

Nanostructures of diblock copolymers under curved confinement

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Introduction

Diblock copolymers form their structure by two chemically different polymers joined together at one end, and they self-assemble into periodic domains^{1,2}. In the bulk, the morphology and structure of a block copolymer is determined by the interactions between segments comprising the copolymer, the volume fraction of the blocks, and the area occupied by each block at the interface between the domains. Diblock copolymer thin film, one-dimensional (1D) confinement, has been the major geometry of confinement effects studies^{3,4}. The morphology of copolymer between hard, flat surfaces is dictated by the interfacial interaction and commensurability. If the copolymer period and the wall separation distance are incommensurate, stretching or compression of the copolymer molecules will occur, altering the fundamental repeat period⁵. When the confining geometry is nonplanar, as with cylindrical pore, then both commensurability and imposed curvature influence the morphology⁵. In this presentation, we will show novel nanostructures and morphology due to the packing frustration inside cylindrical nanopores⁷ as a potential unique nanotemplate together with block copolymer thin film⁸.

Experimental

We used anodized aluminum oxide (AAO) as a nanotemplate. It was synthesized in our lab by two step anodization procedure as described elsewhere.⁶ An aluminum sheet was electropolished, and then anodized in 0.3 M oxalic acid or sulfuric acid at 15 °C, 40 or 25 V for 12 h. The anodized layer was then removed with phosphochromic acid mixture at 60 °C. The plate was then re-anodized. The nanoporous aluminum oxide membrane was placed on top of the 20-30 μm dried diblock copolymer vacuum for 1 d. Capillary force drew the polymer melt into the nanopores. In order to observe the polymeric nanorods, the membrane with the polymer was dipped into NaOH solution (1 wt/wt %) to dissolve aluminum oxide membrane. After the membrane was removed, the polymeric rods were embedded in epoxy and stained with OsO₄. TEM on cross-sections was taken.

Model and simulations

The morphological structure of a block copolymer melt under cylindrical confinement is simulated by a cell dynamics based on the Cahn-Hilliard-Cook (CHC) equation with a bounding surface contribution and with a geometric consideration for cylindrical confinement:

$$\frac{\partial \psi(\mathbf{r})}{\partial t} = \left(\frac{\partial (F + F_{surf})}{\partial \psi} \right) + \xi \quad (1)$$

where the order parameter ψ describes the local constitution of the block copolymer melt at a position \mathbf{r} , M is a mobility constant, F is the free energy functional of the block copolymer, F_{surf} accounts for the interaction between block copolymers and the inner surface of cylindrical pore, and ξ represents the thermal noise. The free energy functional, F , consists of two terms: $F = F_s + F_i$. The first term represents a short-range part expressed by the Landau-Ginzburg free energy functional,

$$F_s(\psi) = \int d\mathbf{r} [H(\psi) + \frac{D}{2}(\nabla\psi)^2] \quad (2)$$

$$H(\psi) = \tau\psi^2 + \nu\psi^3 + \mu\psi^4 \quad (3)$$

Here τ is a temperature-like parameter and D , ν , and μ are phenomenological constants. The second term F_i accounts for the

long-range repulsive interaction inherent to microphase separation of block copolymer and is given by

$$F_i(\psi) = \frac{b}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 G(\mathbf{r}_1 - \mathbf{r}_2) \delta\psi(\mathbf{r}_1) \delta\psi(\mathbf{r}_2) \quad (4)$$

where $G(\mathbf{r}_1 - \mathbf{r}_2)$ is the Green's function and b is related to the degree of polymerization M : $b \sim M^2$. The eq (1) is integrated by the discrete cell dynamics equation on the square grids. For the diffusion flux in the vicinity of surface, a rigid-wall boundary condition, i.e., no flux through the surface, is used.

Results and discussion

When the diameter of the confining cylinder (d) is large in comparison to the copolymer period, L_0 , morphologies were inferable from those observed under planar confinement are found⁷. For symmetric polystyrene-block-polybutadiene (PS-*b*-PBD), when d was much larger than L_0 , multiple concentric cylinders of PS and PBD oriented along the nanorod axis is obtained. The lamellar forming diblock copolymers shows concentric cylinder inside the nanopores. Since PBD domain was preferentially interact with the alumina wall, the outer side of the polymeric nanorod was enclosed by PBD domains. PS domains were covered on the PBD domains due to the chemical connectivity. However, when the cylinder diameter is small and incommensurate with the copolymer period, the imposed curvature produces unusual morphologies. When the ratio of pore diameter to repeat period is incommensurate ($d/L_0 \sim 2.5$), the packing frustration induces morphological transition from concentric cylinder to 'toroidal' structure. (Figure 1) For cylindrically microphase-separated diblock copolymer whose repeat period is much larger than the rod diameter, the domains are aligned along the rod axes. When the rod diameter becomes smaller, then incommensurability started coming into play, and single or multiple helical cylinders were observed instead of straight bundles of cylinders. We will discuss more on the morphology from experiments and simulations depending on compositions of the copolymer and the degree of confinement.

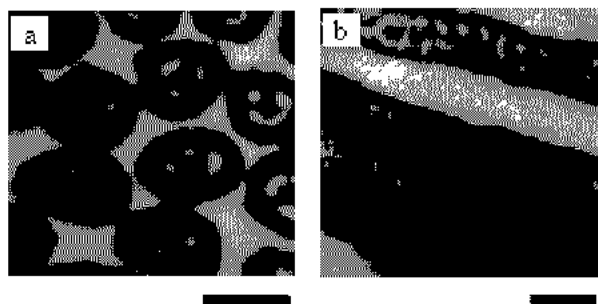


Figure 1. TEM images of PS-*b*-PBD (lamellar in bulk) nanorods from a nanoporous alumina membrane; (a) cross-sectional cut normal to and (b) parallel to the rod axis, respectively. ($L_0 \sim 17.6$ nm. $d \sim 45$ nm) Scale bars, 50 nm.⁷

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