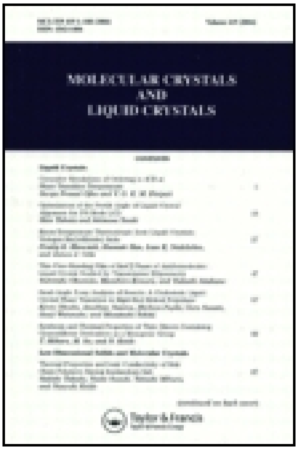

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POLYMERIZATION-INDUCED PHASE SEPARATION OF POLYMER-DISPERSED LIQUID CRYSTAL

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Polymerization-Induced Phase Separation of Polymer-Dispersed Liquid Crystal

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Polymerization-induced phase separation in polymer-dispersed liquid crystal is studied by computer simulations in two dimensions. The domain morphology resulting from phase separation is investigated by solving the couple set of equations for the local volume fraction and the nematic order parameter, taking into account the viscoelastic effects and gelation due to polymerization. Comparing the morphology of phase separation by temperature quench, it is shown that the viscoelastic effects and gelation enable the polymer-rich phase to form a stable interconnected domain even when the polymer component is minority.

Keywords: polymer-dispersed liquid crystal; polymerizaiton; phase separation; viscoelastic effect; gelation

INTRODUCTION

Polymer-dispersed liquid crystals have attracted much attention recently as novel materials for display application. It is the most common method in the technological application that photo-polymerizing induces phase separation between polymers and liquid crystals and freezes the polymer-rich phase formed into network structure. Although this method involves interplay among three kinetic processes: polymerization, phase separation, and nematic ordering, there is little theoretical understanding on influences of polymerization process. In this paper, we focus our attention on viscoelastic effect due to the polymerization which is expected to be more important for the kinetics of domain morphology.

FREE ENERGY AND KINETIC EQUATIONS

Free Energy of Polymer-Dispersed Liquid Crystal

In order to represent the kinetics of polymer-dispersed liquid crystal, one needs two kinds of basic variable. One is the local volume fraction of polymer $\phi(\vec{r},t)$. By assuming the incompressibility, the local volume fraction of LC(liquid crystal) molecules is given by $1-\phi(\vec{r},t)$. The other variable is the tensor order parameter $Q_{\alpha\beta}(\vec{r},t)=\frac{3}{2}S\{n_\alpha n_\beta-\frac{1}{3}\delta_{\alpha\beta}\}$ where $S(\vec{r},t)$ is the degree of nematic order and $n_\alpha(\vec{r},t)$ is the α-th component of the director field $\vec{n}(\vec{r},t)$. $(\alpha=x,y,z)$

We employ a simplified version of the free energy proposed by Motoyama *et al.* [1]. The free energy is a functional of ϕ and $Q_{\alpha\beta}$,

$$F[\phi,Q_{\alpha\beta}]=\int d\vec{r}\,\Big[\frac{C_0}{2}(\nabla\phi)^2+\frac{C_1}{2}(\nabla_\gamma Q_{\alpha\beta})(\nabla_\gamma Q_{\alpha\beta}) + f_p(\phi)+f_L(\phi,Q_{\alpha\beta})\Big] \tag{1}$$

with

$$f_p(\phi)=\frac{1}{N_p}\phi\ln(\phi)+(1-\phi)\ln(1-\phi)+\frac{\chi_0}{T}\phi(1-\phi) \tag{2}$$

and

$$f_L(\phi,Q_{\alpha\beta})=A(\phi)(\mathrm{Tr}Q^2)+B(\mathrm{Tr}Q^3)+D(\mathrm{Tr}Q^2)^2 \tag{3}$$

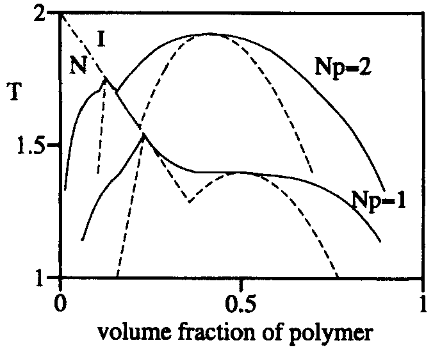

Figure 1: Phase diagram for $N_p = 1$ and $N_p = 2$ fixing other parameters as $\chi_0 = 2.8$, $T_c = 2$, $B = 0$, $C_2 = 2$ and $D = 1$. The symbol I (N) means as isotropic (nematic) phase. The full line is the coexistence curve. The dotted- broken line is the transition line from isotropic to nematic phase. The dotted lines are the spinodal lines.

where the repeated indices imply summation. N_p is given by $N_p = n_p/n_L$ with n_p and n_L the molecular weight of polymers and LCs, respectively. T is the temperature and χ_0 a positive constant. The coupling between ϕ and $Q_{\alpha\beta}$ appears in the coefficient A such that $A(\phi) = T - (T_c - C_2\phi)$ where T_c is the isotropic-nematic transition temperature in the absence of polymers and C_2 a positive constant. Figure 1 is an example of the phase diagram for $N_p = 1$ and $N_p = 2$ obtained from (1).

Equations of Motion

Since the order parameter $Q_{\alpha\beta}(\vec{r}, t)$ is a non-conserved quantity, the simplest form of the time-evolution equation is given by

$$\frac{\partial Q_{\alpha\beta}}{\partial t} = -M_L \frac{\delta F[\phi, Q_{\alpha\beta}]}{\partial Q_{\alpha\beta}} + \lambda_{\alpha\beta} + \eta_{\alpha\beta}, \tag{4}$$

where the constant $\lambda_{\alpha\beta}$ is the Lagrange multiplier and is determined by the condition Tr $Q = 0$, and the last term $\eta_{\alpha\beta}$ is the thermal random forces which satisfy the fluctuation dissipation relation,

$$\langle \eta_{\alpha\beta}(\vec{r}, t)\eta_{\gamma\delta}(\vec{r'}, t')\rangle = M_L(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\delta(\vec{r} - \vec{r'})\delta(t - t'). \tag{5}$$

It should be noted that the traceless property must be taken into account in the generation of the thermal noise $\eta_{\alpha\beta}$ in simulations. M_L is an Onsager coefficient.

Next we need to derive the time-evolution equation for $\phi(\vec{r},t)$. Assuming that LC molecules do not cause any viscoelasticity, we here use the two-fluid model introduced originally for polymer-solvent mixtures [2].

Let $\vec{v}_p(\vec{r},t)$ and $\vec{v}_L(\vec{r},t)$ be the average velocities of polymer and LC-solvent, respectively. Assuming that the two components have the same density ρ, the volume average velocity is given by $\vec{v} = \phi\vec{v}_p + (1-\phi)\vec{v}_L$. The kinetic equations for ϕ, $\vec{v}$ and $\vec{v}_p$ are given in the two-fluid model by

$$\frac{\partial\phi}{\partial t} + \vec{\nabla}\cdot(\phi\vec{v}) = \vec{\nabla}\cdot\frac{\phi(1-\phi)^2}{\zeta}\left[\vec{\nabla}\cdot\Pi - \vec{\nabla}\cdot\sigma\right] \tag{6}$$

$$\vec{v}_p - \vec{v} = -\frac{(1-\phi)^2}{\zeta}\left[\vec{\nabla}\cdot\Pi - \vec{\nabla}\cdot\sigma\right] \tag{7}$$

$$\rho\frac{\partial\vec{v}}{\partial t} \cong -\vec{\nabla}\cdot\Pi + \vec{\nabla}p + \vec{\nabla}\cdot\sigma + \eta_L\nabla^2\vec{v} \tag{8}$$

where ζ is the friction constant, p is a part of the pressure given by $\vec{\nabla}\cdot\vec{v} = 0$, and η_L is the LC-solvent viscosity. Here Π is the osmotic tensor defined through the relation $\vec{\nabla}\cdot\Pi = \phi\vec{\nabla}\left[\frac{\delta F}{\delta\phi}\right]$. The total stress tensor σ can be evaluated from the shear stress σ_S and the bulk stress σ_B by using the relation

$$\sigma = \sigma_S - \frac{1}{d}(\mathrm{Tr}\ \sigma_S)I + \frac{1}{d}(\mathrm{Tr}\ \sigma_B)I, \tag{9}$$

where I is the unit tensor and d $(= 2)$ is the dimensionality of space. The shear stress obeys the upper convective constitutive equation [3]

$$\frac{\partial\sigma_S}{\partial t} + \vec{v}_p\nabla\sigma_S = (\vec{\nabla}\vec{v}_p)^T\cdot\sigma_S + \sigma_S\cdot(\vec{\nabla}\vec{v}_p) - \frac{1}{\tau_S}\sigma_S + M_S\{\vec{\nabla}\vec{v}_p + (\vec{\nabla}\vec{v}_p)^T\}. \tag{10}$$

The bulk stress tensor is assumed to take a diagonal form $\sigma_{B_{ij}} = q\delta_{ij}$ where

$$\frac{\partial q}{\partial t} + \vec{v}_p\nabla q = -\frac{1}{\tau_B}q + M_B(\vec{\nabla}\cdot\vec{v}_p). \tag{11}$$

The relaxation times τ_S and τ_B and the coefficients M_S and M_B used in simulations will be fixed in the next section.

SIMULATIONS

We have to take into consideration of polymerization in our model equations. Polymerization causes two effects. One is the shift of the coexistence curve as shown in Fig. 1. We assume the following form of N_p in the bulk free energy (2).

$$N_p(t) = N_p^\infty - (N_p^\infty - N_p^0)\, e^{-gt}, \tag{12}$$

where N_p^0 and N_p^∞ are the initial and the final values of $N_p(t)$, respectively, and g represents the polymerization rate. In this paper, we fix $N_p^0 = 1$ and $N_p^\infty = 2$.

The other effect of polymerization is a change of the viscoelastic properties, which appear in Eq. (10) and (11). The magnitude of the shear and the bulk moduli, M_S and M_B are assumed to have the same ϕ-dependence as the previous study [3], $M_S = 0.5\ \phi^2$ and $M_B = 5\ \theta(\phi - \phi^*)$. θ is a step function and ϕ^* is the threshold value of ϕ. In the simulations, we choose $\phi^* = \phi_0$. This means that the bulk modulus appears when the volume fraction exceeds the average volume fraction ϕ_0. In simulations, we examine two different sets of the relaxation times

$$\tau_w^{(1)} = \alpha_w\ \phi^2 N_p(t)^3 \tag{13}$$

and

$$\tau_w^{(2)} = \beta_w \left[\exp\left\{aN_p(t)^3(\phi - \phi_0)\right\} + 1\right] \tag{14}$$

where w stands for either B or S. We put $\alpha_S = 5$, $\alpha_B = 10$, $\beta_B = 0.5$, $\beta_S = 0.25$ and $a = 3$ in the simulations. The first ones (13) have the same ϕ-dependence as the previous study [3] but with N_p^3-dependence expected by the reptation theory [4] assuming an incomplete gelation. The second ones (14) mean that if a complete gelation occurs after polymerization, the system is purely elastic so that the relaxation rate becomes infinitesimal and hence has a strong concentration dependence.

In order to simulate the time evolution of the nematic ordering, we choose Q_{zz}, Q_{xz} and Q_{yz} as independent variables. These three components are sufficient to determine the values of S and $\vec{n}$. This numerical scheme will be described in detail elsewhere.

RESULTS OF SIMULATIONS

First we show the phase ordering quenched inside the coexistence line for fixed value of $N_p = 1$. We have used the relaxation time given by (13).

When $\phi_0 = 0.25$, an interconnected domain of polymer-rich phase appears in the intermediate time but it eventually breaks into disconnected domain, which is the phase inversion found by Tanaka and Araki in polymer-solvent mixtures [3].

If we further decrease the average volume fraction, nucleation and growth of the minority phase (polymer-rich phase) occurs as in Fig. 2 for $\phi_0 = 0.2$, which is the same as the case without viscoelasticity.

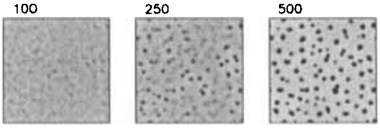

Figure 2: Time evolution of phase separation by temperature quench for $T = 1.2$ and $\phi_0 = 0.2$. (The parameters are fixed as $\chi_0 = 2.8$, $T_c = 2$, $B = -0.01$, $C_0 = 1$, $C_1 = 1$, $C_2 = 2$, $D = 1$, $M_L = 1$, $\eta_L = 0.1$ and $\zeta = 0.1$. Numerical calculations are carried out under the periodic boundary condition with the grid size $\Delta x = \Delta y = 1$ for the system size 128×128. The time step is chosen as $\Delta t = 0.01$. The initial value of ϕ at each sell is generated by random number uniformly distributed in the interval $\phi_0 - 0.001 < \phi < \phi_0 + 0.001$. The initial values of Q_{zz}, Q_{xz} and Q_{yz} are generated by setting $S = 0.1$ and the randomly oriented director $\vec{n}$. Other initial values are set as $\vec{v} = 0$, $\vec{v}_p = 0$ and $\sigma = 0$. The magnitude of the random forces η_{zz}, η_{xz} and η_{yz} is set to be 0.0025.)

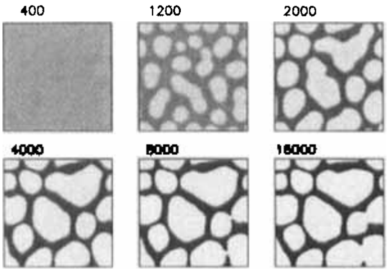

Figure 3: Time evolution of phase separation induced by polymerization for $T = 1.55$, $\phi_0 = 0.2$ and $g = 0.001$.

Now we study polymerization-induced phase separation by changing the molecular weight of polymers as Eq. (12). Figure 3 shows the time-evolution of domains at $T = 1.55$, $\phi_0 = 0.2$ and the polymerization rate $g = 0.001$. We have used the relaxation time given by (14). After polymerization is initiated, the nematic LC domain grows and the polymer-rich phase constitutes an interconnected domain. It is emphasized that this behavior is entirely different from Fig. 2 for temperature quench at the same average volume fraction $\phi_0 = 0.2$. Then the coagulation of LC-rich domains is quite rare in Fig. 3. Thus the interconnected domain of the polymer-rich phase is stable. This is due to the $\phi-$dependence of (14) such that the relaxation rates are vanishingly small for a large value of ϕ. In fact, if one uses (13), the interconnected domain is found to be unstable as in Fig. 2.

DISCUSSION

We have introduced a set of kinetic equations for polymerization-induced phase separation of polymer-dispersed liquid crystals and investigated the morphology and kinetics of phase separation process. The novel aspect in our system is to take account of gelation due to polymerization. To our knowledge, this is the first attempt for modeling gelation in a mesoscopic approach.

In a previous paper [3], the viscoelastic effect in polymer-solvent mixtures causes a phase inversion in the course of phase separation, where an interconnected domain of the polymer-rich phase is stable only transiently. However if we take into account of gelation as (14), the interconnected structure formed by this polymer-rich domain becomes more stable and the phase inversion is not observed within the limit of a simulation time. Thus our model equations are capable to reproduce at least qualitatively the domain morphology observed experiments. In order to make a more quantitative comparison, however, further tuning of the parameters is necessary.

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