Polymerization-Induced Phase Separation in a Liquid-Crystal–Polymer Mixture

J. Y. Kim,[1,2] C. H. Cho,[1] P. Palffy-Muhoray,[1,2] M. Mustafa,[3] and T. Kyu[3]

[1]Liquid Crystal Institute, Kent State University, Kent, Ohio 44242
[2]Department of Physics, Kent State University, Kent, Ohio 44242
[3]Institute of Polymer Engineering, University of Akron, Akron, Ohio 44325

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We have used light scattering to study the kinetics of polymerization-induced phase separation in a liquid-crystal–polymer mixture. The evolution of the structure factor is compared with scaling predictions for thermally quenched systems. We have also observed a cascading phenomenon where phase separated domains become unstable and undergo phase separation for a second time.

Inhomogenous composite materials consisting of liquid crystals and polymers are of considerable current interest for fundamental scientific reasons and because of their very great potential for use in flat panel displays. Polymer stabilized cholesteric materials consist of a small amount of polymer dispersed throughout a continuous cholesteric liquid-crystal phase [1], while polymer dispersed liquid crystals (PDLC) consist of liquid-crystal droplets dispersed in a polymer matrix [2,3]. Both of these materials can be switched between states with different optical properties by modest applied fields, and this property makes them candidate materials for display applications. Both of these materials are formed by the phase separation of an initially homogeneous mixture of the liquid crystal and a prepolymer; typically, the phase separation is caused by polymerization. A great deal is known about the kinetics of phase separation induced by a thermal quench in liquid mixtures, alloys, and polymer blends; however, little work has been done to date on the kinetics of phase separation due to polymerization [4–9].

We have used light scattering to study the kinetics of polymerization-induced phase separation in a PDLC forming liquid-crystal–polymer mixture. The system under study consists of the commercial nematic liquid-crystal mixture E7, the epoxy Epon 828, and the curing agent Capcure [10] 3-800. E7 is a eutectic liquid-crystal mixture of cyanobiphenyls and terphenyls, Epon is a bifunctional epoxide of bisphenol, and Capcure is a trifunctional mercaptan. We studied a ternary mixture consisting of 0.45 weight fraction E7, 0.275 weight fraction Epon, and 0.275 weight fraction Capcure. The components were combined and stirred to form a homogeneous mixture which was centrifuged to remove dissolved air. The sample was contained between parallel glass plates separated by a 30 μm Mylar spacer. The sample temperature was held at $62 \pm 0.5\,°C$, $4\,°C$ above the nematic-isotropic transition temperature of the pure liquid crystal. Static light scattering measurements were carried out using a He-Ne laser.

The scattered intensity $I(q,t)$ is shown in Fig. 1 as a function of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where $\lambda = 6328$ Å and θ is the scattering angle. Although the polymerization process commences on mixing, no evidence of phase separation is seen for 37 min. After this induction period, there is an abrupt increase in the intensity of scattered light. Similar induction periods have also been observed using calorimetry [5]. The maximum scattered intensity increases with time, while q_{max}, the magnitude of the scattering vector where the scattered intensity is a maximum, decreases. After 42 min no further change in the angular distribution of scattered intensity profile can be detected.

The phase separation takes place at constant temperature, and is driven by polymerization instead of the usual thermal quench. As the condensation reaction proceeds, the average degree of polymerization increases, and eventually the system becomes unstable against phase separation. If the prepolymer and the curing agent in the PDLC forming mixture are considered as one species with molecules having the average degree of polymerization, then the system may be regarded as a pseudobinary mixture. The structure factor $S(q,t)$ in this case is the Fourier transform of the spatial correlation function of the dielectric constant at time t, and is proportional to the intensity $I(q,t)$ of the scattered light.

In the theory of Cahn and Hilliard [11–13] for the early stages of spinodal decomposition (SD), the time de-
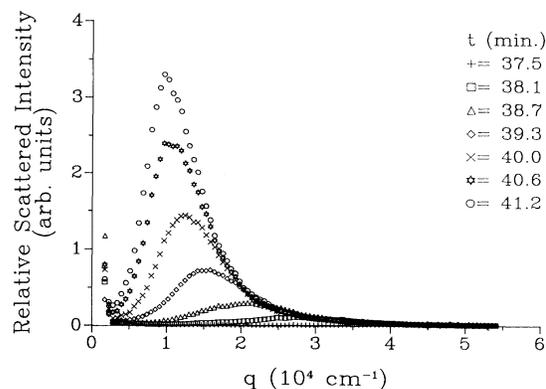

FIG. 1. Scattered intensity $I(q,t)$ vs the scattering vector q.

pendence of the structure factor is given by $S(q,t)$ $=S(q,0)e^{2R(q)t}$, where

$$R(q) = Mq^2 \left[-\left(\frac{\partial^2 f}{\partial \phi^2}\right) - 2\kappa q^2 \right]. \tag{1}$$

Here $R(q)$ is the growth rate, M is the diffusion mobility, f is the free energy density, and ϕ is the liquid-crystal concentration. In a polymerizing system, M and $\partial^2 f/\partial\phi^2$ are both expected to vary with time and the degree of polymerization. Hence, unlike in thermally quenched binary mixtures, q_{max} is expected to change with time even in the early stage.

The liquid-crystal–polymer system under study is a multicomponent mixture, whose components, in addition to the liquid crystal, are the n-mers whose distribution changes with time. A simple stability argument is as follows. An approximate expression for the free energy density of a multicomponent liquid mixture is [14], in the van der Waals approximation,

$$f = -\left(\sum_{i=0} a_i\phi_i\right)^2 + kT\sum_{i=0}\frac{\phi_i}{V_i}\ln\frac{\phi_i}{V_i}, \tag{2}$$

where a_i is a coupling constant (independent of molecular volume) and ϕ_i and v_i are the volume fraction and the molecular volume, respectively, of species i. The stability of the system is determined by the eigenvalues of the Hessian

$$\frac{\partial^2 f}{\partial\phi_i\,\partial\phi_j} = -2(a_0 - a_i)(a_0 - a_j) + kT\left[\frac{1}{v_0\phi_0} + \frac{\delta_{ij}}{v_i\phi_i}\right]. \tag{3}$$

If $i=0$ refers to the liquid crystal and, assuming that for the polymer $a_i = a_p$ for $i \geq 1$, the eigenvalues are the zeros [15] of $f(\lambda) = 1 + \varepsilon\sum 1/(\lambda - b_i)$, where $b_i = kT/v_i\phi_i$ and $\varepsilon = 2(a_0 - a_p)^2 + kT/v_0\phi_0$. The smallest eigenvalue is

$$\lambda_{min} \propto -2(a_0 - a_p)^2 + kT\left[\frac{1}{v_0\phi_0} + \frac{1}{\sum v_i\phi_i}\right]. \tag{4}$$

Since v_i increases with i, as the polymerization proceeds $\sum v_i\phi_i$ increases with time, and λ_{min} decreases. When λ_{min} becomes negative, the system becomes unstable and phase separation begins. Thus polymerization drives the system unstable via the increase in the average size of the polymer molecules, that is, in the volume averaged n-mer volume $\sum v_n\phi_n$.

In the late stage of phase separation, the scaling ansatz [16] for the structure factor is

$$\tilde{S}(q,t) = q_{max}^{-3}(t)F(q/q_{max}). \tag{5}$$

Since $\tilde{S}(q,t) = I_{nor}(q,t)$, $F(q/q_{max}) = I_{nor}q_{max}^3$. Figure 2 shows the scaling function $F(q/q_{max})$ at different times. Some deviation from the scaling prediction is observed near the wings and for the late time data; nonetheless there is reasonable agreement overall.
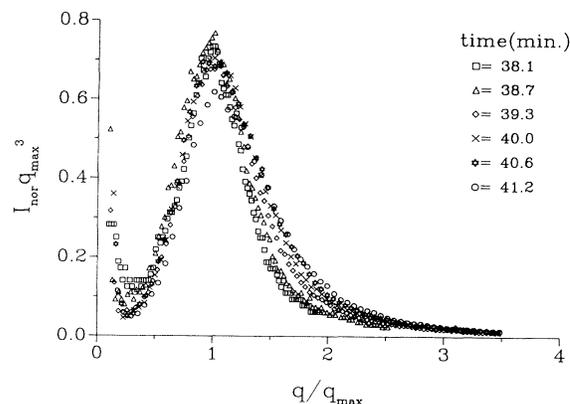

FIG. 2. The scaling function $F(q/q_{max}) = I_{nor}q_{max}^3$ vs the scaled wave vector q/q_{max}.

For the late stage of SD, Langer, Bar-on, and Miller [17], Binder and Stauffer [18], and Siggia [19] have considered, for thermally quenched binary mixtures, a power-law dependence of q_{max} on t:

$$q_{max} \sim t^{-\nu}. \tag{6}$$

Langer, Bar-on, and Miller predicted $\nu = 0.21$. Binder and Stauffer considered cluster dynamics with the result that $\nu = \frac{1}{3}$. Siggia predicted that, for mixtures with the critical composition, the initial growth is diffusional, and $\nu = \frac{1}{3}$, and that at long times the domain growth proceeds by coalescence due to surface tension and $\nu = 1$. Figure 3 shows the dependence of q_{max} on the time $t - t_0$, where t_0 is the induction time. For small $t - t_0$, our results are consistent with an exponent of $-\frac{1}{3}$. However, in this regime, the exponent sensitively depends on the value of t_0, and thus more data are required for its unambiguous determination. At later times, the exponent is clearly -1.

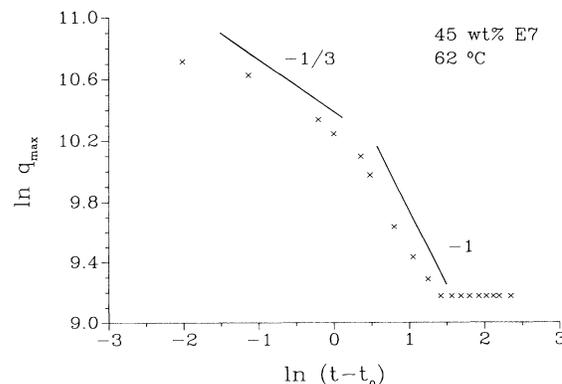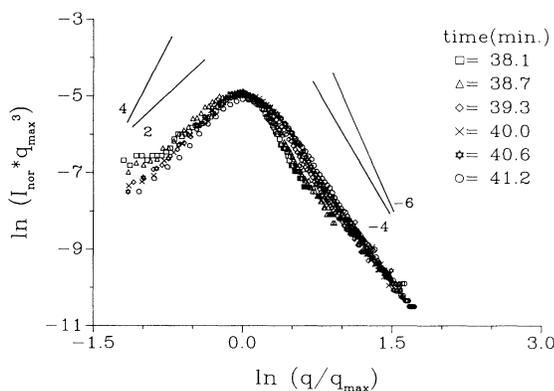Furukawa [20] proposed that the scaling function during the late stage of SD in d dimensions has the form

FIG. 3. $\ln q_{max}$ vs $\ln(t - t_0)$. The slope is a.

FIG. 4. $\ln(I_{nor}q_{max}^3)$ vs $\ln(q/q_{max})$.

$$F(x) = (1 + \gamma/2)x^2/(\gamma/2 + x^{2+\gamma}), \tag{7}$$

where $x = q/q_{max}$, and $\gamma = d + 1$ for an off-critical mixture and $\gamma = 2d$ for a critical mixture. For growth in three dimensions, $F(x) \sim x^2$ for $x < 1$, and $x > 1$, for off-critical quenches $F(x) \sim x^{-4}$, while for a critical mixture $F(x) \sim x^{-6}$. Furukawa subsequently also proposed [21,22] $F(x) \sim x^3/(2 + x^9)$ and $F(x) \sim x^4/(3/2 + x^{10})$ for the late stage of phase separation in three dimensions.

The exponent of the scaled scattering vector x for $x < 1$ in Fig. 4 takes on values between 2 and 4, in agreement with Furukawa's predictions. The exponent for $x > 1$ is -6 near $x \approx 1$, and -4 for $x \gg 1$. The exponent of -6 is typical for a thermally quenched critical binary mixture. In our system it may be manifest if the system is predominantly unstable, rather than metastable, during the phase separation process.

Phase separation was also observed using a microscope while the sample was curing at 45°C. In Fig. 5, two separated phases were observed during the early time of the phase separation. The characteristic domain size here is larger than in samples cured at 62°C. The domains grow both by direct coalescence and by the Lifshitz-Slyozov [23] evaporation-condensation mechanism. A striking phenomenon observed at a later time is that as polymerization continues, the material in both liquid-crystal-rich and polymer-rich phase separated domains again becomes unstable, and undergoes a second phase separation process, as shown in Fig. 5. Although similar observations have been made in systems which have been thermally quenched for a second time [24], we believe this is the first observation of a spontaneous second phase separation in an isothermal system. Our observation suggests the possibility of a sequence of such phase separation processes in polymerizing systems, which could lead to structures with hierarchical domain size distributions.

In summary, we have used light scattering techniques to study polymerization-induced phase separation in a liquid-crystal–epoxy mixture. The scaling relations for quenched binary fluids appear to hold for our system.
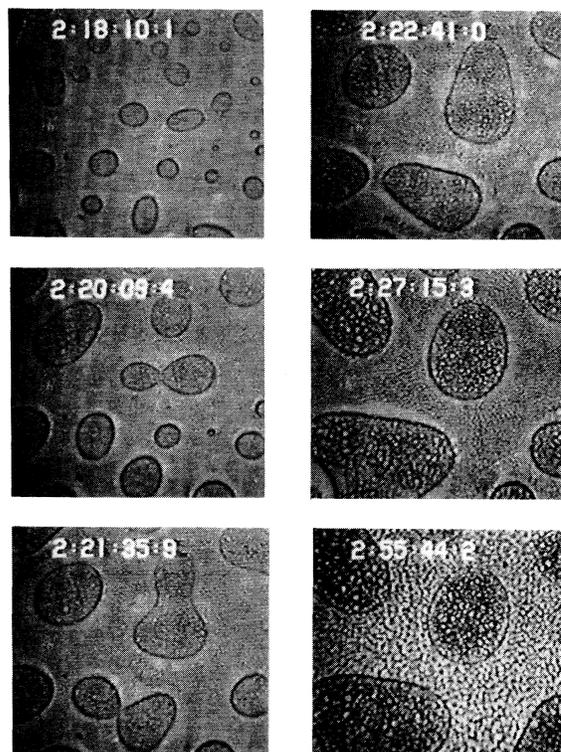
FIG. 5. Micrographs of the cascade phenomena where phase separation occurs for a second time. The horizontal dimension of each micrograph is 180 μm.

We have observed the crossover of q_{max} from a $(t - t_0)^{-1/3}$ to a $(t - t_0)^{-1}$ time dependence as predicted by Siggia for thermally quenched systems. The scaling behavior of the structure factor is in reasonable agreement with Furukawa's predictions. We have also observed a novel cascade phenomenon where spontaneous phase separation takes place for a second time in already phase separated domains.

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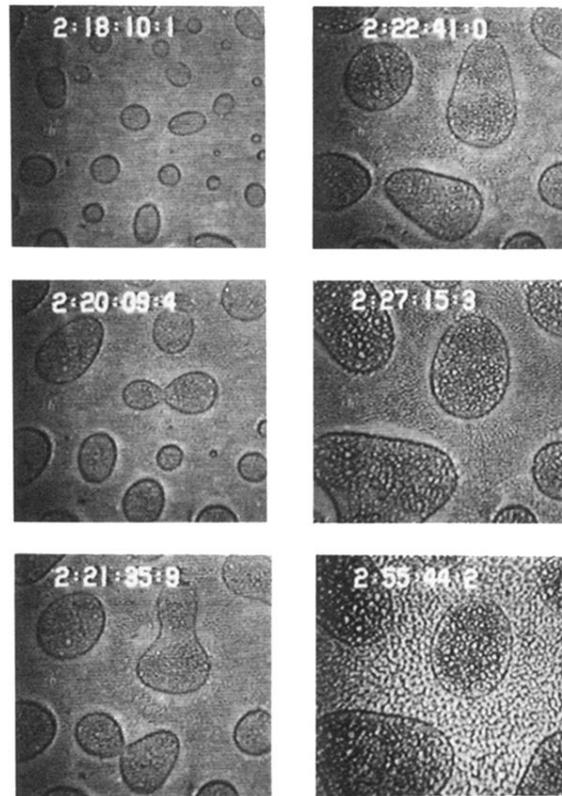[24] C. Casagrande, P. Fabre, M. A. Guedeau, and M. Veyssie, Europhys. Lett. **3**, 73 (1987).

FIG. 5. Micrographs of the cascade phenomena where phase separation occurs for a second time. The horizontal dimension of each micrograph is 180 μm.