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Effect of curvature on properties of diblock copolymers confined between two coaxial cylinders: 2. Domain adjustment in a curved bilayer

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ABSTRACT

We study the phase behavior of diblock copolymers in a curved bilayer. Three aspects are discussed in detail: domain size distributions of the two adjacent monolayers within the film, optimal film thickness for a bilayer, and structural transition from a monolayer to a bilayer. One major finding is the determination of transition point in film thickness where the layer-type structure goes from monolayer to bilayer. At high confinement, the transition point increases as the curvature increases regardless of the symmetry of diblock copolymers. At low confinement, the transition point might increase or decrease, depending on the symmetry of diblock copolymers.

1. Introduction

Polymer nanofibers and nanowires have received broad attention in the past decade due to their great practical application values in semiconductor engineering [1]. For example, material scientists used polythiophene nanofibers to conduct heat on a thermal interface for the development of novel microprocessor with high thermal conductivity. This novel microprocessor was proven to be twenty times better at conducting heat than the traditional ones [2]. In recent several years, block copolymer nanofibers have been studied in experiments since their promising properties [3–8]. Shin et al. produced diblock copolymer nanorods and observed many rare micro-phase structures using transmission electron microscopy, such as multi-layered concentric lamellar, stacked-disc and torodial-type structures [3]. These micro-phase structures had been predicted earlier using simulation and theory [9,10]. Computer simulations [11–17] and theoretical calculations [18–21] have been used to investigate the self-assembly of block copolymers in multi-dimensional confinement systems and provide a nice compliment to experimental studies. Yu et al. [22–26] systematically simulated the phase behaviors of diblock copolymers confined in cylindrical nanopores. Ma et al. [27] combined both simulations

and experiments to study the self-assembled morphologies of gyroid-forming diblock copolymers when confined to cylindrical geometry. They obtained various micro-phase structures in the simulations, which agreed with their experimental observations.

Multi-layered concentric lamellar structures are of particular interest to us, because they are crucial in producing novel multi-data transmission channel in the field of chip and polymer technology. Alternating layers of insulators and superconductors within the multi-layered concentric cylindrical structure not only communicate more electric signals through the superconductor layers, but also alleviate interference between these signals through the insulator layers. Such concentric lamellar structures can be formed by introducing diblock copolymers in coaxial cylinders. We performed Monte Carlo simulations in our previous work [28] to examine the self-assembly of AB diblock and ABA triblock copolymers between two coaxial cylinders, and found that the concentric cylindrical structure appears only when the confined film thickness is compatible with the bulk lamellae period of block copolymers. For a narrow cylindrical confinement system, helical structure was formed instead of the concentric cylindrical structure, even though the coaxial surfaces have a strong preference for each block of diblock copolymers. Same conclusions were also drawn in a latest simulation work from Zuo et al. [29]

To understand the formation mechanism of the multi-layered concentric lamellar structure, we have to solve three problems: (1) the effect of confined curvature on the free energy and layer

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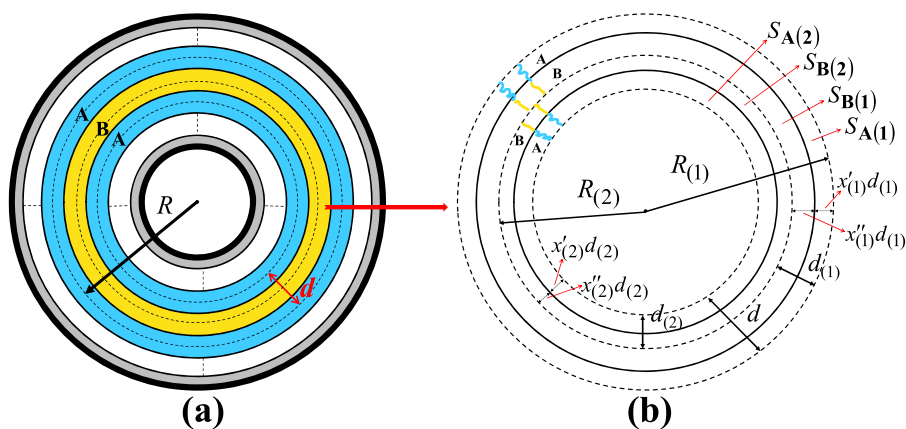E-mail address: xxiao3@ncsu.edu (X. Xiao).

Figure 1. (a) A multi-layered concentric cylindrical structure. The sky-blue and yellow regions correspond to the A-rich and B-rich domains, and the gray regions could be either the A-rich or the B-rich domain. The A-rich and the B-rich domains are sandwiched between two hard coaxial cylindrical walls (bold black circles at the exterior and at the interior layers). The short dotted lines represent multiple microphase domains. The thin black circles stand for real phase interfaces between the A and B blocks, and the thin dotted circles stand for virtual phase interfaces between the homogeneous blocks. (b) A unit cell is one curved (A-B-B-A) bilayer with a total film thickness d, which consists of two curved monolayers with two separate layer thicknesses $d_{(1)}$ and $d_{(2)}$. Without loss of generality, the outer and inner domains for the exterior (A-B) monolayer are assumed to be the rich-A and the rich-B domains, respectively. The layer thicknesses of the A and B domains in the exterior (A-B) monolayer are denoted as $x'_{(1)}d_{(1)}$ and $x''_{(1)}d_{(1)}$, respectively. The domain distribution of the interior (B-A) monolayer is reverse as the exterior (A-B) monolayer. The rich-B domain resides in the outer domain of the interior (B-A) monolayer and the rich-A domain is in the inner domain, of which the layer thicknesses are denoted as $x''_{(2)}d_{(2)}$ and $x'_{(2)}d_{(2)}$, respectively. The notation is explained in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

thickness of a (A-B) monolayer; (2) structural adjustment involving a (A-B-B-A) bilayer in response to the change of film thickness; and (3) morphological transitions between multi-layered concentric structures formed in coaxial cylinders. Problem (1) has been discussed in our previous work [30], wherein we employed Semenov's Strong Segregation Limit (SSL) theory [31,32] to study the dependence of the asymmetry (f) of AB diblock copolymers on the layer thickness of (A-B) monolayer at various confined curvatures [30]. Our theoretical study indicated that for the diblock copolymers of $f = 0.4$, the optimal layer thickness of the (A-B) monolayer has a slight increase firstly and then decrease as the confined curvature increases; while the optimal layer thickness for the diblock copolymers of $f = 0.6$ has a decrease as the curvature increases. A further analysis revealed that the free energy of the (A-B) monolayer increases exponentially with the increase of curvature when $f = 0.4$, but when $f = 0.6$ the free energy decreases slightly at a small curvature and then increases dramatically at a large curvature. Our finding explains well in theory why hexagonal structure can form in the bulk phase when the asymmetry of diblock chains is away from 0.5. Other theory work regarding the coaxial cylindrical and nanopore confinements can be found in Refs. [33–36]. The research efforts, however, did not provide a comprehensive insight on the understanding of such layer-type morphology structure in cylindrical confinement.

In this work, we employed SSL theory to study the problem (2): how the changes of the film thickness affect the sizes of phase domains in a curved (A-B-B-A) bilayer. Understanding the structural adjustments between two adjacent monolayers at various curvatures is essential to explore the morphological transitions of multi-layered concentric cylindrical structures in nanopores. By minimizing the total free energy of the (A-B-B-A) bilayer with respect to the layer thickness of the lamellae, we obtained an equilibrium layer thickness of the exterior (A-B) monolayer which balances the free energies between the exterior (A-B) and interior (B-A) monolayers involved in the (A-B-B-A) bilayer. In this manner, the (A-B-B-A) bilayer can automatically adjust the domain sizes of the monolayers to an equilibrated state. Through plotting the profile of film thickness of the bilayer *vs.* the total free energy per chain, we determined an optimal film thickness, at which the total free energy per chain reaches a global minimum. The optimal film thickness is a function of curvature, which reflects an optimal chain elongation

state under a certain cylindrical confinement. Finally, we evaluated the free energies of a (A-B) monolayer and a (A-B-B-A) bilayer, and located an intersection of the two free energy profiles which signifies the transition point at which a most likely existing structure shifts from the single (A-B) morphology to the dual (A-B-B-A) morphology.

2. Physical model and strong segregation limit theory

A multi-layered concentric cylindrical morphology appears when two coaxial cylindrical walls have a strong preference for one of the blocks of AB diblock copolymers. Figure 1a shows a sketch map of the multi-layered concentric cylindrical morphology, within which a (A-B-B-A) concentric lamellar structure (*viz.* a curved (A-B-B-A) bilayer) is repeated as a unit cell. The (A-B-B-A) bilayer contains two single concentric lamellae: one for exterior (A-B) monolayer and other for interior (B-A) monolayer. Due to geometric symmetry, the two monolayers have opposite domain distributions (see Figure 1b). As a consequence, there are two phase interfaces existing between the A-rich and B-rich domains in the (A-B-B-A) bilayer. As depicted in strong segregation limit theory, all diblock copolymer chains are aligned normal to phase interface. The stretch or compression of the copolymer chains, therefore, affects the size of phase domains (Figure 1b). We define d as a total film thickness of the (A-B-B-A) bilayer, and also define two layer thickness for the two monolayers, *viz.* $d_{(1)}$ for exterior (A-B) monolayer and $d_{(2)}$ for interior (B-A) monolayer. Obviously, $d = d_{(1)} + d_{(2)}$. We introduce two distortion coefficients: x' for block A and x'' for block B. These coefficients measure the extent to which the bending of the lamellae in cylinders affects the layer thickness of phase domains. See the Figure 1b for definition. The variables $x'_{(1)}d_{(1)}$ and $x''_{(1)}d_{(1)}$ are used to measure the layer thickness of the distorted A-rich and B-rich domains in the exterior (A-B) monolayer, respectively. The variables $x'_{(2)}d_{(2)}$ and $x''_{(2)}d_{(2)}$ are the layer thickness of the A-rich and B-rich domains in the interior (B-A) monolayer, respectively. The exterior radii of the two monolayers is assumed to be $R_{(1)}$ and $R_{(2)}$, respectively. Thus we have $R_{(2)} = R_{(1)} - d_{(1)}$.

Since the (A-B-B-A) bilayer consists of two monolayers, the total free energy F_{total}^{Con} of the (A-B-B-A) bilayer can be separated into two parts: one is $F_{(1)}^{Con}$ for the exterior (A-B) monolayer, and the other