

Nanostructures of Block Copolymer under Confined Geometry

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Introduction

During the last decade, nano-sized structures have attracted supreme interest in almost all fields of material science due to the continuing demands for miniaturization of devices and electronic components. Self-assembly of block copolymers has been recognized one of the promising routes to develop nanostructured materials. In bulk or concentrated solution, block copolymers form spatially periodic nanostructures with length scales of the order of 10~100 nm and the best-known structures are the lamellar, the hexagonally arranged cylinders, the sphere arranged on a body-centered cubic, and the bicontinuous gyroid.[1] These abundant nanostructures formed by block copolymer make it possible to be used for a number of potentially exciting applications such as magnetic-storage media, silicon capacitor, flash memory devices, nano-electronics, photonic crystals, and carrier for drug delivery.

These nano-sized, self-organized structures are affected not only by constitutional and thermodynamic conditions such as composition of block copolymer and temperature but also by various type of external conditions such as shear flow, electric field, heat treatment, and spatial confinement. In particular, the self-assembly of block copolymer in confined geometries attracts recent interest both from academia and industry. The spatial confinement can induce, in combination with the block copolymer self-assembly, new morphologies that cannot be observed in bulk.

This paper deals with a simulation work on nanostructure development of block copolymers caged in nano-sized pores with geometries of cylinder and tetragonal pillar. To investigate how these confined geometries affect the block copolymer morphology in a systematic way, a cell dynamics simulation [2,3] is employed.

Model and simulation

The time evolution of the morphological structure of a block copolymer melt under confined geometry is simulated by a cell dynamics based on a coarse-grained discretization of the Cahn-Hilliard-Cook (CHC) equation with a bounding surface contribution and with a geometric consideration:[4,5]

$$\frac{\partial \psi}{\partial t} = M \nabla^2 \left(\frac{\partial (F + F_{surf})}{\partial \psi} \right) + \xi \quad (1)$$

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

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

with

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

Here τ is a temperature-like parameter and D , ν , and μ are phenomenological constants. The second term F_l accounts for the long-range repulsive interaction inherent to microphase separation of block copolymer and is given by

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

where $G(\mathbf{r}_1 - \mathbf{r}_2)$ is the Green's function and b is related to the degree of polymerization N .

The eq (1) is integrated by the discrete cell dynamics equation on the square grids with a bounding surface boundary condition. 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

Figure 1 shows the simulated morphological structures of symmetric block copolymer confined in cylindrical pore with different pore diameter d . The surface of inner pore is modeled to attract one of block components (A) and to repel B-block. The simulated morphologies show simple concentric domains irrespective of the pore diameter when the surface prefers one of the blocks.

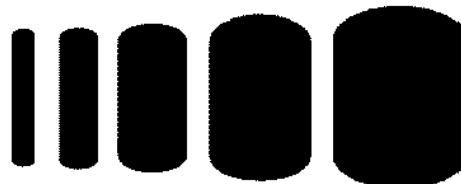


Figure 1. The simulated morphologies of symmetric block copolymer in cylindrical pore with different pore diameter. Only B-domains are represented.

This monotonous morphological variation for symmetric block copolymer becomes largely complicated when the block copolymer is asymmetric. Figure 5 shows the simulated morphologies of cylinder-forming asymmetric block copolymer caged in cylindrical pore, where the inner surface attracts the minor A-block. As the pore diameter increases, a variety of morphologies can form, ranging from simple broken or continuous rods to more complicated structures involving various forms of helices or rings. Figure 6 illustrates the effect of block copolymer composition on the morphology inside the pore when the pore diameter is fixed.



Figure 2. The simulated morphologies of asymmetric block copolymer in cylindrical pore with different pore diameter. The surface attracts minor A-block. Only A-domains are represented.

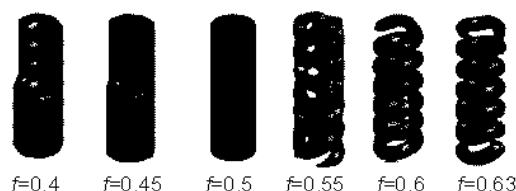


Figure 3. The simulated morphologies of cylindrically confined block copolymer with different block copolymer compositions (f) at a fixed pore diameter. Only B-domains are represented.

Acknowledgement

We thank the Korea Science and Engineering Foundation (KOSEF) for financial support through Hyperstructured Organic Materials Research Center (HOMRC).

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