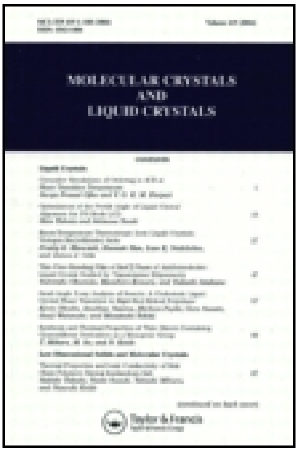

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Phase Separation Kinetics of a Liquid Crystal-Polymer Mixture

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Phase Separation Kinetics of a Liquid Crystal-Polymer Mixture

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Epoxy-based polymer-dispersed liquid crystal (PDLC) materials composed of the liquid crystal E-7, the epoxy Epon 828, and the curing agent Capcure 3-800 are formed via polymerization induced phase separation of the liquid crystal and the polymer. As the polymer reacts with the curing agent, the liquid crystal and the polymer become immiscible and the system phase separates with the liquid crystal eventually forming microdroplets in the polymer matrix. This system is interesting in that the instability of the homogeneous mixture against phase separation is brought about not by the usual temperature quench, but by polymerization of one of the components. The time evolution of the structure factor of the mixture has been studied by light scattering. We discuss the results in view of the predictions of Cahn-Hilliard theory.

1. INTRODUCTION

Phase separation due to a thermal quench in binary mixtures has been the subject of considerable attention,[1-6] and a great deal is known about the kinetics of this process. We report here our studies of the kinetics of phase separation in a fluid mixture where the phase separation is induced by polymerization rather than by a change of temperature. The system under study is a liquid crystal-prepolymer and curing agent mixture, which undergoes phase separation due to polymerization to form a polymer dispersed liquid crystal (PDLC) material. PDLC films are of considerable current importance in display applications,[7] and understanding the phase separation process which forms these materials is important for both fundamental and practical reasons.

In this paper we present our preliminary experimental results of light scattering measurements on the time evolution of the structure factor of the mixture as it undergoes phase separation. An attempt is made to relate these experimental results to simple Cahn-Hilliard theory.

2. SAMPLE PREPARATION

The mixture under study consists of the liquid crystal E7, the epoxy Epon 828 and the curing agent Capcure 3-800 in the ratio 2:1:1 by weight. The homogeneous mixture is placed in a cell consisting of two glass slides separated by a 27 μm thick mylar spacer. The cell is immersed in silicon oil in a thermostatted cylindrical cell housing. The sample temperature is kept at 62°C, above the nematic-isotropic transition of the pure liquid crystal. Polymerization takes place as the result of a condensation reaction between the epoxy and the curing agent. As the polymerization proceeds, the liquid crystal eventually phase separates and finally forms nearly spherical micron sized droplets dispersed in the polymer binder. Figure 1 shows a scanning electron micrograph (SEM) of a typical cured PDLC (33% liquid crystal E7 by weight) material.

3. THEORETICAL BACKGROUND

In order to make some contact with theoretical results for binary mixtures, we regard the liquid crystal E7 as one species, say component A, and consider the epoxy and the curing agent as the second species, component B. The Flory-Huggins free energy[8] for a mixture of polymers A and B is

$$\frac{\mathcal{F}}{kT} = \phi \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi\phi(1-\phi) \qquad (1)$$

where ϕ is the volume fraction of the liquid crystal, N_B is the degree of polymer-

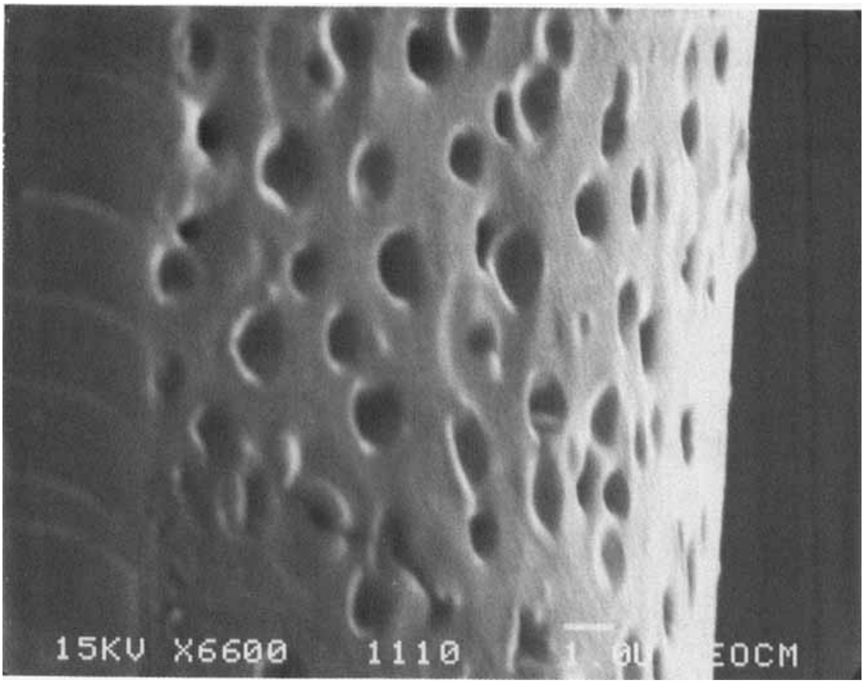

FIGURE 1 Scanning electron micrograph (SEM) of the cured PDLC material.

ization of component B, (the degree of polymerization of the liquid crystal is 1), k is Boltzmann's constant and χ is an interaction parameter. Initially, $N_B = 1$, the second derivative of the free energy with respect to composition is positive, and a homogeneous mixture is stable. As the polymerization proceeds, N_B increases with time, and the free energy takes on a double well form which favors phase separation for certain concentrations.

The theory of Cahn and Hilliard[1] describes the early stages of spinodal decomposition. It is based on the assumption that an inhomogeneous binary mixture can be described by a free energy.

$$F = \int [f(\phi) + \kappa(\nabla\phi)^2]\, d^3r, \tag{2}$$

where $f(\phi)$ is the free energy density of a homogeneous system with concentration ϕ, and κ is constant associated with the interfacial energy. The concentration diffusion is described by

$$\frac{\partial\phi}{\partial t} = M\left[\frac{\partial^2 f}{\partial\phi^2}\nabla^2\phi - 2\kappa\nabla^2\nabla^2\phi\right] \tag{3}$$

where M is the mobility. The time evolution of the structure factor is then given by

$$S(q, t) = S(q, 0)\exp[2R(q)t] \tag{4}$$

where

$$R(q, t) = Mq^2\left[-\left(\frac{\partial^2 f}{\partial^2\phi}\right) - 2\kappa q^2\right] \tag{5}$$

is the growth rate. The structure factor $S(q, t)$ is proportional to the intensity of scattered light, and may be determined from light scattering measurements. The maximum scattered intensity occurs at $q_{\max}{}^2 = -\partial^2 f/4\kappa\partial\phi^2$.

4. DATA ANALYSIS AND EXPERIMENTAL RESULTS

Our system is different from thermally quenched systems in that the second derivative of the free energy and the coefficient κ continuously change with time. We analyzed our results on the basis of Equation (3), and determined the quantities $M\ (\partial^2 f/\partial\phi^2)$ and κM as functions of time.

Figure 2 shows typical scattered intensity at a fixed angle as function of time. The initial homogeneous mixture is prepared at time $t = 0$; the onset of scattering occurs at a later time t_c. Figure 3 shows this onset time t_c as a function of concentration for two different curing temperatures. We assume that t_c is the time when the free energy becomes unstable and the phase separation process begins. Figure

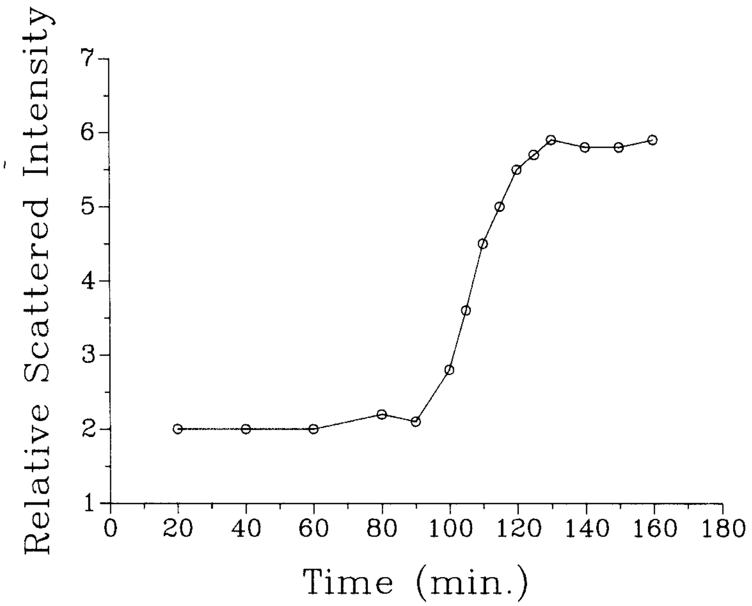

FIGURE 2 Scattered intensity as function of time.

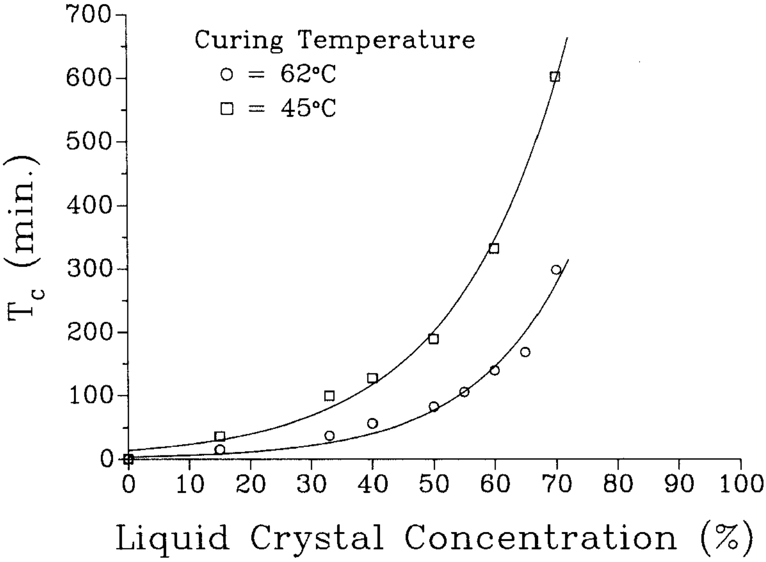

FIGURE 3 Onset time of phase separation as function of composition.

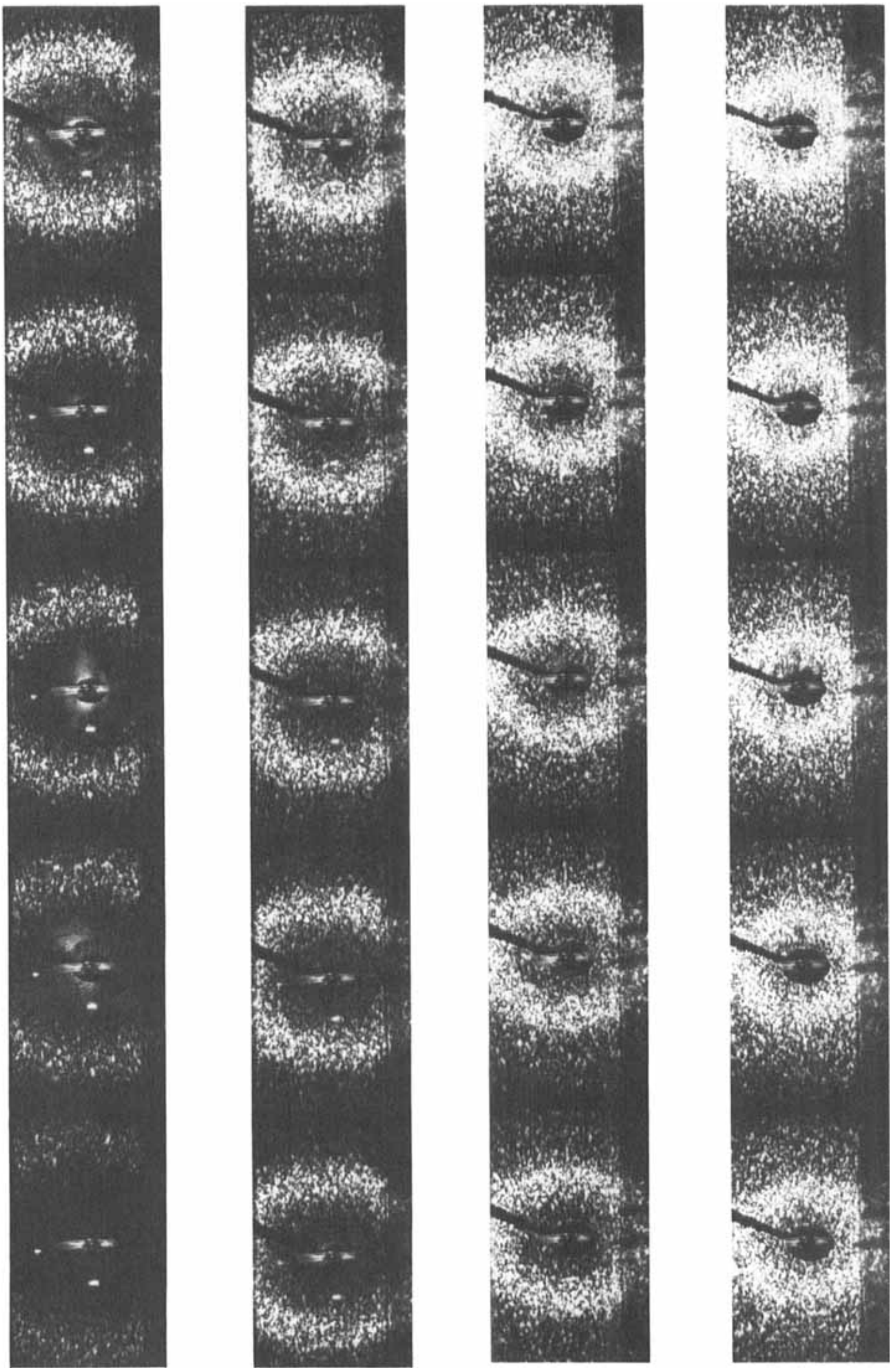

FIGURE 4 Time evolution of the diffraction pattern.

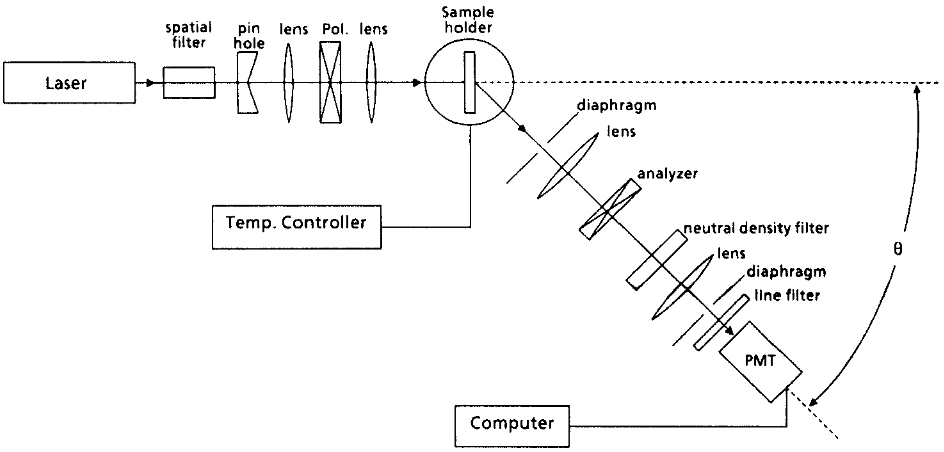

FIGURE 5 Schematic diagram of the light scattering set up.

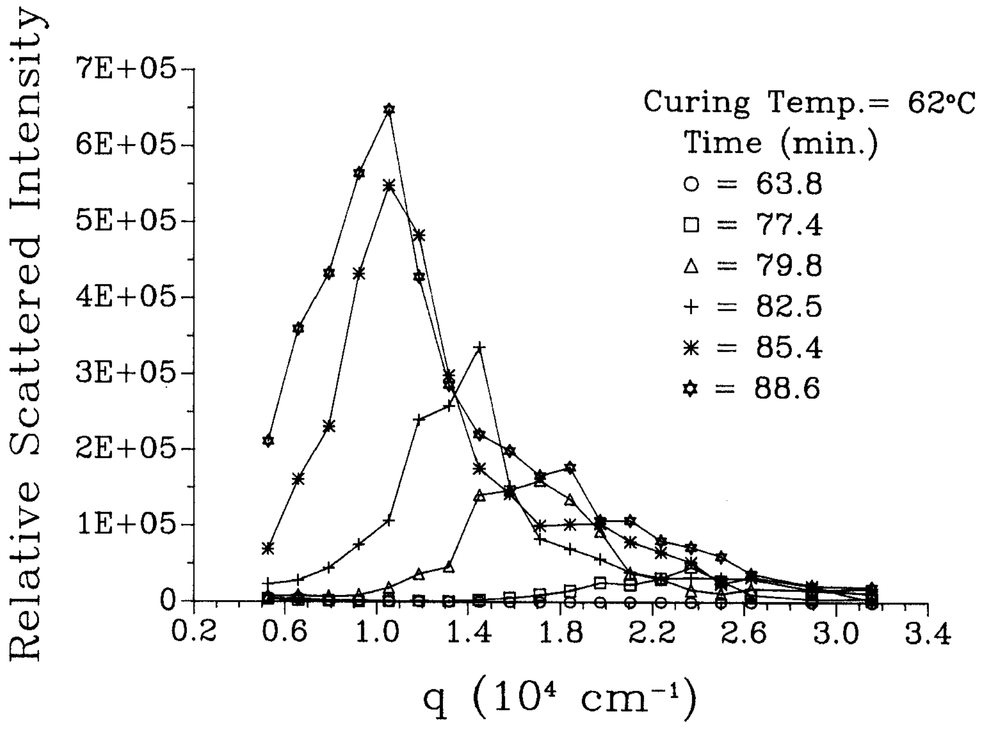

FIGURE 6 Scattered intensity as a function of angle and time.

4 shows the temporal evolution of the diffraction pattern; the elapsed time between photographs is 30 seconds. The decrease in the radius of the ring in the diffraction pattern indicates that $q_{\max}$ is decreasing with time. The structure factor can be more accurately determined by detailed measurements of the intensity of the scattered light as a function of angle. Figure 5 shows the schematic of the light scattering set-up and Figure 6 shows results of our preliminary measurements of the intensity of scattered light from a HeNe laser as a function of scattering angle. The scattering angle θ is related to the wave vector q by $q = 4\pi/\lambda \sin(\theta/2)$.

5. DISCUSSION AND CONCLUSIONS

In our sample, the convexity of the free energy $\partial^2 f/\partial\phi^2$, the mobility M of the liquid crystal and the coefficient κ are all expected to vary with time. On the basis of Equations 4 and 5, we have extracted values of $M\,\partial^2 f/\partial\phi^2$ and κM as functions of time from the results of our light scattering measurements. Values of these quantities are shown in Figure 7; the solid lines in the figure are merely to guide the eye. We expect that $-\partial^2 f/\partial\phi^2$ and κ both increase with time as the degree of polymerization N_B increases. Assuming that the mobility M is a weak function of N_B, this is consistent with our observations. The observed decrease of $q_{max}{}^2 = -\partial^2 f/4\kappa\partial\phi^2$ with time indicates that κ increases more rapidly than the curvature of the free energy.

In conclusion, we have observed phase separation in our liquid crystal-polymer mixture where the phase separation is induced by polymerization. In this system both the curvature of the free energy $\partial^2 f/\partial\phi^2$ and the coefficient κ change with time

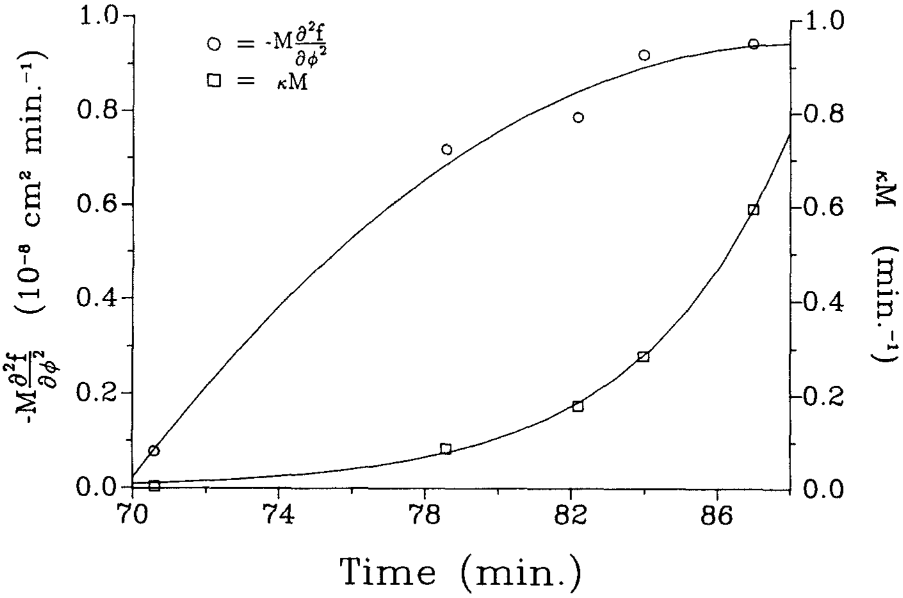

FIGURE 7 Variation of $-M\,\partial^2 f/\partial\phi^2$ and κM with time.

during phase separation. The onset of phase separation occurs well after the start of the polymerization process. The initial phase separation takes place rapidly (~ 8 min.) compared to the total curing time of >2 hrs. Our observations are in rough qualitative agreement with the predictions of simple theory for phase separation in binary mixtures. A detailed model of polymerization induced phase separation is needed to enable interpretation of the experimental results.

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