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Confinement-Induced Novel Morphologies of Block Copolymers

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Self-assembly of block copolymers confined in cylindrical nanopores is studied systematically using a simulated annealing technique. For diblock copolymers which form two-dimensional hexagonally packed cylinders with period L_0 in the bulk, novel structures such as helices and stacked toroids spontaneously form inside the cylindrical pores. These confinement-induced morphologies have no counterpart in the bulk system and they depend on the pore diameter (D) and the surface-polymer interactions, reflecting the importance of structural frustration and interfacial interactions. On tightening the degree of confinement, transitions from helices to toroids to spheres are observed. Mechanisms of the morphological transitions can be understood based on the degree of structural frustration parametrized by the ratio D/L_0.

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Spontaneous formation of ordered structures from amphiphilic molecules has attracted tremendous attention in the last decades. Among the many different amphiphilic systems, block copolymers with their rich phase behavior and ordering transitions have become a paradigm for the study of structural self-assembly [1]. For the simplest case of diblock copolymers, which are linear polymers composed of two different subchains (A and B blocks), their phase behavior is controlled by the competition between the A-B repulsion and chain connectivity. A variety of ordered bulk phases, including lamellae, hexagonally packed cylinders, body-centered-cubic spheres, and a bicontinuous network structure called gyroid, is observed for diblock copolymers [1]. In a physically confined environment, structural frustration, confinement-induced entropy loss, and surface interactions can strongly influence the molecular organization. In particular, it is possible that confinement can lead to unusual morphologies which are not accessible in the bulk, thus providing opportunities to engineer novel structures. The self-assembly of confined diblock copolymers has attracted considerable recent attention [2,3]. In particular, the self-assembly of both symmetric and asymmetric block copolymers under a one-dimensional confinement, imposed by two parallel bounding surfaces, has been extensively studied both experimentally and theoretically. Much attention has been focused on controlling the orientation of the lamellae with respect to the confining surfaces.

For two- or three-dimensional confinement, it is expected that the combination of confinement and curvature will lead to unusual morphologies. In a series of papers, Russell and co-workers reported the study of symmetric [4,5] and asymmetric [3,6] polystyrene-*b*-polybutadiene (PS-*b*-PBD) diblock copolymers confined within nanoscopic cylindrical pores in alumina membranes. For the lamella-forming symmetric diblock copolymers confined in the cylindrical pores, a multiple set of concentric cylinders is observed when the pore diameter (D) is larger than the equilibrium period L_0 [4]. When the pore diameter D is comparable to L_0 and D/L_0 is not an integer, a novel stacked-disk or toroid morphology forms in the pores [5]. Concentric cylinders were also observed in by Sun and coworkers in symmetric polystyrene-*b*-poly(methyl methacrylate) diblock copolymers confined in alumina nanopores [7]. Theoretically, concentric cylinder structures have been predicted by He *et al.* [8] using Monte Carlo simulations and by Sevink *et al.* [9] using dynamical density functional simulations. Furthermore, Li, Wickham, and Garbary [10] have carried out self-consistent field theory (SCFT) calculations for diblock copolymers under cylindrical confinement, and concentric cylindrical structures were obtained among other two-dimensional morphologies. For the cylinder-forming asymmetric PS-*b*-PBD diblock copolymers confined in nanopores, Xiang *et al.* [4] observed that, while large pore diameters ($D/L_0 > 4.1$) lead to hexagonally packed cylindrical domains, the symmetry and domain spacing of the cylinders can be altered by the shape and size of the pores, whereas in nanopores with smaller diameters ($D/L_0 = 1.1$–1.5), alignment of the cylindrical domains along the rod axis is no longer observed. Rather, the morphology has changed from simple cylinders oriented parallel to the nanopores to a morphology where the cylinders form helices within the nanopores [6]. In a related work, Wu *et al.* [11] studied the confined assembly of silica-surfactant composite mesostructures within cylindrical nanopores of varying diameters. They observed that cylinder-forming systems confined in the nanopores spontaneously form unusual silica structures such as helices and toroids, and they have carried out SCFT calculations on a model system composed of diblock-copolymer–

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homopolymer blends to account for the observed self-assembled mesostructures. All these previous studies demonstrated the generality of confinement-induced structural transitions in amphiphilic systems. In order to understand the interplay between the bulk periodic structure and the confinement, it is desirable to carry out systematic studies of the confined self-assembly of diblock copolymers as a function of the degree of confinement and surface interactions.

In this Letter, we report a systematic study of the formation of novel morphologies in confined asymmetric diblock copolymers. The study is based on a lattice model, in which the polymers are modeled by the "single-site bond fluctuation" model proposed by Carmesin and Kremer [12] and by Larson [13]. Equilibrium structures of the system are obtained using a simulated annealing technique, which is a well-known procedure for obtaining the ground states of complex systems [14–16]. Details of the model system and simulation procedure are given elsewhere [17]. Our previous studies on this model system have demonstrated that the simulated annealing is an efficient method for studying self-assembled block copolymer morphologies in solution [18,19] and in a confined environment [17]. In the current study, the simulated annealing method is applied to cylinder-forming asymmetric diblock copolymers confined in cylindrical pores with different pore diameters and surface-polymer interactions. A rich variety of novel morphologies, ranging from helices to toroids to complex networks, is obtained. These structures are very different from those formed in the bulk or under a one-dimensional confinement, thus expanding the repertoire of nanoscopic self-assembled block copolymer structures.

Specifically, A_n-b-B_{N-n} diblock copolymers are used in the study, where N and n are the number of all monomers and A monomers, respectively. The volume fraction of A blocks is $f_A = n/N$. The total monomer concentration is kept at $\rho = 85\%$. The system is embedded in a simple cubic lattice of volume $V = L_x \times L_y \times L_z$. Each monomer occupies one lattice site, and the copolymers are self- and mutually avoiding. The bond length is set equal to 1 and $\sqrt{2}$, thus each site has 18 nearest-neighbor sites. The repulsion between the A-B blocks is modeled by a nearest-neighbor interaction parameter $\epsilon_{AB} = 1.0$. The initial state is an array of parallel copolymer chains along one of the axes. Starting from the initial state, the ground state of the system is obtained by executing a set of Monte Carlo simulations at decreasing temperatures [17].

Equilibrium bulk phases are obtained in rectangular boxes of size $L_x \neq L_y \neq L_z$ with periodic boundary conditions in all three directions. L_x, L_y, and L_z are varied so that the box is commensurate to the period of the ordered structures [20–22]. For the model system with $N = 12$, its phase diagram has been obtained by simulations with $n =$ 2–6. Lamellae and gyroids are found at $n = 6, 5$ and $n =$ 4, respectively. For $n = 3, 2$, the equilibrium bulk phase is the hexagonally packed cylinders along one of the axes. The equilibrium spacing between the cylinders is $L_0 =$ 10.67 lattice spacings for $f_A = 1/4$ and $L_0 = 9.93$ lattice spacings for $f_A = 1/6$, respectively. Another important length scale is the radius of the cylinders, R_0, which can be estimated using the relation $\pi R_0^2 = f_A\sqrt{3}L_0^2/2$. For the two cylinder-forming diblock copolymers with $f_A = 1/4$ and $f_A = 1/6$, the cylinder radius is $R_0 = 0.2625L_0$ and $R_0 = 0.2143L_0$, respectively.

For simulations of confined self-assembly, the cylinder-forming diblock copolymers ($N = 12$, $n = 2, 3$) are confined to a long cylindrical pore of diameter D. The confinement is realized in the volume $V = L_x \times L_y \times L_z$ with $L_x = L_y = D + m$, where $m = 2$ when D is odd and $m = 3$ when D is even. Polymers cannot occupy the wall sites which are the lattice sites outside a cylinder with diameter D. Therefore the polymers are confined in an approximate cylindrical pore of diameter D [23]. The extra m in L_x and L_y ensures that each site inside the cylindrical pore has 18 nearest-neighbor sites. These nearest-neighbor sites are either inside the pore or in the wall. The interaction between the polymers and the wall of the pore is modeled by interactions between the nearest-neighbor pore-wall sites. The polymer-wall interaction (characterized by ϵ_{WA} and ϵ_{WB}) is varied between a neutral wall ($\epsilon_{WA} = \epsilon_{WB}$) to a selective wall which attracts the A blocks ($\epsilon_{WA} < \epsilon_{WB}$) or B blocks ($\epsilon_{WA} > \epsilon_{WB}$). Periodic boundary conditions are adopted in the L_z direction along the pore. Similar to the bulk phases, the pore length is varied to obtain optimum equilibrium ordered structures. It is observed that the equilibrium morphology of the confined system depends sensitively on the pore diameter D and wall-polymer interactions. Typical self-assembled morphologies for different wall-polymer interactions are summarized in Fig. 1. Since structural frustration is characterized by the ratio between the pore diameter and the spacing between the cylinders, the morphologies in Fig. 1 are organized as a function of D/L_0.

For the case where the wall attracts the majority blocks ($f_A = 1/6$, $\epsilon_{WA} = 1.0$, and $\epsilon_{WB} = -1.0$), a layer of B blocks forms close to the pore wall due to the attractive W-B interaction [Fig. 1(a)]. The overall morphology of the diblock copolymers can be classified by viewing the system along the cylindrical pore. When D/L_0 is close to 1 ($D/L_0 \approx 1 \pm 0.3$), the A blocks form one cylinder at the center of the pore. When $D/L_0 \approx 2 \pm 0.5$, the A blocks form a one-ring structure. For $D/L_0 \approx 3 \pm 0.5$, one cylinder and an outer ring are observed. When D/L_0 is near to four ($D/L_0 \approx 4 \pm 0.3$), a two-ring structure is formed. Viewing the system from the side of the pore reveals that the morphologies are very rich and complex. For small pores with $D/L_0 < 0.7$, the A blocks form a chain of spheres at the center of the pore. For larger value of $D/L_0 \approx 1 \pm 0.35$, these spheres connect to form a single straight cylinder. A transition from a single straight cylinder to a stack of tilted disks occurs at $D/L_0 \approx 1.5$. The tilted disks evolves into a single helix (S helix) for

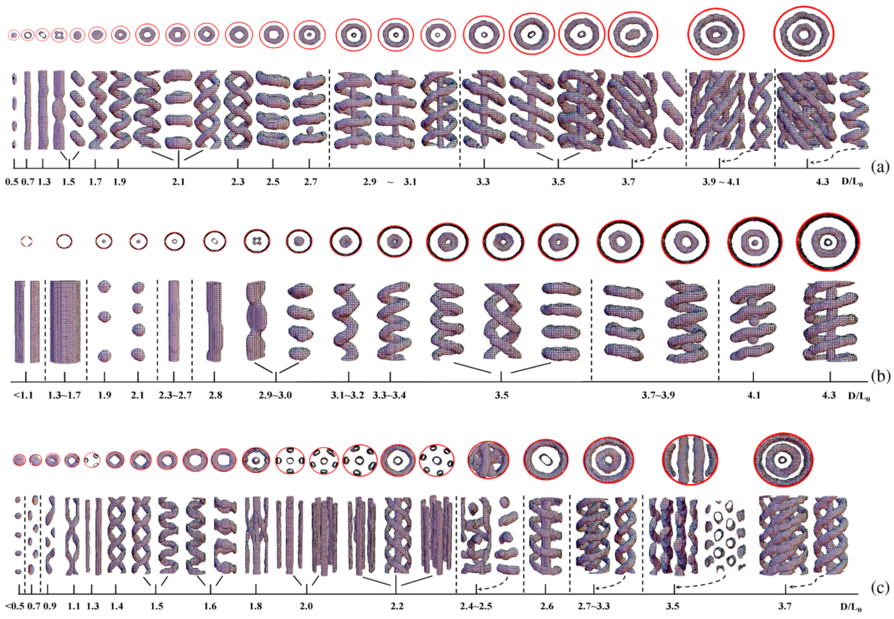

FIG. 1 (color online). Self-assembled morphologies as a function of the ratio D/L_0 for different wall-polymer interactions. The parameter D/L_0 is given underneath each morphology. Both a top view and a side view are given. The outmost circles in the top views indicate the wall of the cylindrical pores. For some large diameters, the inner ring is shown separately. (a) The case where the wall attracts the majority blocks ($f_A = 1/6$, $\epsilon_{WA} = 1.0$, and $\epsilon_{WB} = -1.0$). (b) The case where the wall attracts the minority blocks ($f_A = 1/6$, $\epsilon_{WA} = -1.0$, and $\epsilon_{WB} = 1.0$). (c) The case of a neutral wall ($f_A = 1/4$ and $\epsilon_{WA} = \epsilon_{WB} = 0$). Notice the formation of small A droplets and A cylinders close to the wall.

$1.6 < D/L_0 < 2.0$. A set of degenerate structures (single helices, stacked toroids, and double helices) is found at $D/L_0 = 2.1$. The double helices (D helices) are stable until $D/L_0 \approx 2.5$, at which a stack of larger toroids is obtained. At $D/L_0 = 2.7$, a chain of spheres appears at the center of the stacked toroids, resembling the central spheres in the region $D/L_0 < 0.7$. This chain of spheres evolves into a straight cylinder, while the toroids close to the wall remain or change to S helices or D helices at $D/L_0 \approx 2.9$–3.1, and to tilted toroids and S helices at $D/L_0 = 3.3$ and 3.5, respectively. For larger pores $D/L_0 > 3.7$, the A blocks form a coaxial double ring. The outer ring forms helices or tilted toroids, the inner ring forms S or D helices. The inside ring forms regular tilted toroids and helices, and the transition sequence resembles to that of the single-ring structures at smaller D. For even larger D, a coaxial triple-ring appears, but the structures are plagued with defects. It is interesting to notice that the pitches of the helices and period of the stacked toroids are the same as the spacing between the cylinders in the bulk phase, indicating that the mechanism of the formation of these structures is related to the release of confinement frustrations. Another interesting observation is that, when D/L_0 is close to a half integer ($D/L_0 \approx 1.5$, 2.5, 3.5, and 4.5), the A blocks form stacked discs or stacked toroids in the outer ring. This is likely due to the fact that half-integer D/L_0 presents the most frustrated case. The importance of half-integer D/L_0 is also noticed experimentally for symmetry diblock copolymers [5]. Although experimental studies on cylinder-forming diblock copolymers inside a pore which attracts the majority blocks are lacking, the above predictions can be compared with the morphologies observed by Wu *et al.* [11] in a silica-surfactant composite system confined within cylindrical nanopores in an alumina membrane. The sequence of morphological transitions is consistent with their experimental observations and SCFT simulations [11].

When the wall-polymer interaction is strongly attractive to the minority block ($\epsilon_{WA} < 0, \epsilon_{WB} > 0$), the minority blocks are forced to be in contact with the wall. Typical morphologies as a function of D/L_0 are presented in Fig. 1(b) for the case of $\epsilon_{WA} = -1.0$, $\epsilon_{WB} = 1.0$ and $f_A = 1/6$. For small pores, the A blocks form droplets on the wall because there are not enough A monomers to cover the whole wall surface. For larger enough pores, the A blocks form a layer at the wall. Increasing D further leads to a morphological transition sequence resembling to case of B-attractive wall ($\epsilon_{WA} > \epsilon_{WB}$) described above, with larger transition values of D/L_0. This can be understood from the fact that the A-B monolayer at the pore wall is equivalent to a smaller cylindrical pore with a B-attractive wall. The effective diameter of the pore is roughly given by $D - 3L_0/2$.

For the special case of $\epsilon_{WA} = \epsilon_{WB} = 0$, more complex structures form due to the extra frustrations provided by the neutral wall. Similar behavior as the neutral wall case has been observed for weakly selective walls. Typical morphologies for the case of $\epsilon_{WA} = \epsilon_{WB} = 0$ and $f_A = 1/4$ are summarized in Fig. 1(c). The general trend of the morphological transition is similar to the cases of selective walls. In particular, a chain of spheres in small pores and helices or toroids in larger pores is observed. However, when $D/L_0 < 0.8$, small droplets of A domains are found close to the wall. These droplets rotate around the axis of the cylinder. For larger value of D/L_0, A cylinders form at the pore wall. Three A cylinders are found at $D/L_0 = 1.2$, whereas four, five, and six A cylinders are observed in a very narrow range around $D/L_0 = 2.0$, resembling the two-dimensional structures obtained by Li, Wickham, and Garbary [10]. Furthermore, cylinders oriented nearly perpendicular to the cylindrical pore are formed at $D/L_0 = 2.5$ and 3.5. The distance between the cylinders both oriented parallel and perpendicular to the cylindrical pore is the same as the bulk cylinder spacing. It is interesting to notice that, when D/L_0 is close to an integer, cylinders parallel to the cylindrical pore are observed; when D/L_0 is close to a half integer, cylinders perpendicular to the cylindrical pore are obtained. The helical and toroid structures are the compromise between these two extreme cases. These predicted morphologies can be compared with recent experiments by Xiang and co-workers on asymmetric PS-*b*-PBD diblock copolymers confined within cylindrical nanopores in an alumina membrane [6]. The bulk morphology of this sample consists of PBD cylinders in a PS matrix. For nanopores with diameters D of 33–45 nm ($D/L_0 = 1.1$–1.5), one ring of multiple helices is found within the nanopores. This is in good agreement with our prediction that one layer of helices forms when $D/L_0 = 1.1$–1.6. Although the PBD blocks preferentially segregate to the pore wall, this agreement suggests that the PS-*b*-PBD/alumina system may corresponds to a weakly attractive wall.

In summary, equilibrium morphologies of cylinder-forming asymmetric diblock copolymers confined in cylindrical pores are explored using a simulated annealing method. It is discovered that confined self-assembly leads to a rich variety of morphologies. Many of these ordered structures, such as helices and stacked toroids, cannot form in bulk block copolymers. The formation of these novel structures is correlated with the ratio between the pore diameter D and the bulk cylinder spacing L_0, D/L_0, reflecting that the origin of these novel structures is the confinement-induced structural frustration. For the case of strongly selective walls, a generic morphological transition sequence, from string of spheres to cylinder to helix then toroids, is predicted. The combination of this study with the experiments and self-consistent field theory demonstrates that confined self-assembly of amphiphilic molecules provides a robust method to produce nanoscopic structures which are not accessible in the bulk phases. The predicted sequence of morphological transitions is consistent with all available experiments and recent self-consistent field theory calculations. Furthermore, a wealth of novel structures, not seen by experiments to date, is predicted. It is hoped that our studies will stimulate and help to guide future experiments to locate these structures.

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