

Surface-induced Morphologies of ABC Star Triblock Copolymer in Spherical Cavities^{*}

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Abstract The morphologies and phase diagrams exhibited by symmetric ABC star triblock copolymer nanoparticles are investigated on the basis of real-space self-consistent field theory. The ABC star triblock copolymers were chosen to be tiling-forming with fixed polymer parameter and the spherical boundaries were modeled using the masking technique. We first study a number of examples where the ABC triblock copolymers confined in spherical cavities with neutral surface. Then, two types of spherical cavity distinct preferential surfaces are considered, including both A-block attractive and repulsive preferential surfaces. We aim at the effects due to various spherical cavity diameters and the degree of interactions between the polymer and the spherical surface. A variety of morphologies, such as ring-like structures, concentric sphere, and irregular cylinder, were identified in phase diagrams. The results show that both the degree of interactions and spherical diameters can influence the formation of morphologies so that ring-like structures and other novel structures could be obtained.

Keywords: Morphology; Star triblock copolymer; Spherical cavity; SCFT.

INTRODUCTION

Block copolymer nanoparticles, with either isotropic morphologies or anisotropic morphologies, have gained increasing attention in recent years due to their applications in versatile functional devices, such as the switchable display devices and photonic crystals^[1–6]. For example, the Janus polymeric nanoparticle, a typical anisotropic nanoparticle with a dipolar distribution of composition and electrical properties, was suitable for applications in switchable display devices^[6]. One possible route to obtain the block copolymer nanoparticles is to utilize self-assembly of block copolymers in a spherical confinement, where the block copolymers are enforced into a closed geometry. Block copolymers in spherical cavity undergo severe structural frustration and produce the morphologies that cannot be observed in the film or pore confinements^[7,8].

Due to their potential applications, extensive theoretical and experimental studies of simple AB diblock copolymers in spherical cavity have been carried out^[9–12]. For example, concentric-spherical lamellar structures exhibit a relatively strong surface preference for large spherical pores. In such case, the A segments segregate to the surface, whereas the core of concentric-spherical lamellae can be either A or B, depending on the size of spherical pores. Besides these, the complex morphologies also form in AB diblock copolymer

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nanoparticles^[13, 14]. The results indicate that diameters and preferential surfaces influence the structural formation of AB diblock copolymers in spherical cavity. ABC triblock copolymers, such as linear and star ABC triblock, which exhibit complicated morphologies in bulk^[15–17], which are more potentially possible to obtain novel morphologies within their spherical cavity.

ABC star triblock copolymers having special topological structures, characterized by three ends of blocks connected at one junction point, produce several special structures, which are lacking for their linear counterpart^[18–22]. The special topology always leads to a tendency on linear arrangement of conjunction points in the self-assembly of ABC star triblock copolymers^[23, 24]. The polygon-tiling patterns, such as PT[6,6,6], PT[8,8,4], PT[8,6,4;8,6,6], PT[10,6,4;10,6,6], and PT[12,6,4]^[19, 20], are such striking examples where the conjunction points are arranged into several parallel lines. Recently, Yu *et al.* reported a simulation study on patchy nanoparticles self-assembled from linear triblock copolymers under spherical confinement, where a variety of patchy nanoparticles and multiple morphological transitions are identified^[25]. These authors argued that the number of patches on a nanoparticle surface increases with the diameter and selectivity of surface. For ABC star triblock copolymers, the spherical confinement leads to the novel morphologies in spherical cavity due to the restriction of star topological structure. An example is that the phase diagrams of ABC star triblock copolymers have been recently reported in the spherical cavity with the fixed diameters and preferential interactions^[26]. Various 3D morphologies in various symmetries, including mushroom ring, spherical concentric lamellae (SCL), and spherical ring (SR), have been observed in the system under various physical conditions because of the special architecture of polymer chains and spherical confinements^[26].

However, it is desirable to access the controllable morphologies in spherical cavity by tuning the confinement sizes and selective interactions between surfaces and polymers. In particular, it is interesting to explore how the linear arrangement of the polygon-tiling patterns blends in the crowded 3D confinement spaces when the nanoparticles have different strengths of preferential surfaces and diameters. In the present study, we choose the ABC star triblock copolymers to be tiling-forming in intermediate segregation region in bulk and employ real-space self-consistent field theory (SCFT) in 3D space to explore the morphologies and phase behavior of ABC star triblock copolymers in spherical confinement. This study aims to elucidate the effects of the preferential surfaces and diameters of nanoparticles on the morphological behavior of the tiling-forming ABC star triblock copolymers in spherical confinement, in which a series of ring-like and non-ring-like morphologies were investigated by constructing the phase diagrams.

THEORETICAL METHOD

First, we briefly describe the masking technique for constructing the spherical cavity boundary. The masking technique is originally proposed by Fredrickson *et al.*, and has been used to construct for the film geometry in the previous works^[27–30]. In the masking technique, an interfacial density $\phi_w(\mathbf{r})$ is introduced to describe the boundary following a modified incompressibility constraint^[27],

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_C(\mathbf{r}) + \phi_w(\mathbf{r}) = 1 \quad (1)$$

In this equation, $\phi_i(\mathbf{r})$ represents the volume fraction of three blocks, $i \in (A, B, C)$, $0 < \phi_w(\mathbf{r}) < 1$ represents a region with an overlap between the surface and ABC polymers, $\phi_w(\mathbf{r}) = 0$ represents the region of the ABC polymer mixture, and $\phi_w(\mathbf{r}) = 1$ represents the region of the impenetrable hard wall. By trying different functions, we found that the following cosine function was suitable to construct the spherical boundary:

$$\phi_w(\mathbf{r}) = \begin{cases} 1 & r > R \\ \frac{1}{2} \left\{ 1 + \cos \left[\frac{\pi}{T} (R - r) \right] \right\} & R - T \leq r \leq R \\ 0 & R - T > r \end{cases} \quad (2)$$

where R represents the spherical cavity radius, T represents the wall thickness, and r is the distance from the center of the spherical nanoparticle.

Then, we consider a SCFT model of n star triblock copolymer chains in the spherical cavity with volume of V . Each star triblock copolymer chain presents three branches A, B, and C joined at one junction, where $f_i \in (A, B, C)$ represents the volume fraction of each block. The time-like parameter s begins at the junction point, $s = 0$, and terminates at the end of each branch of the star polymer, $s = f_i$. The central task in SCFT involves solving modified diffusion equations (MDE),

$$\frac{\partial q_i(\mathbf{r}, s)}{\partial s} = R_g^2 \nabla^2 q_i(\mathbf{r}, s) - w_i(\mathbf{r}) q_i(\mathbf{r}, s) \quad (3)$$

$$-\frac{\partial q_i^+(\mathbf{r}, s)}{\partial s} = R_g^2 \nabla^2 q_i^+(\mathbf{r}, s) - w_i(\mathbf{r}) q_i^+(\mathbf{r}, s) \quad (4)$$

All parameters are rescaled with the gyration radius of an ideal Gaussian chain R_g . In star triblock copolymers, the star architecture requires a special initial condition; $q_i^+(\mathbf{r}, f_i) = 1$ and $q_i(\mathbf{r}, 0) = q_j^+(\mathbf{r}, 0) q_k^+(\mathbf{r}, 0)$, where $(i, j, k) \in (A, B, C)$. The local monomer fractions of each block can be obtained as

$$\phi_A(\mathbf{r}) = \frac{V}{Q} \int_0^{f_A} ds q_A(\mathbf{r}, s) q_A^+(\mathbf{r}, s) \quad (5)$$

$$\phi_B(\mathbf{r}) = \frac{V}{Q} \int_0^{f_B} ds q_B(\mathbf{r}, s) q_B^+(\mathbf{r}, s) \quad (6)$$

$$\phi_C(\mathbf{r}) = \frac{V}{Q} \int_0^{f_C} ds q_C(\mathbf{r}, s) q_C^+(\mathbf{r}, s) \quad (7)$$

Here, the single triblock copolymer chain function Q can be calculated as $Q = \int q_i(\mathbf{r}, f_i) d\mathbf{r}$. According to SCFT, the free energy per chain can be expressed as

$$\begin{aligned} \frac{F}{nk_B T} = & -\ln\left(\frac{Q}{V}\right) + \frac{1}{V} \int d\mathbf{r} (\chi_{AB} N \phi_A \phi_B + \chi_{BC} N \phi_B \phi_C + \chi_{AC} N \phi_A \phi_C) \\ & + \frac{1}{V} \int d\mathbf{r} (\chi_{AW} N \phi_A \phi_W + \chi_{BW} N \phi_B \phi_W + \chi_{CW} N \phi_C \phi_W) \\ & - \frac{1}{V} \int d\mathbf{r} (w_A \phi_A + w_B \phi_B + w_C \phi_C) - \frac{1}{V} \int d\mathbf{r} \eta (1 - \phi_A - \phi_B - \phi_C - \phi_W) \end{aligned} \quad (8)$$

In the equation, the Flory-Huggins parameter χ_{ij} represents the interaction between different species i and j , and χ_{iW} expresses the dimensionless measures of the surface interaction between species i and the spherical wall. Consequently, $\chi_{iW} = 0$ represents a neutral polymer-surface interaction, $\chi_{iW} > 0$ indicates a wall surface repelling i -type monomers, and $\chi_{iW} < 0$ indicates the adsorptive interaction between the surface and monomers. The parameter $\eta(\mathbf{r})$ represents the incompressibility condition of the system, and V indicates the effective volume occupied by the copolymers: $V = \int d\mathbf{r} [1 - \phi_W(\mathbf{r})]$, where the effective diameter of spherical cavity d_{eff} can be

calculated as $V = \frac{1}{6} \pi d_{\text{eff}}^3$.

According to mean-field approximation, minimization of the free energy per chain with respect to ϕ_A , ϕ_B , and ϕ_C yields the following equations:

$$w_A(\mathbf{r}) = \chi_{AB} N \phi_B(\mathbf{r}) + \chi_{AC} N \phi_C(\mathbf{r}) + \chi_{AW} N \phi_W(\mathbf{r}) + \eta(\mathbf{r}) \quad (9)$$

$$w_B(\mathbf{r}) = \chi_{AB} N \phi_A(\mathbf{r}) + \chi_{BC} N \phi_C(\mathbf{r}) + \chi_{BW} N \phi_W(\mathbf{r}) + \eta(\mathbf{r}) \quad (10)$$

and

$$w_C(\mathbf{r}) = \chi_{AC} N \phi_A(\mathbf{r}) + \chi_{BC} N \phi_B(\mathbf{r}) + \chi_{CW} N \phi_W(\mathbf{r}) + \eta(\mathbf{r}) \quad (11)$$

Equations (1) to (11) are self-consistently considered in SCFT to calculate ϕ_i , w_i , and η using a numerical approach. One of the principal steps involves solving MDE, given as Eqs. (3) and (4) numerically for a given field, w_i . These equations were numerically solved in the framework of a pseudospectral scheme, which is unconditionally stable and presents second-order accuracy in the contour step length $(\Delta s)^{2[15, 19, 20, 28, 31]}$. The overall strategy follows the combinatorial screening method originally proposed by Drolet and Fredrickson, in which a relaxation process is assumed, starting with an initially guessed mean field^[32, 33]. The relaxation steps are repeated until the relative difference between the free energies of the sequential iteration steps is reduced to less than 10^{-6} . In the present work, the SCFT equations are implemented in 3D space, in which the numerical algorithm is parallelized, similar to the procedure used in previous works^[26, 34]. Periodic boundary conditions in all three directions are used to calculate the polymer structures in bulk, where the domain sizes are optimized by adjusting the simulation-box lengths in all three directions. In order to calculate the structure of ABC star triblock copolymers in spherical cavity, the pseudospectral method based on the parallel fast Fourier transformation technique was employed as well. We searched the local minimum free energy by inputting various values of the initial mean field w_i and selecting the one with the lowest free energy as the stable phase.

In this work, we set the symmetric incompatibility degrees of ABC star triblock copolymers in the intermediate segregation region to be $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 50$, which probably has complicated morphological behavior, similar to the diblock copolymer case^[35]. In addition, we set the volume fraction of the three blocks (A, B, and C) as $f_A:f_B:f_C = 0.2:0.4:0.4$ to observe the evident effect of surface preference on various blocks. Under these polymer parameters, the ABC star triblock copolymer exhibit the PT[8,8,4] morphology in bulk. For the nanoparticle, the spherical diameter d_{eff} is set to range from $1.34 R_g$ to $5.90 R_g$, with a small step of $\Delta d_{\text{eff}} = 0.19 R_g$. We also select two preferential surfaces λ_{aw} and λ_{bcw} , where $\lambda_{i\text{w}} = \chi_{i\text{w}}N/\chi_{AB}N$, $i \in (A, B, C)$, represents the interaction between blocks and spherical nanoparticle boundaries. Here, $\lambda_{i\text{w}} = 0.08\text{--}0.48$, with a small step of $\Delta \lambda_{i\text{w}} = 0.08$.

RESULTS AND DISCUSSION

This study focuses on the surface-induced morphologies for the tiling-forming ABC star triblock copolymers in the spherical cavity with various strengths of surface preference. The morphologies in bulk and in spherical cavity with neutral walls are presented in Fig. 1 and Fig. 2. The morphologies and their corresponding behavior in spherical cavity with A-attractive surfaces are shown in Figs. 3 to 4, whereas those in spherical cavity with A-repulsive surfaces are shown in Figs. 5 to 6. In all morphologies, we cut the dark sections absorbed to the surface so that we can clearly see structures, where red, green, and blue denote A-rich, B-rich, and C-rich domains in space, respectively. Each color is separately plotted in certain cases to clearly demonstrate the inner structures.

Morphologies and Phase Diagram in Spherical Confinement with Neutral Wall

First, we investigate the morphologies of ABC star triblock copolymers in bulk, as shown in Fig. 1. The bulk structure has fixed polymer parameters of $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 50$ and $f_A:f_B:f_C = 0.2:0.4:0.4$. Figure 1(a) shows the polygonal tiling patterns, PT [8,8,4], in 2D and 3D spaces. The density distributions are shown in Figs. 1(a1) and 1(a2), which exactly indicate the translational symmetry in the third direction and periods in the other two directions. Here, we also show the distribution of conjunction points, as shown in Figs. 1(a3) and 1(a4), which indeed exhibits a linear arrangement and concentrates on the zone among the A, B and C block domains. The previous study of dynamic density functional theory on symmetric ABC triblock copolymers reported that the conjunction points were restricted to parallel lines formed by mutual intersection between the three domains,

which is similar to our present results^[24]. In Fig. 1(b), we investigated the monomer density distribution of blocks along the direction labeled as l in Fig. 1(a2). The density distributions show that such PT[8.8.4] has a relatively wide interface with the different block domains, indicating the triblock copolymers are indeed located in the intermediate segregation region. Moreover, the A-rich or B-rich domain size that defined in Fig. 1(b) can be obtained by calculating their full wave at half maximum (FWHM), which are labeled in the corresponding positions. In this manner, we calculate the bulk periods, *i.e.*, $L_1 \approx 4.23 R_g$ and $L_2 \approx 4.27 R_g$, where $L_1 = L_{1C} + L_{1A}$. Within the uncertainty, the L_1 and L_2 can be considered to be equal. Previous works reported the PT[8,8,4] structure in 2D space at $f_A:f_B:f_C = 0.2:0.4:0.4$ and $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35$, which share similar periods of $L_x = 5.60 R_g$ and $L_y = 5.87 R_g$ in two directions^[18–20].

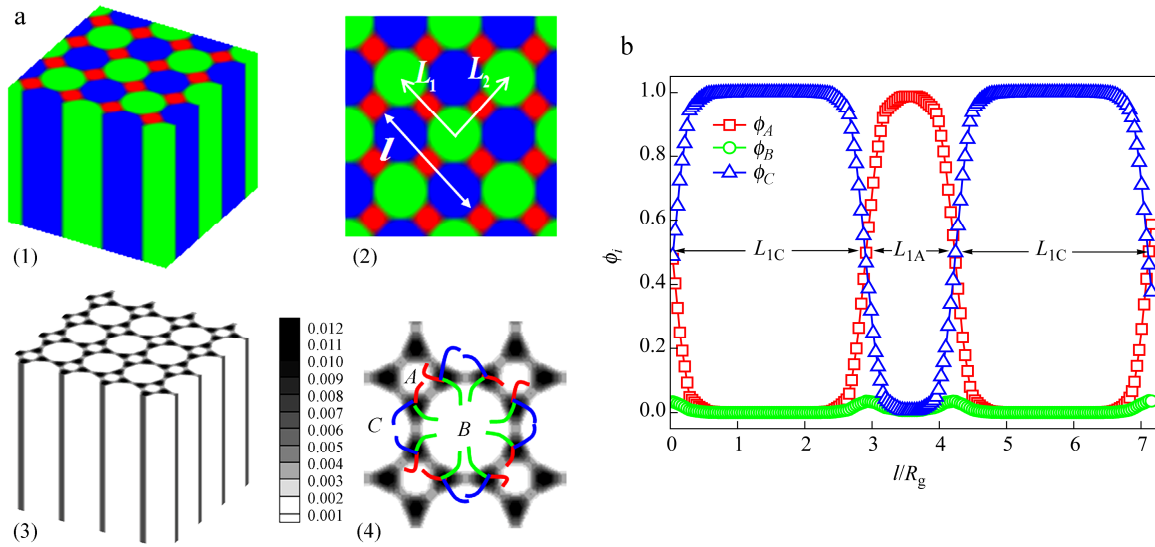


Fig. 1 (a1 and a2) Bulk morphology of symmetric triblock copolymers with $f_A:f_B:f_C = 0.2:0.4:0.4$ and $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 50$, $L_1 \approx 4.23 R_g$ and $L_2 \approx 4.27 R_g$; (a3 and a4) Densities distributions of the junction points and schematic diagram for bulk structure; (b) The monomer density profile ϕ_i ($i \in A, B, C$) as function of l , and corresponding thicknesses domains

Then, we investigate that how such a PT[8,8,4] morphology behaves in the spherical cavity with neutral surfaces and various diameters. Several typical morphologies are shown in Fig. 2(a), where the effective diameter d_{eff} varies from $1.34 R_g$ to $5.90 R_g$ with an increment of $\Delta d_{\text{eff}} = 0.19 R_g$ and the stable regions in the phase diagram are labeled in the corresponding row. In spherical cavity with small diameters, *i.e.*, $d_{\text{eff}} = 1.34 R_g$ to $1.53 R_g$, three components are still not phase separated. This disordered phase was observed due to severe confinement. Disorder phases have also been observed in other types of severe confinement, in which a system of diblock copolymers has been considered in nanorod array confinement^[36]. When $1.53 R_g < d_{\text{eff}} \leq 2.10 R_g$, we observed a phase separation that is similar to the Janus structures in diblock copolymer nanoparticles, or the patchy structure with one patch on the surface in the previous works^[13, 25]. A novel morphology with rotational symmetry was observed at $2.10 R_g < d_{\text{eff}} \leq 2.86 R_g$. Similar morphology appeared at $2.86 R_g < d_{\text{eff}} \leq 3.62 R_g$ as d_{eff} further increased. The morphology that appeared when $3.62 R_g < d_{\text{eff}} \leq 4.76 R_g$ show relaxed confinement, and the structures are similar to those in bulk, which are confirmed in the spherical cavity with large diameters of $4.76 R_g < d_{\text{eff}} \leq 5.90 R_g$. However, unlike the ABC linear triblock copolymers in spherical confinement where the number of patches in the surfaces increases with the diameter^[25], the present observations indicate that patchy structure transits into the other complex structure when the diameter increases. This suggested that it is difficulty to blend the linear arrangement of conjunction points in the spherical cavity with neutral surfaces.

A typical free energy comparison about two represented morphologies is shown in Fig. 2(b), where the free energy depends on d_{eff} , and the free energy per chain is as units of $k_B T$. The stability of each structure is examined by comparing its free energy with other candidate structures. The crossing for two energy curves indicates that the phase transition is to be the first-order between these two morphologies Figs. 2(a4) and 2(a5). Furthermore, the free-energy variation of higher energy branch starts to become more flat as d_{eff} grows. This fact indicates that the morphological behavior is similar to the bulk characteristic when the spherical cavity diameter is large enough. Such similar bulk behavior has also been observed in other diblock copolymer system confinements with large space^[10]. This phase transition behavior is similar to those observed in our previous work where the PT[6,6,6] structure in spherical cavity with neutral surface was considered^[26].

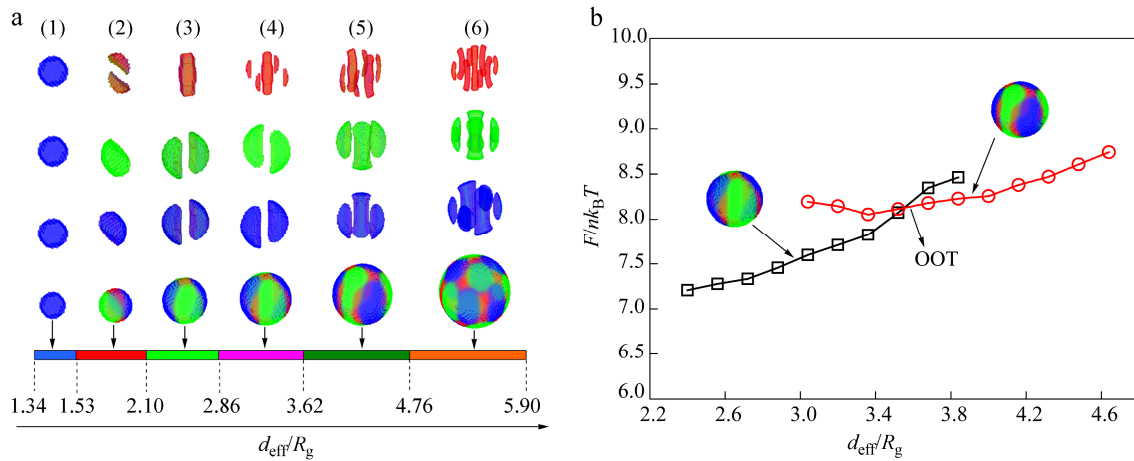


Fig. 2 (a) Morphologies of ABC star triblock copolymers in spherical cavity with neutral surfaces and various diameters (d_{eff} ranges from $1.34 R_g$ to $5.90 R_g$, with an increment of $\Delta d_{\text{eff}} = 0.19 R_g$); (b) An example of free energy curve for ABC star triblock copolymers in spherical cavity with neutral surfaces

Morphologies and Phase Diagram in Spherical Confinement with A-Attractive Surfaces

This subsection focuses on morphologies and the corresponding behavior of ABC star triblock copolymers in the spherical cavity with A-attractive surfaces, in which the surface attracts A-blocks and repels B- and C-blocks. An adsorption degree is defined as $\lambda_{\text{aw}} = \chi_{\text{aw}} N / \chi_{\text{AB}} N$, where λ_{aw} varies from 0.08 to 0.48, with a step of $\Delta \lambda_{\text{aw}} = 0.08$. All morphologies founded in the spherical cavity with A-attractive surfaces are shown in Fig. 3, where phase symbols are also listed in the left column. These morphologies can be sorted into two types, including three ring-like structures and seven non-ring-like structures.

Non-ring-like morphologies include disordered (D), two-colored disk (TCD), dumbbell-like (DL), and irregular cylinder (IC) structures, which are shown in Fig. 3(a). The D structure is due to severe confinement originating from small spherical cavity (Fig. 3(a1)). In Fig. 3(a1), we show the original morphology and cutaway below which is surrounded by dark sections which absorbed to the spherical surface. In order to show the inner morphologies clearly, we cut the dark sections absorbed to the surface in all morphologies as follows. The TCD structure is composed of two disk-like layers formed by B- and C-blocks, accompanying an irregular A-block ring (Fig. 3(a2)). The TCD structure possesses axial symmetry, which is similar to the tennis ball structure formed by diblock copolymers^[13]. The DL structure includes a dumbbell-like C domain, an irregular B-block ring, and two dispersed A-block domains (Fig. 3(a3)). The DL structure has two-fold symmetry, which is a little similar to the previously reported mushroom structures in diblock copolymer spherical cavity^[13]. Then, IC morphologies were observed in nanoparticles with various diameters (Figs. 3(a4)–3(a7)). The cylinders are bent in crowded spaces, whereas the bending degree accords with spherical cavity diameters. Specifically, the cylinders are severely bent in small spherical cavity (Figs. 3(a4), 3(a5) and 3(a6)). By contrast, the bending degree is slight in large spherical cavity, in which the structures are similar to those observed in bulk (Fig. 3(a7)).

Three typical ring-like morphologies were observed in spherical cavity with various diameters (Figs. 3(b1)–3(b3)), as shown in Fig. 3(b). The ring-like structure in Fig. 3(b1), RL-312, presents rotational symmetry and contains double C-block disks, double A-block rings, and a single B-block ring. Figure 3(b2) shows another type of ring-like structure, RL-322, with symmetric B-block and C-block domains formed by a ring and a disk, respectively. In RL-322, the A-block forms triple rings with a spherical core, in which the rings are parallel to each other. The RL-II is to some degree appears as the same with the previous reports MR structure in both diblock and triblock copolymers^[13, 26]. The third typical RL structure, RL-332, in which C-blocks form double rings, A-blocks form triple rings, and the B-domain contains a ring and double disks, is shown in Fig. 3(b3). In fact, these ring-like nanoparticles contain the disk structure near the surfaces, which can be regarded as the ring-like patchy nanoparticles. The distribution of special monomer was turn out to be a useful way to recognize the ring-like structure in the angle of microscopic, which has been employed to describe the morphologies of rod-coil diblock copolymer^[37, 38]. Here, we plotted the distribution of conjunction points in order to observe the RL morphologies in more detail, as shown in the right columns in Fig. 3(b). These distributions clearly exhibit that the conjunction points are blended into the ring-like structures, where all rings found in RL structures are parallel to each other, and the multi-rings appear in spherical cavity with large diameters.

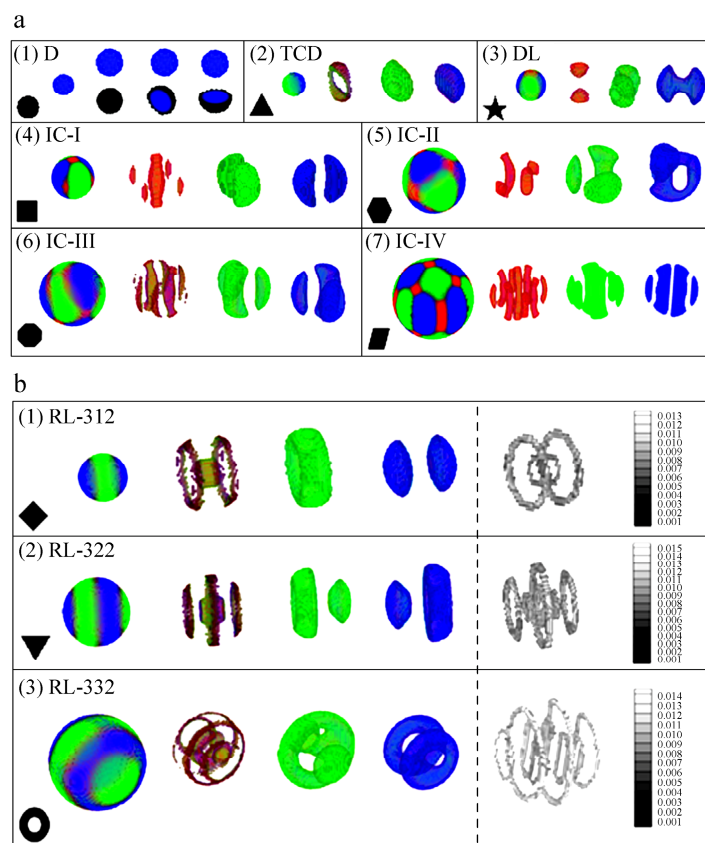


Fig. 3 The morphologies in the spherical cavity with A-attractive surfaces, $\lambda_{aw} = 0.08$ – 0.48 , and various diameters, $d_{eff} = 1.34 R_g$ – $5.52 R_g$: (a) Non-ring-like structures and internal construction; (b) Ring-like structures and internal construction, densities distributions of the junction points (All blocks are shown, and the inner structures are shown under the full structures in different colors.)

All ring-like and non-ring-like morphologies found in the spherical cavity with an A-attractive wall are arranged in a phase diagram (Fig. 4a). This phase diagram is constructed by λ_{aw} and d_{eff} , where the dashed blue and red lines guide the boundaries between the phases. The ring-like morphologies are distributed in a gathered

region where the wall that attracts A-blocks is strong ($\lambda_{aw} \geq 0.24$) and the spherical cavity are relatively large ($d_{eff} \geq 2.48$). When the ABC star triblock copolymers are placed into a spherical cavity, the curved surfaces force the conjunctions into non-linear distributions. The phase diagram indicates that no-ring-like structures were observed in the case where the geometric confinement dominates or the adsorption is weak and the spherical symmetric adsorptions further change the conjunction points into ring-like distributions. Despite the wheel, mushroom and lamella structures obtained in experiments, the experiments in previous studies showed that microphase-separated structures of PS phases in spherical cavity can be categorized as ring ($D/L_0 = 0.66$), helix ($0.97 \leq D/L_0 \leq 1.52$), or branched helix ($1.52 \leq D/L_0 \leq 1.89$)^[12], some of them are quite similar to the observed RL structures. We also compared the observed morphologies of nanoparticles with other results of the simulation in 3D spherical confinement system^[9, 11, 39, 40]. While the ring-like morphology was obtained with low interactive energy for both block copolymers in severely spherical confinement in previous reports, this difference is main due to the different topologies between diblock and star triblock copolymers. The phase diagram suggested that the number of rings and disks increases with the diameters and there needed stronger interactions between the polymers and surfaces to form the ring-like structure in the larger spherical cavity. This result is similar to the patchy nanoparticles where the number of patches increases with the diameter^[25]. It is reasonable to deduce that more rings and disks will appear in the larger spherical cavity. In such case, the stronger adsorption between the surfaces and polymers is suggested.

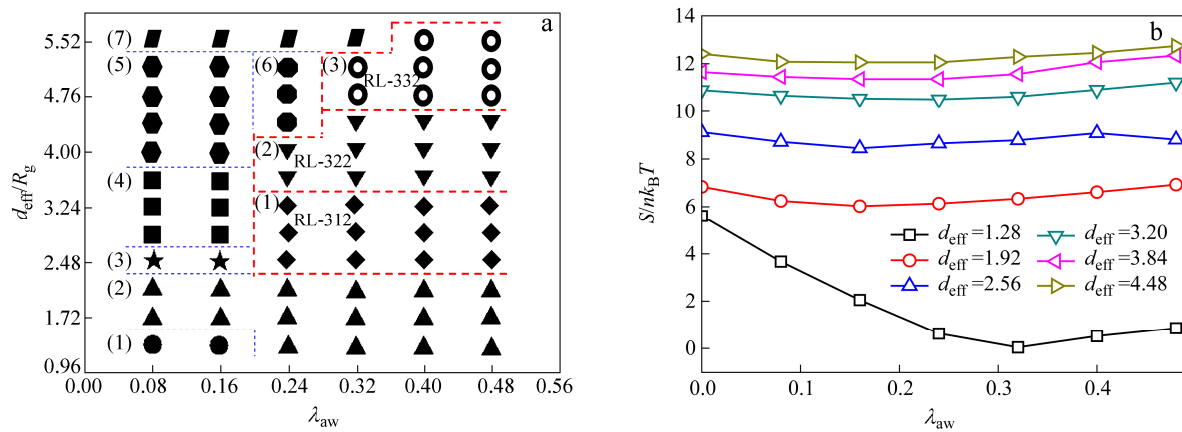


Fig. 4 (a) Phase diagram constructed by A-attractive surface ($\lambda_{aw} = 0.08$ – 0.48) and spherical cavity diameter ($d_{eff} = 1.34 R_g$ – $5.52 R_g$) with dotted lines as eye guide for the phase boundaries; (b) The dependence of entropic energies on A-attractive surfaces (λ_{aw}) for the ABC star triblock copolymers in spherical cavities with various diameters, respectively

To explore the phase behavior in the phase diagram shown in Fig. 4(a), we plotted the entropic curves, as shown in Fig. 4(b), where the different lines represent the entropy as function of surface adsorption strength in spherical cavities of different sizes. In general, the results showed that the value of entropy evidently increases as the spherical cavity diameter increases, whereas the adsorption strength slightly influences the entropy, as shown in Fig. 4(b). On one hand, the value of entropy almost remains constant at the fixed d_{eff} when the adsorption strength (λ_{aw}) increases. This result indicates that the entropic energy mainly comes from the confinement, not the surface preferential interactions. On the other hand, the spherical cavity diameter strongly influences the value of entropy, as shown in Fig. 4(b). The chains extend in a confinement space; thus, the chains are required to continuously fill a larger space as the confinement diameter increases, resulting in increased entropic losses^[41, 42]. The chain will logically approach the bulk conformation when the confinement diameter is sufficiently large, and the chain can be stretched naturally and the entropic energy almost remains unchanged with confinement diameter^[43]. In this case, the origin of RL structures is attributed to the strong interaction between the A-blocks and surfaces in large confinement diameters.

Morphologies and Phase Diagram in Spherical Confinement with A-repulsive Surfaces

In the A-repulsive case, *i.e.*, spherical cavity with A-repulsive and BC-attractive surfaces, we need to define another adsorption degree, $\lambda_{bcw} = \chi_{bcw}N/\chi_{AB}N$, where λ_{bcw} varies from 0.08 to 0.48, with a step of $\Delta\lambda_{bcw} = 0.08$. Several typical morphologies, which are divided into the ring-like and non-ring-like types, are shown in Fig. 5.

Non-ring-like morphologies include D, TCD, difform disk (DD), DL, concentric sphere (CS), and IC structures, which are displayed in Fig. 5(a). The D structures (1) and (2) in Fig. 5(a) can be attributed to the severe confinement originating from the small spherical cavity. The TCD structure in Fig. 5(a3) is composed of two disk-like layers formed by A- and C-blocks, with an irregular B-block ring. The overall structure is similar to the morphology illustrated in Fig. 3(a2). The DD structure in Fig. 5(a4) includes two disk-like layers formed by B- and C- blocks, accompanying another two DD-like layers formed by A-blocks. The CS structure possesses a hollow ball cavity formed by the A-block, with two disk-like layers formed by B- and C- blocks in the central region, as shown in Fig. 5(a6). The CS structure possesses good axial symmetry. The DL structure comprises a DL C-domain, a loose B-block ring, and several A-block domains (Fig. 5(a5)). Several IC structures with various spherical cavity sizes were also formed, as shown in (Figs. 5(a7), 5(a8), 5(a9), 5(a10) and 5(a11)). Structure (8) is similar to the structure in Fig. 3(a4), and structure (9) is similar to the structure in Fig. 3(a7).

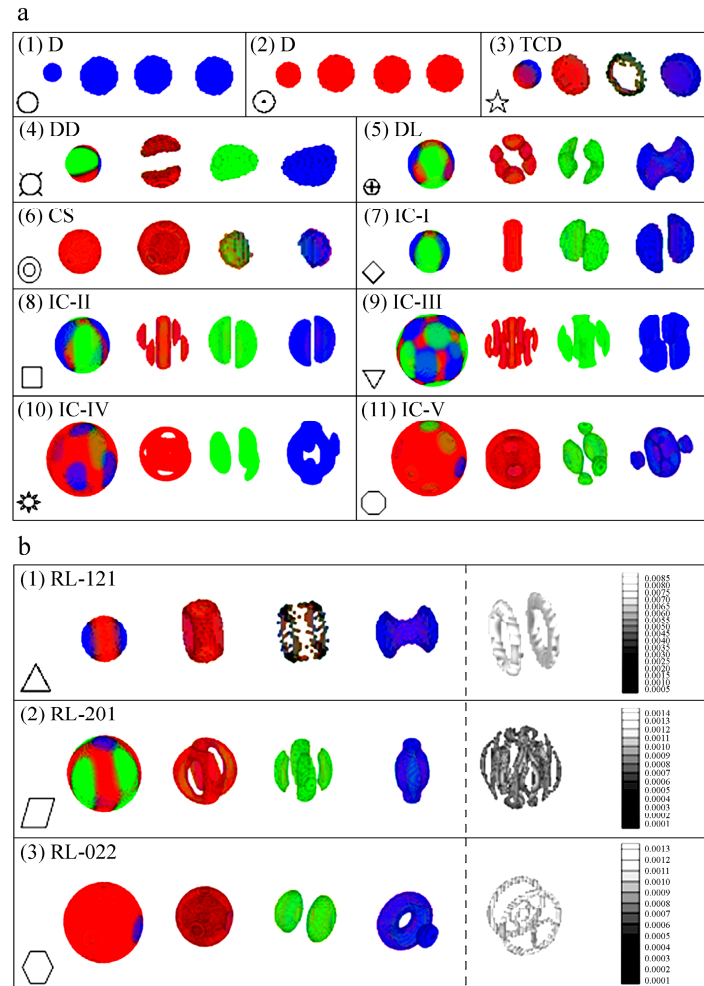


Fig. 5 The morphologies in the spherical cavity with A-repulsive surfaces, $\lambda_{bcw} = 0.08\text{--}0.48$, and various diameters, $d_{\text{eff}} = 1.34 R_g\text{--}5.52 R_g$: (a) Non-ring-like structures and internal construction; (b) Ring-like structures and internal construction, densities distributions of the junction points (All blocks are shown, and the inner structures are shown under the full structures in different colors.)

Moreover, the cylinders are severely bent in small spherical cavity (Figs. 5(a7) and 5(a8)). By contrast, the cylinders are slightly bent in large spherical cavities, which are also relatively similar to the structure in bulk (Fig. 5(a9)). Figure 5(a10) shows another type of IC structure, IC-IV, with an A-block cavernous sphere, B-block disordered cylinders, and C block forming a stretched ring and certain disk structures. Structure (10) in Fig. 5(a) is also similar to a previously observed structure that possesses four or more holes distributed in the spherical surface when $1.8 \leq D/L_0 \leq 2.7$ and $0.1 \leq \alpha \leq 0.15$ ^[9]. The IC structure in Fig. 5(a11), IC-V, has an A-block that forms cavernous sphere, a B-block that forms disks, and a C-block that forms a irregular ring and two symmetrical disks.

Ring-like morphologies contain three novel ring-like structures obtained in various spherical cavities (Figs. 5(b1), 5(b2), and 5(b3)). The corresponding distributions of the junction points are also shown in the right column in Fig. 5(b). The ring-like structure in Fig. 5(b1), RL-121, contains a single A-block ring, an irregular B-block ring, and a C-block DL structure, similar to the structure with two holes obtained in a previous study where $D/L_0 = 1.5$ and $\alpha \leq 0.15$ in previous report^[9]. The ring-like structure in Fig. 5(b2), RL-201, presents rotational symmetry and contains double A-block rings, four B-block distorted cylinders, and a C-block swollen cylinder. The ring-like structure in Fig. 5(b3), RL-022, has an A-block that forms a hollow spherical cavity, a B-block that forms double disks, and a C-block that forms a ring and a disk. We also observe the fact that the distributions of the junction points also exhibit ring-like, which are in according with each RL structures. The result offers a proof again that the distribution of junctions is a powerful method to realize the true structure in microscopic view.

Figure 6(a) shows a phase diagram arranged by λ_{bcw} and d_{eff} , where the dashed blue and red lines distinguish the borders between the phases. The RL structures are distributed within a narrow region. Comparing with the phase diagram in the A-attractive case, the narrow distribution in Fig. 6(a) demonstrates that the RL structures are sensitive to λ_{bcw} and d_{eff} . The RL-022 in Fig. 6(a) is located in a relatively large space where λ_{bcw} is strong and d_{eff} is large, indicating that forming a spherical structure is crucial when λ_{bcw} is strong. However, the RL-121 with a single A-ring appears in a region with weak λ_{bcw} and small d_{eff} ; RL-121 can evolve into RL-201 with a double A-ring when d_{eff} is large. The presence of RL-121 reflects the special requirement of the competition between confinement and surface preference. Similar results have also been obtained in a previous work^[44]. The previous experimental report offer us a ring-like structure^[12], which is quite similar to RL-121, when $D/L_0 = 0.66$. Meanwhile, when $D/L_0 = 1.52$, the helix structures seems the same with RL-201 to some extent. The morphological transitions from ring to helix with the increase of the spherical cavity sizes are in agree with our results. The IC-IV and IC-V looks alike in appearance with the soccer ball morphology in experiment^[45], we can predict that other RL structures may also obtained under this condition when the size of nanoparticles is smaller.

Figure 6(b) presents the entropic energy as function of the adsorption strength (λ_{bcw}) with different confinement diameters. The entropic energy generally increases with increasing adsorption strength (λ_{bcw}) at a fixed d_{eff} , which differs from those in the A-attractive case shown in Fig. 4(b). In other words, the entropic energy is more sensitive to λ_{bcw} than to λ_{aw} . Our results indicate that the adsorption between the surfaces and major blocks significantly influences the entropic energy. This result is similar to a previous observation^[7]. Figure 6(c) shows the entropic energy as function of the confinement diameter with different adsorption strengths (λ_{bcw}). When the adsorption strength is weak ($\lambda_{bcw} \leq 0.24$), it plays an important role to reduce the entropic energy only in some smaller confinement diameters, as the d_{eff} increases, when the confinement is mild, the value of entropic energy will increase as well, the results is corresponding to the previous cylindrical nanopore confinement report when ($f_B = 0.6$)^[46]. On the contrary, when the adsorption strength is strong ($\lambda_{bcw} \geq 0.40$), the value of entropic energy will reduce as the d_{eff} increases. In fact, the confined chains are stretched to fill a larger space as the confinement size increases, which causes increasing entropic losses^[11]. The occurrence of this difference is employed to reflect the importance of the competition between the confinement and surface adsorption. In addition, ABC star triblock copolymers confined in nanopores, can self-assembly into single-helix or double-helix structures in previous report^[47], which are replaced by similar RL structures in spherical

confinement. The main reason is due to the fact that copolymer systems confined in different spaces, nanopores and spherical confinement satisfy with axial symmetries and spherical symmetries, respectively.

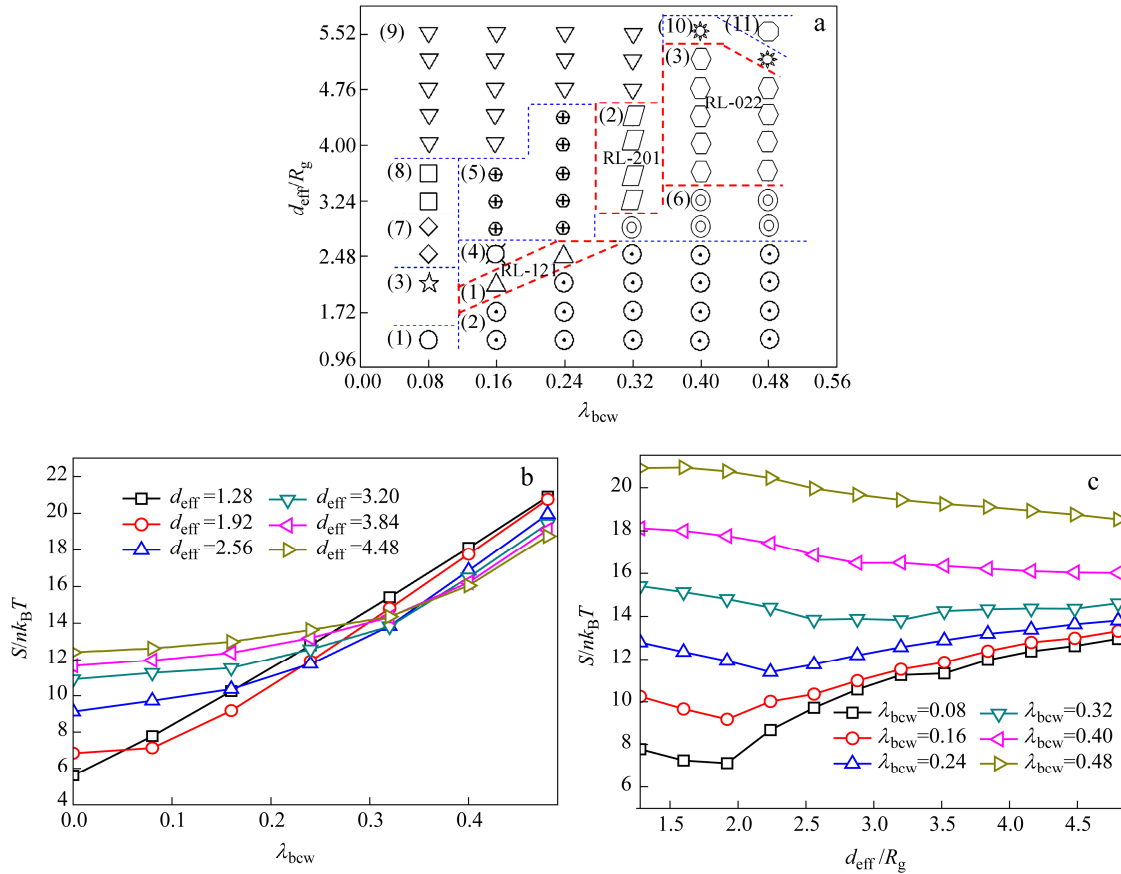


Fig. 6 (a) Phase diagram constructed by A-repulsive surface ($\lambda_{\text{aw}} = 0.08\text{--}0.48$) and spherical cavity diameter ($d_{\text{eff}} = 1.34 R_g\text{--}5.52 R_g$) with dotted lines as eye guide for the phase boundaries; (b) The dependence of entropic energies on A-repulsive surfaces (λ_{bcw}) for the spherical cavity with various diameters, respectively; (c) The dependence of entropic energies on the spherical cavity diameter d_{eff} ($1.34 R_g\text{--}5.52 R_g$) for the spherical cavity with various A-repulsive surfaces λ_{bcw} , respectively

CONCLUSIONS

We analyzed the surface-induced morphologies of ABC star triblock copolymers in spherical cavities on the basis of SCFT. We investigated the self-assembled morphologies by constructing phase diagrams depending on spherical cavity diameters and surface preferential strengths; we considered a spherical confinement environment with neutral surface and obtained several typical morphologies through various spherical cavity diameters; and then we considered two types of adsorption surfaces, which presented different degrees of preferential interactions with the polymer systems.

Various morphologies, including RL and None-RL structures, were obtained at different spherical cavity diameters and surface adsorption strengths. The RL structures contain several ring-like or disk-like A-, B-, or C-domains, which are parallel to each other and have axial symmetry. The RL structures were observed in the spherical cavity with adsorption surfaces, but not in the spherical cavity with neutral surfaces, which indicates that the selectivity of surfaces is crucial to form the RL morphologies in spherical cavities. In the A-attractive case, the RL structures are located in a gathered region in the phase diagram, in which the strength of the preferential surface is relatively strong in spherical cavities with relatively large diameters. However, the RL

structures show a narrow distribution in the phase diagram in the A-repulsive case. The investigations both on the A-attractive and A-repulsive cases suggested the number of rings or disks increases with spherical cavity diameter. The present numerical study on the surface-induced morphologies in spherical cavity is expected to provide certain valuable guidance for future experiments and aid the fabrication of ABC star triblock copolymer spherical cavities with desirable inner morphologies.

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