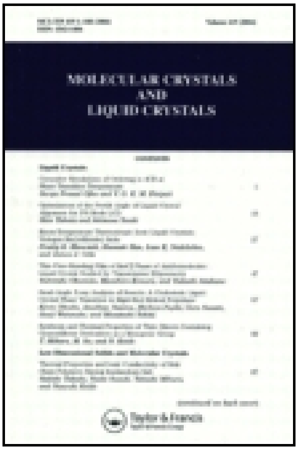

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PHASE SEPARATION KINETICS OF MAIN-CHAIN LIQUID CRYSTALLINE POLYMERS

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Phase Separation Kinetics of Main-Chain Liquid Crystalline Polymers

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We investigate phase separation kinetics of main-chain liquid crystalline polymers (LCP's) by numerical calculations based on a continuum description. We introduce two order parameters, the density and the orientational order of LCP's and construct a set of time-dependent Ginzburg-Landau equations to describe the dynamics of these two order parameters. We show that the morphology of the phase-separated system is crucially influenced by the coupling between the density and the orientational order which appears in the kinetics as well as in the free energy.

Keywords: phase separation; main-chain liquid crystalline polymers; kinetics; orientational order

INTRODUCTION

Much attention has been paid to liquid crystalline polymers(LCP's) because of their technological applications such as optical devices and fibers of high tensile strength. Since appropriate control of the morphology and the orientational order is crucial to attain the material properties desired for the individual applications, it is quite important to understand the mechanism of phase separation and orientational ordering in LCP's. However, the presence of the coupling between the compositional order, or the density, and the orientational order makes the problem interesting but quite complicated, and the understanding of the dynamical properties of such systems is still unsatisfactory.

The aim of this paper is to investigate how the coupling between the compositional order and the orientational order affects the morphology and phase separation kinetics of LCP's. We restrict ourselves to main-chain LCP's and construct a set of dynamic equations for the order parameters representing the density and the orientational order of LCP's. We present the results of the numerical simulations to show the importance of the coupling between the compositional order and the orientational order in the phase separation of LCP's.

MODEL

Order Parameter and Free Energy

First we introduce two order parameters to specify the state of the system. One is a scalar order parameter ϕ representing the volume fraction of LCP's and the other is a tensor order parameter S_{ij}, the orientational order per unit volume. Precise definition of these two order parameters is presented in previous articles [1,2].

The free energy of the system can be written as $v_0\beta F = \int d\boldsymbol{r}(f_{FH}\{\phi\} + f_S\{\phi, S_{ij}\} + f_{grad}\{\phi, S_{ij}, \nabla\})$, where v_0 is the segment volume and β is the inverse temperature. The first term f_{FH} is the Flory-Huggins energy which can be written as

$$f_{FH} = \frac{\phi}{N}\ln\phi + \frac{1-\phi}{N'}\ln(1-\phi) + \chi\phi(1-\phi). \qquad (1)$$

Here N and N' are the degree of polymerization for the LCP and the counter-component, respectively and χ is the isotropic interaction parameter.

The second term f_S is the free energy due to the presence of orientational order:

$$f_S = -\frac{\phi}{2N}\mathrm{Tr}\{\ln(1+dQ) - dQ\} - \frac{1}{2}w\phi^2\mathrm{Tr}Q^2 + \lambda\mathrm{Tr}Q, \qquad (2)$$

where d is the space dimension of the system and $Q_{ij} \equiv S_{ij}/\phi$ stands for the orientational order per segment. Tr implies taking the trace of a matrix. The first term of eq. (2) is the conformational entropy which prefers the isotropic state. The second term is the Maier-Saupe anisotropic interaction term which tend to align LCP molecules, with w being the anisotropic interaction parameter. The last term in eq. (2) is introduced to ensure that the orientational order parameter Q_{ij} (or S_{ij}) is traceless and λ is the Lagrange multiplier.

As the free energy due to the inhomogeneity we take the following form:

$$\begin{aligned} f_{grad}\{\phi, Q_{ij}\} &= \frac{C_0}{2\phi}(1+dQ)_{ij}\partial_i\phi\partial_j\phi \\ &\quad - L_0\left((1+dQ)_{ij}\partial_i\partial_j\phi + d\partial_i\phi\partial_j Q_{ij} + d\phi\partial_i\partial_j Q_{ij}\right) \\ &\quad + \frac{1}{2}L_1\phi(1+dQ)_{ij}(1+dQ)^{-1}_{k\mu}(1+dQ)^{-1}_{l\nu}\partial_i Q_{kl}\partial_j Q_{\mu\nu} \\ &\quad + \frac{1}{2}L_2\phi(1+dQ)^{-1}_{ij}\cdot\frac{1}{2}(\partial_k Q_{ik}\partial_l Q_{jl} + \partial_k Q_{il}\partial_l Q_{jk}), \end{aligned} \tag{3}$$

where $C_0 = L_0 = l^2/12Nd, L_1 = l^2d/24N$, and $L_2 = l^2d/6N$ with l being the length of the LCP molecule. The first line is the contribution of surface tension, which is anisotropic in the presence of orientational order. The second line contains the additional coupling terms between the fluctuation of the density and the orientational order. The last two lines correspond to the Frank elastic energy. The derivation of the above free energy is given in References [1,3].

Kinetic Equations

We construct a set of time-dependent Ginzburg-Landau(TDGL) equations for the order parameters ϕ and S_{ij}. The equations are formally written as $\partial\psi(\boldsymbol{r})/\partial t = \int d\boldsymbol{r}' \sum_{\psi'=\phi,S_{ij}} \Lambda_{\psi\psi'}(\boldsymbol{r},\boldsymbol{r}')\delta(\beta F)/\delta\psi'(\boldsymbol{r}')$, where $\psi = \phi$ or S_{ij} and $\Lambda_{\psi\psi'}(\boldsymbol{r},\boldsymbol{r}')$ is the kinetic coefficient. Here we make a gradient expansion of the kinetic coefficients. When we take only up to the second order terms in the gradients, the kinetic equations are rewritten as

$$\frac{\partial}{\partial t}\phi(\boldsymbol{r}) = \partial_\mu\left(\lambda^{\mu\nu}_{\phi\phi}\partial_\nu\frac{\delta(\beta F)}{\delta\phi(\boldsymbol{r})} + \lambda^{\mu\nu}_{\phi S_{ij}}\partial_\nu\frac{\delta(\beta F)}{\delta S_{ij}(\boldsymbol{r})}\right), \tag{4}$$

$$\frac{\partial}{\partial t}S_{ij}(\boldsymbol{r}) = \partial_\mu\left(\lambda^{\mu\nu}_{S_{ij}\phi}\partial_\nu\frac{\delta(\beta F)}{\delta\phi}\right) + \left(\Lambda^0_{S_{ij}S_{kl}} + \partial_\mu\lambda^{\mu\nu}_{S_{ij}S_{kl}}\partial_\nu\right)\frac{\delta(\beta F)}{\delta S_{kl}}. \tag{5}$$

Here the newly introduced kinetic coefficients λ's and $\Lambda^0_{S_{ij}S_{kl}}$ may depend on $\phi(\boldsymbol{r})$ and $S_{ij}(\boldsymbol{r})$. Notice that the Onsager reciprocal relation leads to $\Lambda_{S_{ij}\phi}(\boldsymbol{r},\boldsymbol{r}') = \Lambda_{\phi S_{ij}}(\boldsymbol{r}',\boldsymbol{r})$ and $\lambda^{\mu\nu}_{S_{ij}\phi} = \lambda^{\nu\mu}_{\phi S_{ij}}$. We also note that the zeroth-order terms in the gradients do not appear in $\Lambda_{\phi\phi}$ and $\Lambda_{\phi S_{ij}}$ because the presence of such zeroth-order terms is inconsistent with the conservation of ϕ.

In the non-dilute regime, the relaxation of rod-like objects is dominated by the translational motion parallel to themselves [4]. The contribution of the translational diffusion to the kinetic coefficients is evaluated by the biased reptation model [2, 5]. Note that the translational diffusion does not contribute to $\Lambda^0_{S_{ij}S_{kl}}$ because the orientational order S_{ij} is conserved when only the translational diffusion takes place [2]. The detail of the evaluation of λ's will be given elsewhere and we give here only the final result:

$$\begin{aligned}
\lambda^{\mu\nu}_{\phi\phi} &= \frac{D_c v_0 N}{d}\phi(1+d\mathrm{Q})_{\mu\nu}, \\
\lambda^{\mu\nu}_{\phi S_{ij}} &= \frac{D_c v_0 N}{d^2}\phi((1+d\mathrm{Q})_{i\mu}(1+d\mathrm{Q})_{j\nu} + (1+d\mathrm{Q})_{j\mu}(1+d\mathrm{Q})_{i\nu}), \\
\lambda^{\mu\nu}_{S_{ij}S_{kl}} &= \frac{D_c v_0 N}{d^3}\phi[((1+d\mathrm{Q})_{ik}(1+d\mathrm{Q})_{jl} + (1+d\mathrm{Q})_{il}(1+d\mathrm{Q})_{jk}) \\
&\quad \times (1+d\mathrm{Q})_{\mu\nu} \\
&\quad + ((1+d\mathrm{Q})_{j\mu}(1+d\mathrm{Q})_{l\nu} + (1+d\mathrm{Q})_{j\nu}(1+d\mathrm{Q})_{l\mu}) \\
&\quad \times (1+d\mathrm{Q})_{ik} + (3 \text{ similar terms})].
\end{aligned} \tag{6}$$

Here D_c is the translational diffusion constant along the chain.

Although the rotational diffusion is far less important in the non-dilute regime compared with the translational diffusion along the chain [4], there may be some cases where rotational diffusion should be taken into account. In our model rotational diffusion is incorporated phenomenologically by setting $\Lambda^0_{S_{ij}S_{kl}} = -\phi\mathcal{D}_r(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - (2/d)\delta_{ij}\delta_{kl})$, where $\mathcal{D}_r$ is proportional to the rotational diffusion constant. For simplicity we set $\mathcal{D}_r$ constant, although the rotational diffusion constant may depend on the degree of orientational order [4].

RESULTS

Numerical calculations are performed on a two-dimensional (d=2) 128×128 square lattice with periodic boundary conditions using the

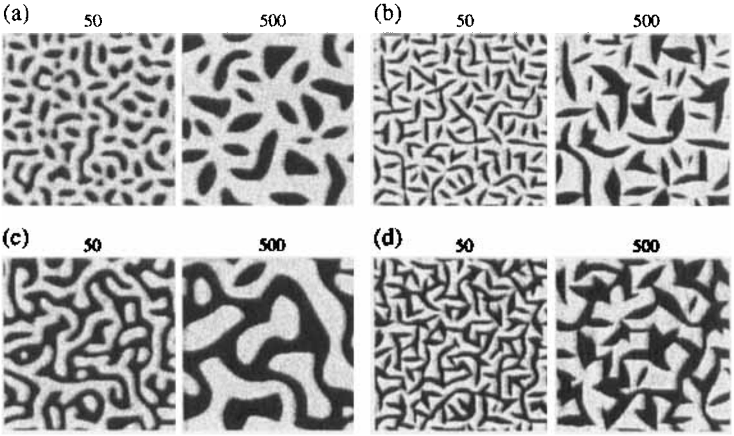

FIGURE 1 Composition(ϕ) profile for (a)$\overline{\phi} = 0.4, wN = 3$, (b)$\overline{\phi} = 0.4, wN = 5$, (c)$\overline{\phi} = 0.5, wN = 3$, (d)$\overline{\phi} = 0.5, wN = 5$. Darkness represents ϕ. The numbers indicate the time after quench in unit of l^2/D_c.

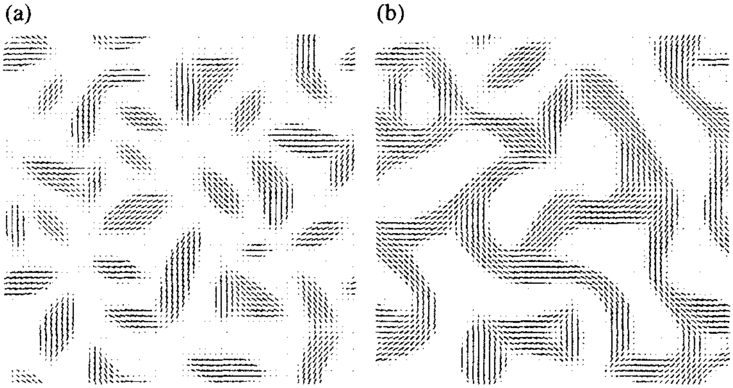

FIGURE 2 Orientation profile at $t = 500 \times l^2/D_c$ for (a)$\overline{\phi} = 0.4, wN = 3$, (b)$\overline{\phi} = 0.5, wN = 3$.

explicit Euler scheme. The lattice size is $\Delta x = l/4$ and we take the time step as $\Delta t = \alpha l^2/D_c$, where we take α between 0.001 and 0.0025 according to the numerical stability of the simulation. In the following simulations we fix some of the parameters as $N = N', \chi N = 2.7, \mathcal{D}_r = 0.001 \times D_c N v_0 / l^2$. In Figures 1 and 2, we show the composition profile and the orientation profile, respectively, for different initial volume fraction($\overline{\phi}$) and strength of anisotropic interaction(w) under an isotropic initial condition. In these simulations, we choose the parameters so that phase separation occurs into an isotropic LCP-poor phase and a nematic LCP-rich phase. Figure 1 indicates that the morphology depends strongly and sensitively on ϕ and w and that the anisotropy of the morphology is stronger with larger anisotropic interaction parameter w. We also note that at the intermediate stage($t = 50 \times l^2/D_c$) with $\overline{\phi} = 0.5$ we can observe a thin network-like structure composed of LCP's similar to that observed in experiments [6]. Orientational profile in Figure 2 shows that in anisotropic droplets the longer axis is parallel to the nematic orientation inside and that in a network-like structure the nematic orientation is parallel to the network. This tendency of the nematic orientation is attributed to the gradient energy (eq. 3) which prefers the interface parallel to the nematic orientation [1].

To check the importance of the orientational order more clearly, we perform simulations also under a nematic initial condition with $\overline{Q_{xx}} = -\overline{Q_{yy}} = 0.3$ and $\overline{Q_{xy}} = 0$. Here we use the parameters $\overline{\phi} = 0.5$ and $wN = 3$. We note here that $(1 + d\mathrm{Q})_{ij}$ in the λ's (eq. 6) reflects the anisotropy of the diffusion which arises from the tendency of LCP molecules to move parallel to the nematic orientation [2]. Therefore, to investigate how the anisotropy of the diffusion affects the morphology and phase separation, we consider the following two cases: the "anisotropic diffusion" case, where we adopt eq. (6) as the λ's, and the "isotropic diffusion" case, where we replace $(1 + d\mathrm{Q})_{ij}$ in eq. (6) by δ_{ij}.

We show in Figure 3 the time evolution of the composition profile. In the "isotropic diffusion" case, the striated pattern parallel to the orientational order is clearly observed, similar to that in the experiment of nematic-nematic phase separation of side-chain LCP's [7]. In the "anisotropic diffusion" case, on the other hand, the anisotropy of the phase separation is much weaker and even domains perpendicular to the nematic orientation can be found. The orientation of the domains parallel to the nematic direction again results from the gradient energy (eq. 3) as noted above, while the anisotropy of the diffusion in the presence of the orientational order leads to the density fluctuation perpendicular to the nematic orientation [2]. The much weaker anisotropy of the morphology in the "anisotropic diffusion" case is therefore attributed to the competition of these two opposite effects. We emphasize that the difference of the morphology here originates purely from the kinetics, because in these two simulations we have used the same free energy and the initial conditions. This result therefore shows that the kinetic coupling of ϕ and S_{ij} which appears as the S_{ij}-dependent kinetic coefficients may have an important effect on the phase separation kinetics of LCP's, although almost no theoretical and numerical studies have paid any attention to it.

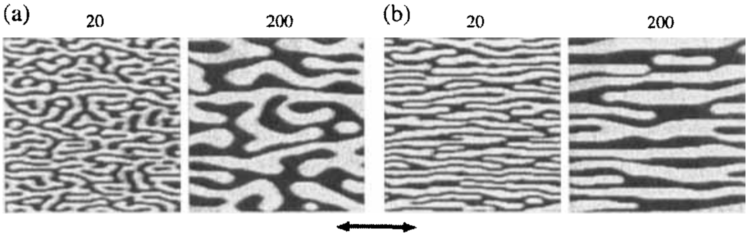

FIGURE 3 Composition(ϕ) profile under a nematic initial condition for (a)"anisotropic diffusion" case, and (b)"isotropic diffusion" case. The direction of the initial nematic order is shown by an arrow.

CONCLUSION

In this paper we have investigated phase separation kinetics of main-chain LCP's by numerically integrating the TDGL equations for the two order parameters: the compositional order ϕ and the orientational order S_{ij}. We have performed simulations under an isotropic initial condition and under a nematic initial condition. Our simulation results have shown that the coupling of the compositional order ϕ and the orientational order S_{ij} in the kinetics as well as in the free energy plays a significant role in the phase separation and the domain morphology of main-chain LCP's.

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