Direct Determination of the Probability Distribution Function of Concentration in Polymer Mixtures Undergoing Phase Separation

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We report here the first use of the digital-image-analysis method to determine the probability distribution function of concentration in binary mixtures undergoing phase separation. This method has been applied to the mixture of poly(vinyl methyl ether) and polystyrene undergoing spinodal decomposition. The distribution function is initially Gaussian, but it becomes broader and turns bimodal upon decomposition. This transformation of distribution is related to the change of phase structure and, particularly, to the sharpening of the interfacial region.

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The dynamics of the phase-separation process has been studied from both theoretical and experimental points of view by many researchers.[1] The phenomena are very general and common in mixtures of liquids, metals, polymers, glasses, etc., because of the universal character. In binary mixtures, the local order parameter is generally the local concentration $c(\mathbf{r})$. The probability distribution function of concentration, $P(c,t)$, is important for the study of phase separation. Theoretically, the non-Gaussian shape of $P(c,t)$ renders the treatment difficult, especially in the late stage of phase separation.

For systems having a nonconserved order parameter where the values of the order parameter at two different spatial points are independent dynamically, $P(c,t)$ was successfully calculated by Kawasaki, Yalabik, and Gunton.[2]

On the other hand, for systems having a conserved order parameter, their $P(c,t)$ is difficult to calculate because of the nonlocal character, in addition to its strong nonlinearity. The higher-order nonlinear terms in free energy play an important role in the late stage of spinodal decomposition. In classical binary liquids, the relevant gross variables for critical dynamics are $c(\mathbf{r})$ and the transverse components of the local velocity. By assuming that the local velocity follows almost instantaneously the change in $c(\mathbf{r})$, we can eliminate the local velocity. In that case, according to Kawasaki and Ohta,[3] the following stochastic equation for $P(\{c(\mathbf{r})\},t)$ is obtained:

$$(\partial/\partial t)P(\{c\},t)=L\{c\}P(\{c\},t), \tag{1}$$

where the stochastic operator $L\{c\}$ is given by

$$L\{c\}=L_0\{c\}+L_{\mathrm{hd}}\{c\}, \tag{2}$$

$$L_0\{c\}=-L\int d^3r[\delta/\delta c(\mathbf{r})]\nabla^2[\delta/\delta c(\mathbf{r})+\delta H(\{c\})/\delta c(\mathbf{r})], \tag{3}$$

$$H(\{c\})=\int\{(K/2)[\nabla c(\mathbf{r})]^2+\tfrac{1}{2}\tau[c(\mathbf{r})]^2+(u/4!)[c(\mathbf{r})]^4\}d^3r. \tag{4}$$

Here $H(\{c\})$ is the Ginzburg-Landau-type free-energy functional and K, τ, and u are constants. L_{hd} is the operator which comes from the hydrodynamic interaction.

In the case of polymer blends having high molecular weights, the hydrodynamic interaction is not as important as in binary liquid mixtures, because of the entanglement effect[4]; accordingly, L_{hd} can be neglected in the above treatment.

The stochastic equation (1) describes the spinodal decomposition in which $P(c,t)$ starts to deviate from its initial value $P_0(c)=N_0\exp[-H_0(c)]$ in the one-phase region to the final equilibrium value $P_{\mathrm{eq}}=N_{\mathrm{eq}}\times\exp[-H(c)]$, where H_0 is given by Eq. (4) with τ replaced by τ_0 (the initial value of τ), and N_0 and N_{eq} are the appropriate normalization constants. On quenching of the system to the unstable region, τ changes its sign from positive to negative.

It is important to see how $P(c,t)$ changes from $P_0(c)$ to $P_{\mathrm{eq}}(c)$ during phase separation. To our knowledge, however, there has been no experimental method for observing $P(c,t)$ directly, except by computer simulation. Recently, we have applied digital image analysis (DIA) to pattern-formation problems in polymers and analyzed various structures in polymers quantitatively.[5,6] In this Letter, we apply the DIA method to the study of spinodal decomposition (SD) in binary mixtures, and show that $P(c,t)$ can be obtained directly and in a simple manner. DIA operations in wave-number space correspond to small-angle light scattering (SALS) and operations in real space give us unique information which cannot be obtained by other methods.

The scattering method SALS is one of the most powerful methods for studying the growth of local concentration fluctuations during the coarsening process, and it has been used mainly for experimental studies of phase-separated structures. Information given by $P(c,t)$

differs from that given by the scattering function $S(k)$. The scattering intensity is also related to the concentration difference between the phases; however, it is not possible to obtain $P(c)$ from $S(k)$ without additional assumptions.

In this Letter, we focus attention on the phase separation of polymer mixtures. The phase-separation process in polymers takes place very slowly and the spatial scale of phase separation is relatively large. Furthermore, the quench depth required for our study is not as small as in liquid binary mixtures. These are great merits for studying phase-separation dynamics in polymer systems. In the case of polymers, we can apply DIA with optical microscopy instead of scattering methods such as SALS. Optical microscopy is suitable for studying the late stages of spinodal decomposition because it is applicable to larger length than the conventional scattering technique.

Samples used in this study were mixtures of polystyrene (PS) and poly(vinyl methyl ether) (PVME). The weight-averaged molecular weight M_w of PVME was 99000, and the number-averaged molecular weight M_n of PVME was 46500. M_w of PS was 101000, and M_n of PS was 100000. The composition of the mixture used in this experiment was 80 wt.% PVME, which was slightly different from a critical composition of this mixture (ca. 70 wt% PVME). This system had a lower-critical-solution-temperature (LCST)-type phase diagram.

Temperature of the sample was controlled by a hot stage (Linkam TH-600) to within ±0.1 °C and the temperature jump could be made with a maximum speed of 90 °C/min. The system was quenched rapidly from the one-phase region to the unstable two-phase region.

Phase-separated structures were observed under a phase-contrast microscope. The spatial concentration distribution $c(\mathbf{r})$ was transferred to the intensity distribution $I(\mathbf{r})$, because the intensity is proportional to the difference in the refractive index $n(\mathbf{r})[\propto c(\mathbf{r})]$ in the phase-contrast microscope.[6] With use of an image processor, we could obtain a digitized image of phase-separated structure having a spatial resolution of 512×512, and an intensity resolution of 256. The real-time measurement had been performed under the control of a microcomputer. The real-time measurement could also be done with the use of a video recording system having a time resolution of 1/30 s. Details about DIA have been described in previous papers.[5,6]

The one-particle distribution $P(c,t)$ is the probability that the concentration in one cell, at time t, has the value c. We could easily obtain $P(c,t)$ by constructing a histogram of the optical intensity. The intensity was digitized with a resolution of 256. $P(c,t)$ is given by $P(c,t) = M(c)N^{-1}(\Delta c)^{-1}$, where $M(c)$ is the number of cells which has the value between c and $c+\Delta c$ (Δc is the width of the concentration interval).

When $P(c)$ had a very narrow distribution, the form of $P(c)$ was sensitive to the instrumental factor such as the inhomogeneity of the optical intensity input to the microscope. To avoid this effect, we made a correction to the original image numerically. In addition, we used the diffusor for the light source of the microscope.

Figure 1 shows the temporal change of a phase-separated structure observed at 133.5 °C. A coarse-graining process characteristic of spinodal decomposition is clearly observed. Figure 2 shows the temporal change of $P(c,t)$ during the spinodal decomposition obtained from images in Fig. 1. In Fig. 2, the intensity of 128 corresponds to the average concentration of the sample (80 wt.% PVME).

At the initial stage, $P(c,t)$ has a very sharp distribution with a Gaussian shape. Then, the shape of $P(c,t)$ becomes broader with time and deviates from the Gaussian shape. Finally, $P(c,t)$ displays two peaks reflecting the separation of the system into two phases. This behavior agrees qualitatively with the numerical calculation of Langer, Bar-on, and Miller,[7] and with the computer simulation of the time-dependent Ginzburg-Landau model carried out by Petscheck and Metiu.[8]

Figure 3 shows the temporal change of the average wavelength of concentration fluctuation, $\lambda_{\max}$ $(=2\pi/k_{\max})$, which is obtained from the peak position of $S(k)$. $S(k)$ is obtained by calculating the power spectrum of two-dimensional Fourier transform (2DFT) of the original images which are the same as those used for calculation of $P(c)$. One of the merits of DIA is that we can get various kinds of information in real space and in $\mathbf{k}$ space from the same image. The power spectrum of 2DFT of an image is equivalent to the structure factor obtained by SALS.[6]

In Fig. 3, there is no simple scaling regime in this composition and quenching condition. The exponent is dependent on time, changing gradually with time. Approximately, the exponent for $\lambda_{\max}$ should change from 0 to 1 through $\frac{1}{3}$. In the case of near-critical quench, we observed the simple scaling law in a certain time regime.

If the nonlinear term is negligible, $P(c,0)$ is expressed by the Gaussian distribution whose variance is $\chi_k(0)$ and $P(c,t)$ is given by

$$P(c,t) = \text{const}\times\exp\left[-\int_k |c_k|^2/2\chi_k(t)\right], \tag{5}$$

$$\chi_k(t) = [\chi_k(0) + K^{-1}(\kappa^2-k^2)^{-1}]\exp(2R_k t) - K^{-1}(\kappa^2-k^2)^{-1}, \tag{6}$$

$$R_k = LKk^2(\kappa^2-k^2), \tag{7}$$

where $\kappa^2 = |\tau|/K$ and $\int_k \equiv (2\pi)^3\int dk$. This corresponds to Cahn's linear theory[9] and gives the Gaussian-shaped dis-

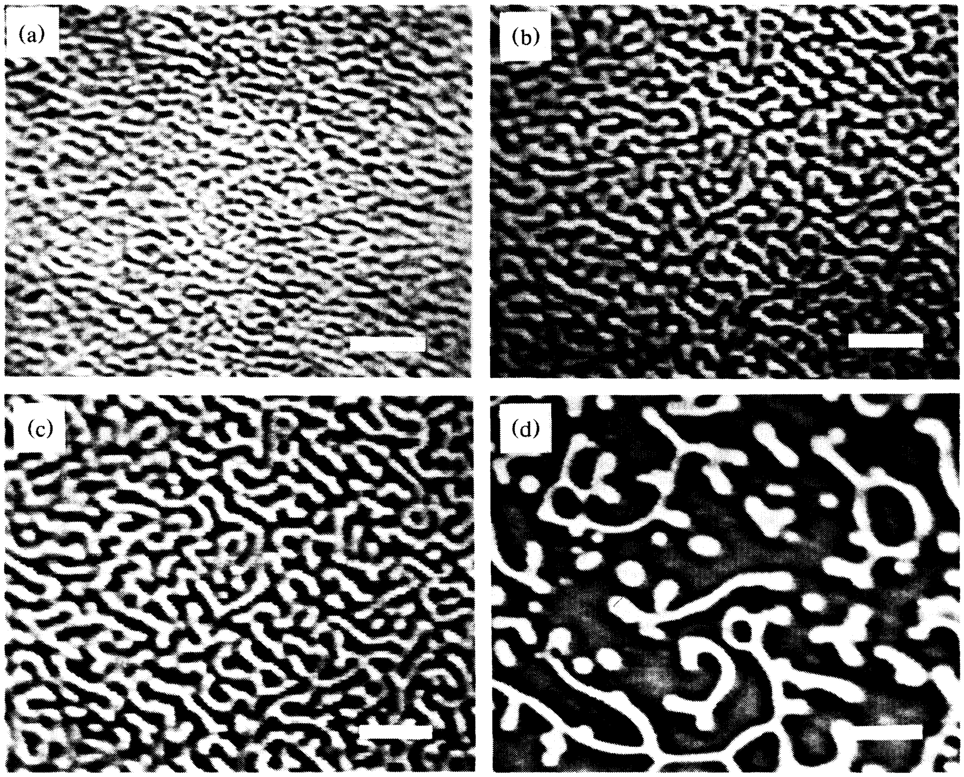

FIG. 1. Temporal change of phase-separated structure observed by optical microscope. Bar corresponds to 20 μm. (a)–(d) Structures at 480, 720, 1200, and 2400 s after quench, respectively.

tribution of $P(c,t)$. In Fig. 2, the probability distribution function is close to the Gaussian shape in the initial stage, but the linear growth is not observed in this system, as can be seen in Fig. 3. This suggests that the dynamics of phase separation is highly sensitive even to weak nonlinearity. The nonlinear term becomes important as the decomposition proceeds and $c(\mathbf{r},t)$ grows. This is the term which slows down the initial exponential growth of the low-k modes. It also contains the thermo-

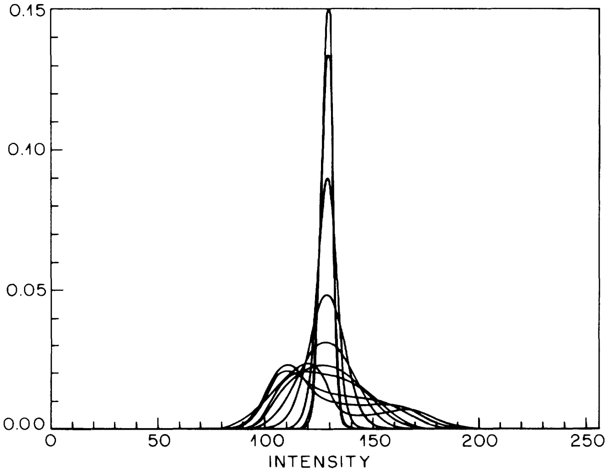

FIG. 2. Temporal change of the probability distribution function for concentration, $P(c)$. Curves correspond to $P(c)$ at 11, 180, 300, 480, 720, 960, 1200, 1500, 1800, and 2400 s after quench, respectively, from the top to the bottom, at the value of intensity at 128.

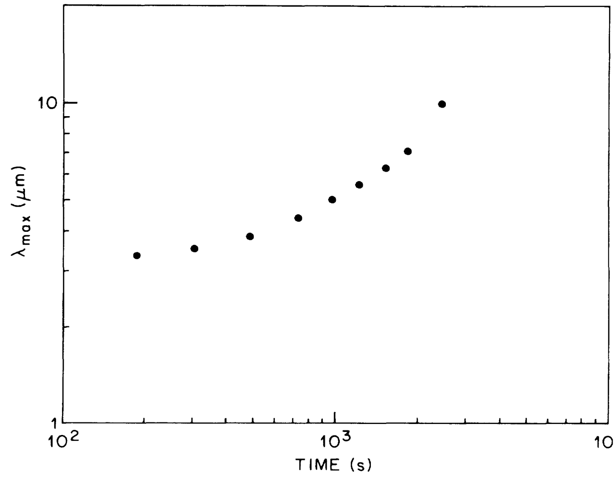

FIG. 3. Temporal change of the average wavelength of concentration fluctuation, λ_{max}.

dynamic information on the relation between the position in the phase diagram and the two final equilibrium phases.

In the regime where the typical wavelength of fluctuation ξ is comparable to the interface thickness δ ($\xi \sim \delta$), $P(c)$ should have a shape similar to Gaussian shape. In the regime $\xi > \delta$, $P(c)$ deviates from the Gaussian shape and transforms into a double-peak shape. In the regime $\xi \gg \delta$, $P(c)$ becomes completely bimodal and $P(\bar{c})$ ($\bar{c}$ the average concentration) becomes small. This behavior is observed in Fig. 2. From the direct observation (see Fig. 1), the time when the interface is clearly formed is about 480 s after the quench. Before this time, the interface is diffuse and its dimension is comparable to the size of inhomogeneity. In this stage, $P(c)$ is almost Gaussian. In the final stage, the interface becomes very sharp and we observe $P(c)$ with double peaks. The growth behavior of the domain in Fig. 3 may also be related to this morphological change.

The value of $P(c,t)$ at $c=\bar{c}$ is closely related to the total amount of interface. $P(\bar{c},t)$ gives us the information on the temporal change of interface length. In the late stage, the interfacial tension plays an important role, as suggested by Siggia,[10] In DIA, we can also extract the motion of the interface and estimate the total length of the interface.

After a very long time following the quench, we should reach an equilibrium state where the system is completely phase separated. In this case, we can obtain the final fractions of two phases, ϕ_A and ϕ_B, by a simple calculation using a phase diagram. If the final concentrations of the two phases are given by c_A and c_B, ϕ_A and ϕ_B are given by $\phi_A = |(\bar{c}-c_A)/(c_A-c_B)|$ and $\phi_B = |(\bar{c}-c_B)/(c_A-c_B)|$. Thus, if we wait for a sufficiently long time, we should be able to obtain the final composition, and we can obtain the absolute value of concentration by this method. In our polymer mixture, however, it takes too long for the system to reach the equilibrium state because of the high molecular weights of polymers. The absolute determination of concentration should be much easier in binary liquid mixtures and polymer solutions.

During the late stage of spinodal decomposition, the amplitude of the concentration fluctuation approaches the equilibrium value c_A and c_B; however, the wavelength or size of the phase-separated structure grows with time. In this regime, the phase-separated structures at different time scale have self-similarity. In addition, the droplet size is much larger than the interface thickness and only the motion of interface becomes important. In this regime, $P(c)$ should be only weakly dependent on time because $P(c)$ is insensitive to the motion of interface change. This regime should be scaled only by the spatial factor and be described by the position of the interface. The phase-separation behavior observed in this Letter did not reach this final stage yet, but the indication of transition to the final stage of spinodal decomposition can be seen in Fig. 2. It is important to see both $P(c)$ and $S(k)$, and to make clear the relation between them in order to study this stage.

A more comprehensive study of the spinodal-decomposition behavior in the polymer mixture having various compositions and quench conditions will be discussed elsewhere.

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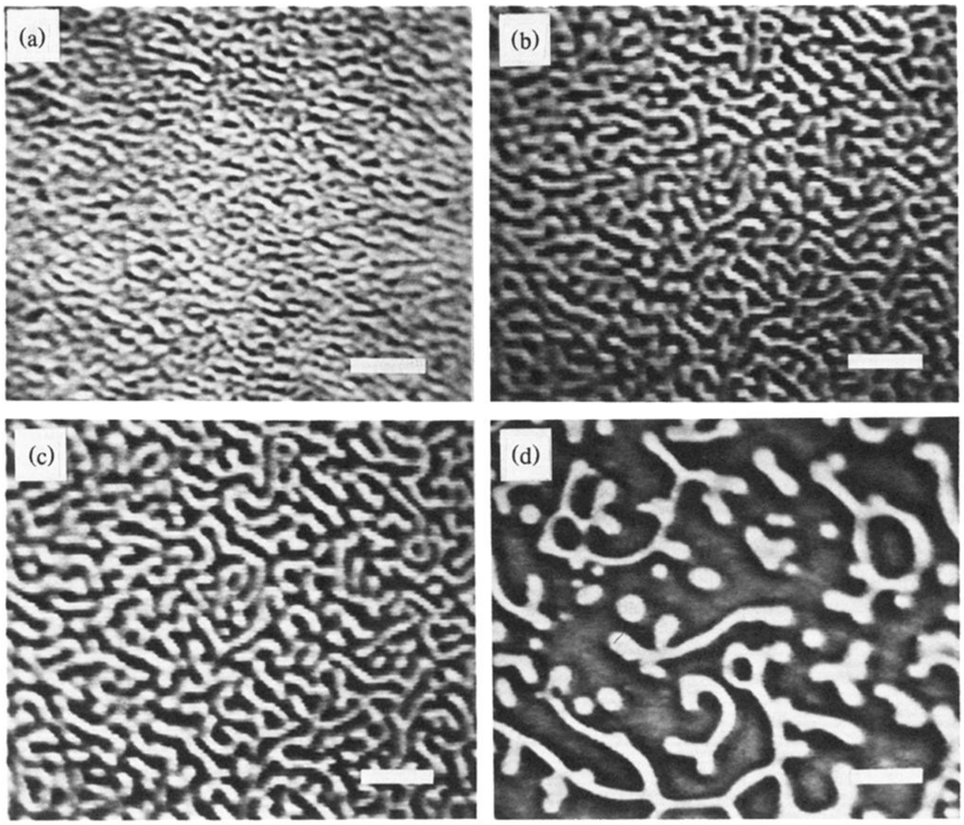

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