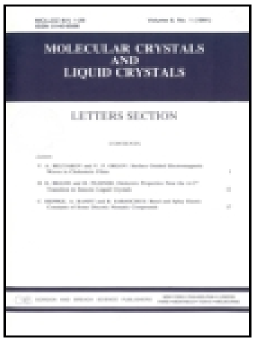

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Akihiko Matsuyama (2015) Phase Separations in Mixtures of a Flexible Polymer and a Cholesteric Liquid Crystal in the Presence of an External Field, Molecular Crystals and Liquid Crystals, 612:1, 33-45, DOI: 10.1080/15421406.2015.1044361

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1044361

Mol. Cryst. Liq. Cryst., Vol. 612: pp. 33–45, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1044361

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Phase Separations in Mixtures of a Flexible Polymer and a Cholesteric Liquid Crystal in the Presence of an External Field

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We present a mean field theory to describe phase behaviors in mixtures of a flexible polymer and a cholesteric liquid crystal under an external magnetic or electric field. Taking into account a chiral coupling between liquid crystals under the external field, we examine twist-untwist phase transitions and phase separations in the mixtures. Depending on the strength of the external field, we predict cholesteric-paranematic (Ch + N), nematic-paranematic (N + pN), cholesteric-nematic (Ch + N) phase separations on the temperature-concentration plane. We also calculate spinodal regions, which are important in phase separation kinetics inside binodal lines.

Keywords Cholesteric Liquid Crystal; External Field; twist-untwist; nematic-cholesteric phase transition

I. Introduction

Untwisting of a cholesteric phase by an external magnetic or electric field has been studied theoretically [1–13] and experimentally [14–21], since it has been first observed by de Gennes [1] and Meyer [14–16]. Applying the external field perpendicular to a helical axis of the cholesteric phase, untwisting of the helix takes place with positive dielectric or diamagnetic anisotropy. On increasing the external field H, the pitch p increases and diverges at a critical value Hc of the external field. When $H > H_c$, we have a nematic phase, oriented uniformly along the external field. This is known as a field-induced twist-untwist transition (or CNT) [22].

Recently, developing the molecular theory of the cholesteric phase presented by Lin-Liu et al. [23, 24], we have presented the mean field theory to describe phase behaviors of binary mixtures of a polymer and a liquid crystal, by taking into account of the chiral coupling between the components [25].

In this paper we develop our previous theory [25] to describe untwisting of cholesteric phases in mixtures of a flexible polymer chain and a cholesteric liquid crystal in the presence of an external magnetic or electric field. We derive the free energy of the mixtures under the external field and calculate the pitch and the critical field as a function of orientational

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order parameters and concentrations. We predict the field-induced CNT on the temperature-concentration plane and phase separations, such as a cholesteric-paranematic (Ch + pN) and nematic-paranematic (N + pN) phase, depending on the strength of the external field. We also calculate spinodal regions, which are important in phase separation kinetics inside the binodal lines.

II. Free Energy of Mixtures of a Flexible Polymer and a Cholesteric Liquid Crystal Under an External Field

A. Chiral Free Energy

Consider a binary mixture of a liquid crystal molecule and a flexible polymer chain. To describe a cholesteric phase of the mixture, we develop a mean field model proposed by Lin-Liu et al. [23, 24] and our previous theory [25].

Let N_P be the number of a polymer chain with n_P segments and N_L be the number of a low-molecular weight liquid crystal molecule of length L and diameter D. The volume of the liquid crystal and that of the polymer chain is given by $v_L = (\pi/4)\, D^2 L$ and $v_P = a^3 n_P$, respectively. Let $\phi_L = v_L \rho_L$ and $\phi_P = v_P \rho_P$ be the volume fraction of the liquid crystal and the polymer, respectively, where ρi is the number density $\rho_i = N_i/V$ of the molecule $i (= L, P) : \phi_L + \phi_P = 1$. Using the axial ratio $n_L = L/D$ of the liquid crystal, the volume per a liquid crystal molecule is given by $v_L = a^3 n_L$ where we define $a^3 = (\pi/4) D^3$.

The free energy consists of the following three terms:

$$F = F_{mix} + F_{ani} + F_{ext}. \tag{1}$$

The first term in Eq. (1) is the free energy of an isotropic mixing of a polymer and a liquid crystal molecule and is given by Flory-Huggins theory for polymer solutions [26]:

$$\alpha^3 \beta F_{mix}/V = \frac{\phi_L}{n_L} \ln \phi_L + \frac{\phi_P}{n_P} \ln \phi_P + \chi \phi_L \phi_P \tag{2}$$

where χ is the Flory-Huggins interaction parameter between a liquid crystal and a polymer in an isotropic phase and $\beta = 1/k_B T;\, T$ is the absolute temperature, k_B is the Boltzmann constant.

The second term in Eq. (1) shows the free energy for cholesteric phases. The configuration of the constituent molecules is characterized by its position vector $\mathbf{r}$ and its orientation unit vector Ω, defined by a polar angle θ and an azimuthal angle ϕ, or solid angle $d\Omega (= \sin\theta d\theta d\varphi)$, in a fixed coordinate frame. Let $f_L(\mathbf{n}(\mathbf{r}) \cdot \Omega)$ be the orientational distribution function of the liquid crystal molecule, where $\mathbf{n}(\mathbf{r})$ is the local director. It should be noted that the distribution function depends only on the relative angle between the local director $\mathbf{n}(\mathbf{r})$ and the molecular orientation vector Ω. The anisotropic part of the free energy in the second virial approximation is given by

$$\begin{aligned}\beta F_{ani} &= \rho_L \int f_L(n(r) \cdot \Omega) \ln 4\pi f_L(n(r) \cdot \Omega) dr d\Omega \\ &\quad + \frac{1}{2} \rho_L^2 \int f_L(r_1, \Omega_1) f_L(r_2, \Omega_2) \beta U_{LL}(r_1, \Omega_1; r_2, \Omega_2) dR,\end{aligned} \tag{3}$$

where $d\mathrm{R} \equiv d\mathrm{r}_1 d\mathrm{r}_2 \mathrm{d}\Omega_1\Omega_2$. The first term in Eq. (3) shows the entropy changes due to an orientational order- ing and U_{LL} is the orientation-dependent intermolecular potential between liquid crystal molecules. The lowest- order contributions to the interaction potential for the cholesteric phase are given by in a series of the Legendre polynomials [24, 25, 27]:

$$\begin{aligned} U_{LL}(\mathbf{r}_1, \boldsymbol{\Omega}_1; \mathbf{r}_2, \boldsymbol{\Omega}_2) = {} & U_{LL,1}(\mathbf{r}_{12})(\boldsymbol{\Omega}_1 \times \boldsymbol{\Omega}_2 \cdot \hat{\mathbf{r}}_{12}) P_1(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) \\ & + U_{LL,2}(\mathbf{r}_{12}) P_2(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2), \end{aligned} \tag{4}$$

where we have truncated by $P_2(x)$. The potential $U_{LL,1}$ shows the chiral interaction between liquid crystals. The term $(\boldsymbol{\Omega}_1 \times \boldsymbol{\Omega}_2 \cdot \hat{\mathbf{r}}_{12})$ represents scalars coupling between orientational and spatial variables, where $\hat{\mathbf{r}}_{12} = (\mathbf{r}_2 - \mathbf{r}_1)/|\mathbf{r}_{12}|$.

The potential $U_{LL,2}$ shows the intermolecular potential that accounts for the formation of a nematic phase, which has been used in Maier-Saupe [28] and Onsager models [29]. Following the symmetry consideration for cholesteric phases, we requires that the first term in Eq. (4) is odd in $\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2$ and the second term be even [30].

The last term in Eq. (1) is the magnetic (or electric) free energy relevant to orientational order. We here consider the coupling between a liquid crystal and an external field because we focus on flexible polymers. When the external magnetic field $\mathbf{H}$ is applied to the liquid crystal molecule having a diamagnetic anisotropy $\Delta\chi_L$, the external free energy is given by [2]

$$F_{ext} = -n_L \rho_L \Delta\chi_L \int H_\alpha Q_{\alpha\beta}(r) H_\beta dr, \tag{5}$$

where $Q_{\alpha\beta}(\mathrm{r})$ is the second rank order parameter tensor of the liquid crystal and in general is a function of position:

$$Q_{\alpha\beta}(r) \equiv \int f_L(n(r)\cdot\Omega)(\tfrac{3}{2}\Omega_\alpha\Omega_\beta - \tfrac{1}{2})d\Omega, \equiv \left\langle \tfrac{3}{2}\Omega_\alpha\Omega_\beta - \tfrac{1}{2}\delta_{\alpha\beta} \right\rangle, \tag{6}$$

where Ω_α is the Cartesian component of the molecular orientation vector $\boldsymbol{\Omega} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ at a position $\mathbf{r}$.

Using Eq. (6), we obtain

$$\iint f_L(n(r_1)\cdot\Omega_1) f_L(n(r_2)\cdot\Omega_2) P_2(\Omega_1\cdot\Omega_2) d\Omega_1 d\Omega_2 = \frac{2}{3} Q_{\alpha\beta}(r_1) Q_{\alpha\beta}(r_2), \tag{7}$$

$$\begin{aligned} & \iint f_L(n(r_1)\cdot\Omega_1) f_L(n(r_2)\cdot\Omega_2)(\Omega_1 \times \Omega_2 \cdot \hat{r}_{12}) P_1(\Omega_1\cdot\Omega_2) d\Omega_1 d\Omega_2 \\ & = \frac{4}{9} \varepsilon_{\alpha\beta\gamma} \hat{r}_{12,\alpha} Q_{\beta\mu}(r_1) Q_{\gamma\mu}(r_2), \end{aligned} \tag{8}$$

where $\varepsilon_{\alpha\beta\gamma}$ is Levi-Civita antisymmetric tensor of the third rank and $r\hat{r}_{12,\alpha}$ is the $\alpha(= x, y, z)$ component of the unit vector $\hat{\mathbf{r}}_{12}$. We here assume that the $Q_{\alpha\beta}(\mathbf{r}_2)$ does not change appreciably over the range of the potential and can be expanded in the Taylor series about $r(= |\mathbf{r}_{12}|)$:

$$Q_{\alpha\beta}(r_2) \approx Q_{\alpha\beta}(r_1) + r_\kappa \frac{\partial Q_{\alpha\beta}(r_1)}{\partial r_\kappa} + \frac{1}{2} r_\kappa r_\lambda \frac{\partial^2 Q_{\alpha\beta}(r_1)}{\partial r_\kappa r_\lambda}. \tag{9}$$

Substituting Eq. (9) into (7) and (8), the anisotropic free energy can be expressed as

$$\beta F_{ani}/V = \rho_L \int f_L(n(r)\cdot\Omega) \ln[4\pi f_L(n(r)\cdot\Omega)] d\Omega + \beta(F_1 + F_2)/V, \tag{10}$$

where we have the chiral component of the free energy

$$\beta F_1 = \frac{1}{2}\rho_L^2 C_{LL} \int \frac{4}{9}\varepsilon_{\alpha\beta\gamma} Q_{\mu\beta}(r_1)\partial_\alpha Q_{\mu\gamma}(r_1)dr_1, \tag{11}$$

and the usual nematic free energy

$$\begin{aligned}\beta F_2 = &\frac{1}{2}\rho_L^2 A_{LL} \int \frac{2}{3} Q_{\alpha\beta}(r_1)Q_{\alpha\beta}(r_1)dr_1 \\ &+\frac{1}{2}\rho_L^2 B_{LL} \int \frac{1}{3} Q_{\alpha\beta}(r_1)\partial_\mu \partial_\mu Q_{\alpha\beta}(r_1)dr_1,\end{aligned} \tag{12}$$

and the coefficients are defined as

$$A_{LL} \equiv \int \beta U_{LL,2}(r_{12})dr_{12}, \tag{13}$$

$$B_{LL} \equiv \int \beta U_{LL,2}(r_{12})z^2 dr_{12}, \tag{14}$$

$$C_{LL} \equiv \int \beta U_{LL,1}(r_{12})\frac{z^2}{r} dr_{12}, \tag{15}$$

We here employ a simple square wall interaction potential with a short range d_0, which is the order of the particle size. With this approximation we can take [25]

$$A_{LL} = -\upsilon_{LL}\nu_{LL}, \tag{16}$$

$$B_{LL} = -\frac{1}{3}\upsilon_{LL}\nu_{LL}d_0^2, \tag{17}$$

$$C_{LL} = -\upsilon_{LL}c_{LL}d_{0,} \tag{18}$$

where $\upsilon_{LL} \left(= (\pi/4)\, L^2 D\right)$ is the average excluded volume between the liquid crystals in random orientations. The interaction parameter $\nu_{LL}(\equiv -U_{LL}, 2/k_B T > 0)$ corresponds to the orientational-dependent (Maier-Saupe) interaction parameter between liquid crystal molecules for a nematic phase [28]. The chiral interaction parameter $c_{LL}(\equiv -U_{LL,1}/k_B T)$ corresponds to the strength of the chirality between liquid crystal molecules and is a pseudoscalar parameter.

In order to calculate the distortion free energy due to the spatial variation of the director in a cholesteric phase, we assume that the director is uniformly twisted along z axis with a pitch $p = 2\pi/q$:

$$\mathbf{n}(\mathbf{r}) = (\cos\theta, \sin\theta, 0), \tag{19}$$

and the tensor order parameter can be expressed as [2]

$$Q_{\alpha\beta}(r_1) = S_L\left(\frac{3}{2}n_\alpha(r_1)n_\beta(r_1) - \frac{1}{2}\delta_{\alpha\beta}\right), \tag{20}$$

where S is the scalar orientational order parameter of the liquid crystal:

$$S_L = \int P_2(n(r)\cdot\Omega)f_L(n(r)\cdot\Omega)d\Omega. \tag{21}$$

The scalar order parameter does not depend on a position $\mathbf{r}$ and the angle θ is a function of a position z along the pitch axis in our model. We here set the magnetic field $\mathbf{H}$ is taken along y axis:

$$\mathbf{H} = (0, H, 0). \tag{22}$$

When $\Delta\chi_L > 0$, the liquid crystal molecules are oriented along the external field. Substituting Eqs. (20) and (22) into Eqs. (5), (11), and (12), we obtain the free energy of the cholesteric phase:

$$F_{ch} = F_{ani} + F_{ext} = F_{nem} + F_{dis}, \tag{23}$$

where we have separated the free energy into two parts for convenience. One is the nematic free energy of Maier-Saupe type [28]:

$$a^3\beta F_{nem}/V = \frac{\phi_L}{n_L}\int f_L(n(r)\cdot\Omega)\ln[4\pi f_L(n(r)\cdot\Omega)]d\Omega - \frac{1}{2}\nu_{LL}\phi_L^2 S_L^2, \tag{24}$$

and the other is the distortion energy due to the spatial variation of the director in the presence of the external field:

$$a^3\beta F_{dis}/V = -\frac{1}{2}\nu_{LL}\phi_L^2 S_L^2\ g(Q), \tag{25}$$

where we define $Q \equiv qd_0$. The function $g\,(Q)$ contains the spatial variation of the twist angle and is written as

$$g(Q) = -\frac{Q}{8\pi^2}\int_0^{1/Q}\left[\left(\frac{\partial\theta}{\partial\tilde{z}}\right)^2 - 4\pi Q_0\left(\frac{\partial\theta}{\partial\tilde{z}}\right) - \left(\frac{2\pi}{\zeta}\right)^2\left(sin^2\theta - \frac{1}{3}\right)\right]d\tilde{z}, \tag{26}$$

and

$$\xi^2 \equiv \frac{\upsilon_{LL}\phi_L S_L}{2h_L^2}, \tag{27}$$

where we define $\tilde{z} \equiv z/(2\pi d_0)$ and $Q_0 \equiv c_{LL}/\nu_{LL}$. The value $Q0$ shows the pitch of the pure cholesteric phase in the absence of an external field [25]. The value of ξ is the magnetic coherence length [2]. The external field is given through the parameters $h_L^2 \equiv 3\beta\Delta\chi_L H^2$.

B. Cholesteric Pitch

The cholesteric pitch $p(= 2\pi d_0/Q)$ in an equilibrium state can be derived by minimizing the distortion free energy F_{dis} (Eq. (25)). The function $\theta(z)$ should satisfy the condition for minimum F_{dis} and the corresponding Euler equation is given by

$$\left(\frac{\zeta}{2\pi}\right)^2\left(\frac{\partial\theta}{\partial\tilde{z}}\right)^2 + \sin^2\theta = c, \tag{28}$$

where c is an arbitrary constant. The pitch p of the cholesteric phase satisfying the condition of a minimum in F_{dis} is

$$p = \int_{0}^{p} dz = \int_{0}^{1/Q} 2\pi d_0 \left(\frac{\partial \tilde{z}}{\partial \theta}\right) d\theta, \tag{29}$$

and using Eq. (28) we obtain

$$\frac{1}{Q} = \left(\frac{2}{\pi}\right) \zeta K(c), \tag{30}$$

where $K(c)$ is the complete elliptic integral of the first kind:

$$K(c) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{c - \sin^2\theta}}. \tag{31}$$

From the behaveor of $K(c)$, the value of 1/Q clearly diverges as $c \to 1$.
Substituting Eqs. (28) and (31) into (26), we obtain

$$g(Q) = \frac{1}{2\zeta^2}\left(c - \frac{1}{3}\right) - Q\left(-Q_0 + \frac{2}{\pi\zeta}E(c)\right), \tag{32}$$

where $E(c)$ is the complete elliptic integral of the second kind:

$$E(c) = \int_0^{\pi/2} \sqrt{c - \sin^2\theta}\, d\theta, \tag{33}$$

The constant c can be determined by $dg(Q)/dc = 0$ and we then obtain

$$E(c) = \frac{\pi}{2}\zeta Q_0, \tag{34}$$

and

$$\frac{p}{p_0} = \frac{Q_0}{Q} = \frac{4}{\pi^2}K(c)E(c), \tag{35}$$

where $p_0 = 2\pi d_0/Q_0$ is the pitch of a pure liquid crystal in the absence of the external field. Eq. (35) has been first derived by de Gennes [2].
Substituting Eq. (34) into (32), the function $g(Q)$ for the minimum of the distortion free energy is given by

$$g(Q) = \frac{1}{2\zeta^2}\left(c - \frac{1}{3}\right), \tag{36}$$

where the constant c is determined by Eq. (34).

The value of second elliptic integral (33) is larger than 1 and increases with increasing c from $c = 1$. When $(\pi/2)\xi Q_0 > 1$, the value of c is determined by Eq. (34) and the pitch Q of the cholesteric phase is given by Eq. (30). When $(\pi/2)\xi Q_0 < 1$, we have $Q = 0$ and $c = 1$ from Eq. (28). The cholesteric phase is defined by $Q > 0$ and $S_L \neq 0$, the nematic phase is given by $Q = 0$ and $S_L \neq 0$, and the isotropic phase is defined by $Q = SL = 0$. The orientational order parameter is determined by minimizing the free energy as shown in the next subsection.

C. Orientational Distribution Function in an Equilibrium State

The orientational distribution function $f_L(\mathbf{n}(\mathbf{r}) \cdot \Omega)$ of the liquid crystals is determined by the cholesteric free energy (Eq. (23)) with respect to these functions: $(\delta F_{ch}/\delta f_L) = 0$, under the normalization condition:

$$\int f_L(n(r) \cdot \mathbf{\Omega}) d\mathbf{\Omega} = 1. \tag{37}$$

We then obtain the distribution function of the liquid crystal molecules:

$$f_L(x) = \frac{1}{Z_L} exp\left[n_L \nu_{LL} \phi_L S_L (1 + g(Q)) P_2(x) \right], \tag{38}$$

The constants Z_L is determined by the normalization condition as $Z_L = 4\pi I_0[S_L]$ and the functions I_m is defined as:

$$I_m[S_L] \equiv \int_0^1 [P_2(x)]^m \exp\left[n_L \nu_{LL} \phi_L S_L (1 + g(Q)) P_2(x) \right] dx, \tag{39}$$

where m = 0, 1, 2.
Substituting Eq. (38) into (21), the scalar orientational order parameter S_L can be determined by the self-consistency equations:

$$S_L = I_1[S_L]/I_0[S_L], \tag{40}$$

Using the distribution function, Eq. (38), the free energy (Eq. (23)) of the cholesteric phase is given by

$$a^3 \beta F_{ch}/V = \frac{1}{2} \nu_{LL} \phi_L^2 S_L^2 (1 + g(Q)) - \frac{\phi_L}{n_L} \ln I_0[S_L]. \tag{41}$$

The total free energy F (Eq. (1)) of our system is given by the sum of Eqs. (2) and (41). The chemical potential of the liquid crystal molecule is given by

$$\begin{aligned} \beta\mu_L &= \beta(\partial F/\partial N_L)_{N_P} \\ &= n_L \left[\frac{1}{n_L} \ln\phi_L + \left(\frac{1}{n_L} - \frac{1}{n_P} \right) \phi_P + \chi\phi_P^2 + \frac{1}{2} \nu_{LL} \phi_L^2 S_L^2 (1 + g(Q)) - \frac{1}{n_L} \ln I_0[S_L] \right], \end{aligned} \tag{42}$$

and that of the polymer:

$$\begin{aligned} \beta\mu_P &= \beta(\partial F/\partial N_P)_{N_L} \\ &= n_P \left[\frac{1}{n_P} \ln\phi_P + \left(\frac{1}{n_P} - \frac{1}{n_L} \right) \phi_L + \chi\phi_L^2 + \frac{1}{2} \nu_{LL} \phi_L^2 S_L^2 (1 + g(Q)) \right]. \end{aligned} \tag{43}$$

III. Numerical Results

In this section we show some numerical results of the phase diagrams on the temperature-concentration plane for the mixtures of a flexible polymer and a cholesteric liquid crystal under an external field. The coexistence (binodal) curve can be calculated by the standard

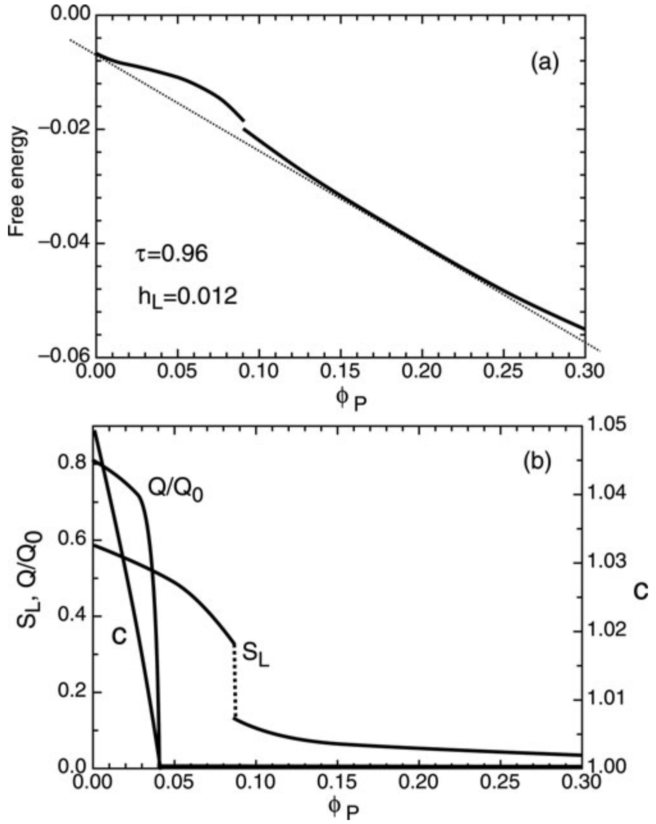

Figure 1. (a) Free energy ($\alpha^3\beta F/V$) plotted against the concentration ϕ_P at $\tau = 0.96$ for $h_L = 0.012$ (b) Orientational order parameter *S*, wavenumber *Q/Q*$_0$, and the constant *c* as a function of ϕ_P.

common-tangent construction in the free energy (Eq. (1)) to find coexisting phases of different concentrations. We here take $\chi/v_{LL} = 0.1$. The binodal curves can be also obtained by solving the two-phase coexistence conditions: the chemical potentials μ_L and μ_P of coexisting phases have to be equal to each other [31].

In the numerical calculation, we here define the reduced temperature

$$\tau \equiv T/T_{CI} = 4.55/(n_L v_{LL}), \tag{44}$$

where T_{CI} shows the cholesteric-isotropic phase transition (CIT) temperature of a pure liquid crystal in the absence of an external field [25]. The value $Q_0 (\equiv c_{LL}/v_{LL} = 2\pi d_0/p_0)$ is the pitch of the pure liquid crystal and we can estimate as $Q_0 = 0.01$ for the typical pitch $Q_0 = 3000$ nm and the length $Q_0 = 30$ nm of a liquid crystal molecule. The chiral coupling parameter between liquid crystals is given as a function of the temperature $\tau : c_{LL} = Q_0 v_{LL}$. The dimensionless parameters of the external field is given by $h_L = (\sqrt{3\Delta\chi_L/k_B T})H$ for $\Delta\chi_L > 0$. For numerical calculations, we here take $n_L = 2, n_P = 20$.

Figure 1(a) shows the free energy ($\alpha^3\beta F/V$: solid curve) plotted against the concentration ϕ_P at $\tau = 0.96$ for *hL* = 0.012. The dotted line shows the common tangent line for coexisting phases. Figure 1(b) shows the orientational order parameter *SL*, wave number *Q/Q*$_0$, and the constant *c* as a function of ϕ_P. At low concentrations $\phi_P < 0.04$,

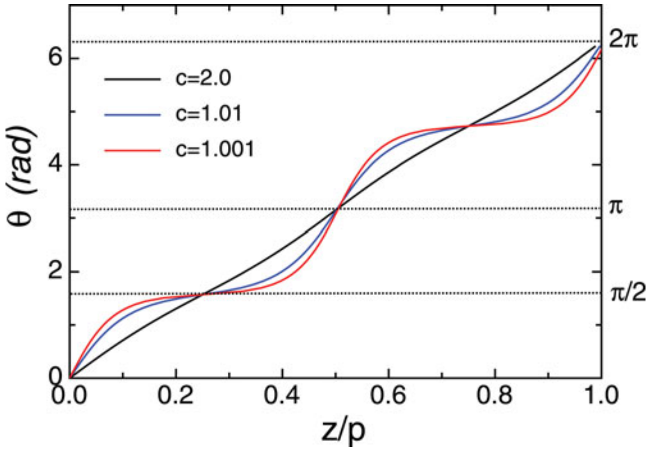

Figure 2. Twist angle θ plotted against a position z along the pitch axis for various values of a constant c.

we have the cholesteric (Ch) phase, where $Q > 0 (c > 1)$ and $S > 0$. On increasing ϕ_P, the Ch phase changes to the nematic (N) phase with $Q = 0 (c = 1)$ and $S > 0$ and the constant c continuously decreases to 1. We find the second- order cholesteric-nematic phase transition (CNT). Further increasing ϕ_P, the orientartional order parameter SL jumps to a lower value and we have a paranematic (pN) phase (or weak nematic phase): the first-order nematic-paranematic phase transition (NpNT). As shown in Fig. 1(a), at this temperature we have the phase separation between the Ch and pN phase (Ch + pN).

From Eq. (28), the profile of the twist angle $\theta(z)$ can be calculated by

$$\frac{z}{p} = \frac{1}{4K(c)} \int_0^\theta \frac{d\theta}{\sqrt{c - \sin^2\theta}}. \tag{45}$$

Figure 2 shows the twist angle θ as a function of a position z/p for various values of a constant c. When $c = 2$ for low external fields, the value of θ lineally changes as a function of z. As increasing the effect of the external field, the equilibrium value of c decreases (see Fig. 1(b)), and the profile of the twist angle θ is changed. When $c = 1.01$, the liquid crystal molecules favor to align along the filed **H** and the plateau regions of $\theta = \pi/2$ and $\theta = 3\pi/2$ expand. In regions of $\theta = 0, \pi, 2\pi$, the twist angle θ is sharply changed as a function of z, where the unfavorable twist energy is stored. When $c = 1$, the Ch phase continuously changes to the N phase.

Figure 3 shows the phase diagram on the temperature (T/TCI)−concentration(ϕ) plane in the absence of the external field. The solid curves show binodal line and the black dotted line corresponds to the CIT line. We have two-phase separation between a cholesteric and an isotropic phase (Ch + I) below $T/TCI = 1$. Inside the binodal lines, we have a spinodal region (horizontal dotted lines), where the free energy becomes unstable.

Figure 4 shows the phase diagram on the temperature-concentration plane in the presence of a weak external field $hL = 0.01$. The solid curves are the binodal line, the dotted line shows the NpNT, and the dashed line is the CNT. The NpNT temperature of the pure liquid crystal ($\phi_P = 0$) shifts to higher temperatures because of the external field. For the weak external field $hL = 0.01$, the nematic phase appears on the narrow region between the Ch and pN phases. The CNT and NpNT temperatures decrease with increasing

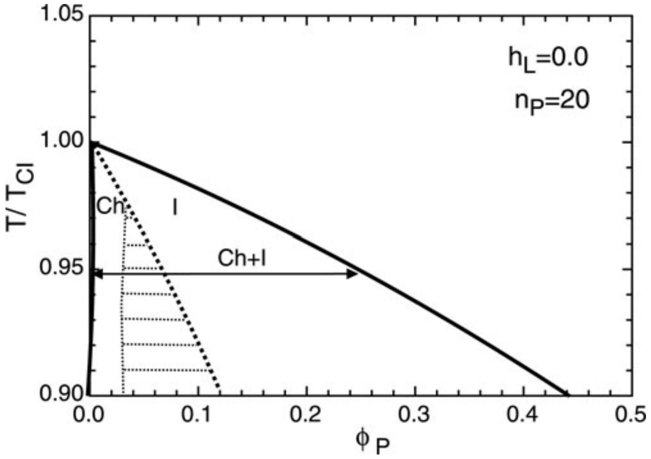

Figure 3. Phase diagram on the temperature (T/T_{CI})− concentration(ϕ_P) plane in the absence of the external field. Phase separation between a cholesteric and an isotropic phase (Ch + I) appears.

the polymer concentration ϕ_P. We find the phase separation (N + pN) between a nematic and a paranematic phase at $1.025 < \tau < 1.03$ and the cholesteric-nematic (Ch + N) phase separations at $\tau < 1.025$. At low polymer concentrations, the stable Ch and N phases appear. We also have the three phase coexistence (Ch + N + pN) between Ch, N, and pN phases at $T/TCI = 1.025$.

Figure 5 shows the phase diagram on the temperature-concentration plane with $hL = 0.012$. On increasing the strength (hL) of the external field, the CNT temperature shifts to lower temperatures and the nematic phase appears on a broad region between the pN and Ch phases. We have the N + pN and Ch + pN phase separations. At $\tau = 1.0$, we find three-phase coexistence (Ch + N + pN) between Ch, N and pN phases. We also have the nematic spinodal region (between CNT and NpNT lines) and cholesteric spinodal one

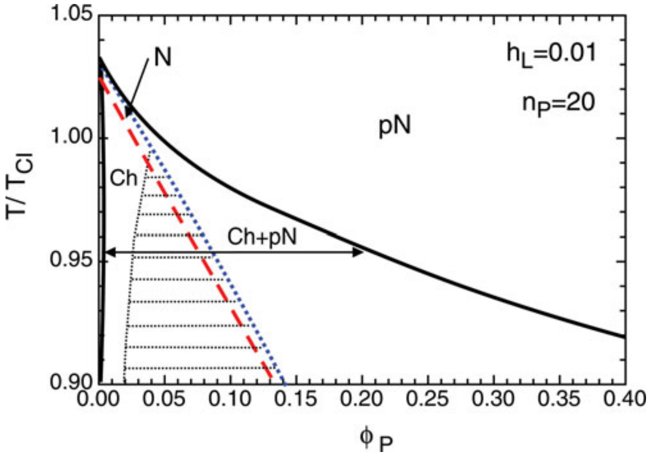

Figure 4. Phase diagram on the temperature-concentration plane in the presence of a weak external field $h_L = 0.01$.

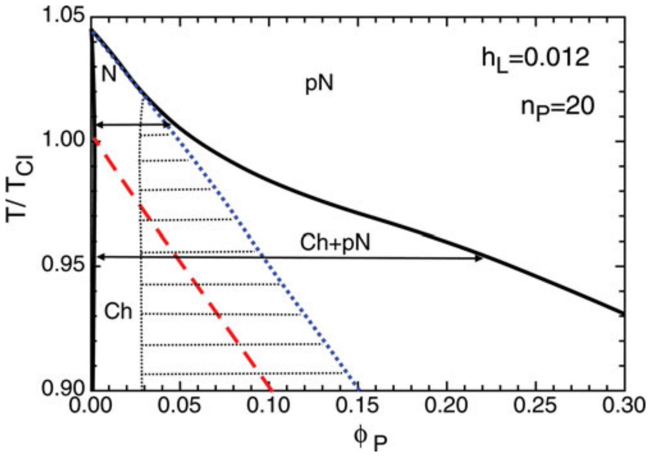

Figure 5. Phase diagram on the temperature-concentration plane in the presence of an external field $h_L = 0.012$.

(below the CNT line) inside the binodal curves. In the nematic spinodal region, it has been shown that the phase separation is induced by the instability of the orientational ordering [32]. In the cholesteric spinodal region, however, the instability of the pitch Q will affect the phase separation dynamics [33]. It will be a challenging subject of phase separations accompanying cholesteric ordering.

Summary

We have presented a mean field theory to describe phase behaviors in binary mixtures of a flexible polymer and a cholesteric liquid crystal in the presence of an external magnetic or electric field. We have calculated the orientational order parameters, the pitch of the cholesteric phase, and the phase diagrams on the temperature-concentration plane. It is found that in the presence of the external field the CNT and NpNT take place in the mixtures, depending on temperature and concentration. The CNT exists at lower temperatures and at lower concentrations of the NpNT line. On increasing the strength of the external field, the CNT temperature shifts to lower temperatures and the nematic phase appears between the pN and Ch phases. We predict Ch + N, N + pN, and Ch + N phase separations on the temperature-concentration plane. We also find the nematic spinodal and cholesteric spinodal regions, which will be an important in phase separation kinetics.

Funding

This work was supported by Grant-in Aid for Scientific Research (C) (Grant No. 26400435) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] De Gennes, P. G. (1968). *Solid State Commun.*, *6*, 163.
[2] De Gennes, P. G., & Prost, J. (1993). *The Physics of Liquid Crystals*, (Oxford University Press, New York).
[3] Parsons, J. D., & Hayes, C. F. (1974). *Phys. Rev. A 9*, 2652.

[4] Yamashita, M., Kimura, H., & Nakano, H. (1981). *Mol. Cryst. Liq. Cryst. 68*, 79.
[5] Lin-Liu, Y. R. (1983). *Phys. Rev. A 27*, 594.
[6] Lee, M. A., & Vlachopoulos, P. (1984). *Mol. Cryst. Liq. Cryst. 110*, 341.
[7] Kedney, P. J., & Stewart, I. W. (1994). *Lett. Math. Phys. 31*, 261.
[8] Shiyanovskii, S. V., & Terentieva, J. G. (1994). *Phys. Rev. E 49*, 916.
[9] Shiyanovskii, S. V., & Terentieva, J. G. (1996). *Liq. Cryst. 21*, 645.
[10] Seidin, R., Mukamel, D., & Allender, D. W. (1997). *Phys. Rev. E. 56*, 1773.
[11] Scarfone, A. M., Lelidis, I., & Barbero, G. (2011) *Phys. Rev. E 84*, 021708.
[12] Barbero, G., & Scarfone, A. M. (2013). *Phys. Rev. E 88*, 032505.
[13] Fukuda, J., & Zumer, S. (2013). *Phys. Rev. E 87*, 042506.
[14] Meyer, R. B. (1968). *Appl. Phys. Lett. 12*, 281.
[15] Meyer, R. B. (1969). *Appl. Phys. Lett. 14*, 208.
[16] Durand, G., Leger, L., Rondelez, F., & Veyssie, M. (1969). *Phys. Rev. Lett. 22*, 227.
[17] Motoc, C., Cuculescu, I., & Honciuc, M. (1978). *Mol. Cryst. Liq. Cryst. 45*, 215.
[18] van Sprang, H. A., & van de Venne, J. L. M. (1985). *J. Appl. Phys. 57*, 175.
[19] Smalyukh, I. I., Senyuk, B. I., Palffy-Muthoray, P., Lavrentovich, O. D., Huang, H., Gartland, E. C. Jr., Bodnar, V. H., Kosa, T., & Taheri, B. (2005). *Phys. Rev. E. 72*, 061707.
[20] Mikityuk, Z., Nevmerzhitska, O., Zaremba, P., & Vistak, M. (1996). *Mol. Cryst. Liq. Cryst. 275*, 3.
[21] Hotra, Z., Mykytyuk, Z., Hotra, O., Fechan, A., Syshynskyy, O., Yasynovska, O., & Kotsun, V. (2011). *Mol. Cryst. Liq. Cryst. 535*, 225.
[22] Oswald, P. (2006). in *Phase Transitions. Applications to Liquid Crystals, Organic Electronic and Optoelectric Fields*, Ed. by Popa-Nita, V. (Research Signpost, Kerala, India).
[23] Lin-Liu, Y. R., Shih, Y. M., & Woo, C. W. (1977). *Phys. Rev. A 15*, 2550.
[24] Lin-Liu, Y. R., Shih, Y. M., Woo, C. W., & Tan, H. T. (1976). *Phys. Rev. A 14*, 445.
[25] Matsuyama, A. (2013). *J. Chem. Phys. 139*, 174906.
[26] Flory, P. J. (1953). *Principles of Polymer Chemistry* (Cornell University, Ithaca).
[27] Goossens, W. J. A. (1971). *Mol. Cryst. Liq. Cryst. 12*, 237–244.
[28] Maier, W., & Saupe, A. (1959). *Z. Naturforsch 14a*, 882.
[29] Onsager, L. (1949). *Ann. N. Y. Acad. Sci. 51*, 627.
[30] Straley, J. P. (1974). *Phys. Rev. A*, *10*, 1881.
[31] Matsuyama, A. (2010). Chap. 2, in *Encyclopedia of Polymer Blends*, Vol.1, Ed. by Isayev, A. I. (WILEY-VCH, Weinheim).
[32] Matsuyama, A., Evans, R. M. L., & Cates, M. E. (2000). *Phys. Rev. E 61*, 2977.
[33] De Luca, G., & Rey, A. D. (2004). *Phys. Rev. E 69*, 011706.

Appendix A: Free Energy in the Absence of an External Filed

In this Appendix, we derive the free energy in the absence of the external field. When $h_L = 0$, Eq. (26) is given by

$$g(Q) = -\frac{Q}{8\pi^2}\int_0^{1/Q}\left[\left(\frac{\partial\theta}{\partial\tilde{z}}\right)^2 - 4\pi Q_0\left(\frac{\partial\theta}{\partial\tilde{z}}\right)\right]d\tilde{z}, \tag{A1}$$

and using $\theta = qz$ we obtain

$$g(Q) = \frac{1}{2}\left[Q_0^2 - (Q - Q_0)^2\right]. \tag{A2}$$

Then the equilibrium value of the pitch is given by $(dg/dQ)_T = 0$ and then we obtain $Q = Q_0$ and

$$g(Q) = \frac{1}{2}Q_0^2. \tag{A3}$$

Substituting Eq. (A3) into Eq. (41), we obtain the cholesteric free energy for $hL = 0$:

$$a^3\beta F_{ch}/V = \frac{1}{2}\nu_{LL}\phi_L^2 S_L^2\left(1 + \frac{1}{2}Q_0^2\right) - \frac{\phi_L}{n_L}\ln I_0[S_L], \tag{A4}$$

The pitch is given by $Q_0 = c_{LL}/\upsilon_{LL}$ in our model. If the interaction parameters have entropic and energy terms, we may set $c_{LL} = A + B/T$ and $\upsilon_{LL} = C + D/T$, where *A, B, C, D* are constants.

Appendix B: Critical Field

The critical field strength $\left(h_L^c\right)$, where the pitch p tends to be infinity, or Q = 0, is given by E(1) = 1 in Eq. (34):

$$h_L^c = \frac{\pi}{2}Q_0\sqrt{\frac{1}{2}\nu_{LL}\phi_L S_L}. \tag{B1}$$

When $h_L < h_L^c$, we have the cholesteric phase, while $h_L < h_L^c$ the untwisting of the cholesteric phase takes place and the nematic phase appears. The term in the distortion free energy (Eq. (25)) proportional to g(Q) can be identified as a bare twist elastic constant (K$_{22}$) and we then obtain

$$\tilde{K}_{22} = \frac{1}{2}\nu_{LL}S_L^2\phi_L^2, \tag{B2}$$

where $\tilde{K}_{22} \equiv a(K_{22}/k_BT)$. Using the twist elastic constant, we obtain the critical value (B1) of the external field for the mixtures:

$$h_L^c = \frac{\pi}{2}Q_0\sqrt{\frac{\tilde{K}_{22}}{\phi_L S_L}}. \tag{B3}$$