PHYSICAL REVIEW E **71**, 051803 (2005)

Orientational order transition of the striped microphase structure of a copolymer-homopolymer mixture under oscillatory particles

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(Received 2 January 2005; revised manuscript received 14 March 2005; published 25 May 2005)

Based on the three-order-parameter model, we investigate the orientational order transition of striped patterns in microphase structures of diblock copolymer-homopolymer mixtures in the presence of periodic oscillatory particles. Under suitable conditions, although the macrophase separation of a system is almost isotropic, the microphase separation of the system will be significantly perturbed by the oscillatory field, and composition fluctuations are suppressed anisotropically. The isotropy of the microphase will be broken up. By changing the oscillatory amplitude and frequency, we observe the orientational order transition of a striped microphase structure from the isotropic state to a state parallel to the oscillatory direction, and from the parallel state to a state perpendicular to the oscillatory direction. We examine, in detail, the microstructure and orientational order parameter as well as the domain size in the process of orientational order transition under the oscillatory field. We study also how the microphase structure changes with the composition ratio of homopolymers and copolymers in mixtures. The results suggest that our model system may provide a simple way to realize orientational order transition of soft materials.

DOI: 10.1103/PhysRevE.71.051803 PACS number(s): 83.80.Uv, 83.80.Tc

I. INTRODUCTION

In the past two decades, there has been great progress in the study of phase-ordering dynamics in many soft matter systems [1–12]. The microphase separation in block copolymers has been investigated both experimentally and theoretically [13–34]. Although block copolymers have been studied extensively, there are only a few works on copolymer-homopolymer mixtures [13–16,20,25,27,28]. Hong and Noolandi [13] studied theoretically the general copolymer-homopolymer mixtures. They predicted that a macrophase separation would take place at low temperatures, which is followed by a microphase separation in the copolymer-rich domain. Later, Koizumi, Hasegawa, and Hashimoto [16] examined experimentally the phase separation of binary mixtures of polystyrene–block-polyisoprene (SI) and homopolystyrene (HI). It was discovered that, when the volume fraction of SI is low, macrophase separation appears during the solvent evaporation process, which is subsequently followed by microphase separation. Ohta and Ito [14,15] further analyzed the dynamics of phase separation in copolymer-homopolymer mixtures. They found many rich structures, such as an "onionlike" pattern. Although these studies have shown that the polymeric materials consisting of copolymer-homopolymer mixtures undergo dramatic changes in the morphology and kinetics of phase separations, the microphase and macrophase separation still led to an isotropic morphology for the coexisting phase. It is important to know in the design of new materials how to adjust the orientation of ordered phases and to obtain the transition of orientational order in a simple way that is technically easy to realize.

Recently, some works have paid attention to the ordered structures formed by externally applied perturbations due to its potential importance in the material engineering. Some previous studies have considered applying a field, such as shear flow, electric field, gravity, or temperature, to perturb phase separations and to cause a self-organization process [12,32–37]. Actually, ordered structures can also be generated by means of introducing mobile particles to polymer blends [38–42]. In technological applications, the use of colloidal or glass particles is a promising route to materials synthesis with the opportunity to create highly ordered structures on wide length scales. Tanaka *et al.* [40] examined experimentally the pattern evolution in a binary mixture into which mobile particles were introduced with different interactions to two immiscible phases. Their results indicated that the presence of mobile particles dramatically changes the morphology and growth kinetics of phase separations. Ginzburg *et al.* [10] studied phase separation in a binary mixture affected by mobile particles in a low density with selective affinity for one of the species, by using cell dynamical simulations (CDSs). On the other hand, Boltau *et al.* [43] showed experimentally that the domains of a phase-separating mixture of polymers in a thin film can be guided into arbitrary structures by a surface with a prepatterned variation of surface energy. One of us has reported numerically structural formation on a solid substrate for phase-separating films containing mobile particles with a preferential attraction for one component of the binary mixture [41]. Later, further work was reported for the structural organization in binary immiscible fluids in the presence of mobile particles [42].

In this paper, we investigate the orientational transition of the microphase in copolymer-homopolymer mixtures by introducing mobile oscillatory particles which wet one block of copolymers. The presence of the oscillating field enforces the movement of particles, and in turn, the mobile particles influence the phase-separating process due to the affinity for one of the components. Therefore, a phase-ordering process can take place by the interplay between the phase separation

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1539-3755/2005/71(5)/051803(9)/$23.00

and the deformation of the favored phase induced by mobile particles, resulting in the development of anisotropic structures. The paper is organized as follows. Section II is devoted to the description of the model and method. In Sec. III the numerical results and discussions are presented. Finally, a brief conclusion is given in Sec. IV.

II. MODEL AND METHOD

We consider a phase-separating film on a substrate surface. The phase-separating film is a diblock copolymer-homopolymer mixture with a small concentration of particles subjected to a periodically oscillatory field. Each copolymer chain is composed of monomers A and B with a shot-rang repulsive interaction between them. The interaction between monomer C in a homopolymer and monomer B in a copolymer is also assumed to be repulsive each other, the mobile particles wet B monomers. The interaction between the mixture and the substrate surface is assumed to be negligible, i.e., the substrate is neutral to the polymer blend. In addition, the hydrodynamic effects, which prevail in the very latest stage of phase separation in polymer blends, are neglected in the present model. The coordinates of the planar surface are defined by the x and y axes. Further, we will assume an alternating "electric" field acting on "charged" mobile particles along the x direction to describe the externally driving force. The interaction between mobile particles is neglected and only their excluded volume effect is considered [44].

For describing the system, several parameters are defined. We take $\phi_{A0}, \phi_{B0}, \phi_{C0}$, and ρ_0 as the average volume fractions of monomers A, B, C, and the mobile particles. In the case of symmetric diblock copolymers which is considered here, the polymerization indices of the A and B blocks are equal; this is assured by $\phi_{A0}=\phi_{B0}$. As for the average particle concentration, we will let ρ_0 equal 5% throughout this paper. An important quantity, the composition ratio of homopolymers and copolymers which can be changed, is defined by $f=\phi_{C0}/(\phi_{A0}+\phi_{B0})$. In the process of phase separations, fluctuations are dominant, so we should investigate the local volume fractions of monomers A, B, C, and the mobile particles. They are denoted, respectively, by $\phi_A(x,y), \phi_B(x,y), \phi_C(x,y)$, and $\rho(x,y)$. Under the incompressibility condition, that is the total density $\phi_A(x,y)+\phi_B(x,y)+\phi_C(x,y)+\rho(x,y)$ is constant, three of the local volume fractions are independent. Then it is reasonable to take $\phi(x,y)=\phi_A(x,y)-\phi_B(x,y)$, $\psi(x,y)=\phi_A(x,y)+\phi_B(x,y)$, and $\rho(x,y)$ as the independent variables. The order parameter $\phi(x,y)$ gives the local concentration difference between monomers A and B, and the order parameter $\psi(x,y)$ describes the segregation of homopolymers and copolymers, whereas the order parameter $\rho(x,y)$ describes the local particle density. According to the phase field dynamic theory, there is a correspondence between the discrete mobile particles and the continuous density function $\rho(x,y)$. In fact $\rho(x,y)$ is understood as the probability of mobile particles to occupy the site (x,y). At the beginning, $\rho(x,y)=1$ or $\rho(x,y)=0$ stands for the site (x,y) occupied or unoccupied by a mobile particle. In the evolution process of the system, $\rho(x,y)$ ranges from 0 to 1. However, when the system approaches equilibrium, the mobile particles can recur at the sites with higher occupation probabilities.

Here we propose a three-order-parameter model instead of previous two-order-parameter model [14,15,45,46]. The free-energy functional of the system is given by

$$F = F_L + F_S. \tag{1}$$

The long-range part F_L and the short-range part F_S are given by

$$F_L = \frac{\alpha}{2}\int\int d\boldsymbol{r}\, d\boldsymbol{r}' G(\boldsymbol{r},\boldsymbol{r}')[\phi(\boldsymbol{r})-\phi_0][\phi(\boldsymbol{r}')-\phi_0], \tag{2}$$

and

$$F_S = \int\int dx\, dy\Bigg[\frac{c_1}{2}(\nabla\psi)^2 + \frac{c_2}{2}(\nabla\phi)^2 + e\rho^2(\rho-1)^2 + g\rho\phi + w(\psi,\phi)\Bigg], \tag{3}$$

respectively, where α, c_1, c_2, e, and g are all positive constants. The long-range part is relatively simple, in which $G(\boldsymbol{r},\boldsymbol{r}')$ is the Green's function defined by the equation $-\nabla^2 G(\boldsymbol{r},\boldsymbol{r}')=\delta(\boldsymbol{r}-\boldsymbol{r}')$ and ϕ_0 is the spatial average of ϕ. We must set $\phi_0=0$ in the case of symmetric copolymers. As for the short-range part, the c_1 and c_2 terms correspond to the surface tensions; the e term allows the coexistence of the two bulk states [45,46], corresponding to $\rho=0$ and 1. The former is the case in which the system is locally occupied by A or B or C, whereas the latter is the case in which the local volume is occupied only by mobile particles. A cross term g between the order parameters ϕ and ρ is taken into account due to the coupling between the copolymer and particles. g is the wetting strength, and $g>0$ means that the particle is energetically favorable in the B phase ($\phi<0$). The local interaction $w(\psi,\phi)$ can be replaced by $w(\eta,\phi)$ where $\eta=\psi-\psi_c$, where ψ_c is the volume fraction at the critical point of the macrophase separation and is a constant determined by the parameters of the system. According to Ito *et al.* [14,15], we find

$$w(\eta,\phi) = v_1(\eta) + v_2(\phi) + b_1\eta\phi - \frac{1}{2}b_2\eta\phi^2, \tag{4}$$

where b_1 and b_2 are positive constants. The functions $v_1(\eta)$ and $v_2(\phi)$ are assumed to be even with respect to the arguments. Equation (4) prescribes the minimal model of the short-range part of the free energy in our system.

In terms of the free energy functional in Eqs. (1)–(3), we have a set of three coupled equations by using the three order parameters, they are

$$\frac{\partial\eta}{\partial t} = M_\eta\nabla^2\frac{\delta F}{\delta\eta}, \tag{5}$$

$$\frac{\partial\phi}{\partial t} = M_\phi\nabla^2\frac{\delta F}{\delta\phi}, \tag{6}$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \boldsymbol{j}_e = M_\rho \nabla^2 \frac{\delta F}{\delta \rho}, \tag{7}$$

where M_η, M_ϕ, and M_ρ are positive transport coefficients. The second term on the left-hand side of Eq. (7) comes from the additive current due to the existence of a driving field acting on mobile particles. As is well known, the periodically oscillatory driving field can be realized in many practical applications such as electrolytes, charged colloids, or granular materials [47]. In the present work, a bias field is analogous to that of an electric field on positive charges. This will cause the local separation of the "charged" particles from the mixture, and the system undergoes a local phase separation between the particles and the mixture along a given driving direction. Such an additionally local separation which breaks up the symmetry of the system may significantly alter the microphase separated structure. In the presence of an externally oscillatory field $\gamma \sin(\omega t)$, pointing along the x direction, a simple form can be modeled by the "Ohmic" current $\boldsymbol{j}_e = \gamma \sin(\omega t)\rho(1-\rho)\boldsymbol{x}$ where γ is the amplitude and ω is the frequency, $\rho(1-\rho)$ reflects the vanishing of $\boldsymbol{j}_e$ in a completely filled or empty system [44].

The numerical simulations of the above model system can be carried out in an $L \times L$ two-dimensional square lattice, with $L=128$ and periodic boundary conditions, using the (CDS) approach proposed by Oono and Puri [48,49]. The CDS equations corresponding to Eqs. (5)–(7), in their space-time discretized form, are written as follows:

$$\eta(x,y,t+\Delta t) = \eta(x,y,t) + M_\eta(\langle\langle I_\eta \rangle\rangle - I_\eta), \tag{8}$$

$$\phi(x,y,t+\Delta t) = \phi(x,y,t) + M_\phi\{(\langle\langle I_\phi \rangle\rangle - I_\phi) - c[\phi(x,y,t) - \phi_0]\}, \tag{9}$$

$$\rho(x,y,t+\Delta t) = \rho(x,y,t) + M_\rho(\langle\langle I_\rho \rangle\rangle - I_\rho) - \gamma \sin(\omega t)(1-2\rho) \times [\rho(x+1,y,t) - \rho(x-1,y,t)]/2, \tag{10}$$

where

$$I_\eta = -c_1(\langle\langle \eta \rangle\rangle - \eta) - A_\eta \tanh \eta + \eta + b_1\phi - \frac{1}{2}b_2\phi^2, \tag{11}$$

$$I_\phi = -c_2(\langle\langle \phi \rangle\rangle - \phi) - A_\phi \tanh \phi + \phi + b_1\eta - b_2\eta\phi + g\rho, \tag{12}$$

$$I_\rho = 2e\rho(\rho-1)(2\rho-1) + g\phi, \tag{13}$$

and

$$\langle\langle x \rangle\rangle = \frac{1}{6}\sum_{\mathrm{NN}} x + \frac{1}{12}\sum_{\mathrm{NNN}} x, \tag{14}$$

where the subscripts NN and NNN stand for the nearest-neighbor and next-nearest-neighbor cells, respectively. For the original cell dynamics system, the lattice size (Δx or Δy) and the time step (Δt) were both set to be unity.

Our simulations of the model system are performed by choosing the parameters $A_\eta=1.3$, $A_\phi=1.1$, $e=0.125$, $b_1=0.05$, $b_2=0.2$, $c=0.02$, $c_1=0.5$, $c_2=0.5$, $g=0.045$, and $M_\eta=M_\phi=M_\rho=1$. The results are obtained by averaging over five independent runs.

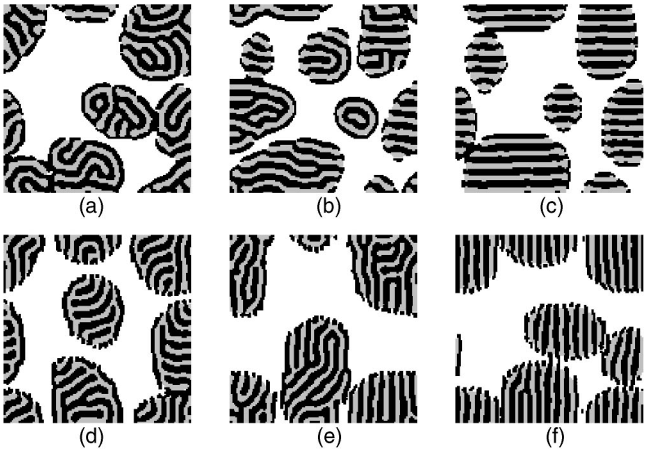

FIG. 1. Patterns of a 128×128 two-dimensional lattice with the composition ratio $f=53.5/41.5$ at time $t=2\,500\,000$. (a) $\gamma=0.001$, $\omega=0.000\,01$; (b) $\gamma=0.07$, $\omega=0.0003$; (c) $\gamma=0.16$, $\omega=0.0006$; (d) $\gamma=0.19$, $\omega=0.1$; (e) $\gamma=0.24$, $\omega=0.13$; (f) $\gamma=0.326$, $\omega=0.14$. Phase A is represented by the black region, phase B by the gray region, and phase C by the white region.

III. NUMERICAL RESULTS AND DISCUSSION

A. Orientational transition of microphases

First, we study how the orientational order of a microphase structure in copolymers transits under oscillatory particles in a thin film of a copolymer-homopolymer mixture. Figure 1 shows the equilibrium patterns with the composition ratio $f=53.5/41.5$ at time $t=2\,500\,000$, when the oscillatory field increases step by step. The black, gray, and white regions stand for A-rich, B-rich, and C-rich regions, respectively. The mobile particles are not shown so as to display clearly the microphase structure. However, it should be pointed out that the mobile particles in general tend to get together in the B-rich region consisting with our physical intuition.

The macrophase structures in Fig. 1 are almost isotropic and the macrodomain size is affected weakly with increasing the oscillatory amplitude γ and frequency ω. Figure 1(a) shows that for small oscillatory frequency and small oscillatory amplitude, the pattern exhibits an isotropic microphase striped structure. As the oscillatory frequency and oscillatory strength are increased, we see that the competition between the motion of particles and microphase separation will effectively break up the isotropy of the microphase striped structure, and drives the isotropic system into an orientational striped structure. We can observe from Fig. 1(a) to Fig. 1(c) that the microphase structures are oriented into the x direction gradually. By selecting suitable oscillatory parameters, the better parallel striped patterns [Fig. 1(c)] are prone to be formed. However, by further increasing the oscillatory parameters, striped microphase domains change their orientation to be isotropic again. Interestingly, the striped structure will be perpendicular to the x direction for higher values of the oscillatory parameters. From Fig. 1(c) to Fig. 1(f) we have observed this orientational order transition. For a suitable oscillatory force, we can obtain a better stripe pattern perpendicular to the x direction [Fig. 1(f)].

The results can be understood as follows. On one hand, the macrophase separation is isotropic. Because the coupling strength ($g=0.045$) is not too strong, the macrophase separation is almost not affected. Meanwhile, the surface tensions of the copolymers and homopolymers dominate in the process of macrophase separation, the macrodomain structure displays an isotropic pattern. On the other hand, the orientational order transition of microphase become true. For a small oscillation field, the effect of particles on the microphase separation can be neglected, the surface tensions and the long-range correlation of copolymers dominate the composition fluctuations, the system of copolymer shows the isotropy [Fig. 1(a)]. As the oscillation is enlarged, the oscillatory motion of particles plays a significant role, and the coupling interaction of particles with the B phase drives the B phase moving along the x direction. At the moment, the oscillatory motion is a perturbation in the x direction. In the phase-separating process, such a perturbation leads to B phase coarsening in the x direction compared to the y direction, and the A phase increases the coarsening too in the x direction by the surface tension and long-range correlation between the B phase and A phase. Both give rise to the slowing coarsening x direction stripes in the copolymer. An oscillatory force with moderate strength may alleviate the topological defects in structures and highly ordered stripes parallel to the x direction are formed [Fig. 1(c)]. When the periodically oscillatory force is strong enough, the particles retain rapid motion along the x direction due to the high oscillatory frequency ω, and the moving range of oscillatory particles becomes larger due to the large oscillatory amplitude γ. The coupling interaction of particles with the B phase drives the B phase to move rapidly within a larger range in the x direction. This rapid motion of the B phase makes the B phase domains jostle each other in the x direction, leading the coarsening of the B phase to be prevented in the x direction, and conversely the coarsening in the perpendicular direction is enforced. This coarsening diffuses the A phase through the B phase, and results in the microphase striped structure perpendicular to the oscillatory direction under the competition between the coarsening in the y direction and the phase separating of the system. Then, the perturbation caused by the strong oscillatory force prevents microdomain coarsening in the x direction but the coarsening persists in the y direction, eventually giving rise to the striped structure in the y direction [Fig. 1(f)]. The same approach can be effectively used to separate binary granular mixtures with different sizes in the presence of a periodic horizontal force [50]. According to the above analysis, we can understand that there are differences between the mechanisms of forming the parallel and perpendicular stripes. These differences manifest at least in the lamellar widths along the x and y directions. Observation shows that the width of stripes in Fig. 1(c) is greater than that in Fig. 1(f).

In order to characterize the orientational order transition of microphase striped domains, we calculate, in detail, the orientational order parameter

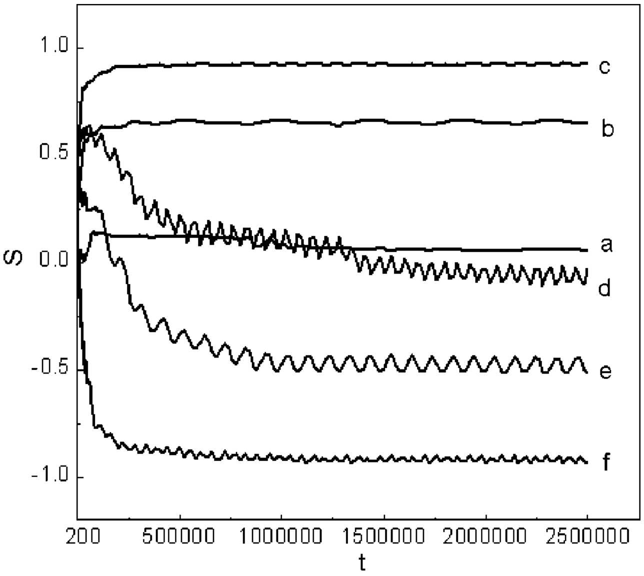

FIG. 2. Alignment kinetics for the composition ratio $f=53.5/41.5$ and different oscillatory forces. Curves a, $\gamma=0.001$, $\omega=0.00001$; b, $\gamma=0.07$, $\omega=0.0003$; c, $\gamma=0.16$, $\omega=0.0006$; d, $\gamma=0.19$, $\omega=0.1$; e, $\gamma=0.24$, $\omega=0.13$; f, $\gamma=0.326$, $\omega=0.14$.

$$S=\langle 2\cos^2\theta-1\rangle, \tag{15}$$

as in two-dimensional nematic liquid crystals [32], where θ is the angle between the unit normal vector of a stripe and the unit normal vector in the oscillatory direction. The spatial average takes the value $S=0$ for an isotropic phase, $S=1$ for a completely oriented phase parallel to the oscillatory direction, and $S=-1$ for another completely orientational phase perpendicular to the oscillatory direction. Figure 2 shows the variation of the order parameter in a process of orientational order transition. From Fig. 2, we can see that the values of the order parameter S in different cases all increase at the early stage. We know from curve a that the order parameter S is near to zero, so the microphase structure shown in Fig. 1(a) is isotropic due to the oscillatory force being weak. As the oscillatory force is enhanced, the value of the order parameter is increased obviously (curves b and c), this indicates that microdomains coarsen along the oscillatory direction. As the oscillatory force increases to a suitable value, the order parameter S near to 1, the microphase striped pattern along the x direction is formed, as in curve c. Here, the microphase structure transits from an isotropic state to a state parallel to the oscillatory direction, as shown in going from Fig. 1(a) to Fig. 1(c). As the oscillatory force further increases, the order parameter decreases gradually, as shown by curves d and e. As the oscillatory force increases to a suitable value, the order parameter changes to near −1, and the microphase striped structure is almost completely perpendicular to the oscillatory direction, as in curve f. From curves a to f, we can also see that the order parameter S changes basically from 0 to 1, and in turn, to −1. This process is a detailed description of the orientational order transition. Interestingly, from curve d to curve f we can find that as S changes from 1 to −1, it decreases oscillatorily, which reflects that the mechanism for forming the perpendicular

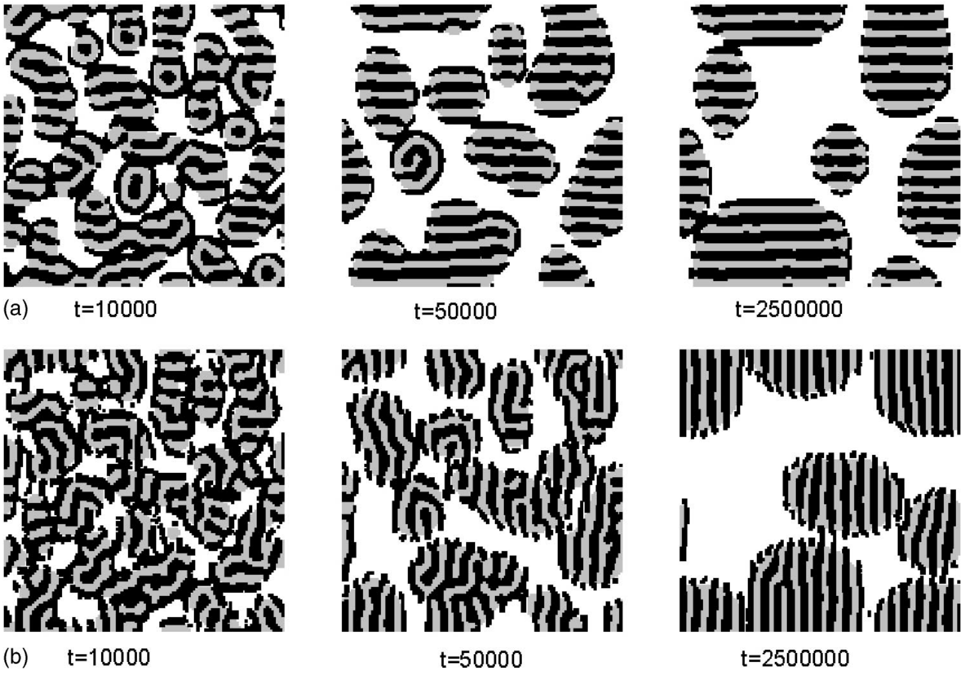

FIG. 3. Pattern evolution of a 128×128 two-dimensional lattice with the composition ratio $f = 53.5/41.5$. (a) $\gamma = 0.16$, $\omega = 0.006$; (b) $\gamma = 0.326$, $\omega = 0.14$. Phase A is represented by the black region, phase B by the gray region, and phase C by the white region.

striped phase is different from that of the parallel striped phase. From Fig. 2 we can also see that the order parameter S almost does not change at the late stage, so the microphase striped structures obtained are stable in the long time limit.

B. Domain growth

Next, we study the domain growth of A, B, and C phases by investigating the pattern evolution with time. Figure 3 displays the pattern evolution with the composition ratio $f = 53.5/41.5$. Figures 3(a) and 3(b) are simulated by using $\gamma = 0.16$, $\omega = 0.006$, and $\gamma = 0.326$, $\omega = 0.14$, corresponding to Figs. 1(c) and 1(f), respectively. In Fig. 3, it is shown that at the early stage (about $t = 10\,000$) the macrophase separation occurs whereas the microdomain growth is weak; as $t = 50\,000$, the microphase separation obviously takes place, and the growth of microdomains is much rapid than that of macrodomains; at the late stage, $t = 2\,500\,000$, the isotropic macrodomains are formed in the mixture, combined with the highly orientationally ordered microdomains in copolymers. It is found that well striped structures along the x direction and y direction have emerged in the long-range process.

We would calculate numerically the domain size $R_i(t)$ ($i = x$ or y) in the x or y direction as a function of time. The domain size $R_i(t)$ can be derived from the inverse of the first moment of the structure factor $S(\boldsymbol{k}, t)$ as

$$R_i(t) = 2\pi / \langle k_i(t) \rangle, \qquad (16)$$

where

$$\langle k_i(t) \rangle = \int d\boldsymbol{k}\, k_i S(\boldsymbol{k}, t) \Bigg/ \int d\boldsymbol{k}\, S(\boldsymbol{k}, t). \qquad (17)$$

In fact, the structure factor $S(\boldsymbol{k}, t)$ is determined by the Fourier component of the spatial concentration distribution [49]. Figures 4 and 5 show the time evolution of the microdomain size $R_i(t)$ in the x and y directions as a function of time in double logarithmic plots. The results are averaged over five independent runs.

From Fig. 4(a), we see that in equilibrium as the oscillatory force is increased, the microdomain size R_x first increases (from curve a to c), but as the oscillatory force is further increased, R_x gradually decreases (from curve c to f). This fact indicates that as the oscillatory force is increased, the coarsening of microdomains is along the oscillatory direction, and is suppressed as the oscillatory force further increases. By contrast, from Fig. 4(b), we see that the microdomain size R_y first decreases, and then increases with increasing the oscillatory force. This means that as the oscillatory force is strong enough, coarsening of microdomain perpendicular to the oscillatory direction is enforced, which is suppressed at first. From Fig. 4, we can also see that at the early stage the microdomain growth is slow, and is not appreciably affected by the variation of oscillatory force. The change of microdomain size is obvious at the middle stage, and is stable at the later stage.

In Fig. 5, R_x and R_y are the microdomain sizes in the x and y directions, while R'_x and R'_y are the macrodomain size in the x and y directions, respectively. Figures 5(a) and 5(b) correspond to Figs. 3(a) and 3(b), respectively, which display the pattern evolution of highly ordered stripe along the x direction and y direction. From Fig. 5, it is easy to find that the growth speed of the macrodomain size is almost same in the x and y directions, so the macrodomain structure is isotropic, and weakly affected by the oscillatory force. On the other hand, the growth speed of macrodomains is faster than that of microdomains at the early stage, but the growth speed of microdomains is much large than that of macrodomains at the middle stage. This fact indicates that the macrophase separation dominates in the process of phase separation in homopolymer-copolymer mixtures at the early stage, and later the microphase separation makes its way obviously.

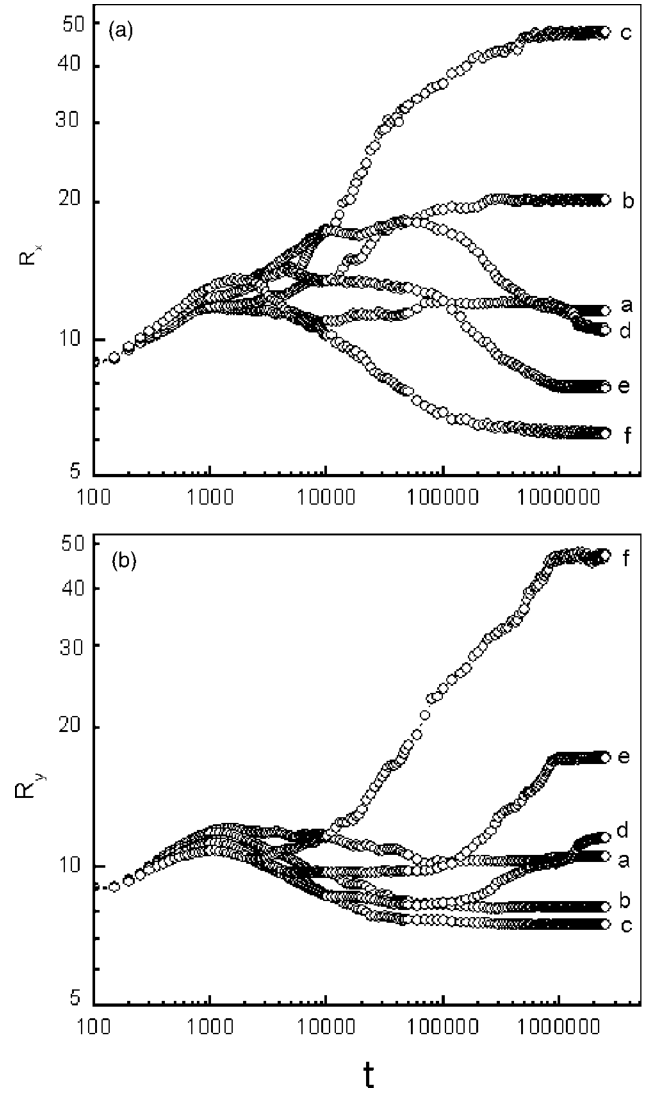

FIG. 4. Time evolution of the characteristic sizes of microdomains $R_x(t)$ and $R_y(t)$ for the composition ratio $f=53.5/41.5$ and different oscillatory forces. Curves *a*, $\gamma=0.001$, $\omega=0.000\,01$; *b*, $\gamma=0.07$, $\omega=0.0003$; *c*, $\gamma=0.16$, $\omega=0.006$; *d*, $\gamma=0.19$, $\omega=0.1$; *e*, $\gamma=0.24$, $\omega=0.13$; *f*, $\gamma=0.326$, $\omega=0.14$.

This phenomenon agrees with experiment [16]. Furthermore, it can be seen that the well striped structure along the *x* direction or *y* direction can be obtained by selecting suitable oscillatory force, such as in Figs. 3(a) and 3(b).

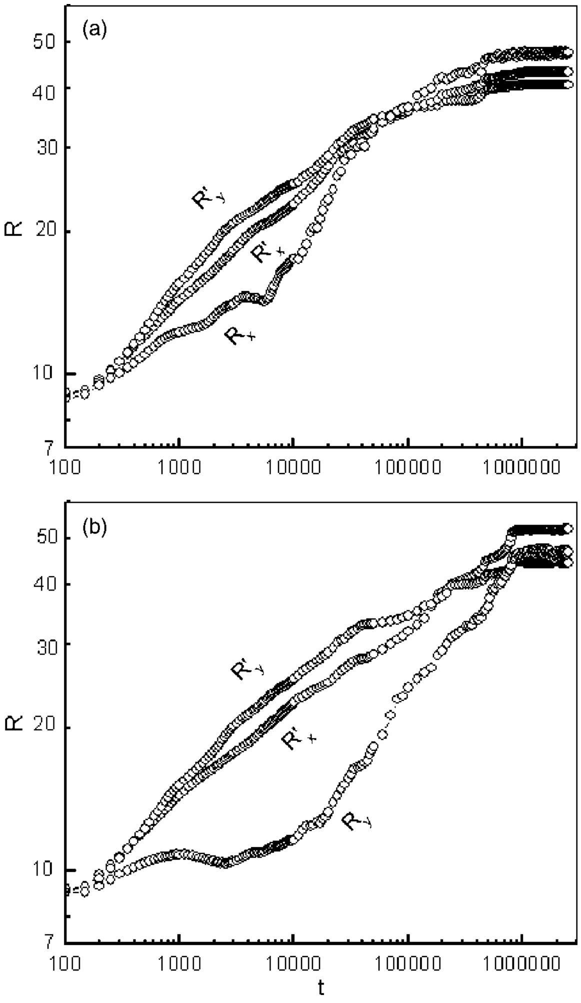

FIG. 5. Time evolution of the characteristic sizes of domains with the composition ratio $f=53.5/41.5$ for suitable oscillatory forces. (a) $\gamma=0.16$, $\omega=0.006$; (b) $\gamma=0.326$, $\omega=0.14$.

C. Variation of morphology with composition

Lastly, we investigate how the orientational order of domain structures changes with the composition ratio of homopolymers and copolymers. Figure 6 displays the orientational order transition of domain structures obtained for the composition ratio $f=18.5/76.5$ at $t=2000000$. From Fig. 6 we can find that the domain structures are reversed compared to Fig. 1. The striped structure of copolymers prevail in patterns, while the domain of homopolymers is minority. It is noted that the domains of the homopolymer (phase *C*) in Fig. 6(c) are elongated, while they are almost isotropic in Fig. 6(f). It means that a weaker field may lead to a more elongated structure. This interesting phenomenon could also be ascribed to the different mechanisms of forming the parallel or perpendicular stripes. From Fig. 7, we can obviously see that the orientational order parameter transits from 0 to 1 and from 1 to −1, and always increases with increasing the oscillatory force at the early stage. It can also be shown that as *S* changes from 1 to −1, the order parameter *S* is oscillatorily decreased from Fig. 7(d) to Fig. 7(f).

As an extreme example, finally we would show the transition process of the orientational order of microphase separation with the composition ratio $f=0/95$ at $t=2\,000\,000$. In fact, it is the case of pure copolymers and particles without homopolymers. From Fig. 8, we can see only the microphase separation in the mixture. As the oscillatory force on the particles is weak (that is, the amplitude and frequency of the oscillatory force are smaller), the domain structure displays isotropic bicontinuous stripes due to the long-range correlation and the surface tensions of copolymers dominating over the phase separation process, as shown in Fig. 8(a). As the oscillatory force is increased, the oscillatory motion of the particles will play an important role, the phase separation of

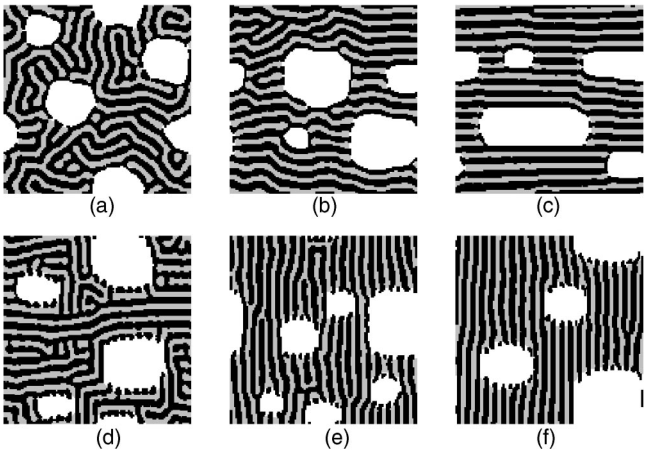

FIG. 6. Patterns of a 128×128 two-dimensional lattice with the composition ratio $f=18.5/76.5$ at time $t=2000000$. (a) $\gamma=0.001$, $\omega=0.00001$; (b) $\gamma=0.09$, $\omega=0.0003$; (c) $\gamma=0.181$, $\omega=0.0006$; (d) $\gamma=0.285$, $\omega=0.11$; (e) $\gamma=0.3143$, $\omega=0.13$; (f) $\gamma=0.331$, $\omega=0.14$. Phase *A* is represented by the black region, phase *B* by the gray region, and phase *C* by the white region.

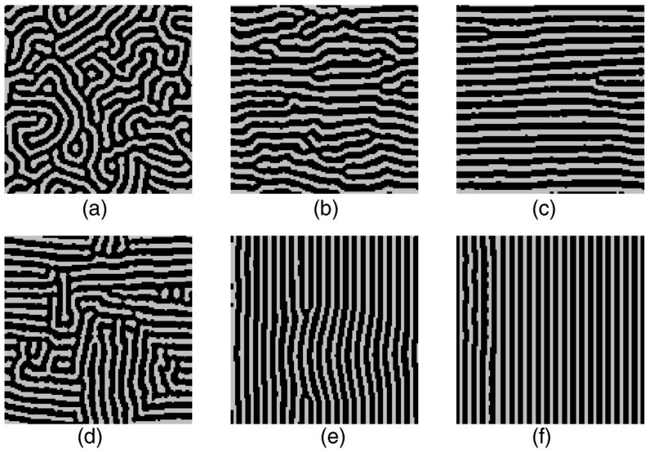

FIG. 8. Patterns of a 128×128 two-dimensional lattice with the composition ratio $f=0/95$ at time $t=2\,000\,000$. (a) $\gamma=0.001$, $\omega=0.000\,01$; (b) $\gamma=0.105$, $\omega=0.0003$; (c) $\gamma=0.181$, $\omega=0.0006$; (d) $\gamma=0.317\,18$, $\omega=0.11$; (e) $\gamma=0.33$, $\omega=0.12$; (f) $\gamma=0.35$, $\omega=0.14$. Phase *A* is represented by the black region, phase *B* by the gray region, and phase *C* by the white region.

the system will significantly be perturbed, and the coarsening process is enforced along the oscillatory direction. So that the isotropic striped structure will be broken, the orientation of striped patterns will tend to be parallel to the oscillatory direction, such as in Fig. 8(b). As the amplitude and frequency of oscillatory force are increased to suitable values, highly ordered striped structure is formed along the oscillatory direction, just as shown in Fig. 8(c). As the oscillatory force is further increased, the particles retain the rapid and large range's motion along the *x* direction due to the higher oscillatory frequency and the larger oscillatory amplitude of the particles. In this time the strong oscillatory force prevents the domain coarsening in the *x* direction, but coarsening exists in the *y* direction. The ordered structure perpendicular to the oscillatory direction is gradually formed, that is displayed in Figs. 8(d)–8(f). From Fig. 8, as well as Fig. 9, we can find that with the oscillatory force increased the striped structure of microphase changes from the isotropic state to the state parallel to the oscillatory direction, and from the parallel state to the state perpendicular to the oscillatory direction. Through adjusting the amplitude and frequency of oscillatory force, we can obtain highly ordered stripes parallel to the

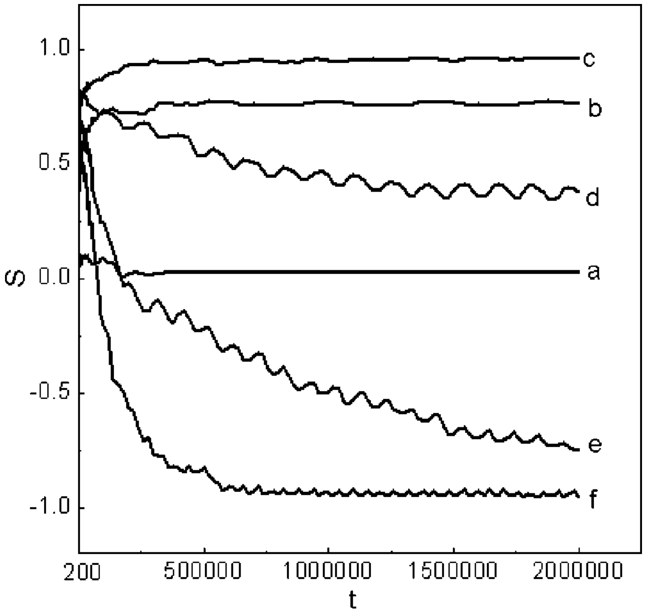

FIG. 7. Alignment kinetics for the composition ratio $f=18.5/76.5$ and different oscillatory forces. Curves *a*, $\gamma=0.001$, $\omega=0.000\,01$; *b*, $\gamma=0.09$, $\omega=0.0003$; *c*, $\gamma=0.181$, $\omega=0.0006$; *d*, $\gamma=0.285$, $\omega=0.11$; *e*, $\gamma=0.3143$, $\omega=0.13$; *f*, $\gamma=0.331$, $\omega=0.14$.

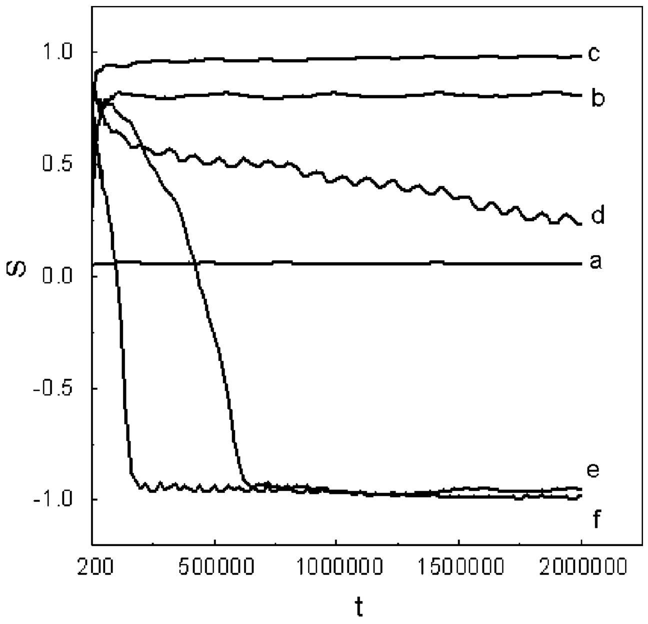

FIG. 9. Alignment kinetics for the composition ratio $f=0/95$ and different oscillatory forces. Curves *a*, $\gamma=0.001$, $\omega=0.000\,01$; *b*, $\gamma=0.105$, $\omega=0.0003$; *c*, $\gamma=0.181$, $\omega=0.0006$; *d*, $\gamma=0.317\,18$, $\omega=0.11$; *e*, $\gamma=0.33$, $\omega=0.12$; *f*, $\gamma=0.35$, $\omega=0.14$.

oscillatory direction or perpendicular to the oscillatory direction.

IV. CONCLUSION

By using the three-order-parameter model, we have studied the orientational order transition in a copolymer-homopolymer mixture under oscillatory particles. It has been found that the microphase separation in copolymers will be followed by the macrophase separation in the system. Imposition of an oscillating field on particles breaks up the rotation symmetry of microphase structure and anisotropically suppresses the composition fluctuations. We have examined the dependence of the morphology, order parameter and domain size on the oscillating field acting on particles, and obtained the orientational order transition of microphase patterns in the copolymer-homopolymer mixture by enhancing the oscillatory frequency and amplitude. Significantly, we have found that the competition between the motion of the oscillatory particles and the phase separation of the mixture can lead to striped microphase domain structure from the isotropic state to the state parallel to the oscillatory direction, and from the parallel state to the state perpendicular to the oscillating direction, depending on the oscillating fields acting on particles. We have also found that the morphology with orientational order transition will be influenced by the composition ratio of homopolymer and copolymer in mixtures. Our results indicate that using oscillatory particles to drive phase separation offers a useful approach to realize the orientational order formation and transition. From our numerical calculations, it could be understood that the orientational order transition of the striped microphase structure is a cooperative effect of the amplitude and frequency of the oscillatory external field. For small amplitude and low frequency, the system is isotropic; when both the amplitude and frequency are increased, microphase stripes along the direction of the external field are formed; as the amplitude and frequency are increased further, the system reenters the isotropic state; in the case of larger amplitude and higher frequency, there are also microphase stripes that appear but orient along the direction perpendicular to the external field. Our results are mainly based on numerical treatments of the three order-parameter coupled equations. It is still a challenge to find the scope for the amplitude and frequency that determine the orientational orders and their transition. The present simulations provide beneficial suggestions for experimentally studying the orientational order transition of a striped structure in soft materials by controlling an oscillatory field.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China under Grants No. 10334020, No. 20490220, and No. 10021001, the Provincial Natural Science Foundation of Jiangsu Grant No. BK2002086, and the Training Program Foundation for the Talents by the State Education Commission.

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