Periodic Spinodal Decomposition in a Binary Polymeric Fluid Mixture

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(Received 16 August 1994)

We demonstrate here a dynamic phase transition between a periodic state without coarsening and a nonstationary state with coarsening, for a binary polymer mixture periodically driven above and below its instability point. For a nonstationary state we have found, in both symmetric and off-symmetric mixtures, the growth of a two-level structure characterized by two length scales. There is no self-similarity in this pattern evolution. A dynamic phase diagram of the dynamic stability of the phase has been obtained for the first time: Hydrodynamic interaction is found to have a strong effect on the *dynamic stability limit* through its dependence on the composition symmetry.

PACS numbers: 64.75.+g, 05.70.Fh, 64.60.Ht, 64.70.Ja

It is well known that phase separation proceeds in an unstable state of a mixture and the system eventually separates into two macroscopic phases. This process of the decay of an unstable state has been intensively studied by many researchers for various kinds of condensed matter, and the universal feature of the phenomenon has been clarified [1]. Phase separation is initiated by the temporal change of a control parameter such as temperature, which brings a system from a stable to an unstable state [1]. Temperature quenches into an unstable state can be classified into three types: (i) a single temperature quench which has been most commonly used for studying phase separation [1], (ii) a multiple temperature quench including a slow continuous quench and a double temperature quench [2–4], and (iii) a periodic temperature quench [5–9]. The last one was first studied theoretically by Onuki to answer what happens when a mixture is periodically brought above and below the critical temperature. Onuki predicted that there exists a new type of *dynamic phase transition* between a periodic and a nonperiodic state. Then this problem was experimentally investigated by Joshua *et al.* [8] for binary fluid mixtures experiencing a periodic pressure change. These pioneering works revealed the physics of periodic spinodal decomposition using early-stage phase separation. However, dynamic competition between phase mixing and *late-stage phase separation* has so far been explored neither theoretically nor experimentally. This competition is particularly interesting, since hydrodynamics plays a dominant role only in the late-stage coarsening.

In this Letter, we are aiming at answering the following questions. (i) How does the periodic phase separation proceed with time? (ii) What determines the dynamic stability limit? (iii) What is the general feature of the dynamic phase transition caused by dynamic competition between an ordering and a disordering process?

The samples used were mixtures of oligomers of ϵ-caprolactone (OCL) and styrene (OS). The number averaged molecular weights of OCL and OS were 2000 and 1000, respectively. Polydispersity ratios of OCL and OS were 1.2 and 1.04, respectively. The critical composition of this mixture was OCL/OS(33/67), and the critical temperature T_c was 135.5 °C. The experiments were performed at compositions where phase separation is not affected by wetting. For a simple liquid mixture, it is rather difficult to use a temperature oscillation to induce periodic phase separation because of its fast phase-separation speed and a pressure oscillation has been used [8]. For a polymer mixture, however, we can use an isothermal temperature oscillation because of the intrinsically slow molecular dynamics. This is a merit of using a polymer mixture for studying periodic phase separation, since we can avoid the problem stemming from the difference between adiabatic and isothermal phase separations [10]. The temperature of the hot stage (Linkam TH-600RMS) was controlled by a computer to have the functional form of $T(t) = \bar{T} + \Delta T \sin(2\pi t/\tau_p)$. For this periodic temperature oscillation, each period can be divided into two parts: (i) a mixing interval in the one-phase region [$T(t) > T_{bn}$; T_{bn} is the binodal temperature] and (ii) a demixing interval in the two-phase region [$T(t) < T_{bn}$]. The latter is further composed of two parts, namely, a deeper-quench demixing period [$\partial T(t)/\partial t < 0$] and a shallower-quench demixing period [$\partial T(t)/\partial t > 0$]. There are a number of key variables in periodic phase separation such as the composition ϕ, $\bar{T}$, ΔT, τ_p, and the functional shape of the temperature change. Here τ_p (10 or 20 s) and ΔT (1 or 2 K) were fixed, and ϕ and $\bar{T}$ were used as variables.

A mixture slowly phase separates with oscillatory behavior only when the system is cool enough to phase separate. First we show such examples. Figure 1(a) shows the coarsening dynamics of periodic spinodal decomposition for a symmetric mixture in a nonsteady coarsening regime. We can clearly see the two-level structure composed of an elementary bicontinuous structure and a large, growing superstructure in the late stage. The two-level structure reflects the existence of *only two types of domains*: One type of domain survives after experiencing the mixing period and continuously grows, while the other type of domain is created and destroyed within each period and thus does not grow with time. Figure 1(b) shows similar coarsening dynamics for an off-symmetric mixture. In

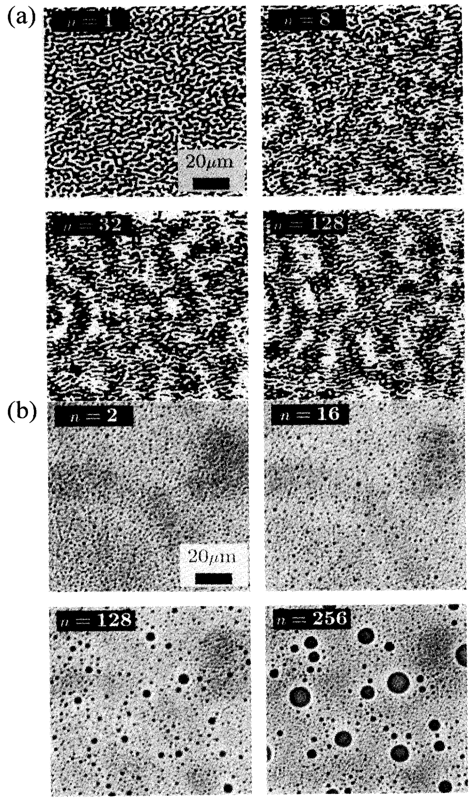

FIG. 1. Coarsening processes of periodic spinodal decomposition for $\bar{T} < T^*$. (a) Bicontinuous patterns observed in the nth period at the phase of 9 s for OCL/OS (35/65). $\bar{T} = 135.8°\text{C}$, $\Delta T = 2$ K, and $\tau_p = 10$ s. The pattern was two-valued by a black and white operation. (b) Droplet patterns observed in the nth period at the phase of 15 s for OCL/OS (38.5/61.5). $\bar{T} = 135.2°\text{C}$, $\Delta T = 2$ K, and $\tau_p = 20$ s.

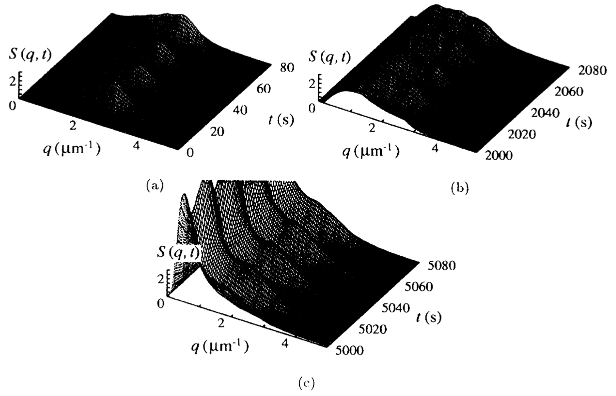

FIG. 2. Temporal change of $S(q)$ in OCL/OS (38.5/61.5), for $\bar{T} = 135.2°\text{C}$, $\Delta T = 2$ K, and $\tau_p = 20$ s.

contrast to Fig. 1(a), there is a long incubation time before large droplets are formed and the two-level droplet structure becomes evident. Figure 2 shows the temporal change in the structure factor $S(q)$ (q is the wave number) for an off-symmetric mixture. $S(\vec{q})$ was obtained by numerically calculating the power spectrum of the 2D Fourier transformation of a digitized image (400 × 400, 8 bit) [11]. Then we get $S(q)$ by averaging $S(\vec{q})$ circularly. The two peaks of $S(q)$ correspond to the elementary-droplet structure and the large superdroplet structure. This double peak is similar to that predicted for periodic spinodal decomposition of solid mixtures by Onuki [5]. We can clearly see the oscillatory behavior of these peaks reflecting the periodic temperature change and, at the same time, the gradual growth of the lower-wave-number peak corresponding to the large superdroplet structure. Figure 3 shows the overall coarsening behavior of the two peaks of the structure factor $S(q)$ corresponding to the elementary-domain and the superdomain structures (see Fig. 1), for both symmetric and off-symmetric compositions. We made a fitting of two Gaussian functions to $S(q)$ and obtained the two peak wave numbers. For bicontinuous phase separation, there is no incubation time and the superstructure coarsens with a time exponent of $\sim 1/3$. For droplet phase separation, on the other hand, there is a long incubation time before the rapid coarsening of the superstructure. The behavior is quite consistent with what is shown in Fig. 1. The appearance of the two-level structure whose component structures coarsen differently indicates strongly that there is no self-similarity in pattern evolution for a nonsteady growth state (see Fig. 3), in contrast to the results reported by Joshua *et al.* [8]. This inconsistency likely reflects the difference between periodic phase separation using early-stage spinodal decomposition and that using the late-stage one.

Figure 4 indicates the temporal change in the intensities $[S(q_p)]$ and wave numbers (q_p) of the peaks of $S(q)$. For the symmetric mixture [see Fig. 4(a)], there is a clear difference in the dynamics between a mixing and a demixing period and thus q_p oscillates in a saw-tooth-like shape. For the off-symmetric mixture [see Fig. 4(b)], on the other hand, there is not such a drastic difference and thus q_p oscillates in a sinusoidal shape. This oscillation amplitude becomes smaller with time, reflecting that the

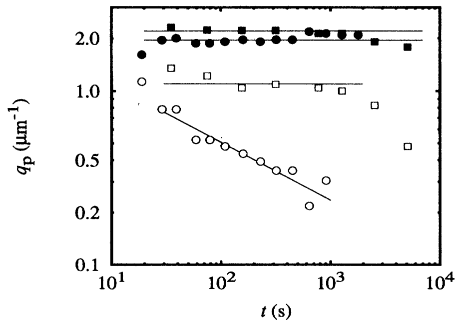

FIG. 3. Time dependencies of the two characteristic peak wave numbers q_p for $\bar{T} < T^*$. Circles correspond to the experiment of Fig. 1(a), while squares to that of Fig. 1(b). Filled symbols are for the elementary small domains, while open symbols are for the superdomains. The solid lines have a slope of 1/3 or 0.

superdroplets become much larger than the characteristic diffusion length of a mixing period.

For $\bar{T} > T^*$, we have only small droplets which periodically appear below T_{bn} and disappear above T_{bn} and thus the system is in a periodic steady state without coarsening. For $\bar{T} < T^*$, on the other hand, we have a nonsteady state which accompanies the coarsening of a phase-separated pattern from period to period, as indicated in Figs. 1–4. Thus there is a dynamic phase transition at T^* between a periodic steady state and a nonsteady growth state, as predicted by Onuki [5]. We have also found that T^* is strongly dependent on ϕ. The ϕ dependence of T^*, $T^*(\phi)$, which has been experimentally obtained for $\tau_p = 10$ s and $\Delta T = 2$ K, is shown in Fig. 5 together with the thermodynamic phase diagram. The most striking feature is that $T^* > T_{bn}$ for bicontinuous phase separation, while $T^* < T_{bn}$ for droplet phase separation. This fact was unambiguously confirmed by checking whether the system finally becomes homogeneous or inhomogeneous after changing the temperature pattern from $T(t) = T^* + \Delta T \sin(2\pi t/\tau_p)$ to $T(t) = T^*$. This $T^*(\phi)$ curve should be called a *dynamic phase diagram*, since its location is determined mainly by dynamic factors such as phase-mixing dynamics in a mixing period and coarsening dynamics in a demixing period.

First, we discuss the elementary process of periodic spinodal composition in each period. During a mixing period in the one-phase region, a domain becomes diffuse and disappears by simple interdiffusion through the domain boundary. The characteristic diffusion length l_d during a mixing period (τ_{mix}) can be estimated as $l_d^2 \sim D\tau_{\mathrm{mix}}$, where D is the diffusion constant and $D = k_B T/5\pi\eta\xi$ (ξ is the correlation length). Thus it takes $\sim R^2/D$ for the memory of a domain structure with a characteristic size of R to be completely lost. In a demixing period in the two-phase region, we can assume that a domain coarsens by the well-known scaling law of normal spinodal decomposition [1]: For a symmetric mixture $R = k_b(\sigma/\eta)t$ [1,12], where k_b is the constant, σ is the interface tension, and η is the viscosity. This fast hydrodynamic coarsening driven by capillary instability is well known as Siggia's mechanism. For an off-symmetric mixture, on the other hand, $R = [(k_d k_B T/5\pi\eta)t]^{1/3}$. Here, $k_d \sim 12\Phi_d$ (Φ_d is the volume fraction of droplets) for the Brownian-coagulation mechanism, while $k_d \sim 0.053$ for the evaporation-condensation mechanism [1,12]. On the basis of this simple model, we can estimate T^* according to the following criterion. When a domain size R after experiencing the coarsening in a demixing period is smaller than l_d, periodic spinodal decomposition should be in a periodic steady state. Otherwise, it is in a nonsteady state with coarsening. T^* can be most easily estimated for a stepwise periodic temperature change: In this case, $\sigma(T^* - \Delta T) \sim \{k_B T/[5\pi\eta\xi(T^* + \Delta T)\tau_p]\}^{1/2}(\eta/k_b)$ for the bicontinuous case, while $\xi(T^* + \Delta T)^3 \sim (12\Phi_d)^{-2}(k_B T/5\pi\eta)\tau_p$ for the droplet case. Here $\sigma \propto \epsilon^{2\nu}$ and $\xi \propto \epsilon^{-\nu}$, where $\epsilon = (T - T_c)/T_c$ and ν is the critical exponent of ξ ($\nu \sim 0.63$). This model explains the ϕ dependence of T^* at least qualitatively.

The fact that $T^* > T_{bn}$ for bicontinuous phase separation and $T^* < T_{bn}$ for droplet phase separation can be explained physically as follows. For a symmetric composition, the hydrodynamic coarsening unique to bicontinuous spinodal decomposition causes a strong asymmetry in be-

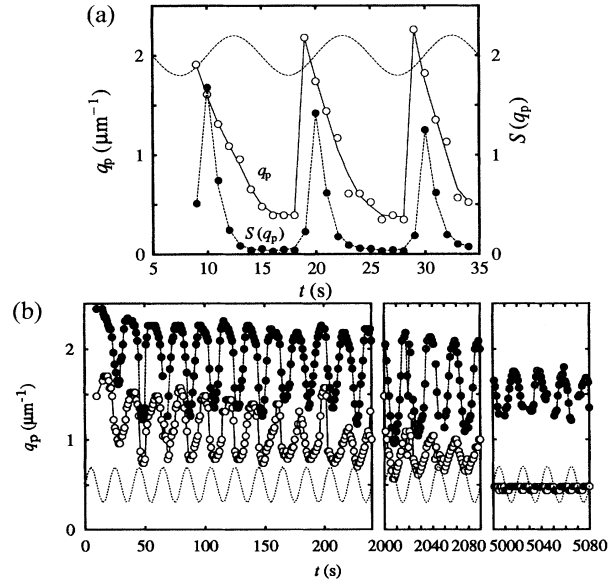

FIG. 4. (a) Temporal change in the intensity (•) and the wave number (◦) of the peak having the temperature oscillation for the experiment of Fig. 1(a). (b) Temporal change in the wave numbers of the two peaks reflecting the two-level structure for the experiment of Fig. 1(b). ◦ is the lower-wave-number peak and • is the higher-wave-number peak. For both (a) and (b) the dashed sinusoidal curves indicate the temperature oscillation behavior.

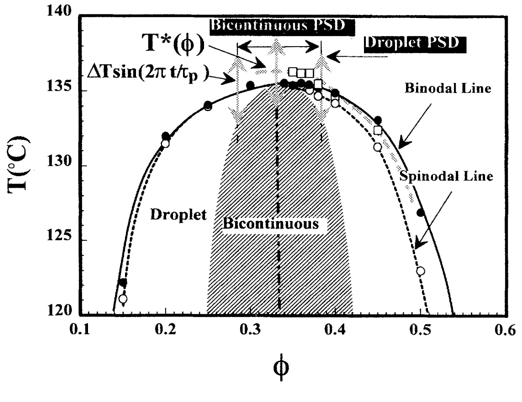

FIG. 5. The dynamic phase diagram $[T^*(\phi)]$ of the OCL/OS mixture together with the thermodynamic phase diagram [filled circle is the binodal line (solid curve), open circle is the spinodal line (black dashed curve)]. ϕ is the weight fraction of OCL. $T^*(\phi)$ (open square with the gray dashed line) is the boundary mean temperature between a periodic steady state and a nonperiodic coarsening state for the temperature oscillation of $\tau_p = 10$ s and $\Delta T = 2$ K (gray arrows). PSD stands for periodic spinodal decomposition.

havior between a mixing and demixing period: In a mixing period, domains dissolve by *slow diffusion*, while in a demixing period domains grow by *quick hydrodynamic coarsening* as $R \sim t$ [see Fig. 4(a)]. Thus only a short demixing period can create a domain which is too large to be destroyed in a mixing period. For off-symmetric mixtures, on the other hand, both phase separation and phase dissolution are dominated mainly by diffusion. Thus there is not such a strong asymmetry in dynamics between a mixing and a demixing period [see Fig. 4(b)]. This effect of the composition symmetry on the coarsening mechanism likely is unique to fluid systems, and there is probably no such drastic effect for solid systems.

Next we discuss why an inhomogeneity with a large spatial scale (the superstructure) is produced by periodic spinodal decomposition. Evidently, the inhomogeneity is enhanced by the selection in a mixing period due to the fact that droplets smaller than l_d disappear, while droplets larger than l_d survive and continuously grow. Further, the process in a shallower-quench demixing period plays a key role in producing the heterogeneity. During this period, there is an outward diffusion field around a domain to reduce the concentration difference between the two phases [4,13]. The concentration in a region sandwiched by two neighboring domains approaches the final equilibrium one faster than that in the other regions simply because of the geometrical reason. The resulting imbalance of diffusion flux causes an attractive interaction between domains, which eventually leads to the formation of the superstructure. This mechanism works for both bicontinuous and droplet phase separations. For a bicontinuous pattern, further, there is an additional effect: Once some difference in tube size is formed, it will be enhanced by tube hydrodynamic instability [12].

The formation of the superstructure can be regarded as an analog of normal phase separation. Here we call the volume fraction of the large domains ϕ_{large}. For $\bar{T} > T^*$, ϕ_{large} is always zero, while ϕ_{large} increases with time for $\bar{T} < T^*$. In this sense, ϕ_{large} is *the characteristic parameter of the dynamic phase transition.* ϕ_{large} is a slowly increasing function of time for $\bar{T} < T^*$ and, finally, approaches the value thermodynamically determined. For an off-symmetric composition, there is a long incubation time for the growth of ϕ_{large}. This incubation time becomes shorter with an increase in the composition symmetry of the mixture, since its increase shortens the interdroplet distance and effectively strengthens the interdroplet interaction. It also becomes shorter with a decrease in $\bar{T}$ which reduces the mixing period, and finally disappears for $\Delta T + \bar{T} < T_{bn}$. Although there is no energy barrier for this process, there is a time barrier for coarsening due to a weak interdroplet interaction. The existence of the incubation period is common to a metastable state, as in nucleation-growth behavior for a normal single quench. For a symmetric composition, on the other hand, ϕ_{large} starts to increase immediately after the initiation of periodic spinodal decomposition. A homogeneous domain structure is unstable even in the early stage, because of a strong interaction between the elementary domains, or the intrinsically nonlocal nature of a bicontinuous pattern. The absence of the incubation period is common to an unstable state, as in spinodal decomposition for a normal single quench. On the analogy of normal phase separation, we can newly define two kinds of dynamic stability, *dynamic instability* for a symmetric periodic quench and *dynamic metastability* for an off-symmetric periodic quench. The boundary composition likely is correlated with the composition of the percolation limit and also with ΔT (see Fig. 5).

Finally, we discuss the general implications derived from our study. The dynamic stability of periodic phase transitions can be generally classified into three types. (i) When the characteristic speed of ordering in an ordering period (v_{ord}) is slower than that of disordering in a disordering period (v_{dis}), the system is in a steady stable state (*dynamic stability*). (ii) When $v_{\text{ord}} \sim v_{\text{dis}}$, the transition takes place very slowly with an incubation time (*dynamic metastability*). (iii) When $v_{\text{ord}} \gg v_{\text{dis}}$, the transition takes place quickly without any incubation time (*dynamic instability*). For a binary fluid mixture, for example, hydrodynamic coarsening increases v_{ord} drastically only for bicontinuous phase separations, and leads to *dynamic instability*. It should be noted that the interdomain interaction sometimes affects the ordering speed strongly. We believe that this classification of the dynamic stability in terms of the relation between v_{ord} and v_{dis} is likely valid for any order-disorder transition, which include not only phase separation but also other ordering processes such as crystallization and magnetic ordering.

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, and Culture, Japan and also by a Grant from Ciba-Geigy Foundation (Japan) for the Promotion of Science.

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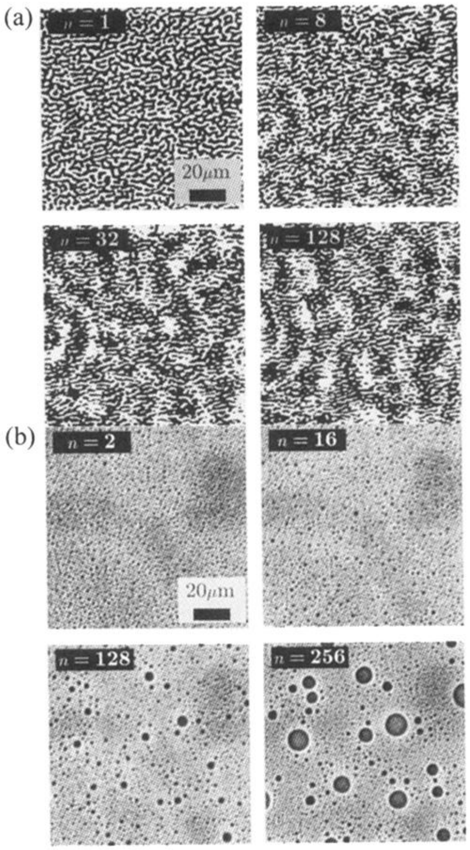

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