

STRUCTURE EVOLUTION OF THE CYLINDRICAL PHASE OF DIBLOCK COPOLYMERS IN FILMS*

Hong-ge Tan^{a**}, Zi-yu Wang^b, Wen-fang Zhu^a, Qing-gong Song^a, Hui Li^c and Cui-qin Bai^a

^aCollege of Science, Civil Aviation University of China, Tianjin 300300, China

^bCollege of Science, Hebei University of Technology, Tianjin 300130, China

^cInstitute of Information Science and Engineering, Hebei University of Science and Technology, Shijiazhuang 050054, China

Abstract In the weak segregation limit, the structure evolution of the hexagonal cylindrical phase of diblock copolymers in films was investigated. Employing the Landau-Brazovskii mean field theory, we obtained three amplitude parameters as functions of temperature, surface field strength and film thickness. By controlling confinement size and surface field strength, lamellae and undulated lamellae appear in the cylindrical bulk phase of diblock copolymers. “Phase diagrams” of confinement-induced structures are constructed at different surface field strengths. The obtained theoretical results are in agreement with relevant theoretical and experimental results.

Keywords: Theory; Block copolymers; Film; Surfaces; Mean field.

INTRODUCTION

Diblock copolymer is an idea model for the study of self-assembly because it can self-assemble into complex nano-scale morphologies^[1–8]. In recent years, confinement is an important method to obtain novel structures of diblock copolymers. The morphology of diblock copolymers in confined environment is more complex and interesting than that in the bulk because of the effect of surface-block interactions and the film thickness.

Much attention has been focused on the self-assembly of symmetric diblock copolymers in a confined environment^[9–17]. Their phase behavior has been understood fair well. Typically, by tuning the surface-block interaction and the thickness of the film, one can obtain alternate morphology between parallel lamellae and perpendicular lamellae. For the lamellar structure, a fairly simple physical picture can be used due to the one dimensional nature of the structure. Theoretical predictions are available for the lamellar structure^[10, 11, 14–16]. For asymmetric block copolymers with cylindrical bulk morphology, a number of studies have been carried out experimentally and theoretically^[18–32]. Some of these studies focused on orientational transition^[18–23]. In principle, cylinder domains often prefer to align parallel to the substrate to reduce the number of cylinder ends. Due to the effects of surface field and confinement, both parallel orientation and perpendicular orientation were observed. The rest of the studies focused on the morphology transition^[24–32]. A variety of structures in thin films have been observed, including a wetting layer, lamella, undulated lamella, a perforated lamella and cylinder with neck. There has been some theoretical work on the film of the cylindrical bulk morphology of diblock copolymers^[18, 19, 21–23, 25, 32]. Those theoretical results were in good agreement with experiments. In this paper, we will apply a simple analytical approximation consisting of a Landau-Brazovskii expansion of the free energy to study the structure evolution of hexagonal phase melt in the film. We obtained some structures observed in

*This work was supported by the National Natural Science Foundation of China (No. 20504027) and Scientific Research Foundation of Civil Aviation University of China (No. 05qd05s).

**Correspondence author: Hong-ge Tan (谭红革), Email: thg75@sina.com.cn

Received November 5, 2007; Revised December 17, 2007; Accepted December 25, 2007

experiments by this simple method. Applying the analogous method, Turner and *co-workers* have studied the effect of one flat surface on the cylindrical bulk phase^[26]. In this paper, we will apply this simple method to diblock copolymers confined in two flat surfaces. The morphologies in the film are different from those induced by one surface because of the effect of film thickness.

This paper is organized as follows. Our study is carried out by employing the Landau-Brazovskii model^[33, 34], which can be derived from the many-chain Edwards Hamiltonian for diblock copolymers in the weak segregation limit^[1, 2]. Since we focus on the confinement-induced behavior in the hexagonal phase close to the ordering transition, the weak segregation theory is appropriate. In section of THE MODEL, we apply the single mode approximation, accurate at weak segregation, to the Landau-Brazovskii model, leading to an amplitude model studied previously in different contents^[15, 26, 34]. In section of RESULTS AND DISCUSSIONS, we study the structural variation of hexagonal bulk phase under different film thicknesses and different surface field strengths. The results are summarized in “phase diagrams” of structure reconstructions. Corresponding discussions are also carried out in this section. Finally, the last section is devoted to conclusions.

THE MODEL

We consider an incompressible melt of n AB diblock copolymers in a volume V_0 at a temperature T . The total degree of polymerization of the diblock copolymer is N . The monomer density is $\rho = nN/V_0$. The degree of polymerization of the A block is $f_A N$, where $0 \leq f_A \leq 1$. The order parameter of diblock copolymers is defined as $\phi(\mathbf{r}_0) \equiv \phi_A(\mathbf{r}_0) - f_A$, the deviation of the local A monomer concentration from its average value. Because we are studying the confinement-induced behavior near the ordering transition, which is in the weak segregation regime, the Landau-Brazovskii model can be used. Specifically, the Landau-Brazovskii free energy F_0 is given by^[33, 34]

$$f_0[\phi(\mathbf{r}_0)] \equiv \frac{F_0}{nk_B T} = \frac{1}{V_0} \int d\mathbf{r}_0 \left\{ \frac{\xi_0^2}{8q_0^2} [(\nabla^2 + q_0^2)\phi]^2 + \frac{\tau_0}{2} \phi^2 - \frac{\gamma_0}{3!} \phi^3 + \frac{\lambda_0}{4!} \phi^4 \right\} \quad (1)$$

Here, f_0 is the Landau-Brazovskii free energy per block copolymer, ξ_0 is the bare correlation length, q_0 is the critical wavevector, τ_0 is the reduced temperature, and γ_0 and λ_0 are expansion coefficients. For stability, $\lambda_0 > 0$. Since the Landau-Brazovskii free energy can be derived from the many-chain Edwards Hamiltonian for diblock copolymers following the method of Leibler^[1] and Ohta and Kawasaki^[2], we can express these parameters in terms of χN , f_A and R_g , which appeared in the Edwards model. Specifically, we have^[1-3, 34]

$$q_0^2 = \frac{x^*}{R_g^2} \quad (2)$$

$$\tau_0 = 2[(\chi N)_s - \chi N] \quad (3)$$

$$\xi_0^2 = 4x^* c R_g^2 \quad (4)$$

$$\gamma_0 = -N\Gamma_3 \quad (5)$$

$$\lambda_0 = N\Gamma_4(0,0) \quad (6)$$

Here, R_g is the radius of gyration of the chains, and x^* is the position of the minimum of the function $F(x, f_A)$ appearing in the scattering function in Ref. [1]. The disorder-to-order spinodal point, $(\chi N)_s$ and the quantity, c , are defined by

$$(\chi N)_s = \frac{1}{2} F(x^*, f_A) \quad (7)$$

$$c = \frac{1}{2} \frac{\partial^2 F(x, f_A)}{\partial x^2} \Big|_{x=x^*} \quad (8)$$

Finally, the vertex functions I_3 and $I_4(0, 0)$, which are functions of f_A are computed in Ref. [1].

It is convenient to rescale Eq. (1) by expressing lengths in units of q_0^{-1} , and the free energy is in units of λ_0 . Under the rescalings

$$\mathbf{r} = q_0 \mathbf{r}_0 \quad (9)$$

$$V = q_0^3 V_0 \quad (10)$$

$$f = \frac{f_0}{\lambda_0} \quad (11)$$

$$\xi^2 = \frac{(q_0 \xi_0)^2}{4\lambda_0} \quad (12)$$

$$\tau = \frac{\tau_0}{\lambda_0} \quad (13)$$

$$\gamma = \frac{\gamma_0}{\lambda_0} \quad (14)$$

the Landau-Brazovskii free energy becomes

$$f[\phi(\mathbf{r})] = \frac{1}{V} \int d\mathbf{r} \left\{ \frac{\xi^2}{2} [(\nabla^2 + 1)\phi]^2 + \frac{\tau}{2} \phi^2 - \frac{\gamma}{3!} \phi^3 + \frac{1}{4!} \phi^4 \right\} \quad (15)$$

For a hexagonal structure in the weak segregation regime, it is sufficient to restrict ourselves to the first mode in reciprocal space, whose reciprocal lattice vectors satisfy $|\mathbf{G}_i| = q_0 = 2\pi/(b/\sqrt{2})$ (b is the lattice parameter and $|\mathbf{G}_i| = 1$ in scaled units), instead of using the complete set of vectors $\mathbf{G}_i$. For a hexagonal phase, the 3 shortest vectors $\mathbf{G}_i$ (in scaled units) may be chosen as:

$$\mathbf{G}_1 = \hat{z}$$

$$\mathbf{G}_2 = \frac{1}{2} (\sqrt{3}\hat{x} + \hat{z})$$

$$\mathbf{G}_3 = \frac{1}{2} (-\sqrt{3}\hat{x} + \hat{z})$$

In the single mode approximation, the order parameter can be written as

$$\phi(\mathbf{r}) = 2a_1(\mathbf{r}) \cos(\mathbf{G}_1 \cdot \mathbf{r}) + 2a_2(\mathbf{r}) [\cos(\mathbf{G}_2 \cdot \mathbf{r}) + \cos(\mathbf{G}_3 \cdot \mathbf{r})] \quad (16)$$

Where a_1 and a_2 are space-dependent amplitude functions describing the variation of microstructure. If we assume that the amplitudes a_1 and a_2 are slowly varying functions on the scale of D_c , which is the period of the hexagonal phase, we can separate the length scale for variations in the amplitude from the length scale of the microstructure. Within this slowly-varying amplitude approximation, the Landau-Brazovskii free energy can be written in terms of the amplitudes as

$$f = \frac{1}{V} \int d\mathbf{r} \left\{ \xi^2 (\nabla^2 a_1)^2 + 2\xi^2 (\nabla^2 a_2)^2 + 4\xi^2 \left[(\mathbf{G}_1 \cdot \nabla a_1)^2 + (\mathbf{G}_2 \cdot \nabla a_2)^2 + (\mathbf{G}_3 \cdot \nabla a_2)^2 \right] \right. \\ \left. + \tau(a_1^2 + 2a_2^2) - 2\gamma a_1 a_2^2 + \frac{1}{4}(a_1^4 + 6a_2^4 + 8a_1^2 a_2^2) \right\} \quad (17)$$

For the equilibrium state of the bulk diblock copolymers, a_1 and a_2 are position independent, leading to a bulk free energy density

$$f_{\text{bulk}} = \tau(a_1^2 + 2a_2^2) - 2\gamma a_1 a_2^2 + \frac{1}{4}(a_1^4 + 6a_2^4 + 8a_1^2 a_2^2) \quad (18)$$

When $a_2 = 0$, the structure is lamellae. When $a_1 = a_2 = a_{\text{hex}}$, the structure is hexagonal arrays of cylinders.

Define an effective temperature $\alpha = \tau/\gamma^2$. The lamella/cylinder phase boundary occurs for

$$\alpha^* = -2.867 \quad (19)$$

When a diblock copolymer melt is put in contact with two flat surfaces, the translational symmetry is broken. In order to study the confinement-induced structures in the hexagonal phase explicitly under interactions between polymers and the surfaces, we choose the surface planes as the $z = 0$ and $z = l$ planes and assume that the surface is presented by a surface potential. Thus, the free energy of the system is given by

$$\Omega = \frac{1}{V} \int d\mathbf{r} \left\{ -\phi(\mathbf{r}) \Delta u [\delta(z) + \delta(z-l)] + f[\phi(\mathbf{r})] \right\} \quad (20)$$

Where Δu is the differential affinity of surfaces with respect to polymer A^[26]. $\delta(z)$ and $\delta(z-l)$ are the delta functions, which mean the interactions are short range and only exist on the surfaces ($z = 0$ plane and $z = l$ plane). We assume that the amplitudes are only z -dependent, and vary slowly on the scale of l_0 , which is the characteristic period of the lamellar component in the bulk melt. Moreover, we neglect the effect of the incommensurability between the film thickness and l_0 (We neglect the orientation effect on the microstructures). We can separate the length scale for variations in the amplitude from the length scale of the microstructure. Because the amplitudes vary slowly on the scale of l_0 , we only retain gradient terms up to quadratic order in the Landau-Brazovskii free energy. Under these assumptions, the free energy per unit surface can be written as

$$\Omega = -2\Delta u a_1(z=0) - 2\Delta u a_1(z=l) + \int_0^l dz \left\{ \xi^2 \left[4 \left(\frac{\partial a_1}{\partial z} \right)^2 + 2 \left(\frac{\partial a_2}{\partial z} \right)^2 \right] \right. \\ \left. + \tau(a_1^2 + 2a_2^2) - 2\gamma a_1 a_2^2 + \frac{1}{4}(a_1^4 + 6a_2^4 + 8a_1^2 a_2^2) \right\} \quad (21)$$

It is convenient to introduce the following new variables,

$$\begin{aligned} a_1 &= \gamma X, & a_2 &= \gamma Y \\ a_3 &= \gamma Z, & z &= \frac{2\xi}{\gamma} t \\ \Delta u &= \xi \gamma^2 \sigma, & \Omega &= 2\xi \gamma^3 \tilde{\Omega} \\ L &= (2\xi/\gamma)L \end{aligned}$$

Thus, $X(t)$ and $Y(t)$ are related to the structures since they are proportional to $a_1(z)$ and $a_2(z)$, respectively. Also, we introduce a reduced distance t and a reduced adsorption strength σ instead of z and Δu , respectively. In terms of these new variables, the free energy density becomes

$$\tilde{\Omega} = -\sigma X(0) - \sigma X(L) + \int_0^L dt \left\{ \left(\frac{dX}{dt} \right)^2 + \frac{1}{2} \left(\frac{dY}{dt} \right)^2 + f[X(t), Y(t)] \right\} \quad (22)$$

where the function $f(X, Y)$ is the bulk free energy and given by

$$f(X, Y) = \alpha(X^2 + 2Y^2) - 2(XY^2) + \frac{1}{4}(X^4 + 6Y^4 + 8X^2Y^2)$$

Minimizing the new free energy per unit surface, we obtain two coupled Euler-Lagrange equations for the amplitudes X and Y ,

$$\frac{d^2 X}{dt^2} = (\alpha + 2Y^2)X - Y^2 + \frac{1}{2}X^3 \quad (23)$$

$$\frac{d^2 Y}{dt^2} = (4\alpha + 4X^2 - 4X)Y + 6Y^3 \quad (24)$$

which can be solved with the boundary conditions

$$\begin{aligned} \left. \frac{dX}{dt} \right|_{t=0} &= -\left. \frac{dX}{dt} \right|_{t=L} = -\sigma \\ \left. \frac{dY}{dt} \right|_{t=0} &= \left. \frac{dY}{dt} \right|_{t=L} = 0 \end{aligned}$$

In the follow section, we can solve these two coupled Euler-Lagrange equations and discuss the results with parameters L , σ and effective temperature α .

RESULTS AND DISCUSSION

In this section, we show that how the film thickness affects the bulk structure under different surface field strengths. As the first step, we linearize the free energy density of the bulk phase $f(X, Y)$ around the hexagonal structure. Minimizing the total free energy given by Eq. (22), we obtain three linear Euler-Lagrange equations. Under the boundary conditions, we obtain the general solutions of these linear equations,

$$\Delta X(t) = X(t) - X_{\text{bulk}} = \sigma \sum_{i=1}^2 \left[C_{Xi}(\alpha, L) e^{-\lambda_i(\alpha)t} + C_{Xi+2}(\alpha, L) e^{\lambda_i(\alpha)t} \right] \quad (25)$$

$$\Delta Y(t) = Y(t) - Y_{\text{bulk}} = \sigma \sum_{i=1}^2 \left[C_{Yi}(\alpha, L) e^{-\lambda_i(\alpha)t} + C_{Yi+2}(\alpha, L) e^{\lambda_i(\alpha)t} \right] \quad (26)$$

where C_{Xi} , etc. are the coefficients of the solutions of the linear equations and are determined by α and L .

In order to study the confinement effect, we fix at first the effective interaction $\sigma = 2$ and the effective temperature $\alpha = -1$ (far from the effective transition temperature $\alpha^* = -2.8697$). We obtain $X_{\text{bulk}} = Y_{\text{bulk}} = Z_{\text{bulk}} = 0.8633$, $\lambda_1 = 2.3841$ and $\lambda_2 = 1.1897$. We change the film thickness and consider two different cases as follows.

The first case is for a thick film, in which we choose $L = 9$. In this case, the corresponding coefficients are $C_{X1} = 1.892 \times 10^{-2}$, $C_{X2} = 0.803$, $C_{X3} = 1.795 \times 10^{-5}$, $C_{X4} = 9.116 \times 10^{-12}$, $C_{Y1} = 0.123$, $C_{Y2} = -0.247$, $C_{Y3} = -5.527 \times 10^{-6}$, $C_{Y4} = 4.271 \times 10^{-11}$. These asymptotic solutions can be used as the initial conditions to obtain the exact numerical solutions of the Euler-Lagrange equations, and then we obtain the amplitudes $X(t)$ and $Y(t)$ varying with t for a given L . The results are shown in Fig. 1. On the surfaces, $Y(t) = 0.188$, which indicates that the cylindrical component exists.

The second case is for a thin film, in which we choose $L = 1$. In this case, the corresponding coefficients are $C_{X1} = 2.091 \times 10^{-2}$, $C_{X2} = 1.153$, $C_{X3} = 0.351$, $C_{X4} = 1.927 \times 10^{-3}$, $C_{Y1} = 0.136$, $C_{Y2} = -0.355$, $C_{Y3} = -0.108$ and $C_{Y4} = 1.252 \times 10^{-2}$. We also obtain the amplitudes $X(t)$ and $Y(t)$ varying with t shown in Fig. 2. Note that all the values of $Y(t)$ become negligible, which indicate that the cylindrical component disappear in the film.

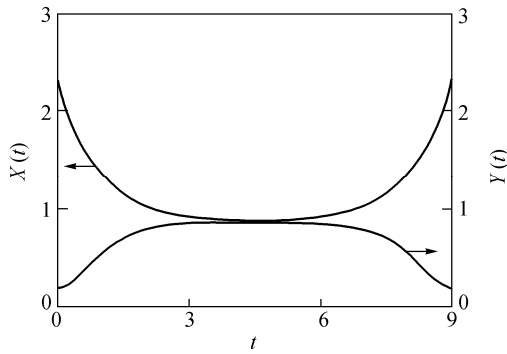


Fig. 1 Reduced amplitudes $X(t)$ and $Y(t)$ as functions of t for $\alpha = 1$, $\sigma = 2$ and $L = 9$

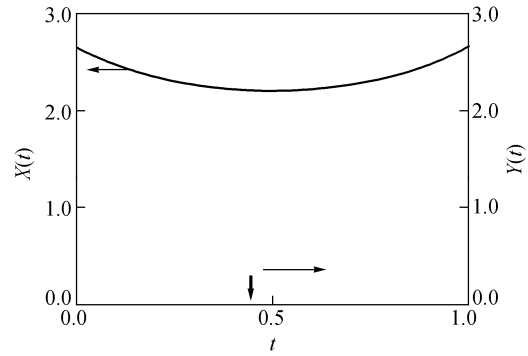


Fig. 2 Reduced amplitudes $X(t)$ and $Y(t)$ as functions of t for $\alpha = 1$, $\sigma = 2$ and $L = 1$

To demonstrate the evolution of the confinement-induced structures explicitly, the real space profiles of the system are presented in Figs. 3 and 4 for $L = 9$ and 1, respectively. From Fig. 3, we find that when the value of L is large, the structures in the film change from undulated lamellae near the surfaces to cylindrical structures near the center of the thin film. Figure 4 shows that when the value of L is small enough, undulated lamellae and cylindrical structures disappear, and lamellar phases extend throughout the thin film.

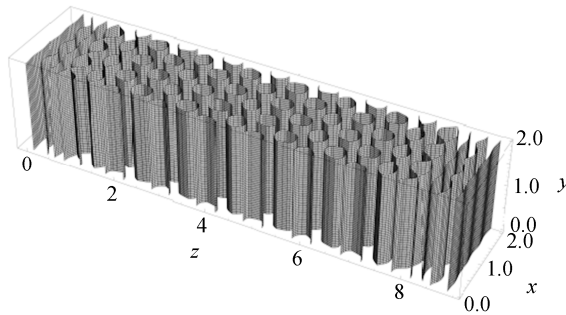


Fig. 3 Three-dimensional contour plot of the order parameter $\phi(x, y, z)$ in the region with amplitudes from the solid lines in Fig. 1
 z is taken as t (in length unit of $q_0^{-1} = 4\pi$).

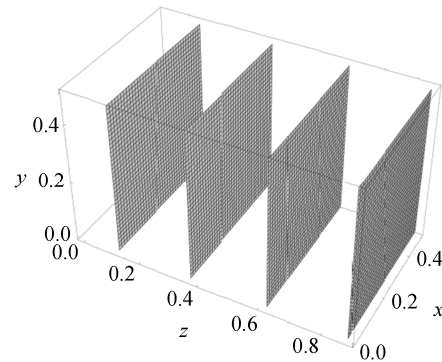


Fig. 4 Three-dimensional contour plot of the order parameter $\phi(x, y, z)$ in the region with amplitudes from the solid lines in Fig. 2

In order to illustrate the structure variation with film thickness, we construct two “phase diagram” for $\alpha = -1$ with $\sigma = 2$ and 15, respectively, which are shown in Figs. 5 and 6. Lines $A(L)$ and $C(L)$ are the distances from the surface ($t = 0$ and $t = L$) to the positions where the amplitudes $Y(t)$ reach 5% of $X(t)$ for $\sigma = 2$ and 15, respectively. Inside these lines, the cylindrical components begin to appreciable and lamellae appear. Lines $B(L)$ and $D(L)$ are the distances from the surface ($t = 0$ and $t = L$) to the positions where the amplitudes $Y(t)$ reach 40% of $X(t)$ for $\sigma = 2$ and 15, respectively. Inside these lines, the cylinder begins to appear. Such two “phase diagrams” qualitatively describe the evolution of the confinement-induced structures in the film under different surface field strengths. In Figs. 5 or 6, one can find the relation of the lamellar thickness and the film thickness.

After lamella appears, the lamellar thickness increases with the decrease of the film thickness until lamellae extend throughout the film.

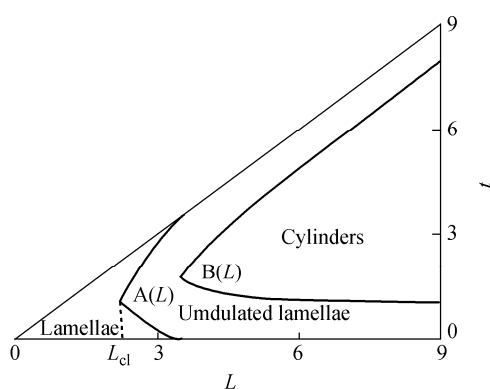


Fig. 5 “Phase diagram”, *i.e.*, reduced film thickness L versus reduced distance t , for $\alpha = -1$ with $\sigma = 2$. Line $A(L)$ describes the positions where the amplitudes $Y(t)$ reach 5% of $X(t)$ from the surfaces ($t = 0$ and $t = L$); Line $B(L)$ describes the positions where the amplitudes $Y(t)$ reach 40% of $X(t)$.

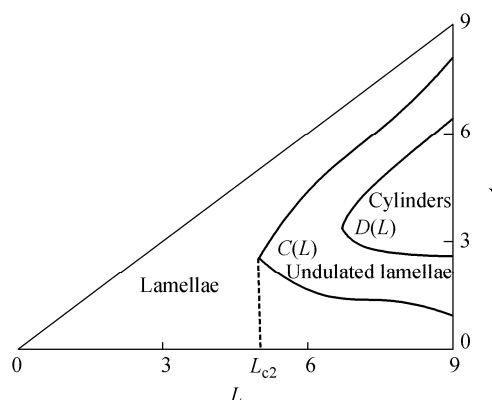


Fig. 6 “Phase diagram”, *i.e.*, reduced film thickness L versus reduced distance t , for $\alpha = -1$ with $\sigma = 15$. Line $C(L)$ describes the positions where the amplitudes $Y(t)$ reach 5% of $X(t)$ from the surfaces ($t = 0$ and $t = L$); Line $D(L)$ describes the positions where the amplitudes $Y(t)$ reach 40% of $X(t)$.

Comparing Fig. 5 with Fig. 6, one can find that the effects of confinement for weaker and stronger surface fields are different. The region where lamellar phase exists for $\sigma = 2$ is smaller than that for $\sigma = 15$. The critical thickness L_{c1} for $\sigma = 2$, below which the lamellar phases extend throughout the film, is smaller than L_{c2} for $\sigma = 15$. The lamellae persist to a larger extent at the stronger surface field. It is because the stronger surface field strength can induce lamellar phases easily and affect the bulk phase to a larger extent.

The structures in the film are different from the surface-induced structures. First, the big difference comes from the cusp of lines A , B , C and D (Figs. 5 and 6). If we only consider the effect of surface field, these lines should be straight to keep the same distances from the surfaces ($t = 0$ and L) and intersect at a point which is in front of the cusp of the lines. This can be considered as the effect of confinement. Second, the value of $Y(t)$ near the surfaces decreases with the decreasing of the film thickness (see Figs. 1 and 2), which indicates that the cylindrical component exists for the thicker film and then disappears little by little near the boundary with the decreasing of the film thickness under the same surface field strength. Finally, the lamellar phase appears in a quite thin film even for a weaker surface field. This means that the confinement makes the lamellar phase appear for a weaker surface field. If we only consider the effect of surface field, only the undulated lamellar phase or cylinder-like phase can be obtained, and no lamellar phase can be obtained for the weaker surface field.

Our theoretical results are in agreement with other theoretical methods and experiments. This method is more simple and less time-consuming.

CONCLUSIONS

In summary, the evolution of the confinement-induced structures is studied based on the Landau-Brazovskii theory. In the weak segregation limit, the confinement-induced structures are determined by the variation of the amplitudes along the direction perpendicular to the surfaces.

For a weaker surface field strength, in thick films, the undulated lamellae appear near the surfaces and then convert to the cylinder structures near the center of the film. If we continue to decrease the film thickness, lamellae appear near the surfaces at first and then extend throughout the space. The evolution of the confinement-induced structures follows these specific deformation modes. For a stronger surface field, the confinement-induced structures are different from those for a weak surface field. The above results are summarized in two “phase diagrams”.

REFERENCES

- 1 Leibler, L., *Macromolecules*, 1980, 13: 1602
- 2 Ohta, K. and Kawasaki, K., *Macromolecules*, 1986, 19: 2621
- 3 Fredrickson, G.H. and Helfand, E., *J. Chem. Phys.*, 1987, 87: 697
- 4 Ge, H., Wang, Z., Li, B.H., Ding, D.T. and Shi, A.C., *Acta Polymerica Sinica*(in Chinese), 2007, (2): 119
- 5 Han, Z.W., Sun, P.C., Li, B.H., Jin, Q.H. and Ding, D.T., *Acta Polymerica Sinica*(in Chinese), 2006, (4): 593
- 6 Li, L.Y., Sun, P.C., Yao, Y., Zhou, H.J., Chen, T.H., Li, B.H., Jin, Q.H. and Ding, D.T., *Acta Polymerica Sinica*(in Chinese), 2006, (1): 124
- 7 Bates, F.S. and Fredrickson, G.H., *Annu. Rev. Phys. Chem.*, 1990, 41: 525
- 8 Matsen, M.W. and Bates, F.S., *Macromolecules*, 1996, 29: 7641
- 9 Lambooy, P. and Russell, T.P., *Phys. Rev. Lett.*, 1994, 72: 2899
- 10 Matsen, M.W., *J. Chem. Phys.*, 1997, 106: 7781
- 11 Turner, M.S., *Phys. Rev. Lett.*, 1992, 69: 1788
- 12 Russell, T.P., Lambooy, P., Kellogg, G.J. and Mayes, A.M., *Physica B*, 1995, 213/214: 22
- 13 Geisinger, T., Muller, M. and Binder, K., *J. Chem. Phys.*, 1999, 111: 5251
- 14 Pickett, G.T. and Balazs, A.C., *Macromolecules*, 1997, 30: 3097
- 15 Tsori, Y. and Andelman, D., *J. Chem. Phys.*, 2001, 115: 1970
- 16 Milner, S.T. and Morse, D.C., *Phys. Rev. E*, 1996, 54: 3793
- 17 Kellogg, G.J., Walton, D.G., Mayes, A.M., Lambooy, P., Russell, T.P. and Gallagher, P.D., *Phys. Rev. Lett.*, 1996, 76: 2503
- 18 Pereira, G.G., *Phys. Rev. E*, 2001, 63: 061809
- 19 Huinink, H.P., Brokken-Zijp, J.C.M., van Dijk, M.A. and Sevink, G.J.A., *J. Chem. Phys.*, 2000, 112: 2452
- 20 Liu, Y., Zhao, W., Zheng, X., King, A., Singh, A., Rafailovich, M.H., Sokolov, J., Dai, K.H., Kramer, E.J.S., Schwarz, A., Gebizlioglu, O. and Sinha, S.K., *Macromolecules*, 1994, 27: 4000
- 21 Suh, K.Y., Kim, Y.S. and Lee, H.H., *J. Chem. Phys.*, 1998, 108: 1253
- 22 Huinink, H.P., van Dijk, M.A., Brokken-Zijp, J.C.M. and Sevink, G.J.A., *Macromolecules*, 2001, 34: 5325
- 23 Yang, Y.Z., Qiu, F., Zhang, H.D. and Yang, Y.L., *Polymer*, 2006, 47: 2205
- 24 Karim, A., Singh, N., Sikka, M., Bates, F.S., Dozier, W.D. and Felcher, G.P., *J. Chem. Phys.*, 1994, 100: 1620
- 25 Wang, Q., Nealey, P.F. and de Pablo, J.J., *Macromolecules*, 2001, 34: 3458
- 26 Turner, M.S., Rubinstein, M. and Marques, C.M., *Macromolecules*, 1994, 27: 4986
- 27 Radzilowski, L.H., Carvalho, B.L. and Thomas, E.L., *J. Polym. Sci., Part B: Polym. Phys.*, 1996, 34: 3081
- 28 Konrad, M., Knoll, A., Krausch, G. and Magerle, R., *Macromolecules*, 2000, 33: 5518
- 29 Harrison, C., Park, M., Chaikin, P., Register, R.A., Adamson, D.H. and Yao, N., *Macromolecules*, 1998, 31: 2185
- 30 Zhang, Q.L., Tsui, O.K.C., Du, B.Y., Zhang, F.J., Tang, T. and He, T.B., *Macromolecules*, 2000, 33: 9561
- 31 Knoll, A., Horvat, A., Lyakhova, K.S., Krausch, G., Sevink, G.J.A., Zvelindovsky, A.V. and Magerle, R., *Phys. Rev. Lett.*, 2002, 89: 035501
- 32 Wang, Q., Nealey, P.F. and de Pablo, J.J., *Macromolecules*, 2003, 36: 1731
- 33 Brazovskii, S.A., *Sov. Phys. JETP*, 1975, 41: 85
- 34 Wickham, R.A., Shi, A.C. and Wang, Z.G., *J. Chem. Phys.*, 2003, 118: 10293