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Equilibrium phase behavior of nematic mixtures

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A phenomenological model for predicting phase diagrams of a binary nematic mixture containing side chain liquid crystalline polymers and/or low molar mass liquid crystals has been proposed by combining Flory–Huggins free energy of isotropic mixing and Maier–Saupe free energy for nematic ordering of the nematogens. Two orientational order parameters, s_1 and s_2 , of the two components in the mixtures having two different clearing temperatures are taken into consideration in the calculation. The Flory–Huggins interaction parameter, χ , and the nematic interaction parameter of the Maier–Saupe theory, ν_{11} and ν_{22} , are assumed to be functions of inverse absolute temperature. Further the cross-nematic interaction is assumed to be proportional to the square root of the product of the nematic interaction parameters of the two mesogens, i.e., $\nu_{12} = c (\nu_{11} \cdot \nu_{22})^{1/2}$. The theory predicts a variety of phase diagrams depending on a single parameter, c , which is a measure of a relative strength of interaction between two dissimilar mesogens to that in the same species. The predicted phase diagrams have been tested rigorously with experimental phase diagrams of various nematic mixtures reported by others as well as by us. © 1995 American Institute of Physics.

INTRODUCTION

In pursuit of liquid crystal optical materials for flat panel display applications,^{1,2} liquid crystal, and polymer mixtures have received considerable attention, particularly polymer dispersed liquid crystals (PDLC)³ and polymer stabilized liquid crystals (PSLC).⁴ These PDLC and PSLC materials are basically inhomogeneous liquid crystal composite films containing dispersions of monomeric liquid crystals stabilized by polymer binders. The domain morphologies of LC dispersions such as size, shape, and uniformity are some of the important criteria for electro-optical performance of these materials.³ It has been recognized that thermodynamic phase diagrams and kinetic of phase separation in liquid crystal/polymer mixtures play an important role in determining these domain structures, and ultimately their electro-optical properties.^{5,6} The fundamental understanding of thermal quench and/or reaction induced phase separation of PDLC systems is essential for their successful applications, and therefore it is of interest to us.

In a previous paper,⁷ we have calculated a “tea-pot” phase diagram for a mixture of homopolymer and monomeric liquid crystals by combining the Flory–Huggins free energy of isotropic mixing^{8,9} and Maier–Saupe free energy for nematic ordering^{10–12} of the liquid crystals. The calculated phase diagram consists of a liquid–liquid coexistence region overlapped with a nematic–liquid coexistence region. A new nematic–liquid spinodal is also predicted to exist in the narrow nematic–liquid coexistence region.⁷ The theoretical prediction is tested favorably well with the experimental cloud point phase diagrams of polybenzyl methacrylate/E7 systems.⁷

In the present study, we focus on the establishment of phase diagrams of nematic mixtures by combining the Flory–Huggins (FH) and Maier–Saupe (MS) theories for a

nematic mixture having two different orientational order parameters, s_1 and s_2 , and two different nematic–isotropic transition points for the constituents.¹³ The combined FH/MS theory is basically a mean-field model in which the detailed chemical structures of the side chain liquid crystalline polymer (SCLCP) or low molecular weight nematic liquid crystal (LC) such as chain rigidity (or persistence length) and length of methylene linkages (spacer units) of the two mesogens are not taken into consideration. We assume that the stability of the nematic phase arises from the anisotropic dispersion forces of the mesogenic dipoles and there is no strong specific interaction between the SCLCP and the nematogen. Further, we neglect the interaction between the side group mesogen and the backbone polymer because the plasticization of the nematic ordering of side group mesogens by the polymer has already been reflected in the lowering of the nematic–isotropic transition of the liquid crystals.¹⁴ Other transitions such as smectic–nematic, crystal–smectic, and polymer glass transitions are not considered here since these phenomena are, if they exist, expected to occur at much lower temperatures and evidently beyond the scope of this work. The Flory–Huggins interaction parameter, χ , and the nematic interaction parameter of the two liquid crystal mesogens, ν_{11} and ν_{22} , are assumed to be repulsive and have inverse temperature dependence. The effects of relative strength of nematic interaction (c parameter), critical temperature (χ interaction parameter), and molecular weight on phase diagrams have been demonstrated. The calculated phase diagrams have been tested critically with the experimental phase diagrams of various side chain liquid crystalline polymer/monomeric liquid crystal mixtures reported by others,^{15–17} and also by us.^{18,19}

THEORY

Model descriptions

In the proposed FH/MS theory, the total Gibbs free energy of mixing for binary nematic mixtures may be ex-

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pressed in terms of a simple addition of the free energy of mixing of isotropic liquids, g^i , and the free energy of nematic ordering of the liquid crystals, g^n , i.e.,

$$g = g^i + g^n, \quad (1)$$

where g represents the dimensionless total free energy density of the system.

The free energy of isotropic mixing of a binary polymer blend may be described in terms of the Flory–Huggins theory,^{8,9} viz.,

$$g^i = \frac{G^i}{nkT} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2, \quad (2)$$

where k is Boltzmann constant and T 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 sites occupied by a single liquid crystalline polymer chain. ϕ_1 and ϕ_2 represent the volume fractions of components 1 and 2, respectively, which may be given by⁹

$$\phi_1 = \frac{n_1 r_1}{n_1 r_1 + n_2 r_2}, \quad \phi_2 = \frac{n_2 r_2}{n_1 r_1 + n_2 r_2}, \quad (3)$$

where, n_1 and n_2 are the numbers of liquid crystal molecules and liquid crystalline 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, i.e.,

$$\chi = A + \frac{B}{T}, \quad (4)$$

where A and B are constants.⁹

The contribution of nematic liquid crystals to the total free energy of binary nematic mixtures has been generally given by the Maier–Saupe mean-field theory^{10–12} representing the free energy of nematic ordering. Following a theoretical scheme of Brochard *et al.*,¹³ the free energy density of binary nematic mixtures containing side chain liquid crystalline polymers and low molar mass liquid crystals may be described as

$$g^n = \frac{G^n}{nkT} = -\Sigma_1 \phi_1 - \Sigma_2 \phi_2 - \frac{1}{2} \nu_{11} s_1^2 \phi_1^2 - \frac{1}{2} \nu_{22} s_2^2 \phi_2^2 - \nu_{12} s_1 s_2 \phi_1 \phi_2, \quad (5)$$

where Σ_1 and Σ_2 represent the decrease of entropy due to the alignment of individual LC molecule of component 1 and the mesogenic group of component 2, respectively. ν_{11} and ν_{22} are the nematic interaction parameters of the pure components whereas ν_{12} represents the cross-interaction between the dissimilar mesogens. The self-consistent orientational order parameters s_1 and s_2 are further defined as¹⁰

$$s_j = \frac{1}{2} (3 \langle \cos^2 \theta_j \rangle - 1), \quad (6)$$

in which θ_j is the angle between a reference axis and the director of a liquid crystal molecule belonging to component j ($j=1$ or 2). The angle bracket, $\langle \rangle$, denotes the ensemble average which is defined as

$$\langle \cos^2 \theta_j \rangle = \int \cos^2 \theta_j \cdot f(\theta_j) d \cos \theta_j. \quad (7)$$

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

$$f(\theta_j) = \frac{1}{4\pi Z_j} \exp\left[-\frac{u(\theta_j)}{kT}\right], \quad (8)$$

where Z_j is the partition function defined as

$$Z_j = \int \exp\left[-\frac{u(\theta_j)}{kT}\right] d \cos \theta_j, \quad (9)$$

and $u(\theta_j)$ is the potential of a director orientation which can be taken to be proportional to the second order Legendre polynomials as

$$\frac{u(\theta_j)}{kT} = -\frac{1}{2} m_j (3 \cos^2 \theta_j - 1), \quad (10)$$

in which m_j is a dimensionless mean field parameter characterizing the strength of the potential field.¹²

The order parameter, s_j , can then be related to Z_j through

$$s_j = \int f(\theta_j) \cdot \frac{1}{2} (3 \cos^2 \theta_j - 1) d \cos \theta_j = \frac{1}{Z_j} \frac{dZ_j}{dm_j}, \quad (11)$$

and the entropy Σ_j can be deduced as

$$\Sigma_j = - \int f(\theta_j) \cdot \ln[4\pi f(\theta_j)] d\Omega_j = \ln Z_j - m_j s_j, \quad (12)$$

where Ω_j denotes the solid angle. In a previous paper, the nematic interaction parameters, ν_{11} and ν_{22} , of the individual mesogenic component have shown to have an inverse temperature dependence as follows:

$$\nu_{11} = 4.541 \frac{T_{NI,1}}{T}, \quad (13)$$

$$\nu_{22} = 4.541 \frac{T_{NI,2}}{T}. \quad (14)$$

The exact relation of ν_{12} to ν_{11} and ν_{22} is not known, thus we propose that $\nu_{12} = \nu_{21}$ and is proportional to the square root of the product of ν_{11} and ν_{22} , i.e.,

$$c = \frac{\nu_{12}}{\sqrt{\nu_{11} \nu_{22}}}, \quad (15)$$

where c is the proportionality constant characterizing the relative strength of the cross interaction between the two dissimilar mesogens as compared to that in the same species. The physical significance of the c parameter will be clarified in a latter section.

Free energy minimization approach

To calculate the free energy of a nematic mixture, the relation between the two orientational order parameters corresponding to the two mesogens in the mixtures needs to be evaluated as a function of composition and temperature. This

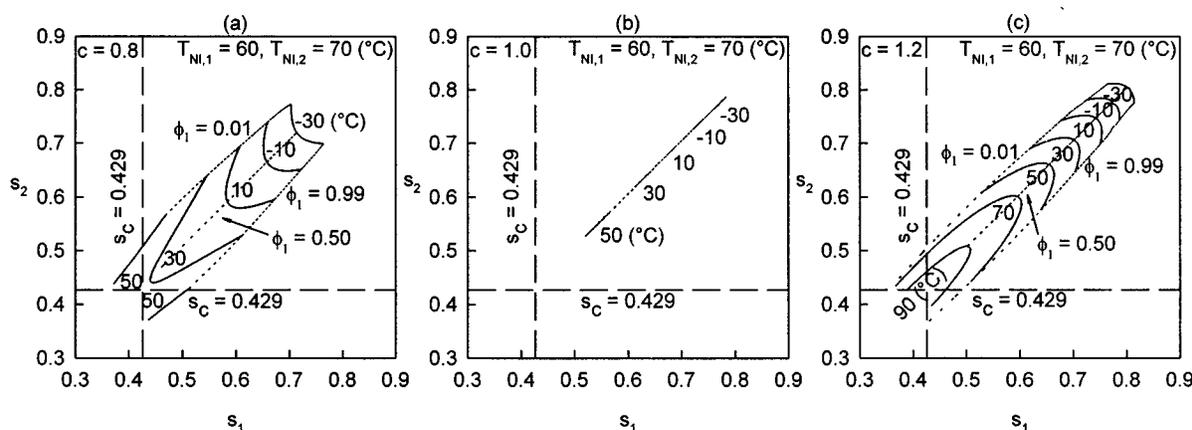


FIG. 1. Orientational order parameters, s_1 and s_2 , as a function of temperature and composition for a mixture of two nematogens having nematic-isotropic transition temperatures of 60 and 70 °C, respectively, for the three cases (a) $c=0.8$, (b) $c=1.0$, and (c) $c=1.2$. The dotted lines represent the constant volume fractions of the nematic component 1.

can be accomplished by minimizing the free energy of nematic ordering with respect to the order parameters, s_1 and s_2 , and then equating them to zero, i.e.,

$$\frac{\partial g^n}{\partial s_1} = 0 \quad \text{and} \quad \frac{\partial g^n}{\partial s_2} = 0, \quad (16)$$

which gives the following equations:

$$-\frac{d\Sigma_1}{ds_1} - \nu_{11}s_1\phi_1 - \nu_{12}s_2\phi_2 = 0, \quad (17)$$

$$-\frac{d\Sigma_2}{ds_2} - \nu_{22}s_2\phi_2 - \nu_{12}s_1\phi_1 = 0. \quad (18)$$

Inserting Eq. (12) into Eqs. (17) and (18) leads to the following equations:

$$m_1 = \nu_{11}s_1\phi_1 + \nu_{12}s_2\phi_2, \quad (19)$$

$$m_2 = \nu_{22}s_2\phi_2 + \nu_{12}s_1\phi_1. \quad (20)$$

From Eqs. (19) and (20), it is obvious that the nematic order parameters (s_1 and s_2) depend on the volume fraction and the nematic interaction parameters (ν_{11} , ν_{22} , and ν_{12}) which themselves are functions of temperature. For a given c value, the s_1 and s_2 can be evaluated numerically as a function of temperature and composition (ϕ) through Eqs. (19) and (20). There is always a solution at $s_1 = s_2 = 0$ corresponding to $g^n = 0$. The critical nematic order parameter is determined to be 0.429. Even if one of the nematic order parameters falls below the critical value, we can still have a minimum free energy to facilitate nematic ordering in the other component. Only when both parameters fall below this critical value, we have a solution corresponding to the local maximum free energy and therefore the nematic ordering would be unstable, leading to the transformation of the nematic to the isotropic state.

Figure 1 shows the relationships between the two orientational order parameters, representing the two mesogens having two different nematic-isotropic transitions (T_{NI}), for three cases (a) $c < 1$, (b) $c = 1$, and (c) $c > 1$. The case (a) $c < 1$, signifies that the cross interaction of the dissimilar me-

sogens is weak as compared to that in the same species. It is seen that the order parameter of the mesogenic mixtures is smaller than that of the pure components at a given temperature, which in turn implies that the mesogenic mixtures are less stable than in their pure states. In the case (c) $c > 1$, the nematic order parameter of the mesogenic mixture is greater than that of the pure mesogens at a given temperature, indicating that the interaction between the dissimilar mesogens is stronger than those of the same mesogens in their neat states. The case (b) $c = 1$ represents the idealized case where the nematic ordering of the different mesogens in the mixture occurs with the same magnitude as compared to those within the same mesogens in their pure states.

Figure 2 shows the temperature dependence of the total free energy of the nematic mixtures as a function of volume fraction for the corresponding three cases (a) $c < 1$, (b) $c = 1$, and (c) $c > 1$. In the case (a), the free energy of the mixtures is higher than that of the pure components at a given temperature, suggesting that the nematic mixtures are less stable than their pure nematics. Thus the condition, $c < 1$, implies that the cross interaction between the dissimilar mesogens is weak relative to that in the same species. The case (c) is just the opposite to the case (a) where the cross interaction between the two mesogens is stronger than the nematic interaction within the same mesogens. As a result, the free energy of the nematic mixtures is lower, and thus the nematics in the mixtures are more stable than in their pure components. Again the case (b) represents an ideal case where all nematics interact with equal strength, thus the free energy of the nematic mixtures follows a simple additivity rule.

Phase equilibrium criteria

The conditions for phase equilibrium require that the chemical potentials of each component in every phase are equivalent. For a binary mixture the criteria can be stated as

$$\mu_1^\alpha = \mu_1^\beta, \quad (21)$$

$$\mu_2^\alpha = \mu_2^\beta, \quad (22)$$

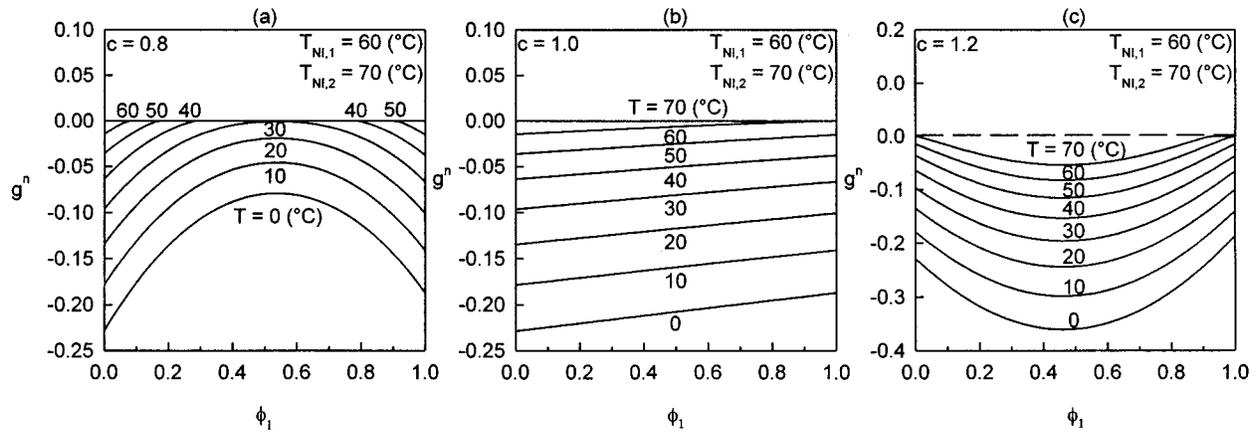


FIG. 2. Temperature dependence of the free energy density of nematic ordering as a function of volume fraction for the three cases (a) $c=0.8$, (b) $c=1.0$, and (c) $c=1.2$.

where α and β represent the two equilibrium phases.

The chemical potentials can be calculated by taking the first derivative of the free energy of the system with respect to the number of molecules of each component. Similar to the free energy of mixing, the total chemical potential of mesogenic mixtures is contributed by the isotropic mixing and the nematic ordering, i.e., $\mu_j = \mu_j^i + \mu_j^n$. The chemical potentials resulting from the isotropic mixing can be derived to give

$$\frac{\mu_1^i}{kT} = \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + \chi r_1 \phi_2^2, \quad (23)$$

$$\frac{\mu_2^i}{kT} = \ln \phi_2 + \left(1 - \frac{r_2}{r_1}\right) \phi_1 + \chi r_2 \phi_1^2, \quad (24)$$

and the chemical potentials due to the nematic ordering can be deduced as

$$\begin{aligned} \frac{\mu_1^n}{kT} &= \frac{1}{2} r_1 \nu_{11} s_1^2 \phi_1^2 + \frac{1}{2} r_1 \nu_{22} s_2^2 \phi_2^2 + r_1 \nu_{12} s_1 s_2 \phi_1 \phi_2 \\ &\quad - r_1 \ln Z_1, \end{aligned} \quad (25)$$

$$\begin{aligned} \frac{\mu_2^n}{kT} &= \frac{1}{2} r_2 \nu_{11} s_1^2 \phi_1^2 + \frac{1}{2} r_2 \nu_{22} s_2^2 \phi_2^2 + r_2 \nu_{12} s_1 s_2 \phi_1 \phi_2 \\ &\quad - r_2 \ln Z_2. \end{aligned} \quad (26)$$

By solving Eqs. (21) and (22) simultaneously, the solutions with respect to temperatures will give the binodal curves of the phase diagram.

Double tangent method

The equilibrium coexistence points at a given temperature can be determined by a double tangent method where the equilibrium volume fractions of the individual phase (ϕ^α and ϕ^β) fall on the same tangent line of the free energy curve. The first derivatives of the total free energy with volume fraction are equivalent at these two compositions and also equal to the slope connecting these two points, i.e.,

$$\frac{g^\alpha - g^\beta}{\phi^\alpha - \phi^\beta} = \left(\frac{\partial g}{\partial \phi}\right)^\alpha, \quad (27)$$

$$\frac{g^\alpha - g^\beta}{\phi^\alpha - \phi^\beta} = \left(\frac{\partial g}{\partial \phi}\right)^\beta. \quad (28)$$

The first derivative of total free energy of the system with volume fraction of component 1 can be deduced to give

$$\begin{aligned} \frac{\partial g}{\partial \phi_1} &= \frac{1}{r_1} \ln \phi_1 - \frac{1}{r_2} \ln \phi_2 + \frac{1}{r_1} - \frac{1}{r_2} + \chi(1 - 2\phi_1) \\ &\quad + \ln \frac{Z_2}{Z_1}. \end{aligned} \quad (29)$$

Figure 3 shows the temperature dependence of total free energy with composition for a hypothetical nematic mixture

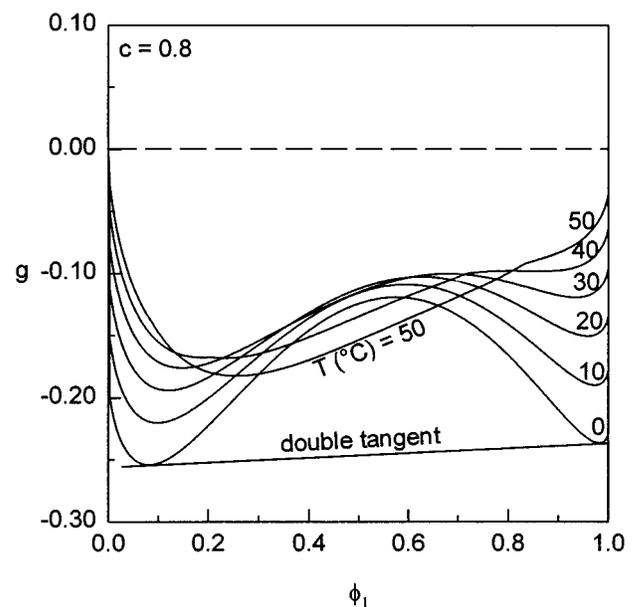


FIG. 3. Variations of the total free energy density with volume fraction of the component 1 for various temperatures.

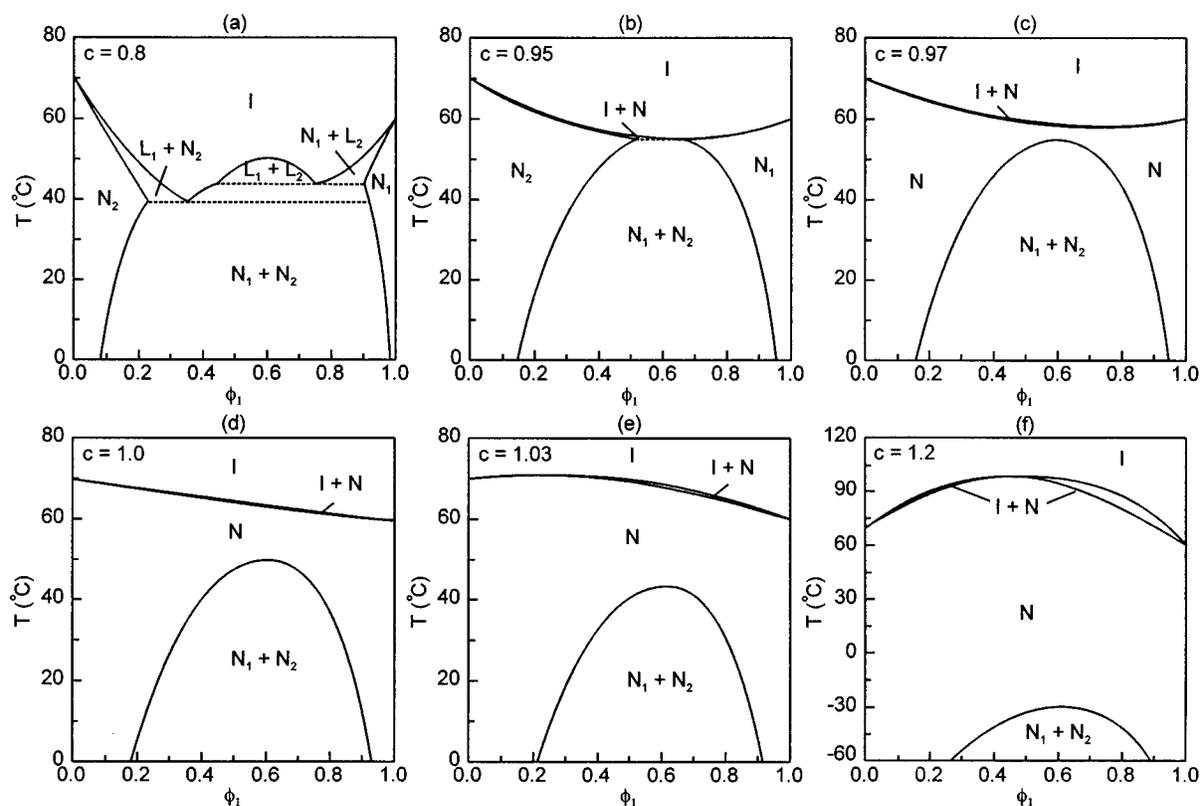


FIG. 4. The effect of “ c ” parameter on phase diagrams of nematic mixtures having T_{NI} of 60 and 70 °C, respectively. The c values signify the relative strength of nematic interactions changing from (a) weak to (f) strong.

with $T_{NI,1}=60$ °C, $T_{NI,2}=70$ °C, and $T_c=50$ °C; $r_2/r_1=2.25/1$ and $c=0.8$. At low temperatures (0–40 °C), dual minima can be discerned in the free energy curves. A double tangent can be drawn through these minimum points to determine the coexistence phases according to Eqs. (27) and (28). When the temperature approaches the nematic–isotropic transitions, a small cusp can be noticed in the total free energy curve (e.g., at 50 °C). It is customary to observe a cusp in the total free energy at a composition where the nematic ordering starts to take into play. At some temperatures near the nematic–isotropic transitions (i.e., 50–70 °C), two or three double tangents or a triple tangent may be drawn in the free energy curves to determine two or more coexistence phases. By connecting the loci of the coexistence points, the temperature versus composition phase diagram can be established as exemplified in the subsequent section.

Determination of c parameter

One of the striking features of the present model is that the c parameter can be actually measured experimentally in some nematic mixtures that exhibit azeotropes. By definition, an azeotrope is the point at which the two equilibrium isotropic and nematic phases have the same composition, i.e., $\phi_1^i = \phi_1^n = \phi_1^{AZ}$.^{13,20} According to Brochard *et al.*,¹³ the orientational order parameters of both components of the mesogenic mixture are equivalent at the azeotropic point, i.e., $s_1 = s_2 = s_{AZ}$. Under these two conditions, Eqs. (19) and (20) may be rewritten as

$$m_{AZ} = \nu_{11}s_{AZ}\phi_1^{AZ} + \nu_{12}s_{AZ}(1 - \phi_1^{AZ}), \quad (30)$$

$$m_{AZ} = \nu_{22}s_{AZ}(1 - \phi_1^{AZ}) + \nu_{12}s_{AZ}\phi_1^{AZ}, \quad (31)$$

and the composition of the azeotrope can then be deduced as^{13,20}

$$\phi_1^{AZ} = \frac{\nu_{22} - \nu_{12}}{\nu_{11} + \nu_{22} - 2\nu_{12}}. \quad (32)$$

By combining Eqs. (13), (14), (15), and (32), the c parameter can be derived to give

$$c = \frac{(1 - \phi_1^{AZ})T_{NI,2} - \phi_1^{AZ}T_{NI,1}}{(1 - 2\phi_1^{AZ})\sqrt{T_{NI,1}T_{NI,2}}}. \quad (33)$$

It is obvious that the c parameter depends only on the composition of the azeotropic point and the NI transition temperatures of the two components. Once the azeotrope is found in the experimental phase diagram, the value of c can be determined easily.

RESULTS AND DISCUSSION

Effect of c parameter on phase diagrams

Figures 4(a)–4(f) depict the predicted phase diagrams for a hypothetical nematic mixture as a function of a single parameter, c , for a situation where the critical point of liquid–liquid equilibrium is located at a lower temperature than the nematic–isotropic transition temperatures of the

constituents. Physically, the c parameter is a measure of the relative strength of interaction of the dissimilar mesogens to that of the same mesogens. The smaller c value implies that the nematic tends to be more stable in their pure phase than in the mixed state, and vice versa.

The phase diagram in Fig. 4(a) belongs to a weakly interacting system ($c=0.8$) which consists of a liquid–liquid (L_1+L_2) equilibrium at the intermediate compositions and two nematic–liquid coexistence (N_2+L_1) and (N_1+L_2) regions at outer compositions being rich in either mesogen. The pure nematic phases (N_1 or N_2) exist at the extreme compositions. The coexistence of nematic–nematic (N_1+N_2) region is predicted below the peritectic lines shown by the dotted lines. As the relative strength of interaction between the dissimilar pair increases, the liquid–liquid coexistence region vanishes and the nematic–liquid region gets narrower [Fig. 4(b)] and is concave upward. Concurrently, the pure nematic regions (N_1 and N_2) expand toward the middle and subsequently form a single phase nematic (N) region [Fig. 4(c)]. The curvature of the nematic–liquid region becomes subtle while the nematic–nematic region is depressed to a lower temperature. At $c=1.0$, where all mesogenic units interact with equal magnitude, isotropic phase, nematic–liquid, single phase nematic, and nematic–nematic coexistence regions can be identified in the descending order of temperature [Fig. 4(d)]. When the c value exceeds unity, the nematic–liquid region becomes convex downward and the single phase nematic region gets larger as the nematic–nematic region is continually suppressed [Fig. 4(e)]. When the c value is increased to 1.2, the nematic interaction between the two mesogens becomes very large so much so that a nematic phase can form in the mixtures above the nematic–isotropic transition temperatures of the individual constituent [Fig. 4(f)].

Effect of T_c on phase diagram

Next we calculate the phase diagrams for the three cases for $c=0.8$, $c=1.0$, and $c=1.2$ by varying the critical point (T_c) of the liquid–liquid equilibrium (UCST) relative to the nematic–isotropic transition points ($T_{NI,1}$ and $T_{NI,2}$) of the constituents. Figures 5(a)–5(f) illustrates such T_c dependence on phase diagrams. Figures 5(a) and 5(b) may be compared with Figs. 4(a) for the case of $c=0.8$. In polymer blends, it is generally known that increase in repulsive interaction (larger positive χ values) raises the UCST temperature. As the critical point of the UCST is raised to a temperature between the two NI transition temperatures, the liquid–liquid region opens up while the area of the N_1+L_2 and N_2+L_1 regions get slightly smaller. Concurrently, the areas of the pure N_1 and N_2 regions at the outer compositions have reduced [Fig. 5(b)]. When the critical point is above the NI transition points of the constituents, the L_1+L_2 region widens, causing the areas of the L_1+N_2 and N_1+L_2 coexistence regions as well as of the neat N_1 and N_2 regions to be somewhat smaller.

Next we examine the effect of T_c on phase diagrams of nematic mixtures by comparing Figs. 5(c) and 5(d) with Fig. 4(d). When T_c is lower than both T_{NI} , there is no liquid–liquid coexistence region. As T_c is raised to a temperature

intermediate between the two T_{NI} , the liquid–liquid coexistence region begins to develop while the I+N region [Fig. 4(d)] separates into the L_1+N_2 and N_1+L_2 regions [Fig. 5(c)]. Concurrently the single nematic region (N) separates into the two pure N_1 and N_2 regions at the extreme compositions. When the T_c is higher than both T_{NI} , the L_1+L_2 region becomes more pronounced [Fig. 5(d)].

In the case of $c=1.2$, the nematic ordering can take place in the mixtures above the NI transition temperatures of both mesogens [Fig. 4(f)]. However, if the Flory–Huggins χ parameter becomes strongly repulsive, the critical point of the liquid–liquid equilibrium (T_c) would increase to a temperature higher than one or both T_{NI} points. When the critical temperature is intermediate between the two T_{NI} points, a liquid–liquid region still cannot exist due to the strong nematic interaction between the two mesogens [Fig. 5(e)], thus it appears to be similar to that of Fig. 4(f), except that the N_1+N_2 region shifts to a higher temperature. Only when the critical point of the liquid–liquid equilibrium is significantly higher than the T_{NI} of both constituents (i.e., above the azeotropic point), the liquid–liquid coexistence region exists above the nematic–liquid regions [Fig. 5(f)]. It may be concluded that a number of phase diagrams can be computed by considering the c parameter representing the relative strength of cross interaction between the two mesogens and their neat phases and the χ interaction parameter representing the intermolecular interaction between the isotropic phases of the monomeric liquid crystal and the side group liquid crystalline polymer.

Effect of molecular weight on phase diagram

Figures 6(a)–6(f) show the molecular weight dependence of phase diagrams for three cases (i) $c=0.8$, (ii) $c=1.0$ and (iii) $c=1.2$ by varying the ratio of r_2/r_1 (from 1/1 to 16/1), representing the relative size of the SCLCP and LC molecules. Figs. 5(b), 5(d), and 4(f) are the intermediate cases with $r_2/r_1=9/1$ corresponding to the above three cases [Figs. 6(a), 6(b); Figs. 6(c), 6(d); and Figs. 6(e), 6(f)]. Increasing the molecular weight of the SCLCP causes the critical point of the liquid–liquid equilibrium to shift to a higher LC content for both $c=0.8$ and 1.0 cases. In the case of $c=1.2$, where the cross-nematic interaction is very strong, the shape of the I+N region changes drastically, especially at the high LC compositions. There is no liquid–liquid region in the system under consideration; it can be discerned only when the χ is strongly repulsive, i.e., T_c is much higher than the T_{NI} of the constituents as shown in Fig. 5(f). The critical composition of the N_1+N_2 region moves to a higher LC content with increasing r_2/r_1 ratio.

Similar phase diagrams, if not all, have been predicted primarily by Brochard *et al.*,¹³ and to a lesser extent by others.^{20–22} In the case of Brochard *et al.*,¹³ the analysis involves considerable adjustable parameters which make the physical interpretation difficult. The present calculation requires a single parameter, viz. c , which is simply a measure of the relative strength of the cross interaction of the two mesogens relative to that in the same species. Another advantage is that the calculated phase diagrams are expressed by the actual temperatures (not by the reduced temperature

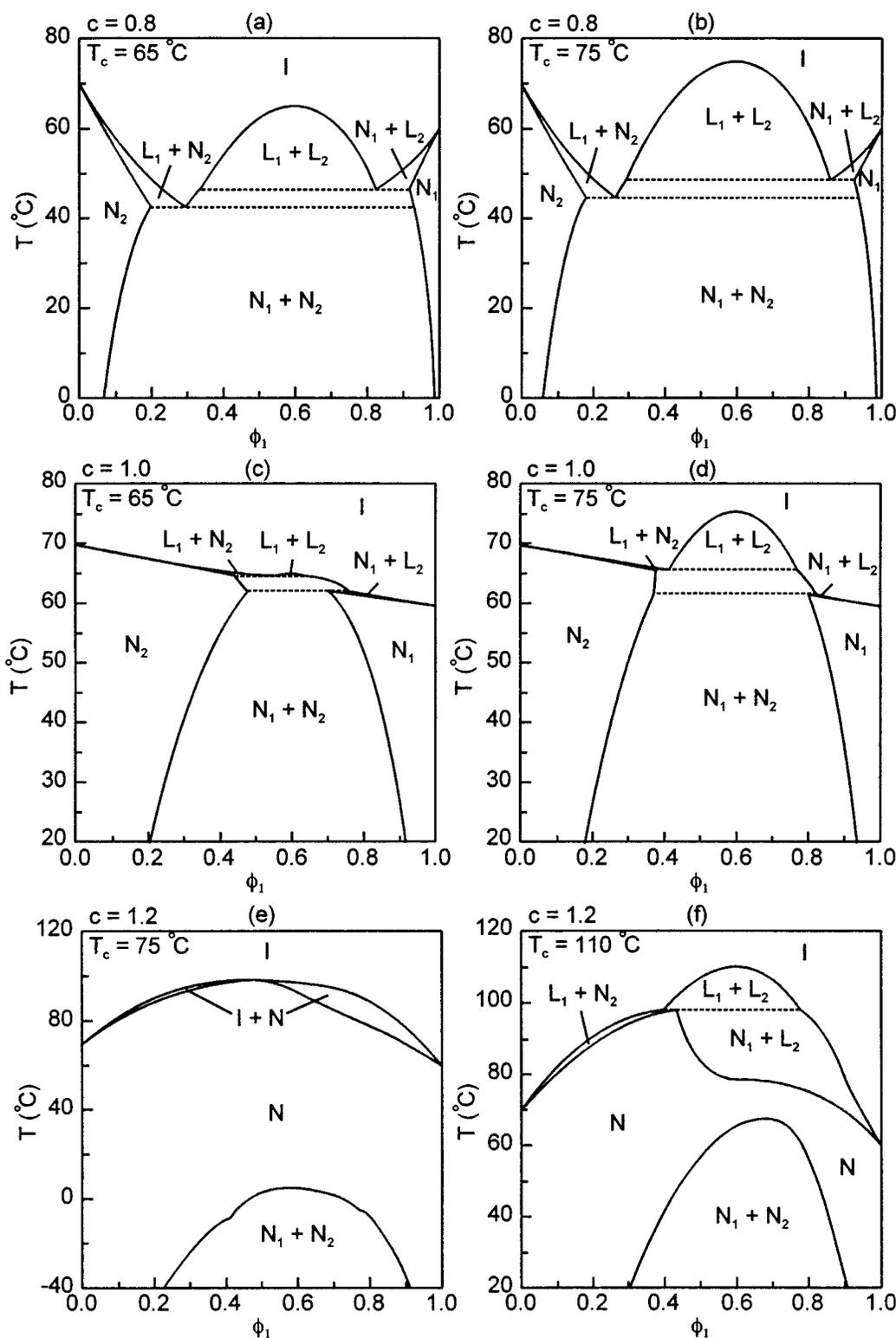


FIG. 5. The effect of T_c (or χ) on phase diagrams of nematic mixtures having T_{NI} of 60 and 70 °C, respectively, for various c values.

as done in the references^{13,20–22}) comparable to the NI transitions of various nematic mesogens in a more realistic temperature range. As pointed out before, this c parameter can be determined experimentally, if an azeotropic point exists in the phase diagram.

Tests with experimental phase diagrams

Figure 7 exhibits a cloud point temperature versus composition phase diagram of a mixture of EGDE-C6/E7. EGDE-C6 is a side chain liquid crystalline polymer in which aminoalkoxy cyanobiphenyl with 6 methylene linkages (des-

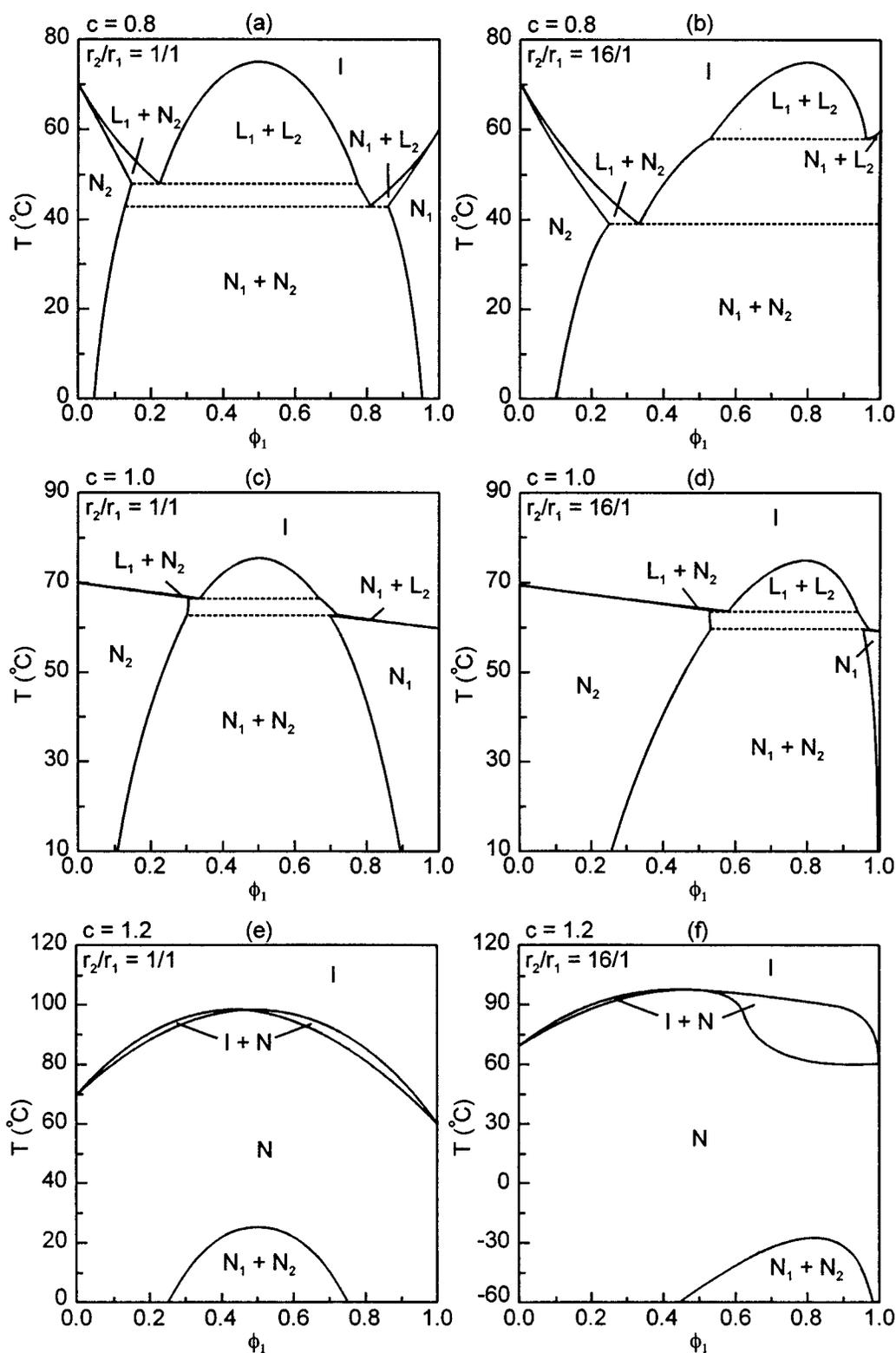


FIG. 6. The effect of molecular weight (r_2/r_1) on phase diagrams of nematic mixtures having T_{NI} of 60 and 70 °C, respectively, for various c values.

ignated C6) is grafted to ethylene glycol diglycidyl ether (EGDE) epoxy backbone chains.¹⁴ The nematic–isotropic transition temperature of pure C6 is about 90 °C, but it reduces to about 30 °C upon grafting to the EGDE backbone chain. This lowering of T_{NI} may be attributed to strong per-

turbation of the polymer chain exerting on the nematic ordering of the side group mesogen. This plasticization effect may be reduced by increasing the spacer length to decouple the polymer and the side group mesogen. E7 is a commercial liquid crystal and reported to consist of cyanobiphenyl, oxy-

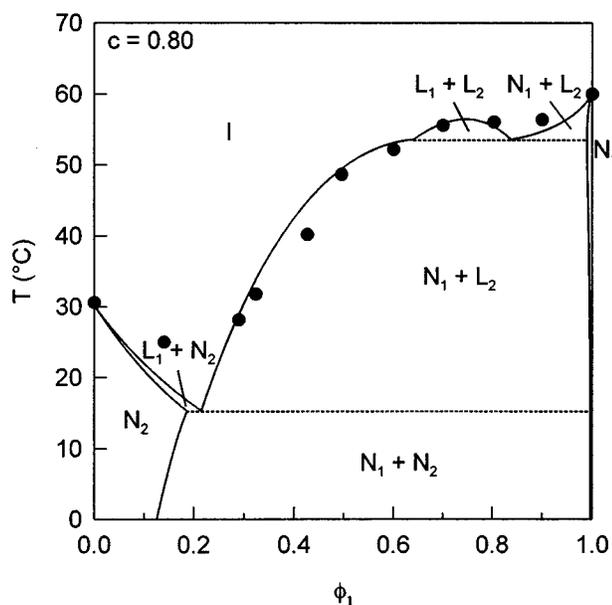


FIG. 7. A temperature versus composition phase diagram of a mixture of slide chain liquid crystalline polymer (ethylene glycol diglycidyl ether with aminoalkoxy cyanobiphenyl side group; EGDE-C6, $T_{NI}=30^\circ\text{C}$) and monomeric liquid crystals (E7; $T_{NI}=60^\circ\text{C}$) in comparison with the predicted phase diagram using $c=0.8$ (solid lines).

cyanobiphenyl and cyanoterphenyl derivatives. Although the chemical composition of E7 is seemingly complex, it is a eutectic nematic mixture having a single nematic–isotropic temperature at 60°C and a single crystal–nematic transition at -30°C , and thus its mixture with EGDE-C6 may be considered as a pseudobinary system.

The solid curve is the theoretical coexistence curve calculated assuming the densities of SCLCP and E7 to be equivalent and using $c=0.8$ and $r_2/r_1=9/1$ (analogous to their molecular weight ratio). The χ_c value is usually dictated by the critical temperature of the liquid–liquid (L_1+L_2) equilibrium which can be estimated from the experimental cloud point curve.^{18,19} Hence, c is the only adjustable parameter used in the present calculation. The dotted lines represent the peritectic lines. The phase diagram consists of a narrow N_1 , but a wide N_2 region at the extreme compositions. There are two nematic–liquid coexistence regions labeled N_1+L_2 and N_2+L_1 . The theory also predicts a coexistence of two separate nematic (N_1+N_2) phases at a lower temperature below the second peritectic line [Figs. 4(a) and 7].

Figure 8 shows the replot of temperature versus composition phase diagram (assuming the densities of the SCLCP and LC are equivalent) for a mixture of a side chain crystalline polymer and a monomeric nematogen reported by Finkelmann and co-workers.¹⁵ As pointed out earlier, the crystal–nematic transition and glass transition of the system are out of the scope of this work, and thus omitted. The SCLCP is poly(dimethyl siloxane) with methoxyphenyl benzoate side groups connected by a flexible spacer (4 methylene units) to the backbone chain. This SCLCP has a T_g of 15°C and T_{NI} of 97°C . The mesogen is 4-propyloxy phenyl 4'-hexyloxy benzoate which has a similar chemical structure

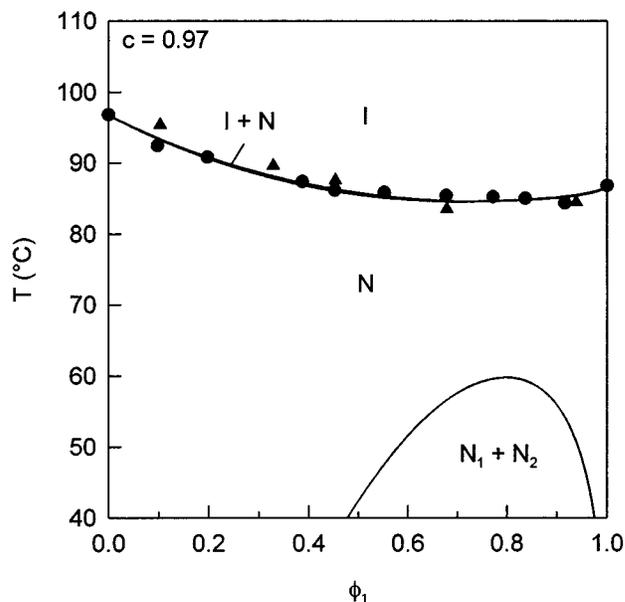


FIG. 8. A temperature versus composition phase diagram of a side chain liquid crystalline polymer (polydimethyl siloxane with methoxyphenyl benzoate side group connected by four methylene units) and monomeric liquid crystal (4-propyloxy phenyl 4'-hexyloxy benzoate) in comparison with the calculated phase diagram using $c=0.97$ (solid lines). The experimental data points are reproduced from Finkelmann *et al.* (Ref. 15). The closed circles and triangles represent data from differential scanning calorimetry and optical microscopy, respectively.

to the mesogenic group of the SCLCP. This mesogen has the crystal–nematic transition at 60°C and the nematic–isotropic transition at 87°C .

The solid curve is calculated using $c=0.97$ and $r_2/r_1=16/1$ as the information on the molecular weights of the SCLCP is not available. The χ parameter is inconsequential in the present calculation as the liquid–liquid phase separation will not affect the azeotropic point once the critical temperature is set to below the azeotrope. The phase diagram of this system is relatively straight forward and consists of isotropic, isotropic–nematic, and a single nematic phase (where the two mesogens are intimately mixed) in the descending order of temperature. The theory predicts the coexistence of nematic–nematic region at a lower temperature, if no other transition such as crystal–smectic, smectic–nematic or glass transition, exists in the vicinity of this region. It should be emphasized that our calculation accords well with their experimental phase diagram [Figs. 4(c) and 8].

Casagrande and co-workers¹⁶ reported another type of phase diagram for a SCLCP/LC system and is replotted here in Fig. 9 in comparison with the theoretical fit. The SCLCP is the same poly(dimethyl siloxane) with a methoxyphenyl benzoate in the side chain, connected to the main chain by a flexible spacer of four methylene units. The mesogen is another type of phenylbenzoate derivative, i.e., 4-octyloxyphenyl 4'-hexyloxy benzoate, which exhibits a smectic C–nematic transition at 65°C a nematic–isotropic transition at 92°C . The phase diagram is more complex than the previous system, but it is well within our predicted capability, that is to say it is strikingly similar to our predicted

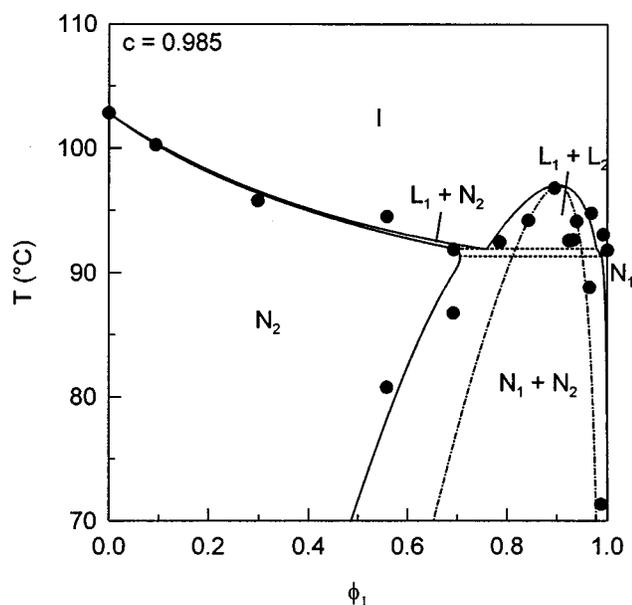


FIG. 9. A temperature versus composition phase diagram of a side chain liquid crystalline polymer (polydimethyl siloxane with methoxyphenyl benzoate side group connected by four methylene units) and monomeric liquid crystal (4-octyloxyphenyl 4'-hexyloxybenzoate) in comparison with the calculated phase diagram using $c=0.985$ (the solid and dashed lines represent binodal and spinodal, respectively). The experimental data points are reproduced from Casagrande *et al.* (Ref. 16).

phase diagram shown in Fig. 6(d). By choosing an appropriate c value = 0.985 and setting $r_2/r_1 = 32/1$ in order to correspond to the critical composition of the phase diagram, it is shown that the calculated coexistence curve (solid line) and liquid-liquid spinodal curve (dashed line) conform very well with the experimental points. Although our calculated coexistence curve is slightly different from the original lines drawn by the authors, it captures all essential features of the phase diagram such as the coexistence of liquid-liquid, liquid-nematic, nematic-nematic, and two pure nematic regions.

Another interesting development is the induced smectic phase in the nematic mixtures of SCLCP and monomeric LC, reported recently by Hwang and co-workers.¹⁷ The induced smectic phase is obviously beyond the scope of the present study, but it should be pointed out that this induced smectic phase is due to the strong interaction between the two mesogens. The SCLCP is a similar polydimethyl siloxane derivative with a phenylbenzoate side group interlinked to the main chain by a flexible spacer of three methylene units, i.e., poly(4-methoxyphenyl 4'-propyloxy benzoate methyl siloxane) (termed PS3EM). It exhibits a nematic-isotropic transition at 61 °C and a T_g of 15 °C. The nematogen is 4-cyano 4'-pentyloxy biphenyl (5OCB) having a nematic-isotropic transition at 68 °C. The phase diagram of the PS3EM/5OCB is reproduced in Fig. 10 which consists of isotropic phase, the coexistence of isotropic-nematic (I+N), a single nematic phase (i.e., two nematogens are intimately mixed) and the coexistence of two separate nematic phases. An azeotrope was found in this phase diagram; therefore, c parameter can

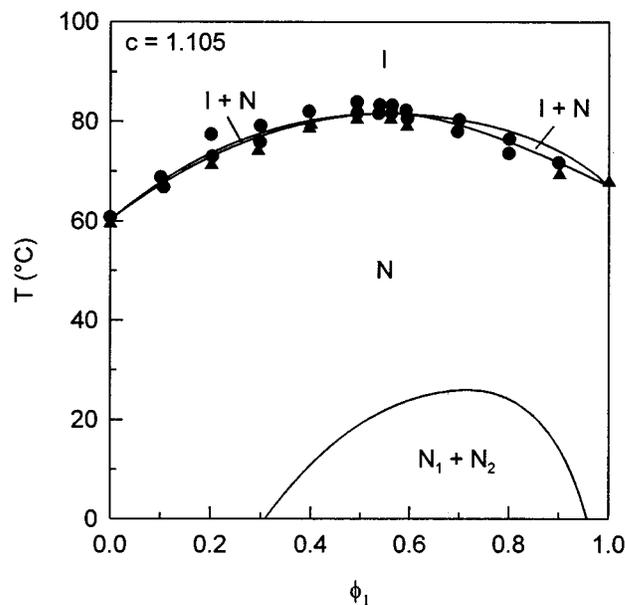


FIG. 10. A temperature versus composition phase diagram of a side chain liquid crystalline polymer (poly[4-methoxyphenyl 4'-propyloxy benzoate methyl siloxane]) and a monomeric liquid crystal [4-cyano 4'-pentyloxy biphenyl (5OCB)] in comparison with the calculated phase diagram using $c=1.105$ (solid lines). The experimental data points are reproduced from Hwang *et al.* (Ref. 17). The closed triangles and circles represent the data from differential scanning calorimetry and optical microscopy, respectively.

be determined directly from this point by applying Eq. (33). The c value was experimentally determined to be 1.105 at $\phi_1^{AZ} = 0.6$. Using the observed c value and taking $r_2/r_1 = 9/1$, the calculated coexistence curve is then compared with the experimental data in Fig. 10. The χ interaction parameter is inconsequential here, except for the position of the coexistence of two separate nematic (N_1+N_2) phases which may be masked in practice by other transitions such as crystal-nematic and glass transitions. It is striking to see a remarkable resemblance between the experiment and the theory [Fig. 4(f)] without using any adjustable parameter. The convex curvature of the I+N coexistence region suggests that nematic ordering can take place even above the T_{NI} of both mesogens, indicating that the cross interaction must be very strong. In their nematic mixture,¹⁷ the cross interaction between the two nematogens is extremely strong so much so that a smectic phase can be induced. This subject is left to the scope of future studies.²³

CONCLUSIONS

We have demonstrated that the combined FH/MS theory with two nematic order parameters is capable of predicting a variety of phase diagrams for binary nematic mixtures with a single parameter, denoted c . Physically, this c parameter is a measure of the relative strength of interaction between the two mesogens as compared to that in the same species. The shape of phase diagrams is extremely sensitive to the c parameter relative to the other effects such as molecular weight (r_2/r_1) and T_c (or χ) parameter. The Flory-Huggins χ interaction parameter may play an important role especially when

a liquid–liquid coexistence region is identified in the phase diagram. If the azeotropic point is known, the c parameter can be determined directly from the experiment, hence it is no longer an adjustable parameter for such systems. It should be emphasized that the present model has been developed specifically for the mixtures of monomeric nematic liquid crystals and side chain liquid crystalline polymers. This theory may be of limited use for mixtures containing main chain liquid crystalline polymers.

ACKNOWLEDGMENT

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