



Electric-field-induced sphere–cylinder phase transitions of diblock copolymers



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ABSTRACT

Using the real space self-consistent field theory, the transitions between the body-centered-cubic phases and the cylindrical phases were studied for the diblock copolymers in the external electrostatic fields along three different orientations [001], [110], and [111]. The different orientations of the external fields resulted in the cylinder structures with various symmetries through the intermediate ellipsoid structures, where the cylinder-to-cylinder transition was also observed in the electric field along the orientation [110]. Furthermore, the size of ellipsoid was investigated by varying the strength of electric field, and the factors that affect the critical values of electric field strengths were also considered for the sphere–cylinder transitions in the electric fields with orientation [001]. Our findings are compared with the available experimental and theoretical works, which is in a general agreement.

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1. Introduction

Block copolymers can be used as functional materials with emerging applications due to their spontaneous formation of ordered structures in nanoscale [1]. For example, several classical ordered structures, such as the lamellae, cylinders, spheres, and gyroids, have been documented for the diblock copolymers. However, the ordered phase of diblock copolymers is not created in one single crystal but in domain with different orientations, thus limiting their application. One means of aligning the domain is to apply an external field, such as shear and electric field. The external electrostatic potential, which is produced by two parallel planar electrodes separated by several micrometers, can effectively align the lamellar or cylindrical domains normal to the surfaces of thin films [2]. In addition to the benefits of electric fields to control the domain orientations, electric fields can also induce phase transitions due to the balance between enthalpic and entropic energies.

A system with inhomogeneous dielectric material affected by the external electric field has attracted considerable attention [2]. The small-angle X-ray scattering is employed to investigate the lamellar domain alignments for various diblock copolymer systems [3–12]. The scanning force microscopy and simulation method are used to observe the three-dimensional (3D) control over the

lamella orientations, in which the orthogonal electric fields are employed [13–15]. Theoretical works have been contributed to the mechanisms of lamellar alignment for the diblock copolymers with various methods, such as the Ginzburg–Landau method and self-consistent field theory (SCFT) method [16–19]. On the other hand, the electric field can control the orientation of cylinders in the system of diblock copolymers, which have been contributed by many theoretical and experimental studies [13,20–22]. For the lamellar alignments, the electric field determines the polarization of the dielectric material. That is to say, the local inhomogeneous dielectric constant depends on the morphology of the ordered phase, which is also determined by the local electric field.

Electric field can not only orient the lamella and cylinder domains but also can induce the phase transitions. Experiments have reported that the sphere phases can be induced into the hexagonal cylinder phases in the diblock copolymer system when the strength of electric field was increased into a certain degree [23–25]. The effect of the interfacial energy on the induced phase transition has been investigated [24]. A number of theoretical calculations, including the SCFT and cell dynamic simulation, have been applied to study the phase transition from the spheres to the cylinders with the effects of external electric field [26–30]. Reciprocal space approach, which solves the SCFT equations numerically using a restricted Fourier basis depending on the assumed morphological symmetries, has been performed [26]. Very recently, a dynamical SCFT study has been performed on the phase transition between the sphere and cylinder, where the different transition kinetic

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pathways, the final cylindrical domains with various symmetries, and various transient states, have been observed depending on the strength and directions of the applied electric fields [30]. Other phases, such as the gyroid and hexagonally perforated lamella, can also be induced into the cylinder phases in the cell dynamic and real-space dynamical SCFT simulations when the strength of applied electric field is increased to a certain degree [31–35].

Although there have been several works contributed to the electric-field induced sphere–cylinder phase transitions, the phase transitions were observed in the electric field with fixed strengths. It is expected to observe the new phase behaviors in the electric fields with various orientations and varying strengths where a *quasistatic* process can be assumed. In the present work, we study the sphere-to-cylinder transition under the effects of the external electric field for the diblock copolymer using a real-space SCFT approach. We solve the set of SCFT equations and the appropriate Maxwell equations under the assumption of a simple constitutive relation between the local dielectric properties and the local volume fractions with the saddle-point approximation. With the external electric fields along the orientations [001], [110], and [111], we observe the different processes of phase transition from spheres to cylinders along with the orientations of the external electrostatic fields, where the body-centered-cubic (bcc) phases are deformed to the cylinders with different symmetries. Furthermore, the parameters affecting the phase transitions were also investigated in the model diblock copolymer system.

2. Calculation method

We consider a system of n AB diblock copolymers, with polymerization index N and A-monomer fraction f in a fixed external electrostatic potential ψ . We assume the monomers A and B to occupy the same volume $1/\rho_0$ and have the same Kuhn length a in an incompressible system with volume V . In real-space SCFT, we consider the statistics of a single copolymer chain in a set of effective chemical potential field ω_i , where the subscript i represents the block species A or B. These chemical potential fields are conjugated to the segment density ϕ_i of the block species i . The free energy functional (in the unit of $k_B T$) with mean-field approximation in a fixed external electric field can be written as follows:

$$\frac{F}{nk_B T} = -\ln Q + \frac{1}{V} \int d\mathbf{r} \left\{ \chi N \phi_A \phi_B - \omega_A \phi_A - \omega_B \phi_B - P(1 - \phi_A - \phi_B) - \frac{1}{2} \varepsilon(\mathbf{r}) |\nabla \psi(\mathbf{r})|^2 \right\}, \quad (1)$$

where, χ is the Flory–Huggins interaction parameter between species A and B, P is the Lagrange multiplier (as a pressure), and $\psi(\mathbf{r})$ denotes the electrostatic potential at position \mathbf{r} . The linear approximation $\varepsilon(\mathbf{r}) = \varepsilon_A \phi_A(\mathbf{r}) + \varepsilon_B \phi_B(\mathbf{r})$, in the unit of $3/(2\pi\rho_0 e^2 a^2)$, was used to describe the position-dependent dielectric constant, where ε_A and ε_B represent the relative dielectric constants of block copolymers A and B, respectively. $Q = \int d\mathbf{r} q(\mathbf{r}, 1)$ denotes the partition function of a single copolymer chain. The end-segment distribution function $q(\mathbf{r}, s)$ provides the probability of the section of a chain, with the contour length s , and contains a free chain end with “connected end” located at \mathbf{r} . The parameterization was chosen such that the contour variable s increases continuously from 0 to 1, corresponding from one end of the chain to the other. With the flexible Gaussian chain model describing the single-chain statistics, the function $q(\mathbf{r}, s)$ satisfies the following modified diffusion equation:

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \nabla^2 q(\mathbf{r}, s) - N \theta_i(s) \omega_i q(\mathbf{r}, s) \quad (i = A, B), \quad (2)$$

where $\theta_i(s)$ is equal to 1 if s belongs to block i ; otherwise it is equal to 0. In Eq. (2), the lengths are scaled by the (overall) radius of the gyration of an unperturbed chain. The appropriate initial condition is $q(\mathbf{r}, 0) = 1$. Similarly, the second distribution function $q'(\mathbf{r}, s)$ should be used to express the diffusion behavior of monomer, which satisfies Eq. (2) only with the right-hand side multiplied by -1 , and the initial condition, $q'(\mathbf{r}, 1) = 1$.

The mean-field SCFT equations are obtained by the saddle point approximation, where one sets $\delta F/\delta \phi_i = \delta F/\delta \omega_i = \delta F/\delta P = \delta F/\delta \psi = 0$, leading to the following set of equations:

$$\omega_A(\mathbf{r}) = \chi N \phi_B(\mathbf{r}) + P(\mathbf{r}) - \frac{1}{2} \varepsilon_A |\nabla \psi(\mathbf{r})|^2, \quad (3)$$

$$\omega_B(\mathbf{r}) = \chi N \phi_A(\mathbf{r}) + P(\mathbf{r}) - \frac{1}{2} \varepsilon_B |\nabla \psi(\mathbf{r})|^2, \quad (4)$$

$$\phi_{A(B)}(\mathbf{r}) = \frac{1}{Q} \int_0^1 ds q(\mathbf{r}, s) q'(\mathbf{r}, 1-s) \theta_i(s), \quad (5)$$

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1, \quad (6)$$

$$\nabla \cdot [\varepsilon(\mathbf{r}) \nabla \psi(\mathbf{r})] = 0, \quad (7)$$

The mean-field SCFT equations (Eqs. (3)–(7)) were solved directly in real space by using a combinatorial screening algorithm proposed by Drolet and Fredrickson [36,37]. Using a “pseudospectral method” [38,39], the modified diffusion equations were solved to obtain the end-integrated propagators, $q(\mathbf{r}, s)$ and $q'(\mathbf{r}, s)$. The effective chemical potential fields were updated through the linear combination of ω^{old} and ω^{new} . This iteration scheme represents a pseudodynamics process with the steepest descent on the energy landscape to the nearest metastable solution.

Numerical simulations were carried out in a 3D space represented by a box $L \times L \times L$, which is divided into a $32 \times 32 \times 32$ lattice, with a periodic boundary condition. This simulation box size can produce one unit cell with precision enough, from which the various phases can be distinguished. This box size is similar to the previous work [37]. In order to eliminate the box size effect, we have optimized the domain size by comparing the free energies in various grid sizes. The simulation results indicate that the phases have the same optimized grid size in different strengths of electric fields as the phase without electric field. In the present work, we optimized the grid size to be $\Delta x = 0.145$ and the box size was set as $L = 4.65$, where all lengths are measured in the unit of R_{g0} (unperturbed mean-square radius-of-gyration of a copolymer chain). We assume that the fixed external electrostatic potential ψ is produced by planar electrodes separated by a distance d (in units of R_{g0}) and subjected to a voltage difference V_{12} . Then, the average electric field strength $E_0 = V_{12}/d$ is introduced to describe the fixed electrostatic field in this system. The corresponding molecular parameters of bcc phase were set as $\chi N = 20$ and $f = 0.24$ in the simulation [40]. The relative dielectric constants $\varepsilon_A = 4.0$ and $\varepsilon_B = 16.0$ were applied in the sphere–cylinder phase transition cases, while the dielectric constants were varied to investigate its dependence of the critical electric field. The average relative dielectric constant parameter is defined as $\varepsilon_{e0} = (\varepsilon_A \times f) + \varepsilon_B \times (1-f)$. Starting from the bcc phase, the simulation for each voltage was carried out until the phase pattern is stable and invariable with time and the free energy change is negligible to $\Delta F < 10^{-6}$.

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