Research Article

Open Access

Bo Lin*, Chen Zheng*, Qingying Zhu and Fang Xie

Surface-induced phase transitions in thin films of dendrimer block copolymers

<https://doi.org/10.1515/epoly-2020-0009>

Received August 11, 2019; accepted December 11, 2019.

Abstract: The phase morphologies and phase transitions of dendrimer block copolymer thin films confined between two homogeneous, planar hard substrates had been investigated by a three-dimensional real space self-consistent field theory (SCFT). From the perspectives of property and strength of the preferential substrate, when the film system confined within neutral substrates, the thinner film was easier to take the undulated and perpendicular cylinder phases. For the attractive preference of the substrate on block segment A, the polymer films tended to take the surface-wetting structures that was composed by block segment A. On the contrary, for the repulsive preference of the substrate on block segment A, a phase transition of cylinder-lamellae could be observed increasing with the relative surface strength of the preferential substrate.

Keywords: dendrimer block copolymer; surface confinement; self-consistent field theory; phase morphology; phase transition

1 Introduction

Block copolymer (BCP) was a class of soft matter capable of self-assembling to form ordered structures with nanodomain (1-3). However, the confinement operation of the BCP in a nanoscale device could significantly change the interfacial interaction and display the symmetry breaking in the molecular organization, which differed

from that of the bulk of BCP. Recently, most of the studies focused at the BCP under one-dimensional (1D) confinement of parallel walls (4-6), 2D confinement of cylindrical pores (7-9), and 3D one of spherical cavities (10). However, both the complexity and variety of self-assembled structure would significantly increase with the number of polymer segment (11,12). The Monte Carlo simulation revealed that there were different morphologies in the confined thin film of linear triblock copolymer including the parallel cylinders, perpendicular cylinders, and distorted mixed structures (11). Tang and Zhang had applied the pseudospectral SCFT to investigate the phase morphologies and phase transitions of star triblock copolymer thin films that were confined between the preferential surfaces (13,14). Their simulation experiments showed that the typically parallel cylinders, perpendicular cylinders, tilted cylinders, lamellae, perforated lamellae, and complex hybrid phases could be stable under the surface confinement.

Dendrimer block copolymer (DBC) as a more complicated block copolymer could be synthesized by controlled procedure to generate ideally branched chains, which had the potential applications in nanoscale catalyst scaffolds, drug delivery vehicles, gene transfection agents, and templates of supramolecular and self-assembly (15-18). These realistic applications were mainly based on different interface condition and the noncovalent interaction between the DBC and various materials such as drug, surfactant, lipid, polymer, protein, and DNA. Recently, the atomistic molecular dynamics simulation had been used to seek the scaling laws and predict the viscoelastic properties of the DBC (15,16), meanwhile, the dissipative particle dynamics simulation and SCFT were both applied to foresee the self-assembly behavior of DBC (19-21). However, the surface confinement would lead to obvious differences in the physical properties for the dendrimer that were quite different from that of dendrimer without surface confinement. So the understanding of phase morphology and phase transition of dendrimer with surface confinement would represent one of the most important prerequisites for the

* Corresponding authors: Bo Lin and Chen Zheng, School of Chemistry and Materials Engineering, Huizhou University, Guangdong 516007, China; Glorious Sun Guangdong School of Fashion, Huizhou University, Guangdong 516007, China, emails: jidalinbo@163.com (Bo Lin), zhengchenkenaf@163.com (Chen Zheng)

Qingying Zhu and Fang Xie, School of Chemistry and Materials Engineering, Huizhou University, Guangdong 516007, China

controllable design of dendrimer. Since the appearance of different morphologies under confinement condition was depended on the interaction between the block segment and the substrate (Λ), namely surface confinement, it was fascinating for us to adopt a SCFT theoretical method to study the self-assembly of confined DBC thin films with different strength of Λ . Therefore, a SCFT model was used in this work to evaluate the equilibrium phase morphologies with their stability regions, and the phase transition of order-to-order of the DBC thin films by regulating the film thickness, the phase segregation regime, and the property and strength of surface field.

2 Theoretical method

A simulation method of self-consistent field theory (SCFT) could be briefly described to predict equilibrium morphologies of confined DBC thin film as follows. A melt system of n AB-type DBC was assumed to be confined inside a spacial volume V with a preferential surface, the distance between the two planar hard substrates was defined as Δ . Each DBC had N total statistical segments with volume fraction f_i for i type of blocks A and B, block segment A of the first generation (G1) joined at a central core O and connected up all block segment B of the second generation (G2) at branching points of A_i ($i = 1, 2, 3$) as shown in Figure 1.

To cope with a many-body system, one considered the statistics of a single dendrimer chain in a set of effective chemical potential fields $\omega_i(\mathbf{r})$ (Eq. 1 and 2), it conjugated to the local segment density fields $\phi_i(\mathbf{r})$ and was normalized by bulk monomer density ρ that was assumed to be the same for all block segments within the theoretical frame of SCFT.

$$\omega_A(\mathbf{r}) = \chi_{AB} N \phi_B(\mathbf{r}) - H(\mathbf{r}) N + \xi(\mathbf{r}) \quad (1)$$

Figure 1: Molecular architecture of a dendrimer copolymer, in which block A (green) and block B (red) represents the first and the second generation of the dendrimer copolymer, respectively.

$$\omega_B(\mathbf{r}) = \chi_{AB} N \phi_A(\mathbf{r}) - H(\mathbf{r}) N + \xi(\mathbf{r}) \quad (2)$$

with a surface field of $H(\mathbf{r})$:

$$H(\mathbf{r}) = \begin{cases} 1/4\Lambda_1(1+\cos(\pi z/\varepsilon)), & 0 \leq z \leq \varepsilon \\ 0, & \varepsilon < z < \Delta - \varepsilon \\ 1/4\Lambda_2(1+\cos(\pi(\Delta - z)/\varepsilon)), & \Delta - \varepsilon \leq z \leq \Delta \end{cases} \quad (3)$$

where z was the coordinate perpendicular to the film, ε was the thickness of the surface. $\Lambda_i = -(\chi_{AS_i} - \chi_{BS_i})$ ($i=1,2$) was the difference between the block–substrate interaction that controlled the strength of the interaction between polymer block and the substrate at the top surface ($z = 0$) and bottom surface ($z = \Delta$), respectively. For the property of the surface, a positive value of Λ_i represented the block A–attractive substrate, on the contrary, a negative one of Λ_i represented the block A–repellent substrate.

In Eq. 1 and 2, $\xi(\mathbf{r})$ was the potential field that ensured incompressibility of the DBC system, which was determined by Eq. 4:

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = \phi(\mathbf{r}) \quad (4)$$

In the bulk, $\phi(\mathbf{r})$ was independent of special position and keeps constant at 1, while in the surface layers, its value was defined as 1/2, which could be shown as Eq. 5:

$$\phi(z) = \begin{cases} 1/2, & 0 \leq z \leq \varepsilon \\ 1, & \varepsilon < z < \Delta - \varepsilon \\ 1/2, & \Delta - \varepsilon \leq z \leq \Delta \end{cases} \quad (5)$$

Accordingly, the definition of $H(\mathbf{r})$ could be changed into:

$$H(\mathbf{r}) = \begin{cases} 1/4\Lambda_1, & 0 \leq z \leq \varepsilon \\ 0, & \varepsilon < z < \Delta - \varepsilon \\ 1/4\Lambda_2, & \Delta - \varepsilon \leq z \leq \Delta \end{cases} \quad (6)$$

Subsequently, the free energy of DBC confined within the preferential surfaces at an appointed temperature T could be given by:

$$F/nk_B T = -\ln(Q/V) + (1/V) \left\{ \int d\mathbf{r} \chi_{AB} N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - \int d\mathbf{r} [\omega_A(\mathbf{r}) \phi_A(\mathbf{r}) + \omega_B(\mathbf{r}) \phi_B(\mathbf{r})] - \int d\mathbf{r} \xi(\mathbf{r}) [\phi_O - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] - \int d\mathbf{r} H(\mathbf{r}) N [\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] \right\} \quad (7)$$

where χ_{AB} was a Flory–Huggins interaction parameter between different block segment A and B. $Q = \int d\mathbf{r} q_i(\mathbf{r}, s) q_i^+(\mathbf{r}, s)$ was the partition function of a single dendrimer chain within the surface field $H(\mathbf{r})$ that could be obtained by the block segment distribution function $q_i(\mathbf{r}, s)$ and $q_i^+(\mathbf{r}, s)$. The distribution function $q_i(\mathbf{r}, s)$ represented the probability of finding segment s at position $\mathbf{r}$, which satisfied a modified diffusion equation by using a flexible Gaussian chain model:

$$\frac{\partial}{\partial s} q_i(\mathbf{r}, s) = \frac{Na^2}{6} \nabla^2 q_i(\mathbf{r}, s) - \omega_i(\mathbf{r}) q_i(\mathbf{r}, s) \quad (8)$$

For the two ends of each block chain were distinct, a second end-segment distribution function $q_i^+(\mathbf{r}, s)$ was needed, it satisfied Eq. 8 only with the right-hand side multiplied by -1 . Each block chain of the dendrimer was parameterized with variable s , which increased along the chain. The branching points A_1 , A_2 and A_3 corresponded to $s = 0$. Along each block chain (e.g. OA_1), the s increased from 0 at the branching point O to $f_{OA_1}N$ at the other end A_1 . The other eight block chains of OA_2 , OA_3 , A_1B_1 , A_1B_2 , A_2B_3 , A_2B_4 , A_3B_5 , and A_3B_6 were parameterized similarly.

With these definitions, the initial conditions of the above diffusion equations were as follows:

$$\begin{aligned} q_{A_1B_1}^+(\mathbf{r}, f_{A_1B_1}N) &= q_{A_1B_2}^+(\mathbf{r}, f_{A_1B_2}N) = q_{A_2B_3}^+(\mathbf{r}, f_{A_2B_3}N) = \\ q_{A_2B_4}^+(\mathbf{r}, f_{A_2B_4}N) &= q_{A_3B_5}^+(\mathbf{r}, f_{A_3B_5}N) = q_{A_3B_6}^+(\mathbf{r}, f_{A_3B_6}N) = 1.0 \end{aligned} \quad (9)$$

$$\begin{aligned} q_{A_iO}(\mathbf{r}, 0) &= q_{A_iO}^+(\mathbf{r}, 0) \cdot q_{A_kO}^+(\mathbf{r}, 0) \\ (i, j, k \in [1, 3]; i \neq j, i \neq k, j \neq k) \end{aligned} \quad (10)$$

$$q_{A_iB_{2i-1}}(\mathbf{r}, 0) = q_{A_iB_{2i}}^+(\mathbf{r}, 0) \cdot q_{A_iO}^+(\mathbf{r}, 0) \quad (i \in [1, 3]) \quad (11)$$

$$q_{A_iB_{2i}}(\mathbf{r}, 0) = q_{A_iB_{2i-1}}^+(\mathbf{r}, 0) \cdot q_{A_iO}^+(\mathbf{r}, 0) \quad (i \in [1, 3]) \quad (12)$$

$$\begin{aligned} q_{A_iO}(\mathbf{r}, f_{A_iO}N) &= q_{A_iB_{2i-1}}^+(\mathbf{r}, f_{A_iB_{2i-1}}N) \cdot q_{A_iB_{2i}}^+(\mathbf{r}, f_{A_iB_{2i}}N) \\ (i \in [1, 3]) \end{aligned} \quad (13)$$

As a result, the local density of block segment A and B could be calculated by:

$$\phi_A(\mathbf{r}) = \frac{V}{NQ} \sum_{i \in [1, 3]} \int_0^{f_{A_iO}N} ds q_{A_iO}(\mathbf{r}, s) q_{A_iO}^+(\mathbf{r}, s) \quad (14)$$

$$\begin{aligned} \phi_B(\mathbf{r}) &= \frac{V}{NQ} \sum_{i \in [1, 3]} \int_0^{f_{A_iB_{2i-1}}N} ds q_{A_iB_{2i-1}}(\mathbf{r}, s) q_{A_iB_{2i-1}}^+(\mathbf{r}, s) \\ &+ \frac{V}{NQ} \sum_{i \in [1, 3]} \int_0^{f_{A_iB_{2i}}N} ds q_{A_iB_{2i}}(\mathbf{r}, s) q_{A_iB_{2i}}^+(\mathbf{r}, s) \end{aligned} \quad (15)$$

Equations 1, 2, 4, 14 and 15 together formed a closed set of self-consistent equations. These equations were numerically implemented in conjunction with a combinatorial screening algorithm that proposed by Drolet and Fredrickson (21-23), and then the free energy converged and was minimized to a stable value with a change decreased to 10^{-6} , finally the phase pattern appeared in the appointed simulation box could be identified clearly.

To demonstrate the availability of the numerical implementation of simulation experiments within theoretical frame of SCFT, the contour length was discretized as the total statistical segments N in the DBC and the grid size in 3D space was set as $\Delta x = \Delta y = \Delta z = 1/6 R_g$ in this work. To minimize the influence of simulation box size, the box size in the x and y directions were set within a reasonable range of $5-7 R_g$ ($R_g = (N/2)^{1/2}$). It assumed that each block segment was equal and enough to reasonably illustrate the complicated microphase structures with $N = 72$, namely, $f_A = 1/3$. To simplify the simulations, the property of two substrates were assumed to be symmetric, i.e. $\Lambda = \Lambda_1 = \Lambda_2$, $\Lambda > 0$ meant an attractive effect for segment A towards the substrate but a repellent effect for segment B towards the substrate. On the contrary, $\Lambda < 0$ indicated a repellent effect for segment A towards the substrate but an attractive effect for segment B towards the substrate in the DBC films. This work focused on the preferential substrate with neutral, weak, and relatively strong surface strength, which was corresponding to the surface property of $\Lambda = 0$, $|\Lambda| = 0.6$ and $|\Lambda| = 3.0$, respectively, to facilitate comparing phase morphologies and phase transitions under different phase segregation regime (χ_{AB}).

3 Results and discussion

The phase morphologies of dendrimer copolymer thin film had been explored and divided into five primary classes and each class of morphology included several subfields of relative structure (5,6). It noted that the colors of green, blue, and magenta totally represented block segment A, while the color of red only represented block segment B in the morphology of thin films.

- (1) Cylinder (C, Figure 2). It included parallel cylinder (C_p), undulated cylinder (C_u), perpendicular cylinder ($C_\perp$), dumbbell cylinder (C_d), and hybrid cylinder ($C_u C_\perp$).
- (2) Lamellae (L, Figure 3). There were two kinds of lamellar structures (L_w and L_{nw}) had been found to be more favorable than the cylindrical structures for the surface interaction energy between the dendrimer copolymer and substrate dominating in the thin film system. The L_w or L_{nw} denoted the lamellae phase with or without wetting surface layer of block segment A, respectively.
- (3) Spherical structure (S, Figure 4). There were three kinds of spherical structures had been found. The numbers on the upper right corner of the structures denoted the number of the sphere layers in thin film counted in the z-direction.
- (4) Perforated lamellae (PL, Figure 5). The results from strong segregation theory and SCFT showed that perforated lamellae structures (PL) were stable under thin film conditions because of the confinement and preference of the substrates.
- (5) Hybrid structure (H, Figure 6). Each stable and hybrid morphology was mixed by two pure phase structures (such as cylinder, lamellae, or sphere).

3.1 Neutral preference dependence

To emphasize the nature of film thickness of dendrimer copolymer effecting on the morphological transformation ($\Lambda = 0$). Figure 7 demonstrated that the morphology in the confined thin film system was quite different from the stable structure in the bulk of DBC (Figure 8). However, the film system without substrate preference (Figure 7) had been composed of the cylinders (C_u and $C_\perp$) within a smaller Δ , especially the undulated cylinder (C_u^1) could be observed with $\Delta \leq 8/6 R_g$ (Figure 9a). The cylinders were contorted as much as possible to reduce the interaction between the block segment A and the substrates, and decrease the unfavorable surface energy. The perpendicular cylinder ($C_\perp$) was a transitional structure among the cylindrical morphologies (Figure 9b). Huinink et al. had found that

Figure 2: Cylindrical morphologies of block A ($f_A = 1/3$).

Figure 3: Lamellar morphologies of block A ($f_A = 1/3$).

Figure 4: Spherical morphologies of block A ($f_A = 1/3$).

Figure 5: Perforated lamellae. The green and red represents isodensity surface distribution of block A ($f_A = 1/3$) and block B ($f_B = 2/3$) in dendrimer copolymer, respectively.

$C_{\perp}$ could be observed under the neutral substrates with a preference for the shorter block by a theoretical method of density functional calculation (24). This phenomenon

Figure 6: Hybrid morphologies of block A ($f_A = 1/3$). A small gap in the morphology deliberately made for better observing the interior of hybrid structure.

Figure 7: Phase diagram under neutral substrates ($\Lambda = 0$).

agreed well with the result from Monte Carlo simulation by Wang et al. (25), and it took a similar square arrange as the structures of the bulk, and then the confined film alternates between $C_{\perp}$ and C_p (Figure 9c) increasing with Δ . The conformation transformation between the adjacent structures resulted from an energy balance between the entropic free energy ($-TS$) and the short-range interaction (U) (5). The entropic free energy difference between the confined thin film system and the bulk ($-TS+TS_0$) decreased with Δ (Figure 9). It revealed that the DBC under confinement conditions was compressed much more than that of the bulk in the weak segregation regime ($\chi_{AB} = 0.60$). The effect of Δ dominated in the morphological transition, which made it take the cylindrical structures in the smaller Δ to decrease the unfavorable surface energy. To sum up, the compression could be released when the Δ increased without substrate preference. It expected that $-TS+TS_0$ will approach to a smaller value even lower than zero, which would induce the appearance of wet-layer structures, and finally the compression became small

Figure 8: Equilibrium morphologies for bulk of dendrimer copolymer: (a) spherical structure for $0.60 \leq \chi_{AB} \leq 0.65$, (b) cylindrical structure for $0.70 \leq \chi_{AB} \leq 0.80$.

Figure 9: Entropic free energy difference between the confined thin film ($-TS$) and the bulk of dendrimer copolymer ($-TS_0$) as a function of film thickness Δ/R_g with $f_A = 1/3$, $\Lambda = 0$, and $\chi_{AB} = 0.60$.

enough to be neglected increasing with the Δ . As a result, the lamellar structure appeared in the thicker film, for the inhibitory action from the small Δ had been released increasing with Δ , and finally the film system took a wet-layer structure of L^3 (Figure 9e) increasing with the surface energy. For bigger χ_{AB} ($\chi_{AB} = 0.65$), the phase behavior was fully released in the thicker film and took the similarly spherical structures as the bulk (Figure 8a) under the same χ_{AB} . When the χ_{AB} increased even further, the thin film was inclined to take the bulk behavior (cylinder) with the bigger χ_{AB} ($\chi_{AB} \geq 0.70$) and displayed a reciprocating phase transition of sphere to cylinder (S $\rightarrow$ C) in the medium segregation degree ($\chi_{AB} = 0.70$), subsequently, the phase behavior were radically controlled by cylindrical structures as the bulk phase behavior when $\chi_{AB} \geq 0.75$ (Figure 8b). On the other hand, the number of layers of the structures increasing with Δ , such as $S_2 \rightarrow S_3 \rightarrow S_4$ (Figure 7), which was another good prove for the existence of the release effect from the thicker film.

3.2 Weak preference dependence

A combined parameter ΔN had been used to denote the interaction between the polymer block and the preferential substrate in the previous works (5,14). Here, an absolute value $|\Delta/\chi_{AB}|$ was intended chosen for representing substrate preference and was a more simple way to illuminate the relative strength of substrate selectivity (Figures 10-13). In order to facilitate comparison, the parameters of horizontal coordinate was uniformly set as χ_{AB} but not Δ/χ_{AB} , which could provide consistency for the case neutral preference dependence (Figure 7).

Under weak preference, the L and PL phases preferred to take a structure of wetting layer (such as L_w and iPL) with $\Delta > 0$ (Figure 10). On the contrary, they were respectively replaced by L_{nw} and $PL_{\perp}$ without any wetting layer (Figure 11) when $\Delta < 0$. This phenomena also took place in the other selective strength of substrate under the repellent case (Figure 13). Fredrickson reported that the appearance of the PL phase was not only dependent on the volume fraction but also strongly dependent on the film thickness (11), which agreed well with the results from this work. Besides, the PL phase regions could expand into the lamellar phase or cylindrical phase under the case of $\Delta < 0$ by varying Δ (Figures 11 and 13), even the hybrid structure (LC) when $\Delta > 0$ (Figures 10 and 12). It showed that two couples of lamellar phase transition $L^1_w \rightarrow L^2_w \rightarrow L^3_w$ and $L_u \rightarrow L_2 \rightarrow L_3$ always successively appeared with increasing Δ , particularly with a bigger Δ . To match Δ under confinement, the flat surfaces of the regular lamellae had to be distorted into undulated surfaces with external strain. Meanwhile, the hybrid structure of LC or LS (except for CS) emerged and arranged with filling phase of cylinder or sphere besides the wetting layer of lamellar phase increasing with Δ (Figure 10). However, it was difficult for the film to take the wet-layer lamellae phase when $\Delta < 0$, then it had to adopt the hybrid structure of CS (Figure 11) increasing with the Δ . Additionally, the phase diagrams under weak preference had been displayed an obvious alternation of PL–H or C–H. For $\Delta > 0$ (Figure 10), there was an alternation between the perforated lamellae (PL) and hybrid structure (H) under the weak segregation regime, and then the film system could appear in the H-region under the strong segregation regime of $\chi_{AB} = 0.80$. For $\Delta < 0$ (Figure 11), the alternation of PL–H changed to C–H

Figure 10: Phase diagram under weak attractive substrate ($\Delta = 0.6$).

Figure 11: Phase diagram under weak repellent substrate ($\Delta = -0.6$).

and finally the film system turned into an entire cylindrical structure. Moreover, it showed that the region of hybrid structure under $\Delta > 0$ were broader than that of $\Delta < 0$, which attributed to the attractive preference of substrate was more easily to induce the appearance of the wetting-layer lamellae phase comparing with the hybrid structure of CS. These results proved that the film was more inclined to choose the lamellar phase under $\Delta > 0$, whereas for $\Delta < 0$, it preferred to adapt cylindrical or spherical phase to decrease the unfavorable surface energy.

3.3 Strong preference dependence

Contrasting with the smaller Δ , the dendrimer copolymer thin films confined with a strong relative strength of substrate selectivity ($|\Delta| = 3.0$) as shown in Figures 12 and 13. Figure 12 showed that the sequence of phase transformation changed from the wet-layer lamellae structures ($L^1_w \rightarrow L^2_w \rightarrow L^3_w$ in smaller Δ) to $L \rightarrow H$ (in middle Δ), and to $L_w \rightarrow PL \rightarrow H$ (in higher Δ) increasing with the Δ . Additionally, there was a cascade of $LC \leftrightarrow LS$ transition ($LC^1_u \rightarrow LS_1 \rightarrow LC^2_u \rightarrow LC^3_u \rightarrow LS_2$) except for $\chi_{AB} = 0.80$ ($LC^1_u \rightarrow LS_1 \rightarrow LC^2_u \rightarrow LC^3_u$). Comparing with the case of neutral substrate (Figure 7), the wetting-layer structure of L^1_w arose in a range of smaller Δ instead of C^1_u and the L_w phase morphology totally replaced the cylindrical structure with $\chi_{AB} \leq 0.65$ (Figure 12). Meanwhile, there was an obvious phenomenon that a predominant wetting-layer phase structure had been always obtained with bigger Δ ($\Delta = 3.0$) and $\Delta/\chi_{AB} = 5.0$ as shown in Figure 12. For bigger Δ ($\Delta = -3.0$, Figure 13), in which the lamellar structure without wetting layer totally replaced the

lamellar structure with wetting layer at $\chi_{AB} = 0.60$, and the PL_w had replaced the L^1_w in the same smaller Δ under the opposite effect of the substrate selectivity (Figure 12). In contrast to the strong A-repellent substrate with the strong A-attractive substrate, the the sequence of phase transformation of $LS_2, LC^2_u, LC^1_u, LS_1$, and LC^1_u for the dendrimer film confined within the repellent substrate had been replaced by the transition sequence of C^3_u (or C^2_u), C^2_u , C^1_u , and C^1_u under the attractive ones, respectively, which agreed well with the deduction from the case of $|\Delta| = 0.6$ (Figures 10 and 11). For decreasing the unfavorable surface energy, the dendrimer thin film was more likely to take the cylindrical or spherical phase without wetting layer and replace the lamellar phase with the wetting layer. It suggested that the confinement effect faded as the film thickness increased, and the phase behavior of the film system tended to approach those in the bulk.

It was significant to investigate the effects of surface field strength on the morphology stability regions for relatively thinner film $\Delta = 1.5\text{--}3.5 R_g$ (Figure 14). The $C_\perp$ phase was found in the lower absolute surface strength ($|\Delta| \leq 0.1$) specially for smaller Δ ($\Delta = 1.5 R_g$). It revealed that the $C_\perp$ phase was largely controlled by Δ but exclusively determined by the weak substrate preference. The perpendicular phase ($C_\perp$) would be replaced by the parallel phase gradually increasing with surface strength, and finally changed to C^1_u and L^1_w structures (Figure 14), for the perpendicular phase costing too much elastic energy to wet the surface of substrates. When the attractive effect ($H > 0$) increased further, the morphology of thin film was mainly occupied by the lamellar structure with wetting layers. On the contrary, when the repulsive effect increased, the cylinder phase (C^1_u) would go on. The two individual free

Figure 12: Phase diagram under strong attractive substrate ($\Delta = 3.0$).

Figure 13: Phase diagram under strong repellent substrate ($\Delta = -3.0$).

Figure 14: Free energy variation and the according morphology stability regions of confined thin film of dendrimer copolymer as a function of the surface field strength (H) with $\chi_{AB} = 0.70$ and the Δ varies from $1.5 R_g$ to $3.5 R_g$.

energy contributions of the film system illuminated that the entropic free energy ($-TS$) decreased distinctly at each appointed relative strength of substrate as Δ increased. Meanwhile, comparing with the short-range interaction (U), $-TS$ still became predominant in the polymer film as shown in Figure 14. For each Δ , the dendrimer polymer chains stretched as far as possible and tended to take the nonoriented phase morphology increasing with strength of surface field, such as the appearance of the parallel undulated cylinders and spheres, or the parallel lamellae and hybrid structures of LC and LS. Figure 14 showed that the undulated cylinder and the hybrid structure with wetting-layer of lamellae could be observed in the region of stronger surface field. Furthermore, it showed that the layer number of cylinder in the undulated phase and the layer number of filling phase of cylinder both increasing with Δ . It indicated that the phase behavior and its corresponding morphology also needed to match the film thickness, and then took a suitable layer number of the cylinders to preserve the phase morphology as the thinner film is. It was a good explanation on the entropy contribution of the film system for these conclusions, the entropic free energy at each appointed surface field decreased with increasing the film thickness, and the film system would become more stable. For the weak surface field, as the film thickness increased, the perpendicular

cylinder phase (Figure 14) was gradually replaced by an analogous cylinder structure (C_d) of the bulk of DBC in the same χ_{AB} . It illuminated that the impact of the surface field on the center of the film would become smaller and smaller increasing with Δ , and the preferential effect of the substrate would be impaired or even inactive.

4 Conclusions

A 3D real space SCFT had been applied to reveal the phase morphologies and phase transitions of AB dendrimer block copolymer films with an asymmetric component $f_A = 1/3$ that were confined between two homogeneous hard substrates. By systematically varying the Δ of thin film and the χ_{AB} between two different block segments in the DBC, the phase diagrams and phase behaviors had been evaluated by the typical strength of Δ . Five main classes of phase structure had been found to be stable for the confined thin films, which included cylinder (C), lamellae (L), sphere (S), perforated lamellae (PL), and hybrid structure (H) that was mixed by two of the pure structures (such as cylinder, lamellae, or sphere). In order to have insight into the phase transition of the polymer film, the preferential effect of the substrate had been taken into account as well.

Within neutral substrates, the cylinder phases were the frequenters in the thinner film, the bulk behavior easily displayed increasing with the film thickness. Under weak preference, the wet-layer structures of L_w , LC, and LS could be found with $\Delta = 1.0\text{--}4.0 R_g$ and $\Lambda > 0$. On the contrary, for $\Lambda < 0$, the wet-layer structures totally disappeared in all over the Δ . Meanwhile, the thin film only displayed the CS structure within the bigger Δ and it took a cylinder-lamellae transition at each appointed thickness increasing with $|\Lambda/\chi_{AB}|$. Under strongly attractive preference, the hybrid phase of LC and LS alternately emerged with an oscillating morphology transformation, especially for the thicker film with $\chi_{AB} \geq 0.65$ (Figure 12). While for the strongly repulsive preference, the hybrid phase of CS could be observed in the thicker film with $0.65 \leq \chi_{AB} \leq 0.75$.

Acknowledgements: B. L. gratefully acknowledged the financial support from the professorial and doctoral scientific research foundation of Huizhou University (Grant No. 2018JB001) and the Guangdong Natural Science Foundation (Grant No. 2017A030313080).

References

- Shi C., Li B.H., Self-assembly of diblock copolymers under confinement. *Soft Matter*, 2013, 9(5), 1398-1413.
- Ramanathan M., Michael Kilbey II S., Ji Q.M., Hillcd J.P., Ariga K., Materials self-assembly and fabrication in confined spaces. *J. Mater. Chem.*, 2012, 22(21), 10389-10405.
- Yager K.G., Lai E., Black C.T., Self-Assembled Phases of Block Copolymer Blend Thin Films. *ACS Nano*, 2014, 8(10), 10582-10588.
- Huinink H.P., Dijk van M.A., Brokken-Zijp J.C.M., Sevink G.J.A., Surface-Induced Transitions in Thin Films of Asymmetric Diblock Copolymers. *Macromolecules*, 2001, 34(15), 5325-5330.
- Yang Y.Z., Qiu F., Zhang H.D., Yang Y.L., Cylindrical phase of diblock copolymers confined in thin films. A real-space self-consistent field theory study. *Polymer*, 2006, 47(6), 2205-2216.
- Li W.H., Liu M.J., Qiu F., Phase diagram of diblock copolymers confined in thin films. *J. Phys. Chem. B*, 2013, 117(17), 5280-5288.
- Sevink G.J.A., Zvelindovsky A.V., Fraaije J., Huinink H.P., Morphology of symmetric block copolymer in a cylindrical pore. *J. Chem. Phys.*, 2001, 115(17), 8226-8230.
- Li W.H., Wickham R.A., Garbary R.A., Phase diagram for a diblock copolymer melt under cylindrical confinement. *Macromolecules*, 2006, 39(2), 806-811.
- Yu B., Sun P.C., Chen T.H., Jin Q.H., Ding D.T., Li B.H., et al., Self-assembly of diblock copolymers confined in cylindrical nanopores. *J. Chem. Phys.*, 2007, 127(11), 114906.
- Yabu H., Higuchi T., Jinnai H., Frustrated phases: polymeric self-assemblies in a 3D confinement. *Soft Matter*, 2014, 10(17), 2919-2931.
- Chen H.Y., Fredrickson G.H.J., Morphologies of ABC triblock copolymer thin films. *J. Chem. Phys.*, 2002, 116(3), 1137-1146.
- Feng J., Ruckenstein E., Monte Carlo simulation of triblock copolymer thin films. *Polymer*, 2002, 43(21), 5775-5790.
- Han W.C., Tang P., Li X., Qiu F., Zhang H.D., Yang Y.L., Self-assembly of star ABC triblock copolymer thin films: Self-consistent field theory. *J. Phys. Chem. B*, 2008, 112(44), 13738-13748.
- Lin B., Zhang H.D., Qiu F., Yang Y.L., Self-assembly of ABC star triblock copolymer thin films confined with a preferential surface: a self-consistent mean field theory. *Langmuir*, 2010, 26(24), 19033-19044.
- Carbone P., Muller-Plathe F., Molecular dynamics simulations of polyaminoamide (PAMAM) dendrimer aggregates: molecular shape, hydrogen bonds and local dynamics. *Soft Matter*, 2009, 5(13), 2638-2647.
- Gupta S., Biswas P., Effect of pH on size and internal structure of poly (propylene imine) dendrimers: a molecular dynamics simulation study. *J. Phys. Chem. B*, 2018, 122(39), 9250-9263.
- Zhang J.H., Hu J.J., Feng X.Y., Li Y.W., Zhao L.B., Xu T.W., et al., Interactions between oppositely charged dendrimers. *Soft Matter*, 2012, 8(38), 9800-9806.
- Wu S.Y., Chou H.Y., Yuh C.H., Mekuria S.L., Kao Y.C., Tsai H.C., Radiation-sensitive dendrimer-based drug delivery system. *Adv. Sci.*, 2018, 5(2), 1700339.
- Kirkensgaard J.J.K., Systematic progressions of core-shell polygon containing tiling patterns in melts of 2nd generation dendritic miktoarm star copolymers. *Soft Matter*, 2011, 7(22), 10756-10762.
- Kalyuzhnyi O., Illytskyi J., Holovatch M.Y., Ferber C. Universal shape characteristics for the mesoscopic star-shaped polymer via dissipative particle dynamics simulations. *J. Phys.-Condens. Mat.*, 2018, 30(21), 215101.
- Lin B., Zhang H.D., Tang P., Qiu F., Yang Y.L., Self-assembly of ABC dendrimer by real-space self-consistent mean field theory in a two-dimensional space. *Soft Matter*, 2011, 7(21), 10076-10084.
- Drolet F., Fredrickson G.H., Combinatorial screening of complex block copolymer assembly with self-consistent field theory. *Phys. Rev. Lett.*, 1999, 83(21), 4317-4320.
- Arora A., Pillai N., Bates F.S., Dorfman K.D., Predicting the phase behavior of ABAC tetrablock terpolymers: sensitivity to Flory-Huggins interaction parameters. *Polymer*, 2018, 154, 305-314.
- Huinink H.P., Brokken-Zijp J.C.M., van Dijk M.A., Sevink G.J.A., Asymmetric block copolymers confined in a thin film. *J. Chem. Phys.*, 2000, 112(5), 2452-2462.
- Wang Q., Nealey P.F., de Pablo J.J., Monte Carlo simulations of asymmetric diblock copolymer thin films confined between two homogeneous surfaces. *Macromolecules*, 2001, 34(10), 3458-3470.