

MICRODOMAIN MORPHOLOGY OF CYLINDER-FORMING DIBLOCK COPOLYMERS UNDER SPHERICAL SHELL CONFINEMENT*

Ai-hua Chai^{a, c} and Lin-xi Zhang^{b**}

^a Department of Physics, Zhejiang University, Hangzhou 310027, China

^b Department of Physics, Wenzhou University, Wenzhou 325027, China

^c College of Mathematics, Physics and Information Engineering, Jiaxing University, Jiaxing 314000, China

Abstract The topic of self-assembly of cylinder-forming diblock copolymers (DBCPs) under spherical shell confinement in different surface fields is explored using real-space self-consistent field theory calculations (SCFT). Using this approach we observed various microstructures of cylinder-forming DBCPs at different confinement dimensions and surface fields. From detailed searching for the microdomain morphologies, an obvious conclusion is that the interactions between the confinement surface and the polymers have a great effect on the self-assembly. Most of the microstructures are unique and not reported in bulk or under planar and cylindrical confinements.

Keywords: Diblock copolymer; Self-assembly; Self-consistent-field theory.

INTRODUCTION

In recent years, the self-assembly of macromolecular systems in particular diblock copolymers (DBCPs) has attracted a huge attention owing to their potential application in the production of polymeric nanostructured materials^[1–7]. These materials are of great interest and importance due to possible applications in nanotechnology, such as the use of block copolymer films as masks for nanolithography, fabrication of nanoporous membranes for advanced separation media, photonic crystals and high-density media storage^[8–11]. In the effort to develop methods to control structures, a number of theoretical and experimental studies have focused on the self-assembly of block copolymers under confining environments. Confined self-assembly provides a novel method of fabricating ordered structures which are not readily available in bulk systems^[12–16]. Various kinds of microphase separation structures have been reported by focusing on the case of one-dimensional (1-D) planar confinement^[17–25] or two-dimensional (2-D) cylindrical confinement^[26–40]. Theoretical studies have predicted further complex micro-structures under 2-D cylindrical confinement. The confinement dimension δ/L_0 , that is, the ratio of confinement diameter δ versus polymer period in the bulk L_0 , is found to control the structure transition in the confinement-induced block copolymer self-assembly^[34, 40, 41].

Fewer studies on the self-assembly of block copolymers under three-dimensional (3-D) spherical confinement have been carried out in the past years. Thomas and co-workers conducted the bulk lamella-forming system, cylinder-forming system and cylinder-forming system in microdroplets. Concentric shell

* This work was financially supported by the National Natural Science Foundation of China (Nos. 20774066, 20974081 and 20934004), the Ph. D. Programs Foundation of Ministry of Education of China (No. 20090101110002) and the Natural Science Foundation of Zhejiang Province (No. Y4080098).

** Corresponding author: Lin-xi Zhang (章林溪), E-mail: lxzhang@zju.edu.cn

Received November 15, 2010; Revised January 10, 2011; Accepted January 25, 2011

doi: 10.1007/s10118-011-1072-4

structures, honeycomb-like structure and curved concentric arrays structure were observed^[42] for the three cases, respectively. Another paper also reported the concentric structure by the Monte Carlo simulation^[12]. Arsenault *et al.* observed similar structures in their study of polystyrene-*b*-polyferrocenylethylmethysilane self-assembly in silica spherical cavity^[43]. A series of unique structures were found under the condition of different block ratios in the study of using self-consistent field theory (SCFT) calculations^[44]. All these previous studies predicted a rich variety of novel micro-structures under 3D spherical confinements.

In the work, we report self-consistent field theory (SCFT) calculations of the structure of cylinder-forming DBCPs under spherical shell cavity confinement. The spherical shell cavity is made up of a spherical solid and a homocentric sphere. The schematic illustration of the 3-D spherical shell cavity confinement is shown in Fig. 1(a), wherein the cylinder-forming DBCPs are confined in a spherical shell cavity. The effects of surface field and confinement interspace on the DBCPs self-assembly have been studied in detail. The result shows that the self-assembled structures and phase behavior of the DBCPs under 3-D spherical shell confinement are far more complex than those under the 1-D and 2-D confining environments.

THEORY

In our study, the DBCPs chain is composed of two blocks (A- and B-blocks) with $f_A = 0.2$, where f_A ($0 < f_A < 1$) is the volume fraction of the A-block. We assume that the melt of DBCPs with a special degree of polymerization N is incompressible. A Flory-Huggins interaction parameter χ_{AB} is used to characterize the repulsion between the A- and B-blocks. For 3-D spherical shell confinement, the DBCPs are confined in a spherical shell cavity of thickness δ and volume V (see Fig. 1b). Periodic boundary conditions are imposed in all three dimensions to obtain the bulk structure of the DBCPs. For the 3-D spherical shell confinement case, there is no periodic boundary condition in any direction in the calculation.

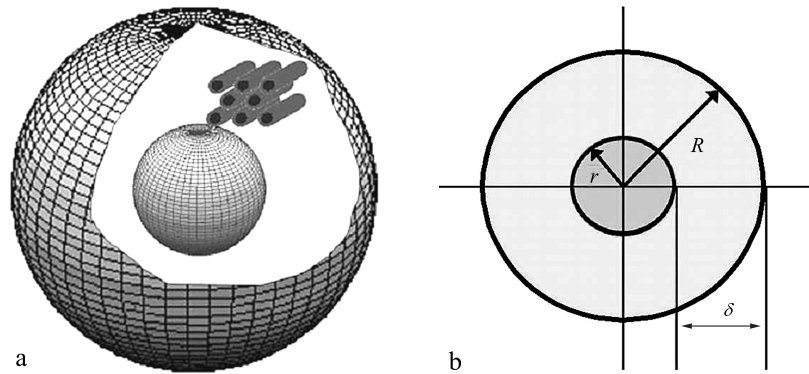


Fig. 1 Schematic illustration of 3-D spherical shell confinement
 r is the radius of the spherical solid, and R is the radius of the homocentric sphere;
 δ is the value of the shell thickness.

We employ the self-consistent field theory (SCFT) to study the morphology of lamella-forming DBCPs confined in a spherical shell cavity. The SCFT is a successful theoretical method for investigation of block copolymer phase diagrams. The real-space approach scheme introduced by Fredrickson and Drolet^[45–47] in solving self-consistent equations is employed in this study. For DBCPs melts under confinement, the SCFT free energy per chain in the unit of $k_B T$ has the form

$$F = -\ln\left(\frac{Q}{V}\right) + \frac{1}{V} \int dr [\chi_{AB} N \phi_A \phi_B - \omega_A \phi_A - \omega_B \phi_B + h_{sA} \phi_A + h_{sB} \phi_B - P(\phi_0 - \phi_A - \phi_B)] \quad (1)$$

where $\omega_{A(B)}$ is the self-consistent field originated from the repulsion interactions between A-block and B-block described by χ_{AB} , and $h_{sA(B)}$ represents the surface field that the inner surface of the confinement acts on A(B)

monomer. The denotation P is a Lagrange multiplier that ensures the system incompressibility. $\phi_{A(B)}$ is the corresponding monomer density field normalized by the local volume fractions of blocks. For the polymer, densities should approach zero at the confinement surface, we generalize incompressibility constraint to $\phi_0 = \phi_A + \phi_B$, ϕ_0 is the total monomer density, and simplify the form

$$\phi_0(r) = \begin{cases} 0 & \text{on the surfaces and outside of the surfaces} \\ 0.5 & \text{on the lattices next to the surfaces} \\ 1 & \text{every where else} \end{cases} \quad (2)$$

$h_{sA(B)}$ represents the surface preference, reflecting surface-polymer interactions between the surface and A(B) blocks that located on the lattices next to the surface. For simplicity, the surface-polymer interaction potential is assumed to be short-ranged and is represented by the following contact interactions:

$$h_{sA(B)} = \begin{cases} H_{A(B)} & \text{on the lattices next to the surfaces} \\ 0 & \text{bulk} \end{cases} \quad (3)$$

where $H_{A(B)}$ is the strength of the surface field, which has the same unit as the Flory-Huggins interaction parameter χ_{AB} .

The end-segment distribution function $q(r, s)$ gives the probability that a chain segment of contour length S and containing a free chain end has its “commented end” located at r . The function $q(r, s)$ and its conjugate $q'(r, s)$ satisfy the following modified diffusion equations:

$$\frac{\partial}{\partial s} q(r, s) = R_g^2 \nabla^2 q(r, s) - N \omega q(r, s) \quad (4)$$

$$-\frac{\partial}{\partial s} q'(r, s) = R_g^2 \nabla^2 q'(r, s) - N \omega q'(r, s) \quad (5)$$

where R_g is the gyration radius for an ideal gaussian chain. $\omega = \omega_A$ for $0 \leq s \leq f_A$, and $\omega = \omega_B$ for $f_A \leq s \leq 1$, with the initial conditions $q(r, 0) = 1$ and $q'(r, 0) = 1$. The Crank-Nicholson scheme has been used for solving these modified diffusion equations. In Eq. (1), $Q = \int dr q(r, 1)$ is the partition function of a single diblock copolymer chain in the mean fields. For minimizing the free energy with respect to the densities and mean fields, a series of SCFT equations are given below:

$$\omega_A(r) = \chi_{AB}(\phi_B(r) - f_B) + h_{sA}(r) + P(r) \quad (6)$$

$$\omega_B(r) = \chi_{AB}(\phi_A(r) - f_A) + h_{sB}(r) + P(r) \quad (7)$$

$$\phi_A(r) = \frac{V}{Q} \int_0^{f_A} ds q(r, s) q'(r, s) \quad (8)$$

$$\phi_B(r) = \frac{V}{Q} \int_{f_A}^1 ds q(r, s) q'(r, s) \quad (9)$$

These equations can be solved self-consistently.

In our study, the chain contour length is divided into 200 segments and the lattice constant is taken as $0.2 R_g$. For systemic comparison, five typical confinement surfaces conditions are considered by the following scheme:

(1) Neutral surface, wherein the surface has no preference for any block ($H_A = 0$ and $H_B = 0$, or in short $H = 0$).

(2) Weak A-attractive surface, wherein the confinement surface weakly attracts A-blocks ($H_A = -8$ and $H_B = 0$).

(3) Strong A-attractive surface, wherein the confinement surface strongly attracts A-blocks ($H_A = -16$ and $H_B = 0$).

(4) Weak B-attractive surface, wherein the confinement surface weakly attracts B-blocks ($H_A = 0$ and $H_B = -8$).

(5) Strong B-attractive surface, wherein the confinement surface strongly attracts B-blocks ($H_A = 0$ and $H_B = -16$).

Under different surface fields, the spherical shell cavity interspace is varied to obtain systematic self-assembled structures of a bulk cylinder-forming DBCPs melt under spherical shell confinement.

RESULTS AND DISCUSSION

In this section, the morphologies of DBCPs confined in spherical shell cavity with variational interspace δ and different surface-polymer interactions $h_{sA(B)}$ are presented. In the calculation, the DBCPs have a volume fraction of A-block $f_A = 0.2$ and a Flory-Huggins parameter $\chi_N = 40$. This DBCPs, in the bulk system, form a hexagonally arranged cylindrical structure and have a repeat period L_0 ^[48]. Our purpose is to clarify the microstructures of cylinder-forming DBCPs confined in a closed spherical shell cavity with different δ and $h_{sA(B)}$. Here $h_{sA(B)}$ represents surface-polymer interaction between the homocentric sphere surface and A(B)-block. Another surface-polymer interaction between the spherical solid surface and A(B)-block is ignored. For comparability, we fix the inner sphere radius, while increase the volume of outer sphere (see Fig. 1b). The self-assembled structures are displayed as a function of confinement factor δ/L_0 . The final morphologies are summarized in Fig. 2, where only the A-blocks are shown for clarity.

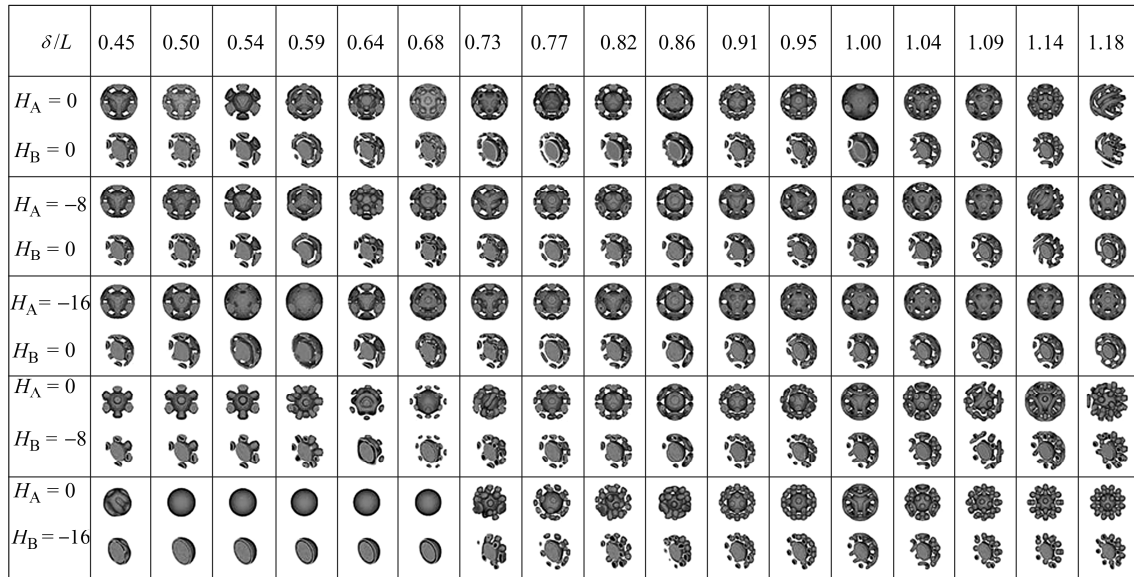


Fig. 2 Spherical shell confinement induced microstructures of the cylinder-forming DBCPs under different surface fields as a function of confinement dimension δ/L_0 (shell thickness δ versus polymer repeat period L_0) Only A-blocks are shown, and inner structures are shown under the full structures by cut views.

Neutral Surface ($H_{A(B)} = 0$)

In the neutral surface case, the DBCPs undergo self-assembly under the pure confinement conditions without surface field influence. As shown in the first row of Fig. 2, the morphologies for this case are very complex. As a matter of convenience, we classify the overall morphologies in terms of the number of A-monolayers (the monolayer structure formed by A-blocks). Most of them have two-layer structures, namely inner layer (A-

monolayer pasted on the spherical solid) and outer layer (A-monolayer pasted on the homocentric sphere). But a few of them are only one-layer structure ($\delta L_0 \geq 0.59$). We also noticed that, in the two-layer structures, the inner layer is incomplete until $\delta L_0 \geq 0.77$, and the outer layer is inconstant in his morphostructure.

Besides the polytrope structures of the outer layer in different confinement factors δL_0 , as shown in the first row of Fig. 2, the outer layer has the common ground that they are all made up of droplets, shorter cylinders, circles and strips. As the values of δL_0 is small, there is only an outer layer. First three structures are made up of six regular A-block droplets with a closed net or twelve shorter cylinders or another six droplets. The fourth is made up of twelve small A-block droplets and a closed net. The remaining space is filled with B-blocks. With the confining space volume increase, the inner layer structure appears. At the values of $0.64 \leq \delta L_0 \leq 0.73$, the inner layers are incomplete and the outer layers are netted texture with six droplets, with one exception. At $\delta L_0 = 0.64$, the outer layer structure is made up of six four-petal and six three-petal flowers, such flower-structure (FS) is not reported before. With the increase of δL_0 , the inner layers form a complete spherical surface covering the spherical solid except the last one. When the volume δL_0 reaches 1.18, the computer performance reaches the limit in our calculation. This anomaly can be seen again under B-attractive surface field case. Let us turn back to the outer layer structures, very complex morphologies are observed. Such as a structure with six A-droplets, shorter cylinders and sector-structures (SS) at $\delta L_0 = 0.77$. Structures are made up of all droplets ($\delta L_0 = 0.82, 0.91, 0.95$) or involuted net with droplets ($\delta L_0 = 1.09$). At $\delta L_0 = 1.04$, the outer layer structure is made up of six circles and six stripes. A similar morphology has been observed in literature^[49]. These stripes also can change into shorter cylinders, such as at $\delta L_0 = 1.14$. At $\delta L_0 = 1.00$, when the size of the confined space is equal to a polymer period, the outer layer structure is found to be an almost closed perforated homocentric sphere with six symmetrically arranged A-block droplets. This morphology is a kind of perforated lamellae (PL) in some degree. At the largest value of $\delta L_0 = 1.18$, the outer layer structure is very different from the others, as shown in the first row of Fig. 2. It is made up of cylinders wrapping around the sphere. This morphology is similar to parallel cylinders ($C_{\parallel}$) in Ref. [50]. These rich morphologies can be generally understood by the competition effects of the confinement-induced entropy.

A-Attractive Surface ($H_A < 0$)

Here the confinement surfaces attracting A-blocks ($H_A < 0$, $H_B = 0$) are considered. It is observed that the morphologies of this section are similar to the neutral surface cases. The confinement dimension δL_0 for the formation of similar multilayer structures is the same: one layer and two layers structure, as shown in the second ($H_A = -8$) and third ($H_A = -16$) rows of Fig. 2. In A-attractive surface cases, the inner layer structures could also be considered as an incomplete sphere, or an empty sphere, which are similar to those in neutral surface cases. The outside layer structures in these cases, owing to the surface preference effect, have their own characteristics.

As exhibited in some local details, the surface fields' effects on the equilibrium structure under 3-D spherical shell confinement are rather complicated. For example, at $\delta L_0 = 0.54$, the droplets structure under a neutral surface field is keeping its feature under weak A-attractive surface field. But under strong A-attractive surface field, they are reconstructed to be almost closed spherical surface with small perforation (PL). A similar evolutionary behavior occurs at $\delta L_0 = 0.59$. On the other hand, at $\delta L_0 = 1.00$, the $C_{\parallel}$ structure under a neutral surface field changed into droplets and net structure under A-attractive surface fields, as Fig. 3 shows, for both strong ($H_A = -16$) and weak ($H_A = -8$) fields. Furthermore, structures could remain unaffected under different surface fields, such as the structures at $\delta L_0 = 0.45$ and 1.09. It is noted that the reason for structure adjustment or unchange under different surface fields could be attributed to the effect of confinement on the self-assembly process. We believe that, in some lenient frustration condition, the equilibrium structure is easily reconstructed by the surface field; thus the copolymer chains could adjust themselves to adapt to the surface preference. However, in some severe frustration condition, the equilibrium structure is highly strengthened; as a result, the surface field could hardly affect the self-assembled structure.

There are some fanciful morphologies under weak A-attractive surface field. For example, at $\delta L_0 = 0.68$ and 0.86, the outer layer structures are made up of eight circle-petal flowers. At $\delta L_0 = 0.82$, it is made up of six

ring cookies and eight triplets. While at $\delta/L_0 = 1.04$, those eight triplets join together to form a intricate net structure. Here these novel morphologies are first reported. A typical morphology appeared at $\delta/L_0 = 1.18$, a classical single perforated lamellae (PL). Under strong A-attractive surface field, an unique morphology of split-leaf net structure appeared at $\delta/L_0 = 0.95$. It was not reported before. Other morphologies under strong A-attractive surface field are similar to those under weak A-attractive case.

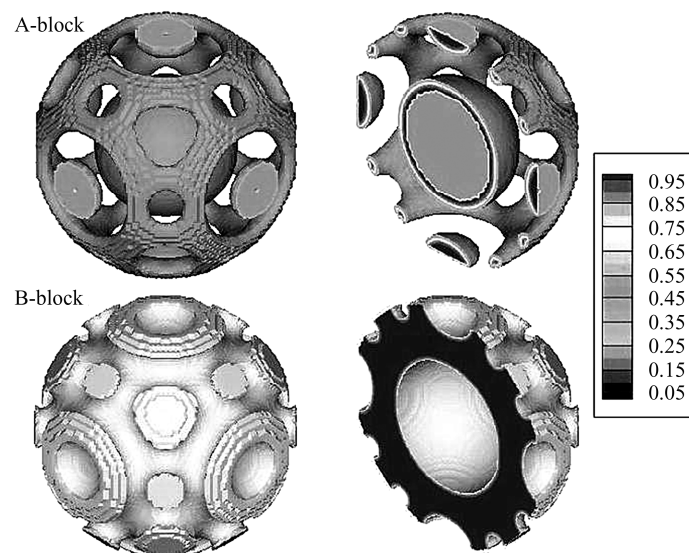


Fig. 3 A(B)-block structure at $\delta/L_0 = 1.00$, $H_A < 0$, $H_B = 0$
The color bar shows the density values.

B-Attractive Surface ($H_B < 0$)

Li and Wickham studied the DBCPs self-assembly under 2-D cylindrical confinement, and found that the cylinder-forming DBCPs systems experienced similar phase behaviors in all kinds of surface field cases, indicating that self-assembled structures under an A-attractive surface field also appeared under a B-attractive surface field or a neutral surface field. On the contrary, our research discovered that in spherical shell confinement self-assembled structures under a B-attractive surface were different from those under neutral and A-attractive surface fields.

In the weak B-attractive surface case ($H_B = -8$), the equilibrium structures are shown in the fourth row of Fig. 2. It was observed that A-blocks were repelled from the surface comparing with the neutral surface and A-attractive surface cases. At the small confining space $\delta/L_0 \leq 0.59$, A-blocks formed droplets and shorter cylinders directed along the diameter. While at $\delta/L_0 \geq 0.64$, an inner layer structure, covering the spherical solid, appeared. The surfaces of these inner layers are glossy. But rugged inner surfaces are also observed at $\delta/L_0 = 0.64$, and 1.18. What's more, at $\delta/L_0 = 0.64$, 0.68, their unique structures of the inner layers are not sphere but cubic. At $\delta/L_0 = 0.73$, there is another distinctive structure. Namely, the inner layer structure is disunited and directed along the diameter, forming shorter laces structure. At $0.77 \leq \delta/L_0 \leq 0.95$, the outer layer structures are made up of droplets in a certain range except at $\delta/L_0 = 0.86$, where it is made up of eight circle-petal flowers. This circle-petal flowers structure has appeared under weak and strong A-attractive surface field at the same confinement conditions. When the confinement space is larger than $\delta/L_0 = 1.00$, the circle-petal changes into large circle and the pistil becomes a small droplet in Fig. 4. Because of the small confinement, its outer layer structure is made up of six circles, not eight, with six small droplets in the centre. A similar structure appeared at $\delta/L_0 = 1.14$, because the space is larger, there are eight droplets inlayed between the six circles. Droplets and ribbons structure appeared at $\delta/L_0 = 1.09$ and 1.18. These morphologies are very different from those under neutral and A-attractive surface fields.

The self-assembled structures under a strong B-attractive surface fields ($H_B = -16$) are exhibited in the fifth row of Fig. 2. By careful inspection of those morphologies, it is found that the phase behaviors are very distinct comparing with the above case. In other words, the structures are extremely terse under the case of strong B-attractive surface fields. For example, at $\delta L_0 \leq 0.68$, the equilibrium structures are sleek homocentric spheres except the first one ($\delta L_0 = 0.45$). The structure of the first one is rough and uneven in surface. At $0.73 \leq \delta L_0 \leq 0.91$, the structures are made up of droplets in a certain range. While at $\delta L_0 \geq 0.95$, a number of A-block copolymer spheres arrange themselves in layers to form the outer layer. Pinna *et al.* observed a similar spherical morphology in their study^[50]. However, as exhibited in some local details, there are two exceptions. The first one appears at $\delta L_0 = 1.00$. Its outer layer structure is made up of six circles and six droplets in the centre of the circles. The second one is found at $\delta L_0 = 1.04$. Its outer layer structure is also made up of six circles and eight triplets, but there are no droplets in the center of the circles. These two typical structures appear under weak B-attractive surface field and strong case at the same confinement conditions.

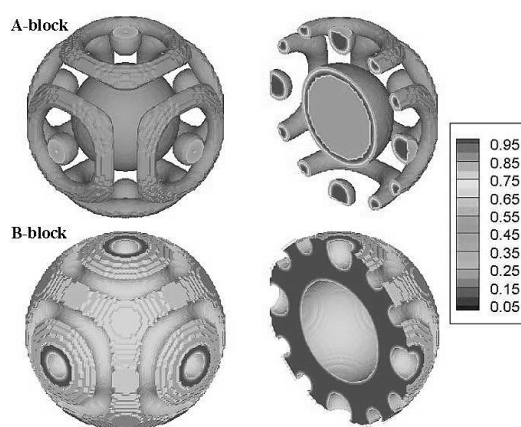


Fig. 4 A(B)-block structure at $\delta L_0 = 1.00$, $H_A = 0$, $H_B < 0$
The color bar shows the density values.

CONCLUSIONS

Using SCFT we performed systematic analysis of cylinder-forming DBCPs confined in a spherical shell cavity. The observed structures are controlled by the interplay of two factors: confinement dimension δL_0 and affinity of the spherical surface to the copolymer blocks (H_A , H_B). That leads to the formation of many structures which are not present in the bulk or other 1-D or 2-D confinement geometries. The self-assembled structures under B-attractive surface fields are clearly different from those observed under neutral and A-attractive surface fields. These rich morphologies can be generally understood by the competition effects of the surface-copolymer interaction energy and confinement-induced entropy.

REFERENCES

- 1 Bates, F.S. and Fredrickson, G.H., *Annu. Rev. Phys. Chem.*, 1990, 41: 525
- 2 Park, M., Harrison, C., Chaikin, P.M., Register, R.A. and Adamson, D.H., *Science*, 1997, 276: 1401
- 3 Bates, F.S. and Fredrickson, G.H., *Phys. Today*, 1999, 52(2): 32
- 4 Pereira, G.G., *Curr. Appl. Phys.*, 2004, 4: 255
- 5 Jackson, A.M., Myerson, J.W. and Stellacci, F., *Nat. Mater.*, 2004, 3: 330
- 6 Grason, G.M., *Phys. Rep.*, 2006, 433: 1
- 7 Sevink, G.J.A. and Zvelindovsky, A.V., *J. Chem. Phys.*, 2008, 128(8): 084901

- 8 Zvelindovsky, A.V., "Nanostructured soft matter", Springer Press, New York, 2007, p. 58
- 9 Hamley, I.W., *Nanotechnology*, 2003, 14(10): 39
- 10 Park, C., Yoon, J. and Thomas, E.L., *Polymer*, 2003, 44(22): 6725
- 11 Urbas, A., Sharp, R., Fink, Y., Thomas, E.L., Xenidou, M. and Fetters, L.J., *Adv. Mater.*, 2000, 12(11): 812
- 12 He, X.H., Song, M., Liang, H.J. and Pan, C.Y., *J. Chem. Phys.*, 2001, 114(23): 10510
- 13 Sevink, G.J.A., Zvelindovsky, A.V., Fraaije, J.G.E.M. and Huinink, H.P., *J. Chem. Phys.*, 2001, 115(17): 8226
- 14 Knoll, A., Horvat, A., Lyakhova, K.S., Krausch, G., Sevink, G.J.A., Zvelindovsky, A.V. and Magerle, R., *Phys. Rev. Lett.*, 2002, 89(3): 035501
- 15 Ludwigs, S., Böker, A., Voronov, A., Rehse, N., Magerle, R. and Krausch, G., *Nature Materials*, 2003, 2: 744
- 16 Park, I., Park, S., Park, H.W. and Chang, T., *Macromolecules*, 2006, 39 (1): 315
- 17 Matsen, M.W., *J. Chem. Phys.*, 1997, 106(18): 7781
- 18 Huinink, H.P., Brokken-Zijp, J.C.M., van Dijk, M.A. and Sevink, G.J.A., *J. Chem. Phys.*, 2000, 112(5): 2452
- 19 Wang, Q., Nealey, P.F. and de Pablo, J.J., *Macromolecules*, 2001, 34(10): 3458
- 20 Huinink, H.P., van Dijk, M.A., Brokken-Zijp, J.C.M. and Sevink, G.J.A., *Macromolecules*, 2001, 34(5): 5325
- 21 Ludwigs, S., Krausch, G. and Magerle, R., *Macromolecules*, 2005, 38(5): 1859
- 22 Ludwigs, S., Schmidt, K., Stafford, C.M., Amis, E.J., Fasolka, M.J., Karim, A., Magerle, R. and Krausch G., *Macromolecules*, 2005, 38(5): 1850
- 23 He, L.L., Zhang, L.X. and Liang, H.J., *J. Polym. Sci. Part B: Polym. Phys.*, 2009, 47(1): 1
- 24 Li, S.B., Chen, P., Wang, X.H., Zhang, L.X. and Liang, H.J., *J. Chem. Phys.*, 2009, 130(1): 014902
- 25 Chen, P. and Liang, H.J., *J. Phys. Chem. B*, 2006, 110(37): 18212
- 26 Wu, Y.Y., Cheng, G.S., Katsov, K., Sides, S.W., Wang, J.F., Tang, J., Fredrickson, G.H., Moskovits, M. and Stucky, G.D., *Nat. Mater.*, 2004, 3: 816
- 27 Shin, K., Xiang, H.Q., Moon, S.I., Kim, T., McCarthy, T. and Russell, T.P., *Science*, 2004, 306: 76
- 28 He, L.L., Zhang, L.X., Xia, A.G. and Liang, H.J., *J. Chem. Phys.*, 2009, 130(14): 144907
- 29 He, L.L., Zhang, L.X. and Liang, H.J., *J. Phys. Chem. B*, 2010, 114(21): 7189
- 30 Xiang, H.Q., Shin, K., Kim, T., Moon, S.I., McCarthy, T.J. and Russell, T.P., *Macromolecules*, 2005, 38 (4): 1055
- 31 He, L.L., Zhang, L.X. and Liang, H.J., *Polymer*, 2009, 50(2): 721
- 32 He, L.L., Zhang, L.X. and Liang, H.J., *Polymer*, 2010, 51(14): 3303
- 33 Feng, J. and Ruckenstein, E., *J. Chem. Phys.*, 2006, 125(16): 164911
- 34 Li, W.H. and Wickham, R.A., *Macromolecules*, 2006, 39(24): 8492
- 35 Chen, P., He, X.H. and Liang, H.J., *J. Chem. Phys.*, 2006, 124(10): 104906
- 36 Feng, J. and Ruckenstein, E., *Macromolecules*, 2006, 39(14): 4899
- 37 Chen, P., Liang, H.J. and Shi, A.C., *Macromolecules*, 2007, 40(20): 7329
- 38 Chen, P. and Liang, H.J., *Acta Polymerica Sinica*(in Chinese), 2009, (4): 298
- 39 Wang, Q., *J. Chem. Phys.*, 2007, 126(2): 024903
- 40 Yu, B., Sun, P.C., Chen, T.H., Jin, Q.H., Ding, D.T., Li, B.H. and Shi, A.C., *J. Chem. Phys.*, 2007, 126(20): 204903
- 41 Li, W.H., Wickham, R.A. and Garbary, R.A., *Macromolecules*, 2006, 39(2): 806
- 42 Cheng, J.Y., Ross, C.A., Smith, H.I. and Thomas, E.L., *Adv. Mater.*, 2006, 18(19): 2505
- 43 Arsenault, A.C., Rider, D.A., Tétreault, N., Chen, J.I.L., Coombs, N., Ozin, G.A. and Manners, L., *J. Am. Chem. Soc.*, 2005, 127 (28): 9954
- 44 Fraaije, J.G.E.M. and Sevink, G.J.A., *Macromolecules*, 2003, 36(21): 7891
- 45 Drolet, F. and Fredrickson, G.H., *Phys. Rev. Lett.*, 1999, 83(21): 4317
- 46 Drolet, F. and Fredrickson, G.H., *Macromolecules*, 2001, 34(15): 5317
- 47 Chen, H.Y. and Fredrickson, G.H., *J. Chem. Phys.*, 2002, 116(3): 1137
- 48 Matsen, M.W. and Bates, F.S., *Macromolecules*, 1996, 29(4): 1091
- 49 Chen, P., Liang, H.J. and Shi, A.C., *Macromolecules*, 2008, 41(22): 8938
- 50 Pinna, M., Guo, X.H. and Zvelindovsky, A.V., *Polymer*, 2008, 49(12): 2797