Symmetric Diblock Copolymers in Nanopores: Monte Carlo Simulations and Strong-Stretching Theory

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INTRODUCTION

Block copolymers have great potential for applications in nanotechnology, due to their microphase separation into spatially periodic structures on the length scale of 10~100 nm, direct control of the self-assembled morphology, and the uniformity of these nanostructures. Nano-confinement of block copolymers can be used to produce novel morphologies that cannot be obtained in the bulk and to control the morphology through the confining surfaces. The influence of confinement on the microphase separation and morphology of block copolymers is also of fundamental interest in polymer science.

Here we focus on the simplest and most studied system of symmetric diblock copolymers, where the two blocks have the same volume fraction and one-dimensional lamellar structure with a characteristic period L_0 forms in the bulk. Xiang et al. recently reported experimental results of symmetric polystyrene-polybutadine (PS-PBD) diblock copolymers confined in nanopores formed in alumina membranes, where the pore surface prefers PBD block.[1-3] Concentric cylinders whose axis is the same as the pore axis were generally observed due to the surface preference.[1-3] A frustrated, stacked-disc or toroidal-type structure was reported when the ratio of the pore diameter D to the bulk lamellar period L_0 is about 2.6.[2] Sun et al. also studied symmetric polystyrene-poly(methyl methacrylate) (PS-PMMA) diblock copolymers confined in nanopores formed in self-ordered alumina, where the confining surface prefers PMMA block.[4] Concentric cylinders were observed when $d \equiv D/L_0 \approx 10.3$, 4.62, and 1.54. When $d \approx 0.64$, the observed morphology is ambiguous, either that of concentric cylinders or a disordered state with preferential segregation of PMMA to the pore surface.[4]

In this work, we use lattice Monte Carlo simulations to study the morphology of symmetric diblock copolymers confined in nanopores, and compare the simulation results with a strong-stretching theory commonly used in the literature.

METHODS

Lattice Monte Carlo Simulations. Our Monte Carlo (MC) simulations are performed in an expanded grand-canonical ensemble with a simple cubic lattice model.[5] Symmetric diblock copolymers $A_{12}B_{12}$ are confined in a cylindrical pore of radius R. The pore surface consists of all the lattice sites with a distance to the pore axis *larger* than R. These surface sites, denoted by S, cannot be occupied by polymer segments, and we denote the number of occupiable lattice sites by V.

Without loss of generality, we assume that the pore surface prefers A segments. We only consider repulsion between nearest-neighbor AB and BS pairs separated by one lattice unit, i.e., $\varepsilon_{AB}>0$ and $\varepsilon_{BS} = \alpha\varepsilon_{AB} \geq 0$, and set all other interactions to be 0. Readers are referred to Ref. [5] for details of our expanded grand-canonical ensemble simulations. In the simulations, we set $\varepsilon_{AB} = 1/2.3$ and the chemical potential of the copolymer chains[6] to be 41.5 (both are in units of k_BT, where k_B is the Boltzmann constant and T the absolute temperature), and allow the total polymer segmental density (ratio of the number of occupied lattice sites to V) to fluctuate[5]. This leads to an average segmental density of about 0.8 and the bulk lamellar period L_0=12 (in units of lattice spacing).[5] For dense polymer systems like what we study here, the expanded grand-canonical ensemble simulations can relax and sample the system configurations much better than the commonly used canonical-ensemble simulations.[5] Our simulations also allow the study of density changes of the confined systems, which is not possible in canonical-ensemble simulations.

Strong-Stretching Theory. The strong-stretching theory (SST) is valid in the strong segregation limit, where the thickness of A-B interfaces is vanishingly small and all A-B junctions are localized at A-B interfaces. Applying this theory requires *a priori* knowledge about the possible morphologies. In this work, we consider only the parallel and perpendicular morphologies in a cylindrical pore. In the former case, the A-B interfaces are circular and parallel to the pore surface, i.e., we have concentric cylinders whose axis is the same as the pore axis. In the latter case, the A-B interfaces orient perpendicular to the pore axis, with the bulk period L_0 maintained along the pore axis. The free energy of each morphology is calculated as a summation of the elastic free energy of the lamellae (associated with chain conformational entropy), the block-block interfacial energy, the surface-copolymer interfacial energy, and the bending free energy of the lamellae if A-B interfaces are not flat.[7] For the perpendicular morphology, we also consider the undulations of A-B interfaces due to the surface preference[7].

RESULTS

Figure 1 shows the typical morphologies observed in our MC simulations as a function of the dimensionless pore diameter d and surface preference α. At large α, concentric cylinders (shown in the right column of Figure 1) are obtained with the number of A-B interfaces n depending on d. A segments segregate to the surface due to the strong surface preference, while the pore center can be either A or B, depending on d. Unlike parallel lamellae in the thin-film case, for concentric cylinders integer values of d are not the most commensurate pore diameters at which the system free energy has a local minimum, due to the broken symmetry between different layers. The MC results indicate that the phase transition between concentric cylinders with different n is of the first order. Due to the underestimation of the elastic free energy associated with chain conformational entropy, SST predicts the transition to be of the second order instead, and underestimates the pore diameter at which the transition occurs.

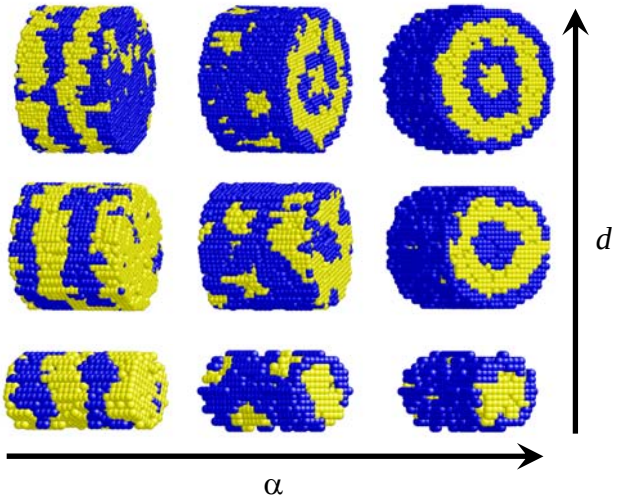

Figure 1. Typical morphologies observed in Monte Carlo simulations as a function of the dimensionless pore diameter $d \equiv 2R/L_0$ and surface preference α. A segments are shown in dark (blue) and B segments in light (yellow).

At neutral (where α=0) or weak surface preferences, lamellae perpendicular to the pore axis (the slab morphology, shown in the left column of Figure 1) is obtained regardless of d. For small α>0, A-B interfaces in this morphology are not flat but undulated due to the surface preference. Although both the MC results and SST show an approximately linear relationship between the undulation amplitude and surface preference, in most cases SST cannot capture other undulation features obtained in MC, including both the packing effects

near the surface and the non-monotonic shape of the undulations; the latter is probably due to the difference in the degree of A-B segregation between the two. As the surface preference increases, the slab morphology changes to a mixed morphology (shown in the middle column of Figure 1) through a first-order phase transition. The mixed morphology is similar to the concentric cylinders in that the A-B interfaces are basically parallel to the pore surface, but B segments protrude through the outer A-rich layer to reach the surface. As α further increases, the mixed morphology gradually changes to concentric cylinders.

Overall, our simulation results agree with the reported experiments[1-4], MC simulations[8-11] and theoretical calculations[12,13]. For lattice simulations of self-assembled structures of block copolymers, however, it is crucial to have a good estimate of the bulk period L_0 and efficient sampling of system configurations. Finally, further theoretical studies using more accurate formalisms are needed to investigate the detailed structures of the mixed morphology and to map out the phase diagram of the system. Using the self-consistent field theory, we are currently conducting 3D calculations of diblock copolymers under cylindrical confinement; the results will be reported in future publications.

ACKNOWLEDGEMENTS

Financial support for this work was provided by Colorado State University, which is gratefully acknowledged.

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