Phase separation and gelation of polymer-dispersed liquid crystals

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Abstract

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 coupled 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. The experimental evidence consistent with this characteristic feature is also given. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymer-dispersed liquid crystals (mixture of liquid crystals with a small amount of polymer) have recently attracted much attention 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 a network structure [1–8].

Polymerization-induced phase separation of polymer-dispersed liquid crystals involves the interplay among three kinetic processes: phase separation, nematic ordering and gelation. Hence, in order to investigate this phase ordering theoretically, we have to introduce a fairly large number of kinetic variables.

So far equilibrium properties such as phase diagram with or without gelation have been studied by several authors [9–13]. Early stage of spinodal decomposition by a temperature quench in polymer-dispersed liquid crystals has been studied theoretically [14]. Simulations of the dynamics of phase separation have been carried out not by polymerization but by a temperature quench [15].

In our previous paper [16], we also studied phase separation in liquid crystal–polymer mixtures induced both by polymerization and by a temperature quench. The basic variables chosen there were the local polymer volume fraction $\phi$ and the nematic order parameter $Q_{\alpha\beta}$. The domain morphology in the process of phase separation was investigated by computer simulations.

One of the most unusual properties of domain morphology in polymerization-induced phase separation is that polymer-rich domains constitute a stable interconnected network even when polymer is the minority component as was shown in the experimental section of Ref. [16]. This feature was not completely realized by our previous theoretical study [16].

In order to overcome this difficulty, we, in this paper, extend our model system to take into account the viscoelastic effects and gelation. The appearance of the interconnected network of a component with slower dynamics is a generic feature of viscoelastic phase separation [17]. Tanaka and Araki have shown by computer simulations of polymer–solvent mixtures that the viscoelasticity of polymer-rich domain causes a transiently interconnected domain [18].

We generalize their model equations based on a two-fluid model [19] to polymer-dispersed liquid crystals. A remaining problem is to model gelation. Although kinetics of gelation have been formulated in terms of a molecular 4
picture [20], such a microscopic description is not suitable for the present mesoscopic approach. Therefore, we assume phenomenologically two different forms of the stress relaxation rates and explore its consequence. This paper is organized as follows. In Section 2, we introduce the set of kinetic equations as well as the free energy functional in terms of $\phi$ and $Q_{a\beta}$. Since the kinetic equations are fairly complicated, we make several simplifications such that the anisotropy of the Onsager coefficient due to liquid crystal molecules and the dynamic cross coupling between $\phi$ and $Q_{a\beta}$ are ignored. In Section 3, we introduce the form of the stress relaxation rates. The domain morphology obtained by simulations for a temperature quench and for polymerization is shown in Section 4 and is compared with experimental results in Section 5. Discussion is given in Section 6. In Appendix A, we describe the methods of simulations of nematic ordering in detail.

2. Kinetic equations for phase ordering

2.1. 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 liquid crystal (LC) molecules is given by $1 - \phi(\vec{r},t)$. The other variable is the tensor order parameter defined by

$$Q_{a\beta} = \frac{3}{2}S\left(n_a n_\beta - \frac{1}{3} \delta_{a\beta}\right).$$  (1)

where $S$ is the degree of nematic order and $n_a$ is the $a$th component of the director field $\vec{n}$. Throughout this article, we consider the situation that phase separation is in two dimensions but the director has three components ($\alpha = x, y, z$).

We employ a simplified version of the free energy introduced by Motoyama et al. [16], which is a functional of $\phi$ and $Q_{a\beta}$ and consists of two parts,

$$F[\phi, Q_{a\beta}] = F_p[\phi] + F_L[\phi, Q_{a\beta}].$$  (2)

The first part depends only on $\phi$ and is given by

$$F_p[\phi] = \int dV \left[ \frac{C_0}{2} (\nabla \phi)^2 + f_p(\phi) \right]$$  (3)

with

$$f_p(\phi) = \frac{1}{N_p} \phi \ln(\phi) + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi),$$  (4)

where $N_p$ is given by $N_p = n_p/n_L$ with $n_p$ and $n_L$ the molecular weight of polymers and LCs, respectively. We have chosen the unit such that the molecular weight of LCs is equal to unity. We assume that $\chi$ is inversely proportional to the temperature $T$ as

$$\chi = \frac{\chi_0}{T}$$  (5)

with $\chi_0$ a positive constant.

The second part of the free energy takes the form that

$$F_L[\phi, Q_{a\beta}] = \int dV (1 - \phi) \times \left[ \frac{C_1}{2} (\nabla \phi)(\nabla \phi) + f_L(\phi, Q_{a\beta}) \right],$$  (6)

where the repeated indices imply summation and

$$f_L(\phi, Q_{a\beta}) = A(\phi)(\text{Tr} Q^2) + B(\text{Tr} Q^3) + D(\text{Tr} Q^2)^2.$$  (7)

The coupling between $\phi$ and $Q_{a\beta}$ appears in the coefficient $A$ such that

$$A(\phi) = T - (T_c - C_2 \phi),$$  (8)

where $T_c$ is the isotropic–nematic transition temperature in the absence of polymers and $C_2$ a positive constant. The relation (8) implies that nematic ordering is disturbed by the existence of polymers so that the transition temperature is a decreasing function of $\phi$.

Since the kinetic equations for polymer-dispersed liquid crystal are fairly complicated, we have made several simplifications in the free energy (7). First of all, we do not consider the case of biaxial nematics ignoring the $(\text{Tr} Q^2)^3$ term. Secondly, there are generally two other terms which contain the spatial gradient of $Q_{a\beta}$ [16,24]. These terms are necessary to control the director configuration along an interface separating polymer-rich and LC-rich domains. In fact, as shown explicitly in Ref. [16] (and see also Ref. [15]), the shape of an LC-rich droplet is affected substantially by the director configuration inside the droplet, which is one of the characteristic features of PDLC. In this paper, however, we do not consider such an effect but rather focus our attention on the viscoelastic effect, which is expected to be more important for the kinetics of polymerization-induced phase separation. Finally we will replace the factor $1 - \phi$ by its average $1 - \phi_0$ in Eq. (6) to avoid an extra term in the evolution equation for $\phi$. This is expected not to be a serious deficiency for the final frozen domain morphology.

The phase diagram can be obtained from Eq. (2). Fig. 1a and b are an example for $N_p = 1$ and $N_p = 2$, respectively, fixing other parameters as $\chi_0 = 2.8$, $T_c = 2$, $B = 0$, $C_2 = 2$ and $D = 1$. The full line is the coexistence line and the broken lines below it are the spinodal line. The straight dotted-line line starting at $T = 2$ and $\phi = 0$ is the transition line below which nematic ordering appears.

2.2. Equations of motion

Now we introduce the full set of the kinetic equations. First, since the order parameter $Q_{a\beta}$ is a non-conserved quantity, the simplest form of the time-evolution equation
for $Q_{ab}$ is given by
\begin{equation}
\frac{\partial Q_{ab}}{\partial t} = -M_L \alpha_b \frac{\partial f(\phi, Q_{ab})}{\partial Q_{ab}} + \lambda_{ab} + \eta_{ab}, \tag{9}
\end{equation}
where $M_L$ is an Onsager coefficient. The constant $\lambda_{ab}$ is the Lagrange multiplier determined by the condition
\begin{equation}
\text{Tr} Q = 0. \tag{10}
\end{equation}

The last term $\eta_{ab}$ in Eq. (9) is the thermal random forces which satisfy the fluctuation dissipation relation
\begin{equation}
\langle \eta_{ab}(\vec{r}, t) \eta_{b'}(\vec{r}', t') \rangle = M_L (\delta_{ab} \delta_{\beta\beta'} + \delta_{ab} \delta_{\rho\rho'} \delta(\vec{r} - \vec{r}') \delta(t - t')). \tag{11}
\end{equation}

It should be noted that the traceless property (10) must be taken into account in the generation of the thermal noise $\eta_{ab}$ in simulations. Substituting Eq. (6) into Eq. (9) yields
\begin{equation}
\frac{\partial Q_{ab}}{\partial t} = C_1 V^2 Q_{ab} - 2A(\phi)Q_{ab} - 4DQ_{ab}\text{Tr} Q^2
\end{equation}
\begin{equation}
-3B \left\{ \sum_{\gamma} Q_{ag}Q_{gb} - \frac{\delta_{ab}}{3} \text{Tr} Q^2 \right\} + \eta_{ab}, \tag{12}
\end{equation}
where we have put $M_L = 1$.

Next we need to derive the time-evolution equation for $\phi(\vec{r}, t)$. Since we are mainly concerned with the polymerization-induced phase separation, we have to take account of the viscoelastic effects due to gelation of polymer chains. Assuming that LC molecules do not cause any viscoelasticity, we here use the two-fluid model introduced originally for polymer–solvent mixtures [19].

Let $\vec{v}_p(\vec{r}, t)$ and $\vec{v}_L(\vec{r}, t)$ be the average velocities of polymer and LC molecules, respectively. Assuming that the two components have the same density $\rho$, the volume average velocity is given by $\vec{v} = \phi \vec{v}_p + (1 - \phi) \vec{v}_L$. The kinetic equations for $\phi$, $\vec{v}$ and $\vec{v}_p$ are given in the two-fluid model by
\begin{equation}
\frac{\partial \phi}{\partial t} + \vec{v} \cdot (\phi \vec{v}) = \vec{v} \cdot \frac{df(1 - \phi)^2}{d\phi} \left[ \vec{v} \cdot \int \vec{\Pi} - \vec{v} \cdot \vec{\sigma} \right], \tag{13}
\end{equation}
\begin{equation}
\vec{v}_p - \vec{v} = -\frac{(1 - \phi)^2}{\zeta} \left[ \vec{v} \cdot \int \vec{\Pi} - \vec{v} \cdot \vec{\sigma} \right], \tag{14}
\end{equation}
\begin{equation}
\rho \frac{\partial \vec{v}}{\partial t} = -\vec{v} \cdot \int \vec{\Pi} + \vec{v} \cdot \vec{\sigma} + \eta_L \nabla^2 \vec{v}, \tag{15}
\end{equation}
\begin{equation}
\vec{v} \cdot \int \vec{\Pi} = \phi \vec{v} \left[ \frac{\delta F}{\delta \phi} \right], \tag{17}
\end{equation}

The total stress tensor $\vec{\sigma}$ can be evaluated from the shear stress $\vec{\sigma}_s$ and the bulk stress $\vec{\sigma}_B$ by using the relation
\begin{equation}
\vec{\sigma} = \vec{\sigma}_s - \frac{1}{d} (\text{Tr} \vec{\sigma}_s) I + \frac{1}{d} (\text{Tr} \vec{\sigma}_B) I, \tag{18}
\end{equation}
where $I$ is the unit tensor and $d(= 2)$ is the dimensionality of space. The shear stress obeys the upper convective constitutive Eq. [18]
\begin{equation}
\frac{\partial \vec{\sigma}_s}{\partial t} + \vec{v}_p \cdot \nabla \vec{\sigma}_s = (\vec{v}_p \cdot \vec{\sigma}_s + \vec{\sigma}_s \cdot (\nabla \vec{v}_p) - \frac{1}{\tau_s} \vec{\sigma}_s
\end{equation}
\begin{equation}
+ M_s \left\{ \vec{v}_p \cdot \vec{\sigma}_s + (\nabla \vec{v}_p) \vec{\sigma}_s \right\}. \tag{19}
\end{equation}
The bulk stress tensor is assumed to take a diagonal form $\vec{\sigma}_{B} = q \delta_{ij}$ where
\begin{equation}
\frac{\partial q}{\partial t} + \vec{v}_p \nabla q = - \frac{1}{\tau_B} q + M_B (\nabla \vec{v}_p). \tag{20}
\end{equation}
The relaxation times $\tau_s$ and $\tau_B$ and the coefficients $M_s$ and $M_B$ used in simulations will be fixed in the Section 3.

Eqs. (12)–(16) and (18)–(20) are the basic kinetic equations for simulations shown in the subsequent sections. Since these are complicated set of equations, we have made several approximations as summarized in the following. First, since LC molecules take a rod-like shape, the coefficient $M_L$ must be generally tensor [15]. However, we omit this complication and simplify it by a scalar constant. Secondly, in Eq. (15), we do not consider the existence of several kinds of viscosities due to the anisotropy of an LC molecule. Third, there is generally a dynamic cross coupling between $\phi$ and $Q_{\alpha\beta}$ through the off-diagonal elements of the Onsager coefficients [15]. However, we do not consider such a cross coupling in Eqs. (12) and (13) since the viscoelastic interaction is expected to be more relevant in the polymerization-induced phase separation. The fourth approximation is that we neglect the hydrodynamic coupling in the kinetic equation for the nematic order parameter in Eq. (12). This is a crude approximation but our main concern is not in the kinetics of nematic ordering but the domain morphology due to gelation.

3. Polymerization and the viscoelastic effect

We have to take into consideration of polymerization in our model equations. It causes two effects. One is the shift of the coexistence curve by changing the molecular weight $N_p$ as shown in Fig. 1. This is a static problem and has been studied in detail previously [10–12].

The time-dependence of the molecular weight $N_p$ is modeled simply by

$$N_p(t) = N_p^\infty - (N_p^\infty - N_p^0)e^{-\gamma t}, \quad (21)$$

where $N_p^0$ and $N_p^\infty$ are the initial and the final values of $N_p(t)$, respectively, and $\gamma$ represents the polymerization rate. In this paper, we fix $N_p^0 = 1$ and $N_p^\infty = 2$. In our simulations, we put $g = 0.1$ or 0.001 for polymerization-induced phase separation, whereas for phase separation by temperature quench we put $g = 0$ and $N_p(t) = N_p^0$.

Here we make a remark about the theoretical treatment of polymerization. In the course of polymerization, the molecular weight of polymers becomes generally polydispersed and hence non-uniform in space. This requires to introduce a space-dependent molecular weight $N_p(\vec{r}, t)$. However, since such a formulation is microscopic and does not conform with our mesoscopic theory based on the two-fluid model, we use the simple form $N_p^0$ as Eq. (21).

The other effect of polymerization is a change of the viscoelastic properties, which appear in Eqs. (19) and (20). The magnitude of the shear and the bulk moduli, $M_s$ and $M_B$ are assumed as follows [18],

$$M_s = 0.5 \phi^2, \quad (22)$$

$$M_B = 5(\phi - \phi^*), \quad (23)$$

where $\theta$ is a step function, i.e. $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$. We have introduced a threshold value $\phi^*$ in $M_B$ such that the bulk modulus does not exist for lower concentration $\phi < \phi^*$. In most of simulations, we choose $\phi^* = \phi_0$ for a technical convenience to enhance the elastic effect. A more realistic case where $\phi^*$ is chosen independently of $\phi_0$ will be described shortly in Section 6.

In simulations, we examine two different sets of the relaxation times

$$\tau_s^{(1)} = 5\phi^2 N_p(t)^3, \quad (24)$$

$$\tau_B^{(1)} = 10\phi^2 N_p(t)^3 \quad (25)$$

and

$$\tau_s^{(2)} = \frac{1}{4}[\exp(an_p(t)^3(\phi - \phi_0)) + 1], \quad (26)$$

$$\tau_B^{(2)} = \frac{1}{2}[\exp(aN_p(t)^3(\phi - \phi_0)) + 1], \quad (27)$$

where $a$ is a constant. The first ones, Eqs. (24) and (25) have the same $\phi$ dependence as the previous study [18] but with $N_p$-dependence expected by the reptation theory [21] assuming an incomplete gelation. The second ones, Eqs. (26) and (27) 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.

One might think that a model where $N_p$ becomes infinite in time is more appropriate for gelation. In this limit, however, the volume fraction $\phi$ is almost equal to 0 and 1 in LC-rich phase and polymer-rich phase, respectively. This causes a technical difficulty in solving numerically Eq. (13) since a random force is added in Eq. (9) and there is a coupling between $\phi$ and $Q_{\alpha\beta}$. In order to avoid this, we here employ Eqs. (21), (26) and (27).

Simulations are carried out under the periodic boundary condition with the grid size $\Delta x = \Delta y = 1$ for the system size $128 \times 128$. The time step is chosen as $\Delta t = 0.01$. The parameters in Eqs. (13)–(15) are fixed as $\eta_L = 0.1$ and $\zeta = 0.1$. The fixed parameters in the model free energy $F$ in Eqs. (2)–(8) are $\zeta_0 = 2.8$, $T_c = 2$, $B = -0.01$, $C_0 = 1$, $C_1 = 1$, $C_2 = 2$ and $D = 1$. The initial value of $\phi$ at each cell is generated by random number uniformly distributed in the interval $\phi_0 = 0.001 < \phi < \phi_0 + 0.001$. Other initial values are set as $\vec{v} = \vec{v}_p = 0$ and $\vec{a} = 0$.

The technical method for calculation of nematic ordering is described in the Appendix A. The initial values of $Q_{xx}$, $Q_{yy}$ and $Q_{xy}$ in simulations are generated by setting $S = 0.1$ and the randomly oriented director $\vec{n}$. The magnitude of the random forces $\eta_{\gamma x}$, $\eta_{\gamma y}$ and $\eta_{\gamma z}$ is set to be 0.0025, unless stated otherwise.
4. Results of simulations

4.1. Phase separation by temperature quench

First we show the phase ordering quenched below the coexistence line for a fixed value of $N_p = 1$. We have used the relaxation time given by Eqs. (24) and (25). Fig. 2 is the result for $T = 1.3$ and $\phi_0 = 0.4$ (marked by the open square in Fig. 1a). The gray region is the uniform state. After temperature quench, the LC-rich droplets of the isotropic state (drawn by light gray color) emerge. As they grow, the nematic ordering proceeds as indicated by the change from light gray color to white color. For instance, a substantial number of domains are white at $t = 3600$ in Fig. 2 but there are a few light gray domains where nematic order is not complete.

In an ordinary binary fluid having low molecular weights, the minority component always constitutes disconnected droplets. Note, however, in Fig. 2 that droplets are in the LC-rich phase which is the major component when the average polymer volume fraction is equal to $\phi_0 = 0.4$. Thus the domain morphology in Fig. 2 clearly indicates the viscoelastic effect [18].

As the droplets become large, polymers are accumulated just outside the droplets, which is indicated by black color. This is because the polymer concentration cannot diffuse rapidly due to the viscoelastic effect. It should be noted that the droplet growth in Fig. 2 is qualitatively different from the Ostwald ripening where a larger droplet grows further at the expense of smaller droplets. In Fig. 2, droplets do not shrink but simply coagulate with the neighboring droplets. This is also a characteristic feature due to the hydrodynamic and viscoelastic effects contained in Eqs. (15) and (19).

Fig. 3 shows the time evolution of the volume fraction $\phi_{\text{max}} (\phi_{\text{min}})$ at a position in a polymer (LC)-rich domain and the nematic order parameter $S$ in an LC-rich droplet. The nematic ordering occurs at about $t = 2700$ where the volume fractions $\phi_{\text{max}}$ and $\phi_{\text{min}}$ in an LC-rich droplet suddenly reach to almost the final equilibrium values. This means that because of the conservation of the total concentration, the total area of LC-rich droplets does not increase appreciably after $t = 3000$.

We have also carried out simulations for a smaller value of the average volume fraction $\phi_0 = 0.35$ quenched at $T = 1.3$ (marked by the filled square in Fig. 1a). Fig. 4 displays the evolution where the LC-rich droplets grow and merge each other but once these droplets are formed, shrinkage of smaller droplets is less frequent similarly to Fig. 2.

A remarkable feature in Fig. 4 is the fact that there is a two-step growth of droplets. At about $t = 2400$, a first nucleation of LC droplets start and after they grow, the second nucleation occurs at about $t = 4000$ in the polymer-rich matrix. In our previous study without considering

![Fig. 3. Time evolution of the minimum and maximum values $\phi$ and the maximum values of $S$ for $T = 1.3$ and $\phi_0 = 0.4$.](image-url)
the viscoelastic effect, a concentric domain pattern of the polymer-rich phase has been observed for the same parameters \( \phi_0 = 0.35 \) and \( T = 1.3 \). However, such a concentric pattern does not appear in Fig. 4 where the viscoelastic effect is present. The origin of concentric pattern is a periodic modulation of polymer concentration around a nucleated droplet [25]. When the viscoelastic effect is strong, the spatial modulation is suppressed so that a concentric pattern does not appear in the present system. Formation of the concentric pattern for an ordinary binary mixture will be discussed separately elsewhere [23].

In order to investigate systematically the morphological change of growing domains, we show the simulation results quenched at \( T = 1.2 \) for \( \phi_0 = 0.35, 0.25 \) and 0.2 in Fig. 5a–c, respectively. These are indicated by the open triangles in Fig. 1a. Since these are inside the spinodal region of nematic

Fig. 4. Time evolution of phase separation by temperature quench for \( T = 1.3 \) and \( \phi_0 = 0.35 \) at \( t = 2400, 3600, 4800, 6000, 8000 \) and 16000.

Fig. 5. Time evolution of phase separation by temperature quench for \( T = 1.2 \) and (a) \( \phi_0 = 0.35 \), (b) \( \phi_0 = 0.25 \) and (c) \( \phi_0 = 0.2 \) at \( t = 50, 100, 150, 250, \) and 500.
ordering in the phase diagram (Fig. 1a), the whole region undergoes nematic ordering at the early stage of the evolution.

In Fig. 5a for $\phi_0 = 0.35$, the LC domains appear as disconnected droplets and enlarge their size by coagulation as phase separation proceeds whereas the polymer-rich phase forms an interconnected domain which is stable within the limit of our simulations. We have verified that this stability of the interconnected domains is not characteristic to the polymer-LC mixtures but it is common even in a mixture of polymer and solvent with low molecular weight as shown in the previous study [18]. An apparently similar behavior has been observed in simulations of the two-fluid model [22]. However, the origin may not be the same because the kinetic equations in Ref. [22] are different from the present ones.

When $\phi_0 = 0.25$ in Fig. 5b, an interconnected domain of polymer-rich phase appears in the intermediate time but it eventually breaks into disconnected domains. This is the phase inversion found by Tanaka and Araki in polymer–solvent mixtures [18].

If we further decrease the average volume fraction, nucleation and growth of the minority phase (polymer-rich phase) occurs as in Fig. 5c for $\phi_0 = 0.2$, which is the same as the case without viscoelasticity.

Therefore the final domain morphology depends drastically on the average volume fraction $\phi_0$. When $\phi_0 \geq 0.35$, an interconnected polymer-rich domain appears whereas when the average volume fraction is smaller, i.e. $\phi_0 \geq 0.25$, the polymer-rich phase eventually constitutes the disconnected droplets. These are the results for temperature quench using the relaxation rates (24) and (25).

In order to see the role of LC molecules for phase separation, we show in Fig. 6 the early stage of phase separation of Fig. 5b. The degree of gray color means $\sin^2 \theta \cos^2 \theta$ where $\theta$ is the angle of the x-axis and the nematic director projected on the xy-plane. At $t = 100$, the whole region is the nematic state with many defects. The region where the polymer volume fraction is larger than $\phi = 0.5$ is indicated by black. In Figs. 6 and 9 below, the defects with topological charge $\pm 1$ exist but those with $\pm 1/2$ are not present. It seems to us that this is an artifact of our algorithm solving Eq. (12). Nevertheless, it is evident that there is a tendency that polymer-rich droplets emerge initially around the defect cores.

### 4.2. Phase separation induced by polymerization

Now we study polymerization-induced phase separation by changing the molecular weight of polymers as Eq. (21). Fig. 7 shows the time evolution of domains at $T = 1.55$, $\phi_0 = 0.2$ (marked by the open circles in Fig. 1a and b) and the polymerization rate $g = 0.001$. We have used the relaxation time given by Eqs. (26) and (27) with $\alpha = 3$.

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. 5c for temperature quench at the same average volume fraction $\phi_0 = 0.2$ where the polymer-rich phase takes disconnected droplets. One of the origin of this morphological difference is the fact that the composition ratio at $T = 1.2$ is given by $r = (\phi_0 - \phi_1)/(\phi_p - \phi_1) = 0.16$ with $\phi_1$ and $\phi_p$ the equilibrium values of LC-rich and polymer-rich phases, respectively, whereas it becomes larger, $r \approx 0.21$ at $T = 1.55$ for the coexistence curve after polymerization $(N_p = 2)$. The latter value of $r$ is closer to that for $T = 1.2$ and $\phi_0 = 0.25$ and hence an interconnected polymer-rich domain is formed as in Fig. 5b. Another reason is, as shown in Fig. 8, the slow increase of the polymer concentration in polymer-rich
domains because of gelation. This effectively increases the composition ratio at the early stage of phase separation.

It is noted that the coagulation of LC-rich domains is quite rare in Fig. 7. Thus the interconnected domain of the polymer-rich phase is stable. This is due to the \( \phi \)-dependence of Eqs. (26) and (27) such that the relaxation rates are vanishingly small for a large value of \( \phi \). In fact, if one uses Eqs. (24) and (25), the interconnected domain is found to be unstable as in Fig. 5b.

Fig. 9 shows the interplay between the nematic ordering and phase separation at the early stage of Fig. 7. The meaning of colors is the same as that in Fig. 6 except that the black region indicates \( \phi > 0.225 \). This nucleation–growth process is followed by spinodal decomposition due to the shift of the phase diagram induced by polymerization. Then, the pattern transforms into an interconnected network due to viscoelastic effects. The domain growth in the course of the polymerization-induced phase separation is investigated at several temperatures for \( \phi_0 = 0.35 \) (indicated by the filled circles in Fig. 1a and b) and \( g = 0.001 \) by using the relaxation time given by Eqs. (26) and (27) with \( a = 3 \).

The domain morphologies for each temperature are shown in Fig. 10. In all cases, the disconnected droplets of the LC-rich phase appear. It is noted that coagulation of droplets is less frequent at lower temperature so that the size of droplets is smaller at lower temperature. At lower temperature, phase separation starts before gelation. Therefore, as the domain grows, the polymer chains accumulate just outside LC-rich domains. Especially, the polymer concentration becomes large in the narrow channel between two adjacent LC-rich droplets. As the polymerization proceeds, this concentration non-uniformity is frozen and inhibits coagulation of LC-rich droplets as in Fig. 10a and b.

At higher temperature, on the other hand, the polymerization proceeds uniformly in space before the system enters into the two-phase region. However, in the present model, the stress relaxation times given by Eqs. (26) and (27) do not increase sufficiently because the factor \( \phi - \phi_0 \) is smaller at higher temperature as is seen in Fig. 1b. This is the reason why the network in Fig. 10c and d are less stable. Although not shown in this paper, the LC-rich droplets at \( T = 1.55 \) and \( T = 1.65 \) is in a nematic phase, whereas they are in an isotropic phase at \( T = 1.7 \) and \( T = 1.75 \) in accord with the phase diagram for \( N_p = 2 \) shown in Fig. 1b.

5. Experimental results

5.1. Experiments on microscopy

We have analyzed time-resolved confocal laser microscopic images in a solution consisting of monomers and
Fig. 9. Time evolution of phase separation and nematic ordering induced by polymerization for $T = 1.55$, $\phi_0 = 0.2$ and $g = 0.001$ at $t = 200, 400, 600, 800, 900$ and $1000$.

Liquid crystal mixtures at the early stage of phase separation to study the kinetics of photo-polymerization-induced phase separation process during UV light-exposure. A Leica's confocal laser microscope allowing us to take digital images through the objective lens with a high resolution of 240 nm horizontal and 643 nm vertical was used to study the kinetics.

The time-resolved microscopic images are stored in a microcomputer connected to the confocal unit every 0.35 s for 60 s. A high-pressure mercury lamp is equipped for the

Fig. 10. Domain patterns at $t = 1600, 2400, 3200, 4000, 8000, 16000$ for $\phi_0 = 0.35$ and $g = 0.001$. (a) $T = 1.55$, (b) $T = 1.65$, (c) $T = 1.7$, (d) $T = 1.75$. 
Fig. 11. Time resolved microscopic photographs for a mixture (80 mol% PAL-746 and 20 mol% of C2000). The length of each square is 31.25 μm.
microscope so that the sample placed on the stage is irradiated over a limited area through the objective lens. The observation of the kinetics was carried out with 20 W/m² of UV-exposure to suppress the rate of evolution on the phase separation. Two beams of Kr laser at 473 and 488 nm are employed in order to improve a poor contrast of images due to a small difference of refractive index between liquid crystal rich phases and monomer-rich phases at the initial stage of phase separation. An optical filter is placed in the front of a detector to eliminate the influence of UV-light.

5.2. Preparation of samples

The C2000 manufactured by Sartomer Inc. was used as a photo curable diacylates. The chemical structure of C2000 was given in Ref. [16]. The low molecular weight liquid crystals used in this study were the fluorinated tolane based liquid crystal mixture of PAL-746 manufactured by Dainippon ink and Chemicals Inc. A 4 mol% of photoinitiator (Irg-651 manufactured by Chiba-Geigy) was added in the total amount of diacrylate. The details of PAL-746 will be given elsewhere. Here we mention some of the characteristics; the anisotropy of birefringence \( \Delta n = 0.266 \), the anisotropy of the dielectric constant \( \Delta \varepsilon = 6.71 \) and the isotropic–nematic transition temperature \( T_{IN} = 92.8^\circ\text{C} \).

The mixture was sandwiched between a slide glass and a cover glass with a cell gap of 50 \( \mu\text{m} \) so that the morphology caused by the phase separation is free from surface effects of the glass walls. UV light at 365 nm was irradiated to the homogeneous solution at 2 K above the isotropic–nematic transition temperature to induce the phase separation for 60 s.

5.3. Kinetics in photo polymerization induced phase separation

The time resolved microscopic photographs in the composition at 80 mol% of PAL-746 and 20 mol% of C2000 (Iso.– Nematic transition temperature: 32°C) are shown in Fig. 11. A white area on the photograph represents
the nematic phase. A black area indicates monomer-rich phases. The phase separation is initiated at 7 s of an elapsed time in UV-light exposure. A number of spherical nematic droplets are nucleated at this time. This contrast to the fact that the minority component always constitutes disconnected droplets in an ordinary fluid having low molecular weights. It is noted that the liquid crystal-rich phase as the majority forms the droplets as shown in Fig. 11. In this point of view, an apparently similar behavior is observed in the simulations mentioned before in Section 4.2. As photo-polymerization goes on, the nucleation and growth of nematic droplets proceeds and the nematic droplets are surrounded with monomer-rich phases in which monomers are enriched near the interface due to the evolution of phase separation.

The nematic domains growing gradually for a period from 7 to 10 s suddenly become large with a frequent coalescence for 11–13 s of the elapsed time. Fluidity on monomer-rich phases is evident at these stages of phase separation, because the rapid growth of size of nematic droplets caused by frequent coalescence is observed. After 13 s, the domain morphology does not change because of an occurrence of gelation. This suggests that gelation rapidly proceeds at the period of phase separation between 12 and 13 s. This is because the reactivity of the monomer-rich phase increases as the accumulation of monomers proceeds.

Therefore one may estimate roughly in this sample the characteristic time of phase separation as a few seconds and that of gelation as about 13 s. The nematic ordering seems more rapid than these time scales.

Table 1 summarizes the kinetics mentioned above. Fig. 11 shows that after about 10 s coalescence of two droplets rapidly forms a large spherical droplet. In the simulations in Fig. 10a, however, the relaxation of the shape after coagulation is rather slow. It is presumed that the differences of the fluidity and the rate of polymerization between the experimental results and the simulations cause this qualitative difference in the droplet kinetics.

In the case that the liquid crystal fraction is at 65 mol% of liquid crystal fraction, the kinetics obviously follow spinodal decomposition as shown in Fig. 12. This change of the domain morphology is also obtained by simulations (see Ref. [16]).

In summary, the domain morphology obtained by experiments and by simulations is qualitatively consistent. However, since there are many parameters in the system such as a rate of polymerization, solubility, phase diagrams, molecular structures, a fraction of liquid crystals, a UV-intensity and a curing temperature, more specific data of both experiments and simulations are necessary to make a quantitative comparison.

6. 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.

As mentioned in Section 3, the crosslinking of molecules for gelation has usually been formulated based on a molecular picture. However, such a microscopic theory is quite inconvenient to study kinetics of phase separation in PDLC where domain size is in a mesoscopic scale. This is the reason as to why we have introduced phenomenologically the effect of gelation as Eqs. (26) and (27). Nevertheless, it should be noted that we have made a clear distinction between simple polymerization and gelation by using the two different sets of relaxation time as Eqs. (24) and (25) for polymerization without gelation and Eqs. (26) and (27) for polymerization with gelation. When the viscoelastic relaxation time is infinite, the polymer-rich domains are purely elastic. One of the advantageous features of the two-fluid model [19] is that this elastic interaction is automatically incorporated into the free energy as it must be. Since this aspect is mathematical, we do not describe the detail here.

In a previous paper [18], 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 Eqs. (26) and (27), the interconnected structure formed by this polymer-rich domain becomes stable and the phase inversion is not observed within the limit of a simulation time especially at lower temperature such as $T = 1.55$ and $g = 0.001$ in Fig. 10a. Thus our model equations are capable to reproduce at least qualitatively the domain morphology observed in experiments as shown in Section 5. In order to make a more quantitative comparison, however, further tuning of the parameters is necessary.

Here we make a remark about another possible origin of the interconnected morphology in PDLC. If the elasticity of the nematic state given by the gradient term in Eq. (6) is strong enough, it is expected that a LC-rich domain becomes a disconnected droplet surrounded by a softer polymer-rich
phase before gelation. In order to examine this interesting property, one needs to carry out simulations by changing the constant $C_1$ in Eq. (6). However, this is left for a future study.

It is noted here that formation of a stable interconnected domain is sensitive to the value of $\phi^*$ in the bulk modulus $M_B$. When $\phi^* = 0.2 = \phi_0$, we have a domain morphology as in Fig. 6, whereas if we put $\phi^* = 0.3 > \phi_0$, polymer-rich domain of the minority phase is disconnected as in an ordinary phase separation in the absence of the viscoelastic effect. It is also mentioned that the relaxation times (26) and (27) have a threshold value of $\phi$. Although we have fixed the threshold to be the average volume fraction $\phi_0$, we may choose another value of the threshold more suitable for comparison with experiments.

In summary, we have shown that the interconnected domain caused by polymerization and gelation in PDLC is quite stable in contrast to polymer–solvent mixtures where the interconnected pattern is only transient and phase inversion takes place at the late stage of phase separation.

Although not shown here, we have carried out preliminary simulations in three dimensions and have a similar behavior of domains if we choose larger values of $\alpha$ in Eqs. (26) and (27).

Another important feature of domain morphology is that almost all LC-rich domains grow expelled from the polymerized polymer-rich phase. This growth kinetic is quite different from that of the usual Ostwald ripening where larger domains grow further at the expense of smaller domains. We will study theoretically this domain growth associated with gelation elsewhere.

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Appendix A. Numerical method for nematic ordering

In order to simulate the time evolution of the nematic ordering, we have to solve Eq. (12) for $Q_{\alpha\beta}$ and to obtain the director field $\vec{n}$ by using the relation (1). In our previous paper [16], we used this numerical scheme. However, as mentioned in the note added in proof of Ref. [16], this method has a difficulty such that the degree of nematic order $S$ becomes imaginary. In order to avoid this unphysical situation, we choose $Q_{zz}$, $Q_{xz}$ and $Q_{yz}$ as independent variables. These three components are sufficient to determine the values of $S$ and $\vec{n}$ as described below.

From definition (1) we have

$$Q_{zz} = \frac{3}{2} \tilde{S} \left( n_z^2 - \frac{1}{3} \right),$$

(A1)

$$Q_{xz} = \frac{3}{2} S n_x n_z,$$

(A2)

$$Q_{yz} = \frac{3}{2} S n_y n_z.$$  

(A3)

When $n_z \neq 0$ and $S \neq 0$ in the nematic phase, $n_x$ and $n_y$ are given by

$$n_x = Q_{xz} \left[ \frac{3}{2} S n_z \right]^{-1},$$

(A4)

$$n_y = Q_{yz} \left[ \frac{3}{2} S n_z \right]^{-1}.$$  

(A5)

From Eqs. (A1), (A4) and (A5) and $|\vec{n}| = 1$, we have a closed equation for $n_z$ whose solution is given by

$$n_z = \left\{ \frac{2J + 3 \pm \sqrt{8J + 9}}{6(J + 1)} \right\}^{1/2},$$

(A6)

where

$$J = \frac{Q_{xz}^2 + Q_{yz}^2}{Q_{zz}^2}.$$  

(A7)

and the $+(-)$ sign should be chosen when $Q_{zz} > 0(<0)$. In Eq. (A6), we have used the fact that $n_z$ is assumed to be positive, without loss of generality. Once $n_z$ is specified, the order parameter $S$ is obtained from

$$S = \frac{2}{3} \left( \frac{Q_{zz}}{n_z^2 - (1/3)} \right).$$

(A8)

The formula (A8) is valid for $Q_{zz} \neq 0$. When $Q_{zz} = 0$, we have $n_z = \sqrt{1/3}$ from Eqs. (A6) and (A7). Substituting this into (A1)–(A3) and using the fact $|\vec{n}| = 1$, we obtain for $Q_{zz} = 0$

$$S = \sqrt{2(2Q_{xz}^2 + Q_{yz}^2)}.$$  

(A9)

When $n_z = 0$, we have $S = -2Q_{zz}$. In this case, one cannot determine the values of $n_x$ and $n_y$ uniquely. This comes from the fact that our method keeps the rotational symmetry of the director space only in the $x$ and $y$ components. Although this is an artifact, we expect that this does not alter the kinetics and the domain morphology unless we set up the situation such that the directors lay completely in the $x$–$y$ plane.

References