Concentric Pattern Formation during Phase Separation Induced by a Cross-Linking Reaction

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Various morphological structures observed in phase separation processes have attracted considerable attention in recent years, and the investigation of mechanisms of their formation constitutes an important field of nonequilibrium statistical mechanics. Phase separation induced by chemical reaction is especially interesting because the interplay between phase separation and chemical reaction is expected to give various novel structural patterns. Tran-Cong et al.[1−3] found that concentric domain structures formed during phase separation of a polymer blend induced by the photochemical cross-linking reaction of one component. An explanation for the mechanism of formation of this remarkable structure was given by Furukawa.[4] The blend is destabilized by an increase in the molecular weight of the component undergoing the cross-linking reaction. Since the blend goes through a metastable region before it reaches the unstable region, phase separation by the nucleation and growth mechanism precedes the spinodal decomposition. In the unstable region, the droplets formed in the metastable region trigger the growth of concentration fluctuations in their adjacent areas, and fluctuations grow concentrically around the droplets. It was demonstrated by computer simulations that when small droplets (triggers) were initially dispersed in the system, a concentric circular pattern was subsequently formed around them by the spinodal decomposition.[4]

However, nucleation and growth in a polymer blend is generally very slow because of its very high viscosity. Thus, it is not obvious that droplets grow large enough to act as triggers in the experimental time scale. In this Communication, we show that concentric circular patterns can form in the unstable region under certain conditions without a preceding phase separation by the nucleation and growth mechanism.[5]

One of the chief characteristics of a reaction-induced phase separation, which distinguishes itself from an ordinary phase separation where no chemical reaction is involved, is that the quench depth changes with time even when the thermodynamic conditions such as temperature and pressure are fixed at constant values.[6] On the other hand, a chief characteristic of a cross-linking reaction is the drastic decrease in the mobility of the system with the progress of the reaction. In this study, phase separation dynamics was simulated by employing a simple model that takes into account these two main characteristics of phase separation induced by a cross-linking reaction, instead of introducing the reaction term explicitly into the model.

The time evolution of the local concentration is described by the Cahn−Hilliard equation, which can be expressed in a reduced form

$$\frac{\partial\psi}{\partial\tau} = \nabla^2(-\psi + \psi^3 - \nabla^2\psi) + \sqrt{g}\zeta \tag{1}$$

where ψ is the reduced concentration, τ is the reduced time,[7,8] and the thermal noise ζ satisfies the following condition in d-dimensional space:

$$\langle\zeta(\mathbf{r},\tau)\,\zeta(\mathbf{r}',\tau')\rangle = -\nabla^2\delta^d(\mathbf{r}-\mathbf{r}')\,\delta(\tau-\tau') \tag{2}$$

A time dependence is introduced into the mobility and the free energy functional to simulate phase separation induced by a cross-linking reaction. Extension of eq 1 to the case where the mobility and the free energy depend on time is straightforward and leads to

$$\frac{\partial\psi}{\partial\tau} = m(\tau)\nabla^2(-a(\tau)\psi + \psi^3 - \nabla^2\psi) + \sqrt{gm(\tau)}\zeta \tag{3}$$

where $m(\tau)$ and $a(\tau)$ are dimensionless quantities representing the time-dependent part of the mobility and the time-dependent coefficient of the free energy, respectively.

The initial composition ψ_0 was assigned at an off-critical value, because in most cases destabilization of the system occurs at an off-critical composition when phase separation is induced by a cross-linking reaction.[4] The quench started from the spinodal point $a(0) = 3\psi_0^2$. The actual forms of $a(\tau)$ and $m(\tau)$ are not known. For simplicity, we assume that $a(\tau)$ increases linearly with time:

$$a(\tau) = a(0) + \frac{1-a(0)}{\tau_e}\tau \tag{4}$$

The time dependence of $m(\tau)$, as well as of $a(\tau)$, arises from the change of the molecular weight of the component undergoing a cross-linking reaction, and it is known that the mobility of a polymer blend depends on the molecular weights of its constituents much more strongly than the mixing free energy (entropy) does. Thus, we assume that $m(\tau)$ is expressed by the $-\alpha$th ($\alpha > 1$) power of time so that it decreases much more rapidly than $a(\tau)$ increases:

$$m(\tau) = [m(0) - m(\infty)]\left(1 + \frac{\tau}{\tau_b}\right)^{-\alpha} + m(\infty) \tag{5}$$

In this study, the following values were used for these parameters:

$$\psi_0 = -0.3,\quad \tau_e = 1.0\times10^7,\quad \tau_b = 1.7\times10^5,$$
$$m(0) = 1.0,\quad m(\infty) = 1.0\times10^{-5},\quad \sqrt{g} = 1.0\times10^{-3}$$

We solved eq 3 numerically on a two-dimensional 128 × 128 square lattice with periodic boundary conditions. An Euler discretization was used with a mesh size $\Delta r = 1$. Because of the drastic decrease of the mobility with time, phase separation becomes very slow in later periods, and it takes an extremely long time to

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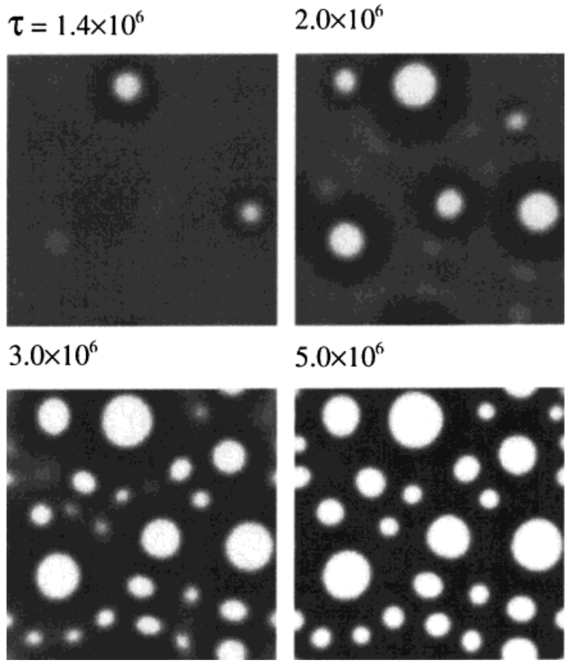

Figure 1. Development of phase separation pattern for α = 3.15.

observe an appreciable change of the morphological structure. To reduce the computation time to a reasonable amount, a variable time step $\Delta\tau = 0.01/m(\tau)$ was adopted. The constant 0.01 was chosen so that the numerical integration did not become unstable. (Note that $\Delta\tau m(\tau)$ corresponds to the time step in the case of a time-independent mobility.[7])

Figure 1 shows the development of the morphological structure during phase separation for α = 3.15. The local concentration was displayed by the brightness of the unit cell, which was divided into 32 levels with the brightest and the darkest level corresponding to $\psi = -1$ and 1, respectively. Droplets of the minor phase ($\psi > -0.3$) appeared, and the concentration inside the droplets increased with time. During the growth of the initially generated droplets, new droplets were generated, leading to the formation of a structure consisting of droplets with a bimodal size distribution. For α smaller than 3.15, a similar droplet structure was observed, but the distribution of the droplet size appeared to be unimodal.

Increasing the power α gave quite different structures as shown in Figure 2 (α = 3.4). Initially droplets appeared as in the case of α = 3.15. However, these droplets subsequently triggered the growth of concentration fluctuations in the surrounding area, which results in formation of a concentric circular pattern. The way in which the concentric circular pattern formed was very similar to those observed in simulations where triggers[4] or filler particles[9] were present in the mixtures as part of the initial conditions.

It is noted that there are discontinuities in the surrounding rings of the concentric patterns. It was found that the number of these discontinuities increased with decreasing α. In the experiments[2,3] the circular layers around the central droplets consisted of droplets rather than continuous rings. A pattern closely resembling the experimental one could be observed around α = 3.35 where most of the surrounding rings broke into droplets.

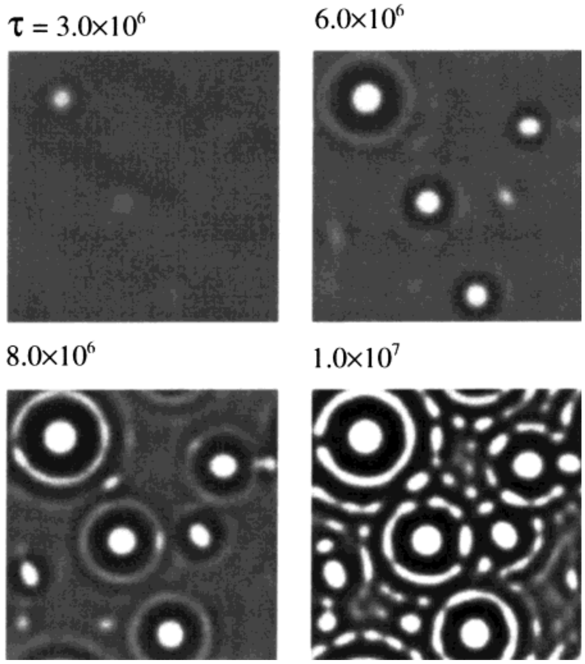

Figure 2. Development of phase separation pattern for α = 3.4.

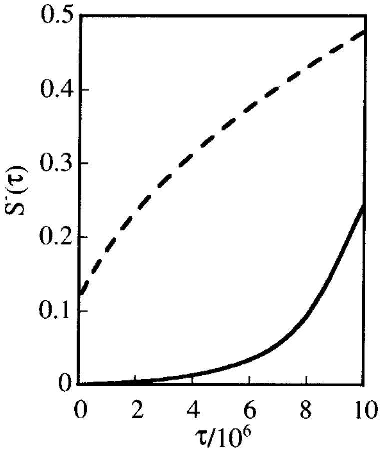

Figure 3. Time evolution of $S^-(\tau)$ (solid line) and $f_{ce}|\psi_{ce}|$ (broken line) for α = 3.4.

To evaluate the dynamics of the concentric pattern formation, we calculated the following quantity.

$$S^-(\tau) \equiv \frac{1}{V}\left|\int_{\psi<\psi_0} d\mathbf{r}\,[\psi_0 - \psi(\mathbf{r},\tau)]\right| \qquad (6)$$

Here, V is the total volume (area, in a two-dimensional space) of the system, and the integration was performed over the regions where $\psi(\mathbf{r},\tau)$ is smaller than ψ_0. In the case of a fixed quench depth, $S^-(\tau)$ increases with time and eventually coincides with the product of the fraction f_{ce} of the total volume of one coexisting phase and its concentration $|\psi_{ce}|$. In Figure 3, $S^-(\tau)$ is plotted against τ for α = 3.4, together with the product of $f_{ce}|\psi_{ce}|$. Because of the time dependence of the quench depth, $f_{ce}|\psi_{ce}|$ increased with time. ($f_{ce}|\psi_{ce}|$ was not zero at $\tau = 0$ because the quench started from the spinodal point.) $S^-(\tau)$ also increased with time, but in the earlier period the increasing rate was very low and the difference between $S^-(\tau)$ and $f_{ce}|\psi_{ce}|$ increased with time. Subsequently, $S^-(\tau)$ increased rapidly. It is noted that the first concentric bright layer emerged at about the same time

($\tau \approx 6 \times 10^6$) as the rapid increase in $S^-(\tau)$ started (see the second panel of Figure 2).

From these results the mechanism for concentric pattern formation was speculated to be as follows. Though the quench depth increased with time, initially the rapid decrease in the mobility suppressed the phase separation. Thus, the difference between $f_{ce}|\psi_{ce}|$ and $S^-(\tau)$ or the thermodynamic driving force of the phase separation increased with time. Eventually the driving force overcame the suppression by the decrease in mobility, and phase separation was accelerated. Since the initial concentration was in the off-critical region, droplets formed in the early period. Since the difference between $S^-(\tau)$ and $f_{ce}|\psi_{ce}|$ was large when the phase separation rate rapidly increased, the average concentration of the sea phase was distant from both binodal points, which led to the formation of continuous domains.

In this Communication, it is shown by computer simulations that concentric circular patterns form during phase separation from the unstable state when the quench depth and the mobility vary with time. No triggering nucleus or filler particle is used as the initial condition. This indicates that the nucleation and growth in the metastable region precedent to the spinodal decomposition in the unstable region is not prerequisite for concentric pattern formation in phase separation induced by a cross-linking reaction. The interplay between the thermodynamic driving force and the mobility played a key role in the formation of the concentric circular pattern.

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