

Phase separation in a dilute polymer solution in a metastable region

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The time evolution of phase separation in a supercooled dilute polymer solution (polystyrene in diethyl oxalate) in a metastable region was studied by time-resolved dynamic and static light scattering. The mean radius $R(t)$ and the total number density $N(t)$ of droplets consisting of the minority phase were obtained as $R(t) \sim t^1$ and $N(t) \sim t^0$ in the growth stage, and as $R(t) \sim t^{1/3}$ and $N(t) \sim t^{-1}$ in the coarsening stage.

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A number of theoretical and experimental studies have been reported on the kinetics of phase-separating systems which were quenched into the unstable two-phase region [1]. Phase separation in the unstable and unmixing mixture may proceed either by nucleation growth (NG) or by spinodal decomposition (SD), depending upon the thermodynamic condition. In general, the dominant mechanism, which limits the dynamical behavior in the process of phase separation, is described by a system-independent universal diffusion process resulting in dynamical universality. However, the polymer system has a characteristic time intrinsic to the polymeric structure, and the dynamic process controlled by its time constant can become an elementary molecular dynamics. A typical example is the glass transition, and SD in the polymer mixture near its glass transition temperature shows a behavior similar to the solid solution [2]. Entropy-induced slowing down of the coarsening of phase separation in a polymer mixture is also such a case [3,4]. In the case of a polymer solution, a strong asymmetry exists in the molecular dynamic properties, e.g., the molecular size and its mobility. This asymmetry could bring a noticeable modification in the phase-separation dynamics [5], and its effect could be enhanced in a supercooled dilute solution in the metastable state.

Nucleation can be induced by quenching an off-critical mixture into the metastable region through its coexisting temperature T_{cx} , and the system evolves to the final coexisting two-phase equilibrium by the growth of droplets consisting of the minority phase with the final equilibrium concentration [increase of droplet size $R(t)$ with time t] [6–8]. Nucleation results from the instability initiated by the local fluctuation to create droplets larger than a certain critical size in a supersaturated mixture. The droplets grow directly from the supersaturated solution in the growth stage. The coarsening following the growth stage occurs due to the Ostwald-ripening and/or diffusion-reaction mechanism [8]. Growth and coarsening of droplets have been considered to be controlled by the diffusion process, assuming that diffusion is the only significant transport process and that adsorption of the solute molecules to droplets occurs very rapidly compared with its diffusion time. Recently, Tokuyama predicted theoretically the existence of an intermediate stage obeying the power law as $R(t) \sim t^{1/4}$ between the growth and coarsening stages [8]. NG experiments on binary mixtures have been performed by cloud point [9,10], by microscopy [11,12], and by light scattering [13,14]. However, little

enough is known about phase separation in polymer systems in a metastable region. Cumming, Wiltzius, and Bates reported that for a polymer mixture the growth of droplets obeys the power law of $R(t) \sim t^{1/2}$ in accordance with the diffusion limited mechanism [13]. On the other hand, Nakata and Kawate obtained $R(t) \sim t^1$ for droplet growth in the dilute polymer solution using the Guinier plots of scattered intensity measurements [14]. It is of great interest to clarify this apparent contradiction of the power-law relationship of the droplet growth and the effect of polymer molecules.

Here, we report the light scattering experiment of the time evolution of phase separation in a supercooled, very dilute solution of polystyrene (PS) and diethyl oxalate (DEO) in a metastable state. The PS sample used has been characterized as $M_w = 60.0 \times 10^4$ with $M_w/M_n < 1.10$, where M_w and M_n are the weight- and number-averaged molecular weight, respectively. DEO was fractionally distilled after drying thoroughly. Since the densities of the PS and DEO at 20 °C are 1.0750 and 1.0785 g/cm³, respectively, a measurement over a long-time period (growth to coarsening) is possible without sedimentation. The phase diagram is shown in Fig. 1. The critical concentration C_C and temperature T_C are 4.66 wt % and 39.630 °C, respectively. We have employed a very

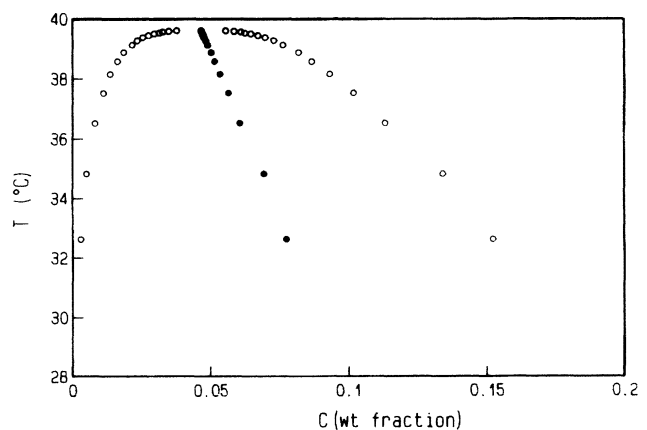


FIG. 1. The coexistence curve for polystyrene ($M_w = 60.0 \times 10^4$) and diethyl oxalate mixture. Solid circles denote the diameter associated with the shape of the coexistence curve. T_C is 39.630 °C and C_C is 4.66 wt %. The concentration and the coexisting temperature of the measured solution are 0.040 wt % and 29.60 °C, respectively.

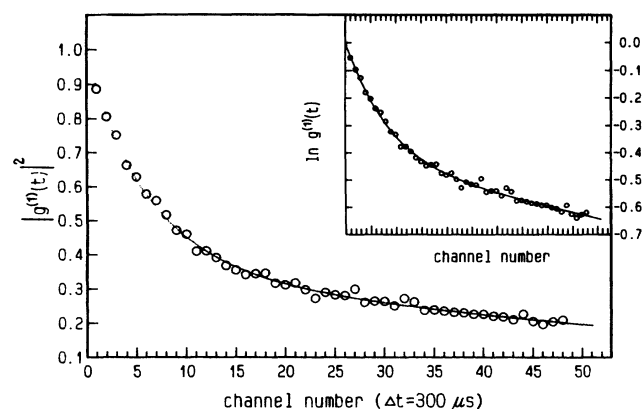


FIG. 2. Correlation function for the PS-DEO mixture ($C=0.040$ wt %) at the quench depth 0.10 °C and 60 min after the quench. The dotted curve is the calculated double-exponential fitting.

dilute solution with a concentration of 0.040 wt % in order to avoid unnecessary interactions between the droplets and the multiple-scattering effect. The coexisting temperature T_{cx} was 29.60 ± 0.01 °C. The sample solution which was maintained at 29.80 °C in the one-phase region was quenched into the metastable region by a rapid temperature drop. The transient time for attaining the new thermal equilibrium was less than 1 min because the quench depths $\delta T = T_{cx} - T$ were as shallow as 0.1 – 0.4 °C. The quenched temperatures T were far above the cloud point, because the cloud point is usually located below T_{cx} by $0.2(T_C - T_{cx})$ [9].

A light scattering method was used to study the growth of droplets. A He-Ne laser operated at $\lambda = 632.8$ nm was used as a light source. The temperature was controlled with an accuracy of ± 2 mK. Scattering measurements over the time range $t < 1000$ min were performed. Multiple scattering estimated from turbidity was sufficiently small because of the very dilute solution of PS in DEO. Hence no multiple-scattering correction was undertaken. The correlation function measurements were performed at a scattering angle of $\theta = 30^\circ$ for the precise determination of the droplet size, because the validity of the Guinier plot method becomes worse for the (sub)micrometer-size droplets in the usual scattering-angle range. The measured correlation functions were analyzed by the least-squares fit to the double-exponential form of the electric-field correlation function. This accounts for the contribution of both the droplets of the minority phase and the polymer chains in the majority dilute phase (where polymer molecules undergo translational diffusion almost independently with sufficient molecular dispersion). A typical correlation function is shown in Fig. 2, with a good reproducibility of the fitting. The static intensity measurements ranging over $\theta = 16^\circ$ – 90° were carried out to determine the zero-angle scattered intensity $I(0^\circ, t)$. The measured scattering function before the quench was subtracted from that after the quench in order to exclude the possible contribution of the scattering in the majority phase, and $I(0^\circ, t)$ was evaluated by the fitting of the measured scattering function to that of spherical particles including the polydispersity of the radius [13]. The average radii were set to those determined by the correlation function, and the fitting was good enough.

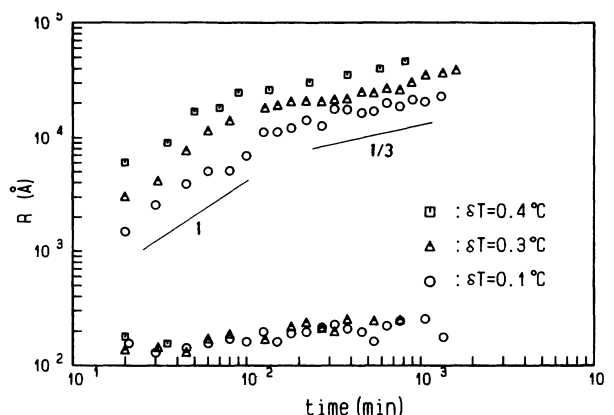


FIG. 3. Mean radius $R(t)$ as a function of time t after the quench for various quench depths. The upper symbols correspond to the droplet radius of the minority (concentrated) phase, and the lower symbols to the hydrodynamic radius of the polymer chain in the majority (dilute) phase. The symbols \circ , Δ , and \square stand for the quench depths 0.10 °C, 0.30 °C, and 0.40 °C, respectively. The two straight lines have the slope of 1 and $\frac{1}{3}$.

Figure 3 shows the time evolution of the droplet size obtained by the correlation function measurements at three quench depths (0.1 °C, 0.3 °C, and 0.4 °C). The lower data points correspond to the hydrodynamic radii of PS molecules in the majority phase. The radii coincide indeed with those of single PS molecules [15], and the time dependence of them is very weak. The upper data points show the temporal growth of the droplets consisting of the minority phase. The nucleation stage could not be detected. It was observed that there exist time regions characteristic of the droplet growth via a crossover regime. This feature is found similarly in the time dependence of $I(0^\circ, t)$ as shown in Fig. 4. Since $I(0^\circ, t) = bN(t)R(t)^6$ with b being some proportional constant, the number density $N(t)$ of droplets is obtained from $I(0^\circ, t)/R(t)^6$.

From these observations of the present mixture, we can derive the following features about the time evolution of the

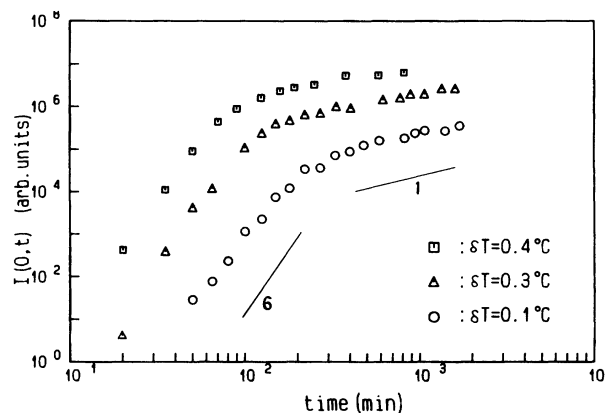


FIG. 4. Double logarithmic plots of zero-angle scattered intensity $I(0^\circ, t)$ vs time t . Symbols are the same as in Fig. 3. It should be noted that the times of measurements of angular dependence of scattered light intensity differ from those of the correlation function measurements. Two straight lines having the slope of 6 and 1 are shown for comparison.

phase separation of the polymer solution in the metastable state. (1) The temporal behavior of the phase separation might be divided into three time regions. (2) $R(t)$ and $I(0^\circ, t)$ [and $N(t)$, too] are rather well expressed by the power-law relations with time in the first and third stages. (3) $R(t) \sim t^1$, $I(0^\circ, t) \sim t^6$, and $N(t) \sim t^0$ in the first stage. (4) $R(t) \sim t^{1/3}$, $I(0^\circ, t) \sim t^1$, and $N(t) \sim t^{-1}$ in the third stage.

The second stage is a crossover regime, and the crossover seems to be smooth and the distinct intermediate stage of NG as suggested by Tokuyama was not observed [8]. However, the characteristic nature of the intermediate stage is not definitive enough in the present result. The third stage is considered to be the coarsening one during which the droplets grow with a constant mass fraction of the minority phase [$N(t)R(t)^3 \sim t^0$] and with a decrease in the number density by the Ostwald-ripening and/or the diffusion-reaction mechanism due to the Brownian motion characteristic of fluid systems [6,7]. The coarsening process was observed clearly by using the polymer solution in which the phase separation is slowed down and the density difference is very small. The first stage can be regarded as the growth stage following nucleation. The constancy of the number density of droplets during this stage is in good agreement with the theoretical prediction [8] and experimental result for a polymer mixture [13], and deviates from the formulation of homogeneous nucleation by Langer and Schwartz [16]. Inhomogeneous nucleation might occur in the present dilute solution; that is, a fixed number of sites grow preferentially by taking the surrounding polymer molecules into the droplet. The t^{-1} dependence of $R(t)$ is contrary to $t^{1/2}$ evolution where the dominant dynamic process is the diffusional process in the supersaturated solution in the period of free growth especially for very small supersaturation [6,8,17]. These points could be explained as follows. In the dilute polymer solution, the mixing of polymer molecules with droplets needs a formation of entanglement and diffusion of polymer chains in the entangled environment. According to de Gennes, the characteristic time τ for this process is evaluated as

$\tau \sim a^2 P^3 \phi^{3/2} / D_1$ with a , P , ϕ , and D_1 being the unit monomer length, degree of polymerization, volume fraction of the polymer in the droplet, and diffusion constant of the monomer, respectively [17]. Assuming $a \sim 0.25$ nm, $P \sim 6000$, $\phi \sim 0.18$, and $D_1 \sim 10^{-6}$ cm²/s [15], we obtain $\tau \sim 10$ s. On the other hand, the diffusional time of a polymer chain in the majority phase is evaluated as $(cR)^2 / (6D_0)$ with c and D_0 being some constant on the order of unity and the diffusion constant of a polymer chain ($\sim 8 \times 10^{-8}$ cm²/s), respectively. This is estimated, e.g., as ~ 0.1 s for $R \sim 1$ μ m. Thus the entanglement formation is much slower than the diffusional time and is the limiting process of phase separation. In this situation, the coalescence might be less effective through the similar mechanism proposed by Tanaka [5]. Since the environment surrounding the droplet is the majority phase with almost constant concentration in the present very dilute solution case, an entanglement formation takes place in proportion to the surface area of droplets and the evolution of droplets $dR(t)^3/dt$ is $\sim R(t)^2$ resulting in $R(t) \sim t^1$. The dominant mechanism which governs the growth stage of droplets of minority phase is not the diffusion process, but the entanglement formation of the polymer chains in the present case. From this viewpoint, the diffusion process in the majority phase for the supersaturated polymer-polymer mixture is itself the diffusion of a polymer chain in the entangled polymer network, and the dominant dynamic process of the phase separation is the diffusion process as in the case of simple binary liquid mixtures in the growth stage. Although the present result is a preliminary one because of various experimental limitations and further studies are still necessary, it should be noted that the asymmetry in the mobilities of the coexisting two phases plays an essential role in the phase-separating kinetics and the polymer solution systems exhibit qualitative modifications to the phase separation.

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