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Spinodals in a Polymer-Dispersed Liquid-Crystal

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Spinodals in a polymer dispersed liquid crystal

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Thermodynamic phase equilibria of a polymer dispersed liquid crystal (PDLC) consisting of monomeric liquid crystals and a polymer have been investigated theoretically and experimentally. The equilibrium limits of phase separation as well as phase transition of a PDLC system were calculated by taking into consideration the Flory–Huggins (FH) theory for the free energy of mixing of isotropic phases in conjunction with the Maier–Saupe (MS) theory for phase transition of a nematic liquid crystal. The correspondence between the Landau–de Gennes expansion and the Maier–Saupe theory was found and the coefficients were evaluated. The calculation based on the combined FH-MS theory predicted a spinodal line within the coexistence of the nematic–isotropic region in addition to the conventional liquid–liquid spinodals. The cloud point phase diagram was determined by means of polarized optical microscopy and light scattering for a polybenzyl methacrylate/E7 (PBMA/E7) PDLC system. The calculated phase diagrams were tested with the experimental cloud points, assuming the Flory–Huggins interaction parameter simply to be a function of temperature. © *1995 American Institute of Physics.*

I. INTRODUCTION

Inhomogeneous mixtures comprising of random coil polymers and liquid crystals (LCs) are of interest due to their potential for application in electro-optical devices.[1–3] The performance of these mixtures, hereafter called polymer dispersed liquid crystals (PDLCs), strongly depends on the final morphology of the dispersed liquid crystal domains. The size (length scale) and shape of the liquid crystal domains are generally determined by both thermodynamics and kinetics of phase separation during the preparation processes.[4] The PDLC systems are generally prepared from an initially homogeneous state via a phase separation process. The demixing process has been dominated initially by the liquid–liquid phase separation in their isotropic state by forming polymer rich and poor regions. When the LC concentration exceeds its critical value within the LC rich domains, a nematic phase develops. It is therefore essential to examine the interplay of phase separation and phase transition mechanisms of PDLCs for the improvement of PDLC's performance.

The phase diagrams for binary mixtures containing anisotropic liquid crystals have been simulated by several researchers,[5–10] based on a simple summation of the free energies from the isotropic mixing and the nematic ordering. The Flory–Huggins theory was commonly used for the isotropic mixing. In the nematic ordering, Ballauff[5] utilized the Flory–Ronca theory for the system containing liquid crystalline polymers. Brochard[6] employed the Maier–Saupe theory for binary nematic mixtures. Palffy-Murhony *et al.*[7] developed a more general approach based on the van der Waal liquid model and subsequently extended to a binary nematic mixture. Other models had their own molecular basis.[8,9] Recently, Fredrickson and Liu[10] had incorporated the free energies from interfaces and fluctuations in their calculation. However, spinodals were not addressed in the above calculations, which may be, if not more, equally important in elucidating the structure evolution and mechanisms of phase transitions of PDLC systems. To fully understand the phase behavior of a PDLC system, it is important to know whether or not a spinodal exists within the nematic and isotropic coexistence region.[11] This is the source of our motivation. Following the reported procedures,[6–8] we have combined the Flory–Huggins theory for the mixing of isotropic liquids and the Maier–Saupe theory for the nematic ordering. The validity of the calculations has been tested with the experimental cloud points of a typical PDLC system.

II. EXPERIMENT

The matrix polymer used in this study was polybenzyl methacrylate (PBMA), purchased from Scientific Polymer Products, Inc. The dispersing liquid crystal (E7) was obtained from the EM industries. E7 is basically a eutectic mixture of cyano-biphenyls (CB) that exhibits a single nematic–isotropic transition at about 60 °C. Hence, the E7 based PDLC systems may be viewed as a quasibinary system. We chose the E7 mixed liquid crystals in preparing PDLCs because a single component liquid crystal such as $4'$-n-pentyl-4-cyano-biphenyl (5CB) usually has a nematic–isotropic transition very close to the crystal–nematic transition temperature.[12]

In the preparation of PDLC films, the polymers and liquid crystals were dissolved in a common solvent such as tetrahydrofuran (THF) or toluene at room temperature. An aliquot of the solution was spread on a glass slide to form a thin film. This sample was dried at room temperature under vacuum for three days. After solvent evaporated, the sample was heated on a hot stage at 100 °C. Subsequently, a cover glass was placed on the sample so that the thin PDLC film was sandwiched between two glasses. Polarized optical microscopy (POM) and small angle light scattering (SALS) were employed to determine the cloud points of the as-prepared PDLC films of various compositions.

The SALS apparatus for the cloud point determination was designed to monitor the scattered intensity at an arbitrary angle (e.g., 20°) by using a photodiode. A 2 mW

He–Ne laser light source having a wavelength of 632.8 nm was utilized. A programmable temperature controller (Omega CN-2012) was linked with a computer (IBM PC2/30) to control the ramp rate and also to record the temperature. The heating rate or cooling rate was 0.5 °C/min unless indicated otherwise. All specimens were subjected to a heating and cooling cycle. In the homogeneous state, the scattered intensity was low, but it increased immensely when the system phase separated into the inhomogeneous two-phase state during the course of cooling. The temperature where the scattered intensity changed abruptly was designated as the cloud point.

As a complementary technique, a polarized optical microscope equipped with a sample heating chamber and a temperature controller was employed to determine the cloud points. The sample was preheated to an elevated temperature above its homogeneous state, and then quenched to an experimental temperature under the microscope. After waiting for about 5 min, we examined whether the two-phase structure was formed. The quench process was repeated at various experimental temperatures by lowering 1 °C interval until a two-phase structure was discerned. The temperature at which a two-phase structure first appeared was regarded as the cloud point.

III. PHASE DIAGRAM CALCULATION

A. Free energy contributions from isotropic mixing and anisotropic ordering

The theoretical model employed here is essentially similar to those reported in the literature,[6–8] but we have emphasized on determining a spinodal within the coexistence of the isotropic and nematic phases. The total Gibbs free energy has been customarily described in terms of a simple combination of the free energy of mixing of isotropic liquids, g^i, and the free energy of anisotropic ordering, g^n, i.e.,

$$g = g^i + g^n, \tag{1}$$

where g represents the dimensionless total free energy density.

The Flory–Huggins theory has been commonly employed to describe the free energy mixing of polymer blends.[13,14] For a binary mixture, the free energy may be expressed as

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

where k is Boltzmann constant, T absolute temperature, G^i the total free energy of mixing of isotropic liquids. The subscript 1 represents the liquid crystal component in a PDLC system, and the subscript 2 denotes the polymer component. r_1 is the number of sites occupied by one liquid crystal molecule, whereas r_2 is the number of segments or sites occupied by a single polymer chain. n_1 and n_2 are the number of liquid crystal molecules and polymer segments, respectively, and n is the total number of segments in the system. The volume fractions, ϕ_1 and ϕ_2, are related to the number of segments as follows:

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

The Flory–Huggins interaction parameter, χ, is assumed to be a function of temperature, i.e.,

$$\chi = A + \frac{B}{T}, \tag{4}$$

where A and B are constants.

To describe the nematic–isotropic transition, the Maier–Saupe mean field approach[15] has been recognized as a popular molecular model because of its inherent simplicity. Further, de Gennes treated the Maier–Saupe theory as a simplified version of the Onsager's expansion,[16] in which the summation of the higher order terms have been replaced by a quadratic order parameter term involving a quadrupole interaction parameter, ν. For a binary LC polymer mixture, the Maier–Saupe equation may be modified to couple with the Flory–Huggins equation via incorporation of the concentration of the nematic liquid crystals as

$$g^n = \frac{G^n}{nkT} = \frac{\phi_1}{r_1} \left(\int f(\theta) \ln[4\pi f(\theta)] d(\cos \theta) \right.$$
$$\left. - \frac{1}{2} \nu \phi_1 s^2 \right), \tag{5}$$

where θ is the angle between a reference axis and the director of a liquid crystal molecule, $f(\theta)$ is the director distribution function, and s represents the orientational order parameter which is defined as

$$s = \tfrac{1}{2}(3\langle \cos^2 \theta \rangle - 1), \tag{6}$$

where $\langle \ \rangle$ denotes the ensemble average which may be defined as

$$\langle \cos^2 \theta \rangle = \int (\cos^2 \theta) f(\theta) d(\cos \theta). \tag{7}$$

Here, the director distribution is considered to be symmetric around the reference axis. The orientation distribution function, $f(\theta)$, can be obtained from the potential by assuming the Gibbs ensemble as

$$f(\theta) = \frac{1}{Z} \exp\left[-\frac{u(\theta)}{kT} \right], \tag{8}$$

where Z is the partition function as defined below

$$Z = \int \exp\left[-\frac{u(\theta)}{kT} \right] d(\cos \theta). \tag{9}$$

The potential of a director orientation, $u(\theta)$, usually called the pseudopotential, can be taken to be proportional to the second order Legendre polynomials viz.,

$$\frac{u(\theta)}{kT} = -\frac{1}{2} m(3 \cos^2 \theta - 1), \tag{10}$$

where m is a mean field parameter characterizing the strength of the potential field, which was originally introduced by de Gennes and later used by Brochard.[6,16]

The Maier–Saupe quadrupole interaction parameter, ν, has the inverse temperature dependence as follow:

$$\nu = 4.54 \frac{T_{NI}}{T}, \tag{11}$$

where T_{NI} is the nematic–isotropic (NI) transition temperature of the pure liquid crystal, but the coefficient value, 4.54, may vary slightly from one material to another.[15]

B. Free energy expression for anisotropic ordering in Landau–de Gennes expansion

To calculate the free energy of an anisotropic system, it is required to know the values of the orientational order parameter as a function of composition and temperature. The orientational order parameter may be evaluated based on the free energy minimization approach by taking the derivative of Eq. (5) with respect to s, and then equating it to zero, i.e.,

$$-\frac{d \ln Z}{ds} + s \frac{dm}{ds} + m - \phi_1 \nu s = 0. \tag{12}$$

Since the first two terms cancel out each other, Eq. (12) reduces to a simple equation as described below

$$m = \phi_1 \nu s. \tag{13}$$

The Maier–Saupe theory may be rewritten in a more practical form by inserting Eq. (13) back into Eq. (5), i.e.,

$$g^n = \frac{G^n}{nkT} = \frac{\phi_1}{r_1}\left(-\ln Z + \frac{1}{2}\nu\phi_1 s^2\right). \tag{14}$$

According to de Gennes,[16] the orientational order parameter, s, may be expressed as a sole function of the mean field parameter, m. We express $s(m)$ by expanding in polynomials to avoid the repetitious numerical integration in the ensemble averaging as follows:

$$s(m) = c_1 m + c_2 m^2 + c_3 m^3 + c_4 m^4, \tag{15}$$

where c_1, c_2, c_3, and c_4 are the coefficients. From the regression analysis, these coefficients can be estimated to give

$$c_1 = 0.1983; \quad c_2 = 0.037\ 68;$$

$$c_3 = -0.016\ 53; \quad c_4 = 0.001\ 458. \tag{16}$$

Here, we adopted the polynomials up to the fourth order to ensure the precision of the regression.[17] Further, the partition function can be obtained from the integral of the function $s(m)$ as[17]

$$\ln Z(m) = \tfrac{1}{2}c_1 m^2 + \tfrac{1}{3}c_2 m^3 + \tfrac{1}{4}c_3 m^4 + \tfrac{1}{5}c_4 m^5. \tag{17}$$

Inserting Eq. (17) back to Eq. (14), one obtains

$$g^n = B_1 s + B_2 s^2 + B_3 s^3 + B_4 s^4 + B_5 s^5 \tag{18}$$

with the coefficients expressed in terms of the volume fraction as

$$B_1 = 0, \tag{19}$$

$$B_2 = \frac{\nu}{2r_1}\phi_1^2 - \frac{c_1 \nu^2}{2r_1}\phi_1^3, \tag{20}$$

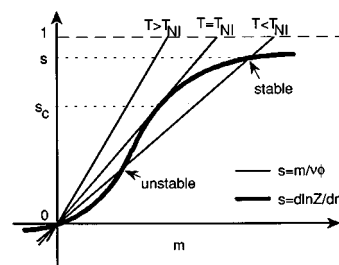$$B_3 = \frac{c_2 \nu^3}{3r_1}\phi_1^4, \tag{21}$$

FIG. 1. Graphical presentation of the self-consistent solution giving the orientational order parameters based on the Maier–Saupe approximation.

$$B_4 = \frac{c_3 \nu^4}{4r_1}\phi_1^5, \tag{22}$$

$$B_5 = \frac{c_4 \nu^5}{5r_1}\phi_1^6. \tag{23}$$

Although our original intention in expanding s in terms of m was to simplify the tedious numerical integration of the partition function of the Maier–Saupe theory, Eq. (18) basically corresponds to the Landau–de Gennes free energy expansion form.[16] It is obvious that any free energy functions can be expanded in the same fashion; therefore, our calculation should not be limited to the Maier–Saupe theory. This free energy expansion will be used in the calculation in the subsequent sections.

C. Evaluation of orientational order parameters

For a given set of temperature and composition, the orientational order parameter, s, is the simultaneous solution of Eqs. (13) and (15). If both equations are plotted together in the form of s versus m, Eq. (13) yields a straight line passing through the origin with a slope of $1/(\phi_1 \nu)$, and Eq. (15) represents a sigmoidal curve increasing from the origin. Figure 1 depicts the graphical presentation of the self-consistent solution giving the order parameter of the Maier–Saupe approximation. The origin is a trivial solution representing the isotropic state, and there is no free energy contribution arising from the nematic ordering. The slopes, $1/(\phi_1 \nu)$, give different values that are proportional to temperature, but inversely proportional to composition. When the slope is greater than a critical value, there is no intersection except at the origin, implying that the system is in the isotropic state, i.e., the temperature must be above the nematic–isotropic transition temperature (T_{NI}) or the LC content must be too low to form a nematic phase. At the critical value, the line represents a tangent to the sigmoidal curve. The tangent point yields the critical order parameter, s_c, and the critical mean field parameter, m_c, of the nematic phase, viz.,

$$s_c \approx 0.44, \quad m_c \approx 2.00. \tag{24}$$

Physically, it means that the liquid crystal phase is unstable below this critical point, but it is stable above it. This gives the limits of the orientational order parameter where nematic ordering can be found, i.e.,
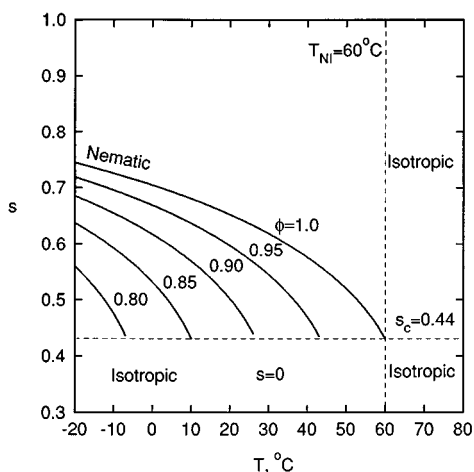
$$s_c \leq s \leq 1. \tag{25}$$

FIG. 2. Variation of the orientational order parameter vs temperature at various concentrations for a PDLC system having a T_{NI} at 60 °C.
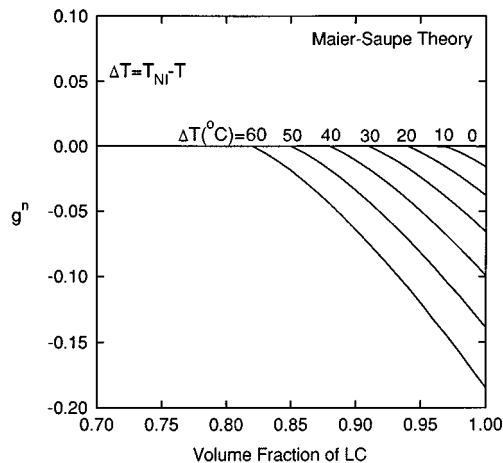

FIG. 3. Variation of the Maier–Saupe free energy vs concentration for various temperature of a PDLC system having a T_{NI} at 60 °C.

The lowest composition to form a nematic phase of a LC/polymer mixture, ϕ_{NI}, can be calculated from the critical value, s_c, from Eq. (13), as follows:

$$\left(\frac{\phi s_c}{T}\right)_{\phi=\phi_{NI}} = \left(\frac{\phi s_c}{T}\right)_{\phi=1, T=T_{NI}}, \tag{26}$$

$$\phi_{NI} = \frac{T}{T_{NI}}, \quad T \leqslant T_{NI}. \tag{27}$$

Therefore, the range of the nematic volume fraction at a constant temperature may be given as

$$\phi_{NI} \leqslant \phi \leqslant 1. \tag{28}$$

If a system has s or ϕ value outside the above limits, the free energy would have no contribution from the nematic ordering, and thus g^n is set to be zero.

   If the slope is lower than the critical value, two intersections can be obtained; but only the one greater than the s_c has a valid solution as the lower intersecting point corresponds to the unstable state. Figure 2 shows the variation of the order parameter versus concentration and temperature for a PDLC system having a T_{NI} at 60 °C. The corresponding Maier–Saupe free energy is shown in Fig. 3. It can be noticed that the free energy curve exhibits a subtle curvature. As will be shown latter, this convex curvature eventually gives rise to the nematic–liquid material.

D. Calculation of binodals, spinodals, and critical point

   Phase equilibrium requires a condition that any components have the same chemical potentials in every phase. For a binary system, the volume fractions, ϕ^α and ϕ^β, of the two equilibrium phases, α and β, can be solved from the following equations, i.e.,

$$\mu_1^\alpha = \mu_1^\beta, \tag{29}$$

$$\mu_2^\alpha = \mu_2^\beta. \tag{30}$$

The chemical potential, μ_i, is defined as the partial molar free energy of component i. The chemical potentials contribution from the Maier–Saupe theory can be deduced as[17]

$$\frac{\mu_1^n}{kT} = -\ln Z + \frac{1}{2}\nu\phi_1^2 s^2, \tag{31}$$

$$\frac{\mu_2^n}{kT} = \frac{1}{2}\frac{r_2}{r_1}\nu\phi_1^2 s^2. \tag{32}$$

Similarly, the chemical potentials contribution from the Flory–Huggins theory may also be calculated.[13] The solutions at different temperatures afford the binodal curves of the phase diagram.

   To check the validity of phase diagram calculation, let us consider a hypothetical PDLC system with the parameters such as $\phi_c = 0.6$, $T_c = 62$ °C, $T_{NI} = 60$ °C. With this set of parameters, the free energy as well as its first and second derivatives may be calculated as a function of composition at different temperatures. We considered two situations for illustration, i.e., at 35 and 45 °C. The first situation corresponds to a case where the equilibrium can be established between the nematic phase and the isotropic polymer-rich phase. In the second situation, the PDLC system can have two sets of phase equilibria depending on the initial compositions; one is the equilibrium of liquid–liquid phases and the other is the equilibrium between isotropic liquid and nematic phases. Figures 4 and 5 depict the free energy and its derivatives versus composition for the above two situations, respectively. It is customary to observe a kink in the total free energy curve at ϕ_{NI} where the nematic ordering free energy starts to take into effect. Such a kink is due to a step change of the order parameter (from $s=0$ to $s=s_c$) during the nematic–isotropic transition which renders the free energy derivatives discontinuous.

   For simplicity, we use ϕ to represent the volume fraction of the liquid crystal (component 1) with superscripts denoting the phases. The equilibrium was established by means of a double tangent method[18] where the equilibrium volume fractions $(\phi^\alpha, \beta^\beta)$ fall on the same tangent line of the free
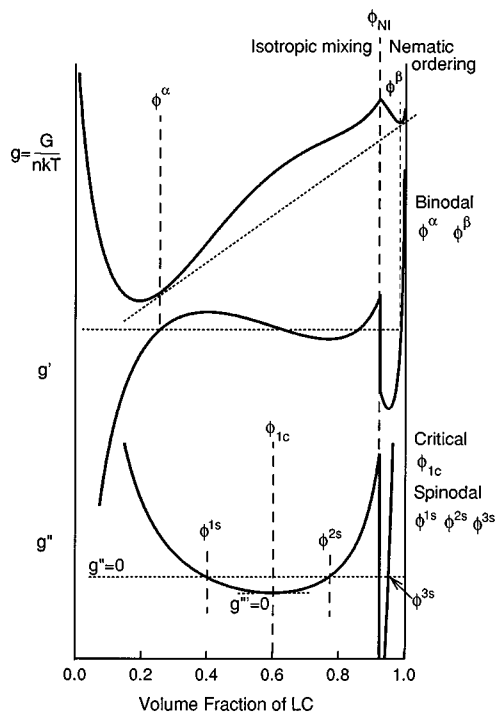
FIG. 4. Variation of free energy and its derivatives as a function of composition for a PDLC system exhibiting one double tangent line in the free energy curve.
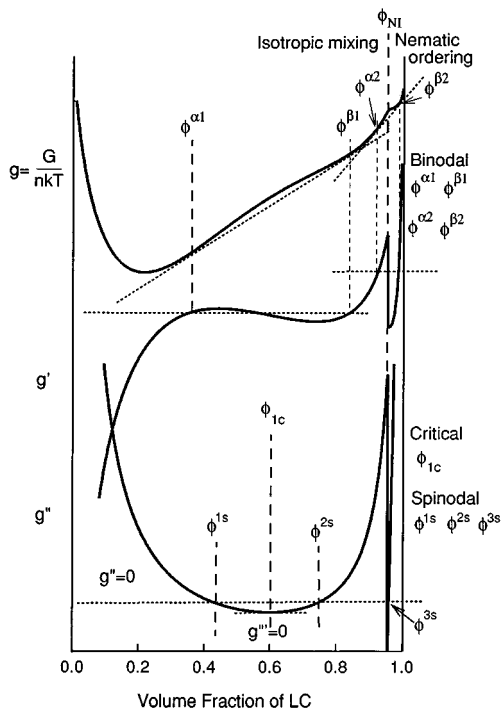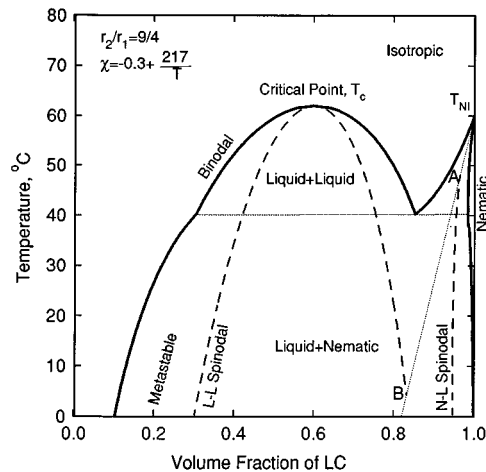

FIG. 6. Phase diagram of a hypothetical PDLC system with parameters used in the calculation.

energy curve, and the first derivatives of the free energy are equal at these two compositions, implying that the isotropic liquid phase, ϕ^α, is in equilibrium with a nematic phase, ϕ^β. At a higher temperature, the equilibrium may be established for two sets of compositions, $(\phi^{\alpha 1}, \phi^{\beta 1})$ and $(\phi^{\alpha 2}, \phi^{\beta 2})$, as shown in Fig. 5. The first set is the liquid–liquid equilibrium which may be described simply by the Flory–Huggins equation. The second set represents the liquid–nematic equilibrium. Similar calculations have been performed for various temperatures to establish a phase diagram for this hypothetical PDLC. As shown in Fig. 6, the phase diagram consists of an upper critical solution temperature (UCST) overlapping with the nematic–isotropic transition.

Now, we turn our attention to the calculation of spinodals. The stable condition requires that the second derivative of the total free energy is greater than zero ($\delta^2 g > 0$), whereas the unstable condition gives the convexity of the free energy curve. The spinodal, that separates the metastable from the unstable state, is defined as the inflection point of the free energy curve ($\delta^2 g = 0$). In a PDLC system, the spinodals may be solved according to

$$\left(\frac{\partial^2 g}{\partial \phi^2}\right)_{T,P} = \left(\frac{\partial^2 g^i}{\partial \phi^2}\right)_{T,P} + \left(\frac{\partial^2 g^n}{\partial \phi^2}\right)_{T,P} = 0. \tag{33}$$

The second derivatives for the Flory–Huggins theory and Maier–Saupe theory may be obtained as follows:[17]

$$\left(\frac{\partial^2 g^i}{\partial \phi^2}\right)_{T,P} = \frac{1}{r_1 \phi} + \frac{1}{r_2(1-\phi)} - 2\chi, \tag{34}$$

$$\left(\frac{\partial^2 g^n}{\partial \phi^2}\right)_{T,P} = -\frac{1}{r_1} \frac{d \ln Z}{d\phi}, \tag{35}$$

where the volume fraction derivative of the partition function can be derived by using Eqs. (13) and (15),[17] i.e.,

$$\frac{d \ln Z}{d\phi} = \nu s^2 \left(1 - \nu\phi \frac{ds}{dm}\right)^{-1}. \tag{36}$$

FIG. 5. Variation of free energy and its derivatives as a function of composition for a PDLC system exhibiting two double tangent lines in the free energy curve.

There are at most three solutions at a given temperature from Eq. (33), which may be represented by ϕ^{1s}, ϕ^{2s}, and ϕ^{3s}. The first two solutions, ϕ^{1s} and ϕ^{2s}, represent the conventional liquid–liquid spinodal points. The third spinodal point, ϕ^{3s}, refers to the spinodal within the coexistence of the nematic–isotropic liquid phase, which will be called hereafter the nematic–liquid spinodal or the NL spinodal.

When the composition is higher than the nematic ordering composition, ϕ_{NI}, the contribution from the Maier–Saupe free energy must be taken into account. Equation (33) suggests that one of the LL spinodals, ϕ^{2s}, cannot exist in a composition greater than the ϕ_{NI}. The temperature at which ϕ^{2s} is equal to ϕ_{NI}, hereafter denoted T_{LL} (point B in Fig. 6), is the lower bound of this LL spinodal.

The spinodals of the hypothetical PDLC at both 35 and 45 °C can be obtained as shown in Figs. 4 and 5, respectively. The $g''(\phi)$ curve crossing the zero line determines the spinodals. In both temperatures, three spinodal points were found, ϕ^{1s}, ϕ^{2s}, and ϕ^{3s}. The last one, ϕ^{3s}, is the NL spinodal point. As the temperature increases, ϕ^{3s} gradually moves toward the ϕ_{NI}, and finally ϕ^{3s} merges to the ϕ_{NI} line (point A in Fig. 6). The merged point represents the upper bound for the NL spinodal, where ϕ^{3s} is equal to ϕ_{NI}. However, the upper bound of the liquid–liquid spinodal curves, ϕ^{1s}, and ϕ^{2s}, is essentially the critical point, ϕ^c, having a critical temperature, T_c.

The existence of the NL spinodal is mainly due to the suble inflection of the free energy curve within the nematic–isotropic coexistence region. This inflection is resulted from the delicate balance between the concave free energy curves of the isotropic mixing and the convex free energy curve from the anisotropic ordering. Physically, the composition above the NL spinodal line is metastable against the nematic ordering. However, the composition below this NL spinodal line may be unstable or metastable against composition depending on whether the temperature is below or above the T_{LL}. To the best of our knowledge, the existence of this NL spinodal line has not been reported in the literature;[6–10] our calculation is probably the first to predict the spinodal line within the nematic–isotropic region.

The critical point, defined as the third derivative of free energy to be zero, can be found consistently from the minimum of the $g''(\phi)$ curves at both 35 and 45 °C cases as depicted in Figs. 4 and 5, respectively.

E. Nematic phase limit

If the liquid crystal rich phase is very close to the nematic phase limit ($\phi^\beta \sim 1$), the binodal calculation needs to be modified in order to avoid a trivial solution. Since the chemical potential of the polymer (component 2) approach negative infinity, Eq. (29) can be dropped out and ϕ^β can be set to unity. The equilibrium composition, ϕ^α, may be solved from the following:

$$(\mu_1^i)_{\phi=\phi^\alpha} = (\mu_1^n)_{\phi=1}. \tag{37}$$

The PDLC system would reach the nematic phase limit under two conditions; one is at temperatures far below T_{NI} ($T \ll T_{NI}$), and the other is at temperatures very close to the T_{NI}. At the nematic phase limit, the nematic rich phase con-
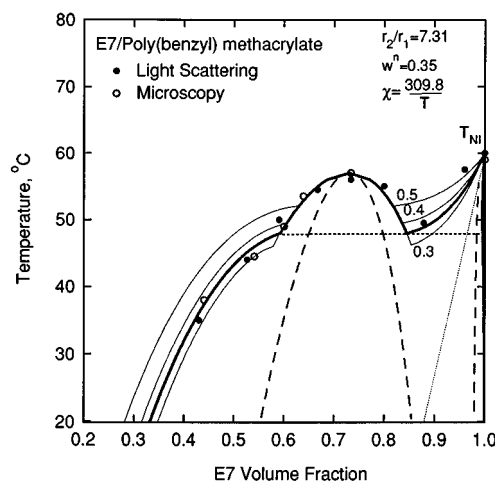

FIG. 7. A calculated phase diagram in comparison with the cloud points of the PBMA/E7 system, showing the w^n dependence.

tains exclusively the liquid crystal molecules in which the polymer molecules may be totally rejected out of the nematic phase. However, the isotropic phase (polymer-rich phase) may still contain some dissolved liquid crystal molecules, which is usually observed in most PDLC systems.

F. Test with experimental results

For the comparison with the experimental cloud points, a parameter, w^n, is introduced to account for the relative contributions of different kinds of potentials. The total free energy, Eq. (1), is then modified as

$$g = (1 - w^n)g^i + w^n g^n, \tag{38}$$

where w^n may be related to polymer–nematic interfaces.[17] Correspondingly, Eqs. (33) and (37) may be modified as follows:

$$\left(\frac{\partial^2 g}{\partial \phi^2}\right)_{T,P} = (1 - w^n)\left(\frac{\partial^2 g^i}{\partial \phi^2}\right)_{T,P} + w^n\left(\frac{\partial^2 g^n}{\partial \phi^2}\right)_{T,P} = 0, \tag{39}$$

$$(1 - w^n)(\mu_1^i)_{\phi=\phi^\alpha} = w^n(\mu_1^n)_{\phi=1}. \tag{40}$$

The temperature versus composition phase diagrams were calculated for various values of w^n and compared with the experimental cloud points of the PBMA/E7 mixture in Fig. 7. The isotropic liquid–liquid phase separation region covers only a small temperature gap. The calculated nematic binodal line is very close to the nematic phase limit, indicating that polymer chains could be excluded totally from the nematic phase. Figure 8 shows a typical polarized optical micrograph of the (50/50) PBMA/E7 mixture that was quenched from the isotropic region (80 °C) to room temperature. The dispersed droplets are strongly birefringent due to the nematic ordering within the domains, whereas the continuum is dark as the polymer-rich phase is isotropic. It may be postulated that the droplet PDLC structure formed because of the off-critical quenching into the metastable region.

It should be pointed out that the χ parameter used here does not account for the molecular weight and volume de-
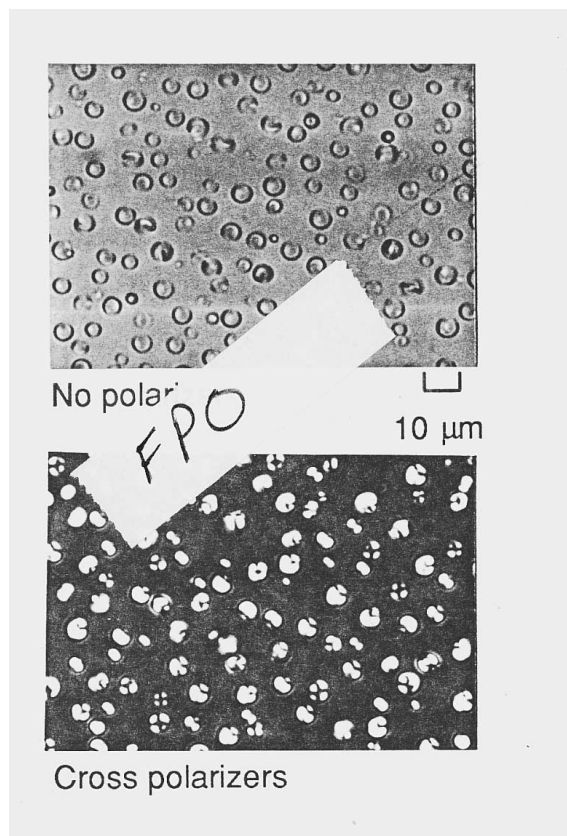
FIG. 8. Unpolarized and polarized optical micrographs of the (50/50) PBMA/E7 mixture taken after 2 days following a temperature quench from an isotropic region (80 °C) to room temperature.

pendence. On the same token, the quadrupole interaction parameter of nematics, ν, was assumed to be simply a function of temperature without considering its volume dependence. In fact the original Maier–Saupe theory[15] predicted that ν has an inverse volume square dependence.[19] However, Cotter[20] argued that ν should have an inverse volume dependence irrespective of the nature of intermolecular pair potential. The present calculation is not intended to fit the experimental results quantitatively, but merely to demonstrate the qualitative comparison. It is reasonable to conclude that the calculated binodal curves certainly capture the trend of the experimental cloud points for the present PDLC system at least qualitatively.

IV. CONCLUSIONS

The combination of free energy of Flory–Huggins and Maier–Saupe free energy predicted the complex phase dia-gram comprising the liquid–liquid equilibrium and the nematic–isotropic transition. Our calculation predicted a nematic–liquid spinodal within the nematic–isotropic coexistence region in addition to the conventional liquid–liquid spinodals. The nematic–liquid spinodal curve has an upper bound and one of the liquid–liquid spinodals has a lower bound. Both limits fall on the ϕ_{NI} line representing the onset of the nematic–isotropic transition. We believe that both spinodals should play important roles in the dynamics of phase separation and pattern formation of PDLC systems.

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