

Interfacial Frustration-induced Novel Self-assembled Structures from Block Copolymers under Janus Spherical Confinement

Xing-Ye Li, Zheng Wang, Yu-Hua Yin, Run Jiang, and Bao-Hui Li*

Key Laboratory of Weak-Light Nonlinear Photonics, Ministry of Education, School of Physics, Nankai University, Tianjin 300071, China

 Electronic Supplementary Information

Abstract Spatial confinement of block copolymers can induce frustrations, which can further be utilized to regulate self-assembled structures, thus providing an efficient route for fabricating novel structures. We studied the self-assembly of AB di-block copolymers (di-BCPs) confined in Janus spherical nanocavities using simulations, and explained the structure formation mechanisms. In the case of a strongly selective cavity wall, all the lamella-forming, gyroid-forming, and cylinder-forming di-BCPs can form interfacial frustration-induced Janus concentric perforated lamellar nanoparticles, whose outermost is a Janus spherical shell and the internal is a sphere with concentric perforated lamellar structure. In particular, Janus concentric perforated lamellar nanoparticles with holes distributed only near the equatorial plane were obtained in both lamella-forming and gyroid-forming di-BCPs, directly reflecting the effect of interfacial frustration. The minority-block domain of the cylinder-forming di-BCPs may form hemispherical perforated lamellar structures with holes distributed in parallel layers with a specific orientation. For symmetric di-BCPs, both the A and B domains in each nanoparticle are continuous, interchangeable, and have rotational symmetry. While for gyroid-forming and cylinder-forming di-BCPs, only the majority-block domains are continuous in each nanoparticle, and holes in the minority-block domains usually have rotational symmetry. In the case of a weakly selective cavity wall, the inhomogeneity of the cavity wall results in structures having a specific orientation (such as flower-like and branched structures in gyroid-forming and cylinder-forming di-BCPs) and a perforated wetting layer with uniformly distributed holes. The novel nanoparticles obtained may have potential applications in nanotechnology as functional nanostructures or nanoparticles.

Keywords Simulated annealing; Diblock copolymer; Self-assembly; 3D confinement; Interfacial frustration

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INTRODUCTION

Block copolymers (BCPs) can self-assemble into a variety of ordered nanostructures which have attracted tremendous attention due to their potential applications in a wide range of fields, such as in lithographic templates for nanowires, high-density magnetic storage media, and material science.^[1–4] The simplest BCPs, linear diblock copolymers (di-BCPs), are known to self-assemble into several ordered microstructures, *i.e.*, lamellae, networks of double gyroid and orthorhombic Fddd, hexagonally packed cylinders, and spherical phase.^[5–12] In the bulk, self-assembly of BCPs is largely driven by the intrinsic frustration due to the existence of two opposite tendencies of immiscible between chemically distinct blocks (that drives different polymeric species to separate from each other) and the covalent bonds connecting different blocks (that prevents macroscopic separation) in molecular architecture.^[13]

The self-assembly of BCPs under various confinements has

been systematically investigated, such as in thin films (one-dimensional (1D) confinement), cylindrical channels (2D confinement), and spherical cavities (3D confinement). These spatial confinements of BCPs can induce additional frustrations, providing a powerful method for breaking the symmetry of an unconfined structure, thus offering an efficient route for fabricating novel structures.^[14] Recent experiments, simulations, and theory have shown that confined self-assembly of BCPs can lead to the formation of a large number of complex ordered structures that are not present in the bulk.^[14] For example, helical structures, stacked toroid structures, cylindrical or spherical concentric lamellar or perforated lamellar structures, Janus-type, wheel-, mushroom-, tennis ball-, or screw-like shaped structures have been observed or predicted for di-BCPs under 2D or 3D confinements.^[15–42]

Compared with 1D and 2D confinements, the 3D confinement of BCPs is much stronger^[22] and hence more fascinating. Experimentally, the 3D confinement of BCPs has been realized using the colloidal crystal template method^[38] or by solvent evaporation of BCP emulsion droplets.^[43,44] Confinement usually means confining BCPs inside a finite space with homogeneous walls. On the other hand, 3D confinement of

* Corresponding author, E-mail: baohui@nankai.edu.cn

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BCPs with Janus spherical cavity walls and inhomogeneous walls has recently been realized experimentally using solvent evaporation of BCP emulsion droplets and interfacial phase separation of an elaborately designed binary surfactant system.^[45] Compared with a spherical cavity with a homogeneous wall, a Janus spherical cavity can be regarded as resulting from symmetry-breaking of the former, and hence can induce additional frustration at the interface of the Janus wall, which may be quite different from the frustration induced by the conventional 1D, 2D, or 3D confinement. This additional interfacial frustration can be further utilized to regulate the self-assembled BCP structures. To the best of our knowledge, there have been two studies related to the self-assembly of BCPs under Janus spherical cavities. In one of these two studies, Cui *et al.* proposed the strategy of Janus cavity fabrication (as mentioned above) and obtained onion nanoparticles experimentally and with simulations for lamella-forming di-BCPs.^[45] The other is a more recent study where Wu *et al.* studied the self-assembly of lamella-forming and cylinder-forming ABC linear triblock copolymers confined in spherical or Janus spherical cavities using self-consistent field theory.^[46] They found that structures induced by the Janus wall are different from those induced by the spherical cavity of the homogeneous wall. To better understand the effect of cavity wall symmetry breaking on the self-assembled structures of BCPs, more studies on the self-assembly of BCPs under Janus cavity confinement are required.

In this study, we investigated the confined self-assembly of AB di-BCPs in Janus spherical cavities using simulated annealing. For all lamella-forming, gyroid-forming, and cylinder-forming di-BCPs, we obtained several series of interfacial frustration-induced or cavity-wall inhomogeneity-induced Janus concentric perforated lamellar nanoparticles, including those with a Janus shell or a perforated Janus shell at the outermost and spherical concentric perforated lamellae inside. In particular, we obtained Janus-perforated lamellar nanoparticles with one or more shells having holes distributed only near the equator plane. For symmetric di-BCPs, both the A- and B-domains are continuous, interchangeable, and exhibit rotational symmetry. We investigated the effect of the degree of confinement and the strength of the interactions between the polymer and cavity walls. The obtained nanoparticles can be used as functional nanostructures.

MODEL AND METHOD

In the current study, we investigated the self-assembly of di-BCP melts confined in a Janus spherical cavity using a simulated annealing method,^[47,48] based on the single-site bond fluctuation model.^[49,50] Our extensive previous studies have established that the method and model are appropriate for investigating the self-assembly of BCPs under confinement.^[21,51] Our model system includes symmetric (lamella-forming), gyroid-forming, or cylinder-forming AB di-BCPs and vacancies. In our model, each AB di-BCP molecule is a chain with N_A A-segments and $(N-N_A)$ B-segments, where $N=12$, $N_A=6, 4$, and 3 , that is, $f_A=1/2, 1/3$, and $1/4$, for lamella-forming, gyroid-forming, and cylinder-forming di-BCPs, respectively. A spherical cavity of diameter D was constructed from a cube of volume $V = L \times L \times L$ on a simple cubic lattice, where $L > D$. The cavity includes lattice sites whose dis-

tance to the cavity center is equal to or less than $D/2$. The lattice sites outside the cavity constitute the cavity wall, which cannot be occupied by the copolymers. To set up a Janus cavity, the properties of the cavity wall sites in the upper (W1) and lower (W2) hemispheres are different.

The model polymer molecules are assumed to be self- and mutually-avoiding in all simulation processes, that is, each segment occupies one lattice site in the cavity, and multiple occupations of any lattice site are not allowed. The bond length between two consecutive segments in each chain is either 1 or $\sqrt{2}$, and thus, each site has 18 nearest-neighbor sites. The polymer concentration was fixed at 85% and the remaining 15% of the sites were set as vacancies. In our simulations, only the nearest-neighbor interactions were considered and modeled by assigning energy $E_{ij} = \epsilon_{ij} k_B T_{\text{ref}}$ to each nearest-neighbor pair of unlike components i and j , where i and $j = A, B, W1$, and $W2$; ϵ_{ij} is the reduced interaction energy; k_B is the Boltzmann constant, and T_{ref} is the reference temperature. The interaction parameters ϵ_{ij} used in our study are listed in Table 1, where $\epsilon_w=1$ and 0.1 for the two cases of strongly and weakly selective walls, respectively. That is, the upper and lower cavity walls were selective to the B- and A-blocks, respectively.

Table 1 The interaction parameters used in our study, where $\epsilon_w=1$ and 0.1 for strongly and weakly selective walls, respectively.

ϵ_{ij}	A	B	W1	W2
A	0	1.0	ϵ_w	$-\epsilon_w$
B	1.0	0	$-\epsilon_w$	ϵ_w
W1	ϵ_w	$-\epsilon_w$	0	0
W2	$-\epsilon_w$	ϵ_w	0	0

RESULTS AND DISCUSSION

In this section, we present our results for the confined self-assembly of diblock copolymers (di-BCPs) in Janus spherical nanocavities using simulated annealing. Our studied systems include AB di-BCPs with volume fractions of the A-block of $f_A=1/2, 1/3$, and $1/4$. Our previous studies, based on the same model and the same method as those used in the present study, established that the studied di-BCPs with $f_A=1/2, 1/3$, and $1/4$ form lamellar phase, double gyroid, and hexagonally packed cylinders, respectively, in the bulk and with a period of $L_0=9.33, 24$, and 10.67 lattice spacings.^[18–22] In the present study, the Janus cavity wall sites in the upper and lower hemispheres are selective to B and A blocks, respectively. Self-assembled structures from AB di-BCPs confined in strongly selective ($\epsilon_w=1$) and weakly selective ($\epsilon_w=0.1$) Janus spherical cavities are presented, where ϵ_w is the strength of the reduced polymer-wall interactions. The effects of the selectivity strength and cavity size on the interfacial frustrations and on the self-assembled structures were analyzed.

Janus Spherical Cavity with Strongly Selective Wall

Symmetric diblock copolymers

Fig. 1 shows the reduced cavity diameter (D/L_0) dependence of the typical morphologies of nanoparticles obtained from lamella-forming (symmetric) di-BCPs confined within a Janus spherical nanocavity with a strongly selective wall, where L_0 is the pe-

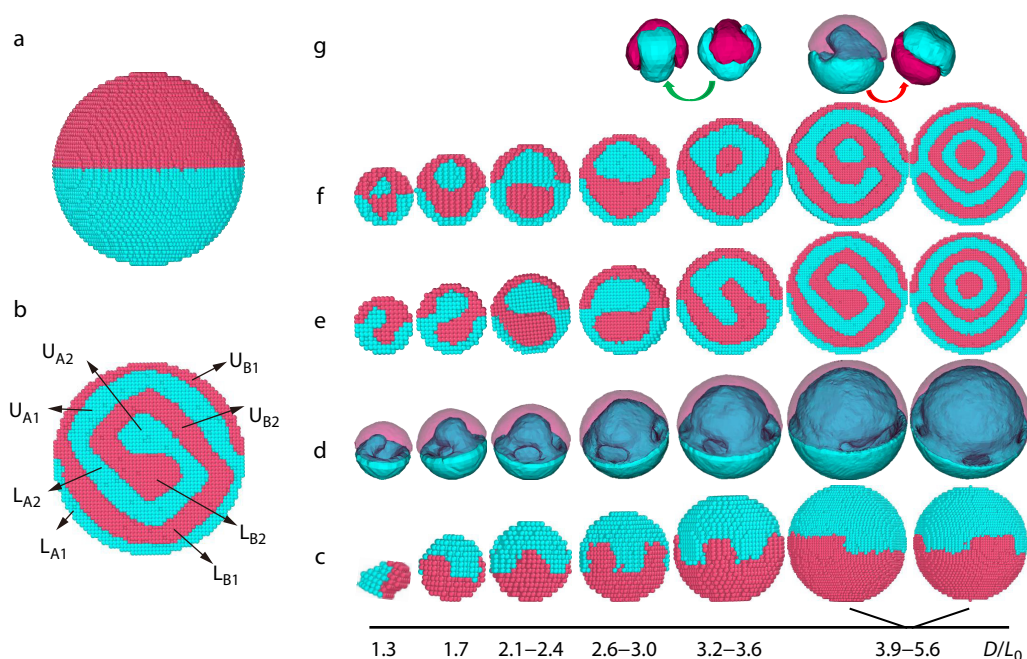


Fig. 1 Typical morphologies obtained from symmetric di-BCPs with $f_A = 1/2$ confined within a strongly selective Janus spherical nanocavity as a function of D/L_0 . (a) The wetting layer close to the cavity wall; (b) The names for each A- and B-hemishells illustrated on a cross-sectional view of a nanoparticle snapshot obtained at $D/L_0 = 5.36$; (c) Nanoparticles without the wetting layer; The isosurface contour plots of the whole nanoparticle (d) and only the inner parts (g); For clarity, the B-domain in transparency in (d), and snapshots in two perpendicular views are shown in (g); (e, f) Cross-sectional views in the planes perpendicular to the equator plane and passing through the center of the cavity in two perpendicular directions. Color scheme: A-domain, blue; B-domain, rose.

riod of the studied block copolymer in the bulk phase. Owing to the strong selectivity of the cavity wall, a Janus wetting layer composed of B- and A-hemishells close to the upper and lower hemispherical cavity walls, respectively, is formed, as shown in Fig. 1(a), where the B- and A-hemishells are directly joined at the equator of the Janus cavity to reduce the interaction energy between the polymer and the cavity wall (surface energy). The size of the Janus wetting layer increased with the cavity size, while its morphology remained unchanged. In this case, the reduction in the surface energy compensated for the increase in the interfacial energy caused by the A/B interface in the wetting layer. For convenience, we defined the distance from a hemishell to the cavity center as its radial distance. Evidently, the pair of wetting hemishells has the same radial distance. In this case, joining does not require extra chain stretching.

In the inner part of the Janus wetting layer, the sequences of the A- and B-hemishells differ between the upper and lower hemispheres because of the connectivity of the A and B blocks. For convenience, we labeled the A- and B-hemishells in the upper and lower hemispheres as $U_{B1}, U_{A1}, U_{B2}, U_{A2}, \dots$, and $L_{A1}, L_{B1}, L_{A2}, L_{B2}, \dots$, respectively, as shown in Fig. 1(b). Here, U and L indicate that the hemishells are in the upper and lower hemispheres, respectively, while the subscripts An and Bm denote the n -th A-hemishell and the m -th B-hemishell counted from the outermost to the innermost. This difference in A- and B-hemishell sequences leads to frustration at the joining interfaces between any pair of U_{jm} and L_{Kn} hemishells that can meet, where J and K can be A or B. On one hand, if each of the $U_{A1}, U_{B2}, U_{A2}, \dots$ hemishells in the upper hemisphere joined directly with the respective $L_{B1}, L_{A2}, L_{B2}, \dots$ hemishells in the lower hemisphere sequentially, to form mul-

tiple Janus spherical shells with interfaces at the equator, this would result in a high interfacial energy due to the increase in AB interfacial area between any pair of would-be joined A- and B-hemishells having the same radial distances, as well as that between any two adjacent shells in the radial direction. However, if the U_{An} (U_{Bm}) hemishell was joined with the hemishell L_{Ai} (L_{Bj}) of the same component at the equator, the chains would be stretched owing to the difference in their radial distances. That is, frustration exists in joining each pair of hemishells (one in the upper and the other in the lower hemisphere) at the interfaces, which we call interfacial frustration. This interfacial frustration drives the formation of novel self-assembled structures of di-BCPs under Janus confinement. The details of these novel structures depend on D/L_0 , as shown in Figs. 1(c)–1(g).

When $D/L_0 \leq 3.0$, there is only one A- or B-hemishell in the upper or lower hemisphere, U_{A1} or L_{B1} , respectively, except for the wetting layer. The U_{A1} and L_{B1} hemishells joined near the equator plane of the Janus cavity, resulting in a wave-like interface, as shown in Fig. 1(c). This wave-like interface indicates a larger interfacial energy between U_{A1} and L_{B1} hemishells than that of a flat interface; however, it can reduce the interfacial energy between U_{A1} (L_{B1}) and the wetting hemishell U_{B1} (L_{A1}) owing to the partial connections of hemishells U_{A1} and L_{A1} , as well as of hemishells L_{B1} and U_{B1} . These partial connections further result in the spherical perforated lamella structures of both A- and B-domains with holes only distributed near the equator-plane of Janus cavity, as shown in Fig. 1(d), and we refer this type of structure as equator-perforated lamella. When $D/L_0 = 1.3, 1.7, 2.1\text{--}2.4$, and $2.6\text{--}3.0$, the numbers of holes in the equator perforated lamella were 1, 2, 3,

and 4, respectively.

When $D/L_0 \geq 3.2$, the number of A- and B-hemishells within the upper and lower hemispherical cavities increases with D/L_0 , leading to more pairs of hemishells joining, and hence stronger interfacial frustration. For $3.2 \leq D/L_0 \leq 3.6$, there were three hemishells within each of the upper and lower hemispheres, with sequences U_{B1} , U_{A1} , and U_{B2} , and L_{A1} , L_{B1} , and L_{A2} , respectively. The joining of U_{A1} and L_{B1} hemishells is similar to that at $D/L_0 = 3.0$, which also results in a wave-like interface (see Fig. 1c) and the partial connections of hemishells U_{A1} and L_{A1} , and L_{B1} and U_{B1} . Hence, both the A- and B-domains for the outermost two shells are equator perforated lamellae with four holes (Fig. 1d). Additionally, the partial connections of hemishells U_{A1} and L_{A2} , as well as of hemishells L_{B1} and U_{B2} result in the formation of an inner equator perforated lamella (see Fig. 1g). Thus, the self-assembled structure for the nanoparticle with $3.2 \leq D/L_0 \leq 3.6$ has two layers of concentric equator perforated lamellae.

From Fig. 1, we notice that two types of degenerate structures were obtained for nanoparticles with $D/L_0 \geq 3.9$. In these structures, both the A- and B-domains are equator perforated lamellae in the outermost two shells, as shown in Fig. 1. However, the structures of the inner shells differed significantly. In one type of degenerate structure, both A- and B-domains appear as spirals in the cross-sectional view perpendicular to the Janus equator plane (see Fig. 1e); hence, we refer to this type of structure as spiral-like structures. In fact, all structures with $D/L_0 \leq 3.6$ belong to spiral-like structures. In this type of structure, a pair of (or two or three pairs of) hemishells with the same radial distance but different chemical species join with a wave-like interface (Fig. 1c), resulting in equator perforated lamellae of different layers (Figs. 1d and 1g). Interestingly, in these spiral-like structures, all A- (or B-) hemi-shells in each nanoparticle are interconnected, indicating that both A- and B-domains are continuous phases. The other type of degenerate structure is referred to as an onion-like structure, where the inner shells form concentric spherical lamellar cores (see Figs. 1(e) and 1(f) at $D/L_0 = 3.9$ –5.6). The core is similar to concentric spherical lamellae self-assembled from symmetric di-BCPs confined in spherical cavities with homogeneous-wall.^[21]

As shown in Fig. 1, at $1.7 \leq D/L_0 \leq 3.6$, holes in the equator perforated lamellae are uniformly distributed and have rotational symmetry about the axis perpendicular to the equatorial plane. However, when $D/L_0 \geq 3.9$, only one or two longer slit-like holes were observed. To understand the variation of the self-assembled structures with D/L_0 , we calculated the surface energy (E_s) per volume and the interfacial energy (E_i) per AB segment for the structures shown in Fig. 1 and plotted them as a function of D/L_0 in Fig. S1 (in the electronic supplementary information, ESI). We notice that at a given D/L_0 , the attractive energy from the wall, E_s , is always stronger than the corresponding repulsive energy from the nearest neighbor AB pairs, E_i , which is the reason why a layer of wetting shell always forms in self-assembled structures. At a relatively smaller D/L_0 , E_s (in absolute value) is much larger than E_i , so that the surface energy dominates the structure. With increasing D/L_0 , both E_s and E_i decreased, and E_s decreased faster than E_i . When $D/L_0 \geq 3.9$, E_i is comparable to E_s ; thus, the influence of the wall is relatively weak in the innermost part of the particle. However, the structure formed in the innermost part of a particle may also influence the structure near the cavity wall. All

of these factors influence the resulting structures.

It should be noted that in each of the structures shown in Fig. 1, both the A- and B-domains are equator-perforated lamellar structures, while only holes in the A-domain are visible in Fig. 1(d), and holes in the B-domain are covered by the L_{A1} wetting hemishell. Furthermore, the A- and B-domains are interchangeable in each nanoparticle, owing to the symmetric composition of the copolymer and the opposite interactions between the cavity wall and the two blocks. The “interchangeable” here means that for a given structure, when its A-domain and B-domain are exchanged, the resulting structure is the same as the unchanged one. Moreover, as shown in Fig. 1(e), after rotating a spiral-like structure 180° about the axis parallel to the equatorial plane, the A(B) domain overlaps with the B(A) domain in the un-rotated structure. On the other hand, two types of onion-like structures were obtained when $D/L_0 \geq 3.9$; in one of them, the inner concentric lamellar core is located in the upper hemispherical cavity (as shown in Figs. 1e and 1f at $D/L_0 = 3.9$ –5.6), whereas in the other type, the core is located in the lower hemispherical cavity (not shown). These two types of onion-like structures are degenerate. When rotating an onion-like structure in one of the two types by 180° about the axis parallel to the equatorial plane, it changes into a structure in the other type.

To better understand the formation mechanisms of the degenerate structures shown in Fig. 1, we investigated the evolution of the structures, as well as the variations in the mean-square radius of gyration $\langle R_g^2 \rangle$ (normalized by the value of the corresponding ideal chain) and total energy $\langle E \rangle$ with the annealing temperature T , as shown in Fig. 2 for nanoparticles

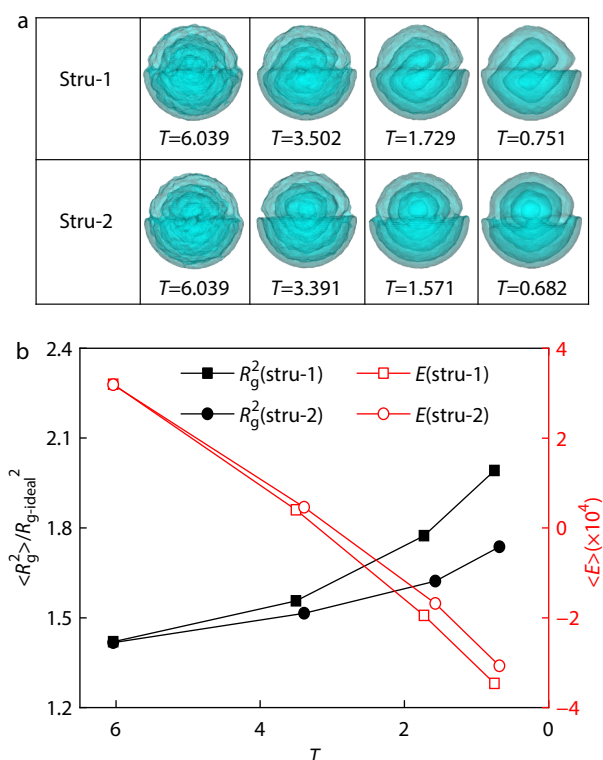


Fig. 2 Typical evolutions with temperature T of (a) the self-assembled structures (only A-domains are shown for clarity), (b) mean-square radius of gyration and total energy for degenerate structures shown in Fig. 1 at $D/L_0 = 5.36$.

at $D/L_0 = 5.36$, where Stru-1 and Stru-2 represent the spiral-like and onion-like structures, respectively. Fig. 2 reveals that at higher T (≥ 6.039) regions, the morphologies of the two degenerate structures are similar, and their corresponding $\langle R_g^2 \rangle$ and $\langle E \rangle$ values are nearly equal. However, at lower T values, the copolymer chains in the spiral-like structure are more stretched than those in the onion-like structure, while $\langle E \rangle$ of the spiral-like structure is lower than that of the onion-like structure. Consequently, the spiral-like structure was enthalpy dominant, whereas the onion-like structure was entropy-dominant.

Asymmetric diblock copolymers

We also studied the self-assembly of asymmetric di-BCPs, including gyroid-forming and cylinder-forming ones, confined in a Janus spherical nanocavity to investigate the effect of BCP composition. Fig. 3 shows the cavity size (D/L_0) dependence of typical self-assembled structures formed by gyroid-forming di-BCPs with $f_A = 1/3$ confined within a Janus spherical nanocavity with a strongly selective wall. Similar to the case of symmetric di-BCPs, a Janus wetting layer is formed near the cavity wall, as shown in Fig. 3, and the morphology of this wetting layer is independent of the Janus cavity size. However, unlike the symmetric di-BCPs, the larger volume fraction of the B-block resulted in a much thicker U_{B1} wetting hemishell than the L_{A1} wetting hemishell. This means that the radial distance of the U_{B1} wetting hemishell is closer to that of the L_{B1} hemishell than that of L_{A1} , resulting in the joining of the U_{B1} and L_{B1} hemishells, which prevents the joining of the L_{A1} wetting hemishell with any other

A-shells. In fact, all B-domains inside each nanoparticle were continuous, while the A-domains were dispersed. When $D/L_0 \leq 1.5$, there is only one A-domain in the upper hemisphere, and with increasing D/L_0 its shape changes from spherical to disc-like to spherical cap-like to hemi-shell. In the lower hemisphere, in addition to the wetting layer, the first inner A-domain occurred at $D/L_0 = 1.2$, and its shape changed with increasing D/L_0 similar to that in the upper hemisphere. When $D/L_0 \geq 1.6$, the U_{A1} and L_{A2} hemishells joined, forming an A-equator perforated lamella. Simultaneously, the U_{B2} and L_{B1} hemishells join, forming a B-equator perforated lamella. Thus, despite the larger volume fraction of the B-block, both the A- and B-domains formed equator perforated lamellar structures, and the number of holes in the equator perforated lamellar structures increased with increasing D/L_0 . When $D/L_0 \geq 1.7$, a new A-domain emerges inside the equator perforated lamellae (as shown in Fig. 3f), and its shape changes from spherical to disk as D/L_0 increases.

Fig. 4 shows the cavity size (D/L_0) dependence of typical self-assembled structures for cylinder-forming AB di-BCPs with $f_A = 1/4$ confined in a Janus spherical nanocavity with a strongly selective wall. Similar to the self-assembled structures formed from gyroid-forming di-BCPs, a Janus wetting layer was formed near the cavity wall. The B-domains inside each nanoparticle are also continuous, while the A-domains are dispersed. However, each A-domain in one hemisphere never meets that in the other hemisphere for all the studied cavity sizes, as shown in Fig. 4, which is different from the structures shown in Fig. 3. As D/L_0 increases, in each hemi-

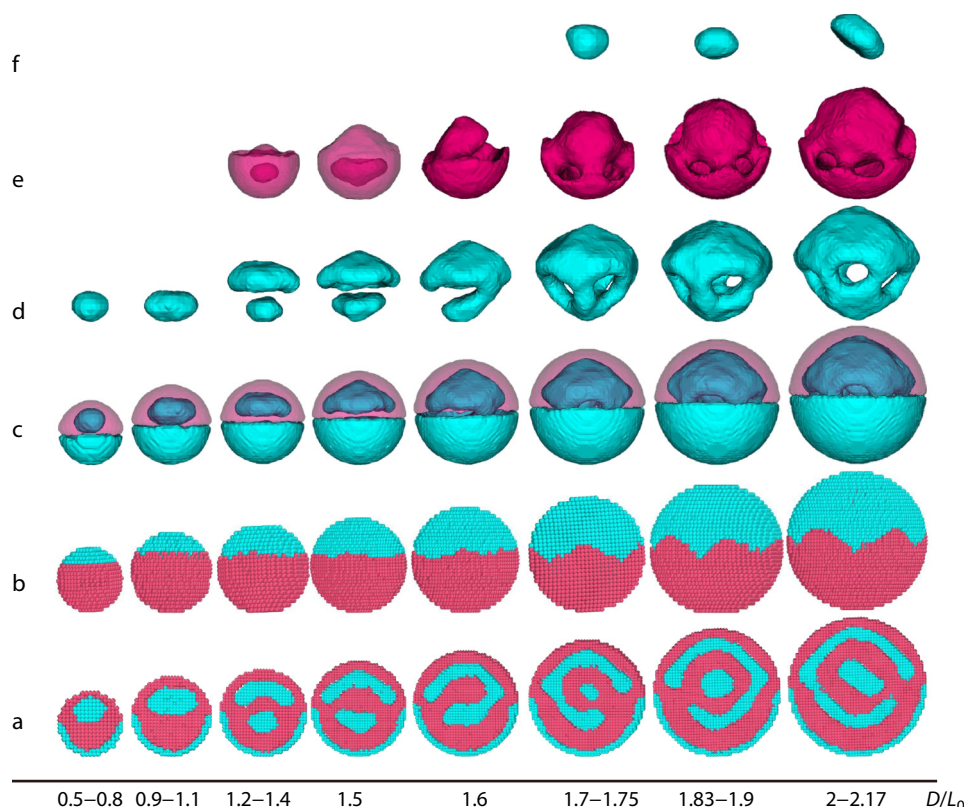


Fig. 3 The D/L_0 dependence of typical morphologies obtained from the gyroid-forming di-BCPs confined within a strongly selective Janus spherical nanocavity. (a) Cross-sectional view; (b) The wetting layer is removed; (c–f) Isosurface contour plots of A- and/or B-domains: (c) B-domains in transparent, (d) the inner A-domain and (e) B-domain, and (f) the innermost A-domain. Color scheme: A-domain, blue; B-domain, rose.

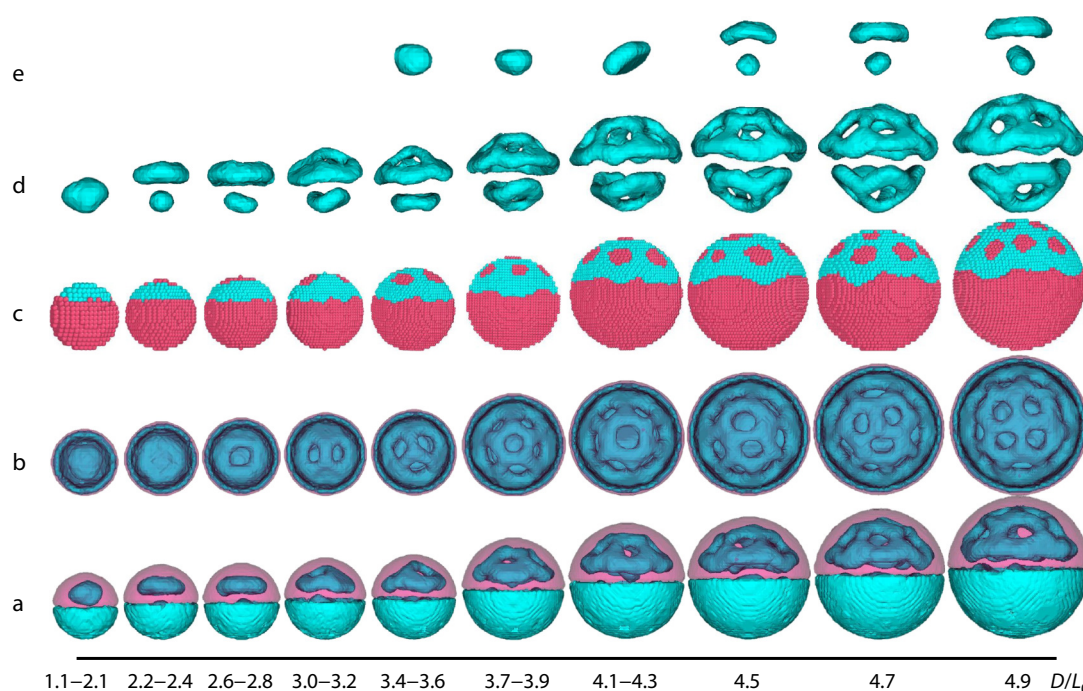


Fig. 4 The D/L_0 dependence of typical snapshots of the self-assembled structures obtained from the cylinder-forming di-BCPs confined within a strongly selective Janus spherical nanocavity. (a, b) In two perpendicular views with the B-domains in transparency; (c) Morphologies without the wetting layer; (d) A-domains without the wetting layer; (e) Inner A-domains. Color scheme: A-domain, blue; B-domain, rose.

sphere, the morphology of the A-domain within the wetting layer changes from a sphere to a disk to a ring to a spherical cap-like or a hemispherical perforated lamellar structure, and further to that with a new inner A-domain, and its morphology repeats the above-mentioned sequence. In each spherical-cap-like or hemispherical A-domain, the holes are packed in layers parallel to the equator plane, and their distribution is relatively uniform in each layer. In other words, the equator plane of the confining cavity wall determines the distribution of the holes. In contrast, the holes in the structures shown in Figs. 1 and 3 are distributed only near the equator plane. The arrangement of holes in Fig. 4 also differs from that of the same di-BCPs confined within a spherical nanocavity with homogeneous and strongly selective walls, where the distribution of holes in the entire layer is relatively uniform.

Janus Spherical Cavity with Weakly Selective Wall

Fig. 5 shows the D/L_0 dependence of typical self-assembled structures of gyroid-forming di-BCPs confined in a Janus spherical cavity with a weakly selective wall. As shown in Fig. 5, the B blocks form a continuous phase, and the L_{A1} wetting layer in the lower hemisphere is not connected to any other A-shell. These characteristics are consistent with those obtained for the same copolymer under the same confinement, but with a strongly selective cavity wall, as shown in Fig. 3. However, the structural details of the A and B domains are different from those shown in Fig. 3. In Fig. 5, the B-domains adopt a flower shape where the petals are single-, double-, and triple-layered at $D/L_0 = 0.5$ –1.0, 1.1–1.7, and 1.75–2.17, respectively. The edge of each layer of the petal joins the upper wetting hemispherical, thereby reducing the A/B interfacial energy. At $D/L_0 = 0.5$ –1.3, the base of the flower converges into a short cylindrical shape, similar to a flower stem, reaching the lowest part of the cavity wall, resulting in a B-hole on the L_{A1} wetting hemispherical. This is due to the small

number of A-segments inside each nanoparticle at $D/L_0 \leq 1.3$ and the weak interactions between the cavity wall and the copolymer. On the other hand, the A-domains (except the L_{A1} wetting hemispherical) mainly constitute branched structures when $D/L_0 \geq 0.9$, where the number of short-cylinder-shaped branches increases with D/L_0 , and they exhibit triple junctions, which are characteristic of gyroid structures. This is similar to that for structures obtained when the same copolymer is confined inside a spherical cavity with a homogeneous weakly selective wall.^[38] Furthermore, each A-branch in the structure reaches the upper cavity wall perpendicularly, resulting in an A-hole on the U_{B1} wetting hemispherical. The number of A-holes in the U_{B1} wetting hemispherical increases with D/L_0 , forming a perforated U_{B1} hemispherical, which is different from that for the same copolymer under the same confinement but with a strongly selective wall, as shown in Fig. 3. It is interesting to note that triple junction features also exist in the U_{B1} wetting hemispherical. The occurrence of holes in the U_{B1} wetting hemispherical is energetically unfavorable; however, it is entropically favorable because a wall always entropically attracts to the minority-block.^[14,38,51] When D/L_0 is small, the A-domain is only a sphere ($D/L_0 = 0.5$ –0.75) or a curved cylinder ($D/L_0 = 0.8$). Similarly, an isolated sphere and curved cylinder also appear at $D/L_0 = 1.1$ –1.3 and $D/L_0 = 1.4$, respectively, which coexist with the branched structures. Furthermore, we noticed that the interface between the A/B wetting hemisphericals shifted to the lower side (lower than the Janus equator) and had a wave-like shape. The downward shift of the interface increases the surface energy; however, it allows the U_{B1} and L_{B1} hemisphericals to join, thereby reducing the A/B interfacial energy. The wave-like features of the interface were determined by the connectivity of the copolymer chains. It is interesting that all the flower-like B-domains and branched A-domains are of the same orientation, which is determined by the polymer-wall in-

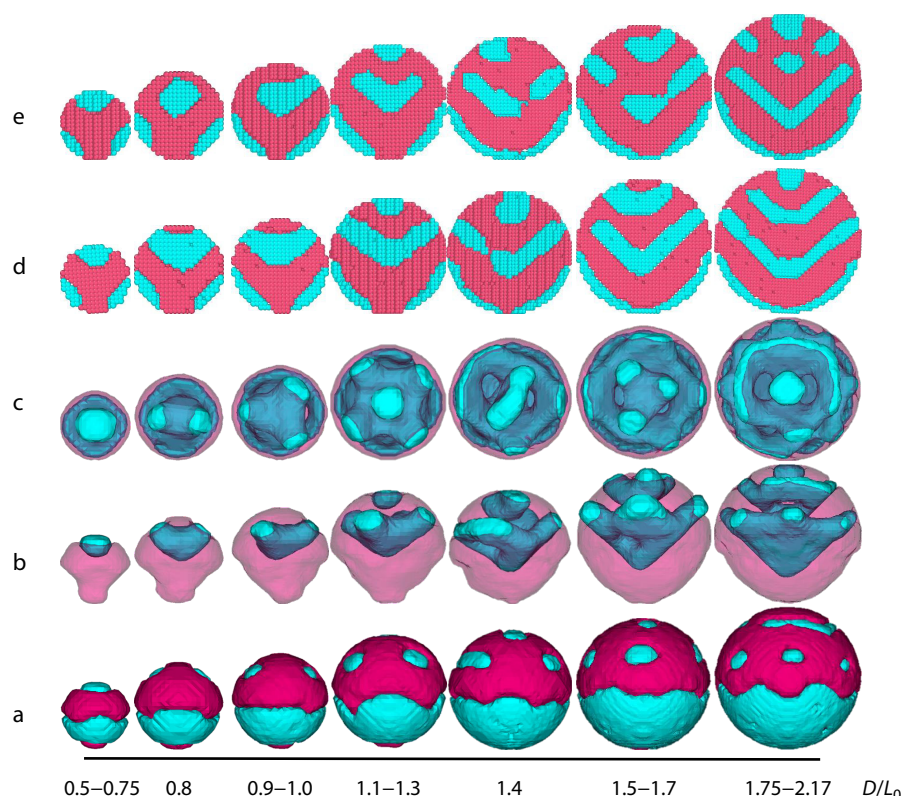


Fig. 5 The D/L_0 dependence of typical morphologies obtained from the gyroid-forming di-BCPs confined in a Janus spherical nanocavity with weakly selective wall. (a–c) The isosurface contour plots, (a) with all the A- and B-domains and (b, c) without the A-wetting layer in two perpendicular views. For clarity, the B-domains in transparency in (b, c). (d, e) Cross-sectional views. Color scheme: A-domain, blue; B-domain, rose.

teractions.

Fig. 6 shows the D/L_0 dependence of typical self-assembled structures formed from cylinder-forming di-BCPs confined in a Janus spherical nanocavity with a weakly selective wall. As D/L_0 increases, the morphology of the minority A-segments changes from a sphere to a curved cylinder and branched structures (except for the L_{A1} wetting hemishell). All A-structures with edges reach the upper cavity wall, resulting in a perforated U_{B1} hemishell. All of these are similar to those in the case of gyroid-forming di-BCPs, as shown in Fig. 5. However, the diameters of the sphere, cylinder, and branch for the structures shown in Fig. 6 are smaller than those for the corresponding structure shown in Fig. 5, owing to the smaller volume fraction of the A-block in this system. Furthermore, in the structures shown in Fig. 6, both the upper and lower wetting hemishells were perforated lamellae.

CONCLUSIONS

We investigated the self-assembly of di-BCPs confined within a Janus spherical nanocavity, using a simulated annealing technique. In our model, wall sites in the upper and lower hemispherical cavities are attractive to the B- and A-blocks, respectively, while being repulsive to the other block. We observed a series of nanoparticles with novel structures induced by interfacial frustration or by the inhomogeneity of the cavity wall for di-BCPs with different compositions, and explained the structure formation mechanisms. The novel nanoparticles obtained may

have potential applications in nanotechnology as functional nanostructures or nanoparticles.

In the case of the strongly selective cavity wall, we observed a series of interfacial frustration-induced structures. In each nanoparticle formed by symmetric di-BCPs, both the A- and B-domains are equator-perforated lamellar structures, where the holes are distributed only near the equatorial plane. Furthermore, both the A- and B-domains are continuous, interchangeable, and with rotational symmetry, whereas only the majority-block domain is continuous in cases of gyroid-forming or cylinder-forming di-BCPs. In each nanoparticle formed by the gyroid-forming di-BCPs, both the minority-block and majority-block domains were equator perforated lamellar structures when the particle size was relatively large. In each nanoparticle formed by the cylinder-forming di-BCPs, depending on the particle size, the minority-block domain can be a sphere, a disk, a ring, a spherical cap-like or a hemispherical perforated lamellar structure in both the upper and the lower hemispheres, minority-block domains from the two hemispheres never meets in all the studied cases. In hemispherical perforated lamellar structures, the holes are distributed in parallel layers of a specific orientation.

In the case of a weakly selective cavity wall, the inhomogeneity of the cavity wall results in structures with an anisotropic orientation and a perforated wetting layer with uniformly distributed holes. In gyroid-forming di-BCPs, the majority blocks form flower-like structures, whereas the mi-

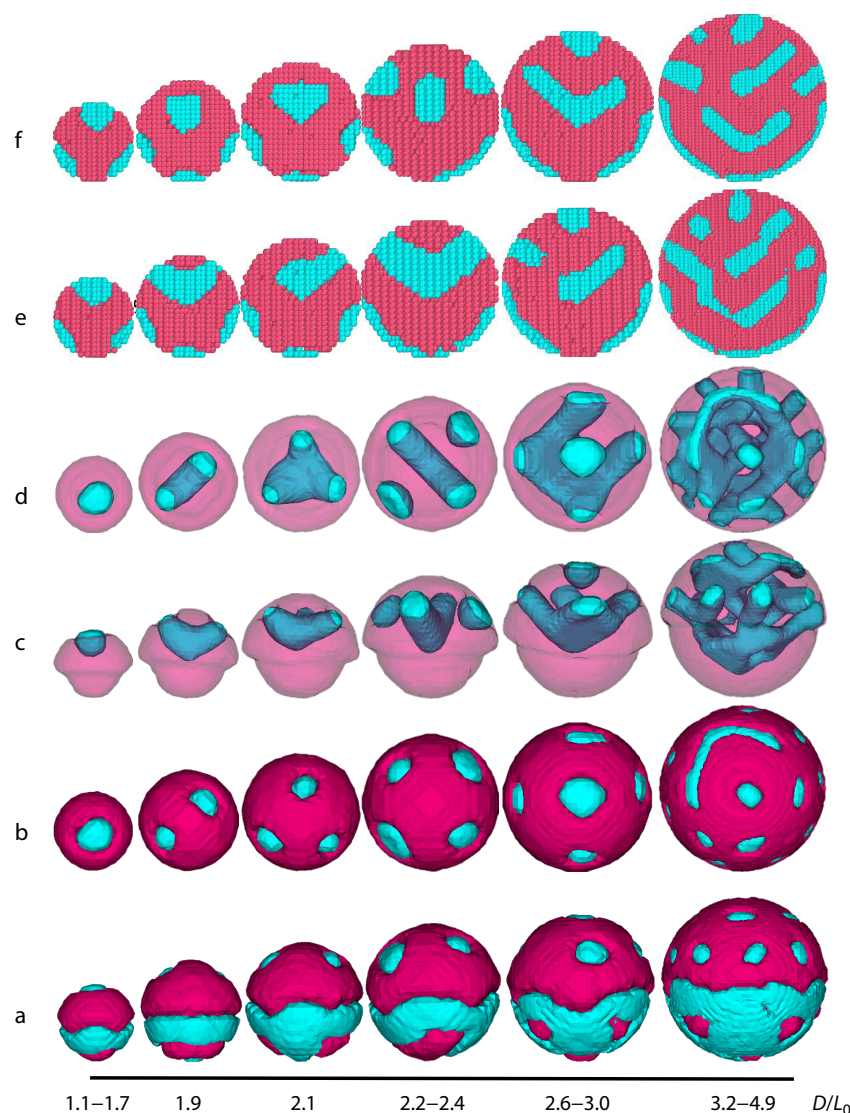


Fig. 6 The D/L_0 dependence of typical particle morphologies obtained from the cylinder-forming di-BCPs confined in the Janus spherical nanocavity with weakly selective wall. (a–d) The isosurface contour plots, (a, b) with and (c, d) without the A-wetting layer in two perpendicular views. For clarity, the B-domains in transparency in (c, d). (e, f) Cross-sections in two perpendicular views. Color scheme: A-domain, blue; B-domain, rose.

nority blocks form branched structures exhibiting the characteristics of triple junctions. In this case, the wetting layer was a spherical perforated lamella with holes distributed only in one hemisphere. In cylinder-forming di-BCPs, the minority blocks also form branched structures. All the flower-like B-domains and branched A-domains were of the same orientation determined by the polymer-wall interactions.

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Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/>

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REFERENCES

- Bates, F. S.; Fredrickson, G. H. Block copolymers—designer soft materials. *Phys. Today* **1999**, 52, 32–38.
- Russell, T. P.; Chai, Y. 50th anniversary perspective: putting the squeeze on polymers: a perspective on polymer thin films and interfaces. *Macromolecules* **2017**, 50, 4597–4609.
- Schacher, F. H.; Rupa, P. A.; Manners, I. Functional block copolymers: nanostructured materials with emerging applications. *Angew. Chem. Int. Ed.* **2012**, 51, 7898–7921.
- Hamley, I. W. Nanostructure fabrication using block copolymers. *Nanotechnology* **2003**, 14, R39–R54.
- Kim, M. I.; Wakada, T.; Akasaka, S.; Nishitsuji, S.; Saijo, K.; Hasegawa, H.; Ito, K.; Takenaka, M. Determination of the Fddd phase boundary in polystyrene-block-polyisoprene diblock copolymer melts. *Macromolecules* **2009**, 42, 5266–5271.
- Lee, S.; Bluemle, M. J.; Bates, F. S. Discovery of a Frank-Kasper σ phase in sphere-forming block copolymer melts. *Science* **2010**, 330, 349–353.
- Matsen, M. W. Effect of architecture on the phase behavior of AB-type block copolymer melts. *Macromolecules* **2012**, 45, 2161–2165.
- Lee, S.; Leighton, C.; Bates, F. S. Sphericity and symmetry breaking in the formation of Frank-Kasper phases from one component materials. *Proc. Natl. Acad. Sci.* **2014**, 111, 17723–17731.
- Kim, K.; Schulze, M. W.; Arora, A.; Lewis, R. M.; Hillmyer, M. A.; Dorfman, K. D.; Bates, F. S. Thermal processing of diblock copolymer melts mimics metallurgy. *Science* **2017**, 356, 520–523.
- Tyler, C. A.; Morse, D. C. Orthorhombic Fddd network in triblock and diblock copolymer melts. *Phys. Rev. Lett.* **2005**, 94, 208302.
- Bates, F. S.; Schulz, M. F.; Khandpur, A. K.; Förster, S.; Rosedale, J. H.; Almdal, K.; Mortensen, K. Fluctuations, conformational asymmetry and block copolymer phase behaviour. *Faraday Discuss.* **1994**, 98, 7–18.
- Xie, N.; Li, W. H.; Qiu, F.; Shi, A. C. σ Phase formed in conformationally asymmetric AB-type block copolymers. *ACS Macro Lett.* **2014**, 3, 906–910.
- Shi, A. C. Frustration in block copolymer assemblies. *J. Phys.: Condens. Matter* **2021**, 33, 253001.
- Shi, A. C.; Li, B. H. Self-assembly of diblock copolymers under confinement. *Soft Matter* **2013**, 9, 1398–1413.
- Xiang, H. Q.; Shin, K.; Kim, T.; Moon, S. I.; McCarthy, T. J.; Russell, T. P. Block copolymers under cylindrical confinement. *Macromolecules* **2004**, 37, 5660–5664.
- Li, W. H.; Wickham, R. A.; Garbary, R. A. Phase diagram for a diblock copolymer melt under cylindrical confinement. *Macromolecules* **2006**, 39, 806–811.
- Dobriyal, P.; Xiang, H. Q.; Kazuyuki, M.; Chen, J. T.; Jinnai, H.; Russell, T. P. Cylindrically confined diblock copolymers. *Macromolecules* **2009**, 42, 9082–9088.
- Yu, B.; Sun, P. C.; Chen, T. H.; Jin, Q. H.; Ding, D. T.; Li, B. H.; Shi, A. C. Self-assembly of diblock copolymers confined in cylindrical nanopores. *J. Chem. Phys.* **2007**, 127, 114906.
- Ma, M. L.; Thomas, E. L.; Rutledge, G. C.; Yu, B.; Li, B. H.; Jin, Q. H.; Ding, D. T.; Shi, A. C. Gyroid-forming diblock copolymers confined in cylindrical geometry: a case of extreme makeover for domain morphology. *Macromolecules* **2010**, 43, 3061–3071.
- Yu, B.; Sun, P. C.; Chen, T. H.; Jin, Q. H.; Ding, D. T.; Li, B. H.; Shi, A. C. Confinement-induced novel morphologies of block copolymers. *Phys. Rev. Lett.* **2006**, 96, 138306.
- Yu, B.; Li, B. H.; Jin, Q. H.; Ding, D. T.; Shi, A. C. Self-assembly of symmetric diblock copolymers confined in spherical nanopores. *Macromolecules* **2007**, 40, 9133–9142.
- Yu, B.; Li, B. H.; Jin, Q. H.; Ding, D. T.; Shi, A. C. Confined self-assembly of cylinder-forming diblock copolymers: effects of confining geometries. *Soft Matter* **2011**, 7, 10227–10240.
- Ok, S.; Vayer, M.; Sinturel, C. A decade of innovation and progress in understanding the morphology and structure of heterogeneous polymers in rigid confinement. *Soft Matter* **2021**, 17, 7430–7458.
- Cheng, M. H.; Hsu, Y. C.; Chang, C. W.; Ko, H. W.; Chung, P. Y.; Chen, J. T. Blending homopolymers for controlling the morphology transitions of block copolymer nanorods confined in cylindrical nanopores. *ACS Appl. Mater. Interfaces* **2017**, 9, 21010–21016.
- Hu, X. J.; Wang, Z.; Yin, Y. H.; Jiang, R.; Li, B. H. Controlling the chirality and number of strands of helices self-assembled from achiral block copolymers confined inside a nanopore: a simulation study. *Soft Matter* **2021**, 17, 4434–4444.
- Yang, J. Y.; Dong, Q. S.; Liu, M. J.; Li, W. H. Universality and specificity in the self-assembly of cylinder-forming block copolymers under cylindrical confinement. *Macromolecules* **2022**, 55, 2171–2181.
- Chen, P.; Liang, H. J.; Shi, A. C. Origin of microstructures from confined asymmetric diblock copolymers. *Macromolecules* **2007**, 40, 7329–7335.
- Li, W. H.; Wickham, R. A. Self-assembled morphologies of a diblock copolymer melt confined in a cylindrical nanopore. *Macromolecules* **2006**, 39, 8492–8498.
- Yu, B.; Jin, Q. H.; Ding, D. T.; Li, B. H.; Shi, A. C. Confinement-induced morphologies of cylinder-forming asymmetric diblock copolymers. *Macromolecules* **2008**, 41, 4042–4054.
- Wang, Y.; Qin, Y.; Berger, A.; Yau, E.; He, C. C.; Zhang, L. B.; Gösele, U.; Knez, M.; Steinhart, M. Nanoscopic morphologies in block copolymer nanorods as templates for atomic-layer deposition of semiconductors. *Adv. Mater.* **2009**, 21, 2763–2766.
- Sun, Y.; Steinhart, M.; Zschech, D.; Adhikari, R.; Michler, G. H.; Gsele, U. J. W. Diameter-dependence of the morphology of PS-*b*-PMMA nanorods confined within ordered porous alumina templates. *Macromol. Rapid Commun.* **2005**, 26, 369–375.
- Li, W. H.; Wickham, R. A. Influence of the surface field on the self-assembly of a diblock copolymer melt confined in a cylindrical nanopore. *Macromolecules* **2009**, 42, 7530–7536.
- Fraaije, J. G. E. M.; Sevink, G. J. A. Model for pattern formation in polymer surfactant nanodroplets. *Macromolecules* **2003**, 36, 7891–7893.
- Higuchi, T.; Tajima, A.; Motoyoshi, K.; Yabu, H.; Shimomura, M. Frustrated phases of block copolymers in nanoparticles. *Angew. Chem. Int. Ed.* **2008**, 47, 8044–8046.
- Chen, P.; Liang, H. J.; Shi, A. C. Microstructures of a cylinder-forming diblock copolymer under spherical confinement. *Macromolecules* **2008**, 41, 8938–8943.
- Rider, D. A.; Chen, J. I. L.; Eloi, J. C.; Arsenault, A. C.; Russell, T. P.; Ozin, G. A.; Manners, I. Controlling the morphologies of organometallic block copolymers in the 3-dimensional spatial confinement of colloidal and inverse colloidal crystals. *Macromolecules* **2008**, 41, 2250–2259.
- Li, S. B.; Chen, P.; Zhang, L. X.; Liang, H. J. Geometric frustration phases of diblock copolymers in nanoparticles. *Langmuir* **2011**, 27, 5081–5089.
- Juan, Y. T.; Lai, Y. F.; Li, X.; Tai, T. C.; Lin, C. H.; Huang, C. F.; Li, B.; Shi, A. C.; Hsueh, H. Y. Self-assembly of gyroid-forming diblock copolymers under spherical confinement. *Macromolecules* **2023**, 56, 457–469.

- 39 He, X. H.; Song, M.; Liang, H. J.; Pan, C. Y. Self-assembly of the symmetric diblock copolymer in a confined state: monte carlo simulation. *J. Chem. Phys.* **2001**, *114*, 10510–10513.
- 40 Mao, X.; Wang, M.; Jin, S. H.; Rao, J. Y.; Deng, R. H.; Zhu, J. T. Monodispersed polymer particles with tunable surface structures: droplet microfluidic-assisted fabrication and biomedical applications. *J. Polym. Sci.* **2022**, *60*, 1653–1669.
- 41 Deng, R. H.; Liang, F. X.; Li, W. K.; Yang, Z. Z.; Zhu, J. T. Reversible transformation of nanostructured polymer particles. *Macromolecules* **2013**, *46*, 7012–7017.
- 42 Staff, R. H.; Rupper, P.; Lieberwirth, I.; Landfester, K.; Crespy, D. Phase behavior of binary mixtures of block copolymers and a non-solvent in miniemulsion droplets as single and double nanoconfinement. *Soft Matter* **2011**, *7*, 10219–10226.
- 43 Deng, R. H.; Li, H.; Liang, F. X.; Zhu, J. T.; Li, B. H.; Xie, X. L.; Yang, Z. Z. Soft colloidal molecules with tunable geometry by 3D confined assembly of block copolymers. *Macromolecules* **2015**, *48*, 5855–5860.
- 44 Deng, R. H.; Li, H.; Zhu, J. T.; Li, B. H.; Liang, F. X.; Jia, F.; Qu, X. Z.; Yang, Z. Z. Janus nanoparticles of block copolymers by emulsion solvent evaporation induced assembly. *Macromolecules* **2016**, *49*, 1362–1368.
- 45 Cui, T. T.; Li, X. Y.; Dong, B.; Li, X.; Guo, M. X.; Wu, L. X.; Li, B. H.; Li, H. L. Janus onions of block copolymers via confined self-assembly. *Polymer* **2019**, *174*, 70–76.
- 46 Wu, J.; Chen, S. T.; Li, S. B.; Liu, L. M.; Wang, X. H.; Lang, W. C. Simulation of surface-induced morphology transition and phase diagram of linear triblock copolymers under spherical confinement. *Chinese J. Polym. Sci.* **2023**, *41*, 166–178.
- 47 Kirkpatrick, S.; Jr, D.; Vecchi, M. Optimization by simulated annealing. *Science* **1983**, *220*, 671–680.
- 48 Kirkpatrick, S. Optimization by simulated annealing: quantitative studies. *J. Stat. Phys.* **1984**, *34*, 975–986.
- 49 Carmesin, I.; Kremer, K. The bond fluctuation method: a new effective algorithm for the dynamics of polymers in all spatial dimensions. *Macromolecules* **1988**, *21*, 2819–2823.
- 50 Larson, R. G. Monte carlo simulation of microstructural transitions in surfactant systems. *J. Chem. Phys.* **1992**, *96*, 7904–7918.
- 51 Liu, Z. Y.; Wang, Z.; Yin, Y. H.; Jiang, R.; Li, B. H. A simulation study of the self-assembly of ABC star terpolymers confined between two parallel surfaces. *Soft Matter* **2021**, *17*, 5336–5348.