

Phase Equilibria of Polymer Dispersed Liquid Crystal Systems in the Presence of an External Electrical Field

TAO CHEN, LIANGSHUN ZHANG, TAO LI, JIAPING LIN, SHAOLIANG LIN

Key Laboratory for Ultrafine Materials of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Received 4 February 2007; revised 11 March 2007; accepted 11 March 2007

DOI: 10.1002/polb.21197

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of an external electrical field on phase behaviors is reported for polymer dispersed liquid crystal films of 4'-pentyl-4-biphenylcarbonitrile/poly(methyl methacrylate) binary mixtures with various polymer molecular weights. The experimental results show that increasing the molecular weight of the polymer or the electrical field intensity can give rise to an increase in the phase-transition temperature and a widening of the binary phase region. The lattice theory, regarding a binary system consisting of a rigid nematic liquid crystal and a random polymer, has been extended to the case in which an external electrical field is present. A comparison of the theoretical predictions with the experimental results has been carried out, and satisfactory agreement has been found. ©2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 45: 1898–1906, 2007

Keywords: electrical field; lattice models; phase behavior; phase diagrams; polymer dispersed liquid crystals

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films, in which nematic liquid crystal (LC) droplets are randomly dispersed in a continuous isotropic polymer matrix,¹ are candidates for applications in electrooptical devices used for switchable privacy windows, optical shutters, colored films with electrically controllable optical density, and various other light-control devices.^{2–4}

In the process of preparing PDLC films, external magnetic or electrical fields are usually applied to obtain the desired overall director orientation in PDLC films and to achieve high optical contrast between off and on states.⁵ On the other hand, the optical response of PDLCs is based on the electrically controlled light scattering properties of LC domains, which depend

strongly on the morphology of the phase-separated structure. Therefore, an understanding of the effect of an external field on the phase behavior of PDLCs is crucial for controlling film properties.

Some experimental reports regarding the effect of an external electrical field on the phase equilibria of PDLC films are available in the literature.^{6–9} By polarized light microscopy (PLM) observation, Yang et al.⁶ investigated the morphologies of phase separation in mixtures of a cyano-biphenyl mixture (E7) and polystyrene with or without an external electrical field applied. They found that an external electrical field makes the binodal curves of the phase diagrams shift to higher temperatures, and the LC domain growth rate is highly accelerated because the electrical-field-oriented LC phase excludes the polymer coils strongly. Manaila-Maximean et al.⁷ studied the dependence of the phase-transition temperatures of E7/poly(methyl methacrylate) (PMMA) PDLC films on a polariz-

Correspondence to: J. Lin (E-mail: jplinlab@online.sh.cn)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 45, 1898–1906 (2007)
©2007 Wiley Periodicals, Inc.

ing electrical field, using the thermally stimulated depolarization currents method and differential scanning calorimetry method. The phase-transition temperatures shift to higher values as the strength of the polarizing electrical field increases. Recently, by using a depolarized light intensity technique, the authors have investigated the influence of the external electrical field on the phase-separation kinetics of LC/monomer mixtures during polymerization.⁸ It was found that the phase-separation process is accelerated and the clearing temperature of the formed PDLC film is raised by the electrical field. Furthermore, the phase diagrams and morphologies for LC/monomer mixtures with an external electrical field applied have been established through PLM by the authors.⁹ It was found that the isotropic–nematic coexistent phase regions shift to higher temperatures as an external electrical field is applied during the crosslinking polymerization process. The processes of phase separation and LC ordering in PDLC formation could be highly accelerated by the electrical field.

There are some theoretical considerations focusing on the phase behaviors for PDLC systems in the absence of an external field.^{10–18} On the basis of the Flory lattice model, Ballauff¹⁰ presented a theory of the nematic–isotropic phase equilibrium in a binary mixture of a thermotropic nematogen and a random coil polymer. The steric part of the partition function was evaluated along the lines given by Flory for the phase equilibria of rods and coils in lyotropic systems. The soft anisotropic forces between the molecules of the nematogenic component were treated by an additional factor in the partition function. A semiquantitative agreement was achieved by the comparison of the theoretical predictions with experimental phase diagrams obtained for mixtures of low-molecular-weight nematogens and flexible solutes. Ballauff's theory has been extended by Lee and Bae¹⁸ to develop a semiempirical model. In this model, the Flory–Huggins interaction parameter, χ , is correlated to both the rodlike solute concentration and temperature. The theoretical result is in good agreement with experimental data obtained for nematic LC and polystyrene mixture systems.

However, limited theoretical work has been reported on the effect of an external field on the phase behaviors of mixtures containing a thermotropic nematogen and a random coil polymer. Combining the Flory–Huggins theory of flexible

polymers mixtures¹⁹ and the Lebwohl–Lasher model of nematogens,^{20,21} Yang et al.²² constructed a theory to predict the influence of an external magnetic field on the phase behaviors for a mixture of a flexible polymer and LC. The theoretical calculations reveal that the external magnetic field promotes the ordering of LC and strengthens the driving force for phase separation. The binodal curves are shifted to higher temperatures, and the spinodal curves are substantially changed.

To the best of our knowledge, however, no theoretical study on the phase behavior of PDLCs in an external electrical field has been reported so far. Such an investigation could be of great importance, not only raising challenging questions addressing very basic aspects of LC research and providing a new way of investigating PDLC films academically but also providing useful information for the fabrication of PDLC films.

In this work, the phase behaviors of a nematic LC in a random coil polymer matrix, that is, 4'-pentyl-4-biphenylcarbonitrile (5CB)/PMMA, were investigated by means of PLM with or without an external electrical field applied. The influence of the external electrical field intensity, molecular weight of the polymer, and content of the LC on the phase behaviors was studied. To theoretically predict the effect of an external electrical field on the phase behaviors of 5CB/PMMA mixtures, an additional energy term related to an external electrical field was introduced to an improved version of Ballauff's theoretical model in which an extended Flory–Huggins equation is employed.¹⁸ Both the experimental and theoretical results show that increasing the polymer molecular weight or the electrical field intensity can shift the phase-transition temperatures upward. The theoretical predictions and experimental results are in good agreement.

EXPERIMENTAL

Materials

The matrix materials, PMMA samples with weight-average molecular weight (M_w) values of 5.0×10^4 , 9.0×10^4 , and 15.0×10^4 , which were named PMMA-5, PMMA-9, and PMMA-15, respectively, were purchased from Shanghai Jiu-long Fine Chemicals Co., Ltd., and used without

further purification. The single-component nematic LC, 5CB, with a nematic–isotropic transition temperature (T_{NI}) of 35.1 °C, was purchased from Yantai Viliant LC Materials Co., Ltd., and used as received.

Preparation of the PDLC Films

PDLC films were prepared by the solvent-induced phase-separation method.²³ Mixtures of PMMA and 5CB with different weight ratios were first dissolved in chloroform at room temperature and stirred for 2 h. Then, an aliquot of the homogeneous solution was spread on an indium tin oxide (ITO) coated conductive glass substrate. This sample was dried at room temperature on ventilation conduction for 12 h until the specimen became turbid. Subsequently, an ITO-coated cover glass was placed on the sample so that the thin PDLC film was sandwiched between two glass plates, separated by a spacer 35 μm thick. Afterward, the sample was moved into an oven to evaporate the remaining solvent for a day at 120 °C. After the elimination of the solvent, the samples were annealed for 1 h at 80 °C (well above the phase-separation temperature) to make the specimens homogeneous and to clear up the thermal history, and then they were naturally cooled to room temperature for PLM observations.

PLM Observations

During the study of the effect of an external field, a direct-current electrical field with an intensity ranging from 1.0 to 5.0 V/ μm was applied perpendicularly to the sample plane.

PLM experiments were carried out on a Leitz-Ortholux II polarized light microscope with a hot stage. The phase-transition temperatures of the 5CB/PMMA mixtures were all detected under a cross-polarizer during the heating of the samples on the hot stage with a programmable temperature controller. The heating rate was 1 °C/min.

THEORETICAL MODEL

The free energy expression of PDLC mixtures in the absence of an external field is given in the improved version of Ballauff's theory in which an extended Flory–Huggins equation is employed.¹⁸ When an external electrical field is applied, the contribution of the electrical field to the free

energy should be considered, and the free energy expression given in ref. 18 should be modified. Because the electrical field is a dipole-type orientational field, according to refs. 24–26, the free energy term associated with the external electrical field (E_{ex}) can be written as follows:

$$E_{\text{ex}}/k_{\text{B}}T = -E_0 n_r x_r \langle \cos \psi \rangle \quad (1)$$

where k_{B} is the Boltzmann constant, n_r is the number of rodlike molecules with axial ratio x_r , and ψ denotes the angle of inclination of the long axis of the nematogen toward the domain axis. The dimensionless parameter E_0 defines the intensity of the external electrical field and can be associated with the experimental electrical field intensity, E , by the multiplication of a physical unit, $\xi = (k_{\text{B}}T/\varepsilon_0 v_{\text{LC}})^{1/2}$,²⁷ where ε_0 is the vacuum permittivity and v_{LC} is the volume per nematogenic molecule. The magnitude of this electrical field unit at the average experimental temperature, $T \approx 306$ K, and for the molecular volume of 5CB, $v_{\text{LC}} = 263.55 \times 10^{-12} \mu\text{m}^3$,²⁸ is $\xi \approx 1.35 \times 10^3$ V/ μm . The dimensionless electrical field is rescaled as $E_0 = E/\xi$.

After the incorporation of eq 1, the mixing free energy expression for a binary system consisting of a rigid nematogenic LC component and a flexible polymer in the presence of the external field becomes

$$\begin{aligned} -\ln Z_{\text{M}} = & -(n_0 - n_r x_r + n_r \bar{y}) \ln \left[1 - \frac{n_r x_r}{n_0} \left(1 - \frac{\bar{y}}{x_r} \right) \right] \\ & + n_r \ln \frac{n_r}{n_0} + n_c \ln \frac{n_c}{n_0} + n_r (\bar{y} - 1) \\ & + n_c (x_c - 1) + (n_0 - n_r x_r - n_c x_c) \\ & \times \ln [(n_0 - n_r x_r - n_c x_c)/n_0] - n_r \sum_y \frac{n_{ry}}{n_r} \ln \frac{n_{ry}}{n_r \omega_y} - \frac{n_r x_r}{2\bar{V}\theta} s^2 \\ & + \chi n_c x_c v_r - E_0 n_r x_r \langle \cos \psi \rangle \quad (2) \end{aligned}$$

where Z_{M} is the mixing partition function, n_0 denotes the total number of lattice sites, n_c is the number of random coils with contour length x_c , \bar{y} is the mean value of the disorientation index of the rodlike component, n_{ry}/n_r is the orientational distribution function for the rodlike component having disorientation y , ω_y is the *a priori* probability of disorientation y for the rodlike solute, \bar{V} represents the reduced volume of the mixture, v_r is the volume fraction of the rodlike solute, s is the order parameter, and θ is the reduced temperature with the value of ratio T/T^* (where T^* is the characteristic temperature

of the nematogen). χ denotes the interaction parameter, which is associated with the exchange energy of creating rodlike/coil-like segment interactions while destroying rodlike/rodlike and coil-like/coil-like segment interactions,¹⁹ and is a function of both the rodlike solute concentration and temperature:¹⁸

$$\chi(T, v_r) = D(T)B(v_r) \quad (3)$$

$$D(T) = d_0 + \frac{d_1}{T} \quad (4)$$

$$B(v_r) = \frac{1}{1 - d_2 v_r} \quad (5)$$

where d_0 , d_1 , and d_2 are adjustable model parameters.

The order parameter, s , and the mean value of the disorientation index of the rodlike component, \bar{y} , are defined in terms of a family of integrals, f_p ($p = 1, 2$, or 3):

$$s = 1 - \frac{3f_3}{2f_1} \quad (6)$$

$$\bar{y} = \frac{4}{\pi} x_r \left(\frac{f_2}{f_1} \right) \quad (7)$$

where

$$f_p = \int_0^{\frac{\pi}{2}} \sin^p \psi \exp \left[-\frac{4}{\pi} x_r a \sin \psi - \frac{3}{2} x_r b v_r \sin^2 \psi + E_0 x_r \cos \psi \right] d\psi \quad (8)$$

$$\langle \cos \psi \rangle = \frac{1}{f_1} \int_0^{\frac{\pi}{2}} \cos \psi \sin \psi \exp \left[-\frac{4}{\pi} x_r a \sin \psi - \frac{3}{2} x_r b v_r \sin^2 \psi + E_0 x_r \cos \psi \right] d\psi \quad (9)$$

Quantities a and b are defined by

$$a = -\ln \left[1 - \frac{v_r}{\bar{V}_r} \left(1 - \frac{\bar{y}}{x_r} \right) \right] \quad (10)$$

$$b = \frac{s}{\bar{V}\theta} \quad (11)$$

The chemical potentials of the components in the anisotropic phase can be readily obtained by the partial differentiation of eq 2 with the auxiliary equations (eqs 3–11). The results are shown

Journal of Polymer Science: Part B: Polymer Physics
DOI 10.1002/polb

as follows:

$$\begin{aligned} \Delta\mu'_r/RT = & \ln \frac{v'_r}{x_r \bar{V}_r} + v'_r (\bar{y} - 1) \\ & + v'_c x_r \left(1 - \frac{\bar{V}_r}{\bar{V}_c x_c} \right) + x_r \left(\frac{\bar{V}_r}{\bar{V}} - 1 \right) \\ & + x_r (\bar{V}_r - 1) \left[a + \ln \left(1 - \frac{1}{\bar{V}'} \right) \right] \\ & - \ln f_1 - \frac{x_r v'_r s}{\bar{V}\theta} \left[1 - \frac{1}{2} s - \frac{1}{2} s v'_r \left(1 - \frac{\bar{V}'}{\bar{V}_r} \right) + \frac{1}{2} s v'_c \right] \\ & + \left(d_0 + \frac{d_1}{T} \right) \left[\frac{1}{(1 - d_2 v'_r)^2} \right] \left(v_c'^2 \frac{\bar{V}_r x_r}{\bar{V}_c} \right) \\ & - E_0 x_r \langle \cos \psi \rangle \quad (12) \end{aligned}$$

$$\begin{aligned} \Delta\mu'_c/RT = & \ln \frac{v'_c}{x_c \bar{V}_c} + v'_r \frac{\bar{V}_c x_c}{\bar{V}_r x_r} (\bar{y} - 1) \\ & + v'_c \left(\frac{\bar{V}_c}{\bar{V}_r} x_c - 1 \right) + x_c \bar{V}_c \left(\frac{1}{\bar{V}'} - \frac{1}{\bar{V}_r} \right) + \bar{V}_c x_c a \\ & + x_c (\bar{V}_c - 1) \ln \left(1 - \frac{1}{\bar{V}'} \right) + \frac{s^2 x_c v_r'^2}{2\bar{V}'\theta \bar{V}_r} (2\bar{V}_c - \bar{V}') \\ & + \left(d_0 + \frac{d_1}{T} \right) \left[\frac{1 - d_2}{(1 - d_2 v_r')^2} \right] x_c v_r'^2 \quad (13) \end{aligned}$$

where the prime symbol denotes the anisotropic phase; v_c is the volume fraction of the polymeric components; and \bar{V}_r and \bar{V}_c are the reduced volumes of the rodlike nematogen and the coiled polymer species, respectively.

The chemical potentials in the isotropic phase are as follows:

$$\begin{aligned} \Delta\mu_r/RT = & \ln \frac{v_r}{x_r \bar{V}_r} + v_r (x_r - 1) + v_c x_r \left(1 - \frac{\bar{V}_r}{\bar{V}_c x_c} \right) \\ & + x_r \left(\frac{\bar{V}_r}{\bar{V}} - 1 \right) + x_r (\bar{V}_r - 1) \ln \left(1 - \frac{1}{\bar{V}} \right) \\ & + \left(d_0 + \frac{d_1}{T} \right) \left[\frac{1}{(1 - d_2 v_r)^2} \right] v_c^2 \frac{\bar{V}_r x_r}{\bar{V}_c} - \frac{\sqrt{3}}{3} E_0 x_r \quad (14) \end{aligned}$$

$$\begin{aligned} \Delta\mu_c/RT = & \ln \frac{v_c}{x_c \bar{V}_c} + v_r \frac{\bar{V}_c x_c}{\bar{V}_r} \left(1 - \frac{1}{x_r} \right) \\ & + v_c \left(\frac{\bar{V}_c}{\bar{V}_r} x_c - 1 \right) + x_c \bar{V}_c \left(\frac{1}{\bar{V}} - \frac{1}{\bar{V}_r} \right) + x_c (\bar{V}_c - 1) \\ & \times \ln \left(1 - \frac{1}{\bar{V}} \right) + \left(d_0 + \frac{d_1}{T} \right) \left[\frac{1 - d_2}{(1 - d_2 v_r)^2} \right] x_c v_r^2 \quad (15) \end{aligned}$$

Table 1. Thermodynamic Properties of 5CB and PMMA^a

5CB		
$x_r = 3.3$	$T_{NI} = 35.1\text{ }^\circ\text{C}$	$\rho (35\text{ }^\circ\text{C}) = 0.9900\text{ g/cm}^3$
$\alpha = 1.00 \times 10^{-3}\text{ K}^{-1}$	$T^* = 371.4\text{ K}$	$V^* = 200.7\text{ cm}^3/\text{mol}$
PMMA		
$v (45.9\text{ }^\circ\text{C}) = 0.8492\text{ cm}^3/\text{g}$	$v^* = 0.7389\text{ cm}^3/\text{g}$	$\alpha = 0.530 \times 10^{-3}\text{ K}^{-1}$

^a ρ is the density of the nematogen at the specified temperature; V^* is the molar hard core volume. The physical senses of the other symbols are expressed in the text.

According to ref. 10, for calculating the phase diagrams, the hard core volume of components, v^* , could be obtained via the following equations with the auxiliary relations of eqs 3–11:

$$\bar{V}^{1/3} - 1 = \alpha T / 3(1 + \alpha T) \quad (16)$$

$$v^* = v / \bar{V} \quad (17)$$

where α denotes the thermal expansion coefficient of the respective component at a given temperature T and v is the specific volume of the respective component.

Biphasic equilibria of a nematic phase and an isotropic phase with an external electrical field applied can be obtained if we equate eq 12 to eq 14 and eq 13 to eq 15 with the auxiliary relations of eqs 3–11 and eqs 16 and 17. For $x_c \geq 50$, however, the nematogen-rich phase approaches complete exclusion of the random coil. This leads to a numerical difficulty for a higher molecular weight.^{16,18} Therefore, calculations for a high molecular weight are performed by the composition of the ordered phase being set to unity and by the one remaining equation being solved for the isotropic phase composition. The details of the calculation steps are similar to those given in ref. 18.

The parameters of the respective compounds used in the calculations are summarized in Ta-

ble 1. The equation-of-state data for 5CB and PMMA were obtained from refs. 16 and 29, respectively. The numbers of segments, x_c , of different PMMA components were obtained from the ratios of their respective hard core volumes to the hard core volumes of one segment.³⁰ The calculated values of three adjustable model parameters (d_0 , d_1 , and d_2) for 5CB/PMMA with different polymer molecular weights are listed in Table 2.

RESULTS AND DISCUSSION

Effect of the Polymer Molecular Weight

Figure 1 presents the dependence of the phase-transition temperatures of 5CB/PMMA mixtures on the polymer molecular weights in the absence of an external field. The phase diagram exhibits an isotropic phase (I) and a binary phase consisting of an isotropic phase mainly containing PMMA (I_p) and a nematic phase (N). The symbols correspond to the experimental phase-transition temperatures. Above the ($I_p + N$)–I phase-transition temperatures, PMMA and 5CB are uniformly mixed. No macroscopic phase separation was found by PLM observation. As can be seen in Figure 1, the ($I_p + N$)–I phase boundary shifts upward to a higher temperature when a higher molecular weight PMMA is employed, and the ($I_p + N$) binary phase

Table 2. Values of the Adjustable Model Parameters for 5CB/PMMA Systems in the Presence of an External Electrical Field

M_w	x_c	$E_0 = 0$			$E_0 = 0.0011$			$E_0 = 0.0014$		
		d_0	d_1	d_2	d_0	d_1	d_2	d_0	d_1	d_2
50,000	595.9	–1.35	416.05	0.99	–1.61	497.33	0.99	–1.70	525.11	0.99
90,000	1072.7	–1.90	585.44	0.99	–1.98	611.78	0.99	–1.81	560.48	0.99
150,000	1787.8	–2.12	654.30	0.99	–2.22	685.03	0.99	–2.18	675.08	0.99

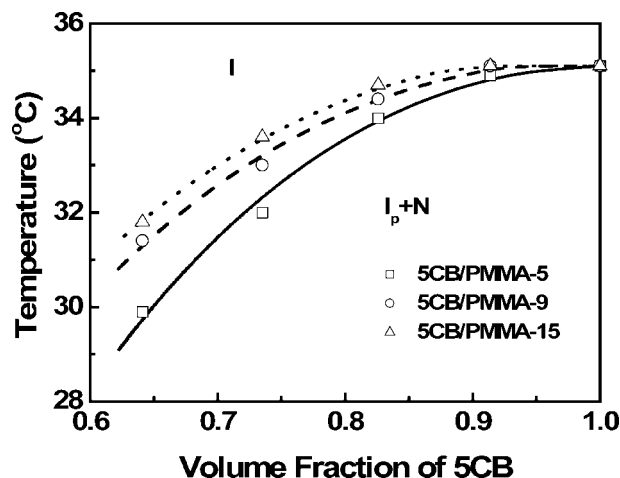


Figure 1. Dependence of the phase-transition temperatures of 5CB/PMMA mixtures on the volume fraction of 5CB for different values of the PMMA molecular weight.

region is hence broadened. The dependence of the phase-transition temperature on the 5CB content becomes weak with increasing 5CB content. At high LC fractions, the $(I_p + N)$ -I phase-transition temperatures approach T_{NI} of 5CB. When the $(I_p + N)$ -I phase transition takes place at the same temperature, the content of 5CB in mixtures with higher PMMA molecular weights is less than that in mixtures with lower molecular weights. Such a polymer molecular weight dependent effect results from the difficulty in mixing the LC component with a high-molecular-weight polymer. In the mixtures with low 5CB fractions, PMMA molecules with a high molecular weight are hardly dissolved in LC domains and are excluded from the nematic phase more strongly than those with a low molecular weight. Thus, the phase separation is enhanced. For this reason, a higher temperature is required for mixing each component well. As for the mixtures with high 5CB contents in which large LC domains form, the polymer molecular weight has less effect on the phase-transition temperature.¹⁰ The extreme situation is that no polymer exists in the system and the phase-transition temperature shifts up to the character-transition temperature of the LC bulk.

The solid line in Figure 1 presents the phase boundary of 5CB/PMMA-5 mixtures calculated with the present theoretical model, whereas the dashed line and dotted line indicate the theoretical phase boundaries of 5CB/PMMA-9 and 5CB/PMMA-15 mixtures, respectively. The theoret-

ical results show that the phase-transition temperatures increase with increasing polymer molecular weight and approach T_{NI} of pure 5CB at a high LC content. Comparing the theoretical phase boundaries with the experimental ones shown in Figure 1, one can recognize a remarkable fit between the theoretical prediction and the experimental data.

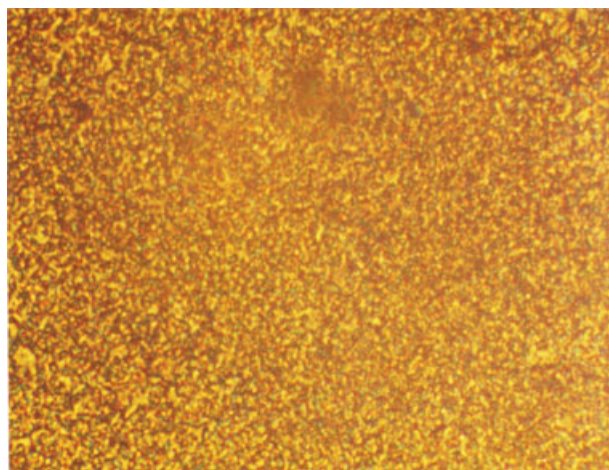
The PLM micrographs for 5CB/PMMA-5 and 5CB/PMMA-15 with a weight ratio of 70/30 can be found in Figure 2(a,b). Both mixtures form the phase-separated structure. The LC domains are embedded in the polymer matrix. The sizes of the 5CB droplets in the PMMA-5 matrix are larger than those in the PMMA-15 matrix.

Effect of an External Electrical Field

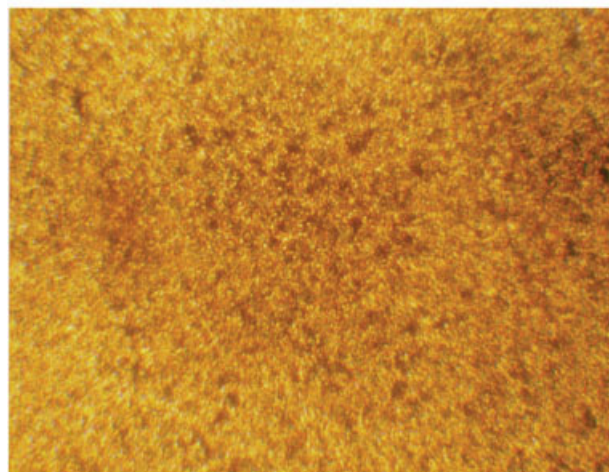
Figure 3 shows the experimental relationship between the LC phase-transition temperature and the electrical field intensity of 5CB/PMMA-5 mixtures. As can be seen in Figure 3, increasing the electrical field intensity raises the $(I_p + N)$ -I phase-transition temperatures and broadens the $(I_p + N)$ binary phase region. For example, for the mixture with 90 wt % 5CB in the absence of an external electrical field, the phase-transition temperature is 34.9 °C. In the case of applying electrical fields with intensities of 1.43 and 1.86 V/ μ m, the transition temperatures become 35.4 and 35.9 °C, respectively. The temperature-rising phenomena are found for all prescriptions, even for pure 5CB, T_{NI} also increases as the external electrical field is applied, and this is similar to the findings of other reports.^{31,32}

The lines in Figure 3 are the calculated results. The solid line is the theoretical phase boundary for $E_0 = 0$, whereas the dashed line and dotted line represent the phase boundaries for $E_0 = 0.0011$ and $E_0 = 0.0014$, which respectively correspond to practical electrical fields with the values of 1.43 and 1.86 V/ μ m. It can be found that this model properly predicts the upward shifting of the phase-transition temperatures in the presence of the external electrical field. In all cases, the theoretical predictions satisfactorily agree with the experimental results.

The upward shifting of the phase-transition temperature can be explained by the external electrical-field-induced alignment of LC molecules. Because of the high dielectric anisotropy of LC molecules,^{8,33} the external electrical field enhances the alignment of LC molecules and



(a)



(b)

Figure 2. Polarized light micrographs of 5CB/PMMA (70/30 w/w) mixtures at room temperature in the absence of an external field: (a) 5CB/PMMA-5 and (b) 5CB/PMMA-15 (crossed polars, 320 \times). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decreases the entropy of mixing. As a result, the polymer coils are excluded from the nematic phase strongly, and this promotes the phase separation.^{6,9} Therefore, the mixing temperature of the two components becomes higher, and this results in the upward shifting of the ($I_p + N$)–I phase boundary. For the 5CB bulk, more energy is required to disturb the alignments of LC molecules in the presence of the external electrical field and results in raising T_{NI} .

Similar effects of an external electrical field on phase transitions are also found in 5CB/PMMA-9 and 5CB/PMMA-15 mixtures, which

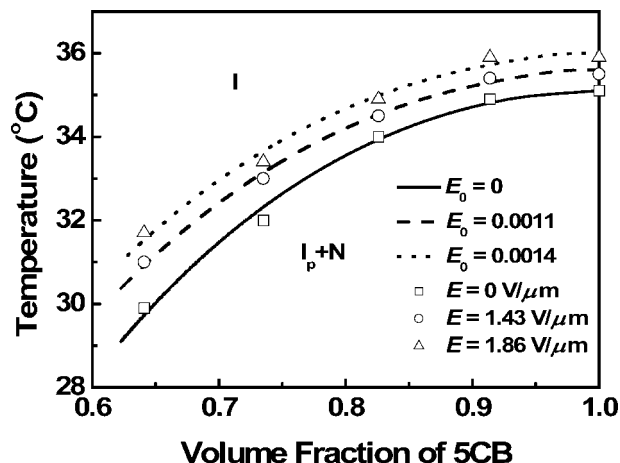


Figure 3. Theoretical predictions and experimental phase diagrams for 5CB/PMMA-5 mixtures in the presence of external electrical fields with various intensities. The symbols are the experimental data; the lines denote the calculation results.

are illustrated in Figures 4 and 5, respectively. Either the experimental results or the theoretical predictions show that the application of the external electrical field shifts the ($I_p + N$)–I phase boundary upward and broadens the ($I_p + N$) binary phase region. The stronger the electrical field intensity is, the higher the phase-transition temperature is and the broader the ($I_p + N$) binary phase region is. This model describes very well phase behaviors of the given systems, except that in Figure 5, a slight deviation from

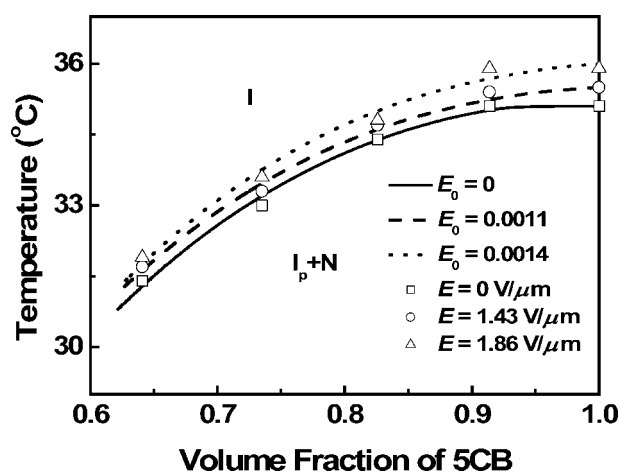


Figure 4. Theoretical predictions and experimental phase diagrams for 5CB/PMMA-9 mixtures in the presence of external electrical fields with various intensities. The symbols are the experimental data; the lines denote the calculation results.

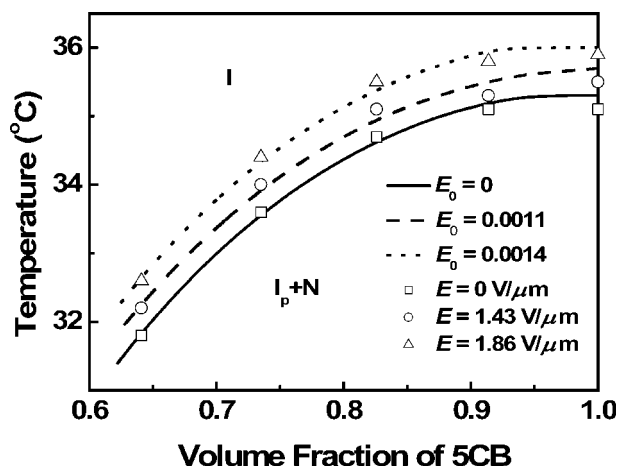


Figure 5. Theoretical predictions and experimental phase diagrams for 5CB/PMMA-15 mixtures in the presence of external electrical fields with various intensities. The symbols are the experimental data; the lines denote the calculation results.

the experimental results appears on the theoretical phase boundaries for high LC content mixtures when a high-intensity external electrical field is applied. The predicted phase-transition temperatures are higher than practical ones. The cause for such deficiency could be that the theory does not consider all interactions that exist in the given systems, especially specific interactions between molecules.¹⁸

Variations of the Order Parameter

The effect of the external electrical field intensity on the order parameter, s , of 5CB in the anisotropic phase is predicted by the present model and illustrated in Figure 6, where s is plotted against system temperature T . The predicted result shows that, whether or not there is an external field, the value of s decreases with increasing temperature, implying that the order of the mixture is disturbed by the heat energy. When an external electrical field is introduced into the system, LC molecules are favored to align to the field direction. As indicated in Figure 6, the alignment of LC molecules increases the order parameter of the system. The driving force for phase separation is thus enhanced.²² A higher temperature is required for mixing each component well. As a result, the phase-transition temperatures are increased, as shown in Figure 3–5.

Although this model overpredicts the effect of an external electrical field on the phase-transi-

tion temperatures for high LC content mixtures containing high-molecular-weight polymers, very good agreement between the theory and experiment is found under most of the experimental conditions. The model predicts many of the salient features of the system composed of thermotropic rods and random polymer coils in the presence of an external electrical field, including the widening of the ($I_p + N$) binary phase region and the raising of the ($I_p + N$)– I phase-transition temperature with increasing polymer molecular weight or external field strength. The quantitative agreement provides strong support for the applicability and validity of the Flory lattice model of the anisotropic energetics responsible for thermotropic behaviors in the presence of an external electrical field.

CONCLUSIONS

In this work, the effects of the polymer molecular weight and an external electrical field on the phase behaviors of PDLC films composed of 5CB and PMMA were investigated with PLM. To account for the electrical field influence, Ballauff's theoretical model, based on the lattice theory, was extended by the introduction of a free energy term contributed by an external electrical field. Both the experimental and theoretical results reveal that increasing the molecular weight of the polymer promotes the phase separation of PDLCs and increases the phase-transition temperature. It is also found that because of

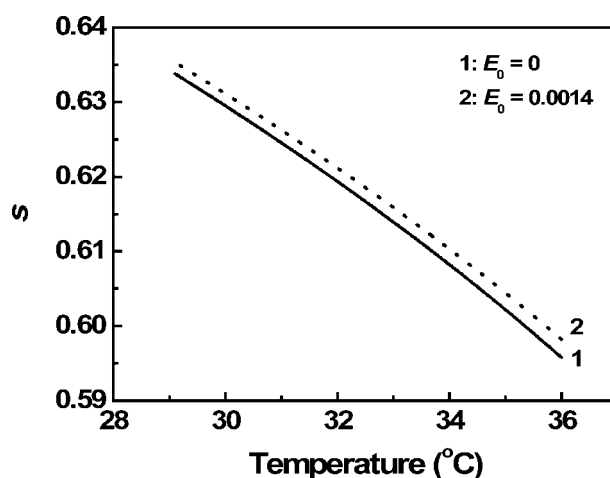


Figure 6. Relationship between the order parameter s and the phase-transition temperatures in the presence of external electrical fields with various intensities.

the effect of the electrical-field-induced alignment of LC molecules, the driving force for the phase separation of PDLC is enhanced. The ($I_p + N$)–I phase boundaries shift upward when the intensity of the external electrical field increases. The theoretical predictions are in good agreement with the experimental results.

This work was supported by the National Natural Science Foundation of China (20574018 and 50673026). Support from the Doctoral Foundation of the Education Ministry of China (grant 20050251008), the Program for New Century Excellent Talents in Universities in China (NCET-04-0410), and the Project of the Science and Technology Commission of Shanghai Municipality (05DJ14005, 06S007002, and 0652nm021) is appreciated.

REFERENCES AND NOTES

- Drzaic, P. S. *Liquid Crystal Dispersions; Series on Liquid Crystals 1*; World Scientific: Singapore, 1995.
- Doane, J. W.; Vaz, N. A.; Wu, B. G.; Zumer, S. *Appl Phys Lett* 1986, 48, 269–271.
- Doane, J. W. In *Liquid Crystals: Applications and Uses*; Bahadur, B., Ed.; World Scientific: Singapore, 1990; p 361.
- West, J. L. In *Technological Application of Dispersions*; McKay, R. B., Ed.; Marcel Dekker: New York, 1994; p 345.
- Drzaic, P. S. *Proc SPIE-Int Soc Opt Eng* 1989, 1080, 11–17.
- Hong, K.; Zhang, H.; Yang, Y. *J Appl Polym Sci* 2002, 86, 250–258.
- Manaila-Maximean, D.; Bena, R.; Rosu, C.; Furlani, M. *Mol Cryst Liq Cryst* 2001, 365, 645–653.
- Zhang, W.; Lin, J.; Yu, T.; Lin, S.; Yang, D. *Eur Polym J* 2003, 39, 1635–1641.
- Yang, D.; Lin, J.; Li, T.; Lin, S.; Tian, X. *Eur Polym J* 2004, 40, 1823–1832.
- (a) Ballauff, M. *Macromolecules* 1986, 19, 1366–1374; (b) Ballauff, M. *Ber Bunsenges Phys Chem* 1986, 90, 1053–1058; (c) Ballauff, M. *Mol Cryst Liq Cryst Lett* 1986, 4, 15–22; (d) Ballauff, M. *Mol Cryst Liq Cryst* 1986, 136, 175–195.
- Brochard, F.; Jouffroy, J.; Levinson, P. *J Phys* 1984, 45, 1125–1136.
- Palfy-Muhoray, P.; De Bruyn, J. J.; Dunmur, D. A. *Mol Cryst Liq Cryst* 1985, 127, 301–319.
- Kelkar, V. K.; Manohar, C. *Mol Cryst Liq Cryst* 1986, 133, 267–276.
- Holyst, R.; Schick, M. *J Chem Phys* 1992, 96, 721–729.
- Liu, A. J.; Fredrickson, G. H. *Macromolecules* 1996, 29, 8000–8009.
- Dorgan, J. R.; Soane, D. S. *Mol Cryst Liq Cryst* 1990, 188, 129–146.
- Shen, C.; Kyu, T. *J Chem Phys* 1995, 105, 556–562.
- Lee, Y. S.; Bae, Y. C. *Macromol Theory Simul* 1999, 8, 544–550.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- Lasher, G. *Phys Rev A* 1972, 5, 1350–1354.
- Lebwohl, P. A.; Lasher, G. *Phys Rev A* 1972, 6, 426–429.
- Lin, Z.; Zhang, H.; Yang, Y. *Phys Rev E* 1998, 58, 5867–5872.
- Zhong, Z. Z.; Schuele, D. E.; Gordon, W. L.; Adamic, K. J.; Akns, R. B. *J Polym Sci Part B: Polym Phys* 1992, 30, 1443–1449.
- Khokhlov, A. R.; Semenov, A. N. *Macromolecules* 1982, 15, 1272–1277.
- Lin, J.; Zhou, H.; Zhou, D. *Polymer* 2001, 42, 549–554.
- (a) Lin, J.; Lin, S.; Chen, T.; Tian, X. *Macromolecules* 2004, 37, 5461–5467; (b) Lin, J.; Lin, S.; Liu, P.; Hiejima, T.; Furuya, H.; Abe, A. *Macromolecules* 2003, 36, 6267–6272.
- Lin, C. Y.; Schick, M. *Macromolecules* 2005, 38, 5766–5773.
- Patnaik, S. S.; Pachter, R. *Polymer* 2002, 43, 415–424.
- Olabisi, O.; Simha, R. *Macromolecules* 1975, 8, 206–210.
- Flory, P. J.; Orwoll, R. A.; Vrij, A. *J Am Chem Soc* 1964, 86, 3507–3514.
- Wojtowicz, P. J.; Sheng, P. *Phys Lett A* 1974, 48, 235–236.
- Lelidis, I.; Durand, G. *Phys Rev E* 1993, 48, 3822–3824.
- Peng, S. C.; Yu, J. W.; Lee, S. N. *J Polym Sci Part B: Polym Phys* 1997, 35, 1373–1381.