PHYSICAL REVIEW E VOLUME 60, NUMBER 1 JULY 1999

Effect of ordering on spinodal decomposition of liquid-crystal/polymer mixtures

Amelia M. Lapeña,[1] Sharon C. Glotzer,[2] Stephen A. Langer,[3] and Andrea J. Liu[1]
[1]*Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095-1569*
[2]*Polymers Division and Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*
[3]*Information Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

(Received 5 October 1998; revised manuscript received 29 April 1999)

Partially phase-separated liquid-crystal/polymer dispersions display highly fibrillar domain morphologies that are dramatically different from the typical structures found in isotropic mixtures. To explain this, we numerically explore the coupling between phase ordering and phase-separation kinetics in model two-dimensional fluid mixtures phase separating into a nematic phase, rich in liquid crystal, coexisting with an isotropic phase, rich in polymer. We find that phase ordering can lead to fibrillar networks of the minority polymer-rich phase. [S1063-651X(99)51207-5]

PACS number(s): 64.70.Md, 64.75.+g, 61.30.Cz, 81.05.Qk

Mixtures of liquid crystals with a small amount of polymer [polymer-stabilized liquid crystals [1–3] (PSLC's)] show promise for electro-optic devices, such as light shutters and displays [4–7], because the polymer tends to form a network that aligns the liquid crystal [8]. Since polymers and liquid crystals tend to be immiscible, the dispersions are prepared by mixing a small amount of miscible monomer with the liquid crystal and photopolymerizing. As the polymers grow, the system phase separates into an ordered phase rich in liquid crystal and an isotropic phase rich in polymer. Long before the system reaches equilibrium, however, the polymerization ‘‘freezes’’ the mixture into a crosslinked network of polymer-rich domains. Thus, the fabrication of PSLC's involves interplay among three kinetic processes: polymerization, phase separation, and phase ordering. Depending on the time scales that control these processes, a rich variety of morphologies has been observed [9–12]. Because of the number of nonequilibrium processes involved, however, there is little theoretical understanding of the factors that control the domain morphology. In this paper, we focus on the interplay between phase-separation and phase-ordering kinetics in mixtures of short, rigid polymers (*rods*) and long, flexible polymers (*coils*), as a first step towards rational design and control of the network morphology.

It is well known that thermodynamic factors, such as the anisotropy of the isotropic/nematic interfacial tension, can influence domain morphology, leading to anisotropic domain shapes. However, there are also kinetic factors that control domain morphology, such as the anisotropic diffusion coefficient of a rod. To capture these thermodynamic and kinetic effects, we use a Cahn-Hilliard framework that allows composition and orientational density to evolve in a coupled fashion as functions of position and time following a temperature quench [13]. In contrast to earlier studies that treat orientational density as a scalar order parameter [14–16], this framework includes the orientational density's second-order tensorial nature [17]. Although it is instructive to study the case of two coupled scalar order parameters (Model *C* [18]), a scalar cannot capture the direction of nematic order. Because a vector does not have head/tail symmetry, it is crucial to retain the tensor order parameter to obtain domain anisotropy [19].

To assess the effects of ordering, we study two systems. The first (denoted RC) is a mixture of rods and coils. The second (denoted CC) is a polymer blend, identical to RC except that the rods are replaced by flexible chains of the same length that do not align. In both cases, we solve the linearized coupled partial differential equations of motion analytically, and the nonlinear equations numerically into the late-time regime, after quenching the isotropic, homogeneous mixture into the coexistence region. We find that ordering dramatically affects morphology, giving rise, for example, to interconnected networks or elongated domains depending on whether ordering or phase separation is the initially dominant process.

We study two-dimensional, incompressible mixtures of chain molecules made up of monomers of the same size. In RC, we have short rods that are $N_A=10$ monomers long, and coils that are $N_B=100$ monomers long. The phase behavior of the system is governed by a bulk free energy [20,21] F_{RC} that couples the area fraction of rods, ϕ, to the orientational density of the rods, $\overleftrightarrow{S}$. This free energy consists of two parts: the Flory-Huggins free energy, which governs phase separation, and the Landau–de Gennes free energy, which governs the isotropic/nematic transition. The free energy was calculated within the random phase approximation [21]. It depends on the rod and coil lengths, and contains only two free parameters. These are the two interaction parameters, namely, the Flory parameter, χ, and the Maier-Saupe parameter, w, which control the isotropic and anisotropic monomer-monomer interactions, respectively. Both of these parameters depend on temperature with entropic and enthalpic contributions: $\chi=\chi_0+\chi_1/T$ and $w=w_0+w_1/T$. We have chosen the parameters χ_i and w_i so that the critical temperature for phase separation according to the Flory-Huggins free energy, T_c, and the isotropic/nematic transition temperature of the pure rod system, T_{ni}, are both of order unity in our (arbitrary) units, with T_{ni} higher than T_c. We use $\chi_0=0.055$, $\chi_1=0.036$, $w_0=0.55$, and $w_1=0.26$, which yield $T_c=1.14$ and $T_{ni}=1.3$. The resulting RC phase diagram is shown in Fig. 1. Below a triple point, the system demixes into an isotropic phase rich in coils and a nematic phase rich in rods.

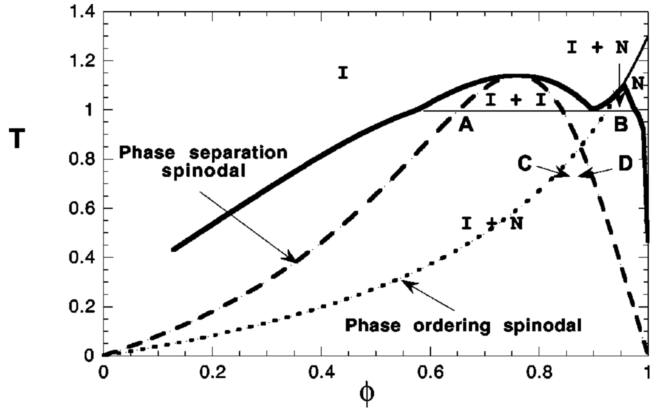

FIG. 1. Phase diagram of a two-dimensional rod/coil blend for the parameters discussed in the text. T is the temperature in arbitrary units chosen so that the IN transition temperature is of order unity, and ϕ is the local area fraction of rods. The heavy solid line is the coexistence curve. The spinodals are the limits of metastability of the isotropic phase. At low temperatures, an isotropic phase rich in coils coexists with a nematic phase rich in rods.

Above the triple point, there is an isotropic-isotropic coexistence region and an isotropic-nematic (IN) coexistence region. The IN coexistence region ends in a critical point that is connected to the IN transition of a pure rod system by a second-order transition line. Note that in three dimensions, the IN transition is first order, so the phase diagram would be different. Below the triple point, however, we find that the IN coexistence curves are qualitatively identical in two and three dimensions. The dashed line represents the spinodal for phase separation, while the dotted line is the spinodal for ordering.

In the CC system, we also use $N_A = 10$ and $N_B = 100$ monomers. Because the ''rods'' are now flexible, the free energy F_{CC} is given by the Flory-Huggins free energy only, without the Maier-Saupe contribution [22]. The parameter χ is exactly the same as in the RC system. Thus, CC is identical to RC except that there is no ordering.

We study the morphology following four quenches from the isotropic, homogeneous phase into the IN coexistence region below the triple point, to the four points marked A–D in the RC phase diagram. We use a simplified version of the equations of motion derived within the dynamical random phase approximation [13,23]

$$\frac{\partial \phi}{\partial t} = \Gamma_{\phi\phi} \nabla^2 \frac{\delta F(\phi, \overset{\leftrightarrow}{S})}{\delta \phi}, \tag{1}$$

$$\frac{\partial S^{ij}}{\partial t} = -\Gamma_{SS}^{ijkl} \frac{\delta F(\phi, \overset{\leftrightarrow}{S})}{\delta S^{kl}}, \tag{2}$$

where $\Gamma_{\phi\phi}$ and Γ_{SS}^{ijkl} are calculated Onsager coefficients that depend on the single chain and single rod diffusion coefficients; expressions for these coefficients are provided in Ref. [13]. The free energy functional $F(\phi, \overset{\leftrightarrow}{S})$ consists of the bulk free energy and a nonlocal free energy that controls the cost of gradients in composition and orientational density [21,23]. The free energy functional $F(\phi, \overset{\leftrightarrow}{S})$ is given by [21]

$$\begin{aligned} F = \int d\mathbf{r} \Bigg\{ & \frac{\phi}{N_A} \log \phi + \frac{1-\phi}{N_B} \log(1-\phi) + \chi \phi (1-\phi) \\ & + \frac{1}{2} [B(\phi) - w] S_{ij} S_{ji} - \frac{1}{3} C(\phi) S_{ij} S_{jk} S_{ki} \\ & + \frac{1}{4} D(\phi) S_{ij} S_{ji} S_{kl} S_{lk} + \frac{1}{2} M_0(\phi) (\boldsymbol{\nabla} \phi)^2 \\ & + L_0(\phi) \partial_i \phi \partial_j S_{ij} + \frac{1}{2} L_1(\phi) (\partial_k S_{ij})^2 \\ & + \frac{1}{2} L_2(\phi) \partial_i S_{ik} \partial_j S_{jk} \Bigg\}. \end{aligned} \tag{3}$$

The coefficients $B(\phi)$, etc., are calculated from a microscopic model in Ref. [21]. For simplicity, we replace the local value of ϕ with its global average when evaluating the coefficients of the gradient terms. $L_1(\phi)$ and $L_2(\phi)$ are related to the Frank elastic constants if the magnitude of S is held constant. The sign of the L_0 term dictates that the liquid crystal molecules will align parallel to the interfaces. For CC, the time evolution is given by Eq. 1 alone, since $\overset{\leftrightarrow}{S} = 0$ and $\delta F_{\mathrm{CC}} / \delta S^{ij} = 0$. We emphasize that the equations of motion are not phenomenological; they are derived from microscopic models. We solve the discretized equations on a square lattice of size 150^2 using a variable timestep Runge-Kutta numerical integration scheme. We have also varied the number of lattice points and the size of the mesh to verify that our observations do not depend on system size or discretization.

Quench A. Here we quench to a point where RC is initially unstable with respect to phase separation, but metastable with respect to ordering. Thus, the point marked A in Fig. 1 lies below the spinodal for phase separation and above the one for ordering. For CC, where ordering is absent, this quench leads to circular droplets rich in the shorter coils, in a matrix rich in the longer coils. RC initially displays almost identical behavior with circular droplets rich in rods. Once the concentration of rods in the droplets is comparable to the

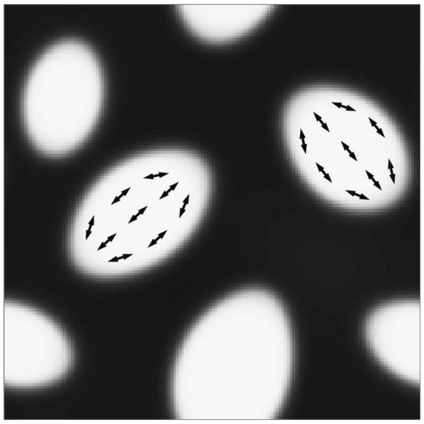

FIG. 2. Late-time snapshot of the local composition for the RC system when quenched to A, as indicated in Fig. 1. We use a gray scale where black corresponds to pure coils and white corresponds to pure rods. The arrows represent the local nematic director (shown for two droplets only).

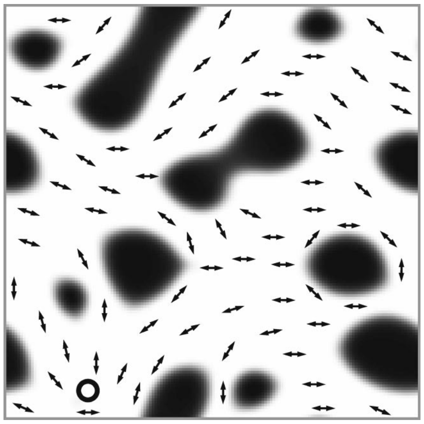

FIG. 3. Snapshot of the local composition for the RC system at a late time following a quench to *C*. Black corresponds to pure coils and white corresponds to pure rods. The arrows illustrate the local nematic director, and a defect is marked with a circle.

concentration at the IN spinodal, however, the rods in the droplets begin to order. At this time, the droplets abruptly expel more coils because the coils are less soluble when the rods are ordered. In addition, the droplets must develop defects because the rods want to be parallel to each other and parallel to the droplet interface. As the rods order, a pair of defects forms inside each droplet and separates, with the two defects moving along the director in opposite directions towards the edge of the droplet. The magnitude of orientational order is lower at the edges than in the center; thus, the defects migrate towards the edges to lower their energy. Since the overall system is isotropic, the long axis of each droplet is randomly oriented. Note that it is essential to retain the tensorial nature of the orientational order parameter in order to obtain *randomly oriented* elongated domains. Figure 2 shows a snapshot of the RC system at a time at which there is significant phase separation and ordering.

Quench B. For this quench, CC is stable with respect to phase separation, so it does not evolve. In this region RC is initially metastable with respect to phase separation, but it is unstable with respect to ordering. The instability towards orientational ordering eventually drives the system to phase separate because the two order parameters are coupled. This makes physical sense; once the rods are strongly aligned, they expel the coils into isolated droplets. Although there is no orientational order within the coil-rich droplets, the droplets are anisotropic because of the nematic elasticity in the surrounding rod-rich matrix.

The appearance of droplets even when the system is only metastable to phase separation is reminiscent of recent theoretical work on protein and polymer crystallization, which shows that a quench below the spinodal for one order parameter (density) can promote domain growth in another order parameter (crystallization) [24,25]. The advantage of our system is that we can calculate the coupled equations of motion for our two order parameters from a microscopic model of rods and coils.

Quench C. In this quench, RC is initially unstable both to phase separation and to ordering, but is more unstable with respect to phase separation. In both RC and CC, the system forms a bicontinuous network that rapidly breaks up into droplets rich in long coils. In RC, however, defects in the surrounding rod-rich domains give rise to droplets that are noncircular, as shown in Fig. 3. Furthermore, the coupling of phase separation and ordering leads to a faster onset of phase separation in RC than in CC, because the rod-rich regions tend to expel coils as the rods order [16].

Quench D. As in Quench *C*, RC is initially unstable both to phase separation and to ordering. However, in this quench it is more unstable with respect to ordering. Once the degree of order is significant, then phase separation begins. Because of ordering, phase separation begins much earlier in RC than in CC; by the time CC displays any noticeable phase separation, the concentration difference between the two phases in RC has already reached its equilibrium value. Figure 4 presents snapshots of RC as it evolves in time. In CC (not shown), the minority phase forms circular droplets. In RC, on the other hand, small highly ordered rod-rich droplets initially form in a coil-rich matrix. As these rod-rich droplets grow, the surrounding coil-rich region shrinks into a network of interconnected domains that are strikingly fibrillar, despite the fact that the coil-rich phase is the minority phase. This is in contrast to systems with only a compositional order parameter (model *B* [18]), where only the majority phase can form networks. Eventually, this network breaks up to form coil-rich droplets; again, these are noncircular because of defects in the surrounding rod-rich regions. However, in experiments the crosslinking of the polymer network may arrest the phase separation at the fibrillar network stage.

In summary, we find that ordering can significantly influence domain morphology, especially when (i) the system is unstable to both phase separation and ordering and (ii) orientational order is significant at the onset of phase separation. This is consistent with morphologies observed in

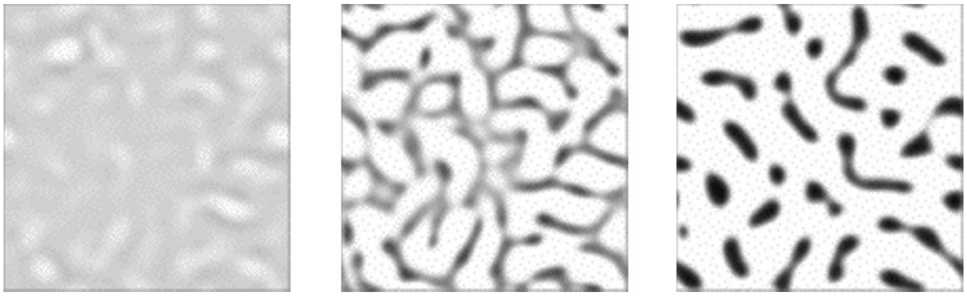

FIG. 4. Snapshots of local composition as a function of time *t* in RC following a quench to point *D* on the phase diagram in Fig. 1. Black corresponds to pure coils while white corresponds to pure rods. Note that ordering drives the system to a fibrillar network morphology of coil-rich domains at intermediate times.

PSLC's, where fibrillar networks of the minority polymer-rich domains form when the system is initially ordered [9–11]. Our results show that we can learn much about domain morphology from the phase diagram and spinodal lines, and that the coupling of phase separation and ordering kinetics leads to rich phenomena that warrant further study.

We thank Abdullah Al Sunaidi, Rashmi Desai, Weinan E, Peter Palffy-Muhoray, and Rebecca M. Nyquist for stimulating and instructive discussions that led to this research. This work was supported by NIST through the Center for Theoretical and Computational Materials Science, and by the NSF through Grant No. CHE-9624090 (A.J.L.).

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