

Phase equilibria of a polymer–smectic-liquid-crystal mixture

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Phase diagrams of nematic–liquid-crystal mixtures have been extensively studied theoretically and experimentally to improve the basic understanding of miscibility and phase separation behavior of polymer-dispersed liquid crystals (PDLC's). To the best of our knowledge, the phase behavior of a PDLC composed of a polymer and a smectic liquid crystal is largely an unexplored area. We have developed a theoretical model for predicting phase diagrams of a polymer/smectic–liquid-crystal mixture by combining the Flory-Huggins (FH) theory for isotropic mixing and the Maier-Saupe-McMillan (MSM) theory for anisotropic ordering of liquid crystals (LC's). Our combined FH-MSM model is capable of predicting the phase diagrams of PDLC systems in which the LC component has either a smectic-*A*–nematic (Sm-*A*–*N*) transition and a nematic-isotropic (*N*-*I*) transition or a smectic-*A*–isotropic (Sm-*A*–*I*) transition.

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INTRODUCTION

Nematic-liquid crystals have customarily been used as the dispersing liquid crystals (LC's) in polymer-dispersed liquid crystals (PDLC's) [1–3]. In this connection, theories for calculating equilibrium phase diagrams of nematic-based PDLC systems have advanced remarkably [4–7]. The calculated phase diagram for a homopolymer–low-molar-mass-nematic-LC mixture essentially resembles a “teapot” phase diagram comprised of liquid-liquid, nematic-liquid, and pure nematic regions. We have shown that the combined Flory-Huggins (FH)/Maier-Saupe (MS) theory is capable of explaining experimental phase diagrams such as the mixtures of polymethyl methacrylate *E7* (a mixture of cyanobiphenyls) and polybenzyl methacrylate/*E7* liquid crystals [4]. Recently, we have generalized the model for predicting various phase diagrams of binary nematic mixtures by introducing a single parameter *c* which is a measure of the relative interaction strength between two dissimilar mesogens to that in the same species [7]. Further, we have demonstrated that the reported experimental phase diagrams for side-chain liquid-crystalline-polymers small-molecule-LC mixtures can be explained remarkably well with this single *c* parameter. In the case where the experimental phase diagram revealed an azeotrope, the *c* parameter can be determined directly from the experimental data, and the phase diagram can be fitted without using any adjustable parameter [7].

It is now of interest to extend the above theory to a PDLC system containing smectic-liquid crystals. One advantage of the smectic-based PDLC is that the switching response (relaxation) time may be expedited significantly relative to the nematic-based PDLC. However, the phase equilibria of a smectic-based PDLC system remain a largely unexplored area which is of interest to us. In this paper, we have developed a theoretical model for predicting phase diagrams of polymer/smectic–liquid-crystal mixtures by combining the Flory-Huggins [8] (FH) theory for isotropic mixing and the Maier-Saupe-McMillan (MSM) theory [9,10] for anisotropic

ordering of smectic LC molecules. Interesting features of the predicted phase diagrams of the polymer/smectic mixtures have been discussed.

THEORETICAL MODEL

The total free energy of mixing for a polymer/smectic–liquid-crystal mixture may be expressed in terms of a simple addition of the free energy of mixing of isotropic liquids, g^i , and the free energy of anisotropic ordering of smectic-liquid crystals, g^s , i.e., $g = g^i + g^s$, where g represents the dimensionless total free energy density of the system. The free energy of the isotropic mixing of a binary polymer blend can be generally described by the Flory-Huggins [8] theory, viz.

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

where k is the Boltzmann constant and T the absolute temperature. r_1 is the number of sites occupied by one liquid-crystal molecule, and is equal to unity for a low molar mass liquid crystal, whereas r_2 represents the number of segments or sites occupied by a single polymer chain. ϕ_1 and ϕ_2 represent the volume fractions of components 1 and 2, respectively, which may be given by [11]

$$\phi_1 = \frac{n_1 r_1}{n_1 r_1 + n_2 r_2}, \quad \phi_2 = \frac{n_2 r_2}{n_1 r_1 + n_2 r_2}, \quad (2)$$

where n_1 and n_2 are the numbers of liquid crystal and polymer molecules, respectively, and $n = n_1 r_1 + n_2 r_2$. χ is known as 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 [11].

The free energy density of the anisotropic ordering of smectic-liquid crystals may be represented in terms of the Maier-Saupe-McMillan mean-field theory [9,10] by coupling the composition of LC's into the free energy equation such that

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$$g^s = \frac{G^s}{nkT} = -\Sigma \phi_1 - \frac{1}{2} \nu (s^2 + \alpha \sigma^2) \phi_1^2, \quad (3)$$

where Σ represents the decrease of entropy due to the alignment of individual LC molecules. ν is the nematic interaction parameter, and is assumed to have an inverse temperature dependence [4,7]. α is the dimensionless interaction strength for the smectic ordering introduced by McMillan [10], which is defined as

$$\alpha = 2 \exp[-(\pi r_0/d)^2], \quad (4)$$

where r_0 represents the molecular length (i.e., it is of the order of the length of the rigid portion of the LC molecule), and d represents the interlayer distance. The α value can vary from 0 to 2. The nematic order parameter s and smectic order parameter σ are further defined as [9,10]

$$s = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (5)$$

$$\sigma = \frac{1}{2} \langle \cos(2\pi z/d)(3 \cos^2 \theta - 1) \rangle, \quad (6)$$

in which θ is the angle between the director of a liquid-crystal molecule and a reference axis z . The angle bracket $\langle \rangle$ denotes the ensemble average, which is defined as

$$\begin{aligned} \langle \cos(2\pi z/d) \cos^2 \theta \rangle &= \int \int \cos(2\pi z/d) \\ &\quad \times (\cos^2 \theta) f(z, \cos \theta) dz d \cos \theta. \end{aligned} \quad (7)$$

Here $f(z, \cos \theta)$ represents the normalized orientation distribution function, and is considered to be symmetric around the reference axis, which may be expressed by

$$\begin{aligned} f(z, \cos \theta) &= \frac{1}{4\pi Z} \exp[\frac{1}{2} m_n (3 \cos^2 \theta - 1)] \\ &\quad \times \exp[\frac{1}{2} m_s \cos(2\pi z/d)(3 \cos^2 \theta - 1)], \end{aligned} \quad (8)$$

where Z is the partition function defined as

$$\begin{aligned} Z &= \int \int \exp[\frac{1}{2} m_n (3 \cos^2 \theta - 1)] \exp[\frac{1}{2} m_s \cos(2\pi z/d) \\ &\quad \times (3 \cos^2 \theta - 1)] dz d \cos \theta, \end{aligned} \quad (9)$$

in which m_n and m_s are dimensionless nematic and smectic mean-field parameters, respectively, which characterize the strength of the potential fields [12]. The order parameters s and σ can then be related to Z through

$$s = \int \int f(z, \cos \theta) \frac{1}{2} (3 \cos^2 \theta - 1) dz d \cos \theta = \frac{1}{Z} \frac{dZ}{dm_n}, \quad (10)$$

$$\begin{aligned} \sigma &= \int \int f(z, \cos \theta) \frac{1}{2} \cos(2\pi z/d) (3 \cos^2 \theta - 1) dz d \cos \theta \\ &= \frac{1}{Z} \frac{dZ}{dm_s}, \end{aligned} \quad (11)$$

and the entropy Σ can be deduced as

$$\begin{aligned} \Sigma &= - \int \int f(z, \cos \theta) \ln[4\pi f(z, \cos \theta)] dz d \Omega \\ &= \ln Z - m_n s - m_s \sigma, \end{aligned} \quad (12)$$

where Ω denotes the solid angle. It should be pointed out that the integration over z in Eqs. (7) and (9)–(12) must be carried out in the limit of $[0, d]$, and then normalized by the distance d .

The two orientational order parameters s and σ may be evaluated by minimizing the free energy of anisotropic ordering with respect to the order parameters, i.e.,

$$\frac{\partial g^s}{\partial s} = 0 \quad \text{and} \quad \frac{\partial g^s}{\partial \sigma} = 0, \quad (13)$$

which yields the following equations:

$$m_n = \nu s \phi_1, \quad (14)$$

$$m_s = \alpha \nu \sigma \phi_1. \quad (15)$$

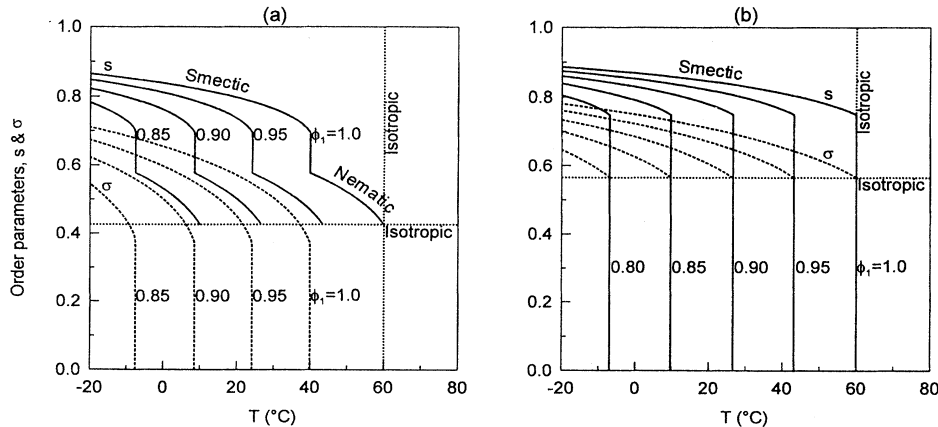


FIG. 1. Temperature and composition dependence of the two order parameters for a mixture of polymer and smectic-A liquid crystal having (a) $T_{NI}=60^\circ\text{C}$ and $T_{SN}=40^\circ\text{C}$ and (b) $T_{SI}=60^\circ\text{C}$.

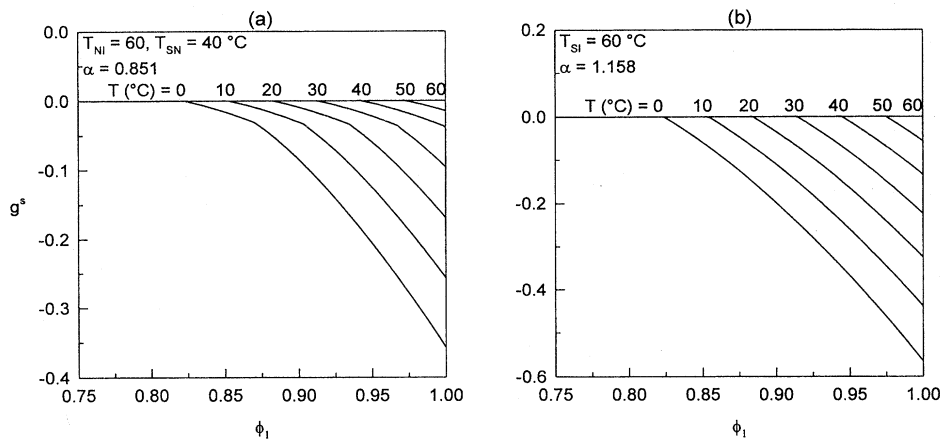


FIG. 2. Temperature and composition dependence of the corresponding free energy curves for a mixture of polymer and smectic-A liquid crystal having (a) $T_{NI}=60\text{ }^{\circ}\text{C}$ and $T_{SN}=40\text{ }^{\circ}\text{C}$ and (b) $T_{SI}=60\text{ }^{\circ}\text{C}$.

From Eqs. (14) and (15), it is obvious that the orientational order parameters (s and σ) depend on the volume fraction of the LC (ϕ_1), the smectic interaction strength (α), and the nematic interaction parameter (ν) which itself is a function of temperature. According to McMillan [10], the smectic-A-nematic transition temperature is an increasing function of α

and reaches T_{NI} at $\alpha=0.98$. The magnitude of α may be taken as an empirical parameter that determines whether the transition occurs from an isotropic phase to a smectic phase directly or via a nematic phase. That is to say, a smectic phase can be melted directly to an isotropic phase when $\alpha>0.98$. However, if $\alpha<0.98$, the transition would occur in

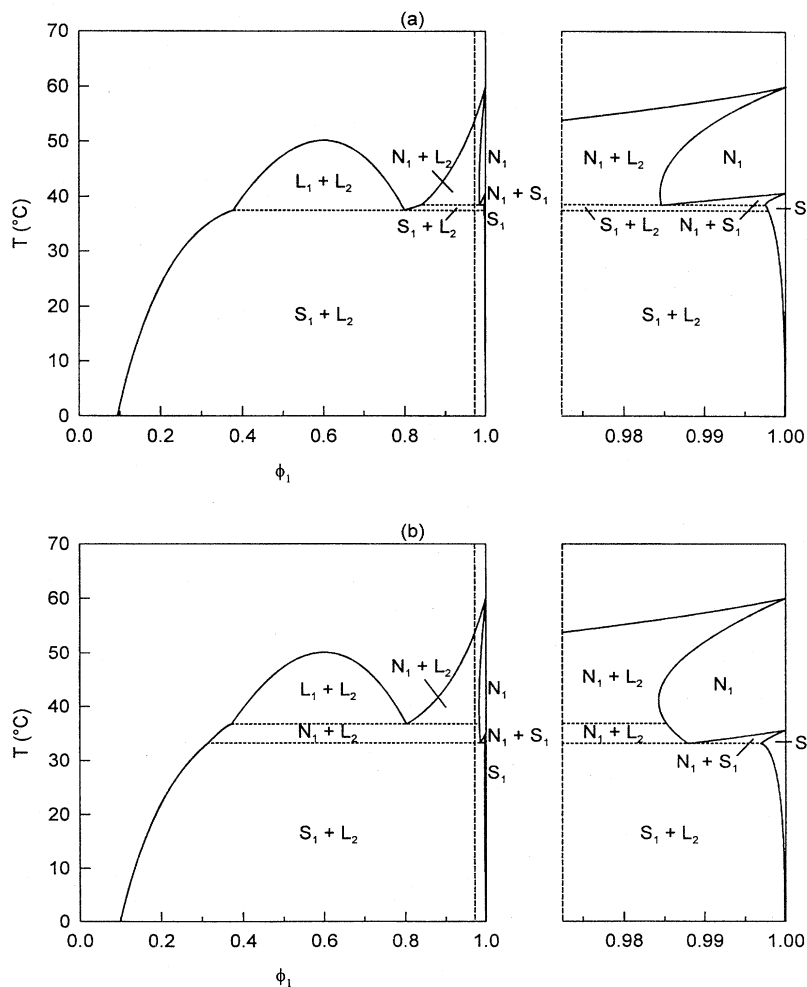


FIG. 3. Temperature vs composition phase diagrams for a mixture of polymer and smectic-A liquid crystal having $T_{NI}=60\text{ }^{\circ}\text{C}$ with (a) $T_{SN}=40\text{ }^{\circ}\text{C}$ and (b) $T_{SN}=35\text{ }^{\circ}\text{C}$ along with their enlarged versions displaying the pure nematic, the pure smectic, and their coexistence gap.

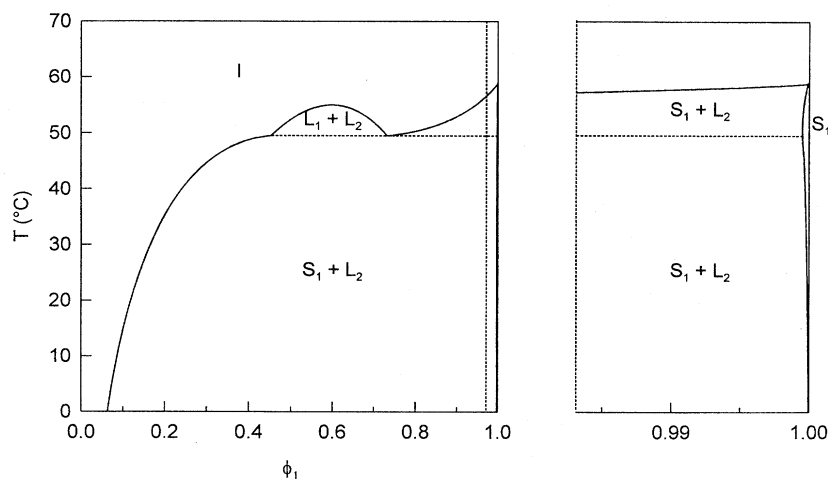


FIG. 4. Temperature vs composition phase diagram for a mixture of polymer and smectic-A liquid crystal having $T_{S1}=60$ °C, and its enlarged version displaying the pure smectic region.

the smectic-nematic-isotropic sequence. The smectic-A-nematic phase transition is first order for $0.70 < \alpha < 0.98$ and is second order if $\alpha < 0.70$. For a given α value, s and σ can be evaluated numerically as functions of temperature and composition (ϕ_1) through Eqs. (14) and (15).

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the two orientational order parameters for two hypothetical PDLC systems in which (a) the LC has a nematic-isotropic transition temperature (T_{NI}) at 60 °C followed by a smectic-A-nematic transition temperature (T_{SN}) at 40 °C, and (b) the LC has a smectic-A-isotropic transition temperature (T_{SI}) at 60 °C. In the former case, the theory predicts a first order SN transition where the smectic order parameter σ drops abruptly to zero at T_{SN} [Fig. 1(a)]. A discontinuity can also be discerned in the nematic order parameter versus temperature curve at T_{SN} . In the latter case, where the smectic-A phase transforms directly to the isotropic phase, both order parameters s and σ exhibit a discrete transition at the T_{SI} [Fig. 1(b)].

The corresponding free energy curves for the two cases are shown in Fig. 2. In Fig. 2(a), the free energy curve shows an abrupt change in the curvature at the smectic-A-nematic transition, where the smectic order parameter undergoes a discontinuous transition. In the latter case, where the smectic-A transforms directly to the isotropic phase [Fig. 2(b)], the free energy curves show a subtle convex curvature with composition at various temperatures which is reminiscent of the composition dependence of the free energy of the polymer/nematic mixture [4].

Figure 3(a) depicts the predicted temperature versus composition phase diagram for a hypothetical polymer/smectic-liquid-crystal mixture by setting $r_2/r_1=2.25/1$ and $\chi=-1+772/T$. The smectic-A-nematic and the nematic-isotropic transition temperatures of the smectic LC are assumed, respectively, to be 40 and 60 °C, from which the α value has been estimated to be 0.851 [10]. The predicted phase diagram is basically an upper critical solution temperature (UCST) overlapped by liquid-crystal phase transitions such

as smectic-nematic-isotropic transitions. It comprises a liquid-liquid (L_1+L_2) region, a nematic-liquid phase (N_1+L_2), a smectic-liquid phase (S_1+L_2), a nematic-smectic phase (N_1+S_1), a pure nematic phase (N_1) and a pure smectic-A phase (S_1) at extreme compositions of LC's. A nematic-liquid coexistence region (N_1+L_2) exists in a small region between the isotropic liquid and the pure nematic region. Between the pure nematic and the pure smectic regions, our theoretical calculation predicts a narrow gap in which the nematic and smectic phases can coexist. This N_1+S_1 coexistence region can also be identified at the extreme LC-rich region of the polymer/smectic phase diagram in which the T_{SN} (35 °C) is located below the peritectic line [Fig. 3(b)]. Upon lowering the temperature, a smectic-A-liquid (S_1+L_2) coexistence region appears below the peritectic lines. At extreme LC compositions, the pure nematic region is generally larger than the pure smectic region since most polymer molecules may be rejected more readily from the highly ordered smectic phase relative to the less ordered nematic phase.

In Fig. 4 we show a phase diagram for a polymer/smectic-liquid-crystal system with the LC having a smectic-A-isotropic transition temperature at 60 °C. The solid curve was calculated by using $\alpha=1.158$, $r_2/r_1=2.25/1$, and $\chi=-1+784/T$. The phase diagram consists of a liquid-liquid equilibrium (L_1+L_2) at the intermediate compositions and a pure smectic-A phase (S_1) at extreme compositions of LC's. The coexistence of the smectic-A-liquid region (S_1+L_2) is also predicted to exist below the peritectic line (the dotted line), as well as in a region between the isotropic liquid (I) and the pure smectic region S_1 . This phase diagram appears quite similar to that of the polymer/nematic-liquid-crystal system [4], except that the nematic phase has been replaced by the smectic phase.

CONCLUSIONS

We have demonstrated that the combined Flory-Huggins/Maier-Saupe-McMillan theory is capable of predicting various phase diagrams for binary polymer/smectic-liquid-crystal mixtures whether the smectic mesophase of LC's

transforms to the isotropic phase directly or through the nematic phase. The calculated phase diagram consists of the L_1+L_2 region due to the UCST, and the nematic-liquid (N_1+L_2), smectic-liquid (S_1+L_2), nematic-smectic (N_1+S_1), pure N_1 , and pure S_1 regions. To the best of our knowledge, our theoretical calculation is the first to predict the possible coexistence of the nematic-smectic (N_1+S_1) region. In the case where the smectic-*A* phase transforms directly to the isotropic phase, the calculated phase diagram is reminiscent of that of the polymer/nematic-liquid-crystal mixtures [4]. Although we have limited our calculation

mainly to the liquid crystals having a smectic-*A* mesophase, our approach can be extended to other smectic phases such as smectic-*C*.

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