

Defect-free hexagonal patterns formed by AB diblock copolymers under triangular confinement

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HIGHLIGHTS

- Only perfect hexagonal patterns are stable in triangularly confined systems.
- Multi-step annealing process leads to defect-free hexagonal patterns.
- DSA in regular triangles does not exhibit an incommensurability problem of size.

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ABSTRACT

The self-assembly of a hexagonal cylinder-forming diblock copolymer melt under the hexagonal confinement provides a useful method for the fabrication of defect-free hexagonal patterns. However, the validity of this method depends on the commensurability of the hexagonal size to the domain spacing. Here we turn to another lateral confinement whose shape adapts to the hexagonal lattice, i.e. the regular triangle. First, we attempted to verify that the perfect hexagonal patterns are exclusively the thermodynamic stable morphologies in the triangles with whatever sizes using the self-consistent field theory (SCFT). Then, we simulate the annealing kinetics of the confined melt using the SCFT iteration process. We find that a small number of defects are usually formed in a large triangle even with a commensurate size to the domain spacing. Finally, we propose a multi-step annealing process, where the perfect hexagonal patterns are yielded via a heterogenous nucleation process. Importantly, the achievement of the perfect hexagonal patterns does not exhibit a size-incommensurability issue with the triangles, and thus could become a promising nanolithography scheme.

1. Introduction

The self-assembly of block copolymers provides a powerful platform for the fabrication of ordered nanostructures which have wide potential applications in many fields [1–5]. One of the promising applications is to extend the nanolithography technique for reaching smaller feature size at a lower cost via the directed self-assembly (DSA) of block copolymers. The bottom-up pattern strategy based on DSA has been regarded as one of the most appealing next-generation lithography techniques [3,6–9]. Two kinds of guiding patterns on the substrate for DSA, i.e. chemical (chemoepitaxy) [6,10–13] and topographical (graphoepitaxy) [7,14–18], have been demonstrated to achieve the structures satisfying the demands of semiconductor. Moreover, DSA of block copolymers via chemoepitaxial and graphoepitaxial techniques can be applied to fabricate not only large-scale ordered geometrically simple patterns [6–8,19,20] but also device-oriented irregular structures

[21–25].

For graphoepitaxy, one of the simple but efficient guiding patterns is acted by the geometrical confinements. On one hand, geometrical confinements are capable to alter the self-assembly behavior of block copolymers drastically due to the breaking of the translational symmetry of the bulk phase as well as the incommensurability between the geometrical size and the domain spacing, leading to novel nanostructures different from the bulk phases [26–35]. On the other hand, some geometrical confinements with proper size conditions can guide the self-assembly of block copolymers into defect-free patterns [19,20,36–38]. For example, ordered hexagonal patterns can be achieved from the self-assembly of hexagonal cylinder-forming diblock copolymers under an angle-matched geometrical confinement, e.g. lateral hexagonal confinement, where each sidewall aligns the cylindrical domains and each corner helps register the positions of domains [19,20,39]. It is necessary to note that long-range order cannot be

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achieved in two-dimensional (2D) systems due to thermal fluctuations, which has been verified in conventional condensed matter systems [40]. This is why an additional guiding pattern is needed for the fabrication of 2D ordered patterns.

The formation of hexagonal patterns in the hexagonal cylinder-forming diblock copolymers under the hexagonal confinement has been well studied by both theory and experiment [19,20,30,36,38,39,41]. In experiments by Xu et al. [38], the defect-free hexagonal pattern is successfully achieved with the diagonal size of hexagon $D \approx 15L_0$, where L_0 indicates the cylinder-to-cylinder distance in the bulk. However, small amount of defects are present in the patterns for larger hexagons, and the defect concentration increases as the hexagonal size. From the aspect of thermodynamics, the self-consistent field theory (SCFT) study reveals that imperfect or defective hexagonal patterns could become stable in the hexagons with incommensurate size to the domain spacing [19]. From the other aspect of kinetics, the cell dynamics simulations (CDSs) based on the time-dependent Ginzburg-Landau theory (TDGL) predict that there exists a commensurability window with respect to the hexagonal size for the fabrication of defect-free patterns even through an ideal heterogeneous nucleation process [20].

For the hexagonal pattern, there is an alternative geometrical confinement with the adaptable symmetry, i.e. the regular triangle. Instructively, previous theoretical studies suggest that diblock copolymers confined in hexagons and triangles exhibit notably different self-assembly behaviors [19,30,39]. In fact, experimentalists have also demonstrated that the triangular confinement is able to guide the self-assembly of cylinder-forming diblock copolymers to form defect-free hexagonal patterns, but they have not examined the size effect yet [38,41]. Monte Carlo (MC) simulations by Yu et al. suggest that some interesting three-dimensional structures (e.g. helices) are observed in long hexagonal nanopores while the main structures in long triangular nanopores are hexagonal patterns [30]. The MC results about the hexagonal confinement have been confirmed by later SCFT calculations [19]. Very recently, large-scale TDGL simulations were performed to investigate the formation kinetics of the hexagonal patterns under triangular confinement [39]. Interestingly, it is observed that the defect concentration does not exhibit obvious dependence on the triangular size. Moreover, defect-free hexagonal patterns could be formed via the optimized heterogeneous nucleation process in triangles with large size ranging from $48L_0$ to $53L_0$. This observation implies that there should be no commensurability issue with the application of the triangular confinement to DSA for the yield of defect-free hexagonal patterns. If this speculation is true, the triangular confinement should be a promising guiding pattern for DSA. However, a systematic study is lacking to provide a direct evidence for the validity of the DSA scheme based on the triangular confinement.

2. Theory and method

We consider an incompressible melt of volume V , consisting of n AB diblock copolymer chains, laterally confined in a regular triangle. The A and B blocks in each copolymer consist of fN and $(1-f)N$ segments, respectively. For simplicity, we assume that all segments have the same statistical length b and density ρ_0 , such that $V = nN/\rho_0$. As the depth of the triangular well is a relatively trivial factor for the fabrication of film-through standing cylinders in graphoepitaxy, we simplify the system to be two-dimensional (2D), i.e. in the plane of the triangle. For convenience of computation, we put the triangle into a square box with side length slightly larger than that of the triangle D and use a third component to fill the outside region of the triangle, ϕ_w , thus preventing the polymers from going there (Fig. 1 (a)). Specifically, the wall component ϕ_w is set to be 1 outside the triangle and it decreases as $\phi_w(\mathbf{r}) = 1 - \tanh(d/\sigma)$ from the wall surface, where d is the closest distance to one of the three sidewalls and σ indicates the interfacial width between the wall component and the copolymer (Fig. 1(b)). The

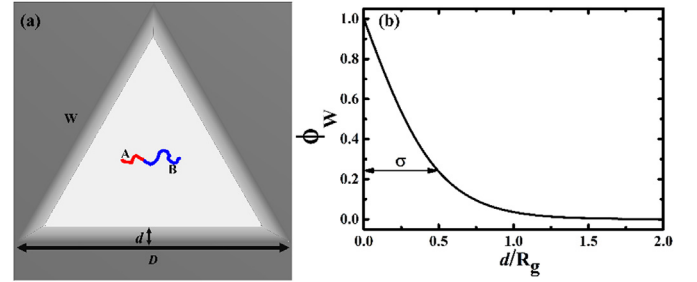


Fig. 1. (a) Schematic illustrating the triangular confinement on the asymmetric AB diblock copolymer melt. The confining effect is implemented by the wall density with a prior-given distribution, $\phi_w(\mathbf{r})$. $\phi_w(\mathbf{r})$ is set to be zero outside the triangle, and otherwise it attenuates as $\phi_w(\mathbf{r}) = 1 - \tanh(d/\sigma)$, where d is the closest distance to one of the three sidewalls and σ is a constant measuring the interfacial width between the wall component and the copolymer. (b) Plot of $\phi_w(\mathbf{r})$ for $\sigma = 0.5R_g$.

radius of gyration, $R_g = N^{1/2}b/\sqrt{6}$, is chosen as the length unit in our SCFT calculations.

Within the mean-field approximation to statistical mechanics of the Edwards model of polymer [42], the free energy functional F for this geometrically confined system at a given temperature T is written as,

$$\begin{aligned} \frac{F}{nk_B T} = & -\ln Q + \frac{1}{V} \int d\mathbf{r} [\chi_{AB} N\phi_A(\mathbf{r})\phi_B(\mathbf{r}) + \chi_{AW} N\phi_A(\mathbf{r})\phi_w(\mathbf{r}) \\ & - w_A(\mathbf{r})\phi_A(\mathbf{r}) + \chi_{BW} N\phi_B(\mathbf{r})\phi_w(\mathbf{r}) - w_B(\mathbf{r})\phi_B(\mathbf{r}) \\ & - \eta(\mathbf{r})[1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r}) - \phi_w(\mathbf{r})]] \end{aligned} \quad (1)$$

where $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are the local volume fractions of A and B components, and $w_A(\mathbf{r})$ and $w_B(\mathbf{r})$ are the potential fields acting on the two components, respectively. $\chi_{\alpha\beta}$ is the Flory-Huggins interaction characterizing the immiscibility between α and β components ($\alpha, \beta = A, B$ and W). $\eta(\mathbf{r})$ is a Lagrange multiplier used to enforce the incompressibility condition $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_w(\mathbf{r}) = 1$. The constant quantity Q is the partition function of a single copolymer chain interacting with the mean fields $w_A(\mathbf{r})$ and $w_B(\mathbf{r})$ produced by surrounding chains. Note that the distribution of the wall component is fixed. So the free energy functional is minimized with respect to the distributions of A/B volume fractions and the conjugate potential fields, leading to the following SCFT equations [42].

$$w_A(\mathbf{r}) = \chi_{AB} N\phi_B(\mathbf{r}) + \chi_{AW} N\phi_w(\mathbf{r}) + \eta(\mathbf{r}), \quad (2)$$

$$w_B(\mathbf{r}) = \chi_{AB} N\phi_A(\mathbf{r}) + \chi_{BW} N\phi_w(\mathbf{r}) + \eta(\mathbf{r}), \quad (3)$$

$$\phi_A(\mathbf{r}) = \frac{1}{Q} \int_0^f ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s), \quad (4)$$

$$\phi_B(\mathbf{r}) = \frac{1}{Q} \int_f^1 ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s), \quad (5)$$

$$Q = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s). \quad (6)$$

In above equations, $q(\mathbf{r}, s)$ and $q^\dagger(\mathbf{r}, s)$ are the two conjugate propagator functions, satisfying the modified diffusion equations,

$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}, s) q(\mathbf{r}, s), \quad (7)$$

$$-\frac{\partial q^\dagger(\mathbf{r}, s)}{\partial s} = \nabla^2 q^\dagger(\mathbf{r}, s) - w(\mathbf{r}, s) q^\dagger(\mathbf{r}, s), \quad (8)$$

where $w(\mathbf{r}, s) = w_A(\mathbf{r})$ for $s < f$ and otherwise $w(\mathbf{r}, s) = w_B(\mathbf{r})$. The initial conditions are $q(\mathbf{r}, 0) = q^\dagger(\mathbf{r}, 1) = 1$. To solve the modified diffusion equations, we employ the second-order pseudo-spectral method for numerical solutions [43,44].

In our calculations, periodic boundary conditions are imposed automatically on the cubic simulation box with sizes $L_x = L_y > D$. In

order to obtain reliable accuracy, the lattice size $N_x \times N_y$ is varied in accord with the box size ensuring the grid spacing $\Delta_x = L_x/N_x = \Delta_y = L_y/N_y \sim 0.1R_g$, typically chosen as 128×128 , 256×256 , 384×384 and 512×512 . The chain contour is discretized into 100 pieces, i.e. $\Delta s = 0.01$. Moreover, a stringent convergence criteria is employed for the solving iteration of the SCFT equations, i.e. that the free energy, the volume fractions (or mean fields) and the incompressibility condition converge to a computational error less than 10^{-6} [45].

3. Results and discussion

To concentrate on the direction effect of the triangular confinement on the formation of hexagonal cylinder patterns, we first choose a typical group of parameters as $\chi N = 20$ and $f = 0.26$ that leads to the hexagonal cylinders in bulk with the cylinder-to-cylinder distance $L_0 \approx 3.98R_g$. Moreover, we fix $\chi_{AW}N = 30$ and $\chi_{BW}N = 15$ such that the wall surface prefers the majority B-blocks. The exploration of the stable morphology in a given block copolymer system is to search the global minimum in a complex free-energy landscape. Usually it is a difficult unsolved problem, especially when there are too many local minima (i.e. SCFT solutions) in the free-energy landscape to be examined. In the pseudo-spectral method of SCFT, different SCFT solutions can be achieved by using different random initial conditions. Nevertheless, it is never possible to make sure that all SCFT solutions are found.

In this triangularly confined 2D system, the number of possible SCFT solutions increases rapidly as the side size D increases. By solving the SCFT equations with different initial conditions many times for fixed D , we find that different solving processes converge to a same solution when $D \lesssim 5.5L_0$, that is a perfect hexagonal pattern. While other SCFT solutions corresponding to imperfect/defective hexagonal patterns are observed for $D \gtrsim 5.5L_0$. This observation presents a challenge to verify if there are stable imperfect hexagonal patterns in the entire size range of confining triangles. Here we try to answer the question by two steps. First, we identify the phase diagram of stable perfect hexagonal morphologies with respect to D by comparing their free energy. Then we generate a large number of imperfect hexagonal morphologies for different sizes of triangular confinements to compare their free energy with the corresponding stable perfect hexagonal morphology in the phase diagram. If there exists one imperfect pattern having lower free energy than the perfect one, we will prove that there are stable imperfect patterns in the triangularly confined system. Otherwise, although we cannot exclude the existence possibility of imperfect patterns, we could speculate a safely low probability for the formation of stable imperfect patterns as long as the number of samples examined is large enough.

We denote the perfect hexagonal pattern as C_k , where k indicates the number of cylindrical domains arranged along one sidewall of the triangle. The total number of domains in the pattern of C_k is $n_{\text{dmn}} = k(k+1)/2$. The density plots of the perfect hexagonal patterns from C_1 to C_9 are shown in Fig. 2(a) and the phase diagram for $\chi N = 20$ and $f = 0.26$ is presented in Fig. 2(b). The free-energy comparisons between these different morphologies are provided in Fig. 3. For $L_0 < D \lesssim 2.2L_0$, only one domain is formed at the center of the triangle (i.e. C_1). Considering that the effective size of the triangle is reduced due to the presence of the wall component inside the triangle, the stability region of C_1 is in good agreement with that of $0.8L_0 \lesssim D < 2L_0$ obtained in long triangular pores using MC simulations by Yu et al. [30] As D increases, the stable morphology transforms into C_2 , C_3 , C_4 , ..., in sequence. The hexagonal patterns of C_2 , C_3 and C_4 are also observed in the similar ranges of triangular size by MC simulations. Obviously, the size range for each pattern is nearly constant, i.e. L_0 , and the stable region of C_k is about $(k+0.3)L_0 \lesssim D \lesssim (k+1.3)L_0$.

In nanolithography, the nonuniformity of domains is an important measurement for the pattern quality. In the confined system, the wall boundary should have some influence on the size and shape of these

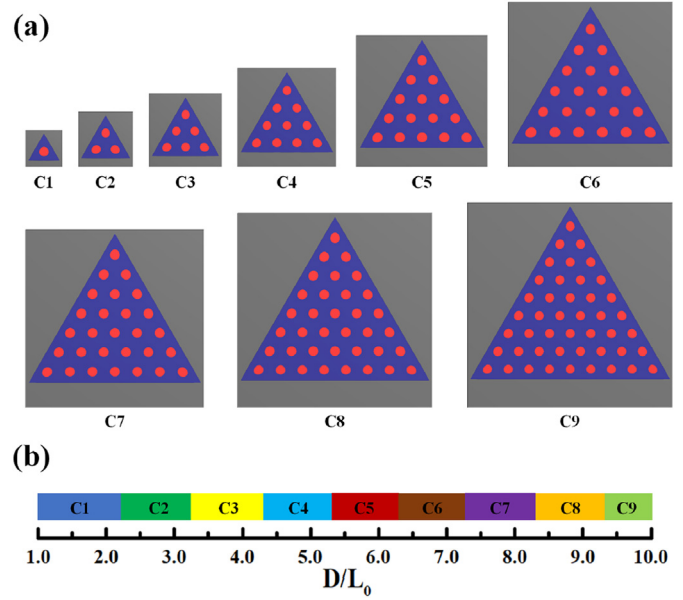


Fig. 2. (a) Density plots of stable perfect hexagonal morphologies observed in the hexagonal cylinder-forming diblock copolymer melt with $\chi_{AB}N = 20$ and $f = 0.26$ under the lateral confinement of two-dimensional triangle with variable side size of D . (b) Phase sequence of morphologies as a function of D/L_0 , where $L_0 = 3.98R_g$.

domains. Here we introduce the relative standard deviation (RSD) of the domain area to quantify the nonuniformity of domain size, $\text{RSD} = \sqrt{\sum_{i=1}^{n_{\text{dmn}}} (S_i - \bar{S})^2 / n_{\text{dmn}}} / \bar{S}$, where S_i and $\bar{S}$ are the area of domain i and the average area of all domains in a given triangle. The values of RSD for different hexagonal morphologies are given in Fig. 4. The observation of $\text{RSD} < 2\%$ indicates that these domains in one morphology are rather uniform. In fact, the nonuniformity in these morphologies listed in Fig. 4(b–f) are hardly detectable. However, RSD always decreases as D increases for a given morphology, implying that chain stretching favors the formation of uniform domains. In other words, as the triangular size increases, the domains expand and become more uniform. Note that there are slight deformations about the domains near the sidewalls, especially at the corners, which is caused by the breaking of the translational symmetry.

As mentioned previously, there is no rigorous method for identifying the stable morphology in a given block copolymer system when there are an unknown number of possible competing metastable morphologies. Here we simply generate a large number of morphologies using SCFT with different random initial conditions for these systems with the triangular size within a specific range, $16.4L_0 \leq D \leq 17.8L_0$, which covers the C_{16}/C_{17} boundary. We plot the free energies of these randomly generated morphologies as well as the perfect C_{16} and C_{17} morphologies in Fig. 5(a) for $\chi N = 20$ and $f = 0.26$. The systems are selected in the considered size range with an interval of $\Delta D = 0.2L_0$, and four different morphologies are generated for each system. We find that most of these hexagonal morphologies contain a small number of defects, thus exhibiting higher free energy than that of the respective stable C_{16} or C_{17} . Two typical morphologies are shown in Fig. 5(b) and (c) for the systems of $D = 16.6L_0$ and $D = 17.4L_0$, respectively, of which the free energies indicated by enclosed points are significantly higher than that of the respective C_{17} and C_{16} . It is interesting to note that the morphology in Fig. 5(c) even consists of 18 domains arranged along the triangular side, two more domains than those in the stable C_{16} morphology. The total domain number $n_{\text{dmn}} = 164$ in Fig. 5(c) is less than $n_{\text{dmn}} = 171$ in C_{18} , however, considerably larger than $n_{\text{dmn}} = 153$ in C_{17} and 136 in C_{16} . Therefore, the occurrence of defects is not the main causing effect for the high penalty of free energy, but the large compression of the domains. In

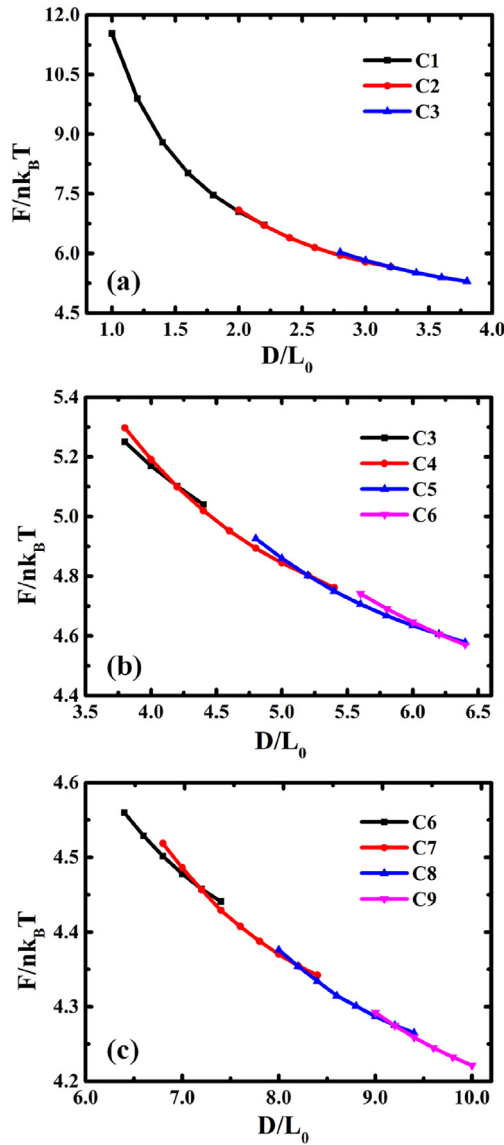


Fig. 3. Free-energy comparisons of candidate 2D morphologies as function of D for $\chi_{AB}N = 20$ and $f = 0.26$. For the reason of clarity, the parameter range of $L_0 \leq D \leq 10L_0$ is divided into three sub-ranges shown in (a), (b) and (c), respectively.

fact, the free energy of the perfect C18 morphology is even higher.

The above discussions can roughly lead to a conclusion that the thermodynamic equilibrium morphologies are always the perfect hexagonal ones in the triangularly confined block copolymer system with whatever triangular size. However, it is difficult to achieve the perfect hexagonal pattern in a large confining triangle via a simple thermal annealing process due to the intervention of a large number of metastable defective morphologies in the kinetic pathway. An optimized kinetic pathway is still needed for the fabrication of the perfect hexagonal pattern in the confined system, e.g. the heterogeneous nucleation process [20,46].

Although SCFT was originally built up for the thermodynamic study on the phase separation of inhomogeneous polymeric systems, its dynamic version has also been developed, i.e. dynamic SCFT (DSCFT) [47–50]. DSCFT is good at examining the collective kinetics of phase separation in inhomogeneous polymeric systems. However, the dynamic simulation of DSCFT is quite time expensive. Alternatively, the phase separation kinetics of block copolymers can be roughly mimicked by the iteration process of solving SCFT equations [37]. The iteration

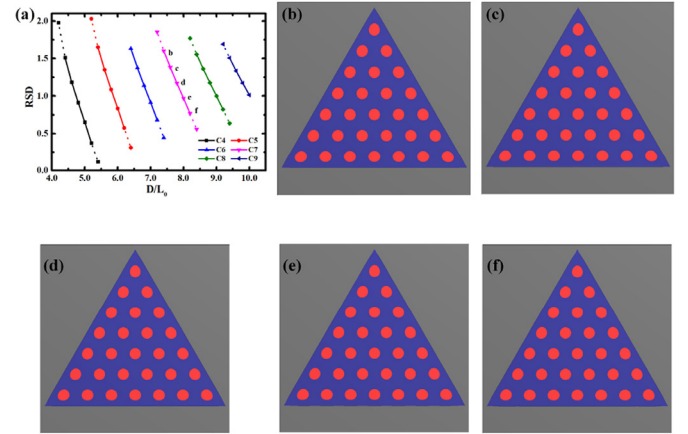


Fig. 4. Relative standard deviation (RSD) of areas of these domains formed in the same triangle as a function of D . The symbols connected by solid lines indicate the stable hexagonal morphologies, while those connected by dashed lines indicate the metastable morphologies. (b–f) shown the C7 hexagonal patterns formed in the triangles of different sizes.

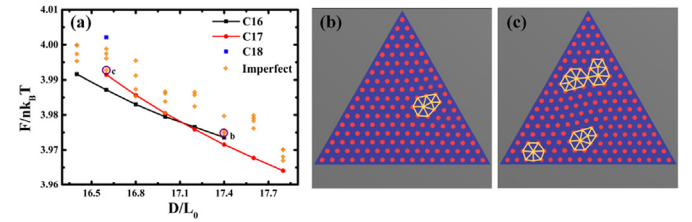


Fig. 5. (a) Free-energy comparison of perfect and imperfect hexagonal morphologies, including perfect C16 (black filled squares), C17 (red filled circles), imperfect morphologies (yellow filled diamonds) and perfect C18 (blue filled square). (b) and (c) imperfect or defective morphologies for the two enclosed points by circles in the free energy plot, where the bonds connecting neighboring domains are plotted to indicate the defects. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

process can be written as

$$\frac{w_A^{k+1}(\mathbf{r}) - w_A^k(\mathbf{r})}{\Delta t} = \chi_{AB} N \phi_B^{k+1}(\mathbf{r}) + \eta^{k+1} +$$

$$\chi_{AW} N \phi_W(\mathbf{r}) - w_A^k(\mathbf{r})$$

$$\frac{w_B^{k+1}(\mathbf{r}) - w_B^k(\mathbf{r})}{\Delta t} = \chi_{AB} N \phi_A^{k+1}(\mathbf{r}) + \eta^{k+1} +$$

$$\chi_{BW} N \phi_W(\mathbf{r}) - w_B^k(\mathbf{r}) \quad (9)$$

where k denotes the k -th step and the updating constant is chosen as $\Delta t = 0.05$.

To obtain the perfect hexagonal patterns kinetically, we propose a multi-step annealing process. In the dynamic simulations, we first simulate the block copolymer melt under the triangular confinement at a low initial value of $\chi N = (\chi N)_I$ corresponding to a high annealing temperature for k_s steps starting from a randomly initialized disordered state. Then we increase χN by Δc every k_s steps until $\chi N = (\chi N)_T$, $(\chi N)_T$ is the targeting segregation degree. This multi-step annealing process is controlled by a few variables, $(\chi N)_I$, Δc and $k_s \Delta t$, and thus is facile to be realized and even optimized in experiment.

In Fig. 6, we present the density snapshots obtained by the SCFT simulations with $(\chi N)_I = 15$, $\Delta c = 0.5$ and $K = 2000$ for (b) $D = 16.6L_0$ and (c) $D = 17.6L_0$. In Fig. 6(b1), $\chi N = (\chi N)_I = 15$ is significantly lower than the bulk order-disorder transition (ODT), i.e. $(\chi N)_{ODT} \approx 16$ for $f = 0.26$, the entire system remains disordered except for the area near the boundary where the B-preference surface field induces the short-range spinodal phase separation. When χN is increased to 16 within the

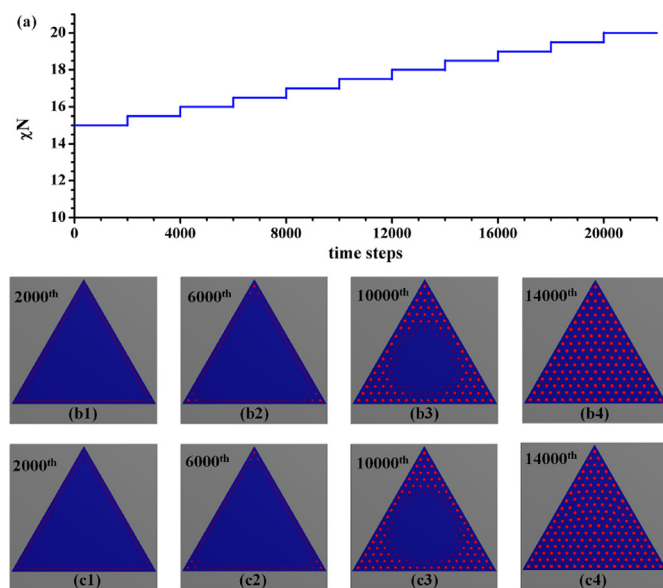


Fig. 6. (a) Schematic illustrating the variation of χN during the multi-step annealing process for $(\chi N)_I = 15$, $\Delta c = 0.5$ and $k_s = 2000$. (b1–b4) Snapshots of the morphologies obtained during the multi-step annealing process for $D = 16.6L_0$. (c1–c4) Snapshots of morphologies for $D = 17.6L_0$.

time steps from 4000 to 6000, the phase separation expands slightly. In particular, a few discrete domains are formed at each corner, which would act as the nuclei for the further nucleation process during the next stage of annealing at an increased χN . In Fig. 6(b3), each nucleus at each corner grows into a defect-free grain of hexagonal cylinders. Finally, the three domain grains with consistent orientation and coherent positions merge into a defect-free hexagonal pattern in Fig. 6(b4). It is interesting to note that the final pattern is C17, but not the thermodynamically stable C16 for $D = 16.6L_0$. The main reason is that the domain size at the early stages is smaller than that at $(\chi N)_T = 20$ due to the decreased value of χN , leading to the packing of more domains into the triangular space than those in the equilibrium morphology. Importantly, the metastable perfect pattern in Fig. 6(b4) usually can be maintained for a long period during the further annealing stage at the enhanced values of χN , e.g. from 18 to 20. More surprisingly, the perfect hexagonal patterns could be yielded via this multi-step annealing process in the triangles with whatever size, where the number of domains is automatically regulated to accommodate the triangular space. For instance, the C18 pattern is obtained for $D = 17.6L_0$ (Fig. 6(c4)). It is important to note that this multi-step annealing process may be optimized further by tuning $(\chi N)_I$, Δc and $k_s \Delta t$. As here our main aim is to qualitatively demonstrate the validity of the DSA scheme by the triangular confinement, we do not perform a systematic optimization.

4. Conclusions

In summary, the self-assembly of a cylinder-forming diblock copolymer melt under the lateral triangular confinement has been investigated using the SCFT, focusing on the thermodynamic and kinetic stability of perfect hexagonal patterns. We have attempted to verify that the thermodynamically stable morphologies are exclusively the perfect hexagonal patterns in the triangularly confined system with whatever size, which is in contrast to the hexagonally confined diblock copolymer system where non-hexagonal patterns could become the equilibrium morphologies when the hexagonal size is incommensurate to the domain spacing. However, we find that it is difficult to obtain the perfect hexagonal patterns due to the kinetic reason. Accordingly, we propose a multi-step annealing process to achieve the perfect patterns, where the

heterogeneous nucleation process is realized. An important conclusion is that the perfect patterns could be achieved via this multi-step annealing process in large triangles with whatever size, where the number of domains is automatically regulated to accommodate the triangular confinement. In other words, this topographical direction method for large-scale ordered hexagonal patterns does not exhibit an incommensurability issue and thus may become a promising nanolithography scheme. It is important to note that defects could be caused when the confining triangle is very large (e.g. $D/L_0 > 20$) because thermal fluctuations will disrupt the long-range correlation of block copolymer domains [40].

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