Orientational phase transitions in the hexagonal cylinder phase and kinetic pathways of lamellar phase to hexagonal phase transition of asymmetric diblock copolymers under steady shear flow

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Abstract

For asymmetric diblock copolymers under steady shear flow, the orientational phase transitions in the hexagonal cylinder phase and the kinetics of lamellar to hexagonal phase transition were studied based on the time-dependent Ginzburg–Landau approach. As to orientational phase transitions in the hexagonal cylinder phase, the simulation results show that the parallel orientation is stable at low shear rate and the perpendicular orientation is stable at high shear rate. In addition, different kinetic pathways of lamellar phase to hexagonal phase transition are observed after a sudden temperature jump from one phase to other. When the temperature jump is deep into the hexagonal phase from the shear-orientated lamellar phase under steady shear flow, the lamellae are transformed into hexagonally ordered cylinders directly via the short so-called modulated instability of the lamellar layers. However, if the temperature jump is only slight into the hexagonal phase with or without steady shear flow, lamellae are transformed into hexagonally ordered cylinders going through a distinct modulated and perforated lamellar phase stage. Moreover, without steady shear flow the perforated lamellar phase stage can survive for longer time, indicating that the steady shear flow cannot lead to stabilization of perforated lamellar phase. The simulation results also indicate that the perforated lamellar phase has \textit{abab}...stacking.

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1. Introduction

Shear-induced structural changes in complex fluids with anisotropy are very general topics encountered not only in polymer blends [1–7], but also in block copolymers [8–36]. Block copolymer melts have received much attention over the past years due in large part to their ability to self-assemble into a variety of ordered microstructures [37–39], such as body-center-cubic (BCC) spheres, hexagonally ordered cylinders (HEX), lamellae (LAM) and more complex bicontinuous structures. Application of shear flows breaks the symmetry and leads to macroscale ordering in block copolymers. In the case of lamellae, by varying the shearing conditions and the temperature, the ‘parallel alignment’, i.e. lamellar normal is parallel to the velocity gradient direction, and the ‘perpendicular alignment’ in which the lamellar normals are parallel to the vortex direction have been observed [8–36]. In addition, Zhang and Wiesner [24] have identified a ‘transverse alignment’, in which the lamellar normal is parallel to the velocity direction.

In equilibrium, between BCC spheres and LAM phases, a HEX microstructure exists. However, few studies have been carried out on the orientation of the HEX microstructure under shear flow. Recently, Tepe et al. [40] have reported that by varying experimental temperature and shear rate, two distinct cylinder orientations, which show an analogy with the orientation behavior of the lamellar phase, are observed in asymmetric PE-PEP diblock copolymers.

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under reciprocating shear. In the vorticity-shear gradient plane, the symmetry patterns have ‘2 dots up’ (see Fig. 1(a)) under slow flow, and ‘1 dot up’ (see Fig. 1(b)) under fast flow, respectively. In order to keep the universality of terminology, we call the former as parallel orientation and the latter as perpendicular orientation. In order to understand this behavior theoretically, Morozov et al. [41] have generalized the earlier analytical theory by Fredrickson [34] to study the orientation behavior of the HEX phase of diblock copolymer melt subjected to steady shear flow. The results show that the parallel orientation is stable at low shear rate while the perpendicular orientation is stable at high shear rate. The theory also shows that the difference in the free energies between parallel and perpendicular orientations is extremely small and a particular orientation is only slightly more stable than the other one. Ohta et al. [42,43] have carried out the numerical simulation for regular hexagonal phase subjected to strong cross-axis shear. But their simulation is in shear plane of two-dimensional (2D) systems. It must be pointed out that the simulation carried out in 2D cannot determine the morphological formation accurately. To our knowledge, as to orientation of the hexagonally ordered cylinders in copolymers, the simulation in three-dimensional (3D) systems under shear flow has never been reported. So it is very necessary to carry out the numerical simulation in 3D to examine the effects of the shear flow on the morphological formation.

In addition, more recent experiments have revealed three additional ‘complex’ morphologies: the bicontinuous double gyroid (G) [44,45], hexagonally modulated layers (HML) [46], hexagonally perforated layers (HPL). [46,47] From small-angle neutron scattering and TEM studies [46, 48,49], it is believed that the HML phase consists of alternating minority and majority component layers in which the thickness of the minority component domains is modulated with a hexagonal in-layer symmetry. In the HPL phase, the majority component is envisioned to form hexagonally ordered channels that extend through the minority component and connect the layers formed by the majority component. Qi and Wang [50,51] have suggested the possibility that the HML and HPL structures may be kinetic, intermediate states rather than new equilibrium phases. Based on their analysis [51], they suggested two possibilities concerning the HML and HPL structures observed in experiments. One possibility is that these structures are indeed kinetic, intermediate states en route from the LAM to HEX and other higher temperature phases. Another possibility is that thermal fluctuation or other symmetry-breaking fields can lead to stabilization of a pseudostable or metastable state. So in this paper, we also investigate whether the steady shear flow can lead to stabilization the HPL structure or not.

In this paper, the orientation of the hexagonally ordered cylinders and kinetic pathways of lamellar to hexagonal phase transition in asymmetric diblock copolymers was examined under steady shear flow in 3D based on a time-dependent Ginzburg–Landau (TDGL) approach. The organization of this paper is as follows. In Section 2, the model equations and algorithm are introduced. In Section 3, discussions of the results are given. In Section 4, we draw our conclusions.

2. Model equations and algorithm

To be concrete, we consider A–B diblock copolymers. The appropriate order parameter is \( \psi(\mathbf{r}) = 2(\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})) = \phi_B(\mathbf{r}) - \phi_A(\mathbf{r}) - (1 - 2f) \), where \( \phi_A(\mathbf{r}) \) and \( \phi_B(\mathbf{r}) \) are, respectively, the local volume fraction of A and B monomers, and \( f \) is the fraction of A monomers in the diblock. The kinetics and morphological evolution are described, in the spirit of linear irreversible thermodynamics, by the TDGL equation for diffusive field coupled with an external velocity field, which can be written as [2]

\[
\frac{\partial \psi(\mathbf{r}, t)}{\partial t} + \mathbf{v} \cdot \nabla \psi(\mathbf{r}, t) = M \nabla^2 \frac{\delta F[\psi(\mathbf{r}, t)]}{\delta \psi(\mathbf{r}, t)} + \eta(\mathbf{r}, t),
\]

(1)

where we have used the fact that \( \psi(\mathbf{r}) \) is a conserved order parameter. In Eq. (1), \( M \) is a mobility coefficient, which we assume to be a constant; \( \mathbf{v} \) is an external velocity field describing shear flow profile

\[
\mathbf{v} = \gamma \mathbf{e}_x,
\]

(2)

where \( \gamma \) is the shear rate and \( \mathbf{e}_x \) is the unit vector in the \( x \) direction; and \( \eta(\mathbf{r}, t) \) is a Gaussian white noise, representing thermal fluctuation, with mean zero and correlation \( \langle \eta(\mathbf{r}, t) \eta(\mathbf{r}, t') \rangle = -2k_B T M \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \)

(3)

where \( T \) is the temperature of the system, and \( \langle \ldots \rangle \) denotes the ensemble average. As a minimal model, any hydrodynamic effect and possible nonlocality in the mobility coefficient are ignored. The thermal noise is also neglected in this simulation, as its effect is not crucial.

The equilibrium free energy functional, consisting of short-range and long-range interaction terms is written as [9, 39,50–52]
where \( g(\psi) \) for the asymmetric diblock copolymers reads
\[
g(\psi) = \left[ -\frac{a}{2} + \frac{b}{2} \left( 1 - 2f \right) \right] (\psi)^2 + \frac{v}{3} (1 - 2f)(\psi)^3 + \frac{u}{4} (\psi)^4.
\]

The second term in Eq. (4) represents the long-range interaction, which arises from the connectivity of the two blocks and is typical of amphiphilic system. The Green’s function \( G(\mathbf{r} - \mathbf{r}’) \) satisfies \( \nabla^2 G(\mathbf{r} - \mathbf{r}’) = -\delta(\mathbf{r} - \mathbf{r}’) \). In fact, \( D \) is proportional to \( \sigma^2 \) and \( \alpha \) is scales as \( \sigma^{-2} \), where \( \sigma \) is Kuhn’s statistical segmental length of individual component (\( \sigma_1 \) and \( \sigma_2 \)) and \( \sigma_1 = \sigma_2 \) is assumed. In Eq. (5), \( \alpha \) is related to the depth from the ODT temperature, and the coefficients \( b \), \( v \) and \( u \) are phenomenological parameters. It can be seen that the phase diagram is very complex since \( D \) and \( \alpha \) in Eq. (4) and the coefficients in the Landau free energy, Eq. (5), can all be varied. Following Ref. [52], the Landau free energy is used as a guide to the morphology to be expected.

Inserting Eqs. (2), (4) and (5) to Eq. (1) and ignoring the thermal noise term, we obtain
\[
\frac{\partial \psi}{\partial t} + \gamma \frac{\partial \psi}{\partial x} = M\nabla^2 \left[ (-a + b(1 - 2f)^2)\psi \right] + v(1 - 2f)\psi^2 + u\psi^3 - D\psi^2 \psi - M\alpha\psi.
\]

Eq. (6) can be rewritten in a dimensionless form with \( a_0 = \sigma \) and \( L_0 = \frac{a_0^2}{M} \) as the unit of length and time scales, respectively,
\[
\frac{\partial \psi}{\partial \tau} + S\frac{\partial \psi}{\partial \xi} = \nabla^2 \left[ (-a + b(1 - 2f)^2)\psi \right] + v(1 - 2f)\psi^2 + u\psi^3 - D\psi^2 \psi - \alpha\psi.
\]

where \( \tau = t/r_0 \), \( S = \gamma/L_0 \), \( \xi = x/a_0 \), \( \eta = y/a_0 \), \( \zeta = z/a_0 \), and \( D = D/a_0^2 \). For the clarity, in the following we still use \( x, y, z \) instead of \( \xi, \eta, \zeta \).

Eq. (7) is numerically solved by using the cell dynamical scheme (CDS) proposed by Puri and Oono [53, 54]. In three-dimensional CDS, the system is discretized on a \( L\times L\times L \) cubic lattice of cell size \( a_0 \), and the order parameter for each cell is defined as \( \psi(\mathbf{n}, \tau) \), where \( \mathbf{n} = (n_x, n_y, n_z) \) is the lattice position and \( n_x, n_y, \) and \( n_z \) are integers between 1 and \( L \). The Laplacian in CDS is approximated by
\[
\nabla^2 \psi(\mathbf{n}) = \frac{1}{a_0^2} \left( \langle \psi(n) \rangle - \psi(\mathbf{n}) \right)
\]

where \( \langle \psi(n) \rangle \) represents the following summation of \( \psi(n) \) for the nearest neighbors (n.), the next-nearest neighbors (n.n.), and the next-next-nearest neighbors (n.n.n.) [54]:
\[
\langle \psi(n) \rangle = B_1 \sum_{\mathbf{n}=\mathbf{m}+\mathbf{n}_1} \psi(\mathbf{n}) + B_2 \sum_{\mathbf{n}=\mathbf{m}+\mathbf{n}_2} \psi(\mathbf{n}) + B_3 \sum_{\mathbf{n}=\mathbf{m}+\mathbf{n}_3} \psi(\mathbf{n})
\]

where \( B_1, B_2, \) and \( B_3 \) are 6/80, 3/80, and 1/80.

Then Eq. (7) is transformed into the following difference equation:
\[
\begin{align*}
\psi(\mathbf{n}, \tau + 1) &= \psi(\mathbf{n}, \tau) - \frac{1}{2} \left( S \psi(x + 1, y, z, \tau) - \psi(x - 1, y, z, \tau) \right) \\
&\quad - \left( \psi(x, y + 1, z, \tau) + \psi(x, y - 1, z, \tau) \right) \\
&\quad - \left( \psi(x, y, z + 1, \tau) + \psi(x, y, z - 1, \tau) \right) \\
&\quad - \left( \psi(x, y, z, \tau + 1) \right) - \psi(x, y, z, \tau) \\
&\quad + v(1 - 2f)\psi(x, y, z, \tau)^2 + u\psi(x, y, z, \tau)^3 \\
&\quad - \langle \psi(\mathbf{n}, \tau) \rangle - \psi(\mathbf{n}, \tau)
\end{align*}
\]

with
\[
I(\mathbf{n}, \tau) = [-a + b(1 - 2f)^2]\psi(\mathbf{n}, \tau)
\]

where \( \gamma = 3 \), \( L = 32 \) nm, and \( \tau = 3 s \). Because the reduced shear rate \( \dot{\gamma} = \gamma/L_0 \), the real shear rate is \( \dot{\gamma} = S\gamma_0 = S \times 10^3 \) s\(^{-1}\).

3. Simulation results and discussion

In this section, we present the results from direct numerical simulation of Eq. (10). Following the Ref. [52], the parameters are chosen to be \( b = 1.5 \), \( v = 2.3 \), \( u = 0.38 \). The other parameters are set as \( D = 0.5 \) and \( \alpha = 0.02 \).

3.1. Orientational phase transitions in the hexagonal cylinder phase under shear flow

Here, we choose \( f = 0.40 \). We fix temperature-like parameter as \( a = 0.14 - 0.25 \), and investigate the effect of
the different shear rate. The mean-field equilibrium phase corresponding to this set of parameters is the HEX structure.

We solved Eq. (10) quiescently for $10^4$ time steps to from an ordered phase before turning on the shear field. The results for $a=0.16$ are shown in Fig. 2. It is clearly seen that the ordered cylinders consisting of randomly orientated grains occur. Such quenched cylindrical phases have local uniaxial order but lack of long-ranged order. Correspondingly, the scattering functions in three different directions are all the isotropic rings. After $10^4$ time steps, the shear fields with different shear rates are turned on.

First, high shear rate $S$ is chosen as 0.001. The evolution of the morphology is shown in Fig. 3(a). It can be seen that the perpendicular orientation formed. The forming process of the perpendicular hexagonal cylinder can be divided into two distinct stages. During the first stage, the domains orient rapidly along the flow directions to form the cylinder phase but no hexagonal lattice appeared. The second stage is the slow ordering of the cylinder to form the complete perpendicular hexagonal lattice. It should be pointed out that the second stage needs longer time than the first stage. When the shear strain $\gamma \sim 5$, the randomly orientated cylinder evolves into highly orientated cylinder along the flow direction and then more or less the perfect perpendicular hexagonal lattices form when $\gamma \sim 40$. To see it more clearly, the morphologies in the vorticity-shear gradient plane ($z$–$y$ plane) are shown in Fig. 3(b). It is clearly seen that the perpendicular orientation with 1 dot up occurs. Next, the low shear rate $S$ is set as 0.0002. Fig. 4 shows the evolution of the morphology. The similar process of morphological evolution is observed as the high shear rate case. But it can be seen that pattern selection tends to form the parallel hexagonal cylinder, which is completely different from the high shear rate case discussed above.

Here we should point out that with different temperature-like parameters, the parallel and perpendicular orientations are observed in our simulations for low and high shear rates, respectively. Our simulation results are in agreement with the experimental [40] and theoretical [41] results very well.

3.2. Lamellae to hexagonal transition under shear flow

To investigate the kinetic pathways of lamellar to hexagonal phase transition, we choose $f=0.45$. The initial
value of the temperature-like parameter $a = 0.4$, which is more deeply quenched than the cases discussed in Section 3.1. The mean-field equilibrium structure corresponding to this set of parameters is the LAM phase. The typical results for the shear rate $S = 0.001$ are given in the following.

We first simulate the occurrence of the LAM phase under steady shear flow. The shear flow was turned on just after the quench. For $a = 0.4$, the highly orientated LAM phase is formed when the shear strain $\gamma = 30$, as shown in Fig. 5.

Under the framework of our coordinates, it is clearly seen that the orientation of the LAM phase belongs to parallel alignment with some defects. Later, the formed parallel-aligned LAM phase is subjected to a sudden temperature jump into hexagonal phase.

In the case that the temperature jump is deep into hexagonal phase, $a = 0.2$, just after temperature jump the HML phase reported in the literature [46] is observed during $\tau = 1000–3000$, as shown in Fig. 6. With the increase of the shear strain, the perfect parallel-aligned HEX phase forms.

The simulation also indicates that, with the temperature jump into the range of $a = 0.18–0.21$, similar process of evolution can be observed. In this region under shear flow,
the HML phase is indeed transient kinetic, intermediate states en route from LAM to HEX phases and the shear flow cannot stabilize this intermediate state. It is also important to mention that, in this region the HPL phase was not observed.

However, when the LAM phase is quenched into \( a = 0.22–0.23 \), which is only slightly higher than \( a \) in Fig. 6, different morphological evolution is observed as in Fig. 7. It is seen from Fig. 7 that the HML phase occurs rapidly and then HPL phase start to emerge. Before the perfect HPL phase can be fully established, the HPL phase starts to transform into HEX cylinders under steady shear flow. Finally, HPL phase transforms into HEX cylinders. When the LAM phase is quenched into \( a = 0.24 \), the parallel-aligned LAM phase persists. For the sake of simplicity, we do not show the results here.

For comparison, we also take account of the case without shear flow. The temperature is still quenched into \( a = 0.22 \). The morphological evolution is shown in Fig. 8. Similar to the kinetics in Fig. 7, the perfect HPL phase emerges at first, but it eventually slowly transforms into the HEX cylinders. But for the present case without shear flow, the HPL structure is more obvious and can survive for longer time. The simulation result also indicated that HPL phase has \( abab \) stacking. Different reduced shear rates are also applied in our simulations, such as \( S = 0.0002, 0.0005, 0.001, 0.002 \), but similar results are observed. So it is apparent from Figs. 7 and 8 that the steady shear flow cannot lead to the stabilization of the HPL structure, on the contrary, without steady shear flow the HPL structure can survive for longer time.

4. Conclusions

In this paper, for asymmetric diblock copolymer under steady shear flow we use the TDGL approach to investigate orientational phase transitions in the hexagonal cylinder phase and the kinetics of lamellar phase to hexagonal phase transition. Through the simulation, the following conclusions can be drawn.

(1) As to orientational phase transitions in the hexagonal cylinder phase under steady shear flow, parallel orientation is stable at low and perpendicular orientation at high shear rates.

(2) When the temperature jump is deep into the hexagonal phase from the lamellar phase, the lamellae transform to hexagonal cylinders directly by the short undulation instability of the lamellar layers. But if the temperature jump is only slight into the hexagonal phase, lamellae transform into hexagonal cylinders through a distinct so-called modulated and perforated lamellar phase stage. The perforated lamellar phase has \( abab \)...stacking. Steady shear flow cannot lead to stabilization of HML and HPL phase.

Fig. 7. The evolution of morphology for the case of \( a = 0.22, f = 0.45 \) under reduced shear rate \( S = 0.001 \).

Fig. 8. The evolution of morphology for the case of \( a = 0.22, f = 0.45 \) without shear flow.
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References