Phase diagrams of mixtures of a polymer and a cholesteric liquid crystal under an external field

Akihiko Matsuyama

Articles you may be interested in

Theory of polymer-dispersed cholesteric liquid crystals
J. Chem. Phys. **139**, 174906 (2013); 10.1063/1.4828940

Solvent effect on phase transition of lyotropic rigid-chain liquid crystal polymer studied by dissipative particle dynamics
J. Chem. Phys. **138**, 024910 (2013); 10.1063/1.4774372

Phase diagrams of binary mixtures of liquid crystals and rodlike polymers in the presence of an external field
J. Chem. Phys. **136**, 224904 (2012); 10.1063/1.4728337

Theory of binary mixtures of a rodlike polymer and a liquid crystal
J. Chem. Phys. **132**, 214902 (2010); 10.1063/1.3447892

Induced nematic phase in a polymer/liquid crystal mixture
J. Chem. Phys. **112**, 1046 (2000); 10.1063/1.480628

Phase diagrams of mixtures of a polymer and a cholesteric liquid crystal under an external field

Akihiko Matsuyama[a)]

Department of Bioscience and Bioinformatics, Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology, Kawazu 680-4, Iizuka, Fukuoka 820-8502, Japan

We present a mean field theory to describe phase behaviors in mixtures of a polymer and a cholesteric liquid crystal under an external magnetic or electric field. Taking into account a chiral coupling between a polymer and a liquid crystal under the external field, we examine twist-untwist phase transitions and phase separations in the mixtures. It is found that a cholesteric-nematic phase transition can be induced by not only the external field but also concentration and temperature. Depending on the strength of the external field, we predict cholesteric-paranematic (Ch+pN), nematic-paranematic (N+pN), cholesteric-nematic (Ch+N) phase separations, etc., on the temperature-concentration plane. We also discuss mixtures of a non-chiral nematic liquid crystal and a chiral dopant. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901085]

I. INTRODUCTION

The behaviors of liquid crystals in the presence of an external field are of important for many technological applications as well as fundamental physical researches.[1] The effects of an external field have been studied on the nematic-isotropic phase transition (NIT) of nematic liquid crystals,[2,3] the cholesteric-nematic phase transitions (CNT) of cholesteric liquid crystals,[4–10] liquid crystalline elastomers,[11–13] and the phase diagrams of mixtures of polymers and nematic liquid crystals.[14–16]

The influence of an external magnetic or electric field on a cholesteric liquid crystal has been studied theoretically[17–27] and experimentally.[28–32] This problem in an external field was first studied by de Gennes[6] and Meyer.[7–9] 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. We here assume that the thickness of the sample is sufficiently large and the boundary conditions can be neglected. On increasing the external field H, the pitch p increases and diverges at a critical value H_c 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),[10] which has been used in liquid crystal displays.

Most experiments of the field-induced CNT have been carried out, not on pure cholesteric liquid crystals, but on mixtures of a nematic liquid crystal and a chiral dopant.[7,8,31] It is well known that the critical field H_c is a linear function of the concentration of dopants in the dilute regime and the pitch of a helix is inversely proportional to the concentration.[1] There are many studies of the CNT based on the Frank's elastic theory,[1,17–26] however, it cannot describe the concentration

dependences. To describe the concentration dependences, we need to consider binary mixtures of a liquid crystal and another molecule. Recently, developing the molecular theory of the cholesteric phase presented by Lin-Liu *et al.*,[33,34] we have presented the molecular theory to describe phase behaviors of binary mixtures of a liquid crystal and a polymer, by taking into account of the chiral coupling between the components.[35] We have obtained the expression of the pitch of a cholesteric phase and the twist elastic constant as a function of orientational order parameters and concentrations and found various phase separations between a cholesteric and an isotropic phases (Ch+I) and two cholesteric phases (Ch$_1$+Ch$_2$).

In this paper, we develop our previous theory[35] to describe cholesteric phases in mixtures of a cholesteric liquid crystal and a polymer chain 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 order parameters and concentrations. We predict the field-induced CNT on the temperature-concentration plane and novel phase behaviors, such as a cholesteric-paranematic (Ch+pN) and cholesteric-nematic (Ch+N) phase separations, etc., depending on the strength of the external field. Our theory can also apply to mixtures of a non-chiral nematic liquid crystal and a chiral dopant, where the cholesteric phase is induced by the chiral coupling between the liquid crystal and dopant under an external field. Our results are consistent with experimental observations.

In Sec. II, we extend a mean field theory to describe binary mixtures of a cholesteric liquid crystal and a polymer chain in the presence of an external field. In Sec. III, we show some numerical results of pitch, the strength of a critical field, and phase diagrams on the temperature-concentration plane for the mixtures. In the Appendix, we discuss mixtures of a nematic liquid crystal and a chiral dopant.

[a)]Electronic mail: matuyama@bio.kyutech.ac.jp. URL: http://iona.bio.kyutech.ac.jp/~aki/.

II. FREE ENERGY OF MIXTURES OF A POLYMER AND A CHOLESTERIC LIQUID CRYSTAL

A. Chiral free energy

Consider a binary mixture of a liquid crystal molecule and a polymer chain for which liquid crystalline ordering is forbidden in the constituent pure polymers, such as a flexible polymer chain. To describe cholesteric phases of the mixtures, we develop a mean field model proposed by Lin-Liu *et al.*[33,34] We here take into account an anisotropic coupling between polymers and liquid crystals.

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, where a^3 is the volume of a polymer segment. 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 ρ_i 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 here assume $a^3 = (\pi/4)D^3$ for simplicity.

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[36]

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

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 $\boldsymbol{\Omega}$, 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 $f_i(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega})$ be the orientational distribution function of the constituent molecule $i(= L, P)$, 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 $\boldsymbol{\Omega}$. The anisotropic part of the free energy in the second virial approximation is given by

$$\beta F_{ani}/V = \sum_{i=L,P} \rho_i \int f_i(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega}) \ln 4\pi f_i(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega}) d\mathbf{r} d\Omega$$
$$+ \frac{1}{2} \sum_{i,j=L,P} \rho_i \rho_j \int f_i(\mathbf{r}_1, \boldsymbol{\Omega}_1) f_j(\mathbf{r}_2, \boldsymbol{\Omega}_2)$$
$$\times \beta U_{ij}(\mathbf{r}_1, \boldsymbol{\Omega}_1; \mathbf{r}_2, \boldsymbol{\Omega}_2) d\mathbf{R}, \tag{3}$$

where $d\mathbf{R} \equiv d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1 \Omega_2$. The first term in Eq. (3) shows the entropy changes due to an orientational ordering and U_{ij} is the orientation-dependent intermolecular potential between

two particles i and j ($i, j = L, P$). We here take $U_{PP} = 0$ because we consider non-nematic polymer chains for the constituent pure polymers. The lowest-order contributions to the interaction potential for the cholesteric phase are given by in a series of the Legendre polynomials[33,35]

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

where we have truncated by $P_2(x)$. The potential $U_{ij,1}$ shows the chiral interaction between two particle i and j. 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 $U_{ij,2}$ shows the intermolecular potential that accounts for the formation of a nematic phase. We here assume that the potentials are short range interactions which have been used in Maier-Saupe[38] and Onsager models.[39] We employ a simple square wall interaction potential with a short range d_0, which is the order of the particle size. Following the symmetry consideration for cholesteric phases, we require that the first term in Eq. (4) is odd in $\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2$ and the second term be even.[37]

The last term in Eq. (1) is the magnetic (or electric) free energy relevant to orientational order. When the external magnetic field $\mathbf{H}$ is applied to the molecule $i(= L, P)$ having a diamagnetic anisotropy $\Delta \chi_i$, the external free energy is given by[1]

$$F_{ext} = - \sum_{i=L,P} n_i \rho_i \int \Delta \chi_i H_\alpha Q_{\alpha\beta}^{(i)}(\mathbf{r}) H_\beta d\mathbf{r}, \tag{5}$$

where $Q_{\alpha\beta}^{(i)}(\mathbf{r})$ is the second rank order parameter tensor of the molecule i[1]

$$Q_{\alpha\beta}^{(i)}(\mathbf{r}) = S_i \left(\frac{3}{2} n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}) - \frac{1}{2} \delta_{\alpha\beta} \right), \tag{6}$$

and S_i is the scalar orientational order parameter of the particle $i(= L, P)$

$$S_i = \int P_2(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega}) f_i(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega}) d\Omega. \tag{7}$$

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 $p = 2\pi/q$

$$\mathbf{n}(\mathbf{r}) = (\cos\theta, \sin\theta, 0). \tag{8}$$

The scalar order parameters do not depend on position $\mathbf{r}$ and θ is a function of z in our mean field approximations. We here set the magnetic field $\mathbf{H}$ is taken along y axis

$$\mathbf{H} = (0, H, 0). \tag{9}$$

When $\Delta \chi_i > 0$, the molecules are oriented along the external field.

Substituting Eqs. (6) and (9) into Eqs. (3)–(5), we obtain the free energy of the cholesteric phase (refer to previous paper[35] for details)

$$F_{ch} \equiv F_{ani} + F_{ext} = F_{nem} + F_{dis}, \tag{10}$$

where we have separated the free energy into two parts for convenience. One is the nematic free energy of Maier-Saupe type[38]

$$a^3 \beta F_{nem} / V = \sum_{i=L,P} \frac{\phi_i}{n_i} \int f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) \ln 4\pi f_i(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega}) d\Omega$$

$$- \frac{1}{2} v_{LL} \phi_L S_L (\phi_L S_L + 2\epsilon_n \phi_P S_P), \quad (11)$$

where the interaction parameter $v_{LL}(\equiv -\beta U_{LL,2} > 0)$ corresponds to the orientational-dependent (Maier-Saupe) interaction parameter between liquid crystal molecules[38] and $\epsilon_n \equiv v_{LP}/v_{LL}$: the parameter $v_{LP}(\equiv -\beta U_{LP,2})$ is the orientational-dependent interaction parameter between a liquid crystal and a polymer. When $v_{LP} > 0$, it means the attractive interaction between a liquid crystal and a polymer chain.

The second term of Eq. (10) shows the distortion energy due to the spatial variation of the director in the presence of an external field

$$a^3 \beta F_{dis} / V = -\frac{1}{2} v_{LL} \phi_L S_L (\phi_L S_L + 2\epsilon_n \phi_p S_P) g(Q) \quad (12)$$

where we define $Q \equiv q d_0$. The function $g(Q)$ contains the spatial variation of the twist angle and is given as

$$g(Q) \equiv -\frac{Q}{8\pi^2} \int_0^{1/Q} \left[\left(\frac{\partial \theta}{\partial \tilde{z}} \right)^2 - 4\pi Q^* \left(\frac{\partial \theta}{\partial \tilde{z}} \right) \right.$$

$$\left. - \left(\frac{2\pi}{\xi} \right)^2 \left(\sin^2 \theta - \frac{1}{3} \right) \right] d\tilde{z}, \quad (13)$$

$$Q^* \equiv Q_0 \frac{\phi_L S_L + 2\epsilon_x \phi_P S_P}{\phi_L S_L + 2\epsilon_n \phi_P S_P}, \quad (14)$$

and

$$\xi^2 \equiv \frac{v_{LL} \phi_L S_L (\phi_L S_L + 2\epsilon_n \phi_P S_P)}{2(\phi_L S_L h_L^2 + \phi_P S_P h_P^2)}, \quad (15)$$

where we define $\tilde{z} \equiv z/(2\pi d_0)$, $Q_0 \equiv c_{LL}/v_{LL}$, and $\epsilon_x \equiv c_{LP}/c_{LL}$. The chiral interaction parameter $c_{LL}(\equiv -\beta U_{LL,1} > 0)$ corresponds to the chirality between cholesteric liquid crystal molecules and $c_{LP}(\equiv -\beta U_{LP,1})$ is that between a liquid crystal and a polymer. The larger values of c_{ij} shows the stronger chiral coupling between molecules. The value of Q^* has the same form with the cholesteric pitch ($p^* = 2\pi d_0/Q^*$) of the mixtures in the absence of an external field and Q_0 shows the pitch of the pure cholesteric liquid crystals in the absence of an external field.[35] The value of ξ is the magnetic coherence length.[1] The external field is given through the parameters $h_L^2 \equiv 3\beta \Delta \chi_L H^2$ and $h_P^2 \equiv 3\beta \Delta \chi_P H^2$ for $\Delta \chi_i > 0$.

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. (12)). The function $\theta(z)$ should satisfy the condition for minimum F_{dis} and the corresponding Euler equation is given by

$$\left(\frac{\xi}{2\pi} \right)^2 \left(\frac{\partial \theta}{\partial \tilde{z}} \right)^2 + \sin^2 \theta = c, \quad (16)$$

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

$$p = \int_0^p dz = \int_0^{1/Q} 2\pi d_0 \left(\frac{\partial \tilde{z}}{\partial \theta} \right) d\theta, \quad (17)$$

and using Eq. (16) we obtain

$$\frac{1}{Q} = \left(\frac{2}{\pi} \right) \xi K(c), \quad (18)$$

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

$$K(c) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{c - \sin^2 \theta}}. \quad (19)$$

From the behavior of $K(c)$, the value of $1/Q$ clearly diverges as $c \to 1$.

Substituting Eqs. (16) and (19) into (13), we obtain

$$g(Q) = -\frac{1}{2\xi^2} \left(\frac{1}{3} - c \right) - Q \left(-Q^* + \frac{2}{\pi \xi} E(c) \right), \quad (20)$$

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

$$E(c) = \int_0^{\pi/2} \sqrt{c - \sin^2 \theta} d\theta. \quad (21)$$

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

$$E(c) = \frac{\pi}{2} \xi Q^* \quad (22)$$

and

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

$$= \frac{4}{\pi^2} K(c) E(c) \left[\frac{\phi_L S_L + 2\epsilon_n \phi_P S_P}{\phi_L S_L + 2\epsilon_x \phi_P S_P} \right], \quad (23)$$

where $p_0 = 2\pi d_0/Q_0$ is the pitch of a pure liquid crystal in the absence of the external field. When $\phi_P = 0$, Eq. (23) results in the pitch of the pure liquid crystal derived by de Gennes.[1]

Substituting Eq. (22) into (20), the function $g(Q)$ for the minimum of the distortion free energy is given by

$$g(Q) = \frac{1}{2\xi^2} \left(c - \frac{1}{3} \right), \quad (24)$$

where the constant c is determined by Eq. (22).

The value of second elliptic integral (21) is larger than 1 and increases with increasing c from $c = 1$. When $(\pi/2)\xi Q^* > 1$, the value of c is determined by Eq. (22) and the pitch Q of the cholesteric phase is given by Eq. (18). When $(\pi/2)\xi Q^* < 1$, we have $Q = 0$ and $c = 1$ from Eq. (16). The cholesteric phase is defined by $Q > 0$, $S_L \neq 0$, and $S_P \neq 0$, the nematic phase is given by $Q = 0$, $S_L \neq 0$, and $S_P \neq 0$, and the isotropic phase is defined by $Q = S_L = S_P = 0$. The orientational order parameters are determined by minimizing the free energy as shown in Subsection II C.

C. Orientational distribution functions in an equilibrium state

The orientational distribution function $f_L(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega})$ of the liquid crystals and $f_P(\mathbf{n}(\mathbf{r}) \cdot \mathbf{\Omega})$ of the polymer chains are

determined by the cholesteric free energy (Eq. (10)) with respect to these functions: $(\delta F_{ch}/\delta f_i) = 0$, under the normalization condition

$$\int f_i(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega})d\Omega = 1. \tag{25}$$

We then obtain the distribution function of the liquid crystal molecules

$$f_L(x) = \frac{1}{Z_L} \exp[n_L v_{LL}(\phi_L S_L + \epsilon_n \phi_P S_P)$$
$$\times (1 + g_L(Q))P_2(x)], \tag{26}$$

where we define

$$g_L(Q) \equiv -\frac{Q}{8\pi^2} \int_0^{1/Q} \left[\left(\frac{\partial\theta}{\partial\tilde{z}}\right)^2 - 4\pi Q_1^* \left(\frac{\partial\theta}{\partial\tilde{z}}\right) \right.$$
$$\left. - \left(\frac{2\pi}{\xi_1}\right)^2 \left(\sin^2\theta - \frac{1}{3}\right)\right]d\tilde{z}, \tag{27}$$

$$Q_1^* \equiv Q_0 \frac{\phi_L S_L + \epsilon_x \phi_P S_P}{\phi_L S_L + \epsilon_n \phi_P S_P}, \tag{28}$$

and

$$\xi_1^2 \equiv \frac{v_{LL}(\phi_L S_L + \epsilon_n \phi_P S_P)}{2h_L^2}. \tag{29}$$

The distribution function of the polymer chains is given by

$$f_P(x) = \frac{1}{Z_P} \exp[n_P v_{LP}\phi_L S_L(1 + g_{LP}(Q))P_2(x)], \tag{30}$$

where we define

$$g_{LP}(Q) \equiv -\frac{Q}{8\pi^2} \int_0^{1/Q} \left[\left(\frac{\partial\theta}{\partial\tilde{z}}\right)^2 - 4\pi\alpha_x \left(\frac{\partial\theta}{\partial\tilde{z}}\right) \right.$$
$$\left. - \left(\frac{2\pi}{\xi_2}\right)^2 \left(\sin^2\theta - \frac{1}{3}\right)\right]d\tilde{z}, \tag{31}$$

$\alpha_x \equiv c_{LP}/v_{LP}$, and

$$\xi_2^2 \equiv v_{LP}\phi_L S_L/(2h_P^2). \tag{32}$$

The constants Z_L and Z_P are determined by the normalization condition as $Z_L = 4\pi I_0[Q]$ and $Z_P = 4\pi J_0[Q]$, respectively. The functions I_m and J_m are defined as

$$I_m[Q] \equiv \int_0^1 [P_2(x)]^m \exp[n_L v_{LL}(\phi_L S_L + \epsilon_n \phi_P S_P)$$
$$\times (1 + g_L(Q))P_2(x)]dx, \tag{33}$$

$$J_m[Q] \equiv \int_0^1 [P_2(x)]^m \exp[n_P v_{LP}\phi_L S_L$$
$$\times (1 + g_{LP}(Q))P_2(x)]dx, \tag{34}$$

respectively, where $m = 0, 1, 2, \ldots$.

Using Eqs. (16), (18), and (22) we obtain

$$g_L(Q) = \frac{1}{2\xi_1^2}\left(c - \frac{1}{3}\right)$$
$$- Q\left[-Q_1^* + \left(\frac{1}{\xi^2} + \frac{1}{\xi_1^2}\right)\frac{\xi}{\pi}E(c)\right] \tag{35}$$

for Eq. (27) and

$$g_{LP}(Q) = \frac{1}{2\xi_2^2}\left(c - \frac{1}{3}\right)$$
$$- Q\left[-\alpha_x + \left(\frac{1}{\xi^2} + \frac{1}{\xi_2^2}\right)\frac{\xi}{\pi}E(c)\right] \tag{36}$$

for Eq. (31).

Substituting Eqs. (26) and (30) into Eq. (7), the scalar orientational order parameters S_L and S_P can be determined by the two coupled-self-consistency equations

$$S_L = I_1[Q]/I_0[Q], \tag{37}$$

$$S_P = J_1[Q]/J_0[Q]. \tag{38}$$

Using the distribution functions, Eqs. (26) and (30), the free energy (Eq. (10)) of the cholesteric phase is given by

$$a^3\beta F_{ch}/V = \frac{1}{2}v_{LL}\phi_L S_L(\phi_L S_L + 2\epsilon_n \phi_P S_P)(1 + g(Q))$$
$$- \frac{\phi_P}{n_P}\ln J_0[Q] - \frac{\phi_L}{n_L}\ln I_0[Q]. \tag{39}$$

The total free energy F of our system is given by the sum of Eqs. (2) and (39).

The chemical potential of the liquid crystal molecule is given by

$$\beta\mu_L = \beta(\partial F/\partial N_L)_{N_P}$$
$$= n_L\left[\frac{1}{n_L}\ln\phi_L + \left(\frac{1}{n_L} - \frac{1}{n_P}\right)\phi_P + \chi\phi_P^2\right.$$
$$+ \frac{1}{2}\phi_L S_L(\phi_L S_L + 2\epsilon_n \phi_P S_P)(1 + g(Q))$$
$$\left. - \frac{1}{n_L}\ln I_0[Q]\right], \tag{40}$$

and that of the polymer

$$\beta\mu_P = \beta(\partial F/\partial N_P)_{N_L}$$
$$= n_P\left[\frac{1}{n_P}\ln\phi_P + \left(\frac{1}{n_P} - \frac{1}{n_L}\right)\phi_L + \chi\phi_L^2\right.$$
$$+ \frac{1}{2}\phi_L S_L(\phi_L S_L + 2\epsilon_n \phi_P S_P)(1 + g(Q))$$
$$\left. - \frac{1}{n_P}\ln J_0[Q]\right]. \tag{41}$$

In Sec. III, we show some numerical results of the physical properties of the cholesteric phase in the presence of the external field.

III. MIXTURES OF A CHOLESTERIC LIQUID CRYSTAL AND A POLYMER

In our numerical calculation, we have three interaction parameters related to cholesteric ordering: the chiral interaction parameter $\epsilon_x = c_{LP}/c_{LL}$, the nematic interaction $\epsilon_n = v_{LP}/v_{LL}$ between a polymer and a liquid crystal, and $Q_0(\equiv c_{LL}/v_{LL} = 2\pi d_0/p_0)$ is the pitch of the pure liquid crystal. We can estimate as $Q_0 \simeq 0.01$ for the typical pitch $p_0 = 3000$ Å and the length $d_0 = 30$ Å of a liquid crystal molecule.

The cholesteric phase of a pure liquid crystals in the absence of an external field appears at

$$n_L v_{LL} = \frac{n_L U_{LL,2}}{k_B T_{CI}} \simeq 4.55, \qquad (42)$$

where T_{CI} shows the cholesteric-isotropic phase transition (CIT) temperature of a pure liquid crystal in the absence of an external field. We then define the reduced temperature

$$\tau \equiv T/T_{CI} = 4.55/(n_L v_{LL}). \qquad (43)$$

The numerical parameters are given as a function of the temperature τ: $c_{LL} = Q_0 v_{LL}$, $c_{LP} = \epsilon_x c_{LL}$, and $v_{LP} = \epsilon_n v_{LL}$. The estimations of the interaction parameters ϵ_n and ϵ_x have been discussed in our previous paper[35] and are of the order of 0.1–1, resulting the twist elastic constant $K_{22} \sim 10^{-6}$ dyn of a typical value.

A. Twist-untwist transitions and a critical field

In this subsection, we first show the twist-untwist transitions in the mixtures. For numerical calculations, we here take $n_L = 2$, $\epsilon_n = 0.3$, and $h_P = 0$ (note that when $h_P = 0$ we have $1/\xi_2^2 = 0$).

Figure 1 shows order parameters S_L, S_P, and the pitch $Q/Q_0(\propto p^{-1})$ plotted against the temperature T/T_{CI} at the polymer concentration $\phi_P = 0.001$ for $\epsilon_x = 0.3$, $n_P = 10$, and $h_L = 0.014$. The pitch Q is normalized by Q_0 of the pure liquid crystal in the absence of the external field. At low temperatures, we have the cholesteric phase with $S_L > 0$, $S_P > 0$, and $Q > 0$. As increasing temperature, the value of Q decreases and becomes zero, where the cholesteric (Ch) phase changes to the nematic (N) phase with $Q = 0$. We find the
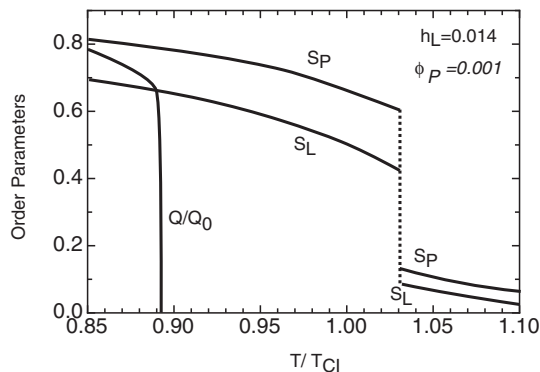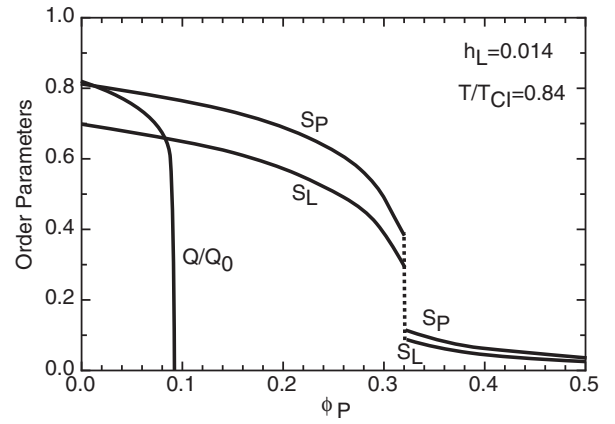

FIG. 2. Order parameters S_L, S_P, and the pitch $Q/Q_0(\propto p^{-1})$ plotted against the concentration ϕ_P at the temperature $T/T_{CI} = 0.84$ for $\epsilon_x = 0.3$, $n_P = 10$, and $h_L = 0.014$.

twist-untwist CNT, which depends only on the pitch while the orientational order parameters continuously change. Further increasing temperature, orientational order parameters jump to nonzero values and the system shows a weak nematic (or paranematic: pN) phase. We find the nematic-paranematic phase transition (NpNT). The order parameter S_P is larger than S_L because of the anisotropic coupling ϵ_n between the polymer and liquid crystal. The NpNT is the first-order phase transition, while the CNT is the second-order one.

Figure 2 shows order parameters S_L, S_P, and the pitch $Q/Q_0(\propto p^{-1})$ plotted against the concentration ϕ_P at the temperature $T/T_{CI} = 0.84$ for $\epsilon_x = 0.3$, $n_P = 10$, and $h_L = 0.014$. On increasing the polymer concentration, the value of Q decreases and we have the CNT and NpNT. As shown in Figs. 1 and 2, we find that the CNT and NpNT can be induced by temperature and concentration. On increasing the external field h_L, the CNT shifts to lower temperatures and lower concentrations. When $h_L = 0$, we only have the CIT.[35]

The critical field strength (h_L^c), where the pitch p of a twist in the cholesteric tends to infinity, or $Q = 0$, is given by $E(1) = 1$ in Eq. (22)

$$h_L^c = \frac{\pi}{2} Q^* \sqrt{\frac{1}{2} v_{LL}(\phi_L S_L + 2\epsilon_n \phi_P S_P)}. \qquad (44)$$

When $h_L < h_L^c$ we have the cholesteric phase, while $h_L > h_L^c$ the untwisting of the cholesteric twist takes place and the nematic phase appears. The term in the distortion free energy (Eq. (12)) proportional to $g(Q)$ can be identified as a bare twist elastic constant (K_{22}) and then we obtain

$$\tilde{K}_{22} = \frac{v_{LL}}{2} S_L \phi_L (\phi_L S_L + 2\epsilon_n \phi_P S_P), \qquad (45)$$

where $\tilde{K}_{22} \equiv a(K_{22}/k_B T)$. Using the twist elastic constant, we obtain the critical value (44) of the external field for the mixtures

$$h_L^c = \frac{\pi}{2} Q^* \sqrt{\frac{\tilde{K}_{22}}{\phi_L S_L}}. \qquad (46)$$

The orientational order parameters can be calculated by Eqs. (37) and (38) with $Q = 0$, $c = 1$, and $\xi_{1,c} \equiv \xi_1(h_L^c)$. When

FIG. 1. Order parameters S_L, S_P, and the pitch $Q/Q_0(\propto p^{-1})$ plotted against the temperature T/T_{CI} at the polymer concentrations $\phi_P = 0.001$ for $\epsilon_x = 0.3$, $n_P = 10$, and $h_L = 0.014$.
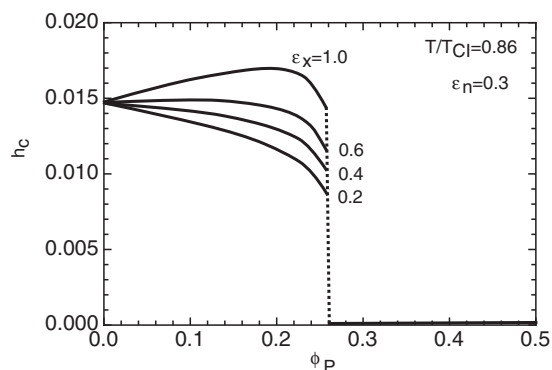
FIG. 3. Critical field h_L^c as a function of ϕ_P for various values of the chiral interaction ϵ_x at $T/T_{CI} = 0.86$ for $\epsilon_n = 0.3$ and $n_P = 10$.

$\phi_P \ll 1$, Eq. (14) can be expanded as

$$Q^* \simeq Q_0 \left[1 + 2(\epsilon_x - \epsilon_n) \frac{S_P}{S_L} \phi_P \cdots \right]. \qquad (47)$$

When $\epsilon_x > \epsilon_n$ ($\epsilon_x < \epsilon_n$), the pitch $p(\propto 1/Q)$ decreases (increases) with increasing ϕ_P. The value of $(\epsilon_x - \epsilon_n)S_P/S_L$ corresponds to the "microscopic twisting power" of the solute, depending on the nature of both solute and solvent molecules.[1] Then the strength of the critical field depend on the chiral interaction parameter ϵ_x.

Figure 3 shows the critical field h_L^c as a function of ϕ_P for various values of the chiral interaction ϵ_x at $T/T_{CI} = 0.86$ for $\epsilon_n = 0.3$ and $n_P = 10$. When $h_L < h_L^c$ we have the cholesteric phase, while $h_L > h_L^c$ the untwisting of a cholesteric twist takes place and the nematic phase appears. When $\epsilon_x = 0.2$, the value of the critical field decreases with increasing ϕ_P and jumps to zero at $\phi_P \simeq 0.26$. When $\phi_P > 0.26$, the system always shows a nematic or paranematic phase in the presence of an external field. When the chiral interaction between a polymer and a liquid crystal is strong ($\epsilon_x = 1$), the critical field h_L^c has a maximum as a function of ϕ_P.

Figure 4 shows the order parameters S_L, S_P, and the pitch wavenumber $Q/Q_0 (\propto p^{-1})$ plotted against the external field h_L at the polymer concentrations $\phi_P = 0.01$, $T/T_{CI} = 0.95$
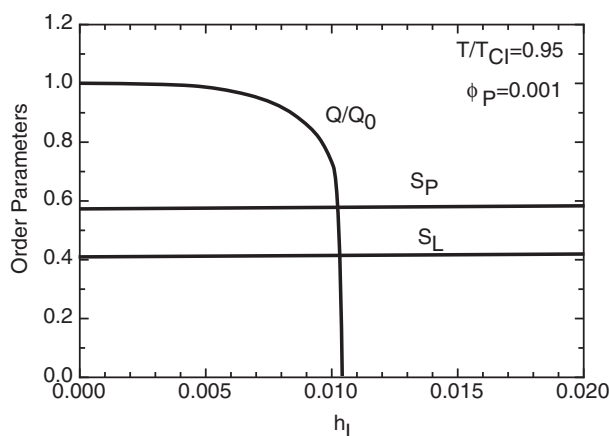
for $\epsilon_x = 0.2$. On increasing the strength of the external field, the pitch p diverges to infinity ($Q \to 0$) and the CNT takes place due to the external field. The orientational order parameters slightly increase with increasing h_L. As shown in Figs. 1, 2, and 4, our theory demonstrates that the CNT can be induced by not only external field but also temperature and concentration.

B. Phase separations under an external field

In this subsection, we show some numerical results of the phase diagrams on the temperature-concentration plane for the mixtures of a polymer and a cholesteric liquid crystal under an external field. The equilibrium free energy is calculated by substituting Q into Eq. (39). The coexistence (binodal) curve can be calculated by the standard 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 also be 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.[40]

The phase diagrams in the absence of an external field have been discussed in our previous paper,[35] where we find the phase separation (Ch+I) between a cholesteric and an isotropic phase. Under an external field, the CNT takes place, depending on the temperature and concentration, as shown in Figs. 1 and 2, and then the phase diagrams are drastically changed.

Figure 5 shows the phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 10$ in the presence of a weak external field $h_L = 0.01$. The solid curves are the binodal line, the dotted line shows the NpNT, and the dashed line is the CNT, which corresponds to the critical field in Fig. 3. The NpNT temperature of the pure liquid crystal ($\phi_P = 0$) shifts to higher temperatures because of the external field. When $h_L = 0$, we have the CIT at $T/T_{CI} = 1$ and the (Ch+I) phase separation appears below $T/T_{CI} = 1$.[35] For the weak external field $h_L = 0.01$, the nematic phase appears on the narrow region between the Ch and pN phases. The CNT
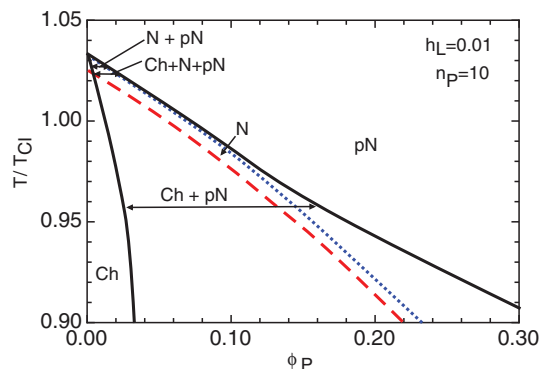

FIG. 4. Order parameters S_L, S_P, and the pitch $Q/Q_0 (\propto p^{-1})$ plotted against the external field h_L at the polymer concentrations $\phi_P = 0.001$, $T/T_{CI} = 0.95$ for $\epsilon_x = 0.2$.

FIG. 5. Phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 10$ in the presence of a weak external field $h_L = 0.01$. The cholesteric, nematic, and paranematic states are denoted by Ch, N, and pN, respectively. The solid lines represent binodal lines, dotted lines show the first-order phase transitions, and dashed lines correspond to continuous phase transitions.
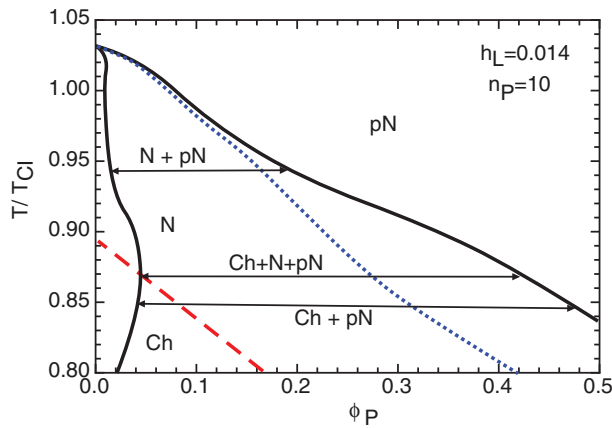
FIG. 6. Phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 10$ in the presence of an external field $h_L = 0.014$.

FIG. 8. Phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 50$ in the presence of an external field $h_L = 0.014$.

and NpNT temperature decrease with increasing 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-paranematic (Ch+pN) phase separations at $\tau < 1.025$. The N+pN coexistence is known in mixtures of a nematic liquid crystal and a polymer under external fields.[14] 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 $T/T_{CI} \simeq 1.025$. As shown in Figs. 1 and 2, the orientational order parameters in the pN phase have small values.

Figure 6 shows the phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 10$ with $h_L = 0.014$. On increasing the strength (h_L) 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+N phase separations. At $\tau \simeq 0.87$, we find three-phase coexistence (Ch+N+pN) between Ch, N, and pN phases. As shown in Figs. 1 and 2, the orientational order parameters jump at the NpNT and the pitch become infinity at the CNT.

Figure 7 shows the phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 20$ with $h_L = 0.014$.
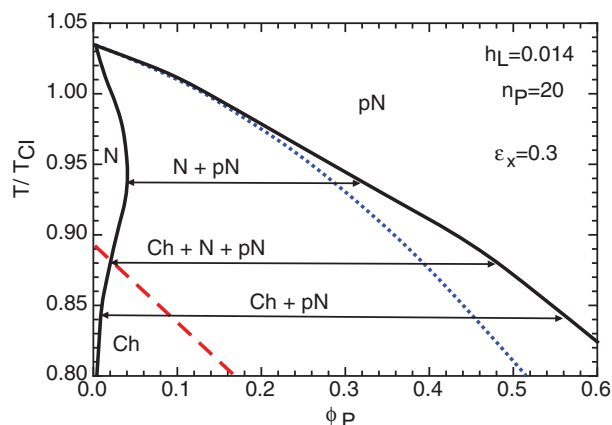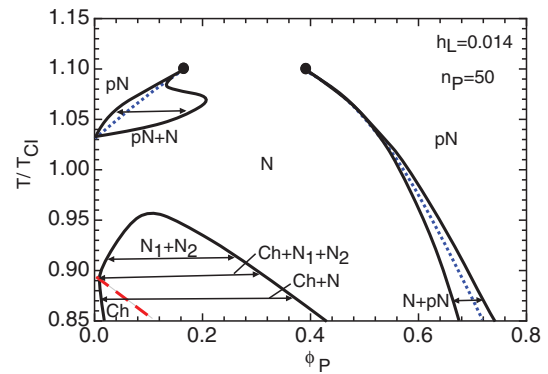
On increasing the molecular weight of the polymer n_P, the anisotropic coupling between a polymer and a liquid crystal becomes strong and the NpNT line shifts to higher temperatures and we have broad biphasic regions, compared to $n_P = 10$ (see Fig. 6).

Further increasing the molecular weight of the polymer, the phase behavior is drastically changed. Figure 8 shows the phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 50$ with $h_L = 0.014$. We find that the NpNT temperature increases from $\tau = 1.03$ with increasing ϕ_P and the pN+N phase separation appears. The NpNT line terminates at a critical point (closed circle), where the orientational order parameters are continuously changed (see Fig. 9). The nematic phase is stabilized by the anisotropic coupling between a polymer and a liquid crystal in the presence of the external field. At high concentrations, the NpNT line with a critical point decreases with increasing ϕ_P and the (pN+N) phase separations appears. At the lower temperatures of the N phase, we have the phase separation between two nematic phases (N_1+N_2) with different polymer concentrations and Ch+N phase separation. We also find the triple point at $\tau \simeq 0.89$, where three phases (Ch+N_1+N_2) coexist. On decreasing the strength of the external field h_L, the CNT line moves to upward and merges into the NpNT line (see Fig. 5). When $h_L = 0$, the nematic phase and critical points disappear and we only have a cholesteric and an isotropic phases, as
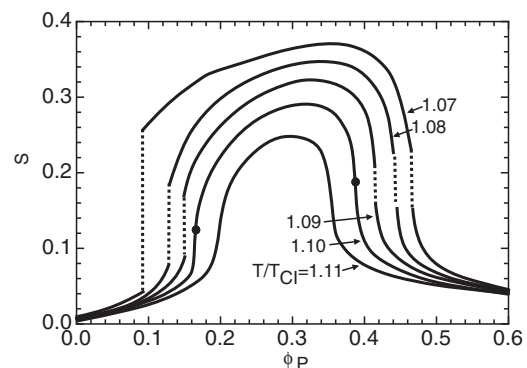

FIG. 7. Phase diagram on the temperature-concentration plane for $\epsilon_x = 0.2$ and $n_P = 20$ in the presence of an external field $h_L = 0.014$.

FIG. 9. The average orientational order parameter $S(= S_P \phi_P + S_L \phi_L)$ plotted against ϕ_P for various temperatures near the critical points in Fig. 8. The closed circles show critical points.
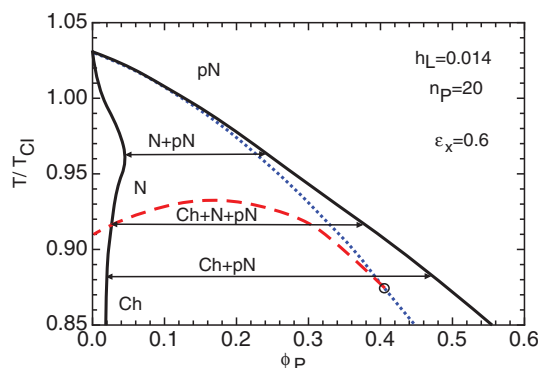
FIG. 10. Phase diagram on the temperature-concentration plane for $\epsilon_x = 0.6$ and $n_P = 20$ in the presence of an external field $h_L = 0.014$. The open circle shows critical end point.

shown in Fig. 9 of the previous paper.[35] When the anisotropic coupling ϵ_n between a polymer and a liquid crystal is zero, the NpNT temperature decreases with increasing the polymer concentration (see Figs. 5–7) and the critical points disappear.

Figure 9 shows the average orientational order parameter $S(= S_P \phi_P + S_L \phi_L)$ plotted against ϕ_P for various temperatures near the critical points in Fig. 8. Below $\tau < 1.1$, the order parameter jumps at the two NpNT concentrations and has a maximum between them. At $\tau = 1.1$, we have two critical points, where the order parameter continuously changes as a function of ϕ_P and temperature.

When the chiral coupling (ϵ_x) between a polymer and a liquid crystal is strong, a cholesteric phase becomes stable at higher temperatures. Figure 10 shows the phase diagram on the temperature-concentration plane for $\epsilon_x = 0.6$ and $n_P = 20$ with $h_L = 0.014$. As compared with Fig. 7, the CNT line shifts to higher temperatures and has a maximum as a function of ϕ_P. The CNT and NpNT lines meet at a critical end point (CE), which is indicated by the open circle. Such CE has been theoretically predicted in cholesteric liquid crystals.[24] Below CE temperature we find the first-order cholesteric-paranematic transition (CpNT) inside the binodal lines. We find the chiral coupling between components strongly affects the CNT.

Our theory demonstrates that the phase behaviors in binary mixtures of a polymer and a cholesteric liquid crystal strongly depend on the external fields. When $h_L = 0$, we only have the coexistence region Ch+I on the temperature-concentration plane, although, we find various phase separations in the presence of external fields. The CNT and NpNT can be controlled by the strength of the external field and the molecular weight of a polymer.

IV. SUMMARY

We have presented a mean field theory to describe phase behaviors in binary mixtures of a polymer and a cholesteric liquid crystal in the presence of an external magnetic or electric field.[35] We have calculated the orientational order parameters, the pitch of the cholesteric phase, the critical fields for twist-untwist transitions, and the phase diagrams on the temperature-concentration plane. It is found that in the pres-

ence 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.

In the presence of the external field, we find the various phase separations: Ch+pN, N+pN, N_1+N_2, and Ch+N, although we only have the Ch+I coexistence in the absence of the external field. It is also found the triple point where three phases Ch+N+pN coexist. Due to the anisotropic coupling between a polymer and a liquid crystal, the phase behaviors drastically change depending on the length of a polymer. For the strong coupling, the critical point appears at the end of the NpNT curves. We demonstrate that a strong coupling between a polymer and a liquid crystal under the external field takes place various phase separations.

Our theory takes into account both orientational order parameters S_P and S_L. For mixtures of a liquid crystal and a flexible polymer chain,[16] we can take $S_P = 0$: $\nu_{LP} = 0$ and $c_{LP} = 0$. In this paper, we did not show the phase diagrams for the mixtures of a cholesteric liquid crystal and a flexible polymer, however, the phase diagrams calculated with $S_P = 0$ are qualitatively the same as Figs. 5 and 6.[45]

Field-induced cholesteric-nematic phase transitions have been observed in a mixtures of cholesterol chloride, nonanoate, and oleyl carbonate at a field of $3–5 \times 10^5$ V/m.[5] It has been shown that CNT temperature decreases with increasing the applied field and a nematic phase appears for wide temperature ranges. Our results of the CNT lines are consistent with these experimental results. Although the phase diagrams calculated in this paper have not been experimentally observed yet, we believe that mixtures of a polymer and a cholesteric liquid crystal under an external field have various phase separations and provide novel materials for liquid crystalline composites and biological liquid crystals.[46,47] The problems of the boundary conditions in a cell of finite thickness[26] can also be important in these mixtures.

APPENDIX: MIXTURES OF A NEMATIC LIQUID CRYSTAL AND A CHIRAL DOPANT

When $U_{LL,1} = 0$ in Eq. (4), or $c_{LL} = 0$ in Eq. (13), our theory can describe mixtures of a non-chiral nematic liquid crystal ($i = L$) and a chiral dopant ($i = P$). In this appendix, we focus on the critical value of the external field. The cholesteric pitch (Q^*) in the absence of the external field, Eq. (14), is given as a function of the volume fraction ϕ_P of the chiral dopant

$$Q^* = \frac{2\epsilon_n \alpha_x \left(\frac{S_P}{S_L}\right)\phi_P}{1 - \left[1 - 2\epsilon_n \left(\frac{S_P}{S_L}\right)\right]\phi_P}, \tag{A1}$$

and we also have Eq. (28)

$$Q_1^* = \frac{2\epsilon_n \alpha_x \left(\frac{S_P}{S_L} \right) \phi_P}{1 - \left[1 - \epsilon_n \left(\frac{S_P}{S_L} \right) \right] \phi_P}, \quad (A2)$$

where $\alpha_x (\equiv c_{LP}/v_{LP})$ shows the chiral coupling between a liquid crystal and a dopant ($\epsilon_n \alpha_x = c_{LP}/v_{LL}$). The critical field h_L^c is given by Eq. (46).

When $\phi_P \ll 1$, Eq. (A1) is given by

$$Q^* \simeq H_{TP} \phi_P, \quad (A3)$$

where

$$H_{TP} \equiv 2\epsilon_n \alpha_x \frac{S_P}{S_L} \quad (A4)$$

is called the helical twisting power of a chiral dopant.[1,35,41] The larger values of H_{TP} correspond to the smaller pitch. For $H_{TP} > 0$, the wave number Q^* of the twist pitch linearly increases with increasing ϕ_P at dilute solutions, consisting with the experiments.[41–44] The temperature and concentration dependences of H_{TP} are given through the ratio S_P/S_L. Some estimations of the parameters have been studied in our previous paper.[35] Using Eq. (A3), the critical field (46) is approximately given by

$$H_c \simeq \frac{\pi}{2} H_{TP} \phi_P \sqrt{\frac{K_{22}}{\Delta \chi_L}}, \quad (A5)$$

which is a linear function of ϕ_P with $S_L \simeq 1$. Our theory is in agreement with the experimental results.[6,9] The critical field increases with increasing the helical twisting power and the twist elastic constant.

[1]P. G. De Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1993).

[2]P. Korpiun, W. Albrecht, T. Muller, and E. Luscher, Phys. Lett. A **48**, 253 (1974).

[3]P. Sheng, Phys. Rev. A **26**, 1610 (1982).

[4]J. J. Wjsocki, J. Adams, and W. Haas, Phys. Rev. Lett. **20**, 1024 (1968).

[5]H. Baessler and M. M. Labes, Phys. Rev. Lett. **21**, 1791 (1968).

[6]P. G. De Gennes, Solid State Commun. **6**, 163 (1968).

[7]R. B. Meyer, Appl. Phys. Lett. **12**, 281 (1968).

[8]R. B. Meyer, Appl. Phys. Lett. **14**, 208 (1969).

[9]G. Durand, L. Leger, F. Rondelez, and M. Veyssie, Phys. Rev. Lett. **22**, 227 (1969).

[10]P. Oswald, in *Phase Transitions: Applications to Liquid Crystals, Organic Electronic and Optoelectric Fields*, edited by V. Popa-Nita (Research Signpost, Kerala, India, 2006).

[11]M. Warner and E. M. Terentjev, *Liquid Crystal Elastomers* (Oxford University Press, New York, 2003).

[12]A. M. Menzel and H. R. Brand, Phys. Rev. E **75**, 011707 (2007).

[13]A. Matsuyama and T. Kato, J. Chem. Phys. **114**, 3817 (2001).

[14]Z. Lin, H. Zhang, and Y. Yang, Phys. Rev. E **58**, 5867 (1998).

[15]C. Shen and T. Kyu, J. Chem. Phys. **102**, 556 (1995).

[16]A. Matsuyama and T. Kato, J. Chem. Phys. **105**, 1654 (1996).

[17]J. D. Parsons and C. F. Hayes, Phys. Rev. A **9**, 2652 (1974).

[18]M. Yamashita, H. Kimura, and H. Nakano, Mol. Cryst. Liq. Cryst. **68**, 79 (1981).

[19]Y. R. Lin-Liu, Phys. Rev. A **27**, 594 (1983).

[20]M. A. Lee and P. Vlachopoulos, Mol. Cryst. Liq. Cryst. **110**, 341 (1984).

[21]P. J. Kedney and I. W. Stewart, Lett. Math. Phys. **31**, 261 (1994).

[22]S. V. Shiyanovskii and J. G. Terentieva, Phys. Rev. E **49**, 916 (1994).

[23]S. V. Shiyanovskii and J. G. Terentieva, Liq. Cryst. **21**, 645 (1996).

[24]R. Seidin, D. Mukamel, and D. W. Allender, Phys. Rev. E **56**, 1773 (1997).

[25]A. M. Scarfone, I. Lelidis, and G. Barbero, Phys. Rev. E **84**, 021708 (2011).

[26]G. Barbero and A. M. Scarfone, Phys. Rev. E **88**, 032505 (2013).

[27]J. Fukuda and S. Zumer, Phys. Rev. E **87**, 042506 (2013).

[28]C. Motoc, I. Cuculescu, and M. Honciuc, Mol. Cryst. Liq. Cryst. **45**, 215 (1978).

[29]H. A. van Sprang and J. L. M. van de Venne, J. Appl. Phys. **57**, 175 (1985).

[30]I. I. Smalyukh, B. I. Senyuk, P. Palffy-Muthoray, O. D. Lavrentovich, H. Huang, E. C. Gartland, Jr., V. H. Bodnar, T. Kosa, and B. Taheri, Phys. Rev. E **72**, 061707 (2005).

[31]Z. Mikityuk, O. Nevmerzhitska, P. Zaremba, and M. Vistak, Mol. Cryst. Liq. Cryst. **275**, 3 (1996).

[32]Z. Hotra, Z. Mykytyuk, O. Hotra, A. Fechan, O. Syshynskyy, O. Yasynovska, and V. Kotsun, Mol. Cryst. Liq. Cryst. **535**, 225 (2011).

[33]Y. R. Lin-Liu, Y. M. Shih, and C. W. Woo, Phys. Rev. A **15**, 2550 (1977).

[34]Y. R. Lin-Liu, Y. M. Shih, C. W. Woo, and H. T. Tan, Phys. Rev. A **14**, 445 (1976).

[35]A. Matsuyama, J. Chem. Phys. **139**, 174906 (2013).

[36]P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953).

[37]J. P. Straley, Phys. Rev. A **10**, 1881 (1974).

[38]W. Maier and A. Saupe, Z. Naturforsch. **14a**, 882 (1959).

[39]L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).

[40]A. Matsuyama, in *Encyclopedia of Polymer Blends*, edited by A. I. Isayev (Wiley-VCH, Weinheim, 2010), Chap. 2.

[41]M. A. Osipov and H.-G. Kuball, Eur. Phys. J. E **5**, 589 (2001).

[42]H. Baessler and M. M. Labes, J. Chem. Phys. **52**, 631 (1970).

[43]H. M. von Minden, V. Vill, M. Pape, and K. Hiltrop, J. Colloid Interface Sci. **236**, 108 (2001).

[44]J. Yoshida, H. Sato, A. Yamagishi, and N. Hoshino, J. Am. Chem. Soc. **127**, 8453 (2005).

[45]A. Matsuyama, "Phase separations in mixtures of a flexible polymer and a cholesteric liquid crystal in the presence of an external field," Mol. Cryst. Liq. Cryst. (to be published).

[46]G. de Luca and A. D. Rey, Phys. Rev. E **69**, 011706 (2004).

[47]A. D. Rey and E. E. Herrera-Valencia, Biopolymers **97**, 374 (2012).