Sphere-forming diblock copolymers confined in a square well

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Hongge Tan [a],*, Meiling Zhang [a], Yajing Deng [a], Qinggong Song [a], Dadong Yan [b],**

[a] College of Science, Civil Aviation University of China, Tianjin 300300, China
[b] Department of Physics, Beijing Normal University, Beijing 100875, China

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ABSTRACT

By means of the mean-field dynamic density functional theory (DDFT), the self-assembly behavior of the sphere-forming diblock copolymers confined in the square well has been studied systematically. Various novel structures are predicted, such as a string of spheres, stacked square bricks, a row of elongated potato-like micelles rotated with respect to each other, a single helix, two staggered helices, well-ordered square array of cylinders, highly ordered body-center-cubic (BCC) spheres, highly ordered face-center-cubic (FCC) spheres and concentric layers. Those morphologies provide the theoretical evidence for the experimental observations. Moreover, some interesting phenomena are found, such as the decrease of the number of layers with the increase of the surface field and the formation of the soft spheres, which can be observed in the experiments. Furthermore, a new order parameter is defined to characterize the degree of micro-phase separation for each kind of microscopic structure, and the key factor in affecting micro-phase separation is discussed.

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1. Introduction

Block copolymers are macromolecules composed of two or more chemically distinct subchains. Those subchains are joined chemically to prevent macrophase separation of different species. The self-assembly of block copolymers has attracted abiding attentions over the past few decades due to their ability to form various ordered nanoscale structures. For the potential application of microstructures, various approaches are employed to expand the types of morphology and control the microdomain ordering. Geometric confinement is proved to be an effective tool to fabricate unique nanostructure material and improve long-range order experimentally and theoretically [1–26].

In the beginning, the block copolymers were confined in thin films (one-dimensional confinement) and many novel self-assembled nanostructures with well controlled orientations were produced through the adjustment of the film thickness and the interaction between the copolymers and the surface [2–6]. Then, two-dimensional (2D) geometric confinement was also used in the self-assembly of the block copolymers [7–26]. Most of the work has focused on 2D confining channel with circular cross section (circular cylindrical channel) and confined copolymers which formed lamellae and cylinders in the bulk.

The effect of the confinement for lamella-forming block copolymers in the pore with circular cross section has been extensively studied in theories and experiments. Sevink et al. applied mean-field dynamic density functional theory to the study of the influence of circular cylindrical channel on the morphology of the symmetric block copolymer system [10]. They found two new phases: stacked disks and concentric lamellae. Meanwhile, using the Monte Carlo simulation, He et al. also obtained concentric lamellae in their study of lamella-forming diblock copolymers confined in circular cylinder [11]. Experimentally, Russell and co-workers reported the same stacked disks and concentric lamellae in the self-assembly of lamella-forming poly-(styrene-b-butadiene) (PS-b-PBD) diblock copolymers under cylindrical confinement [12–14]. Moreover, Sun et al. investigated symmetric poly-(styrene-b-methyl methacrylate) diblock copolymers confined in alumina nanopores and also experimentally observed the concentric lamellae [15].

For cylinder-forming block copolymers confined in the pore, much work has also been carried out. Using self-consistent field theory (SCFT), Chen et al. studied the self-assembly of cylinder-forming asymmetric diblock copolymers confined in cylindrical pores [16]. By choosing suitable chain parameters, various nanostructures were observed, and the dependence of these microstructures on the ratio between the pore diameter D and the bulk cylinder spacing L_0 (D/L_0) was investigated [16]. Yu et al. systemically studied the equilibrium morphologies of cylinder-forming diblock copolymers confined in cylindrical pores using a simulated annealing method [17,18]. They also found that the equilibrium

* Corresponding author. Tel.: +86 10 5880 7604.
** Corresponding author.
 E-mail addresses: thg@iccas.ac.cn (H. Tan), yandd@bnu.edu.cn (D. Yan).

morphology was largely controlled by the ratio D/L_0. These studies show that the commensurability between the pore diameter and the bulk periodicity of the diblock copolymers is one of the key factors in determining the equilibrium states. Experimentally, Russell and co-workers reported the self-assembly of cylindrical diblock copolymers (PS-b-PBD) under cylindrical confinement [13,14,20]. At larger ratios of the pore diameter to the copolymer natural period D/L_0, the copolymers retained their cylindrical morphology with the hexagonal packing, and the cylinders were aligned along the pore axis due to the preferential wetting of the pore wall with the PBD block. Under severe confinement (in small pore), morphologies different from the bulk were observed, which included stacked torus-type structures and helical cylinder.

Contrast to the confinement of lamella-forming and cylinder-forming diblock copolymers, less attention has been paid to the 2D geometric confinement of sphere-forming block copolymers. Experimentally, Russell and co-workers investigated the morphologies of bulk sphere-forming block copolymers under the cylindrical confinement. They observed that large pores caused spherical domains to be aligned along the pore axis, while in pores with smaller diameters, core–shell cylindrical morphologies, single column of spherical microdomains, and spirals of doubly and triply paired spherical microdomains were observed [13,14]. Additionally, spherical domains in rows along the nanorod axis and spheres arranged in concentric shells parallel to the core–shell interface were found by Ma et al. for sphere-forming diblock copolymers poly (styrene-b-isoprene) in the nanorod [21]. Thomas et al. studied the assembly of spherical micelles in alumina nanochannels using polyethylene-co-butylene-block-polyethylene oxide (PHB-b-PEO), and obtained many novel nanostructures [22]. Using the cell dynamics simulation, Pinna et al. studied the lamella-, cylinder-, and sphere-forming diblock copolymers confined in circular cylinder [23]. However, only a few phases have been studied in a limited parameter space in those papers. The knowledge of sphere-forming diblock copolymers confined in cylinder is really fragmentary.

Besides, the effect of different confining geometry of pores on the self-assembly of block copolymers has also been investigated. Yu et al. studied cylinder-forming diblock copolymers confined in channels with various shapes using a simulated annealing method [24]. Experimentally, Russell and co-workers also studied the effect of different confining geometry of pores on morphologies of cylindrical PS-b-PBD [25]. Hur et al. conducted two-dimensional SCFT simulations to determine optimal conditions under which cylindrical block copolymer laterally confined in a square well could form perfect long-range tetragonal order [26]. It was found that self-assembled morphologies were strongly affected by the boundary shapes.

Motivated by these experimental and theoretical studies, we carry out a systematic study of sphere-forming diblock copolymers confined in the square well by the mean-field dynamic density functional theory (DDFT). To our knowledge, this is the first simulation of sphere-forming polymers in a square well. In this paper, we investigate the effects of a square well confinement on the self-assembly of sphere-forming diblock copolymers. Especially we focus on the effects of the size and the interaction between the surface and the diblock copolymers on the microstructures.

This paper is organized as follows. In Section 2, the mean-field dynamic density functional theory is described simply. In Section 3, deviations of the bulk morphology are observed for the copolymers in the square well and novel long-range ordered nanoscopic structures are obtained. In particular, some results are compared with the corresponding experimental and theoretical results. In Section 4, the degree of microphase separation for each kind of nanostructure is discussed and corresponding curve is obtained. Finally, the conclusions about this work are drawn.

2. Model and methods

The computer simulation is carried out by the MESODYN technique, which is based on the mean-field DDFT approach [27–32]. In the DDFT model, the polymer melt consists of n Gaussian chain molecules in a mean-field environment. Langevin equation for the diffusive dynamics of the density fields is used to describe the time evolution of the density.

$$\frac{\partial \rho_I}{\partial t} = M_I \nabla \cdot \rho_I \nabla \mu_I + \eta_I. \tag{1}$$

Here M_I is the mobility parameter of a bead of type I, η_I is Gaussian noise which satisfies the fluctuation-dissipation theorem [32], ρ_I is the density of the copolymer bead I, and $\mu_I = \delta F / \delta \rho_I$ is intrinsic chemical potential field of a bead of type I. F is the free energy of the system and is defined as [28,30]

$$F[\rho] = -kT \ln \frac{\phi^n}{n!} - \sum_I \int_V u_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} + F^{nid}[\rho], \tag{2}$$

where ϕ is the single-chain partition function for ideal Gaussian chains in an external field u_I [28], and non-ideal term $F^{nid}[\rho]$ includes bead–bead and bead–surface interaction as well as Helfand penalty function [31,33]. The details of non-ideal term $F^{nid}[\rho]$ can be found in Refs. [3,30].

In this paper, we consider a melt of n A_8B_2 diblock copolymers with the total degree of polymerization $N = 10$ in a volume V at temperature T. We take the volume fraction as $f_A = 0.8$, which is similar to the value used in the experiment to obtain the spherical phase in the bulk [13]. The simulations are completed on a cubic grid of dimensions $X \times Y \times Z$ with a mesh size h ($h = 1$ nm). For the simulation, the square well axis is along the X direction and the periodic boundary condition is applied along this direction. The length of the square well is fixed to be 64 nm. The cross section of the square well is a square with the side length L. Polymers cannot occupy the lattice sites outside the square well. Thus, polymers are confined in the square well with the side length L. Analogous to our previous work [5], the interaction between different blocks is characterized by the interaction parameter ε_{AB} in units of kJ/mol and the interaction between blocks and interfaces is characterized by corresponding mean field interaction parameters ε_{AM} and ε_{BM}. An effective interface–copolymer interaction parameter is $\varepsilon_M = (\varepsilon_{BM} - \varepsilon_{AM})$, which characterizes the strength of the surface field. Simulation parameters are the same as those in our previous work [5]. The mobility parameters are assumed to be equal, that is, $M_A = M_B = M$. The temperature is 413 K, which is close to the experimental temperature used to anneal PS–PBD copolymers confined in pores to obtain the equilibrium structures [13,14]. The dimensionless parameters in MESODYN are chosen as follows: the grid parameter $d = a/h = 1.1543$; the time step $\Delta \tau = M \Delta t / h^2 kT = 0.5$; the noise scaling parameter $\Omega = h^3/v = 100$; and the compressibility parameter $\kappa_H/vkT = 8$. We follow the temporal evolution in the system and stop it when both the free energy and the order parameter do not change significantly. In this paper, the units of ε and the side length L are kJ/mol and nm respectively, and we neglect them from now on.

3. Results and discussion

For A_8B_2 diblock copolymer, it forms spherical bulk phase at $\varepsilon_{AB} = 10$ with bulk sphere spacing $L_0 = 6-7$ nm, which has been reported in our previous study [5]. The Flory-Huggins parameter χN and ε_{AB} are related by $\chi = \varepsilon_{AB}/RT$ (R is universal gas constant). When $\varepsilon_{AB} = 10$, $\chi N \approx 29$. The formation of spherical phase at