

Fast growth in phase-separating A - B -copolymer ternary mixtures with a chemical reaction

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We study the dynamics of phase separation of a binary A - B -polymer mixture with copolymer C , which is produced by the reaction of two counterpart reactive polymers A and B at the interface via the chemical reaction $A + B \rightleftharpoons C$. For low interfacial energy between the A and B phases, where the copolymer prefers to locate at interfaces, we show that the chemical reaction accelerates the phase separation of the system dramatically, because the backward reaction always drives the creation of immiscible A and B pairs at interfaces, which speed up the phase separation of the system, while the forward reaction process becomes more and more difficult as the interfaces are gradually saturated by copolymers. We also indicate that for a fixed chemical reaction rate constant, as the initial concentration of the copolymers increases, the domain growth at the late stage is speeded up as a result of the backward chemical reaction. However, when the interfacial energy is high, both forward and backward reactions coexist due to the occurrence of unsaturated interfaces, but the relative strength of reaction rates has no appreciable effect on domain growth during spinodal decomposition, because the interfacial energy dominates phase separation.

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I. INTRODUCTION

Phase-separation phenomena in a binary mixture have been the subject of recent research in complex fluids [1]. A bulk, homogeneous mixture of two fluids A and B will spontaneously separate into distinct A -rich and B -rich domains when it is quenched below the spinodal line. These domains grow as time goes on, and finally phase separation becomes macroscopic.

Recently, many studies have been devoted to address the influences of competing interplay on the growth kinetics of the phase-separating systems [2]. There has been a growing interest in the systems of phase separation coupled with chemical reaction [3–11]. Glotzer *et al.* [3] first studied the phase-separation dynamics of a binary (A - B) mixture coupled with the simplest chemical reaction of the form $A \rightleftharpoons B$. Their result indicated that, unlike the usual phase separation, the externally induced chemical reactions will compete with a thermally driven diffusion mechanism, and lead to a crossover from two macroscopic-segregated phases into steady-state labyrinthine morphology at a microscopic domain size [3]. As a consequence, it becomes very important to be able to identify the different mechanisms involved in the phase separation and the various growth stages. Experimentally, Tran-Cong and co-workers [12] have observed several kinds of regular patterns in polymer blends induced by chemical reactions, where the system is irradiated to induce photo-cross-linking reactions among polymer chains.

On the other hand, there has been much interest in the study of the kinetics of phase separation in a binary mixture with a third component such as surfactants and colloidal particles [13–22]. A well-known example is the use of copolymers in immiscible polymer blends, which tends to tune the interfacial structure and surface tension, leading to a notably different growth dynamics in multicomponent polymer mix-

tures. Since the copolymers act to lower the interfacial tension, and then the driving force for phase separation is decreased, the dynamics of domain growth becomes significantly slower in the presence of copolymers. The A - B -copolymer system has been described using various microscopic and macroscopic models in recent studies [13–19].

In the industry, the A - B -copolymer system is prepared by very different techniques [23]. One of the most important and practical methods of introducing copolymers to the immiscible polymer interfaces is the so-called *in situ* reaction [23,24], and more A - B -copolymer blends can be prepared via *in situ* reactive processing, where the block copolymer is synthesized from a reaction of different homopolymers A and B through their functionalized end groups at the interface. The reaction produces A - B copolymers, which eventually crowd the interface. Most experimental works have focused on the influence of reactive polymers on morphological changes, which can be explained in terms of the decrease of interfacial tension due to the creation of block copolymers at interfaces [25–28].

While there have been many theoretical and experimental studies [25–30] displaying the formation of a copolymer at the interface by a chemical reaction of functionalized chains, very little is known about how to control the domain patterns and growth kinetics by changing reaction conditions such as temperature or diffusion control, etc. [23,31,32,9]. In fact, some blends are produced in *in situ* processes, which involve simultaneous polymerization, phase separation, and structure formation under a suitable condition [23,32]. This coupled competing process of mixing and demixing significantly increases the system complexity, and modifies its morphologies and growth kinetics. Therefore, studying the effect of the reversible chemical reaction, which occurs between two kinds of homopolymers on the dynamics of phase separation, is an important subject in polymer engineering. In this paper, we study the phase separation of a ternary system composed of two immiscible homopolymers A and B with copolymers C in which the copolymer C is simultaneously produced and

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can also dissociate into A and B through the reversible chemical reaction $A + B \rightleftharpoons C$. Since the reactive groups are located only at chain ends, the reactive product is the symmetric A - B diblock copolymer and is produced directly at the interface [29]. We examine the competition between the phase separation and chemical reaction of the ternary A - B -copolymer mixture, and find that the presence of the chemical reaction can dramatically speed up the phase separation of the system, contrary to the slowing-down growth in chemically reactive systems studied previously. When the interface is saturated with copolymers so that the creation of interfaces does not cost any energy, at the late stage, the backward reaction always drives the creation of immiscible A and B pairs at interfaces, but the forward reaction process becomes less important. Thus the chemical reaction speeds up the phase separation of the system. However, when the interfacial energy is high, phase separation is mainly dominated by the interfacial tensions, and the relative strength of the reaction rates has no appreciable effects on domain growth during spinodal decomposition, while forward and backward reactions are simultaneously performed due to the occurrence of unsaturated interfaces. We believe that the present study may be a good guide for further experimental works.

The paper is organized as follows. Section II is devoted to the model and the basic formulation for the dynamics of phase separation coupled with chemical reaction. In Sec. III the simulation results are obtained and discussed. Finally, a main conclusion is given in Sec. IV.

II. MODEL

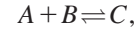
We consider the A - B - C , two-dimensional system where A and B denote different homopolymer components, and C denotes a random copolymer composed of equal volume fractions of A and B components. The local volume fractions of the components A , B , and C are denoted by $\psi_A(x, y)$, $\psi_B(x, y)$, and $\phi(x, y)$, respectively, and the total density $\psi_A(x, y) + \psi_B(x, y) + \phi(x, y)$ is assumed to be a constant normalized to unity. Under the incompressibility condition, two of the local volume fractions will be independent. We take $\psi(x, y) = \psi_A(x, y) - \psi_B(x, y)$ and $\phi(x, y)$ as the independent variables. The order parameter, $\psi(x, y)$ gives the local concentration difference between A and B phases, whereas the order parameter $\phi(x, y)$ describes the local copolymer concentration. We use a two-order-parameter model proposed by Komura and Kodama [17]. The free-energy function of the system is given by

$$F = \int d\mathbf{r} \left[-\frac{a}{2} \psi^2 + \frac{b}{4} \psi^4 + \frac{d}{2} (\nabla \psi)^2 + \frac{w}{2} (\nabla^2 \psi)^2 + e \phi^2 (\phi - \phi_s)^2 - \frac{s}{2} \phi (\nabla \psi)^2 \right], \quad (1)$$

where parameters a , b , d , w , e , and s are positive constants. The interfacial energy between the two components of binary mixtures is represented by the term $(d/2)(\nabla \psi)^2$, and the free energy is bounded by the term $(w/2)(\nabla^2 \psi)^2$. The

term $e \phi^2 (\phi - \phi_s)^2$ allows the coexistence of the two bulk states, i.e., $\phi = 0$ and $\phi = \phi_s$. The state $\phi = 0$ corresponds to the case in which the system is locally occupied either by A or B , whereas $\phi = \phi_s$ corresponds to the case in which the local volume is occupied only by the copolymers. The term $-(s/2)\phi(\nabla \psi)^2$ drives the copolymer to the interfaces between the A and B phases. Since the interface tension vanishes when the interface is saturated with copolymers [33], we are mainly concerned with the case $d = s\phi_s$, so that the creation of interfaces does not cost any energy when the local copolymer concentration is saturated.

We denote a reversible chemical reaction occurring in the A - B - C mixture by



and the forward and backward reaction rates are denoted by $\Gamma_1 (\geq 0)$ and $\Gamma_2 (\geq 0)$, respectively. The system is quenched to a thermodynamically unstable state to cause phase separation, and simultaneously undergo the above reversible chemical reaction. The equations of motion for the order parameters $\psi(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$ can be obtained from the coupled set of equations [17,20]

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= M_\psi \nabla^2 \frac{\delta F}{\delta \psi}, \\ \frac{\partial \phi}{\partial t} &= M_\phi \nabla^2 \frac{\delta F}{\delta \phi} + \Gamma_1 \psi_A \psi_B - \Gamma_2 \phi, \end{aligned} \quad (2)$$

where M_ψ and M_ϕ are transport coefficients.

We carry out numerical simulations of the model system in a $L \times L$ two-dimensional square lattice with $L = 256$ and periodic boundary conditions, using the cell dynamical system (CDS) approach proposed by Oono and Puri [34]. The CDS is a computationally efficient space-time discretized variation of the Cahn-Hilliard-Cook model. The CDS equations corresponding to Eq. (2) are written as follows:

$$\psi(x, y, t+1) = \psi(x, y, t) + M_\psi \tilde{\Delta} I_\psi \quad (3)$$

and

$$\begin{aligned} \phi(x, y, t+1) &= \phi(x, y, t) + M_\phi \tilde{\Delta} I_\phi + \frac{\Gamma_1}{4} [(1 - \phi)^2 - \psi^2] \\ &\quad - \Gamma_2 \phi, \end{aligned} \quad (4)$$

where

$$\begin{aligned} I_\psi &= -A \tanh \psi + \psi + w(\tilde{\Delta})^2 \psi - (d - s\phi) \tilde{\Delta} \psi \\ &\quad + s(\tilde{\nabla} \psi) \cdot (\tilde{\nabla} \phi) \end{aligned} \quad (5)$$

and

$$I_\phi = E \phi (\phi - \phi_s) (2\phi - \phi_s) - \frac{1}{2} s (\tilde{\nabla} \psi)^2. \quad (6)$$

For the original cell dynamics system, the lattice size (Δx or Δy) and the time step Δt were both set to unity. The CDS

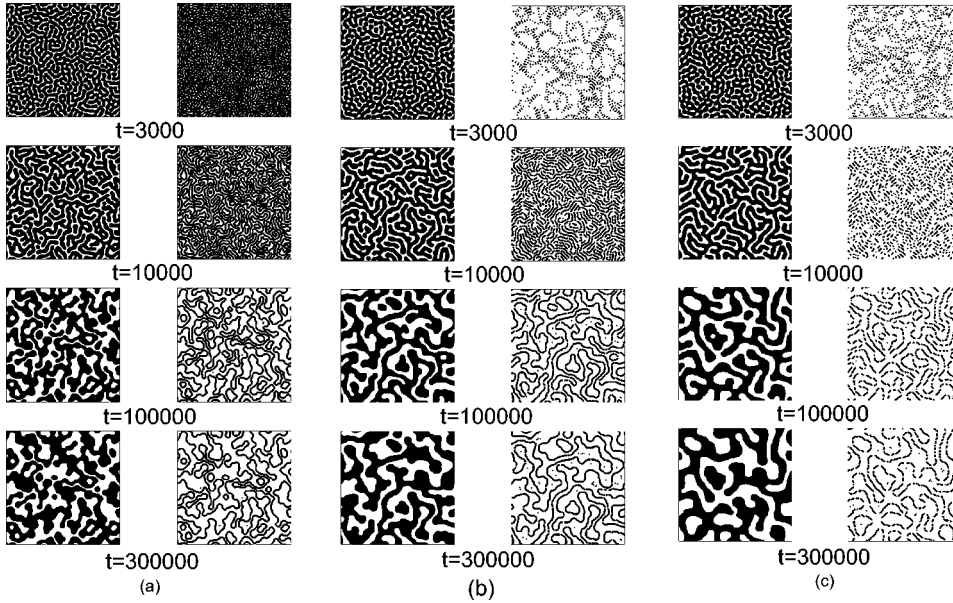


FIG. 1. Time evolution of ψ (left column) and ϕ (right column). The dark area denotes the region of higher values of ψ and ϕ . The parameters are $\bar{\psi}=0$, $\bar{\phi}=0.2$, $d=0.5$, $\Gamma_2=0.001$, $s=0.5$. (a) $\beta=5.0$, (b) $\beta=1.0$, and (c) $\beta=0.2$.

parameters A and E in Eqs. (5) and (6) are related to the free-energy parameters in Eq. (1) by $A=1+a$ and $E=2e$.

The discretized differential operators $\tilde{\nabla}$ and $\tilde{\Delta}$ on the two-dimensional square lattice are defined as [34]

$$\tilde{\nabla}X = \frac{1}{2}[X(x+1,y) - X(x-1,y), X(x,y+1) - X(x,y-1)] \quad (7)$$

and

$$\tilde{\Delta}X = \frac{1}{2} \sum_{NN} X + \frac{1}{4} \sum_{NNN} X - 3X, \quad (8)$$

respectively. Here NN and NNN represent nearest-neighbor and next-nearest-neighbor cells, respectively. $\tilde{\Delta}X$ is essentially the isotropized discrete Laplacian $\nabla^2 X$, but the choice of Eq. (8) will give the better isotropy of the patterns [34].

In our simulations, we start from initial random conditions. The ranges of ψ and ϕ at $t=0$ are $[\bar{\psi}-0.01, \bar{\psi}+0.01]$ and $[\bar{\phi}-0.01, \bar{\phi}+0.01]$, and $\bar{\psi}$ and $\bar{\phi}$ are the spatial averages of ψ and ϕ , respectively. We fix the parameters as $A=1.3$, $E=0.25$, $w=0.2$, $\phi_s=1$, and $M_\psi=M_\phi=0.05$ [17]. The results are averaged over ten independent runs. For the sake of convenience, we introduce two parameters:

$$\alpha = \Gamma_1 + \Gamma_2, \\ \beta = \frac{\Gamma_1}{\Gamma_2},$$

where the parameters α and β remain unchanged during the phase-separating process, and can be adjusted by controlling the reaction rates in the chemical system. In fact, the relative ratio of reaction rates, β , presents the dominant role, which is either the forward or backward reaction.

The mean domain size $R(t)$ is derived from the inverse of the first moment of the spherically averaged structure factor $S(\mathbf{k}, t)$ as $R(t) = 2\pi / \langle k(t) \rangle$, where $\langle k(t) \rangle$ is defined as

$\langle k(t) \rangle = \int d\mathbf{k} k S(\mathbf{k}, t) / \int d\mathbf{k} S(\mathbf{k}, t)$. The structure factor $S(\mathbf{k}, t)$ is defined by $S(\mathbf{k}, t) = \langle |\psi(\mathbf{k}, t)|^2 \rangle$, where $\psi(\mathbf{k}, t)$ is the Fourier component of the order parameter $\psi(x, y, t)$ and $\langle \dots \rangle$ denotes the thermal average over a number of repeating runs from independent initial conditions.

III. SIMULATION RESULTS AND DISCUSSION

We first study the effect of varying the relative ratio of the forward and backward reaction rates on domain patterns and growth of the system with the parameters $\bar{\psi}=0$, $\bar{\phi}=0.2$, $d=0.5$, $\Gamma_2=0.001$, and $s=0.5$. Figures 1(a)–1(c) show the time evolution patterns for $\beta=5.0$, $\beta=1.0$, and $\beta=0.2$ at times in the simulation corresponding to $t=3000$, 10 000, 100 000, and 300 000, respectively. The left and right columns show the spatial distribution of ψ and ϕ fields, respectively. The dark area presents the region of higher values of ψ and ϕ . It is seen from Fig. 1 that the domain sizes of the high β constant are smaller than those of the low β constant, and the unsaturated interfaces increase as the value of β decreases and still exist for small β even at the late stage of phase separation. As the phase separation between A and B components proceeds, the domain sizes of the A -rich and B -rich phases still increase, while the copolymers are gradually pushed to the interfaces between A -rich and B -rich domains which lower the driving force for phase separation. This is attributed to the backward chemical reaction, which induces the creation of the unsaturated interfaces between A and B components. When the forward reaction rate constant is very large, at the early stage, the amount of copolymers formed by homopolymers A and B is more than that of the copolymers decomposed into A and B , and then the domain size is greatly decreased. With gradual aggregation of the copolymers at the interfaces, the forward reaction has lesser important effects on the domain growth, because the chemical reaction can occur only at domain interfaces between the A and B components. The fast growth is mainly dominated by the backward reaction.

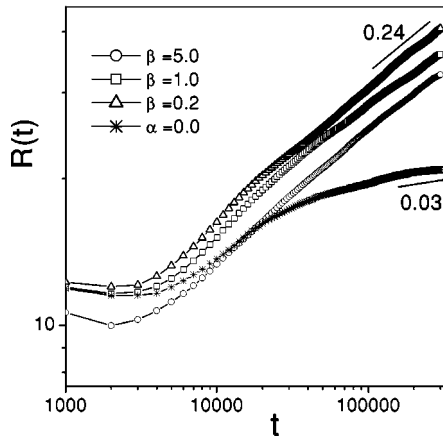


FIG. 2. Log-log plots of characteristic domain size $R(t)$ vs time t for the parameters $\bar{\psi}=0$, $\bar{\phi}=0.2$, $d=0.5$, $\Gamma_2=0.001$, and $s=0.5$.

Figure 2 shows the domain size $R(t)$ as a function of time on a log-log plot for different values of β . We can clearly find that the characteristic domain size for large β is smaller than that of small β due to the forward reaction induced slowing-down growth at the early stage. The simulation also reveals that at the late stage, the domain growth rate of the characteristic length $R(t)$ is nearly independent of the value of β for a fixed value of Γ_2 . The growth gives almost algebraical behavior due to the presence of the chemical reaction, which differs obviously from the ordinary $A-B$ -copolymer system (i.e., $\alpha=0$) [15,17]. In the present case, the chemical reaction speeds up the phase separation of the system, in contrast to the slowing-down growth of the systems studied

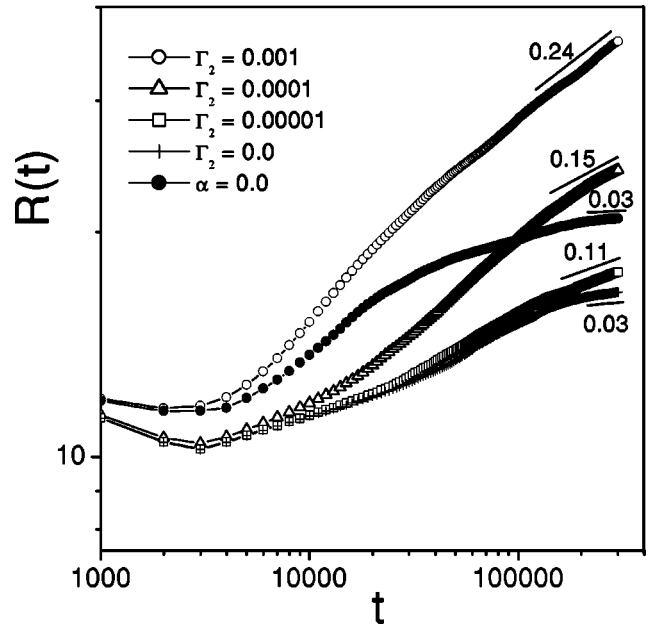


FIG. 3. Log-log plots of characteristic domain size $R(t)$ vs time t for the parameters $\bar{\psi}=0$, $\bar{\phi}=0.2$, $d=0.5$, $\Gamma_1=0.001$, and $s=0.5$.

previously [3,5,6]. In particular, the backward reaction plays an important role on the late-stage growth of the phase separation. An interesting case is that even if β is very large, the domain growth is still faster than that of the case $\alpha=0$, due to the lack of the contact between the A and B components at the late stage, leading to the difficulty of forward reaction. Actually, we can also find that for the $\beta=1$ case, i.e., when

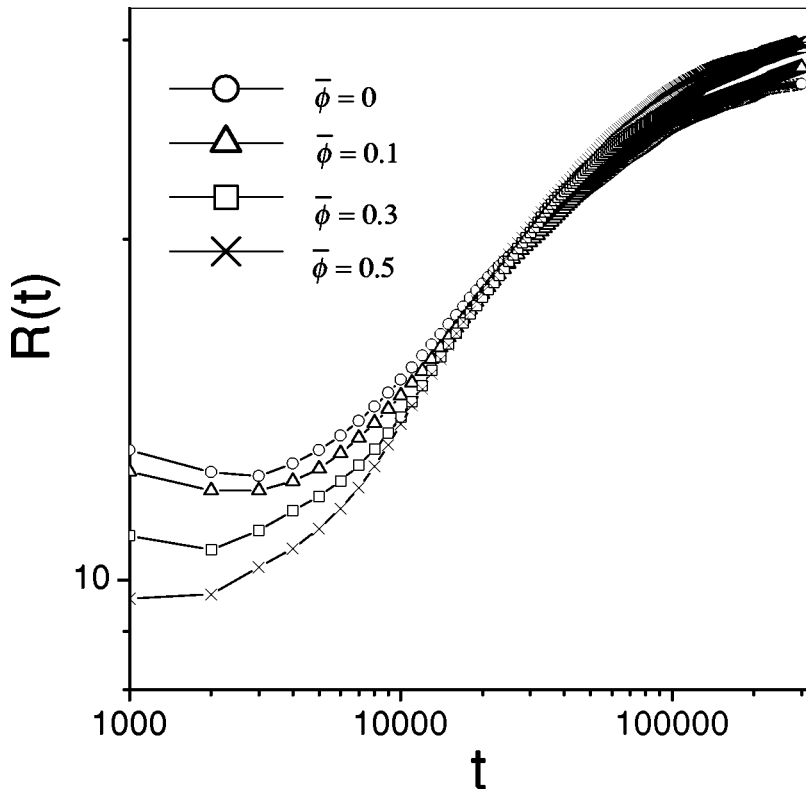


FIG. 4. Log-log plots of characteristic domain size $R(t)$ vs time t for the parameters $\bar{\psi}=0$, $d=0.5$, $\Gamma_1=\Gamma_2=0.0001$, and $s=0.5$.

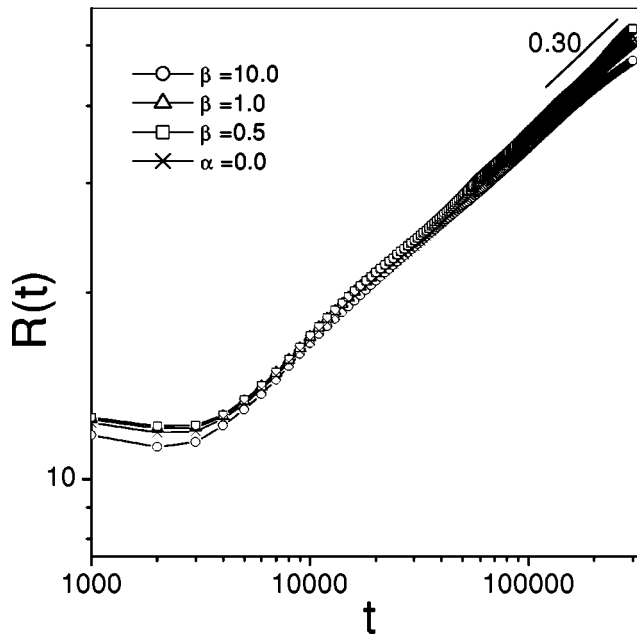


FIG. 5. Log-log plots of characteristic domain size $R(t)$ vs time t for the parameters $\bar{\psi}=0$, $\bar{\phi}=0.3$, $d=0.5$, $\Gamma_2=0.001$, and $s=0.2$.

the forward and backward reaction rates remain equal, the growth behavior is clearly distinct from the case without the chemical reaction ($\alpha=0$), indicating that at the late stage, the forward reaction has lesser important effects on the domain growth, and the backward reaction dominates the domain growth.

To further elucidate the importance of the backward chemical reaction on the domain growth at the late stage, we consider the evolution of the domain size for the variation of the backward reaction rate constant, but the forward reaction rate constant is fixed as $\Gamma_1=0.001$. Figure 3 shows the growth curves of domain sizes with time on a log-log plot for $\Gamma_2=0.001$, 0.0001, 0.00001, and 0.0, respectively. The backward reaction plays a vital role in domain growth at the late stage. It can be seen from Fig. 3 that as the backward reaction rate constant $\Gamma_2 \neq 0$, the chemical reaction dramatically affects the growth dynamics of phase separation, and speeds up the domain growth compared to the case $\alpha=0$. This means that at the late stage, the amount of the copolymers continually decreases due to the backward reaction, i.e., the copolymers are easy to decompose into polymers A and B even if the forward reaction is large ($\Gamma_1=0.001$). With the increase of the backward reaction rate constant Γ_2 , the late-stage domain growth is further speeded up, indicating that the backward reaction always speeds up the domain growth, while the forward reaction easily loses its role when the interfaces are saturated by the copolymers at the late stage. When the backward reaction rate constant $\Gamma_2=0.0$, Fig. 3 shows that the domain growth is suppressed. This clearly indicates that phase separation is mainly dominated by the backward reaction with a large reaction rate constant Γ_2 .

We now consider how the domain growth evolves with time due to the variation of the initial concentration of the copolymers, but the reaction rate constant is fixed to be Γ_1

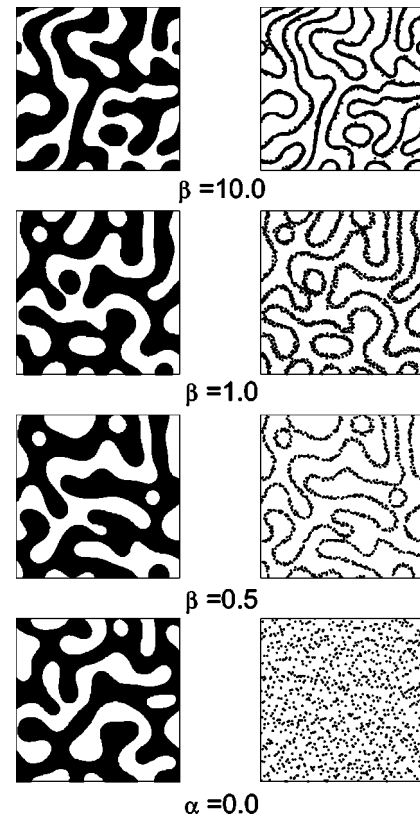


FIG. 6. Domain pattern of ψ (left column) and ϕ (right column) at $t=300\,000$. The parameters are the same as in Fig. 5. (a) $\beta = 10.0$, (b) $\beta = 1.0$, (c) $\beta = 0.5$, and (d) $\alpha = 0.0$.

$=\Gamma_2=0.0001$. In Fig. 4, we show the time evolution of the domain size $R(t)$ for $\bar{\phi}=0$, 0.1, 0.3, and 0.5. Before $t < 20\,000$ the domain size decreases as $\bar{\phi}$ is increased, which is characteristic of the A-B-copolymer system in the absence of the chemical reaction [15,17], but its differences gradually become smaller as the copolymers are decomposed into A and B monomers via chemical reaction, i.e., the chemical reaction alters the diffusion-driven domain growth at the late stage. When t is about 20 000, the domain sizes of various $\bar{\phi}$ are almost of the same values. The fact that the domain size at the late stage is enlarged for high initial concentrations of $\bar{\phi}$ shows that the backward reaction at the late stage becomes more and more important compared to the forward reaction.

Finally, we consider the case $d > s\phi_s$, where the copolymer cannot cancel the interfacial tension of the A-B interfaces. The parameters are chosen as $\bar{\psi}=0$, $\bar{\phi}=0.3$, $d=0.5$, $s=0.2$, and $\Gamma_2=0.001$. Figure 5 shows the time evolution of the characteristic domain length for $\beta = 10.0$, $\beta = 1.0$, $\beta = 0.5$, and $\alpha = 0$, respectively. We can see from Fig. 5 that compared to the case without the chemical reaction, the relative strength of reaction rates has no appreciable effects on domain growth during spinodal decomposition within the suitable regions of the relative ratio β . This means that the phase separation at the late stage is mainly governed by the surface tensions. However, we should point out that in this case, forward and backward reaction processes have the same effects on domain growth, due to the unsaturated inter-

faces. We can easily see that, when $\beta=1$, the domain growth curve overlaps that without chemical reaction ($\alpha=0$), indicating that for high interfacial energy, forward and backward reaction processes balance. Figure 6 shows domain patterns at $t=300\,000$ with various values of β . It can be seen from Fig. 6 that the copolymers are mainly dispersed in the interfaces between A -rich and B -rich phases due to the chemical reaction, contrary to the case $\alpha=0$ where the copolymers are randomly distributed. Interestingly, the presence of the chemical reaction has a tendency to drive the copolymers to form a continuous and well-distributed shape at interfaces, while the domain growth is not appreciably changed by the chemical reaction.

IV. SUMMARY

In this paper, using the CDS approach, we have numerically investigated the dynamics of phase separation of a two-dimensional A - B -copolymer system on the basis of the two-order-parameter time-dependent Ginzburg-Landau model coupled with the reversible chemical reaction. We have examined the effects of chemical reactions on the domain morphology and growth of the system, and show that for a non-zero backward reaction rate, the chemical reaction promotes the phase separation between the A and B phases dramatically no matter how large or small the reaction rate is. The domain size of the high β constant is smaller than that of the

low β constant due to the forward reaction at the early stage, but the domain growth at the late stage is mainly governed by the backward reaction. The fast growth at the late stage is attributed to the backward reaction, which speeds up the phase separation of the system by decomposing the copolymer into A and B monomers, while the forward reaction becomes more and more difficult with the gradual aggregation of copolymers at interfaces or the increase of the initial concentration of copolymers. As Γ_2 is increased, the unsaturated interface increases and the phase separation becomes faster. When the surface tension dominates phase separation ($d > s\phi_s$), as the chemical reaction is introduced, the copolymers tend to form a continuous distributed shape at interfaces. However, for suitable ratios β , the chemical reaction has no significant effect on the growth dynamics of the system. This is due to the fact that both forward and backward reactions exist as a result of the unsaturated interfaces, which confine the amount of copolymers at interfaces, and phase separation is mainly dominated by interface tensions.

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