

2-22-1998

Phase Equilibria of a Nematic and Smectic-A Mixture

Hao-Wen Chiu

Thein Kyu

University of Akron Main Campus, tkyu@uakron.edu

Please take a moment to share how this work helps you [through this survey](#). Your feedback will be important as we plan further development of our repository.

Follow this and additional works at: http://ideaexchange.uakron.edu/polymer_ideas

 Part of the [Polymer Science Commons](#)

Recommended Citation

Chiu, Hao-Wen and Kyu, Thein, "Phase Equilibria of a Nematic and Smectic-A Mixture" (1998). *College of Polymer Science and Polymer Engineering*. 52.

http://ideaexchange.uakron.edu/polymer_ideas/52

This Article is brought to you for free and open access by IdeaExchange@UAkron, the institutional repository of The University of Akron in Akron, Ohio, USA. It has been accepted for inclusion in College of Polymer Science and Polymer Engineering by an authorized administrator of IdeaExchange@UAkron. For more information, please contact mjon@uakron.edu, uapress@uakron.edu.

Phase equilibria of a nematic and smectic-A mixture

Hao-Wen Chiu and Thein Kyu^{a)}

Institute of Polymer Engineering, The University of Akron, Akron, Ohio 44325

(Received 6 October 1997; accepted 20 November 1997)

A phase diagram of a mixture consisting of nematic and smectic liquid crystals has been calculated self-consistently by combining Flory–Huggins (FH) theory for isotropic mixing and Maier–Saupe–McMillan (MSM) theory for smectic-A ordering. However, the MSM theory can be deduced to the original Maier–Saupe (MS) theory for nematic ordering. To describe the phase transitions involving induced smectic phase and nematic + smectic equilibrium, two nematic and two smectic order parameters for the nematic/smectic mixtures have been coupled through the normalized partition function and the orientation distribution function. Self-consistent numerical solution has been sought in establishing nematic/smectic phase diagrams involving (i) phase separation between nematic and smectic liquid crystals and (ii) occurrence of induced smectic in a nematic/smectic mixture. The predictive capability of this combined FH/MSM theory has been tested critically with a reported phase diagram of a nematic/smectic liquid-crystal mixture and also with our experimental phase diagram of a mixture consisting of a nematic side-on side-chain liquid-crystalline polymer and a smectic low molar mass liquid crystal. © 1998 American Institute of Physics.
[S0021-9606(98)50708-8]

I. INTRODUCTION

Recently, it has been recognized that understanding phase behavior of polymer/liquid-crystal mixtures is essential for their full utilization in electro-optical applications.¹ Of particular interests are polymer-dispersed liquid crystals (PDLC) and polymer stabilized liquid crystals (PSLC) because of their potential for electro-optical switches and flat panel displays.^{1,2} Theoretical prediction and experimental determination of those polymer/liquid-crystal mixtures have been of immense interest to scientists^{1–12} working in polymer and liquid-crystal materials, therefore is of interest to us.^{8–12}

In previous papers,^{8,9} we have demonstrated that the coupling between phase separation and liquid-crystal ordering can be modeled by a simple combination of Flory–Huggins (FH) theory^{13,14} for isotropic mixing and Maier–Saupe (MS) theory for nematic ordering.^{15,16} The predictive capabilities of the combined FH/MS theory have been tested rigorously with various experimental phase diagrams for polymer-nematic and two-nematic mixtures.⁹ Recently, this combined theory has been extended to polymer-smectic¹⁰ and subsequently to binary smectic mixtures¹¹ by replacing the MS theory with the Maier–Saupe–McMillan (MSM) theory for smectic ordering.¹⁷ The combined FH/MSM theory was further modified to describe the phenomenon of induced smectic phase in a nematic mixture.¹² Our preference of choosing the combined FH/MSM theory is because of inherent simplicity of the FH theory for demixing of polymer/LC mixtures in the isotropic phase and the predictive capability of MSM theory on the first-order phase transitions. Other theories^{5,18–21} based on a generalized van der Waals approach for quasihard anisotropic particles and/or

Landau–de Gennes free-energy expansion^{13,14} for nematic ordering, if not more, may be equally effective particularly for predicting phase diagrams of nematic mixtures. However, to the best of our knowledge, our approach based on the combined FH/MSM theory is probably the first to predict a variety of phase diagrams for binary smectic mixtures.¹¹

As part of our continuing effort in the same area, we have investigated theoretically the phase diagrams of a nematic/smectic mixture for cases involving (i) phase separation between nematic and smectic liquid crystals (LC) and (ii) occurrence of induced smectic phase in the smectic/nematic mixture. A variety of phase diagrams can be predicted by this combined FH/MSM theory. Of particular interest is the induced smectic phase in the mixture although smectic phase is forbidden in one of the constituents, as it is merely a nematic liquid-crystalline polymer. The present combined FH/MSM theory has been tested with a reported phase diagram of a nematic/smectic LC mixture and also with our experimental phase diagram of a mixture consisting of a nematic side-on side-chain liquid-crystalline polymer (s-SCLCP) and a smectic low molar mass liquid crystal.

II. THEORETICAL SCHEME

The total free-energy density of mixing for a binary smectic mixture, g , may be customarily expressed in terms of a simple addition of free energy of mixing of isotropic liquids, g^i , and free energy of anisotropic (smectic or nematic) ordering of a liquid-crystal mixture, g^a , i.e., $g = g^i + g^a$.³ In general, the free-energy density of isotropic mixing of a binary liquid-crystal/polymer mixture is customarily described according to the Flory–Huggins theory,^{13,14} viz.,

$$g^i = \frac{G^i}{nkT} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2, \quad (1)$$

^{a)} Author to whom correspondence should be addressed.

where k is Boltzmann constant and T absolute temperature. r_1 is the number of sites occupied by one liquid-crystal molecule, whereas r_2 represents the number of statistical segments or sites occupied by a single polymer chain. ϕ_1 and ϕ_2 , representing the volume fractions of components 1 and 2, respectively, may be given by $\phi_1 = n_1 r_1 / n$, $\phi_2 = n_2 r_2 / n$, and $n = n_1 r_1 + n_2 r_2$. n_1 and n_2 are the numbers of liquid-crystal and polymer molecules, respectively. χ represents the Flory-Huggins interaction parameter which is generally assumed to be a function of reciprocal absolute temperature, viz., $\chi = A + B/T$, where A and B are constants.¹⁴

On the other hand, the anisotropic part of the free-energy density of a smectic/nematic mixture may be expressed in what follows:¹¹

$$g^a = \frac{G^a}{nkT}$$

$$= -\Sigma_1 \phi_1 - \Sigma_2 \phi_2 - \frac{1}{2} v_{11} (s_1^2 + \alpha_1 \sigma_1^2) \phi_1^2 - \frac{1}{2} v_{22} s_2^2 \phi_2^2 - v_{12} (s_1 s_2 + \alpha_{in} \sigma_1 \sigma_2) \phi_1 \phi_2, \quad (2)$$

where α_1 is the dimensionless interaction strength for the smectic ordering defined as $\alpha = 2 \exp[-(\pi d_0/d)^2]$. d_0 is the molecular length representing the length of the rigid portion of the LC molecules and d represents the interlayer distance. α_{in} is a parameter characterizing the strength of induced smectic in the mixture. The cross-nematic interaction term v_{12} may be described as $v_{12} = c \sqrt{v_{11} v_{22}}$ by allowing any departure from its geometric mean.⁹ The coupling between c parameter, characterizing the relative strength of cross-nematic interaction with respect to that of the pure mesogens, and the α_{in} parameter [or the product of v_{12} and α_{in} in Eq. (2)] determines whether or not an induced smectic occurs.¹² Further, the nematic order parameters, s_1 and s_2 , and smectic order parameters, σ_1 and σ_2 , are defined as usual,¹⁵⁻¹⁷ i.e.,

$$s_j = \frac{1}{2} \langle 3 \cos^2 \theta_j - 1 \rangle, \quad (3)$$

$$\sigma_j = \frac{1}{2} \langle \cos(2\pi z/d_j) (3 \cos^2 \theta_j - 1) \rangle, \quad (4)$$

in which the subscript $j = 1, 2$ and θ_j is the angle between the LC director and the reference axis z . It should be pointed out that σ_2 has a finite value in the mixtures due to the induced smectic although the smectic phase is forbidden in the pure nematic constituent (i.e., component 2). The normalized orientation distribution function $f(z, \cos \theta_j)$ is further defined as

$$f(z, \cos \theta_j) = \frac{1}{4\pi Z_j} \exp\left[\frac{1}{2} m_{n,j} (3 \cos^2 \theta_j - 1)\right] \times \exp\left[\frac{1}{2} m_{s,j} \cos(2\pi z/d_j) (3 \cos^2 \theta_j - 1)\right], \quad (5)$$

where Z_j is the partition function given as

$$Z_j = \int \int \exp\left[\frac{1}{2} m_{n,j} (3 \cos^2 \theta_j - 1)\right] \times \exp\left[\frac{1}{2} m_{s,j} \cos(2\pi z/d_j) (3 \cos^2 \theta_j - 1)\right] dz d\Omega_j, \quad (6)$$

in which Ω_j is a solid angle. $m_{n,j}$ and $m_{s,j}$ are dimensionless nematic and smectic mean-field parameters, respectively, that characterize the strengths of the respective potential fields.¹⁶ Further, the order parameters s_j and σ_j can be expressed customarily as a function of $f(z, \cos \theta_j)$:

$$s_j = \int \int f(z, \cos \theta_j) \cdot \frac{1}{2} (3 \cos^2 \theta_j - 1) dz d\Omega_j = \frac{1}{Z_j} \frac{dZ_j}{dm_{n,j}}, \quad (7)$$

$$\sigma_j = \int \int f(z, \cos \theta_j) \cdot \frac{1}{2} \cos(2\pi z/d_j) (3 \cos^2 \theta_j - 1) dz d\Omega_j = \frac{1}{Z_j} \frac{dZ_j}{dm_{s,j}}, \quad (8)$$

while the entropy Σ_j may be deduced as

$$\Sigma_j = - \int \int f(z, \cos \theta_j) \cdot \ln[4\pi f(z, \cos \theta_j)] dz d\Omega_j = \ln Z_j - m_{n,j} s_j - m_{s,j} \sigma_j. \quad (9)$$

The orientational order parameters s_j and σ_j may then be evaluated by minimizing the free energy of anisotropic ordering with respect to the nematic and/or smectic order parameters, i.e.,

$$\frac{\partial g^a}{\partial s_j} = 0 \quad \text{and} \quad \frac{\partial g^a}{\partial \sigma_j} = 0. \quad (10)$$

The purpose of the free-energy minimization with order parameters is to determine the composition-dependence of orientational order parameters (s_j and σ_j) through which a free-energy versus composition curve may be established for a given temperature. Then, temperature dependence of the free energy is evaluated through the temperature dependence of the nematic interaction parameters (v_{11} , v_{22} , and v_{12}), i.e.,⁸

$$v_{11} = 4.541 \frac{T_{NI,1}}{T}, \quad v_{22} = 4.541 \frac{T_{NI,2}}{T}; \quad (11)$$

where $T_{NI,j}$ is the NI transition temperature of the component j . By choosing an appropriate α_1 value the smectic-nematic ($S_{mA} - N$) transition temperatures can be computed easily through the relationship between α_1 and phase transition temperatures involving $N - I$, $S_{mA} - N$, or smectic-isotropic ($S_{mA} - I$) transitions as demonstrated by McMillan.¹⁵⁻¹⁷ The $S_{mA} - N$ transition is a first order for $0.7 < \alpha_1 < 0.98$, but the transition is a second order for $\alpha_1 < 0.7$. When $\alpha_1 > 0.98$, the smectic transforms directly to an isotropic phase. Temperature dependence of the smectic interaction parameter (α_1) may be expressed by coupling with v_{11} as follows:¹¹

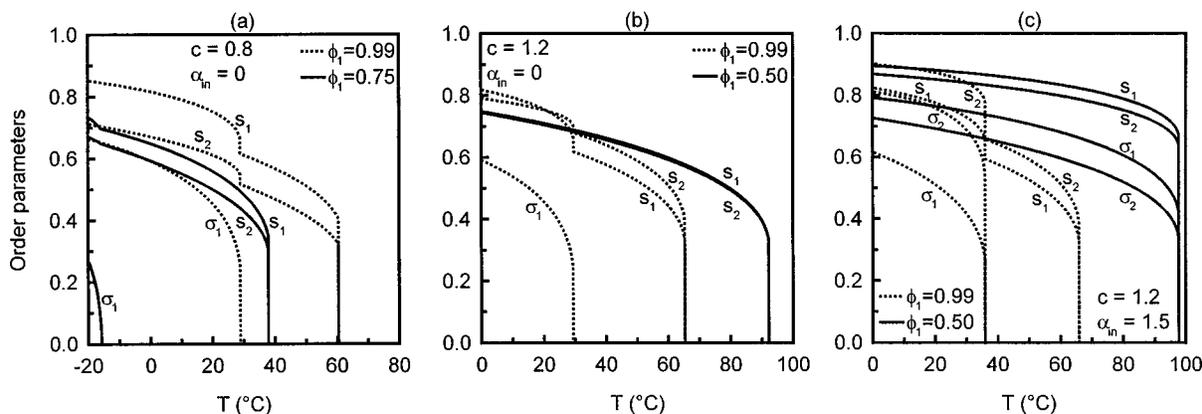


FIG. 1. Temperature dependence of the nematic and smectic order parameters of the neat component ($\phi_1=0.99$) and some intermediate mixtures ($\phi_1=0.5$ or 0.75) for three cases: (a) weak cross-nematic interaction without induced smectic ($c=0.8$, $\alpha_{in}=0$); (b) strong cross-nematic interaction without induced smectic ($c=1.2$, $\alpha_{in}=0$); and (c) strong cross-nematic interaction with induced smectic ($c=1.2$, $\alpha_{in}=1.5$).

$$v_{11}\alpha_1 = 4.541 \frac{T_{SI,1}}{T}, \tag{12}$$

where $T_{SI,1}$ represents temperature of the $S_{MA} - I$ transitions of the component 1. For a given c value, the s_1 and σ_1 can be evaluated numerically as functions of temperature (T) and composition (ϕ_1) from Eq. (10). It should be pointed out that if no induced smectic phase exists, i.e., $\alpha_{in}=0$, the smectic field strength of the nematic LC (component 2), $m_{s,2}$, must be zero. This means that the Maier-Saupe-McMillan representation of the nematic order parameter s_2 is simply reduced to the original Maier-Saupe theory.

Once the nematic and smectic order parameters have been determined, the free-energy density of anisotropic ordering can be calculated readily. The equilibrium coexistence points of the phase diagram may then be computed self-consistently from the total free-energy density by equating the chemical potentials of each component in two equilibrium phases (I and II), viz., $\mu_1^I = \mu_1^{II}$ and $\mu_2^I = \mu_2^{II}$. Alternatively, the binodal points at a given temperature may be established by a double tangent method where the equilibrium volume fractions of the individual phase (ϕ^I and ϕ^{II}) fall on the same tangent line of the total free-energy curve. The interested readers are referred to our previous paper for the detailed calculations.^{9,11}

III. RESULTS AND DISCUSSION

Let us first consider a case of a smectic/nematic mixture in which the smectic LC undergoes smectic-A - nematic ($S_{MA} - N$) phase transition at 30 °C and nematic - isotropic ($N - I$) transition at 60 °C, while the nematic LC reveal a nematic - isotropic ($N - I$) transition at 50 °C. The purpose of minimizing the anisotropic free energy with respect to the nematic and smectic order parameters is to determine the temperature and composition dependence of these order parameters. In Figs. 1(a)-1(c) the temperature dependence of nematic and smectic order parameters for the constituent nematic and smectic LCs ($\phi_1=0.99$) and their intermediate mixtures ($\phi_1=0.5$ or 0.75) are shown. Three cases were considered: (i) weak cross-nematic interaction without induced smectic ($c=0.8$, $\alpha_{in}=0$); (ii) strong cross-nematic

interaction without induced smectic ($c=1.2$, $\alpha_{in}=0$); and (iii) strong cross-nematic interaction with induced smectic ($c=1.2$, $\alpha_{in}=1.5$). In the case (i) for $c=0.8$, the smectic-A - nematic transition as well as the nematic - isotropic transition temperatures are lower for the mixture (e.g., 75/25) as compared to those of the pure smectic-A LC (component 1) and also to the $N - I$ transition of the nematic LC (component 2). This suggests that the nematic is favored to form in the pure constituents relative to that in the mixtures, i.e., the smectic ordering is possible only in the constituent smectic LC.

When the cross-interaction gets stronger ($c=1.2$) as in cases (ii) and (iii), the coupling term involving c (or v_{12}) and α_{in} will determine whether or not an induced smectic phase can occur in some intermediate mixtures although it is forbidden in the pure nematic LC. In the case (ii), the nematic order parameters are higher for the mixture ($\phi_1=0.50$) than that of pure constituents ($\phi_1=0.99$) showing enhanced nematic-isotropic transitions of the induced nematic phase in the mixtures. However, no induced smectic ordering can occur in the pure nematic LC or in the mixtures. In Fig. 1(c) the temperature dependence of the order parameters for strong cross-nematic interaction with the induced smectic ($c=1.2$ and $\alpha_{in}=1.5$) is shown. The smectic order parameter shows a larger value in the mixture than in the pure constituent suggesting that the induced smectic phase occurs in the mixture.

Once the nematic and smectic order parameters have been determined through the free-energy minimization, the composition and temperature dependence of the anisotropic free-energy density can be evaluated for the corresponding three cases [Figs. 2(a)-2(c)]. In the case (i) where the relative cross interaction is weak, the free energy is lowest at the pure constituent LCs, indicating that the anisotropic LC phase is favored to form within the same mesogens. On the contrary, when the relative cross interaction becomes stronger than that in the pure LCs [(i.e., case (ii)], the free-energy curves become concave upward, suggesting that the nematics in the intermediate compositions are more stable relative to those in the pure LC phases. These stable nematics are induced by the strong cross interactions of the dissimilar me-

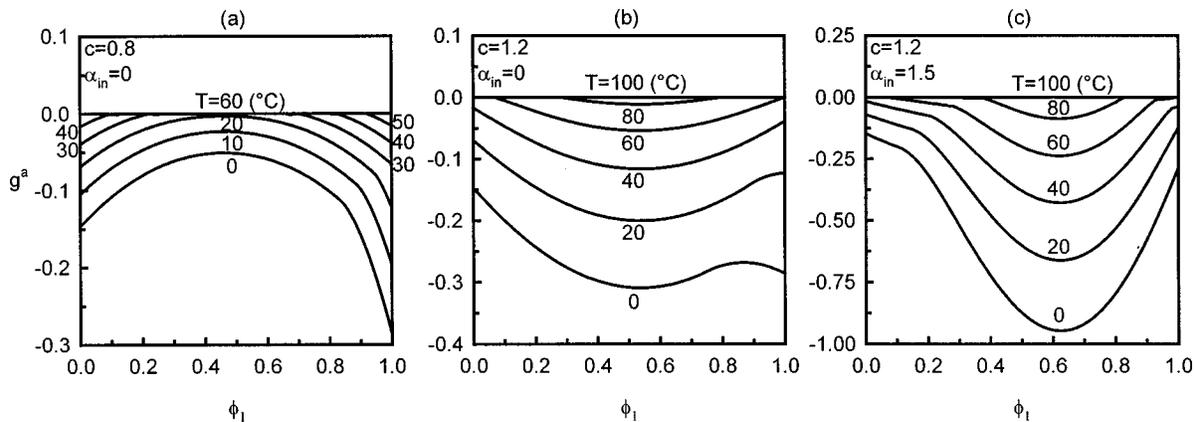


FIG. 2. Temperature and composition dependence of the anisotropic free-energy density for the corresponding three cases of Fig. 1.

sogens; thus they may be regarded as induced nematics. The change of the curvatures of the free-energy curves can be noticed at high smectic LC contents due to the occurrence of smectic ordering. In the case (iii) the free-energy curves show the concave upward trend, thus are similar to the case (ii), suggesting that a smectic phase can be induced in some intermediate mixtures, although one of the constituents is purely a nematic LC. Moreover, the free-energy curves at the nematic LC rich contents exhibit the curvature change, which may be a consequence of a nematic–smectic-A phase transition.

A. Effect of c , α_{in} , and T_c parameters

To illustrate the effect of a c parameter on phase diagrams of a smectic/nematic mixture, numerical simulations have been performed for the case (i), a weak cross-mesogenic interaction, $c=0.8$, in comparison with the case (ii), a strong cross-mesogenic interaction, $c=1.2$, keeping $\alpha_{in}=0$ (no induced smectic). In the calculations, the ratio of the segment length, r_2/r_1 is taken as 2.25/1 with $A=-1$, and $T_c=60$ °C. Figure 3(a) depicts the calculated phase diagram for a weak cross-mesogenic interaction [case (i)]. In the nematic LC (component 2) rich compositions, the coexistence of the liquid and nematic (L_1+N_2) is observed between the single isotropic phase (I) and the pure nematic

(N_2). In the other compositions rich in the smectic LC (component 1), the coexistence of N_1+L_2 , the pure N_1 , $N_1+S_{mA,1}$, and the pure $S_{mA,1}$ regions can be discerned in the order of descending temperature. The theory further predicts various coexistence regions consisting of L_1+L_2 , N_1+L_2 , N_1+N_2 , and $S_{mA,1}+N_2$ regions in the intermediate compositions.

For the case (ii) of strong cross-mesogenic interactions, the coexistence curves of the isotropic (I) + nematic (N) are convex [Fig. 3(b)]. A single nematic phase (N) induced by the strong cross-mesogenic interaction is evident in the wide temperature gap across all compositions, suggesting that the nematic phase is more stable than those of the neat constituents. Concurrently, the coexistence region of $N+S_{mA,1}$, that appears between the induced nematic (N) and the pure $S_{mA,1}$ regions, has been depressed with increasing nematic LC (constituent 2). The enhancement of the $N-I$ transition temperature relative to those of the constituents can be attributed to the induced nematic phase associated with the strong cross-mesogenic interaction. Because of the enhancement of the nematic-isotropic transition in conjunction with the depression of the $N+S_{mA,1}$ coexistence curve, the induced nematic region becomes wider. This broadened nematic region is exactly the reason that the mixed liquid crystals at the

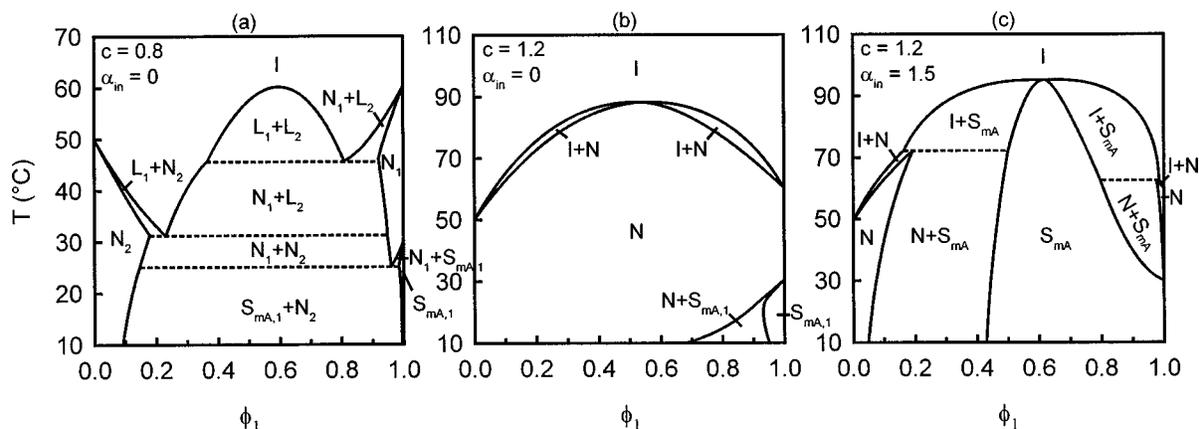


FIG. 3. Phase diagrams of the smectic/nematic mixture in which the constituent smectic displays a smectic–nematic–isotropic transition (i.e., $\alpha_1=0.7861$) for the corresponding three cases of Fig. 1, calculated by setting $r_2/r_1=2.25/1$, $\chi=-1+795.9/T$, $T_{N1,1}=60$ °C, $T_{S_{mA,1},1}=30$ °C, and $T_{N1,2}=50$ °C.

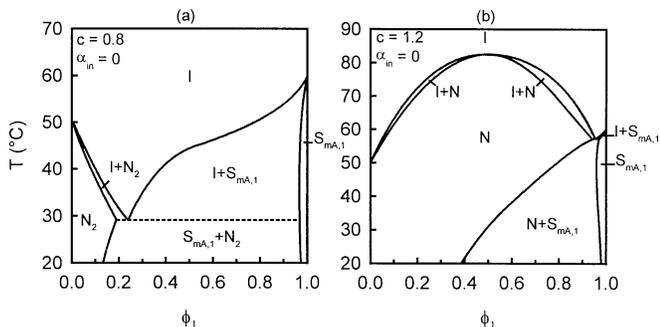


FIG. 4. Calculated phase diagrams for a nematic/smectic mixture having a smectic–isotropic transition in the smectic constituent with $\alpha_1 = 1.0719$ for two situations: (i) $c = 0.8$, $\alpha_{in} = 0$, and (ii) $c = 1.2$, $\alpha_{in} = 0$, showing the effect of the c parameter.

azeotropic point have found extensive use in many commercial applications.

To demonstrate the role of the induced smectic parameters, α_{in} , we have calculated the phase diagram by setting $\alpha_{in} = 1.5$ and $c = 1.2$. As shown in Fig. 3(c), the phase diagram becomes more complex. At the nematic LC (component 2) rich region, the coexistence of isotropic + nematic ($I+N$) is seen between the isotropic and the single nematic phase (N). In the intermediate compositions, we observed the coexistence of isotropic + induced smectic ($I+S_{mA}$) and the single induced S_{mA} . Below the peritectic line consisting of I , N , and S_{mA} phases, the coexistence of $N+S_{mA}$ can be discerned in some compositions high in nematic LC. Below the second peritectic line, a similar observation was made for the region high in smectic LC contents, except that the line separating the induced smectic and the $N+S_{mA}$ regions was converged to that dividing the induced N and the $N+S_{mA}$ regions at the $S_{mA}-N$ transition temperature of the constituent smectic LC. It is apparent that the present phase diagram has been dominated by the induced smectic; thus it may be useful in the area that requires the wide smectic temperature range.

To establish phase diagrams for a nematic/smectic mixture where the constituent LCs have only a single transition, i.e., a nematic–isotropic transition in the component 2 and a smectic–isotropic transition in the component 1 for which α_1 is chosen to be 1.0719. Again, the effect of the c parameter has been investigated for two cases (i) $c = 0.8$, $\alpha_{in} = 0$, and (ii) $c = 1.2$ and $\alpha_{in} = 0$, setting $T_{SI,1} = 60$ °C, and $T_{NI,2} = 50$ °C. As shown in Fig. 4(a), the theory predicts various coexistence regions comprised of $I+N_2$ and the pure N_2 regions in the nematic LC rich region and the $I+S_{mA,1}$ and the pure $S_{mA,1}$ where the smectic component is rich. Below the peritectic line, the $S_{mA,1}+N_2$ phases coexist. In the case of strong cross-nematic interaction, the pure N_2 region can no longer exist in the mixtures as the induced nematic phase (N) becomes dominant, showing the coexistence of the isotropic + nematic ($I+N$) region and the $N+S_{mA,1}$ region. $I+N$ coexistence curves are convex upward which is followed by the wide induced nematic region with decreasing temperature [Fig. 4(b)]. However, the $I+N$ binodal curves intersect with the $N+S_{mA,1}$ coexistence curve at the high smectic LC contents. A narrow $I+S_{mA,1}$ coexistence region

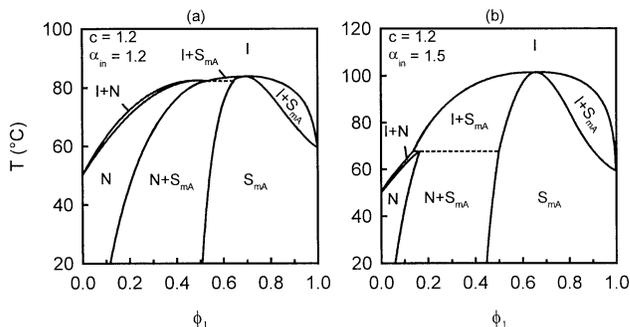


FIG. 5. Simulated phase diagrams for a nematic/smectic mixture for two situations having a smectic–isotropic transition in the smectic constituent (a) $c = 1.2$, $\alpha_{in} = 1.2$ and (b) $c = 1.2$, $\alpha_{in} = 1.5$ showing the effect of α_{in} .

can also be identified at a small temperature gap at very high smectic LC compositions. This narrow $I+S_{mA,1}$ coexistence gap is depressed with increasing nematic LC content.

To appreciate the effect of α_{in} , we seek the numerical self-consistent solution for two situations (a) $c = 1.2$, $\alpha_{in} = 1.2$ and (b) $c = 1.2$, $\alpha_{in} = 1.5$. In Figs. 5(a) and 5(b) the respective phase diagrams are shown, exhibiting the coexistence of $I+N$, the induced nematic (N), the induced smectic (S_{mA}), $N+S_{mA}$, and $I+S_{mA}$ regions. When the α_{in} value increases from 0 [Fig. 4(b)] to 1.2 [Fig. 5(a)], the pure smectic region found originally in the mixtures vanishes. Instead, an induced smectic region develops in the smectic LC rich region with an azeotrope. Concurrently, the $N+S_{mA}$, and $I+S_{mA}$ coexistence regions appear. Upon further increasing the α_{in} value from 1.2 to 1.5, the $I+S_{mA}$ coexistence regions become wider as the coexistence regions containing N phase get reduced while the azeotropic temperature increases.

When the c value is reduced to 0.8 representing the weak cross-mesogenic interaction, keeping the same α_{in} value of 1.2, no induced smectic phase can develop in the phase diagrams [Figs. 6(a) and 6(b)]. This fact suggests that the cross-mesogenic interaction must be strong to observe an induced nematic or an induced smectic phase. What we are seeing in Figs. 6(a) and 6(b) is the appearance of the liquid + liquid (L_1+L_2) coexistence region in the smectic/nematic phase diagrams depending on the critical temperature of the L_1+L_2 equilibrium. Such $L+L_2$ phase separation is discernible only if the critical temperature (T_c) is higher than the

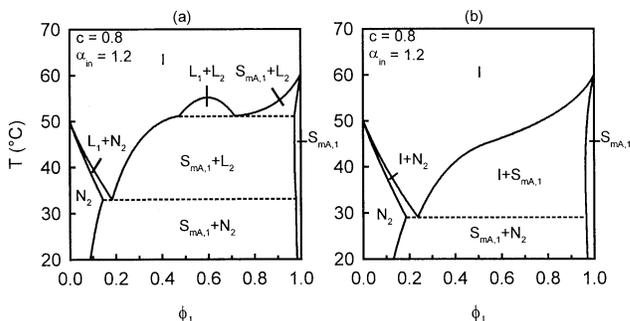


FIG. 6. Simulated phase diagrams for a nematic/smectic mixture for two situations having a smectic–isotropic transition in the smectic constituent (a) $c = 0.8$, $\alpha_{in} = 1.2$, $T_c = 55$ °C and (b) $c = 0.8$, $\alpha_{in} = 1.2$, $T_c = 20$ °C, showing the effect of T_c .

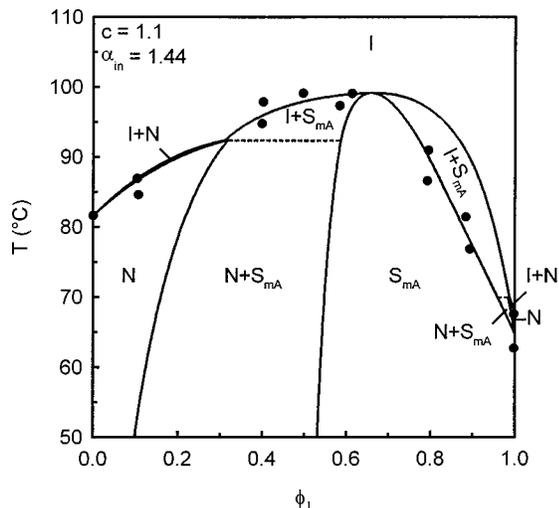


FIG. 7. Comparison of the theoretical prediction (solid curves) and the experimental coexistence points of a mixture of 4-nitrophenyl 4'-n-octyloxybenzoate and 4-n-octyloxyphenyl 4'-n-pentyloxybenzoate (filled circles) from Ref. 21.

$S_{mA,1}+L_2$ coexistence temperature. It should be borne in mind that the χ interaction parameter is directly related to T_c through the temperature dependence of χ , i.e., $\chi = A + (\chi_c - A)T_c/T$, where χ_c is the critical interaction parameter at the critical point. The examination of the influence of T_c on the smectic/nematic phase diagrams therefore signifies the effect of the χ parameter. For low T_c , there is no liquid + liquid phase separation taking place [Fig. 6(b)]. Instead, the $I+N_2$ coexistence region appears between the isotropic and the pure nematic region in the nematic LC rich region. On the same token, $I+S_{mA,1}$ is evident between the isotropic and the pure smectic region.

B. Test with experiments

It has been demonstrated that a rich variety of phase diagrams for the mixtures of smectic and nematic liquid crystals can be predicted theoretically. However, these predictions must be verified by comparing rigorously with the reported experimental results. In Fig. 7 the theoretical prediction (solid curve) in comparison with the experimental results of a mixture of 4-nitrophenyl 4'-n-octyloxybenzoate and 4-n-octyloxyphenyl 4'-n-pentyloxybenzoate (filled circles) is shown.¹⁸ The phase diagram was solved self-consistently by setting $\alpha_1=0.9549$, $\alpha_{in}=1.44$, $c=1.1$, $\chi = -1 + 999.5/T$, and $r_2/r_1=1/1$ since both constituents are monomeric liquid crystals. The choice of χ is inconsequential since there exists no liquid + liquid equilibrium. Note that the value of $c=1.1$ was determined from the azeotrope, hence α_{in} is the only adjustable parameter to fit the experimental phase diagram. Obviously, the theoretical curves capture the experimental trend, except that the coexistence region of $N+S_{mA}$ (at nematic LC rich compositions) is opened because the present theory neglects the crystal phase transition that occurs at a lower temperature in the actual experiment.

Recently, we have experimentally established a phase diagram for a mixture of a cyanobiphenyl derivative com-

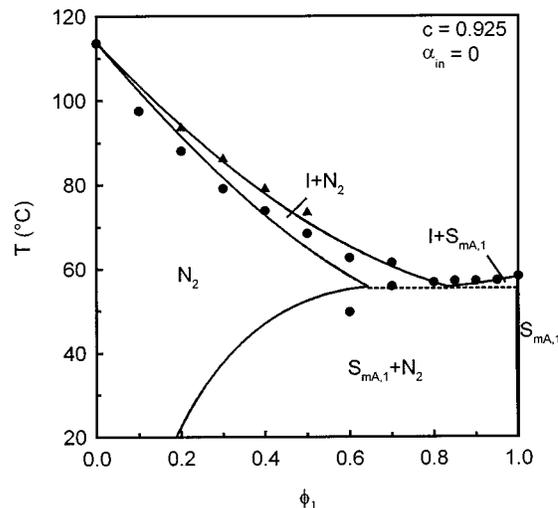


FIG. 8. Comparison of the calculated theoretical curves (solid lines) and the experimental coexistence points of a mixture of a cyanobiphenyl derivative (K36) and a side-on side-chain liquid-crystalline polymer (polymethacrylate grafted with 2,5 bis-4-butoxy benzoyloxy benzoate mesogen via a butyl spacer) (filled symbols). The filled circles and triangles were determined by polarized optical microscopy during the cooling and heating cycles, respectively.

mercially known as K36 and a side-on side-chain liquid-crystalline polymer (polymethacrylate grafted with 2,5 bis-4-butoxy benzoyloxy benzoate mesogen via a butyl spacer).²² K36 is a smectic liquid crystal that shows a smectic-isotropic transition and a crystal-smectic transition, whereas the s-SCLCP exhibits a nematic-isotropic transition. In the numerical solution, we set $c=0.925$, $\alpha_1=1.0575$, $\alpha_{in}=0$, $\chi = -1 + 522.2/T$, and $r_2/r_1=16/1$ (ratio of statistical segment length or degree of polymerization of s-SCLCP and LC), but the crystal phase transition is not taken into consideration in the theory. Again, the choice of χ is not important here because of the lack of liquid + liquid phase separation. c is used as an adjustable parameter. Figure 8 shows the comparison of the theoretical curves (solid lines) and the experimental coexistence data points as determined by polarized optical microscopy with a heating and cooling rate of 0.5 °C/min. However, slower rates (e.g., 0.1–0.2 °C/min) were needed for the s-SCLCP rich regions due to high viscosity of the polymer.²² As can be seen in Fig. 8, the theoretical curves fit with the experimental data remarkably well, thereby attesting to the excellent predictive capability of the present theory.

IV. CONCLUSIONS

We have shown that a rich variety of phase diagrams of a mixture consisting of nematic and smectic liquid crystals can be predicted based on the combination of the Flory–Huggins (FH) theory for isotropic mixing and the Maier–Saupe–McMillan (MSM) theory for nematic/smectic ordering. The effects of various parameters such as c , α_{in} , and T_c on the nematic/smectic phase diagrams have been demonstrated. The predictive capability of the present combined FH/MSM theory has been tested favorably well with the reported experimental nematic/smectic phase diagrams that showed (i) phase separation between nematic and smectic

LCs and (ii) the induced smectic phase. We, however, by no means claim that our combined FH/MSM theory is the only approach. Other theories based on generalized van der Waals-type theory for quasihard anisotropic liquids or Landau-de Gennes theory could be equally effective for prediction of nematic phase diagrams, but such an approach has yet to emerge for predicting smectic/nematic phase diagrams.

ACKNOWLEDGMENT

Support of this work by the National Science Foundation, Grant No. DMR-9529296 is gratefully acknowledged.

¹P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore, 1995).

²J. West in *Technological Applications of Dispersions*, edited by R. B. McKay (Marcel Dekker, New York, 1994), p. 345.

³F. Brochard, J. Jouffrey, and P. Levinson, *J. Phys. (France)* **45**, 1125 (1984).

⁴M. Nakamura, *Mol. Cryst. Liq. Cryst.* **130**, 349 (1985).

⁵P. Palffy-Muhoray, J. J. de Bryun, and D. A. Dunmur, *Mol. Cryst. Liq. Cryst.* **127**, 301 (1985).

⁶A. J. Liu and G. H. Fredrickson, *Macromolecules* **25**, 551 (1992).

⁷P. I. C. Teixeira and B. M. Mulder, *J. Chem. Phys.* **105**, 10145 (1996).

⁸C. Shen and T. Kyu, *J. Chem. Phys.* **102**, 556 (1995).

⁹H. -W. Chiu and T. Kyu, *J. Chem. Phys.* **103**, 7471 (1995).

¹⁰T. Kyu and H. -W. Chiu, *Phys. Rev. E* **53**, 3618 (1996).

¹¹H. -W. Chiu and T. Kyu, *J. Chem. Phys.* **107**, 6859 (1997).

¹²T. Kyu, H. -W. Chiu, and T. Kajiyama, *Phys. Rev. E* **55**, 7105 (1997).

¹³P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).

¹⁴O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility* (Academic, New York, 1979).

¹⁵W. Maier and A. Saupe, *Z. Naturforsch. A* **14**, 882 (1959); **15**, 287 (1960).

¹⁶P. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, London, 1993).

¹⁷W. L. McMillan, *Phys. Rev. A* **4**, 1238 (1971).

¹⁸H. B. Callen, *Thermodynamics*, 2nd ed. (Wiley, New York, 1985).

¹⁹J. -P. Hansen and I. R. McDonald, *The Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1985).

²⁰D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, Oxford, 1987).

²¹E. P. Sokolova, *Russ. J. Appl. Chem.* **67**, 798 (1994).

²²T. Kyu, S. X. Liang, and H.-W. Chiu (unpublished).