

SELF-ASSEMBLY OF LINEAR TRIBLOCK COPOLYMERS UNDER CYLINDRICAL NANOPORE CONFINEMENTS*

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Abstract The self-assembly of linear ABC triblock copolymers under cylindrical confinements is investigated in two-dimensional space using the real-space self-consistent field theory. The effects of confinement degrees and preferential strengths on the triblock copolymer phase behaviors with special polymer parameters are first considered. On one hand, different confinement degrees cause different phase behaviors in nanopores with the neutral surfaces. Moreover, the strongly preferential surface fields can surpass the confinement degrees and volume fractions in determining the confined phase behaviors. On the other hand, in contrast, confined morphologies are more sensitive to the variations in the A-preferential surface field strength. Subsequently, the incompatibility degrees between different blocks are systematically varied under cylindrical nanopore confinements. Under cylindrical nanopore confinements, the morphologies are very sensitive to the variations in the incompatibility degrees. Meanwhile, nanopore confinements can affect order-disorder and order-order transition points in the bulk. The corresponding free, internal, and entropic energies as well as the order parameters are also quantitatively examined to deeply investigate the confined phase mechanisms, and a number of morphological transitions are confirmed to be of first-order. These findings may guide the design of novel nanostructures based on triblock copolymers by introducing confinements.

Keywords: Triblock copolymers; Cylindrical confinements; Self-assembly; Self-consistent field theory.

INTRODUCTION

Block copolymers consisting of two or more chemically immiscible polymer blocks can self-assemble into a rich variety of ordered structures with space periodicities on the nanometer scale. The nanostructures formed by such phase separation have attracted considerable attention due to their potential applications in various fields^[1–4]. Self-assembled nanostructures can be used as templates for preparing titania films that may enhance the solar efficiency of titania-based photovoltaic cells^[5]. Two approaches, namely, introducing confinements and multi-blocks, are usually adopted to obtain novel nanostructures based on block copolymers. Evidently, confinement surfaces influence the molecular conformation during the self-assembly process of block copolymers, resulting in either a reorientation of bulk structures on surfaces or the deviations from bulk structures^[6, 7]. On the other hand, the multi-block copolymers such as linear triblock copolymers have more complicated morphologies in bulk due to their large parameter spaces. Consequently, triblock systems under confinement conditions are more capable of obtaining novel functional nanostructures by tuning confinement and polymer parameters.

There are a large number of experimental and theoretical studies on the self-assembly of bulk triblock

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copolymers. ABC linear triblock copolymers are good benchmarks for exploring novel complicated nanostructures. In bulk, ABC linear triblock copolymers usually self-assemble into several classical-ordered structures, such as lamellar, cylindrical and spherical, which bear the same basic structural features as corresponding structures in AB diblock copolymers^[8, 9]. These periodic-ordered morphologies have been reported in several experiments^[10–14] and have been reproduced in studies on self-consistent field theory (SCFT) and Monte Carlo (MC) simulations^[15–19]. More complicated morphologies, such as lamella-cylinder combination phases, lamella-sphere combination phases, cylinder-ring combination phases and core-shell phases, have also been identified for ABC linear triblock copolymers in bulk^[19–22].

Additional constraints, such as film thickness as well as the interaction between confinement surfaces and polymer segments, also play important roles in the self-assembly of triblock copolymers in thin films. Investigations on the self-assembly of linear triblock copolymer thin films have been extensively carried out using various methods^[23–39]. Perforated lamella as well as parallel- and perpendicular-oriented cylinders are observed with increasing film thickness using a scanning force microscope (SFM)^[27]. The perforated lamella is confirmed in an SFM study on poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer thin films, where a phase diagram was constructed by varying the film thickness^[29]. On the other hand, the MC method was used to investigate asymmetric $A_{13}B_2C_3$ triblock copolymer thin films. In these copolymers, transformations among parallel and perpendicular cylinders, as well as distorted mixed structures are observed with increasing film thickness^[31]. The phase behaviors of cylinder-forming ABA block copolymer thin films have also been investigated by the dynamic density functional theory (DDFT); the phase regions are determined by the interplay between surface fields and confinement effects^[26]. Several SCFT simulations have also been performed to study the self-assembly of triblock copolymer thin films. Specifically, symmetric ABC triblock copolymers have been investigated, and the results show morphological deviations from bulk structures by tuning the surface potentials and film thicknesses^[24]. Recently, sphere-cylinder phase transitions in triblock copolymer thin films have been investigated. The phase transition points are observed to be affected by the film thickness^[37]. In these flat surface confinements, the incommensurability between the film thickness and bulk triblock copolymer periodicity, and surface fields are crucial in the conformational reconstructions of triblock copolymers. These reconstructions lead to the abovementioned rich variety of novel nanostructures. The similar confinement-induced reconstructions has also confirmed by diblock copolymer thin films^[40, 41].

A cylindrical confinement has a curved surface where an additional cylindrical symmetry is introduced, and more complex microstructures are expected. For example, lamella-forming poly(styrene-*b*-isoprene-*b*-styrene) triblock copolymers can self-assemble into concentric lamellar (CL) structures in cylindrical fibers, similar to the behaviors of diblock copolymers^[42]. These CL structures have also been reproduced in the MC and SCFT simulations^[43–45]. $A_3B_5C_5$, $A_3B_{10}C_5$ and $A_3B_5C_{10}$ triblock copolymers in cylindrical tubes can self assemble into a number of novel morphologies with various diameters and preferential surfaces^[43]. These novel morphologies, such as ABC double helixes, AB single helix+C double helixes, AB double helixes+C quadruple helixes, plate morphologies with fins, dendrites, *etc.*, were identified and located in the phase diagram between the stacked disks and the curved lamellar structures. The dependence of self-assembled morphologies on the degrees of confinements and strengths of surface preferences has also been systematically investigated for lamella-forming ABA triblock copolymers in cylindrical nanopores^[45]. For cylinder-forming triblock copolymers, an MC study has been carried out to investigate novel structures of triblock copolymers in nanopores by varying pore diameters^[46]. Furthermore, several studies have focused on the effects of chain architectures on the chain conformations of cylinder-forming ABA triblock copolymers under cylindrical confinements^[47, 48]. A simple model is proposed to explain the mean square radius of gyration for the “bridge” and “loop” chains^[47]. Although there are several polymer parameters (such as fraction volumes and incompatibility degree) involved in the abovementioned studies, the effects of polymer parameters on nanostructures in the self-assembly process are not systematically investigated and are often ignored. Confinement parameters (including confinement degrees and surface fields), especially the confinement degrees, are also not large enough to elucidate the relationship between self-assembled morphologies and confinement parameters. Consequently, the effects of wide ranges of

confinement and polymer parameter space on the self-assembly process of triblock copolymers warrant further study.

In the present work, the self-assembly of ABC linear triblock copolymers under cylindrical nanopore confinements is investigated using SCFT calculations in two-dimensional (2D) space. The self-assembled nanostructures of ABC triblock copolymers confined in cylindrical nanopores are obtained by gradually varying several system parameters over a wide range. These studied parameters include confinement degrees, surface preferential strengths and incompatibility degrees. The confinement-induced self-assembling mechanisms are then given by systematically examining morphological transitions. The total free energy per chain, entropic free energy per chain and internal energy per chain, as well as the order parameters, are also discussed to elucidate further the obtained morphological transition behaviors. Obviously, the results presented in this paper are subject to the 2D calculation, and thus may not obtain certain intrinsic 3D structures, such as perpendicular lamellae. However, the 2D structures are very meaningful and not artificial. Even in the 3D calculation, lots of 3D morphologies have the translational invariance along the z -axis, and thus 2D morphologies can present sufficient information about the 3D morphologies. Moreover, our 2D calculation can not only efficiently carry out the exploration of nanostructures over a wide range of confinement parameter space, but also provide a direct comparison between the 2D simulative results and experimental results obtained by using 2D transmission electron microscopy images. Hence, we hope our findings can provide some valuable theoretical guidance for designing novel functional nanostructures.

THEORETICAL METHOD

A system of n incompressible ABC linear triblock copolymer melts confined in a cylindrical nanopore with diameter d/R_g and volume V is considered. The diameter is rescaled by the gyration radius R_g of an ideal Gaussian chain, and all spatial lengths in the calculations are in R_g units. The ABC triblock copolymers are regarded as Gaussian chains and assumed to be monodisperse with the degree of polymerization N . The chain lengths of different A, B and C chemical incompatible blocks are $f_A N$, $f_B N$ and $f_C N$, respectively. f_A , f_B and f_C are their corresponding volume fractions, and $f_A + f_B + f_C = 1$. Differences in the statistical segment lengths, *i.e.*, $b_A = b_B = b_C = a$, where a is the Kuhn segment length, are neglected. Within the field approximation to the many-chain Edwards theory, at a temperature T , the free energy F for the n Gaussian triblock copolymer chains confined in a cylindrical pore has the following form:

$$\frac{F}{nk_B T} = -\ln\left(\frac{Q}{V}\right) + \frac{1}{V} \int d\vec{r} \left\{ \sum_i \left[\frac{1}{2} \sum_{j \neq i} \chi_{ij} N \phi_i(\vec{r}) \phi_j(\vec{r}) - W_i(\vec{r}) \phi_i(\vec{r}) + H_i(\vec{r}) \phi_i(\vec{r}) \right] - \varepsilon(\vec{r}) \left[\phi_0(\vec{r}) - \sum_i \phi_i(\vec{r}) \right] \right\} \quad (1)$$

The free energy $F/nk_B T$ can be decomposed into two physically relevant contributions^[8, 9, 49], namely,

$$\frac{F}{nk_B T} = \frac{U}{nk_B T} - \frac{S}{nk_B T}, \quad (2)$$

with

$$\frac{U}{nk_B T} = \frac{1}{V} \int d\vec{r} \left\{ \sum_i \left[\frac{1}{2} \sum_{j \neq i} \chi_{ij} N \phi_i(\vec{r}) \phi_j(\vec{r}) + H_i(\vec{r}) \phi_i(\vec{r}) \right] \right\} \quad (3)$$

and

$$-\frac{S}{nk_B T} = -\frac{1}{V} \int d\vec{r} \sum_i W_i(\vec{r}) \phi_i(\vec{r}) - \ln\left(\frac{Q}{V}\right) \quad (4)$$

In the above equations, i and j represent the A, B, and C blocks, namely $i, j \in A, B, C$. Here, $U/nk_B T$ represents

the internal energy per chain from polymer-polymer and polymer-surface interactions. In confined melts, the spatial integration is restricted to the pore volume V . The interactions among three dissimilar monomers are characterized by three Flory-Huggins interaction parameters, namely, χ_{AB} , χ_{BC} , and χ_{AC} . On the other hand, the surface preference is introduced by including an adsorption surface field $H_i(\vec{r})$ in Eq. (3). $H_i(\vec{r})$ is in the units of $\chi_0 N$ (where $\chi_0 N = 35$), reflecting short-ranged surface-polymer interactions and has the form^[50]:

$$H_i(\vec{r}) = -\chi_0 N \gamma_i \frac{\exp(\beta_1) - 1}{\exp(\beta_2) - 1}, \quad \left(\frac{d}{2} - \sigma \leq |\vec{r}| \leq \frac{d}{2}, 0 \leq \gamma_i \leq 1 \right) \quad (5)$$

$|\vec{r}|$ is the absolute distance away from the center of the confining nanopore. $\beta_1 = \frac{1}{\lambda} \cdot \left[|\vec{r}| - \left(\frac{d}{2} - \sigma \right) \right]$ and $\beta_2 = \sigma \lambda$ control the variation in the shape of the pore adsorption surface field $H_i(\vec{r})$ near the pore surface region. The decreased strength of the surface preference γ_i is non-negative, and $\gamma_i = 0$ when $|\vec{r}| \leq \frac{d}{2} - \sigma$. In the present work, the coefficient σ is set to $\sigma = 0.8R_g$, which denotes the cutoff distance of the surface field, and the decay length λ is set to $\lambda = 0.4R_g$. $\phi_i(\vec{r})$ is the monomer density normalized by local volume fractions of blocks, and is imposed with the incompressibility of the system by a Lagrange multiplier $\varepsilon(\vec{r})$. In other SCFT calculations, the incompressibility constraint is set to be a step function^[51] or a cosine function^[52]. In recent years, Meng and Wang have suggested that the microstructures of equilibrium states are not significantly affected by the functional form for the incompressibility constraint^[53]. In the present work, we generalize the incompressibility constraint to be the form

$$\phi_0(\vec{r}) = \sum_i \phi_i(\vec{r}) \quad (6)$$

with $\phi_0(\vec{r}) = 1$ inside the cylindrical nanopore, $\phi_0 = 0.5$ on the lattice near the boundary, and $\phi_0 = 0$ on the boundary. The generalization ensures the representation of an impenetrable boundary and causes the triblock copolymers to be confined inside the cylindrical space. On the other hand, $-S/nk_B$ in Eq. (4) denotes the entropic free energy per chain from the chain stretching. The partition function Q is for a single chain in the mean chemical potential fields $W_i(\vec{r}) = Nw_i(\vec{r})$ produced by surrounding chains, where $W_i(\vec{r})$ conjugates to $\phi_i(\vec{r})$, and can be expressed in terms of propagators $q(\vec{r}, s)$ and conjugated $q^+(\vec{r}, s)$. The contour length is parameterized with a variable s that starts from one end ($s = 0$) to the other ($s = 1$), where the contour step size is set to $\Delta s = 1/N$. The propagators $q(\vec{r}, s)$ and $q^+(\vec{r}, s)$ satisfy the following modified diffusion equations

$$\frac{\partial q(\vec{r}, s)}{\partial s} = R_g^2 \nabla^2 q(\vec{r}, s) - W_{k(s)} q(\vec{r}, s) \quad (7)$$

and
$$-\frac{\partial q^+(\vec{r}, s)}{\partial s} = R_g^2 \nabla^2 q^+(\vec{r}, s) - W_{k(s)} q^+(\vec{r}, s) \quad (8)$$

with the initial conditions $q(\vec{r}, 0) = 1$ and $q^+(\vec{r}, 1) = 1$, respectively. $k(s)$ is the subscript of $W_{k(s)}$; $k(s) = A$ if $0 \leq s \leq f_A$ and $k(s) = B$ if $f_A < s \leq f_A + f_B$; otherwise, $k(s) = C$. The product of $q(\vec{r}, s)q^+(\vec{r}, s)$ proportional to the distribution of the S_{th} segment provides the partition function for a molecule with its S_{th} segment at the position $\vec{r}$. Consequently, the partition function Q for an unconstrained chain evaluated by summing all possible position $\vec{r}$ of the S_{th} segment is given by $Q = \int d\vec{r} q(\vec{r}, s)q^+(\vec{r}, s)$.

To obtain the equilibrium microstructure, the total free energy per chain of confined triblock copolymers should be minimized to a stable value. The minimization of the free energy per chain with respect to the

monomer densities and mean fields leads to the following set of self-consistent mean-field equations:

$$W_A(\vec{r}) = \chi_{AB}N(\phi_B(\vec{r}) - f_B) + \chi_{AC}N(\phi_C(\vec{r}) - f_C) + \varepsilon(\vec{r}) + H_A(\vec{r}), \quad (9)$$

$$W_B(\vec{r}) = \chi_{AB}N(\phi_A(\vec{r}) - f_A) + \chi_{BC}N(\phi_C(\vec{r}) - f_C) + \varepsilon(\vec{r}) + H_B(\vec{r}), \quad (10)$$

$$W_C(\vec{r}) = \chi_{AC}N(\phi_A(\vec{r}) - f_A) + \chi_{BC}N(\phi_B(\vec{r}) - f_B) + \varepsilon(\vec{r}) + H_C(\vec{r}), \quad (11)$$

$$\phi_A(\vec{r}) = \frac{V}{Q} \int_0^{f_A} ds q(\vec{r}, s) q^+(\vec{r}, s), \quad (12)$$

$$\phi_B(\vec{r}) = \frac{V}{Q} \int_{f_A}^{f_A+f_B} ds q(\vec{r}, s) q^+(\vec{r}, s), \quad (13)$$

$$\phi_C(\vec{r}) = \frac{V}{Q} \int_{f_A+f_B}^1 ds q(\vec{r}, s) q^+(\vec{r}, s). \quad (14)$$

Here, Eqs. (6) and (7)–(14) are directly solved using a combinatorial screening method based on the real space implementation of the SCFT, originally proposed by Drolet and Fredrickson^[54, 55]. The implementation is suitable in exploring the novel morphologies of copolymers without requiring assumptions as to the system symmetry, and is started by randomly generating the initial values of the fields $W_i(\vec{r})$. The diffusion equations are solved using a Crank-Nicholson scheme by updating $W_i(\vec{r})$. Then, Q and the right-hand sides of Eqs. (12)–(14) are evaluated to obtain new expression values for the volume fractions of A, B, and C blocks. At the same time, $\varepsilon(\vec{r})$ is obtained by solving Eqs. (6) and (9)–(11). Subsequently, the above obtained quantities are substituted into Eq. (1) to obtain the free energy per chain. To obtain the resulting density profiles and the free energy independent of its particular value, the above obtained quantities are updated by the linear mixing of new and old solutions. These steps are repeated until the relative difference of free energy between the sequence iteration steps is reduced to 10^{-11} , i.e., $\Delta F/nk_B T < 10^{-11}$. Each minimization is run several times using different initial random potential fields $W_i(\vec{r})$ to ensure that the exact equilibrium morphology has been obtained. In this manner, the novel ordered morphologies of the confined triblock copolymers can be obtained for these specific system parameters.

In the present study, the SCFT equations are implemented in a 2D space in all calculations. $\Delta x = \Delta y = 0.2R_g$ is taken as the grid size, and the chain contour length is divided into 200 monomers, similar to our previous works^[56, 57]. Three types of system parameters are used to investigate their corresponding effects. Specifically, the degree of confinement d/R_g is changed from 6 to 30 with an increment of $\Delta d/R_g = 2$, the surface preference strength $\gamma_{A(B)}$ is changed from 0 to 1 with an increment of $\Delta\gamma_{A(B)} = 0.09$, and the incompatibility degrees $\eta\chi_0 N \equiv \chi_{AB}N = \chi_{BC}N = \chi_{AC}N$ (where $\chi_0 N = 35$) with η are changed from 0.08 to 1.29 with an increment of $\Delta\eta = 0.06$ as well as from 1.29 to 2.43 with $\Delta\eta = 0.14$. Some interesting typical phase behaviors can be expected by varying these phase parameters over broad ranges.

RESULTS AND DISCUSSION

To conveniently compare with the bulk phase structures of the selected symmetric triblock copolymer models, we first perform the SCFT simulation on the bulk phase behaviors of these studied copolymer models (with $f_A = f_C$) in the paper. The simulation results present their corresponding bulk structures (satisfying $\eta = 1$), which are lamellae (with $f_B = 0.2$ or 0.4) and cylinders (with $f_B = 0.6$), respectively^[15, 17]. These bulk phase structures and their corresponding periods are shown in Figs. 1(a)–1(c). Here, all morphologies obtained are presented in the

form of three different colors (red, green, and blue) denoting the density distributions of monomers belonging to the A-, B-, and C-blocks, respectively. In Figs. 1(a) and 1(b), we see that the periods of “three color” lamellar structures with $f_B = 0.2$ and $f_B = 0.4$ are almost similar, which are $L_x = 5.65R_g$ and $L_x = 5.6R_g$, respectively. The similarity of lamellar periods can be attributed to the fact that the variations in volume fractions and interactions/incompatibility degrees have less influence on the lamellar period. However, as shown in Fig. 1(c), the period of cylinders with $f_B = 0.6$ satisfies $L_x = 5.1R_g$ and $L_y = 5.34R_g$, which is different from those of lamellar structures. The difference is mainly caused by different structural symmetries.

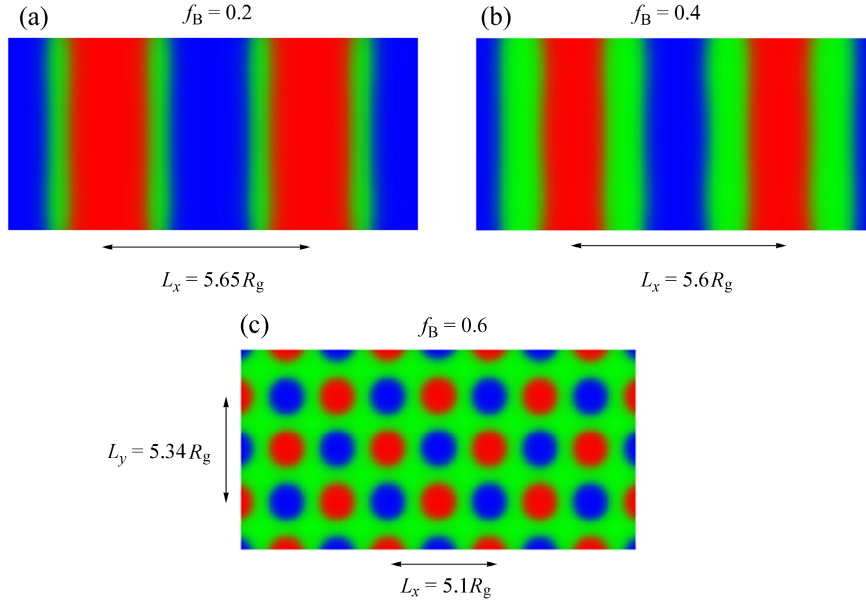


Fig. 1 Bulk structures of symmetric triblock copolymers with $f_A = f_C$ and $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35$ (*i.e.*, $\eta = 1$): (a) lamellar structures of symmetric triblock copolymers with $f_B = 0.2$, (b) lamellar structures of symmetric triblock copolymers with $f_B = 0.4$ and (c) cylindrical structures of symmetric triblock copolymers with $f_B = 0.6$

Then, the effects of confinement degrees, preferential strengths and incompatibility degrees on the self-assembly of linear triblock copolymers under cylindrical confinements are investigated. The effect of each individual factor is clearly observed by changing the corresponding parameter and setting the other phase parameters to specific fixed values.

A. Confinement Degrees

The incompatibility degrees $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 35$ (*i.e.*, $\eta = 1$), which constrain the triblock copolymers to be located in an experimentally significant intermediate-segregation regime, are chosen^[9, 58]. The volume fractions of middle blocks f_B are set as 0.2, 0.4 and 0.6, respectively. Two end-blocks A and C of these symmetric triblock copolymers satisfy $f_A = f_C$. Under these considerations, the phase structures and their corresponding energies are obtained as functions of d/R_g , shown in Figs. 2 and 3, respectively.

Figure 2 shows the phase structures and their corresponding entropic energies as functions of confinement degrees in pores with neutral surfaces. Figure 2(a) displays a series of random phase structures (RAN) at $f_B = 0.2$ over a wide range. These RAN phases are similar to those observed in a previous MC work under similar confinements where the diblock copolymers were found to be symmetric^[59]. The results indicate that the influence of a mid-block can be almost neglected in the self-assembling process of a RAN phase when its volume fraction is relatively smaller (namely, $f_B \leq 0.2$), which has also been confirmed in the bulk phase diagram of ABC triblock copolymers^[15]. The slight difference is that the triblock copolymers exhibit RAN phases with sandwich-type structures. At the same time, the difference also demonstrates that the short middle B blocks are

preferred to be enriched between A- and C-rich lamellae rather than on the pore walls under the neutral nanopore confinements, which results from the special position of the middle B block in the molecular architecture. Subsequently, a series of ordered structures with cylindrical arrangements almost over all ranges for triblocks with $f_B = 0.4$ and 0.6 are observed. Interestingly, several heterogeneous concentric lamellar (HCL) structures appear in the large pore diameter region in the $f_B = 0.4$ case. There is more than one block in each layer, which is similar with hierarchical concentric lamellar structures observed in the ABC star triblock copolymers^[60]. The morphological transitions are relatively simple, and the cylindrical symmetry of the confined morphologies is gradually enhanced with continuously increasing d/R_g in large pore diameter regions. Such phase transition behaviors may be attributed to the two reasons. First, cylindrical confinement requires copolymers to break their natural symmetries to meet the cylindrical symmetry imposed by the confinement geometric boundary^[7, 61]. The weak preference resulting from entropic effects^[53] of a neutral nanopore for short blocks (namely, A and C blocks) can partially release these additional free energies caused by deforming bulk structures. Second, large pores can provide a sufficient space to fit the cylindrical arrangement in the confined morphologies since the structural frustration in the form of chain stretching can be distributed over more layers of structures. Consequently, the structural frustration from the confinement can progressively weaken and the effect of the confinement degree on morphologies also obviously weakens with increasing d/R_g from 10 to 30. However, there is an obvious morphological transition between non-cylindrically symmetric structures for the narrow pores with $d/R_g < 10$, especially in the $f_B = 0.4$ case. The findings indicate that the variations in small pore diameters significantly influence the morphologies and the confinements are severe in the narrow pore region. Notably, the effects of severe confinements have also been observed in previous investigations on the self-assembly of cylindrically confined diblock^[62–64] and triblock^[43, 48] copolymers.

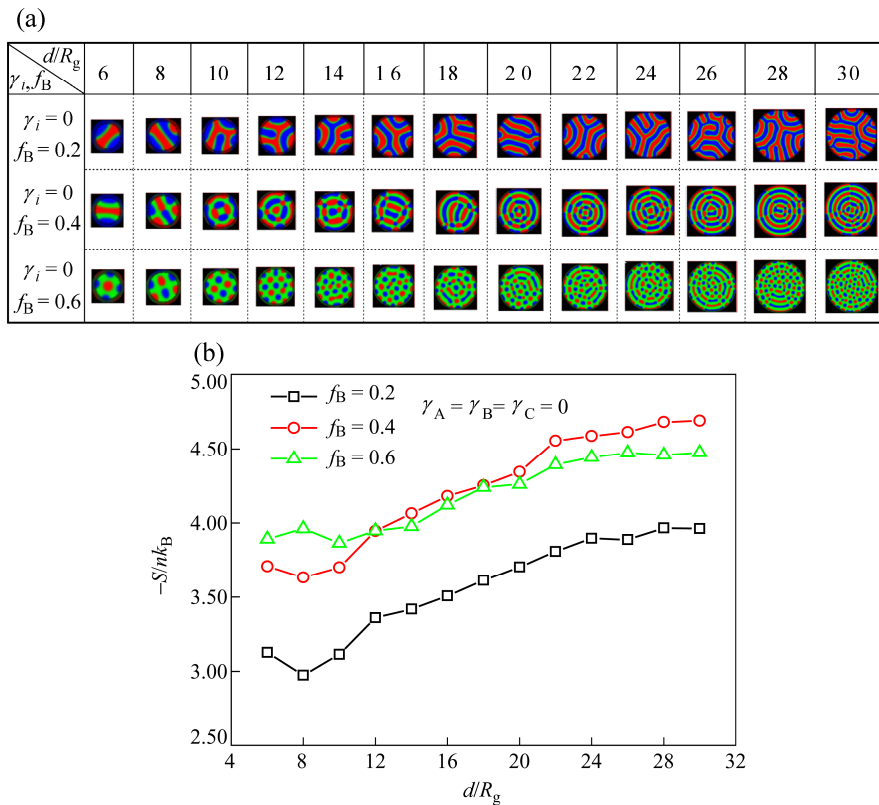


Fig. 2 The dependences of nanostructures and entropic energies on the confinement degrees for the symmetric triblock copolymers (with $f_A = f_C$, $\eta = 1$) confined in nanopores with neutral surfaces (*i.e.*, $\gamma_A = \gamma_B = \gamma_C = 0$): (a) nanostructures of linear ABC triblock copolymers as functions of confinement degrees d/R_g for various f_B values, (b) corresponding entropic energies, $-S/nk_B$, as functions of confinement degrees d/R_g for several f_B values

Figure 2(b) shows the dependence of entropic energies on the confinement degrees. Although the general trend of entropic energies, $-S/nk_B$, gradually increases with d/R_g , there are several differences between small and large degrees of confinement. Specifically, $-S/nk_B$ slowly increases when the confinements are not severe enough in large pores with $d/R_g = 14\text{--}30$, whereas they fluctuate at severe confinements with $d/R_g = 6\text{--}12$. The fluctuation reflects the significant effects of the confinement degrees on the morphologies in the severe confinement region. The slow variation in $-S/nk_B$ indicates the similar morphologies of triblock copolymers under mild confinements. In fact, confined chains have a natural tendency to extend in space and thus chains are continuously stretched to fill a much larger space as d/R_g increases, which causes increasing entropic losses^[50, 65]. Subsequently, it is reasonable to deduce the fact that the chain conformation will approach to that in the bulk state^[45] when the confinement is mild enough, in which the chain stretching nature can be adequately released and the entropic energy penalties reach maximum values and almost maintain unchanged with d/R_g .

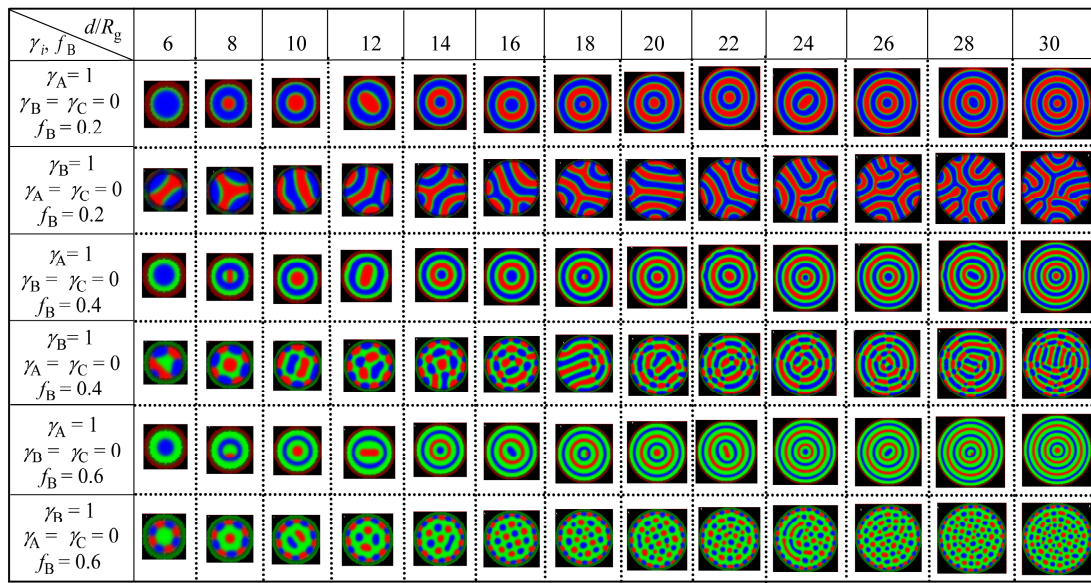


Fig. 3 The dependences of nanostructures on the confinement degrees for the symmetric triblock copolymers (with $f_A = f_C$, $\eta = 1$) confined in nanopores with A-preferential surfaces (i.e., $\gamma_A = 1$, $\gamma_B = \gamma_C = 0$) and B-preferential surfaces (i.e., $\gamma_B = 1$, $\gamma_A = \gamma_C = 0$), respectively. Nanostructures are as functions of confinement degrees d/R_g for various f_B values.

Different phase behaviors of triblock copolymers in the pores with preferential surfaces are expected. Here, we consider two types of preferential surfaces, namely, A-preferential ($\gamma_A = 1$, $\gamma_B = \gamma_C = 0$) and B-preferential surfaces ($\gamma_B = 1$, $\gamma_A = \gamma_C = 0$). Figure 3 presents the phase structures as functions of confinement degrees in nanopores of the two types of preferential surfaces. Generally speaking, the cylindrical symmetries of the morphologies in Fig. 3 are obviously enhanced relative to those in Fig. 2. Specifically, the CL structures with ABC sequence domains are observed in the strongly A-preferential surface field. In the A-preferential surface field case, these CL surface reconstructions are independent of the confinement degrees and volume fractions of mid-blocks, as shown in Fig. 3. As aforementioned, CL structures have also been experimentally and theoretically studied for triblock copolymers under cylindrical confinements^[42–45]. Here, the variations in the volume fraction of mid-blocks only affect the layer thicknesses of CL structures, which has also been mentioned in bulk triangular phase diagrams of triblock copolymers and is similar to that of confined diblock copolymers^[15, 50]. The minus adsorption surface energies of the nanopores for A-blocks can well counteract the extra free energies resulting from the deformation of bulk structures into CL structures. Thus, the CL structures dominate in the strongly A-preferential surface field case, which is completely different from that in Fig. 2.

Simultaneously, several obvious morphological deviations from those in the neutral surface case are also found with $f_B = 0.4$ or 0.6 due to the strongly B-preferential surface field. One such deviation is that a perfect B-rich concentric lamella appears in the outermost layer. Another is that an unbroken circular ring consisting of alternate A- and C-rich domains is independent of d/R_g , and appears in the first AC layer counted from the pore walls. In this case, the strongly B-attractive surface field sufficiently draws the B blocks to wet the pore wall. Subsequently, the A and C blocks are pushed away into the first AC layer underneath the outermost B-rich concentric layer and form an unbroken circular ring. The differences illustrates the strongly attractive surface fields can significantly enhance the symmetric constraint from the confining geometric boundary over the confinement degree. However, due to the special position of B blocks, the phase behaviors in the strongly A- and B-preferential surface field cases present some differences. Partial similarities of morphologies are also found for several f_B values in the strongly B-preferential and neutral surface field cases. When the mid-blocks are short *i.e.*, $f_B = 0.2$, the confined triblock copolymers exhibit similarly random phases to those in the neutral surface, indicating that the effect of the B-preferential surface field can be neglected in this case^[56]. The similarity can be attributed to the fact that the extreme short B block length as well as the “loop” conformation constraint (resulting from the special position of B blocks in the molecular chain architecture) significantly weakens the attractive effect of the B-preferential surface field. Moreover, some morphological similarities of the inner layers between the neutral and B-preferential surfaces are also observed when the mid-blocks are longer ($f_B = 0.4$ or 0.6) and especially the confinement degrees are relatively large ($d/R_g = 14\text{--}30$). Such similarities can be well understood by considering the fact that the B-attractive surface field is short-range interaction as well as the “loop” conformation constraint of B blocks, which result in the sharply weakening of the B-attractive surface field in the inner region of the large pore. Consequently, the B-attractive surface field exhibits less influence on the inner layer structures in these large pore regions^[46].

B. Preferential Strengths

The different morphologies observed at strong $\gamma_{A(B)}$ values prompt us to study the influence of preferential surfaces on the phase behaviors of confined triblock copolymers. Three types of confinement degrees, *i.e.*, $d/R_g = 10, 20$, and 30 , with $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = \chi_0N = 35$ are selected to systemically investigate such effects, as shown in Figs. 4 and 5. For type $d/R_g = 10$, Fig. 4 displays the morphologies and their corresponding internal energies as functions of the attractive strength $\gamma_{A(B)}$ for various f_B values, respectively. For the A-preferential surfaces, the morphological transition subsequently undergoes four types of morphologies in the $f_B = 0.2$ or 0.4 case, namely, the initial morphologies ($\gamma_A = 0$), perfect CL structures, defective concentric lamellar (DCL) structures (or complex morphologies) and CL structures. The CL structures initially appear over the range of $\gamma_A = 0.09\text{--}0.43$ in the $f_B = 0.2$ case, and over $\gamma_A = 0.09\text{--}0.17$ in the $f_B = 0.4$ case, respectively. Subsequently, with continuously increasing γ_A , DCL structures with non-constant mean curvature surfaces occur over a range of $\gamma_A = 0.51\text{--}0.77$ in the $f_B = 0.2$ case, and over $\gamma_A = 0.26\text{--}0.60$ in the $f_B = 0.4$ case. Similar DCL structures have been observed in a previous study on cylindrically confined diblock copolymers^[65]. The phenomenon of some complex morphologies (such as V- or U-shape lamellae) in relatively weak or intermediate adsorption surface field strength cases has also been observed in previous investigations of the self-assembly of diblock^[63] or triblock^[45] copolymers confined in cylindrical nanopores. The occurrence of the complex structures is claimed to reflect the importance of the competition between the confinement and surface preference. Again, the CL structures stably exist over the range of $\gamma_A = 0.86\text{--}1.00$ in the $f_B = 0.2$ case, and over $\gamma_A = 0.69\text{--}1.00$ in the $f_B = 0.4$ case. The reoccurrence of CL structures may be attributed to the fact that the surface energies between A-blocks and pore surfaces dominate in the strongly preferential surface fields and are large enough to compensate for this conformational penalty^[63]. This similar conclusion is also confirmed in a previous investigation on the effect of the chain architecture and surface energies on the ordering behavior of lamella- and cylinder-forming block copolymers^[32]. Generally, there is a relatively simple morphological transition sequence in the $f_B = 0.6$ case. The triblock copolymers only undergo one transition from mixed morphologies ($\gamma_A = 0.00\text{--}0.43$) to CL morphologies ($\gamma_A = 0.51\text{--}1.00$). Notely, these mixed structures consist of A- and C-rich parallel cylinders covered by an A-wetting layer, which are similar to those in previous observation work^[48, 51].

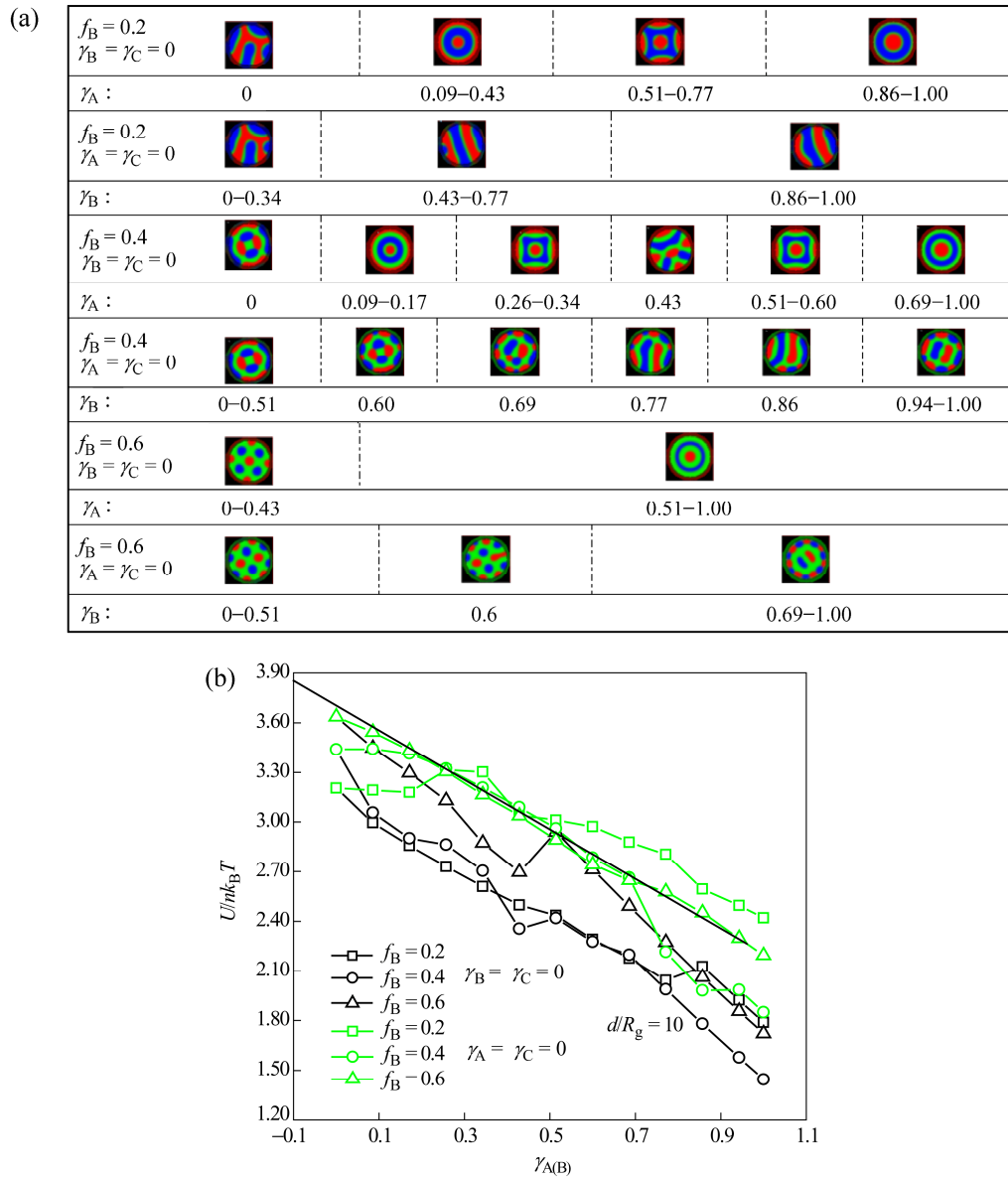


Fig. 4 The dependences of nanostructures and internal energies on the preferential strengths for the symmetric triblock copolymers (with $f_A = f_C$, $\eta = 1$) confined in nanopores with A-preferential surfaces and B-preferential surfaces, respectively: (a) nanostructures as functions of preferential strength $\gamma_{A(B)}$ for various f_B values, (b) corresponding internal energies, $U/nk_B T$. The confinement degree is selected to be $d/R_g = 10$, and f_B is selected to be 0.2, 0.4, 0.6, respectively.

For the B-preferential surfaces, the morphologies are almost unchanged with γ_B over the region of $\gamma_B = 0.43$ –1.00 in the $f_B = 0.2$ case. The triblock copolymers maintain the same morphologies as those in the neutral surfaces over the range of $\gamma_B = 0.00$ –0.34, which reflects the insufficient strength of the surface fields for deforming the initial structure. Similar invariable morphologies are also observed over the range of $\gamma_B = 0.00$ –0.51 in both the $f_B = 0.4$ and 0.6 cases, indicating that the initial structures are insensitive to the weak surface fields. For the $f_B = 0.4$ case, a long period of partial adjustments ($\gamma_B = 0.60$ –1.00) with slight defects occurs in the inner regions to meet the competition between the internal and entropic energies. However, the morphological

transitions are relatively simple in the $f_B = 0.6$ case when the B-preferential surface field is varied and only two distinct morphologies are observed. Similar simple morphological transitions as functions of γ_B are supported by the investigations of the self-assembled morphologies of triblock copolymer films^[31, 43]. This simplicity arises from the “loop”^[44–47] conformation constraint of B-blocks in ABC triblock copolymers, in which a high entropic energy penalty is required to pull B blocks to the surfaces such that the effect of the B-preferential surface field is sharply weakened^[25, 32, 43]. By comparing the three cases with various f_B values, the lengths of mid-blocks are recognized to be crucial for the formation of complex structures in pores with B-preferential surfaces because of their architectures^[32, 47, 66].

Figure 4(b) shows their corresponding internal energies as functions of $\gamma_{A(B)}$ for various f_B values. As a whole, the internal energies continuously decrease with increasing $\gamma_{A(B)}$. The internal energies are contributed by the two components, namely, repulsion interactions from different blocks and adsorption interactions between polymers and surfaces, as demonstrated in Eq. (3). A previous report has shown the internal energy curves as functions of the incompatibility degrees of multi-block copolymers in bulk state^[49]. In the present study, variations in the internal energies with the preferential strength $\gamma_{A(B)}$ are investigated. The adsorption energies between the polymers and nanopore surface fields are of negative values; hence, the increasing $\gamma_{A(B)}$ directly results in the descending trends of the internal energies, as shown in Fig. 4(b). We can see that the $U/nk_B T$ curves as functions of γ_A are underneath those as functions of γ_B . The phenomenon again illustrates that the end-blocks are more easily attracted by the surface to pore walls than the mid-blocks. The internal energy gap caused by the factual adsorption effect difference between γ_A and γ_B (where γ_A and γ_B are of the same values) is decreased with increasing f_B . This decreasing trend of the internal energy gap can be explained by the conjecture that as f_B increases, the behavior of middle B blocks is more and more similar to that of end-blocks. Second, although the internal energies have some general characteristics as abovementioned, some obvious fluctuations appear in the $f_B = 0.4$ case. This finding is consistent with our observations on their corresponding morphologies where there are some complicated subtle (partial) morphological transitions with $\gamma_{A(B)}$.

Figure 5(a) shows the $-S/nk_B$ curves as functions of $\gamma_{A(B)}$ for the symmetric polymers with $f_B = 0.4$ and a fixed pore with $d = 20R_g$, where the representative morphologies are inserted in corresponding positions. There are four morphologies, namely, HCL at $\gamma_A = 0$, CL at $\gamma_A = 0.09–0.69$, DCL at $\gamma_A = 0.77–0.86$ and CL at $\gamma_A = 0.94–1.00$. However, the morphologies as a function of γ_B almost remain unchanged in all regions of $\gamma_B = 0.00–1.00$. Generally speaking, these morphological transition sequences as functions of $\gamma_{A(B)}$ are very similar to those in Fig. 4(a). However, there are morphological deviations between the two different confinement degrees. First, the cylindrical symmetry of the initial morphologies with $d = 20R_g$ is obviously enhanced relative to that with $d = 10R_g$. Second, the DCL structures with $d = 20R_g$ occur in a much smaller region, and are of slighter defects. These deviations indicate that due to confinement, the frustration in the $d = 20R_g$ case is much more mild than that in the $d = 10R_g$ case. Figure 5(b) shows the $\gamma_{A(B)}$ dependence of free energies of the confined triblock copolymers with $d = 30R_g$ and $f_B = 0.6$. For the B-preferential surface, the initial morphology almost remains unchanged in all regions of γ_B , which is consistent with its variation in free energy. However, this is not the case in the A-preferential surfaces where the maximum free energy value appears at a fixed γ_A value. In particular, the general trend of $F/nk_B T$ with γ_A initially increases ($\gamma_A = 0.00–0.34$), and then decreases ($\gamma_A > 0.34$), which is in agreement with that for cylindrically confined diblock copolymers^[50]. The free energy gives a maximum value at $\gamma_A = 0.34$. Subsequently, with increasing γ_A from 0.34 to 1, the free energy is gradually compensated by the negative surface energy, where the absolute value of the surface energy gradually increases and finally dominates the minimum free energy. The $F/nk_B T$ curve as a function of γ_A is also underneath that of γ_B in the region of $\gamma_{A(B)} = 0.69–1.00$. This phenomenon can mainly be attributed to the “loop” conformation constraint of B-blocks, which causes high entropic energy penalties required to pull B blocks to pore surfaces.

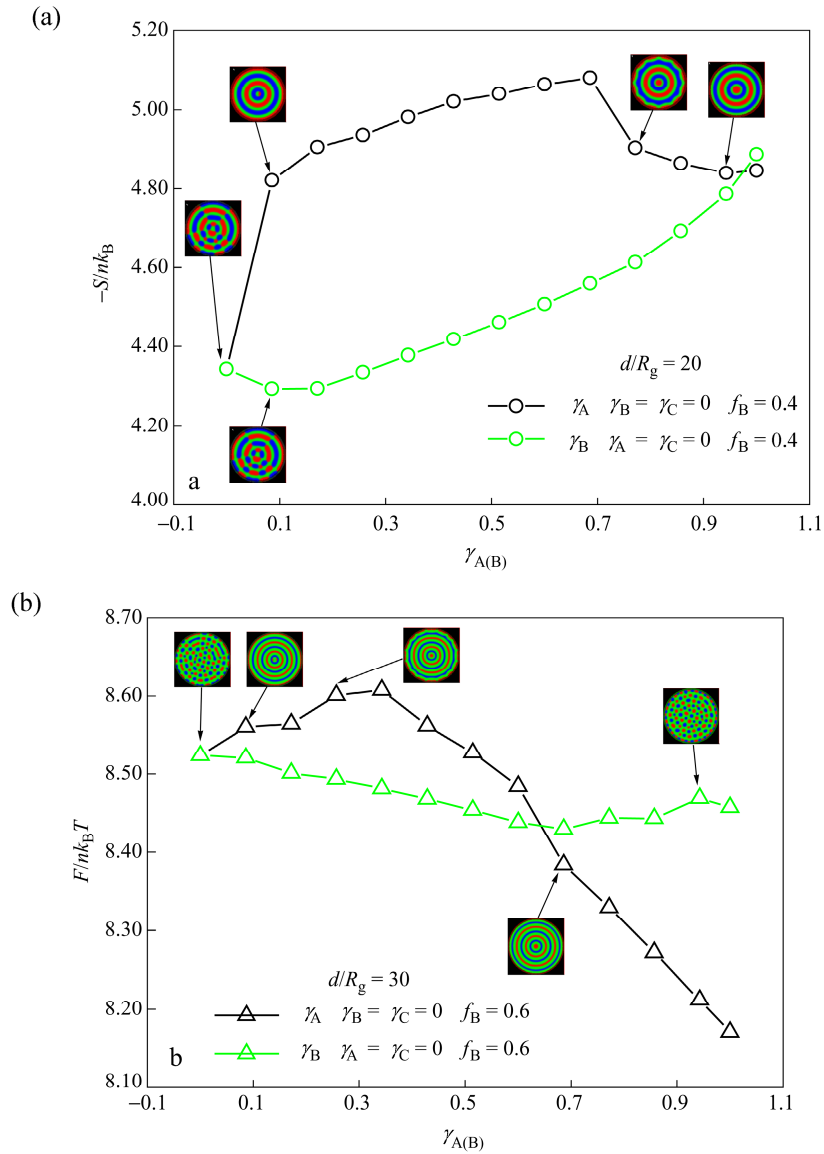


Fig. 5 The dependences of entropic and free energies on the preferential strengths for the symmetric triblock copolymers (with $f_A = f_C$, $\eta = 1$) confined in nanopores with A-preferential surfaces and B-preferential surfaces, respectively: (a) entropic energies, $-S/nk_B$, as functions of preferential strength $\gamma_{A(B)}$ for $f_B = 0.4$ and $d = 20R_g$, (b) free energies, $F/nk_B T$, as functions of preferential strength $\gamma_{A(B)}$ for $f_B = 0.6$ and $d = 30R_g$

C. Incompatibility Degrees

The effect of incompatibility degrees, $\chi_{ij}N$, on the phase behaviors of confined triblock copolymers is then investigated. Figure 6 shows the phase structures as a function of η for a series of χ and f_B values. These phase structures in Fig. 6 correspond to the three types of surface fields. According to the values of η , the phase segregation degrees are roughly divided into three scales for clarity, *i.e.*, the weak-segregation regime ($0.08 < \eta < 0.71$), the intermediate-segregation regime ($0.71 < \eta < 1.71$), and the strong-segregation regime ($1.71 < \eta < 2.43$). The incompatibility degree corresponds to the annealing temperature, which is crucial to the order-disorder transitions (ODTs). ODTs are observed for the confined triblock copolymers with various f_B values and neutral surfaces, as shown in Fig. 6. The ODT points are shifted to the right side with increasing f_B , *i.e.*, $\eta_{ODT} =$

0.37, 0.54, 0.77, and 1.71 for $f_B = 0.2, 0.4, 0.6$, and 0.8 , respectively. With increasing f_B , the volume fractions of A and C blocks are gradually decreased. Especially for $f_B = 0.8$, the minority components A and C are easily mixed and pulled free from their domains, swelling the matrix and evolving to disordered (DIS) phases.

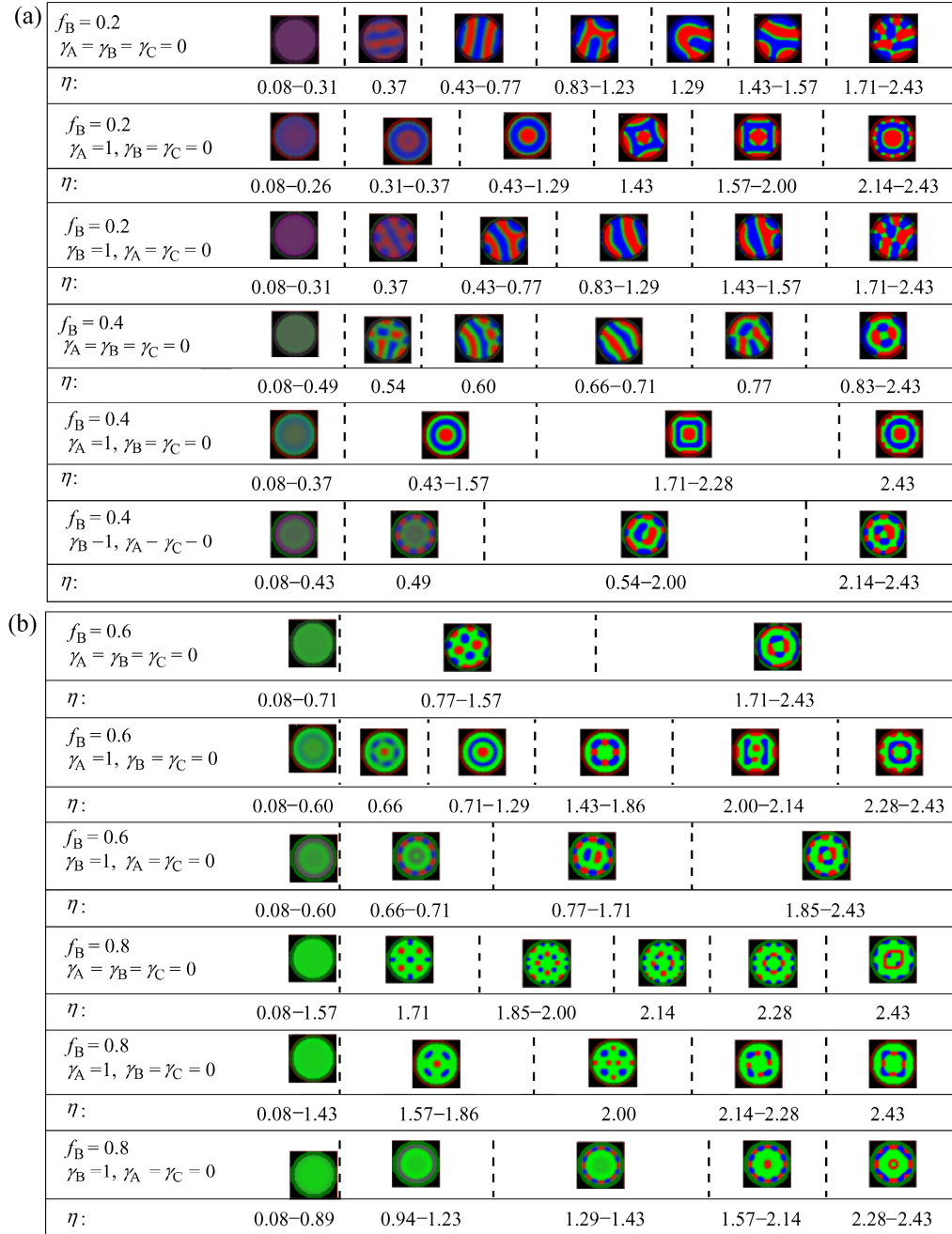


Fig. 6 The dependences of nanostructures on the incompatibility degrees for the symmetric triblock copolymers (with $f_A = f_C$) confined in nanopores with the A-preferential surfaces ($\gamma_A = 1, \gamma_B = \gamma_C = 0$) and B-preferential surfaces ($\gamma_A = 1, \gamma_B = \gamma_C = 0$), respectively: (a) $f_B = 0.2$ and 0.4 , (b) $f_B = 0.6$ and 0.8

The confinement degree is selected to be $d/R_g = 10$.

Consequently, the corresponding η_{ODT} obviously shifts to a high value. The shifting trend of the η_{ODT} value as f_B continuously increases from 0.2 to 0.8 is very similar to that in the mean-field phase diagrams (*i.e.*, $\chi N - f$ phase diagrams) of ABA triblock copolymers^[67]. Generally, for symmetric confined triblock melts with the same f_B value, the η_{ODT} value in the neutral surface field case is relatively higher than that in strongly preferential surface fields.

We see that when the strongly preferential surface fields are introduced, some weakly/partially ordered phase structures (with partially mixed blocks) instead of DIS structures occur in some weak-segregation regimes. For instance, for $f_B = 0.4$, some weakly ordered structures are present in the weak-segregation regime of $0.08 < \eta < 0.37$ in the strongly A-preferential surface field. The reason is that strongly preferential surface fields promote phase segregations between the liked and disliked blocks by surfaces^[58]. Previous studies based on mean fields have reported that the ODT point is dependent on the cylindrical confinement, and that thin film confinement results in the shift of order-order transition (OOT) points for triblock copolymers^[37, 51, 68, 69]. In terms of the order-order transitions (OOTs), the morphological transitions of confined triblock copolymers are much more complicated than those of bulk cases, indicating that confined morphologies are more sensitive to interaction parameter variations between different species^[51, 58, 70]. In the strong-segregation regime, the confined morphologies almost remain unchanged with η , indicating that the variations in η have less influence on the morphological transitions in this regime. The general trends of morphological transitions with increasing η for the symmetric triblock copolymers are similar. Specifically, the transitions are from some weakly ordered DIS simple structures to relatively complex frustration phases^[57]. Here, the occurrence of these complex frustration phases can be attributed to the fact that packing frustration continuously increases with the degree of segregation^[8,9]. Furthermore, the partially cylindrical symmetries of these complex phases originate from the symmetry constraint in the confining geometric boundary.

In order to elucidate further the ODTs and OOTs, we introduce the order parameter, $\langle |\phi_A - \phi_C| / \phi_0 \rangle$, as functions of η with $d/R_g = 10$ and $f_A = f_C$ as well as $f_B = 0.6$ in the cases of neutral (with $\gamma_A = \gamma_B = \gamma_C = 0$) and strongly A-preferential surfaces (with $\gamma_A = 1$, $\gamma_B = \gamma_C = 0$), as shown in Fig. 7. The order parameter, $\langle |\phi_A - \phi_C| / \phi_0 \rangle$, presents the average difference between A and C density concentration. Thus, the values of $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ means microphase segregated degrees. Here, the zero values of $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ denote DIS structures and the nonzero values mean ordered phase structures (including weakly ordered structures). In Fig. 7, the general $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ curve in the neutral surface field case is underneath the one in strongly A-preferential surface field case. Especially in the region of $0.08 < \eta < 0.71$ (with $\gamma_A = 1$, $\gamma_B = \gamma_C = 0$), the values of $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ are nonzero, where some weakly ordered/ segregated phase structures occur. The obvious difference can be attributed to the effect of the strongly A-preferential surface field, which enhances the phase-segregated degree between blocks A and C. On the other hand, except for the weak-segregation regime, the general variation trends of $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ curves as η increases are similar in the intermediate- and strong-segregation regimes. For instance, in the neutral surface field case, the values of $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ keep zero in the weak-segregation regime, where the incompatibility degrees η are not sufficient to induce phase-segregation and thus some DIS structures occur. As η further increases, an ODT is found in the region of $0.71 < \eta < 0.77$, where the $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ curve presents an obvious jump. Subsequently, as η continues increasing in the intermediate-segregation regime, the ordered phase-segregated degrees are continuously enhanced and some OOTs are observed. We find that these ODTs and OOTs are first-order in Fig. 7. Whereas, as η continuously increases in the strong-segregation regime with $1.71 < \eta < 2.43$, the values of $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ almost keep constant, which implies the variation of η has less influence on the ordered phase-segregated degree.

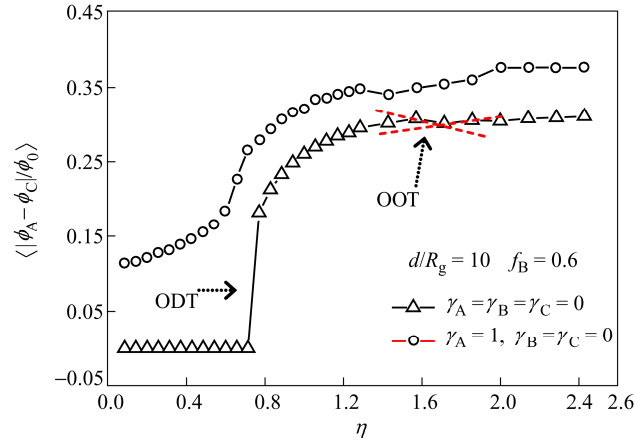


Fig. 7 Order parameter $\langle |\phi_A - \phi_C| / \phi_0 \rangle$ as functions of incompatibility degrees η with $d/R_g = 10$ and $f_A = f_C, f_B = 0.6$ in the cases of neutral (with $\gamma_A = \gamma_B = \gamma_C = 0$) and A-preferential surfaces (with $\gamma_A = 1, \gamma_B = \gamma_C = 0$)

CONCLUSIONS

A systematic study on the self-assembly of ABC linear triblock copolymers under cylindrical confinements in 2D space is performed using the real-space SCFT. The effects of confinement degrees, preferential strengths and incompatibility degrees on the self-assembly of confined triblock copolymers are investigated by singly varying the corresponding parameter. Lots of novel nanostructures are obtained over a large phase parameter space. Meanwhile, their corresponding free, entropic and internal energies as well as order parameters are discussed to deeply illustrate these phase transition behaviors. The main findings are as follows:

First, the different confinement degrees cause different morphologies in the small and large nanopore diameter regions. Severe confinement results in non-cylindrical symmetry structures, and mild confinement causes morphologies with cylindrical symmetry in pores with neutral surfaces. Furthermore, the symmetric triblock copolymers clearly exhibit different phase behaviors in the pores with strongly A- and B-preferential surfaces. For several selected f_B values, CL structures independent of d/R_g are observed in the strongly A-preferential surface field. However, some RAN, HCL and mixed HCL structures are observed in the strongly B-preferential surface field. The interesting phenomenon illustrates that the effects of strongly preferential surface fields can surpass those of confinement degrees and volume fractions to determinate phase behaviors. At the same time, it also implies that the special molecular architecture of triblock copolymers plays an important role on the formation of the confined morphologies. Second, for the effects of preferential strengths, we note that morphologies are more sensitive to the variations in γ_A than to those in γ_B , and some complex morphologies always appear in the intermediate A-preferential surface field strength case. The phase behavior difference mainly results from the “loop” conformation constraint of B-blocks, which causes high entropic energy penalties and weakens the attractive effect of the B-preferential surface field. Third, considering the effect of incompatibility degrees, it is noted that confined morphologies are more sensitive to the variations in η , especially in the intermediate-segregation regime, compared with those in the bulk state. Lots of morphological transitions (including ODTs and OOTs) are confirmed to be of first-order by further quantificationally analyzing order parameter. Although our simulated results may have some deviations from real experimental results, we believe that our findings can still provide some valuable theoretical guidance for future experiments and production industries.

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