Phase separations and orientational ordering of polymers in liquid crystal solvents

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A mean-field theory is introduced to describe nematic-isotropic phase transitions and phase separations in binary mixtures of a liquid-crystal molecule and a semiflexible polymer chain. On the basis of the Onsager model for excluded volume interactions, the Maier-Saupe model for orientational-dependent attractive interactions, and the Flory-Huggins theory for isotropic mixings, we derive the free energy of the binary mixtures. We examine the co-occurrences of the partial orientational ordering of the polymer chains in the liquid-crystal solvents and the phase separations, depending on the stiffness of the polymer chain and the strength of anisotropic interactions. The new phase behaviors, such as nematic unstable regions, nematic metastable regions, a critical solution point in a nematic phase, azeotrope points, and triple points, are examined on the temperature-concentration plane. [S1063-651X(99)06501-0]

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I. INTRODUCTION

Mesomorphic mixtures comprised of polymers and liquid-crystal molecules are of interest because of their important technological applications in high modulus fibers, nonlinear optics, and electro-optical devices. The performances of these systems are closely related to a chain extension in a liquid-crystal phase and phase separations [1–3]. Low-molecular-weight liquid crystals are modeled as rigid rodlike molecules. On the other hand, polymer chains have a variety of stiffnesses and so when the polymer chains are mixed with the liquid-crystal molecules we can expect various types of phase separations depending on the stiffness of the polymer chain.

In mixtures of a flexible polymer and a liquid crystal, broad biphasic regions between an isotropic phase and a nematic phase appear below the nematic-isotopic transition (NIT) temperature of the pure liquid-crystal molecule. The liquid-crystalline phases are destroyed on increasing the polymer concentration. These nematic-isotropic phase separations have been investigated both experimentally [4–8] and theoretically [9–15]. In contrast, mixtures of a liquid-crystalline polymer and a liquid-crystal have good miscibility even in a liquid-crystalline phase [1,16–23]. Flory and his collaborators have described the various types in the phase diagrams of liquid-crystalline polymers [24–29]. Recently the phase behaviors in binary mixtures of liquid-crystal molecules have been analyzed by combining the Flory-Huggins theory for isotropic mixing and the Maier-Saupe theory for anisotropic ordering [30–33]. These theories, however, have not considered the induced rigidity, or straightening, of polymer chains in a nematic phase. In these systems it is important to consider the co-occurrences of orientational ordering of the polymer chains in the liquid-crystal solvents and phase separations [16–23]. Some years ago, based on an elastic chain model, some authors examined the phase behaviors and the orientations of polymer chains in liquid-crystal solvents [17–19].

In this paper we present a mean-field theory to describe phase behaviors in binary mixtures of a liquid-crystal molecule and a polymer chain which has various degrees of flexibility. To describe the orientational ordering of polymer chains, we extend the previous model for liquid-crystalline polymers [34,35] to the mixtures of a liquid crystal and a semiflexible polymer chain. We assume here that two neighboring bonds on the polymer chain have either bent or straightened conformations and the straightened conformation gives rise to a rigid rodlike shape. The liquid crystals of low molecular weight are modeled by rigid rodlike molecules. On the basis of the Onsager model for excluded volume interactions [36], the Maier-Saupe model for orientational-dependent attractive interactions [37,38] between rigid rodlike molecules, and the Flory-Huggins theory for binary mixtures [39], we derive the free energy of our systems. The nematic-isotropic transitions, the order parameter of polymer chains, and that of liquid crystals are examined as a function of the flexibility of a polymer chain and the strength of anisotropic interactions and we calculate the phase diagrams including binodal, spinodal, and the NIT lines on the temperature-concentration plane. These lines will be important to study not only equilibrium properties but also phase separation dynamics such as spinodal decompositions and metastable phase growth [40]. We also derive the Landau–de Gennes expansion of our free energy. This expansion facilitates an intuitive understanding of the underlying physics.

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

Consider binary mixtures of a semiflexible polymer and a liquid crystal. The polymers and liquid crystals interact through orientational-dependent van der Waals interactions and excluded volume interactions. In these systems, it is important to consider both orientational ordering, or straightening, of polymer chains and nematic ordering of liquid-crystal molecules. In order to take into account the partial orientational ordering of the polymer chains in a nematic phase, we assume here that two neighboring bonds on the polymer

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chain have either bent or straightened conformations and the conformational energy of the straightened bond is $|\epsilon_0|$ less than that of the bent bonds [34]. The straightened state of the bonds on a polymer chain is energetically favored, however it is entropically unfavorable. The nematic behaviors of the straightened bonds as well as liquid crystals can be induced by the anisotropic interactions. To describe the nematic-isotropic phase transition (NIT) and phase separations, we consider thermodynamics of our systems. Hereafter we refer to the segments in straightened bonds as ''rigid'' segments.

Let N_p and N_ℓ be the number of the semiflexible polymers and the liquid crystals, respectively. Let n_p be the number of segments on the polymer and n_ℓ be that of the liquid crystal. The free energy of our systems can be given by

$$F = F_{\text{bent}} + F_{\text{mix}} + F_{\text{nem}}. \qquad (2.1)$$

The first term shows the free-energy change needed to straighten bent bonds on the polymers and is given by

$$\beta F_{\text{bent}} = N_p[n_r(\beta f_0) - S_{\text{comb}}/k_B - \Delta S_{\text{conf}}/k_B], \quad (2.2)$$

where $\beta \equiv 1/k_B T$, T is the absolute temperature, k_B is the Boltzmann constant, f_0 is the local free-energy difference between the bent and straightened conformations, and n_r shows the number of rigid segments on the polymer chain. We assume here that each chain has the same conformation. The second term in Eq. (2.2) is the combinatorial entropy related to the number of ways to select n_r rigid segments out of the n_p segments on the polymer and is given by

$$S_{\text{comb}}/k_B = \ln \frac{n_p!}{n_r!(n_p - n_r)!}. \qquad (2.3)$$

By using Stirling's approximation, Eq. (2.3) can be rewritten as

$$S_{\text{comb}}/k_B = -n_p[x \ln x + (1-x)\ln(1-x)], \qquad (2.4)$$

where

$$x \equiv n_r/n_p \qquad (2.5)$$

shows the fraction of rigid (straightened) segments on the polymer chains. The third term in Eq. (2.2) shows the change in conformational entropy to bring a chain from a crystalline (straightened) state to a flexible amorphous state. This entropy was omitted in the earlier work [34]. According to Flory's lattice theory, the conformational entropy $S_{\text{conf}}(n_p)$ of the polymer chain with the n_p flexible segments is given by [39]

$$S_{\text{conf}}(n_p)/k_B = \ln \left[\frac{n_p z(z-1)^{n_p-2}}{\sigma \exp(n_p - 1)} \right], \qquad (2.6)$$

where z is the lattice coordination number and σ is the symmetry number of the chain. When the n_r segments out of the n_p segments on a polymer chain are replaced by rigid segments, the conformational entropy change ΔS_{conf} is given by

$$\Delta S_{\text{conf}} = S_{\text{conf}}(n_p - n_r) - S_{\text{conf}}(n_p) \qquad (2.7)$$

$$= -k_B \ln \left[\frac{n_p}{n_p - n_r} \left(\frac{z-1}{e} \right)^{n_r} \right]. \qquad (2.8)$$

From Eqs. (2.4) and (2.8), the free energy (2.2) can be expressed as

$$\beta F_{\text{bent}}/N_t = \phi \left[x\beta f_0 + x \ln \left(\frac{z-1}{e} \right) \right.$$
$$\left. + x \ln x + \left(1 - x - \frac{1}{n_p} \right) \ln(1-x) \right], \quad (2.9)$$

where $N_t = n_\ell N_\ell + n_p N_p$ is the total lattice sites of our systems and $\phi = n_p N_p/N_t$ is the volume fraction of the polymer chains. The volume fraction of the liquid crystals is given by $\phi_\ell = 1 - \phi$. The volume fraction ϕ_r of the rigid (straightened) segments on a polymer chain is given by

$$\phi_r = n_r N_p/N_t = x\phi. \qquad (2.10)$$

The second term in Eq. (2.1) is the free energy of the isotropic mixing for a polymer and a liquid crystal. According to the Flory theory, the free energy is given by [39]

$$\beta F_{\text{mix}}/N_t = \frac{1-\phi}{n_\ell} \ln(1-\phi) + \frac{\phi}{n_p} \ln \phi + \chi \phi(1-\phi), \qquad (2.11)$$

where χ ($\equiv U_0/k_B T$) is the Flory-Huggins interaction parameter related to isotropic interactions between unlike molecular species [39].

The third term in Eq. (2.1) shows the free energy for the nematic ordering. To describe the nematic behaviors, we take into account both the excluded volume interactions [36] and the orientational-dependent (Maier-Saupe) interactions [37,38]. We consider three coupling terms of the anisotropic interactions. Let $\nu_{\ell\ell}$ be the orientational-dependent (Maier-Saupe) interactions between the liquid crystals, $\nu_{\ell r}$ be that between the liquid crystal and the rigid segment on the polymer chains, and ν_{rr} be that between the rigid segments on the polymer chains.

On the basis of both the Maier-Saupe model for orientational-dependent attractive interactions and the Onsager model for excluded volume interactions, the free energy of the nematic ordering is given by [15,41,35]

$$\beta F_{\text{nem}}/N_t = \frac{1-\phi}{n_\ell} \int f_\ell(\theta) \ln 4\pi f_\ell(\theta) d\Omega$$

$$+ \frac{\phi_r}{n_r} \int f_r(\theta) \ln 4\pi f_r(\theta) d\Omega - \tfrac{1}{2} \nu_{\ell\ell} S_\ell^2 (1-\phi)^2$$

$$- \nu_{\ell r} S_\ell S_r (1-\phi)\phi_r - \tfrac{1}{2} \nu_{rr} S_r^2 \phi_r^2$$

$$+ (\rho_{\ell\ell} - 1)(1-\phi)^2 + 2(\rho_{\ell r} - 1)(1-\phi)\phi_r$$

$$+ (\rho_{rr} - 1)\phi_r^2, \qquad (2.12)$$

where $d\Omega \equiv 2\pi\sin\theta\,d\theta$, θ is the angle between the rigid segments and the director of the orienting field. Equation (2.12) is the second virial approximation and, strictly speaking, can be justified in the limit of sufficiently large values of n_ℓ and n_r only. The $f_\ell(\theta)$ and $f_r(\theta)$ show the orientational distribution functions of the liquid crystals and that of the rigid segments on the polymers, respectively. The first two terms represent the decrease of entropy due to the nematic ordering. The orientational-order parameter S_ℓ of the liquid crystals is given by

$$S_\ell = \int P_2(\cos\theta)f_\ell(\theta)d\Omega \qquad (2.13)$$

and the orientational-order parameter S_r of the rigid segments on the polymers is given by

$$S_r = \int P_2(\cos\theta)f_r(\theta)d\Omega, \qquad (2.14)$$

where $P_2(\cos\theta) \equiv 3(\cos^2\theta - 1/3)/2$. The last three terms in Eq. (2.12) show the excluded volume interactions between rigid segments and the function ρ_{ij} $(i,j = \ell,r)$ is given by

$$\rho_{ij} = \frac{4}{\pi}\int\int \sin\gamma(\theta,\theta')f_i(\theta)f_j(\theta')d\Omega\,d\Omega'. \quad (2.15)$$

In the isotropic phase, we have $f_i(\theta) = 1/(4\pi)$ and $\rho_{ij} = 1$ [36].

In the next section, we derive the order parameters S_ℓ, S_r, and the fraction x in thermal equilibrium conditions.

III. NEMATIC ORDERING OF POLYMERS AND LIQUID CRYSTALS

The orientational distribution function $f_\ell(\theta)$ of the liquid crystals and $f_r(\theta)$ of the rigid segments on the polymers are determined by the free energy (2.12) with respect to these functions:

$$[\partial F_{\text{nem}}/\partial f_\ell(\theta)]_{x,f_r} = 0, \qquad (3.1)$$

$$[\partial F_{\text{nem}}/\partial f_r(\theta)]_{x,f_\ell} = 0, \qquad (3.2)$$

with the normalization conditions

$$\int f_i(\theta)d\Omega = 1, \qquad (3.3)$$

$i = \ell,r$. Here we expand the kernel $\sin\gamma$ of Eq. (2.15) in Legendre polynomials:

$$\sin\gamma = \frac{\pi}{4} - \frac{5\pi}{32}P_2(\cos\theta)P_2(\cos\theta'). \qquad (3.4)$$

Substituting Eq. (3.4) into Eqs. (2.15), Eqs. (3.1), (3.2), and (3.3) lead the distribution function:

$$f_\ell(\theta) = \frac{1}{Z_\ell}\exp[\eta_\ell P_2(\cos\theta)], \qquad (3.5)$$

$$\eta_\ell \equiv n_\ell[(\nu_{\ell\ell} + \tfrac{5}{4})S_\ell(1-\phi) + (\nu_{\ell r} + \tfrac{5}{4})S_r x\phi], \quad (3.6)$$

for the liquid crystals and

$$f_r(\theta) = \frac{1}{Z_r}\exp[\eta_r P_2(\cos\theta)], \qquad (3.7)$$

$$\eta_r \equiv n_p x[(\nu_{\ell r} + \tfrac{5}{4})S_\ell(1-\phi) + (\nu_{rr} + \tfrac{5}{4})S_r x\phi], \quad (3.8)$$

for the rigid segments on the polymer chains, where the constants Z_i $(i = \ell,r)$ are determined by the normalization condition (3.3). The terms ν_{ij} and $\tfrac{5}{4}$ in Eqs. (3.6) and (3.7) correspond to the attractive and excluded volume interactions. From Eqs. (3.3), (3.5), and (3.7), the constant Z_i is given by

$$Z_\ell = 4\pi I_0[\eta_\ell], \qquad (3.9)$$

$$Z_r = 4\pi I_0[\eta_r], \qquad (3.10)$$

where the function $I_0[\eta_i]$ is defined as

$$I_q[\eta_i] \equiv \int_0^1 [P_2(\cos\theta)]^q \exp[\eta_i P_2(\cos\theta)]d(\cos\theta),$$
$$(3.11)$$

$q = 0,1,2,\dots$. Substituting Eqs. (3.5) and (3.7) into Eqs. (2.13) and (2.14), we obtain two self-consistency equations for the two order parameters S_ℓ and S_r:

$$S_\ell = I_1[\eta_\ell]/I_0[\eta_\ell], \qquad (3.12)$$

$$S_r = I_1[\eta_r]/I_0[\eta_r], \qquad (3.13)$$

and the average value of the order parameters is given by

$$S = S_\ell(1-\phi) + S_r\phi_r,$$
$$= S_\ell(1-\phi) + S_r x\phi. \qquad (3.14)$$

The order parameter S_p of the polymer chain is given by $S_p = xS_r$. The function $\sigma_i \equiv \int f_i(\theta)\ln 4\pi f_i(\theta)d\Omega$ and ρ_{ij} in Eq. (2.12) are now given as a function of order parameters S_ℓ and S_r as follows:

$$\sigma_i = \eta_i S_i - \ln I_0[\eta_i], \qquad (3.15)$$

$$\rho_{ij} = 1 - \tfrac{5}{8}S_i S_j. \qquad (3.16)$$

Substituting Eqs. (3.15) and (3.16) into Eqs. (2.12), the free energy for the nematic ordering is given by

$$\beta F_{\text{nem}}/N_t = \tfrac{1}{2}(\nu_{\ell\ell} + \tfrac{5}{4})S_\ell^2(1-\phi)^2$$
$$+ (\nu_{\ell r} + \tfrac{5}{4})S_\ell S_r(1-\phi)x\phi$$
$$+ \frac{1}{2}(\nu_{rr} + \tfrac{5}{4})S_r^2 x^2\phi^2$$
$$- \frac{1-\phi}{n_\ell}\ln I_0[\eta_\ell] - \frac{\phi}{n_p}\ln I_0[\eta_r]. \quad (3.17)$$

The fraction x of the rigid segments on a polymer chain is determined by minimizing the free energy (2.1) with respect to x: $(\partial F/\partial x)_{S_\ell,S_r} = 0$. From Eqs. (2.9) and (3.17), we obtain

$$(\nu_{rr}+\tfrac{5}{4})x\phi S_r^2+(\nu_{\ell r}+\tfrac{5}{4})(1-\phi)S_\ell S_r - D(x)=0, \tag{3.18}$$

with

$$D(x)\equiv\frac{1}{\phi}\left[\ln\left(\frac{x}{(1-x)\lambda}\right)+\frac{1}{n_p(1-x)}\right]\geq 0, \tag{3.19}$$

and the solution for S_r with $\phi\neq0$ is given by

$$S_r=\frac{1}{2(\nu_{rr}+5/4)x\phi}\{-(\nu_{\ell r}+\tfrac{5}{4})(1-\phi)S_\ell$$
$$+\sqrt{[(\nu_{\ell r}+\tfrac{5}{4})(1-\phi)S_\ell]^2+4(\nu_{rr}+\tfrac{5}{4})x\phi D(x)}\}, \tag{3.20}$$

where λ is defined as

$$\lambda\equiv\left(\frac{e}{z-1}\right)\exp(-\beta f_0). \tag{3.21}$$

By solving the coupled equations (3.12), (3.13), and (3.20), we can obtain the values of the orientational-order parameters S_ℓ,S_r, and the fraction x of the rigid segments on a polymer chain as a function of temperature and concentration. From Eq. (3.20) the order parameter S_r is given as a function of S_ℓ and x and so we only solve the coupled equations (3.12) and (3.13) for S_ℓ and x.

We further split the local free-energy difference f_0 in Eq. (3.21) into two parts:

$$f_0=\epsilon_0-Ts_0, \tag{3.22}$$

where s_0 $(=k_B\ln\omega_0)$ is the local entropy loss and ϵ_0 (<0) the energy change needed to straighten a bent bond. The ω_0 is defined as $\omega_0\equiv\omega_1/\omega_2$, where ω_1 (ω_2) is the number of states of a straightened (bent) bond. If the segments are placed on a lattice of coordination number z, we have $\omega_0=1/(z-2)$ [24]. The stiffness of a polymer chain is controlled by the ϵ_0. The larger values of ϵ_0 correspond to the stiffer chains. The most flexible polymer chain is realized when $\epsilon_0=0$. Substituting Eq. (3.22) into Eq. (3.21), we obtain

$$\lambda=\omega\exp(-\beta\epsilon_0), \tag{3.23}$$

where $\omega\equiv e/[(z-1)(z-2)]$.

The chemical potentials are given by

$$\beta\mu_p=\beta(\partial F/\partial N_p)_{N_\ell}$$
$$=n_p\left[-x\ln\lambda+x\ln x+\left(1-x-\frac{1}{n_p}\right)\ln(1-x)\right]+\ln\phi+\left(1-\frac{n_p}{n_\ell}\right)(1-\phi)$$
$$+n_p\chi(1-\phi)^2+n_p\left(\tfrac{1}{2}(\nu_{\ell\ell}+\tfrac{5}{4})S_\ell^2(1-\phi)^2+(\nu_{\ell r}+\tfrac{5}{4})S_\ell S_r(1-\phi)x\phi+\tfrac{1}{2}(\nu_{rr}+\tfrac{5}{4})S_r^2x^2\phi^2-\frac{1}{n_p}\ln I_0[\eta_r]\right) \tag{3.24}$$

for the polymer chain and

$$\beta\mu_\ell=\beta(\partial F/\partial N_\ell)_{N_p}$$
$$=\ln(1-\phi)+\left(1-\frac{n_\ell}{n_p}\right)\phi-n_\ell\chi\phi^2$$
$$+n_\ell\left(\tfrac{1}{2}(\nu_{\ell\ell}+\tfrac{5}{4})S_\ell^2(1-\phi)^2+(\nu_{\ell r}+\tfrac{5}{4})S_\ell S_r(1-\phi)x\phi\right.$$
$$\left.+\tfrac{1}{2}(\nu_{rr}+\tfrac{5}{4})S_r^2x^2\phi^2-\frac{1}{n_\ell}\ln I_0[\eta_\ell]\right), \tag{3.25}$$

for the liquid crystal. When $x=0$, Eqs. (3.24) and (3.25) show the chemical potentials in binary mixtures of a flexible polymer and a liquid crystal [15] and when $x=1$, the theory results in that for binary mixtures of rigid rodlike molecules [9,30].

The coexistence curves (binodal) of the phase equilibrium are derived by the coupled equations $\mu_p(\phi')=\mu_p(\phi'')$ and $\mu_\ell(\phi')=\mu_\ell(\phi'')$, where the volume fraction ϕ' and ϕ'' corresponds to that of the lower and higher concentration phases, respectively. Spinodal lines are derived by the condition $(\partial\mu_\ell/\partial\phi)=0$. The region $(\partial\mu_\ell/\partial\phi)>0$ corresponds to the unstable region.

In our numerical calculations, we define here the ratio ξ of the anisotropic interaction as

$$\xi \equiv \nu_{rr}/\nu_{\ell\ell} \qquad (3.26)$$

and assume that the orientational-dependent interaction $\nu_{\ell r}$ is proportional to the square root of the product of $\nu_{\ell\ell}$ and ν_{rr} [42,31]:

$$\nu_{\ell r} = b\sqrt{\nu_{\ell\ell}\nu_{rr}}, \qquad (3.27)$$

where b is the constant. We then obtain

$$\nu_{rr} = \xi\nu_{\ell\ell}, \qquad (3.28)$$

$$\nu_{\ell r} = b\sqrt{\xi}\nu_{\ell\ell}. \qquad (3.29)$$

The orientational-dependent interaction parameter $\nu_{\ell\ell}$ between the liquid-crystal molecules is given to be inversely proportional to temperature [38]:

$$\nu_{\ell\ell} = U_a/k_B T. \qquad (3.30)$$

We also define the dimensionless nematic interaction parameter α:

$$\alpha \equiv \nu_{\ell\ell}/\chi = U_a/U_0. \qquad (3.31)$$

When $\phi = 0$, Eq. (3.17) represents the free energy for the pure liquid-crystal molecule:

$$\beta F = \tfrac{1}{2}(\nu_{\ell\ell} + \tfrac{5}{4})S_\ell^2 - \frac{1}{n_\ell}\ln I_0[\,\mathring{\eta}_\ell], \qquad (3.32)$$

$$\mathring{\eta}_\ell \equiv n_\ell(\nu_{\ell\ell} + \tfrac{5}{4})S_\ell. \qquad (3.33)$$

The nematic phase appears at $n_\ell(\nu_{\ell\ell} + 5/4) = 4.54$ [34,38] and so the NIT temperature $T_{\mathrm{NI},\ell}$ of the pure liquid crystal is given by

$$T_{\mathrm{NI},\ell} = \frac{n_\ell(U_a/k_B)}{4.54 - 1.25n_\ell}. \qquad (3.34)$$

In our theory, the stiffness of the polymer chain is characterized with a single parameter ϵ or ϵ_0. The larger values of ϵ correspond to the stiffer polymers. The most flexible polymer chain is realized when $\epsilon = 0$ or $x = 0$, in which our theory describes binary mixtures of a flexible polymer and a liquid crystal [15]. In contrast, when $\epsilon \gg 0$ or $x = 1$, the theory results in that for binary mixtures of rigid rodlike molecules [9,30]. Our theory connects the two limiting theories.

IV. PHASE SEPARATIONS

In this section, we calculate the equilibrium values of order parameters S_ℓ, S_r, and the fraction x of rigid segments on a polymer chain as a function of temperature and concentration and derive the phase diagrams on the temperature-concentration plane. In the numerical calculations of Sec. III, we define here the stiffness parameter $\epsilon \equiv |\epsilon_0|/U_a$ of a semiflexible polymer chain. The values of ϵ_0 and U_a are of the order of thermal energy. In the following calculations we use $\omega = 0.025$ ($z = 12$), $b = 1$, $\xi = 1$, $\alpha = 5$, $n_\ell = 2$, and $n_p = 20$ for example.
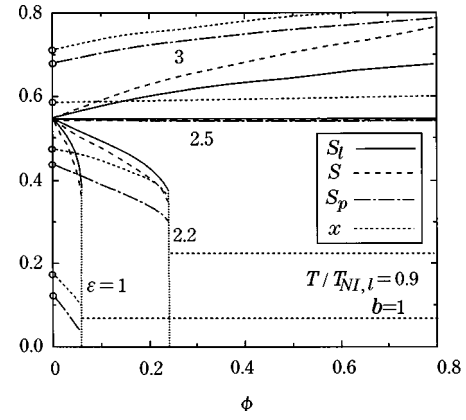

FIG. 1. Orientational-order parameters and the fraction x of the straightened segments on the polymer chain plotted against the polymer concentration ϕ for the reduced temperature $T/T_{\mathrm{NI},\ell} = 0.9$. The value of stiffness parameter ϵ of the polymer chain is changed.

Figure 1 shows the orientational-order parameters and the fraction x of the straightened segments on the polymer chain plotted against the polymer concentration ϕ with the reduced temperature $T/T_{\mathrm{NI},\ell} = 0.9$, where $T_{\mathrm{NI},\ell}$ is the NIT temperature of the pure liquid-crystal molecule. The value of stiffness parameter ϵ of the polymer chain is changed. The larger values of ϵ correspond to the stiffer polymer chains. The solid curve refers to the order parameter S_ℓ of the liquid crystal and the dash-dotted line shows the average-order parameter S_p ($\equiv xS_r$) of the polymer chain. The short-dashed line shows the average-order parameter S of the system and the dotted line corresponds to the fraction x of the rigid segments on the polymer chain. When $T/T_{\mathrm{NI},\ell} = 0.9$, the pure polymer chains of $\epsilon < 2.25$ are in an isotropic state, and so if there are no correlations between polymers and liquid crystals, the nematic ordering of the polymer chains cannot take place. However, we find, for small values of ϵ, a first-order NIT at a certain polymer concentration where the nematic ordering of the polymer chains is induced by the liquid crystals. The values of x and S_p in the nematic phase are small and the polymer chains are slightly ordered. The nematic phase is almost stabilized by the orientational ordering of the liquid-crystal molecule. In the case of $\epsilon = 0$, or a sufficiently flexible polymer, the nematic ordering of the polymer chain cannot occur and the orientational ordering of the liquid crystal only takes place at $\phi \approx 0.06$ [15]. On increasing the stiffness ϵ, the value of x becomes large and the order parameter S_p is increased and so the polymer chain and the liquid crystal are highly ordered in the nematic phase.

Figure 2 shows the phase diagrams on the temperature-concentration plane for (a) $\epsilon = 2$ and (b) $\epsilon = 2.5$. The solid curve refers to the binodal and the dotted line shows the first-order NIT line. The dash-dotted line shows the spinodal. In the biphasic regions between the nematic and the isotropic phases, we have two different metastable regions: an isotropic metastable (IM); a nematic metastable (NM), and a nematic unstable region (NU). When the value of ϵ is small, the theory represents the phase diagrams of flexible polymer–liquid-crystal mixtures and the broad biphasic region between a nematic and an isotropic phase appears [34]. On increasing the ϵ, the NIT temperature $T_{\mathrm{Ni},p}$ of the pure poly-
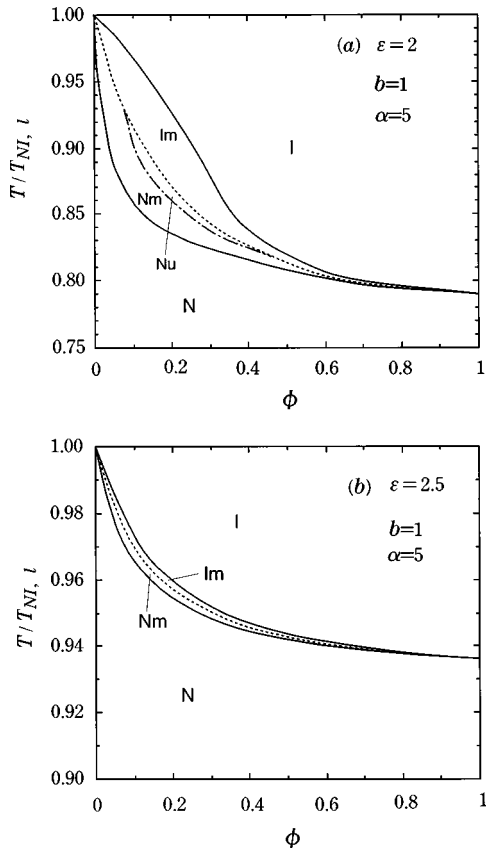
FIG. 2. Phase diagrams on the temperature-concentration plane for (a) $\epsilon = 2$ and (b) $\epsilon = 2.5$.

mer chain increases and the biphasic region becomes narrow. The nematic unstable region (NU) disappears in Fig. 2(b). The type of the phase diagrams strongly depends on the stiffness of the polymer chains. The same results are also derived for the dependence on the molecular weight of the polymer chain. On increasing the length n_p of the semiflexible polymer chain, the $T_{NI,p}$ is increased and the biphasic region becomes narrow. Flexible polymers almost do not dissolve in liquid-crystal solvents at low polymer concentrations and the broad biphasic region between the nematic and isotropic phases appears below the NIT temperature of the pure liquid crystal. The free energy is minimized by the phase separation rather than the straightening of the polymer chains. For stiffer polymer chains, the mixtures have the narrow nematic-isotropic biphasic region and the spinodal region disappears. The free energy is minimized by the partial ordering of the polymer chain in liquid-crystal solvents rather than the phase separation. The former can be classified as the polymer-induced phase separation. The latter, however, can be classified as the polymer-induced stabilization of nematic ordering. The stiffness of the polymer chain strongly affects the nematic ordering of the polymer chain in the liquid-crystal solvent and plays an important role in characterizing the unstable regions and the width of the biphasic region between a nematic and an isotropic phase.

On decreasing the value of the nematic interaction parameter α, the unfavorable interaction parameter (χ) between the polymer and the liquid crystal becomes dominant in the free energy. Figure 3 shows the phase diagrams on the temperature-concentration plane for (a) $\alpha = 2.6$, (b) $\alpha = 2.5$,
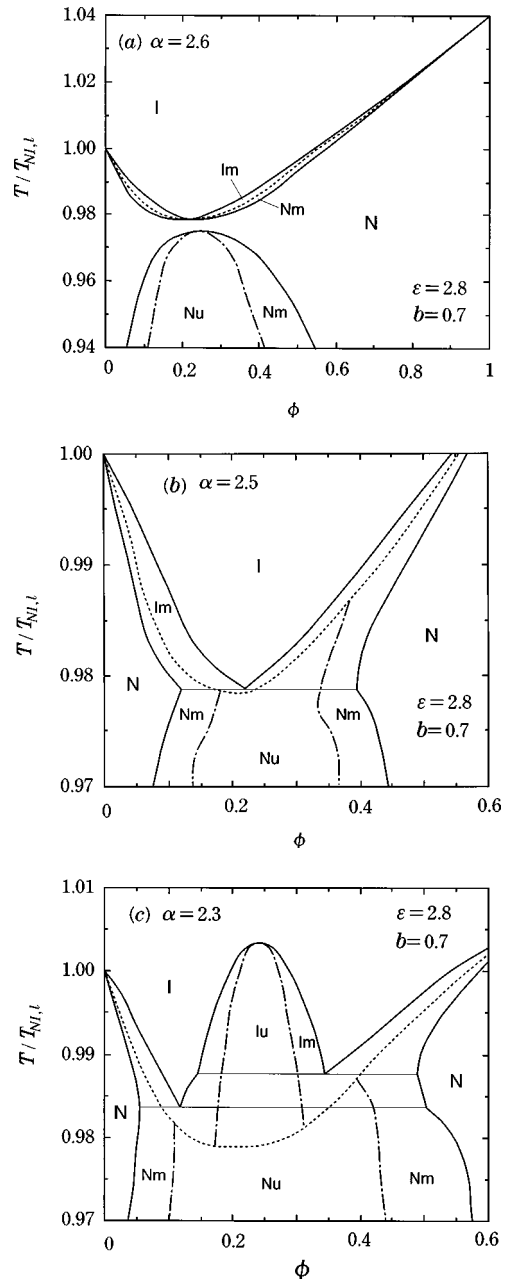

FIG. 3. Phase diagrams on the temperature-concentration plane for (a) $\alpha = 2.6$, (b) $\alpha = 2.5$, and (c) $\alpha = 2.3$ with $\epsilon = 2.8$ and $b = 0.7$.

and (c) $\alpha = 2.3$ with $\epsilon = 2.8$ and $b = 0.7$. When the value of b is small ($b < 1$), the nematic-isotropic liquid coexistence appears below the NIT temperature of the individual element. In Fig. 3(a), we find the spinodal line and the two-phase coexistence between nematic phases with an upper critical solution temperature (UCST) in the nematic phase [23]. We also find the azeotrope point at which two equilibrium nematic and isotropic phases have the same composition. On decreasing the value of α, the UCST in the nematic phase increases and we find the coexistence of two isotropic liquid phases with an UCST as shown in Fig. 3(c). In Figs. 3(b) and 3(c), the spinodal lines of the nematic phase intersect at the NIT curve. We also find two triple points. The upper triple point shows the coexisting of two isotropic liquid phases and a nematic phase. The lower triple point corresponds to the

nematic-isotropic-nematic phase separation. Below the triple point we have broad biphasic regions between two nematic phases. The two-phase coexistence in a nematic phase is controlled by the nematic interaction parameter $\alpha \equiv U_a/\chi$.

V. CONCLUSION

We have presented a mean-field theory to describe the phase separations in binary mixtures of a liquid-crystal molecule and a polymer chain which has various degrees of flexibility. The theory takes into account both the partial orientational ordering of the polymer chain and the nematic ordering of the liquid crystal. The phase diagrams, including binodal, spinodal, and the NIT lines, on the temperature-concentration plane predict the unstable and metastable regions in the nematic-isotropic, nematic-nematic, and three-phase coexistence regions. These regions should play important roles not only in the static properties but also in the dynamics of phase separations.

APPENDIX A: LANDAU−de GENNES EXPANSIONS

In this appendix, we focus on the vicinity of the NIT point in binary mixtures of polymer and liquid crystals. In order to obtain the approximate formulas of the NIT temperature T_{NI} and the order parameter S, we derive the Landau−de Gennes expansion of our free energy (3.17). This expansion helps an intuitive understanding of the underlying physics. Here we assume $\nu \equiv \nu_{\ell\ell} = \nu_{\ell r} = \nu_{rr}$ and the value of x is a constant for simplicity. The larger values of x correspond to the stiffer polymers. The characteristic ratio $l_c \equiv \langle \mathbf{R}^2 \rangle / R_{max}$ of the polymer chain is given by $l_c = (1+x)/(1-x)$ for large n_p [24,34], where $\langle \mathbf{R}^2 \rangle$ shows the mean-square end-to-end distance of the polymer chain, $R_{max} = an_p$ is the length of the chain at full extension, and a is a bond length. Equations (3.6) and (3.8) become

$$\eta_\ell = n_\ell (\nu + \tfrac{5}{4}) S, \qquad (A1)$$

$$\eta_r = n_p x (\nu + \tfrac{5}{4}) S, \qquad (A2)$$

respectively. Equation (3.11) can be expanded in the η_i as

$$\ln I_0[\eta_i] = \frac{1}{10} \eta_i^2 + \frac{1}{105} \eta_i^3 - \frac{1}{700} \eta_i^4 \cdots. \qquad (A3)$$

Substituting Eq. (A3) into Eq. (3.17), we obtain the nematic free energy as an expansion in the order parameter S:

$$\beta F_{nem}/N_t = (\nu + \tfrac{5}{4})(AS^2 - BS^3 + CS^4), \qquad (A4)$$

$$A \equiv \tfrac{1}{2}(1 - \tfrac{1}{5} a_1 \eta), \qquad (A5)$$

$$B \equiv \tfrac{1}{105} a_2 \eta^2, \qquad (A6)$$

$$C \equiv \tfrac{1}{700} a_3 \eta^3, \qquad (A7)$$

$$a_1 \equiv (1 - \phi)g + \phi x^2, \qquad (A8)$$

$$a_2 \equiv (1 - \phi)g^2 + \phi x^3, \qquad (A9)$$

$$a_3 \equiv (1 - \phi)g^3 + \phi x^4, \qquad (A10)$$

with $g = n_\ell / n_p$ and

$$\eta \equiv (\nu + \tfrac{5}{4}) n_p. \qquad (A11)$$

The η is given as a function of temperature through the anisotropic interaction ν, which is inversely proportional to temperature. The equilibrium value of S is given by minimizing the free energy. The discontinuous phase transition occurs at the NIT point η_{NI},

$$\eta_{NI} = \frac{1}{2} \left(\frac{a_1}{10} + \frac{a_2^2}{63 a_3} \right)^{-1}, \qquad (A12)$$

where the free energies Eq. (A4) of the isotropic and nematic phases are equal. For $\eta < \eta_{NI}$, we have $S = 0$. For $\eta > \eta_{NI}$, the order parameter is given by

$$\begin{aligned} S &= \frac{3B}{8C} \left[1 + \sqrt{1 - \frac{32AC}{9B^2}} \right] \\ &= \frac{5a_2}{2 \eta a_3} \left[1 + \sqrt{1 + \frac{28 a_1 a_3}{5 a_2^2} \left(1 - \frac{5}{a_1 \eta} \right)} \right]. \end{aligned} \qquad (A13)$$

The order parameter S_{NI} at the NIT point is given by

$$S_{NI} = \frac{B}{2C} = \frac{20 a_2}{3 a_3} \left(\frac{a_1}{10} + \frac{a_2^2}{63 a_3} \right). \qquad (A14)$$

The equilibrium order parameter S starts at S_{NI} and gradually approaches 1 with increasing $\eta (< 5/a_1)$. From Eqs. (A11) and (A13), the NIT temperature is given by

$$T_{NI} = \frac{U_a/k_B}{(\eta_{NI}/n_p - 1.25)}. \qquad (A15)$$

For $T < T_{NI}$, the nematic phase becomes stable. When $x = 1$, Eq. (A15) shows the NIT temperature for the binary mixtures of rigid rodlike molecules.

Here we derive the approximate formulas for the NIT temperature and the order parameter at the NIT point for the following three cases. For mixtures of a sufficiently flexible polymer and a liquid crystal, we can set $x = 0$ and so we obtain $\eta_{NI} = 315/[73(1-\phi)g]$. From Eq. (A15), the NIT temperature is given by

$$T_{NI} = \frac{4(U_a/k_B)(1-\phi)}{5[3.45/n_\ell - (1-\phi)]}. \qquad (A16)$$

The NIT temperature is decreased with increasing ϕ at $\phi > 1 - 3.45/n_\ell$. The order parameter S_{NI} at the NIT point is decreased with increasing ϕ as

$$S_{NI} = 0.772(1 - \phi). \qquad (A17)$$

For pure liquid crystals without polymer chains, we can set $\phi = 0$ and obtain

$$T_{\mathrm{NI},\ell} = \frac{4(U_a/k_B)}{5(3.45/n_\ell - 1)} \qquad (A18)$$

and $S_{\mathrm{NI}} = 0.772$. The $T_{\mathrm{NI},\ell}$ increases with increasing n_ℓ and diverges at $n_\ell = 3.45$. In our mean-field approximations, when the axial ratio n_ℓ of the liquid crystal is larger than 3.45, the nematic phase is stable at all temperature. For larger values of n_ℓ, the repulsive interactions between rigid rods dominate and the attractive interaction plays only an auxiliary role in the NIT and so the T_{NI} diverges [15,27,43].

When $\phi = 1$, we can obtain the formula for pure semiflexible polymers [34]. The stiffness of the polymer is controlled by $x \equiv n_r/n_p$. From Eq. (A15), we obtain

$$T_{\mathrm{NI},p} = \frac{4(U_a/k_B)n_p}{5(3.45/x^2 - n_p)} \qquad (A19)$$

and $S_{\mathrm{NI}} = 0.772x$. The temperature $T_{\mathrm{NI},p}$ is increased with increasing n_p when $n_p < 3.45/x^2$. For long-semiflexible chains ($x \ll 1$), the order parameter at the NIT point is small and the transition becomes almost second order [44].

From Eqs. (A18) and (A19), we obtain

$$T_{\mathrm{NI},p} = T_{\mathrm{NI},\ell} \qquad (A20)$$

at $x = x^* (\equiv \sqrt{n_\ell/n_p})$. When $x < x^*$, the temperature T_{NI} of Eq. (A15) decreases with increasing the polymer concentration ϕ and the polymer chains destroy the orientational ordering of the liquid crystals. In contrast, when $x > x^*$ the temperature T_{NI} increases with increasing polymer concentration ϕ and the polymer chains promote the orientational ordering of the liquid crystals.

[1] *Liquid Crystalline and Mesomorphic Polymers*, edited by V. P. Shibaev and L. Lam (Springer-Verlag, New York, 1993).

[2] *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor & Francis, London, 1996).

[3] *Liquid Crystalline Polymers*, edited by R. A. Weiss and C. K. Ober (American Chemical Society, Washington, D.C., 1990).

[4] B. Kronberg, I. Bassignana, and D. Patterson, J. Phys. Chem. **82**, 1714 (1978).

[5] A. Dubault, C. Casagrande, M. Veyssie, and B. Deloche, Phys. Rev. Lett. **45**, 1645 (1980).

[6] H. Orendi and M. Ballauff, Liq. Cryst. **6**, 497 (1989).

[7] W. Ahn, C. Y. Kim, H. Kim, and S. C. Kim, Macromolecules **25**, 5002 (1992).

[8] G. W. Smith, Phys. Rev. Lett. **70**, 198 (1993).

[9] F. Brochard, J. Jouffroy, and P. Levinson, J. Phys. (France) **45**, 1125 (1984).

[10] M. Ballauff, Mol. Cryst. Liq. Cryst. **136**, 175 (1986).

[11] R. Holyst and M. Schick, J. Chem. Phys. **96**, 721 (1992).

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

[13] T. Kyu and H. W. Chiu, Phys. Rev. E **53**, 3618 (1996).

[14] P. I. C. Teixeira and B. M. Mulder, J. Chem. Phys. **105**, 10145 (1996).

[15] A. Matsuyama and T. Kato, J. Chem. Phys. **105**, 1654 (1996); **108**, 2067 (1998); Prog. Colloid Polym. Sci. **106**, 175 (1997); A. Matsuyama, R. Morii, and T. Kato, Mol. Cryst. Liq. Cryst. **312**, 117 (1988).

[16] C. Casagrande, M. Veyssie, and H. Finkelmann, J. Phys. (France) Lett. **43**, L371 (1982).

[17] A. ten Bosch, P. Maissa, and P. Sixou, J. Chem. Phys. **79**, 3462 (1983).

[18] P. Maissa and P. Sixou, Liq. Cryst. **5**, 1861 (1989).

[19] M. Warner, J. M. F. Gunn, and A. Baumgartner, J. Phys. A **18**, 3007 (1985); X. J. Wang and M. Warner, *ibid*. **19**, 2215 (1986).

[20] G. Sigaud, M. F. Achard, F. Hardouin, M. Mauzac, H. Richard, and H. Gasparoux, Macromolecules **20**, 578 (1987); **23**, 5020 (1990).

[21] C. Casagrande, M. A. Guedeau, and M. Veyssie, Mol. Cryst. Liq.. Cryst., Lett. Sect. **4**, 107 (1987).

[22] J. F. D'Allest, P. Maissa, A. ten Bosch, P. Sixou, A. Blumstein, R. Blumstein, J. Teixeira, and L. Noirez, Phys. Rev. Lett. **61**, 2562 (1988); Mol. Cryst. Liq. Cryst. **155**, 581 (1988).

[23] W. R. Krigbaum, J. Watanabe, and T. Ishikawa, Macromolecules **16**, 1271 (1983).

[24] P. J. Flory, Proc. R. Soc. London, Ser. A **234**, 60 (1956).

[25] P. J. Flory, Proc. R. Soc. London, Ser. A **234**, 73 (1956).

[26] P. J. Flory, Macromolecules **11**, 1141 (1978).

[27] P. J. Flory and G. Ronca, Mol. Cryst. Liq. Cryst. **54**, 289 (1979); **54**, 311 (1979).

[28] M. Warner and P. J. Flory, J. Chem. Phys. **73**, 6327 (1980).

[29] R. R. Matheson and P. J. Flory, Macromolecules **14**, 954 (1981).

[30] H. W. Chiu and T. Kyu, J. Chem. Phys. **103**, 7471 (1995).

[31] H. W. Chiu, Z. L. Zhou, T. Kyu, L. G. Cada, and L. C. Chien, Macromolecules **29**, 1051 (1996).

[32] H. W. Chiu and T. Kyu, J. Chem. Phys. **107**, 6859 (1997).

[33] T. Kyu, H. W. Chiu, and T. Kajiyama, Phys. Rev. E **55**, 7105 (1997).

[34] A. Matsuyama, Y. Sumikawa, and T. Kato, J. Chem. Phys. **107**, 4711 (1997).

[35] A. Matsuyama and T. Kato, Phys. Rev. E **58**, 585 (1998); J. Chem. Phys. **109**, 2023 (1998).

[36] L. Onsager, Ann. (N.Y.) Acad. Sci. **51**, 626 (1949).

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

[38] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford Science, London, 1993).

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

[40] R. M. L. Evans and M. E. Cates, Phys. Rev. E **56**, 5738 (1997).

[41] T. Odijk and H. N. W. Lekkerkerker, J. Phys. Chem. **89**, 2090 (1985); H. N. W. Lekkerkerker, P. Coulon, P. V. D. Haegen, and R. Deblieck, J. Chem. Phys. **80**, 3427 (1984).

[42] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).

[43] G. Ronca and D. Y. Yoon, J. Chem. Phys. **76**, 3295 (1982).

[44] A. ten Bosch, P. Maissa, and P. Sixou, J. Phys. (France) Lett. **44**, L105 (1983).