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Segmented helical structures formed by ABC star copolymers in nanopores

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Self-assembly of ABC star triblock copolymers confined in cylindrical nanopores is studied using self-consistent mean-field theory. With an ABC terpolymer forming hexagonally-arranged cylinders, segmented into alternative B and C domains, in the bulk, we observe the formation in the nanopore of a segmented single circular and non-circular cylinder, a segmented single-helix, and a segmented double-helix as stable phases, and a metastable stacked-disk phase with fourfold symmetry. The phase sequence from single-cylinder, to single-helix, and then to double-helix, is similar as that in the cylindrically-confined diblock copolymers except for the absence of an equilibrium stacked-disk phase. It is revealed that the arrangement of the three-arm junctions plays a critical role for the structure formation. One of the most interesting features in the helical structures is that there are two periods: the period of the B/C domains in the helix and the helical period. We demonstrate that the period numbers of the B/C domains contained in each helical period can be tuned by varying the pore diameter. In addition, it is predicted that the period number of B/C domains can be any rational in real helical structures whose helical period can be tuned freely. © 2013 American Institute of Physics.

I. INTRODUCTION

The self-assembly of block copolymers under confinement in nanopores is of great interest because confinement can cause the block copolymer to self-assemble into nanostructures beyond those formed in bulk samples. Even with the simplest diblock copolymer, which is characterized by the volume fraction of the minority block, and the product of the Flory-Huggins interaction and is the total degree of polymerization, the introduction of confinement can enrich the structure formation significantly. In recent years, a large number of studies have been dedicated to explore novel structures formed by bulk lamella-forming, cylinder-forming, and gyroid-forming diblock copolymers under cylindrical confinement by experiments, computer simulations, and theoretical calculations. In the case of bulk lamella-forming diblock copolymers, concentric layers parallel to the pore wall prefer to be formed when the pore wall has a strong preferential interaction to either block. The number of such layers is determined by the pore size relative to the bulk lamellar period. If the pore wall is neutral, perpendicular lamellae, with layer normal along the pore axis, are formed, which have a similar period as that in the bulk. The self-assembly behavior becomes more complicated if the pore wall has an interaction with an intermediate strength because no complete wetting layer is formed by either block along the perimeter. For example, Li and Wickham observed I- and Y-shaped structures with translational symmetry along the pore axis, and a perforated-concentric layer structure, using a slightly asymmetric diblock copolymer confined in a cylindrical pore with an intermediate surface interaction. Similarly, in the case of bulk cylinder-forming diblock copolymers, a strong preferential surface interaction can reduce the complexity of self-assemblies, and the corresponding phase behaviors have been well understood by both experiments and theories. A generic phase sequence, from a single straight cylinder (C1) phase, to a stacked-disk (DK) phase, to a single-helix (H1) phase, to a double-helix (H2) phase, and so on, has been constructed. One of the most attractive features in this system is the formation of helical morphologies by the self-assembly of achiral block copolymers, imposed by the cylindrical confinement. It has been proposed that to curve the cylinder into a helix is an efficient way to reduce the entropy loss due to chain stretching induced by a mismatched large pore size while keeping the size of the cylinder formed by the minority block close to the bulk radius. One expects that the formation of helical morphologies is generic in confined block copolymers, including geometrical confinement, and soft confinement which is effectively formed by external environments, such as micelles in solution, and the self-assembly of a cylindrical domain of B/C blocks in an A matrix, in linear ABC triblock terpolymers. Until now, to our best knowledge, all of observed helical structures contain only homogeneous helix which has the screw symmetry. No doubt we can obtain more intriguing helical morphologies by varying the confining boundary or the block copolymer itself. Recently, a few studies have turned to focus on the self-assemblies of ABC triblock terpolymers confined in nanopores. In the ABC star triblock terpolymers, one of the most fascinating features is the assembly of the three-arm junctions during the structure formation, which is usually aligned along straight lines as along as the three blocks are long enough to phase separate. After a cylindrical confinement imposed, the assembly of the junctions is enforced to be changed.

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Xu et al. observed both straight alignment of the junctions in a number of metastable two-dimensional (2D) flower-petal patterns and curved alignment of the junctions in the three-dimensional (3D) morphologies with a hierarchical-lamella forming star terpolymer. As we know, a hexagonally-arranged cylinder phase, where each cylinder segments into alternative B and C domains, can become stable instead of the hierarchial lamella in the bulk when the volume fraction of the symmetric B and C blocks is reduced. Intuitively, it is expected to observe inhomogeneous helical morphologies because of the B/C phase separation within the helix when the hierarchical-lamella forming star terpolymer is replaced by a hierarchical-cylinder forming one in the cylindrical confinement. In this paper we will extend our knowledge on the formation of homogeneous helical morphologies to that of inhomogeneous ones by carrying out a study of the self-assembly of a hierarchical-cylinder forming star terpolymer confined in nanopores using the pseudo-spectral method of the self-consistent field theory (SCFT), which has been often used for the complex block copolymer systems. Our study of the formation of inhomogeneous helical morphologies is motivated by the extensive studies of homogeneous helical morphologies formed in the cylindrically-confined diblock copolymers, and thus our results can be directly compared with those results in the reference model system to reveal the similarity or the difference between them. Furthermore, the alignment of the three-arm junctions in the confinement is more frustrated than that in the bulk. Therefore, the self-assembly of a hierarchical-cylinder forming terpolymer confined in narrow pores is an excellent example to study the impact of the junction alignment on the formation of morphologies, specifically, on the generic phase sequence seen in the confined diblock copolymers. In particular, different morphologies have different ability to release the energy penalty induced by the frustration of the junction alignment. For example, in the straight-cylinder or helical morphologies, the junctions can be readily aligned on precisely or roughly parallel rings. However, for the stacked-disk phase, where B/C co-formed oblate domains are stacked along the pore axis when the A blocks are attracted to the wall surface by the surface preferential interaction and to fill the space between the disks, the junction alignment becomes extremely complicated, and thus may result in the formation of many disk-type morphologies with different junction alignments. In general, the different frustration degrees of the junction alignment can change the relative stability of these phases, and thus change the phase sequence. The theoretical results from the current study can be used to gain a further understanding on the impact of the junction alignment upon the complex self-assembly beyond the bulk system.

II. THEORY AND METHOD

We consider an incompressible melt of ABC star triblock terpolymers confined in a cylindrical pore of diameter 2R = D, where R is the corresponding radius. The ABC terpolymer, with a total degree of polymerization N, has three block lengths as fAN, fBN, and fCN (fA + fB + fC = 1), respectively. The immiscibility between the three blocks is characterized by the products of χABN, χACN, and χBCN, respectively, where χij (i, j = A, B, C) is the corresponding Flory-Huggins interaction parameter. Spacial lengths in our calculations are expressed in units of the radius of gyration, Rg, of the polymer. Within the mean-field approximation to the many-chain Edwards theory, at a temperature T, the free energy F for n Gaussian terpolymer chains confined in a cylindrical pore has the form

\[
\frac{F}{nk_BT} = -\ln Q + \frac{1}{V} \int_{|r|\leq R} d\mathbf{r}[\chi_{ABN}\phi_A(r)\phi_B(r) + \chi_{ACN}\phi_A(r)\phi_C(r) + \chi_{BCN}\phi_B(r)\phi_C(r) - w_A(r)\phi_A(r) - w_B(r)\phi_B(r) - w_C(r)\phi_C(r) + H(\phi_A(r) - \phi_B(r) - \phi_C(r))].
\]  

(1)

where \(\phi_A(r), \phi_B(r), \) and \(\phi_C(r)\) are the volume fractions as function of position. The partition function Q is for a single polymer interacting with the mean fields \(w_A, w_B,\) and \(w_C\) produced by the surrounding chains. In the confined melts, the spatial integration is restricted to the pore volume, taken to be V. The preference of the pore wall is introduced by including a surface field \(H(\mathbf{r}), H(\mathbf{r})/\chi = V_0|\exp[(\sigma + |\mathbf{r} - R|/\lambda) - 1] for R - 1/4|\mathbf{r}| < R, while H(\mathbf{r}) = 0 for |\mathbf{r}| < R - 1/4.\) In this work, we choose the cutoff distance for the surface interaction to be \(\sigma = 0.5R_g,\) and the decay length to be \(\lambda = 0.25R_g,\) \(V_0 = -0.1\) gives a rather strong preference of the pore wall to A block.

Minimization of the free-energy with respect to the volume fractions and the mean fields leads to the following standard mean-field equations:

\[
w_A(\mathbf{r}) = \chi_{ABN}\phi_B(\mathbf{r}) + \chi_{ACN}\phi_C(\mathbf{r}) + H(\mathbf{r}) + \eta(\mathbf{r}),
\]  

(2)

\[
w_B(\mathbf{r}) = \chi_{ABN}\phi_A(\mathbf{r}) + \chi_{BCN}\phi_C(\mathbf{r}) - H(\mathbf{r}) + \eta(\mathbf{r}),
\]  

(3)

\[
w_C(\mathbf{r}) = \chi_{ACN}\phi_A(\mathbf{r}) + \chi_{BCN}\phi_B(\mathbf{r}) - H(\mathbf{r}) + \eta(\mathbf{r}),
\]  

(4)

\[
\phi_A(\mathbf{r}) = \frac{1}{Q} \int_0^{f_A} ds q_A(\mathbf{r}, s) q_A^\dagger(\mathbf{r}, s),
\]  

(5)

\[
\phi_B(\mathbf{r}) = \frac{1}{Q} \int_0^{f_B} ds q_B(\mathbf{r}, s) q_B^\dagger(\mathbf{r}, s),
\]  

(6)

\[
\phi_C(\mathbf{r}) = \frac{1}{Q} \int_0^{f_C} ds q_C(\mathbf{r}, s) q_C^\dagger(\mathbf{r}, s),
\]  

(7)

\[
Q = \frac{1}{V} \int d\mathbf{r} q_K(\mathbf{r}, s) q_K^\dagger(\mathbf{r}, s),
\]  

(8)

\[
\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_C(\mathbf{r}) = 1,
\]  

(9)

where the field function \(\eta(\mathbf{r})\) is a Lagrange multiplier used to enforce the incompressibility condition, \(\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_C(\mathbf{r}) = 1.\) In the above equations, Q is the partition function of single chain in these fields, and \(q_K(\mathbf{r}, s)\) and \(q_K^\dagger(\mathbf{r}, s)\) are the quantum operators of the field.
\( K = A, B, C \) are end-segment distribution functions. The distribution function \( q_K(r, s) \) is proportional to the probability that a polymer chain segment, of contour length \( s \) and with one free end, has its other end located at \( r \). These distribution functions satisfy the modified diffusion equations

\[
\frac{\partial q_K(r, s)}{\partial s} = \nabla^2 q_K(r, s) - w_K(r, s)q_K(r, s),
\]

\[
-\frac{\partial q_K(r, s)}{\partial s} = \nabla^2 q_K(r, s) - w_K(r, s)q_K(r, s).
\]

The initial conditions are \( q_K(r, 0) = q^0_K(r, 0)q^0_M(r, 0) \), where \( (KLM) \in \{(ABC), (BCA), (CAB)\} \), and \( q^0_K(r, f_K) = 1 \). For numerical solution, we employ the pseudo-spectral method of Tzeremes et al.\(^{41}\) and Rasmussen and Kalosakas\(^{42}\) to solve the modified diffusion equations for the end-segment distribution functions. Similar to our previous work,\(^{19}\) the cross-section of the pore is put in a rectangular cell which is a little larger than the diameter of the pore. In our calculations, we discretize the cell into \( N_x \times N_y \times N_z = 128 \times 128 \times 64 \) lattice, and the chain contour is divided into 100 segments. More details of the calculations can be found in our previous work.\(^{19}\)

### III. RESULTS AND DISCUSSION

To form the hexagonally-arranged segmented cylinders, we choose an ABC terpolymer with fixed symmetry volume fraction of \( \{f_A, f_B, f_C\} = \{0.78, 0.11, 0.11\} \), and fixed interactions of \( \chi_{AB}N = \chi_{AC}N = \chi_{BC}N = 60 \).\(^{37}\) Two feature sizes are introduced to characterize the periodicity of the bulk hierarchical-cylinder phase, \( \text{L}_0 \) and \( \text{h}_0 \), which measures the nearest-neighbor cylinder-to-cylinder distance and the alternative B/C domain period along the cylinder axis, respectively. And they are determined as \( \text{L}_0 \approx 4.05 \text{R}_g \) and \( \text{h}_0 \approx 1.72 \text{R}_g \) for this given group of parameters. The pore diameter, \( D \), is varied to examine the structure formation of the ABC terpolymer. Here we focus on the case that the pore surface has a strong preferential interaction to the longest A block. In fact, it is a challengeable task to find complex morphologies without a high symmetry in the SCFT calculations. Usually, the employment of special initial conditions for the mean fields is helpful during the search of new morphologies. For example, a random initial condition but with a screw symmetry can facilitate the localization of the saddle point to-
The nonuniformity of the mean curvature is amplified as the pore size is raised, and thereby it drives the phase to transform into segmented single-helix, $H_1$. As we mentioned previously, the repeating number of B/C segments in a helical period, $n_{BC}$, can be tuned during the formation of the single helix. In our theoretical calculations, only integer $n_{BC}$ can be considered because of the implementation of the periodic boundary condition. Of course, $n_{BC}$ is not necessary to be an integer and can be any rational when the helical structure contains a large number of helical periods in real experimental samples. To estimate the average value of $n_{BC}$ per helical period more accurately, we have to consider helical structures with many helical periods, which would raise the burden of calculations. However, the integer $n_{BC}$ is a reasonable approximation for the rational value when there are many repeating B/C domains in one helical period. This approximate value can be used to estimate the other characteristics of helix, including the pitch angle, the average B/C-domain period along the helix, and the helical screw radius. Consequently, the third intriguing feature is that there are a few artificial morphologies of $H_1$ with $n_{BC} = 5$, 6, 7, and 8 in the phase diagram. In addition, the phase transition between $H_1$ and $H_2$ occurs at $D \approx 1.96 L_0$, which is very close to the value, $D \approx 2.04 L_0$ of Figure 1(a) in Ref. 19. When the single-helix phase transfers to the double-helix phase, the pitch angle or the helical period becomes much larger in order to keep a reasonable length ratio between the helices and the pore. Under the strong-segregation approximation, the sine value of the pitch angle in the double-helix morphology is only half of the single-helix one (see Eq. (12) in Ref. 19). As a consequence, each helix in the double-helix phase has a slightly larger $n_{BC}$ than the single-helix phase at the transition point between $H_1$ and $H_2$. It is observed that the double-helix phase of one helical period with the lowest free energy is $n_{BC} = 10$ at $D \approx 1.96 L_0$.

Different from the cylindrically-confined diblock copolymer, there is no stable stacked-disk phase. In the simple diblock copolymer system, the stacked-disk phase appears as an intermediate phase between $C_1$ and $H_1$, and occupies a narrow phase region, where the chain packing is extremely frustrated. Compared with the previous system, the constraint on the arrangement of the three-arm junctions in the present system adds more frustration onto the chain packing. In another word, the phase separation between B and C blocks enrich the formation of stacked-disk type morphologies by varying the arrangement of B and C domains in the disk. In Figure 2(a), we present the free-energy comparisons between those morphologies of $C_1$, stacked-disk, and $H_1$. Here the free energy of only one of stacked-disk morphologies is plotted as an example, which is denoted as DK$_4$ as it has fourfold symmetry. This symmetry makes it have lower free energy than other stacked-disk morphologies with poorer symmetry. The concave property at the central portion of the disk is noticeable. Figure 2(a) suggests that DK$_4$ becomes more favorable than $C_1$ when $D \gtrsim 1.44 L_0$, but has consistent higher free energy than $H_1$ of $n_{BC} = 5$. Therefore, $C_1$ directly transfers to $H_1$ of $n_{BC} = 5$ without DK$_4$ as an intermediate stable phase. In Figure 2(b), the free-energy comparison between the $H_1$ morphologies with various $n_{BC}$ shows that there are first-order transitions between these artificial morphologies.
energy is reduced, and thus DK₄ will become stable as an intermediate phase between C₁ and H₁.

In Figure 3, we present the free-energy comparisons between H₁ and H₂ for two pore sizes near their transition, D = 7.8Rₘ (filled symbols) and D = 8.0Rₘ (unfilled symbols), respectively. Here we examine two helical periods for the two helical phases to show the impact of inaccurate value of nBC on the free energy. We can see that the optimum value of nBC of H₁ is very close to 16, and that of H₂ is close to 19 with D = 7.8Rₘ in the case of double helical periods. After minimizing the free energy of H₁ and H₂ with respect to the ratio between the helical period and the B/C-domain period, we can see that H₁ has lower free energy than H₂ at D = 7.8Rₘ. When the pore diameter is increased to 8.0Rₘ, the stable phase becomes H₂. In addition, the optimum values of nBC of both phases shift toward the increasing direction. This suggests that we have to take a large number of helical periods into account in order to determine the relative stability between segmented helical phases more accurately. Fortunately, the influence of nBC on the free energy, thus on the relative stability between phases, is limited even though we simply use the optimum integer nBC contained in only one helical period as the approximation of its optimum rational. Of course, the choice of integer nBC gives rise to those artificial morphologies and their phase transitions for H₁ in Figure 1. In fact, the value of nBC can be varied continuously as the pore size in experiments usually has a large length. We also find that the impact of inaccurate nBC on the pitch angle, \( \theta = \arctan(L_p/2\pi R_s) \), where \( L_p \) is the helical period and \( R_s \) is the helical screw radius, is also small. For example, the difference of the pitch angle of H₁ induced by two neighboring nBC integers is within one degree (see Figure 5(a)). The change of the pitch angle as function of the pore diameter in Figure 5(b) is similar as that of the homogeneous single helix formed in the cylindrically-confined diblock copolymers. The B/C-domain period in the segmented helix, h, is readily calculated by

\[
h = \sqrt{L_p^2 + (2\pi R_s)^2/n_{BC}}.\]

The data of h for different H₁ morphologies are shown in Figure 5(b). The three unfilled circles indicate the corresponding data of 2nBC = 13, 15, and 17.
IV. CONCLUSIONS

In summary, we have studied the formation of hierarchical morphologies by the ABC triblock terpolymers under the confinement of narrow pores. Specifically we have focused on the ABC star terpolymer, which forms hexagonally-arranged segmented cylinders in the bulk. As the pore size varies, a number of novel morphologies are observed. Though these morphologies resemble the hierarchical feature of the bulk phase, they have their own distinct properties. In very narrow pores, segregated single circular cylinder is formed. Then, as the pore size deviates from the optimum value for single cylinder, the circular cylinder is deformed continuously to be non-circular. And finally, the segmented non-circular cylinder becomes metastable, and is replaced by the segmented single helix. For the segmented helical phase, one of the most attractive features is that its length can be tuned by varying the repeating number of B/C domains along the helix to accommodate the change of pore size. In our SCFT calculations, an integer repeating number of B/C segments in one helical period is considered to be an approximation of the optimum number per helical period in real helical structures with a large length which should contain a large number of helical periods. As a consequence, there are artificial phase transitions between the morphologies of the same helical phase, but with various repeating number of B/C segments in one helical period. Our calculations also predict that the ratio between the helical period and the B/C-domain period can be any rational in real segmented helical morphologies. The phase sequence, from single cylinder, to single-helix, and then to double-helix, is similar as that in the cylindrically-confined diblock copolymers except for the absence of the stacked-disk phase. This similarity indicates that the formation and stability of helical structures is generic. The absence of a stable stacked-disk phase in the present system is mainly induced by the phase separation between B and C blocks as well as the constrain of the three-arm junctions. Our results provide a further understanding on the self-assembly of ABC terpolymer systems beyond the bulk one, and might motivate relative experimental research.

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