3)$$

The initial condition is  $q_G(\vec{r}, 0) = 1$ . The second end-segment distribution function  $q_G^+(\vec{r}, s)$  satisfies Eq. (3) but with the initial condition of  $q_G^+(\vec{r}, 0) = \exp[-\alpha \omega_p(\vec{r}, s)] q_G(\vec{r}, 1)^{\sigma-1}$ . In terms of  $q_G(\vec{r}, 1)$ , the partition function of polymer-grafted nanoparticle can be expressed as  $Q_G = \int d\vec{r} \exp[-\alpha \omega_p(\vec{r})] q_G(\vec{r}, 1)^\sigma$ . For solvent S, the partition function is generally expressed as  $Q_s = \int d\vec{r} \exp[-\omega_s(\vec{r}) / N]$ .

In terms of these partition functions and end-segment distribution functions, the local densities of each

component is obtained by

$$\phi_A(\vec{r}) = \frac{f_T V}{Q_T} \left[ \int_0^{f_A} ds \cdot q_T(\vec{r}, 1) q_T^+(\vec{r}, 1-s) \right] + \frac{f_G \sigma \beta V}{(\alpha + \sigma \beta) Q_G} \left[ \int_0^1 ds \cdot q_G(\vec{r}, s) q_G^+(\vec{r}, 1-s) \right] \quad (4)$$

$$\phi_B(\vec{r}) = \frac{f_T V}{Q_T} \left[ \int_{f_A}^{f_A+f_B} ds \cdot q_T(\vec{r}, s) q_T^+(\vec{r}, 1-s) \right] \quad (5)$$

$$\phi_C(\vec{r}) = \frac{f_T V}{Q_T} \left[ \int_{f_A+f_B}^1 ds \cdot q_T(\vec{r}, s) q_T^+(\vec{r}, 1-s) \right] \quad (6)$$

$$\phi_P(\vec{r}) = \frac{f_G \alpha V}{(\alpha + \sigma \beta) Q_G} \exp[-\alpha \omega_P(\vec{r})] q_G(\vec{r}, 1)^\sigma \quad (7)$$

$$\phi_S(\vec{r}) = \frac{f_S V}{Q_S} \exp[-\omega_S(\vec{r}) / N] \quad (8)$$

From the equilibrium condition, the minimization of free energy with respect to density and Lagrange multiplier (*i.e.*,  $\delta F / \delta \phi = \delta F / \delta \eta = 0$ ), we can obtain the following Eqs.:

$$\omega_I(\vec{r}) = \sum_{I \neq J} \chi_{IJ} N(\phi_J(\vec{r}) - f_J) + \eta(\vec{r}) \quad (9)$$

$$\omega_A(\vec{r}) + \omega_B(\vec{r}) + \omega_C(\vec{r}) + \omega_P(\vec{r}) + \omega_S(\vec{r}) = 1 \quad (10)$$

Equations (2–10) can be solved self-consistently in the real-space SCFT by the combinatorial screening algorithm proposed by Drolet and Fredrickson<sup>[29–31]</sup>. In this work, the numerical simulations were carried out in 3D cubic lattice with a volume of  $V = 50^3$ . Periodic boundary conditions were imposed in all three directions. The grid size was  $\Delta x = 0.333$  and the time step  $\Delta t$  was set to be 0.3. The volume fraction of the ABC triblock copolymer was fixed at  $f_T = 0.1$  and the volume fraction of polymer-grafted nanoparticle was fixed at  $f_G = 0.01$ . All the simulations were carried out until the morphologies were stable.

## RESULTS AND DISCUSSION

The hybrid morphology formed by linear ABC triblock copolymer/nanoparticle was investigated using SCFT simulation. In this study, we focus on the effect of nanoparticle size as well as the length and number of grafted polymer chains on the morphologies of bump-surface multicompartment micelles<sup>[32]</sup>. To obtain the multicompartment micelles, we set  $\chi_{CS}N = -0.765$  (the C block is hydrophilic). The total chain length of the triblock copolymer is  $N = 26$  with  $N_A = 8$ ,  $N_B = 16$ , and  $N_C = 2$ . Three mutually immiscible blocks in simulation can be realized by setting  $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 30$ . The interactions between particle P and other blocks are set as  $\chi_{BP}N = \chi_{CP}N = 30$  and  $\chi_{AP}N = -5$ . These values remain unchanged in the simulations.

### **Bump-surface Disk-like Micelle Formed by the ABC Triblock Copolymer**

Figure 1(a) shows the bump-surface disk-like micelle formed by the ABC triblock copolymer with the interactions of  $\chi_{AS}N = 37$  and  $\chi_{BS}N = 45$ . For clarity, hydrophobic cores formed by blocks A and B are drawn in blue and red, respectively. The hydrophilic shell formed by block C is omitted in this work. Figure 1a shows that small, uniform, round bumps are located only on the edge of the disk. No bumps can be observed on the flat surface of the disk. To reveal the detailed structure, the hydrophobic cores formed by blocks A and B are respectively plotted in Figs. 1(b) and 1(c). Figure 1(b) shows that block A forms the inner hydrophobic core. All the bumps shown in Fig. 1(a) are generated from this inner core, thus yielding a gear-like structure in the inner core. Meanwhile, all blocks B (Fig. 1c) aggregate on the surface of the inner core, covering the A-formed gear-like inner core tightly and leaving several holes on the edge.

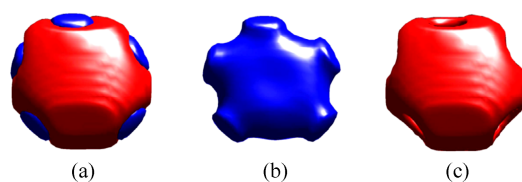


**Fig. 1** Bump-surface multicompartment disk-like micelle formed by pure ABC triblock copolymer: (a) hydrophobic core formed by block A and B, (b) inner hydrophobic core, (c) outer hydrophobic core (The blue and red represent blocks A and B, respectively.)

### Effect of Nanoparticle Size

To study the effect of nanoparticle size  $\alpha$ , the length and number of the grafted chains are fixed at  $N_G = 2$  and  $\sigma = 2$ , respectively. Figures 2(a) to 2(e) show the bump-surface disk-like hybrids formed by ABC triblock copolymer and grafted polymer nanoparticle at different particle sizes. The corresponding inner hydrophobic cores formed by blocks A are presented in Figs. 2(f) to 2(j) for clarity. The disk-like hybrids with several uniform round bumps along the edge are formed with smaller particle size (Figs. 2a and 2b). The bumps are uniformly distributed along the edge, as clearly shown in Figs. 2(f) and 2(j). When the nanoparticle size increases, two round bumps tend to merge to form belt-like bumps (see Figs. 2c, 2d, 2h and 2i). The number of round bumps decreases because of the mutual fusion of round bumps. With further increasing the nanoparticle size, more round bumps fuse with one another to form belt-like bumps, as shown in Figs. 2(e) and 2(j). From Figs. 2(a) to 2(e), we can see that both round and belt-like bumps are distributed along the edge of the disk-like hybrid. Moreover, we also find that the disk-like morphology of the hybrid remains almost unchanged with increasing nanoparticle size.

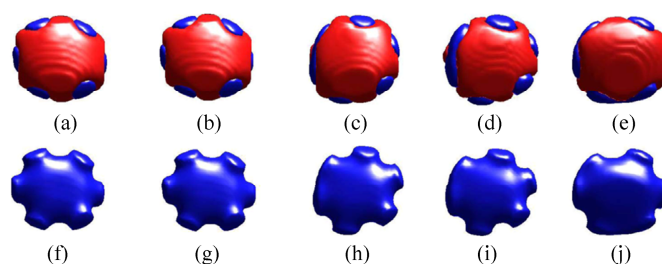


**Fig. 2** Hybrids formed by ABC triblock copolymer/nanoparticle hybrids with different nanoparticle sizes: (a)  $\alpha = 0.01$ , (b)  $\alpha = 0.03$ , (c)  $\alpha = 0.05$ , (d)  $\alpha = 0.09$  and (e)  $\alpha = 0.13$ ; (f)–(j) inner hydrophobic cores corresponding to (a)–(e), respectively

To reveal the distribution of hydrophobic components and nanoparticle P in the hybrid, the hydrophobic blocks A and B and nanoparticle P are given in Fig. 3(a), which shows the location of blocks A and B and nanoparticle P in the disk-like hybrid. For clarity, block A and nanoparticle P as well as pure nanoparticle P are also given in Figs. 3(b) and 3(c), respectively. We can see clearly that all nanoparticles are distributed in the hydrophobic core formed by blocks A because the nanoparticles are grafted by homopolymer A, which is compatible with block A. The total free energy, energy from entropy, and energy from enthalpy were calculated to reveal the effect of the nanoparticles on the bump-surface multicompartment micelles. The calculated results are shown in Fig. 4. Figure 4(a) shows that the total free energy of the system increases with increasing nanoparticle size. Figure 4(b) shows that the energy from entropy increases with increasing nanoparticle size, whereas the energy from the enthalpy decreases (Fig. 4c). By comparing Figs. 4(b) and 4(c) with Fig. 4(a), we can conclude that entropy is a more important factor than enthalpy in the bump merging induced by particle size.

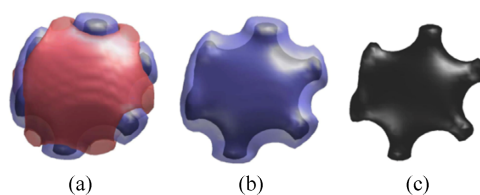


**Fig. 3** Distribution of blocks A, B and nanoparticle P in the hybrid with the nanoparticle size  $\alpha = 0.05$ : (a) formed by blocks A, B and P, (b) formed by block A and nanoparticle P, (c) formed by pure nanoparticle P

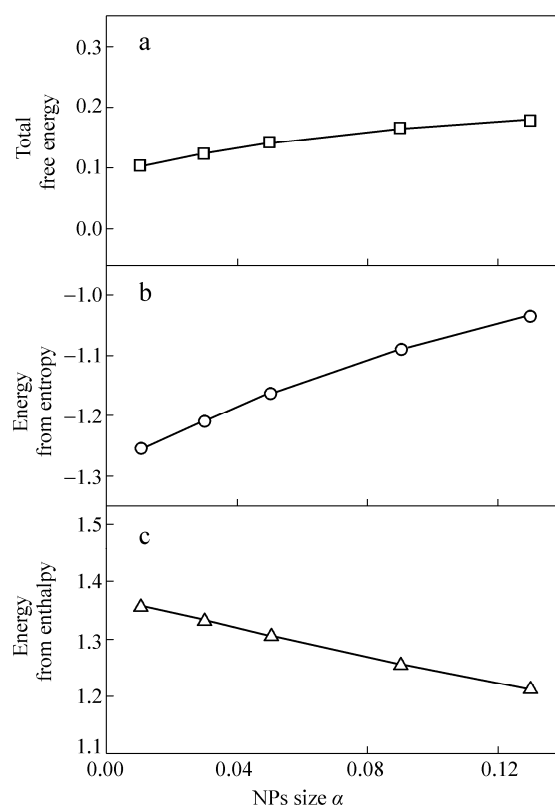


**Fig. 4** Variation of the various energies with nanoparticle size at  $\sigma = 2$  and  $N_G = 2$

### Effect of Grafted Chain Length

The nanoparticle size and number of grafted chains are respectively fixed at  $\alpha = 0.01$  and  $\sigma = 2$  to study the effect of grafted chain length  $N_G$  on the disk-like hybrid morphology. Figure 5 shows the typical results obtained at different grafted chain lengths ( $N_G = 2, 4, 6$ , and  $8$ , respectively). For clarity, side views corresponding to Figs. 5(a) to 5(d) are given in Figs. 5(e) to 5(h), respectively. Figure 5 shows that the shape of the round bumps remain unchanged as grafted chain length increased. However, the corresponding side views (Figs. 5e to 5h) evidently show that the thickness of the disk-like hybrid increases with increasing grafted chain length, which indicates that the hybrid morphology tends to change from disk to sphere with increasing grafted chain length.

Similarly, we calculated the total free energy, energy from entropy, and energy from enthalpy of the system for different grafted chain lengths. The calculated results are given in Fig. 6. As grafted chain length increased, both the total free energy (Fig. 6a) and the energy from entropy (Fig. 6b) increased, whereas the energy from enthalpy decreased (Fig. 6c). This result suggests that entropy is a more important factor than enthalpy in the morphological change induced by grafted chain length.

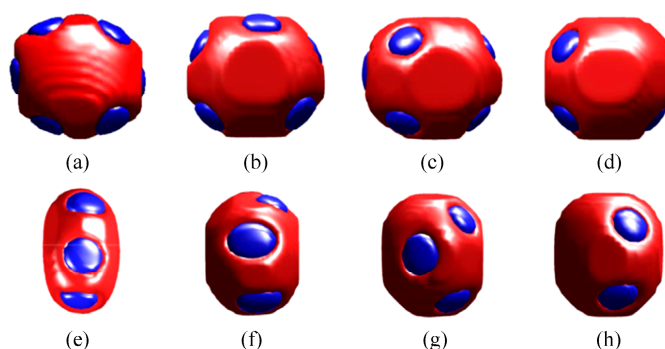


**Fig. 5** Hybrids formed by ABC triblock copolymer/nanoparticle for different grafted chain lengths  $N_G$  with  $\alpha = 0.01$  and  $\sigma = 2$ : (a)  $N_G = 2$ , (b)  $N_G = 4$ , (c)  $N_G = 6$  and (d)  $N_G = 8$ ; (e)–(h) side views corresponding to (a)–(d), respectively

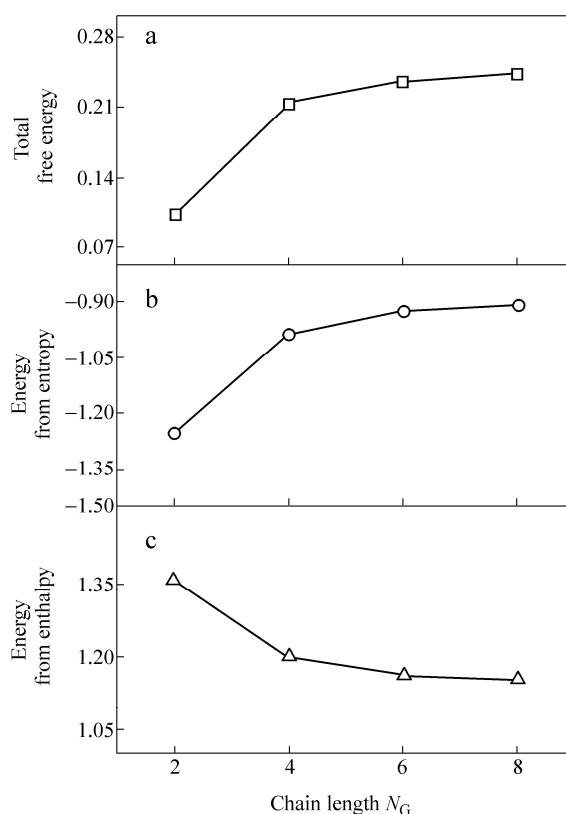


**Fig. 6** Variation of the various energies with grafted chain length at  $\alpha = 0.01$  and  $\sigma = 2$

### Effect of Grafted Chain Number

To study the effect of the number of grafted chains, the nanoparticle size and the grafted chain length are fixed at  $\alpha = 0.01$  and  $N_G = 2$ , respectively. Four typical grafted chain numbers ( $\sigma = 2, 4, 6$  and  $8$ ) were employed. Figure 7 shows the simulation results for various grafted chain numbers. Figures 7(a) to 7(d) show that the number of bumps decreases as the number of grafted chains increases. At the same time, the morphology of the micelle changes gradually from disk-like to spherical with increasing number of grafted chains (Figs. 7e and 7h). In addition, the hybrid morphologies shown in Figs. 7(a) to 7(d) are respectively similar to those shown in Figs. 5(a) to 5(d). This similarity implies that changing the grafted chain length and changing the grafted chain number have an equivalent effect on co-assembly.

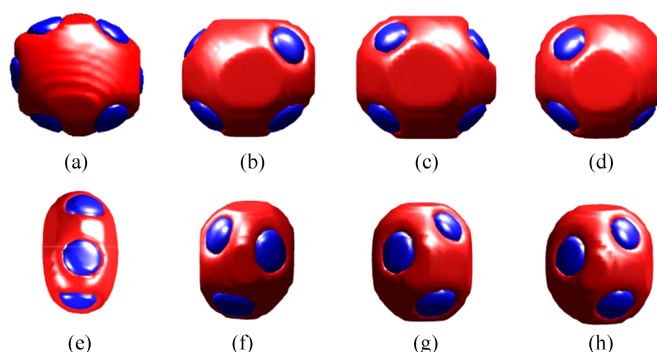


**Fig. 7** Hybrids formed by ABC triblock copolymer/nanoparticle for different grafted chain number  $\sigma$  with  $\alpha = 0.01$  and  $N_G = 2$ : (a)  $\sigma = 2$ , (b)  $\sigma = 4$ , (c)  $\sigma = 6$  and (d)  $\sigma = 8$ ; (e)–(h) side views corresponding to (a)–(d), respectively

To confirm equivalency further, the product of  $N_G$  and  $\sigma$  is considered in this study. In the four cases studied in the above section (see Fig. 5), the grafted chain number is fixed as 2, and the grafted chain length is variable. The products of  $N_G$  and  $\sigma$  are 4, 8, 12, and 16. In this section (Fig. 7), the grafted chain length is fixed as 2, whereas the grafted chain number varies from 2 to 8. Figures 7(a) to 7(d) respectively correspond to the products of  $N_G$  and  $\sigma$  at 4, 8, 12, and 16. Therefore, compared with the length and number of grafted chains separately, their product is a more universal factor that determines the co-assembly result.

## CONCLUSIONS

SCFT was successfully used to study ABC linear triblock copolymer/nanoparticle co-assembly into the bump-surface multicompartment disk-like hybrid in selective solvent. The three-dimensional simulation results showed that nanoparticle size determines the number and shape of bumps on the edge of the disk-like hybrid, whereas the length and number of grafted chains determine the hybrid morphology. Moreover, compared with the length and number of grafted chains separately, their product is a more universal factor that determines the co-assembly result. The calculated results revealed that entropy is a more important role factor than enthalpy in the co-assembly. These results can be helpful for related experimental studies.

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