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Phase transitions in mixtures of a side-on-side chain liquid crystalline polymer and low molar mass nematic liquid crystals

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Miscibility phase diagrams of mixtures of side-on side chain liquid crystalline polymers (s-SCLCP) and low molar mass liquid crystals (E48 and E44) have been established by means of polarized optical microscopy and light scattering. E48 and E44 are cyanobiphenyl-based eutectic nematic liquid crystal (LC) mixtures with nematic–isotropic transition temperatures of 93 and 105°C, respectively. The phase diagram of the s-SCLCP/E48 system reveals the coexistence of an isotropic + nematic region and a single nematic phase in order of descending temperature. The single nematic phase suggests that the pair is miscible in the nematic region. On the other hand, the s-SCLCP/E44 mixture shows liquid + liquid and nematic + nematic coexistence phases, suggestive of the immiscibility character of the pair. These nematic phase diagrams of the s-SCLCP/E48 and s-SCLCP/E44 have been analysed in the context of the combined Flory–Huggins (FH) free energy for isotropic mixing and the Maier–Saupe (MS) free energy for nematic ordering of the mesogens. This combined FH/MS theory is capable of predicting the observed nematic phase diagrams consisting of liquid + liquid, liquid + nematic, nematic + nematic, and the pure nematic regions. The change of colour accompanying the appearance and disappearance of the inversion walls may be attributed to the temperature dependence of birefringence.

1. Introduction

One of the inherent problems associated with polymer dispersed liquid crystals (PDLCs) may be identified as poor wide-angle viewability when subjected to an applied electric field [1, 2]. To circumvent such a problem, an epoxy-based end-on side chain liquid crystalline polymer (e-SCLCP) was grafted with a mesogenic amine by linking through a flexible methylene spacer [3]. In this way it may be possible to match the refractive index of the mesogenic side group with that of the dispersing LC molecules in all directions, thereby improving the wide-angle viewability. The stability limit of the dispersing low molar mass liquid crystals (LCs) in the above e-SCLCP matrix has been investigated by establishing miscibility phase diagrams and examining the dynamics of phase separation of these SCLCP/LC mixtures [3, 4].

As part of our continuing effort in this area, we have synthesized a polymethacrylate-based side-on-side chain liquid crystalline polymer (s-SCLCP) in which the benzoate mesogen was suspended from its side through a flexible butyl spacer that, in turn, was grafted to the backbone chain [5]. In this paper, the s-SCLCP has been mixed with commercial eutectic liquid crystals (E48 and E44) by dissolving in a common solvent such as tetrahydrofuran (THF). E48 and E44 are cyanobiphenyl- and cyanotriphenyl-based eutectic LC mixtures, exhibiting a single nematic–isotropic (NI) transition at about 93°C and at 105°C, respectively. Phase equilibria and structural evolution in these systems have been investigated by using light scattering and optical microscopic methods. The nematic phase diagrams have been analysed in the context of the combined Flory–Huggins (FH) theory for isotropic mixing and Maier–Saupe (MS) theory of nematic ordering [4]. The development of iridescent colour in a narrow temperature gap of the nematic phase diagrams is discussed in terms of director tilting leading to birefringence change with temperature.

2. Theory of nematic phase equilibria

The total free energy of mixing of a binary nematic mixture, g, is customarily described by a simple addition of the free energy of mixing of isotropic liquids, g^i, and the free energy of nematic ordering of the constituent

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liquid crystals, g^n, i.e. $g = g^i + g^n$. The free energy of isotropic mixing of a binary polymer blend is expressed generally in terms of the Flory–Huggins theory [6, 7]:

$$g^i = \frac{G^i}{nk_B T} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2 \tag{1}$$

where k_B is the Boltzmann constant and T the absolute temperature. r_1 is the number of sites occupied by one liquid crystal molecule, whereas r_2 represents the number of sites occupied by a single liquid crystalline polymer chain. ϕ_1 and ϕ_2, representing the volume fractions of component 1 and 2, respectively, are defined as $\phi_1 = n_1 r_1 / n$ and $\phi_2 = n_2 r_2 / n$ with $n = n_1 r_1 + n_2 r_2$ [4, 7]. n_1 and n_2 are the numbers of liquid crystal molecules and liquid crystalline polymer chains, respectively. χ is known as the Flory–Huggins interaction parameter and is generally assumed to be a function of reciprocal absolute temperature, i.e. $\chi = A + B/T$, where A and B are constants [7].

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 [4, 8–10] representing the free energy of nematic ordering:

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

where Σ_1 and Σ_2 represent the decrease of entropy due to the alignment of individual LC molecules of component 1 and the mesogenic groups of component 2, respectively. The last three terms of equation (2) represent the enthalpic contribution. ν_{11} and ν_{22} are the nematic interaction parameters of the pure constituent LCs, 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 as [9, 10]

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

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

$$\langle \cos^2 \theta_j \rangle = \int \cos^2 \theta_j f(\theta_j) \, \mathrm{d} \cos \theta_j. \tag{4}$$

Here, $f(\theta_j)$ represents the normalized orientation distribution function and is considered to be symmetric around the reference axis. It is further given as

$$f(\theta_j) = \frac{1}{4\pi Z_j} \exp \left[-\frac{u(\theta_j)}{kT} \right] \tag{5}$$

where Z_j is the partition function defined as

$$Z_j = \int \exp \left[-\frac{u(\theta_j)}{kT} \right] \mathrm{d}\Omega_j \tag{6}$$

where Ω_j denotes the solid angle. $u(\theta_j)$ is the potential of a director orientation; it is taken to be proportional to the second order Legendre polynomials as

$$\frac{u(\theta_j)}{kT} = -\frac{1}{2} m_j (3 \cos^2 \theta_j - 1) \tag{7}$$

in which m_j is a dimensionless mean field parameter characterizing the strength of the potential field [10].

The order parameter s_j can then be related to Z_j through

$$s_j = \int f(\theta_j) \frac{1}{2} (3 \cos^2 \theta_j - 1) \, \mathrm{d} \cos \theta_j = \frac{1}{Z_j} \frac{\mathrm{d} Z_i}{\mathrm{d} m_j} \tag{8}$$

and the entropy Σ_j can be deduced as

$$\Sigma_j = -\int f(\theta_j) \ln [4\pi f(\theta_j)] \, \mathrm{d}\Omega_j = \ln Z_j - m_j s_j. \tag{9}$$

The nematic interaction parameters, ν_{11} and ν_{22}, of the individual mesogenic component are shown to have inverse temperature dependence as $\nu_{jj} = 4.541 \, (T_{\mathrm{NI},j}/T)$. It is assumed that $\nu_{12} = \nu_{21}$ and $\nu_{12} = c(\nu_{11} \nu_{22})^{1/2}$ to accommodate any departure from its geometric means [4]. c is the proportionality constant characterizing the relative strength of the cross-interaction between the two dissimilar mesogens as compared with that in the same mesogens. Equations (1) and (2) can be solved self-consistently by minimizing the free energy with order parameter to establish the free energy curves as a function of temperature. From these free energy curves, the coexistence points may then be determined by using a double tangent method. The detailed calculation of nematic phase diagrams may be referred to in a previous paper [4].

3. Experimental

A side-on side chain liquid crystalline polymer (s-SCLCP) was synthesized by grafting polymethacrylate with a 2,5-bis(4-butoxybenzoyloxy)benzoate mesogen interlinked with a butyl spacer [5]. The weight average molecular weight was 48 000. The dispersing liquid crystals, commercially known as E48 and E44, were purchased from EM Industries. The exact compositions of these commercial liquid crystals are not known, except that both LCs contain cyanobiphenyl- and cyanotriphenyl-based eutectic LC mixtures exhibiting a single nematic–isotropic (NI) transition at 105°C for E44 and at 93°C for E48. Various ratios of s-SCLCP and LC (E48 or E44) mixtures were dissolved together in tetrahydrofuran (THF) and stirred vigorously at ambient temperature.

Polymer dispersed liquid crystal (PDLC) films were then solvent cast onto glass slides. The thin film (about 10 μm thick) thus formed was heated on a heating block at 120°C for 2 min, then covered with a cover glass.

Temperature versus composition phase diagrams of s-SCLCP/E48 and of s-SCLCP/E44 mixtures were established by means of a cloud point method at a heating and cooling rate of 1°C $\min^{-1}$. The evolution of phase-separated structure and concomitant nematic formation was studied by light scattering and optical microscopy. A polarizing optical microscope (Nikon, Optiphot 2-pol), equipped with polarizers and a Nikon camera (FX-35DX), was utilized to determine the coexistence regions by monitoring the change of mesophase structures during heating and cooling cycles. A Mettler hot stage (FP82HT) having a resolution of ±0.1°C was used for temperature control. The heating scans were undertaken at a rate of 0.5 or 1°C $\min^{-1}$.

4. Results and discussion

4.1. *Characterization of s-SCLCP*

Figure 1 shows the side-on side chain liquid crystalline polymer (s-SCLCP) synthesized in this laboratory which consisted of polymethacrylate grafted with a 2,5-bis(4-butoxybenzoyloxy)benzoate mesogen interlinked through a butyl spacer. In fact, the benzoate mesogen was suspended from its side at the *ortho*-position of one of the benzene rings, therefore the resulting asymmetric linkage may have caused twisting of the mesogen about the flexible spacer. According to the results of our associated DSC study, the s-SCLCP exhibits a glass transition temperature around 50°C and a nematic–isotropic transition at 114°C in the pure state [5]. This nematic–isotropic transition was confirmed here to be about 115°C in the light scattering studies.

4.2. *Phase diagrams and evolution of mesophase structure in s-SCLCP/E48*

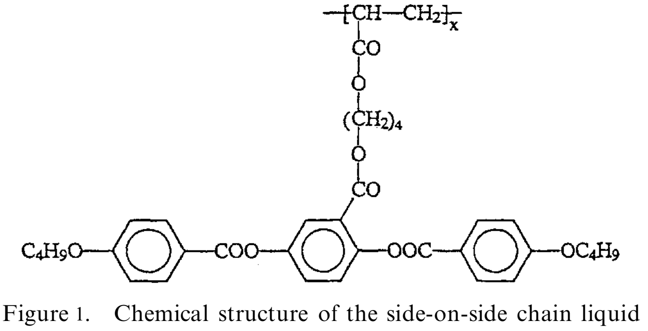

Figure 1. Chemical structure of the side-on-side chain liquid crystalline polymer based on polymethacrylate grafted with a 2,5-bis(4-butoxylbenzoyloxy)benzoate mesogen and connected via a butyl spacer at its side.

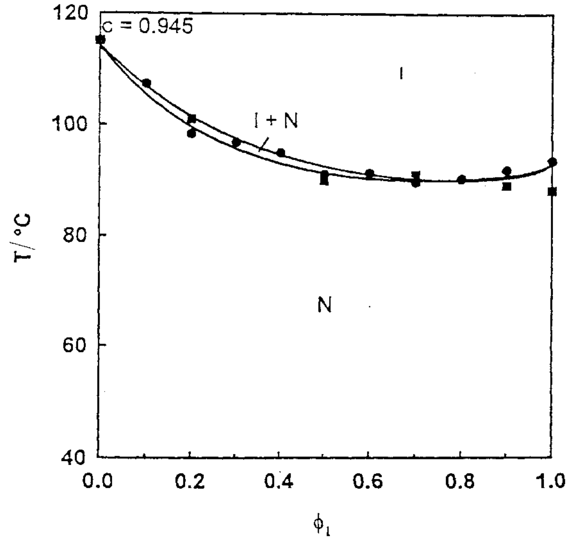

Figure 2. Phase diagrams (filled symbols) of s-SCLCP/E48 mixtures in comparison with the theoretical prediction (solid curves) based on the combined FH/MS theory. The filled circles and square symbols were obtained from light-scattering and polarized optical microscopy, respectively.

Figure 2 depicts the cloud point temperatures of the side-on SCLCP/E48 system along with the calculated phase diagram (solid lines). The calculation was carried out by setting the c parameter, which represents the relative strength of the cross-nematic interaction to that of the pure mesogens, to be 0.945, and the ratio of the polymer segment and the LC molecule, r_2/r_1, to be 9/1. The combined Flory–Huggins/Maier–Saupe (FH/MS) theory used here is basically a mean-field model in which stability of the nematic phase is assumed to arise from the nematic interaction of the mesogenic groups [4]. The flexibility of polymer backbone chains was neglected here as it may be insignificant for the ordering of the side group LCs in the side chain liquid crystalline polymers. Other transitions associated with crystal, smectic, cholesteric, or twisted mesophases, even if they exist, were ignored in the present calculation. The temperature dependence of χ has been estimated by choosing an appropriate A value. The B value in turn may be estimated from the critical temperature of the liquid–liquid equilibrium through the relationship of $B=(\chi_c - A)T_c$. Since there appears no liquid + liquid coexistence region in the phase diagram, the choice of A or χ value is inconsequential in calculating the isotropic + nematic (I + N) coexistence curve.

As shown in figure 2, the phase diagram consists of isotropic (I), isotropic + nematic, and a single-phase nematic (N) region in the order of descending temperature. A similar phase diagram was reported by Finkelmann and co-workers [11] for a mixture containing an end-on SCLCP, namely poly(dimethyl siloxane), to which was attached a methoxyphenylbenzoate side group, and

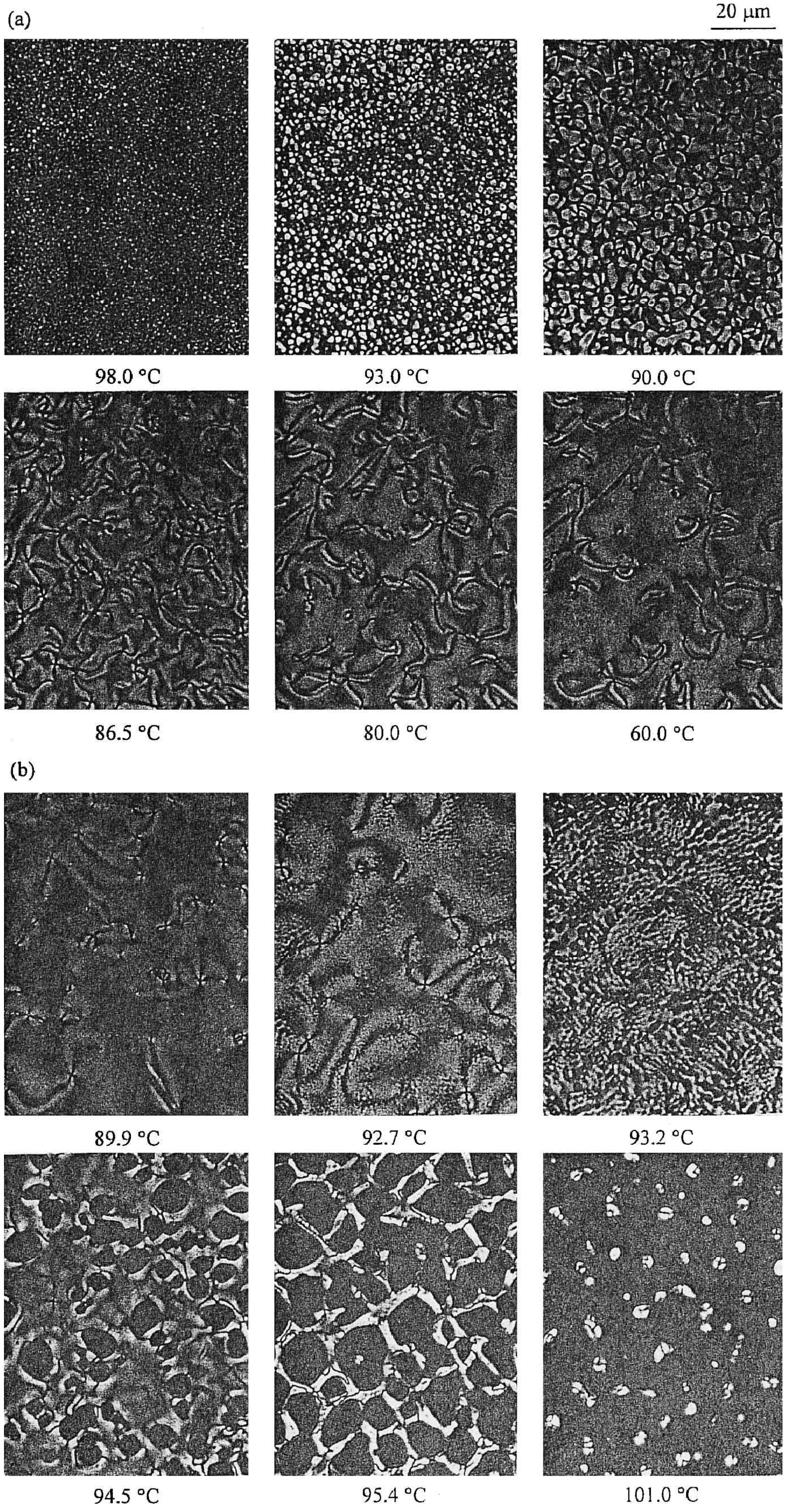

Figure 3. Evolution of mesophase structure of the 80/20 (v/v) s-SCLCP/E48 composition during (*a*) cooling and (*b*) heating cycles. The ramp rate was 1°C min^{-1}.

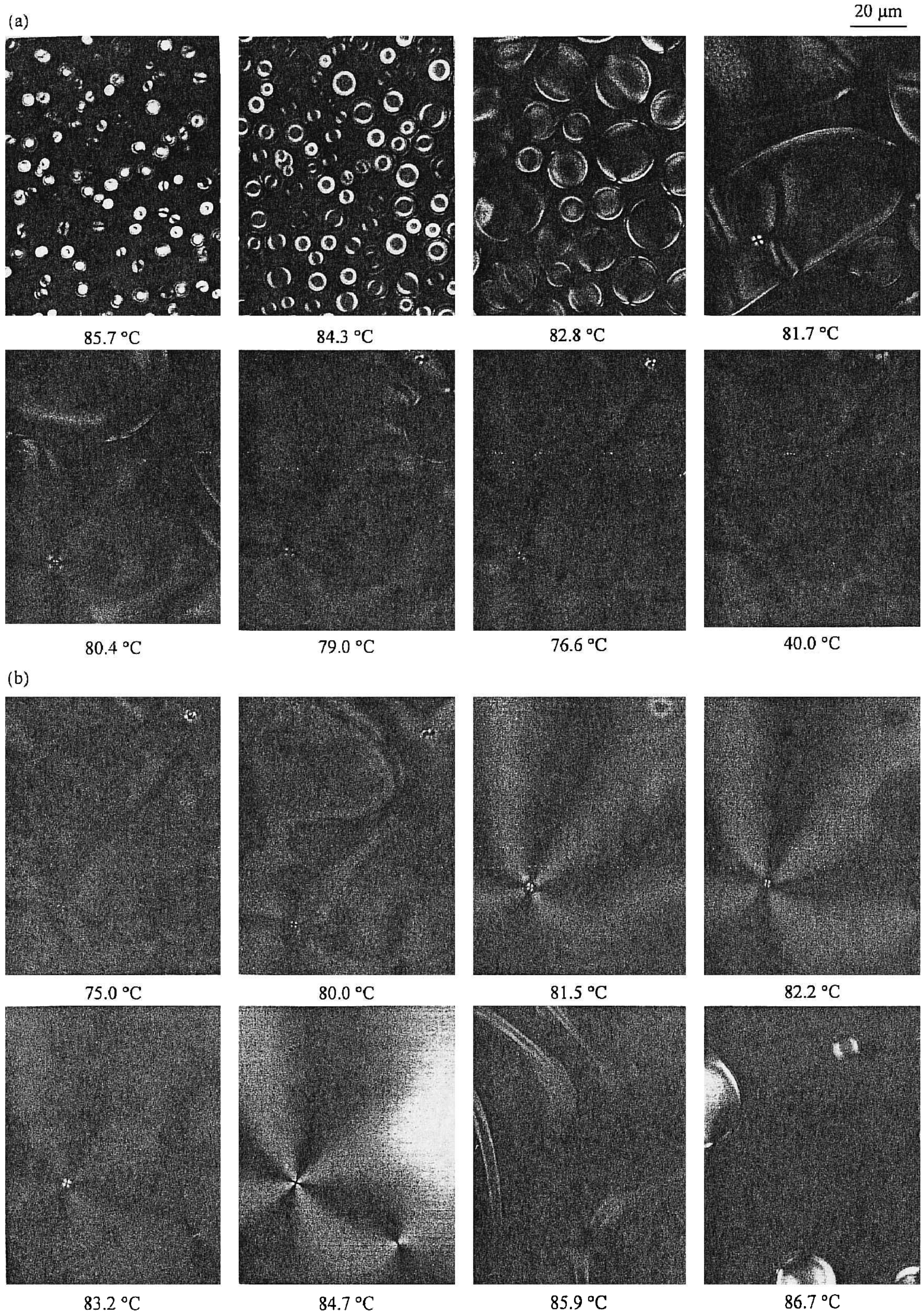

Figure 4. Evolution of mesophase structure of the 10/90 (v/v) s-SCLCP/E48 composition during (*a*) cooling and (*b*) heating cycles. The ramp rate was 1°C min^{-1}.

4-propyloxyphenyl 4′-hexyloxybenzoate liquid crystals. The phase behaviour of such a nematic phase diagram is relatively straightforward, and thus it can be fitted remarkably well with our theoretical calculation for two nematic mixtures.

At the 20 vol % liquid crystal (E48) composition, the phase transformation occurs in a sequence of I, I+N, and the pure N reversibly in the order of descending temperature [figures 3 (*a*) and 3 (*b*)]. Upon cooling, multiple droplets first develop at 98°C and grow through coalescence. Concurrently, nematic line disclinations with the strength of ±1 appear within the growing domains. As the domains coalesce, the annihilation of line disclinations occurs concurrently, exhibiting the so-called schlieren textures [9]. In this region, LC directors are substantially aligned parallel to the supporting glass substrates. The dark brushes grow in size while their numbers decrease due to annihilation. Upon heating above the NI transition temperature of E48, thermal and concentration fluctuations increase, leading to the isotropicalization of the nematic LC-rich region. This temperature gap corresponds to the I+N coexistence region. The dark isotropic region appears and gets wider while the s-SCLCP forms a network, which breaks down with continued heating. It should be emphasized that the phase transition in the 80/20 s-SCLCP/E48 occurs reversibly as required by thermodynamics, but the evolution of the phase-separated structures show considerably different characteristics during cooling and heating cycles, suggesting that the kinetic path is different.

In the composition which is rich in the low molecular weight LC such as the 10/90 s-SCLCP/E48 composition, multiple droplets appear in the isotropic medium since the system recognizes that it passes through the I+N region during cooling, figures 4 (*a*) and 4 (*b*). These droplets grow in diameter via coalescence with time as well as with continued cooling. Nematic structures develop within these growing droplets leading to the bipolar structure. The initial birefringent colour in the bipolar droplets may result from the tilt angles of the LC molecules or the LC director anchoring on the surface or droplet walls. When these droplets touch each other and coalesce, the bipolar structure disappears and eventually transforms to a schlieren texture with a four-dark-brush pattern, suggesting a strength of disclination of ±1. Concurrently, the distinct iridescent colour appears in a narrow temperature gap that changes from green (81.7°C) to red (80.4°C). In the heating runs, the iridescent colour changes in the sequence of rose (81.5°C) to greenish (82.2°C) to blue (83.2°C) and to yellow (84.7°C) in a narrow temperature gap as depicted in

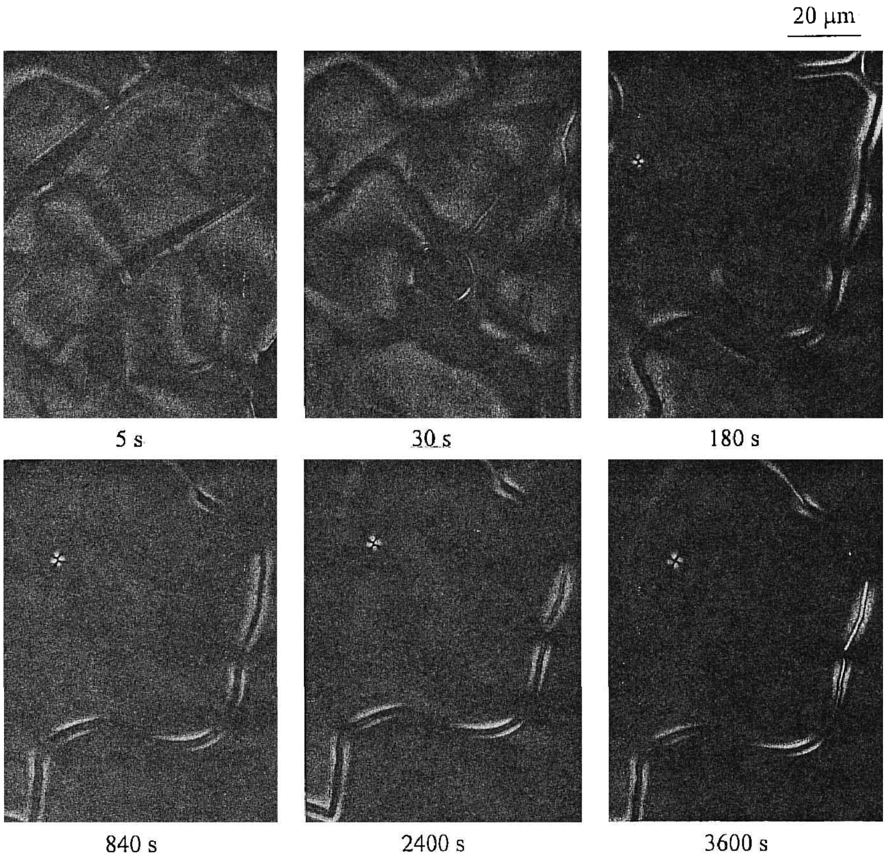

Figure 5. Temporal evolution of the mesophase structure of the 10/90 (v/v) s-SCLCP/E48 composition following a temperature quench from a single phase (100°C) to a temperature gap exhibiting iridescent colours (80°C).

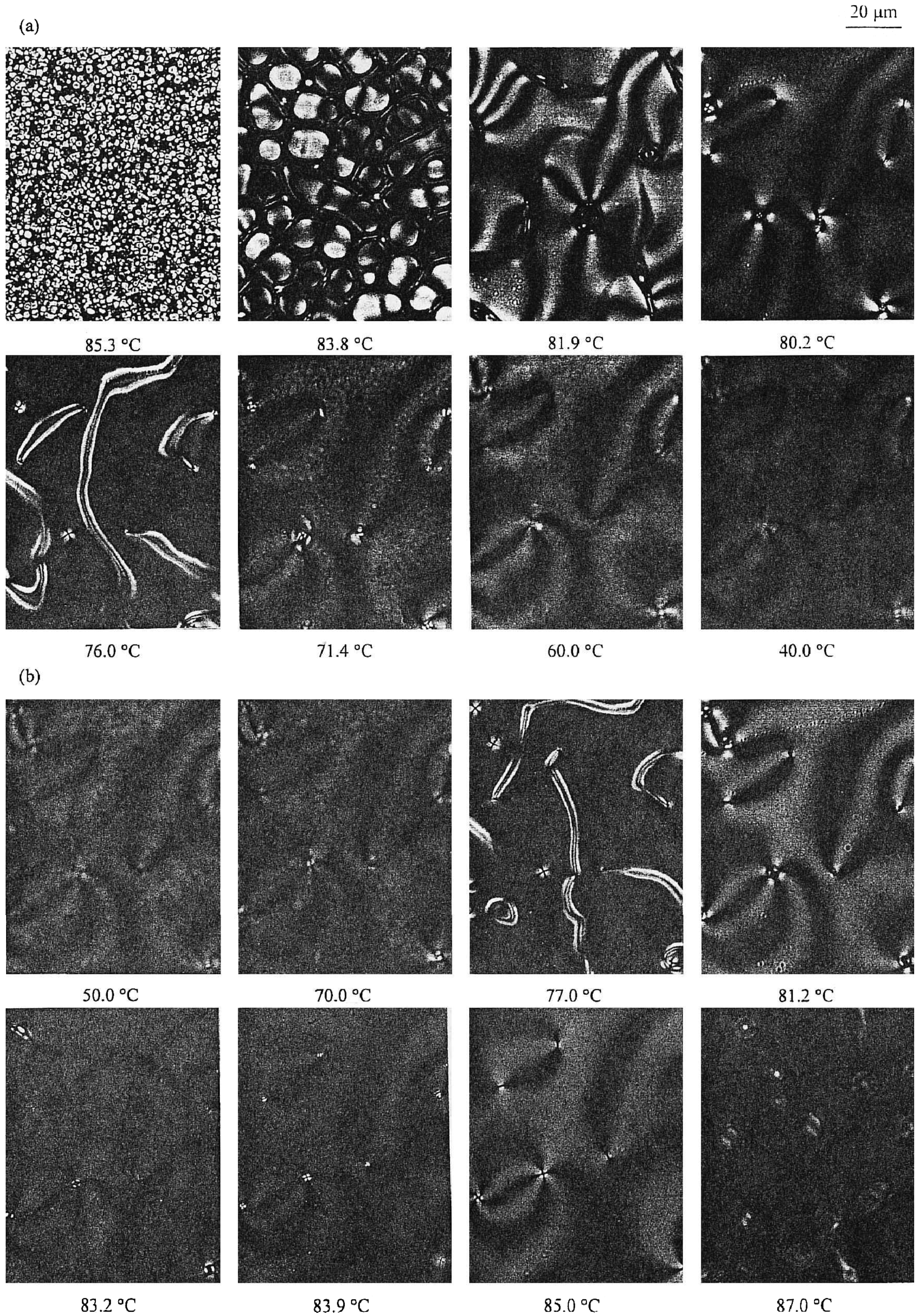

Figure 6. Evolution of the mesophase structure of the 50/50 (v/v) s-SCLCP/E48 composition during (*a*) cooling and (*b*) heating cycles. The ramp rate was 1°C min^{-1}.

figure 4 (*b*). It should be noted that the characteristic of the iridescent colour change in this narrow temperature gap is similar in character to that of a blue phase found in some twisted nematics [12–14]. At present, we do not have independent evidence to substantiate the existence of a blue phase, although such a possibility cannot be ruled out in this system.

When the temperature quench experiment is performed from the isotropic state (100°C) into this narrow temperature gap, e.g. 80°C, some colourful disclinations appear which subsequently annihilate while displaying a thread-like structure characteristic of an inversion wall (figure 5) [9, 10]. This kind of inversion wall may be simply due to the orientation of LC directors aligned in opposite directions. It seems to suggest that the LC tilting or director reorientations may affect birefringence, resulting in change of colour with temperature. However, the change of director tilt angles is often accompanied by change of textures, such as the appearance and disapearance of inversion walls with continued cooling.

Figures 6 (*a*) and 6 (*b*) depict the evolution of mesophase structures of the 50/50 mixture during heating and cooling. A similar droplet formation and coalescence can be discerned. In the temperature range 81.9–76.0°C where the change of iridescent colour is dominant, annihilation of the disclinations occurs while formation and disappearance of the inversion wall can be seen reversibly in conjunction with the iridescent colour changes, figure 6 (*a*). At 76°C, a spectrum of colours develops which may be attributed in part to the temperature dependence of birefringence resulting from the opposite orientations of the LC directors near the inversion walls, creating singularities. It appears that the LC tilt angles continue to change with temperature with further cooling to lower temperatures (60–40°C) which may be attributed to the change of residual birefringence (or residual stress) as SCLCP vitrifies in the vicinity of its glassy state. As expected, this colour change is also thermally reversible, figure 6 (*b*). A similar development of line disclinations and colour change phenomenon can be confirmed in the 30/70 s-SCLCP/E48 composition during the course of cooling and heating cycles.

4.3. *Phase diagram and mesophase structure in s-SCLCP/E44*

Figure 7 depicts the cloud point temperatures of the side-on SCLCP/E44 system in comparison with the calculated coexistence curves (solid lines) of the nematic phase diagram. The *c* parameter was set to be 0.95 and the ratio of polymer segment and the LC molecule was taken as $r_2/r_1 = 9/1$. The temperature dependence of χ may be estimated by choosing an appropriate A value (-1.0 in the present case) to account for the broadness of the liquid–liquid coexistence curve. The B value in turn was estimated from the critical temperature of the liquid–liquid equilibrium, i.e. $B = (\chi_c - A)T_c$, where T_c and χ_c represent the critical temperature and critical interaction parameter, respectively. The value of A is generally dictated by the critical temperature and broadness of the liquid–liquid coexistence curve, but the influence of χ is insignificant for the isotropic–nematic coexistence region. It is significant that the choice of the cross-nematic interaction parameter c and T_c predominates in the nematic coexistence regions as compared with the χ effect.

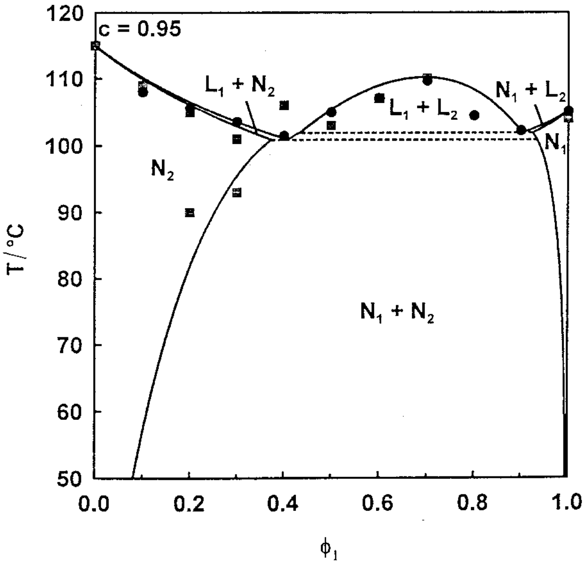

Figure 7. A cloud point phase diagram of the s-SCLCP/E48 mixture in comparison with the calculated coexistence curves, showing liquid + liquid, liquid + nematic, single phase nematic and nematic + nematic coexistence regions. The filled circles and the square symbols were obtained from light-scattering and optical microscopic measurements, respectively.

The calculated phase diagram, as depicted in figure 7, reveals the existence of liquid + liquid, and nematic + nematic phases in the intermediate compositions, and two pure nematic regions at high E44 content (N_1) and high concentration of s-SCLCP (N_2), respectively. The two dotted lines are the peritectic lines, which represent coexistence of three different phases consisting of two liquids plus one nematic or one liquid plus two nematics. There are two narrow nematic–liquid coexistence regions labelled $N_1 + L_2$ and $L_1 + N_2$ where subscripts 1 and 2 represent the LC and s-SCLCP constituents, respectively. When the temperature falls below the second peritectic line, a two-phase nematic region ($N_1 + N_2$) appears. This observed behaviour of phase-separated nematics is strikingly different from that of the s-SCLCP/E48 system in which the two constituents have formed a single nematic phase suggestive of miscible character. The major differences between E44 and E48 is the NI transition temperatures (T_{NI}) in which E44 presumably contains more rigid cyanotriphenyl mesogenic moieties than E48, thereby exhibiting a higher T_{NI} and poorer miscibility with the s-SCLCP.

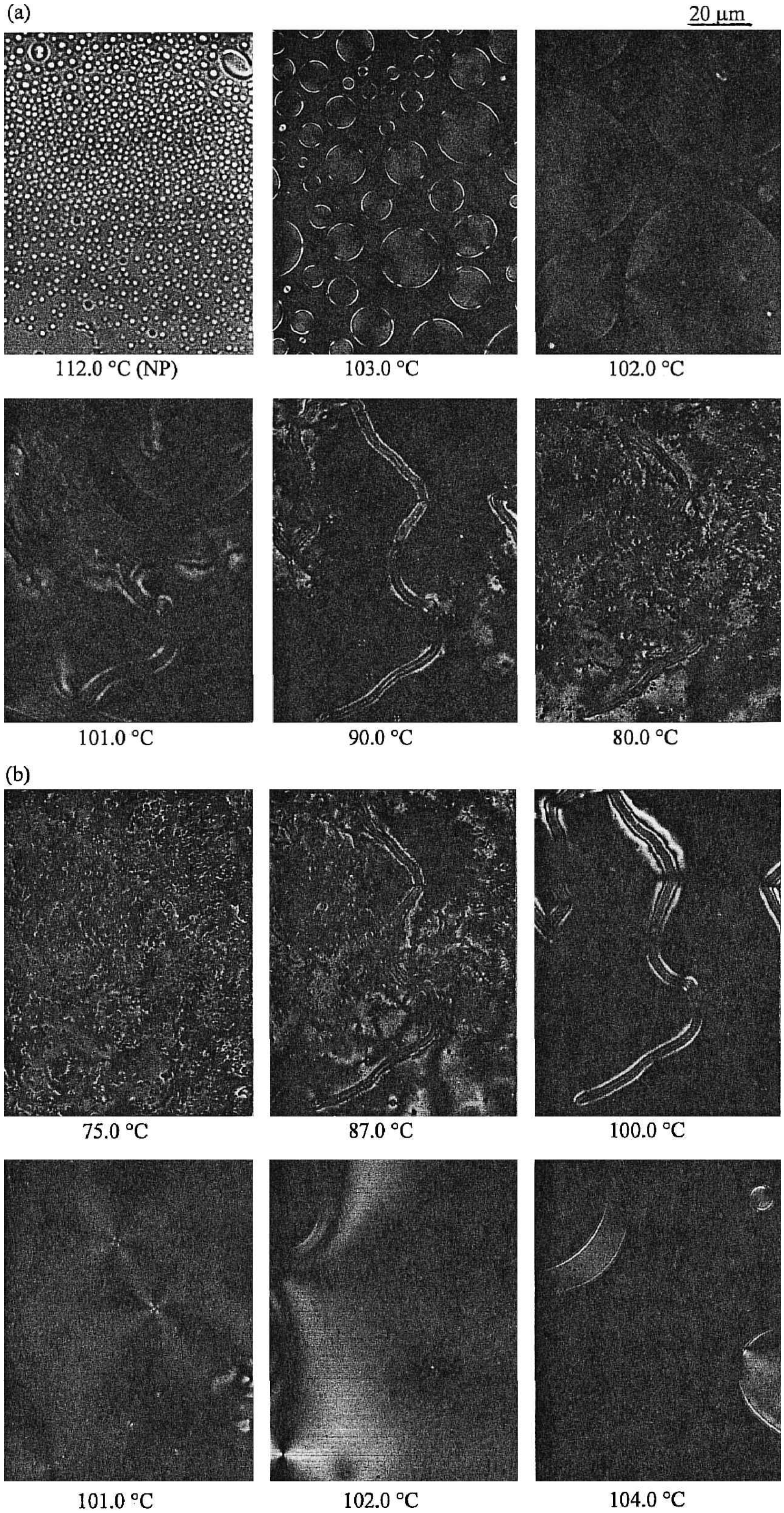

Figure 8. Evolution of the mesophase structure of the 30/70 (v/v) s-SCLCP/E44 composition during the course of (*a*) cooling and (*b*) heating cycles. The ramp rate was 0.5°C min^{-1}.

To identify these coexistence regions, the evolution of structure was investigated at various compositions by polarized optical microscopy. Figures 8 (*a*) and 8 (*b*) exhibit the structure development at the 30/70 s-SCLCP/E44 composition during heating and cooling cycles at a rate of 0.5°C min^{-1}. Upon cooling from the isotropic state (120°C), tiny droplets appear first around 110°C. The droplet formation in the early stage of phase separation is observable only under the unpolarized condition, indicative of liquid–liquid phase separation. With continued cooling, these droplets grow in size through coalescence. Concurrently, nematic ordering takes place within the growing domains in which bipolar droplet structures appear predominantly while exhibiting some iridescent colour. In the vicinity of 103–101°C, annihilation of the LC defects occur within the droplets during coalescence. The droplet structures eventually transform to a thread-like structure characteristic of an inversion

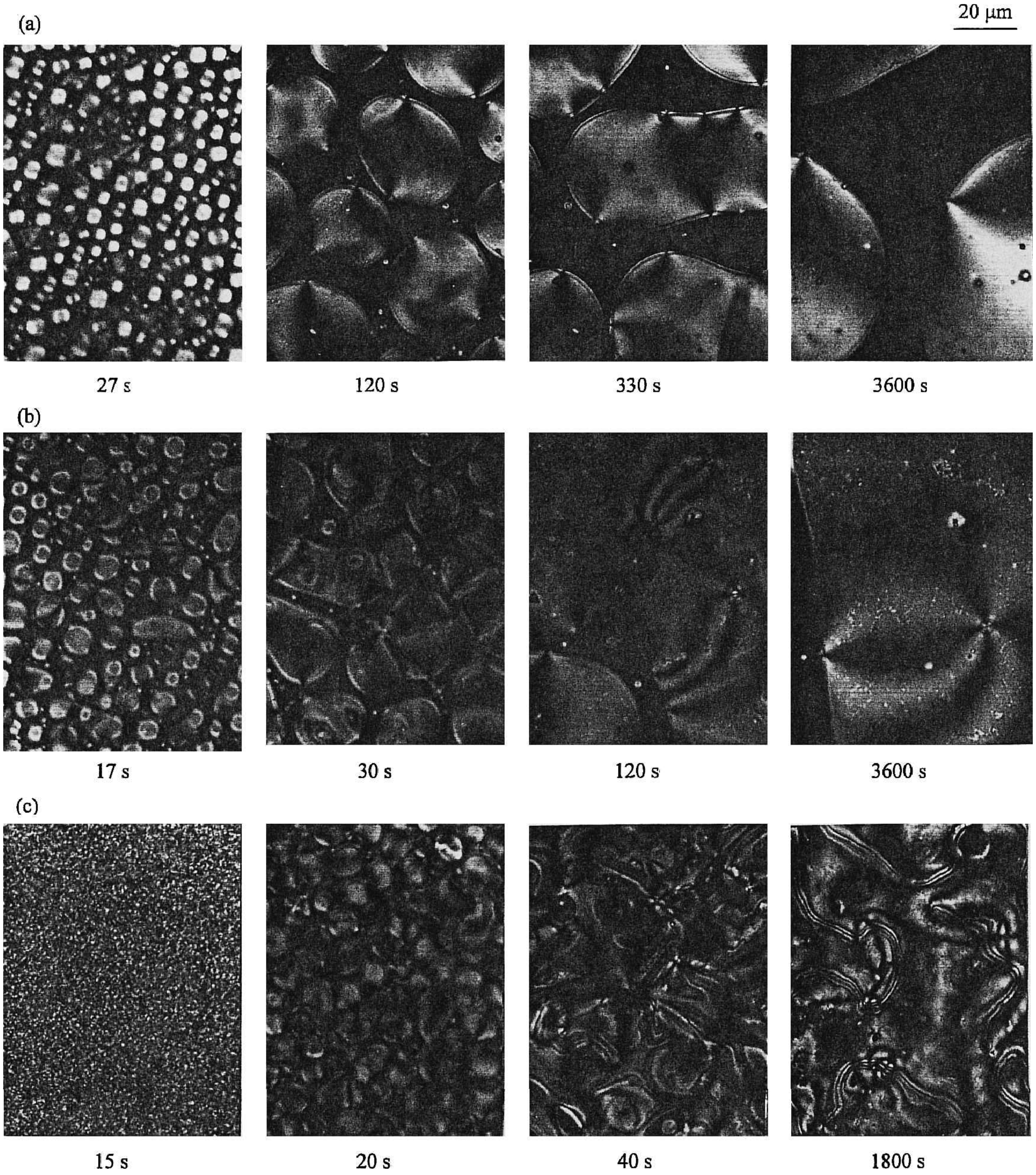

Figure 9. Time evolution of mesophase structure following temperature quenches from 120°C to (*a*) 100, (*b*) 98, and (*c*) 95°C for the 30/70 (v/v) s-SCLCP/E44 mixture.

wall [9]. Newer tiny droplets appear in the background and become birefringent during coarsening with continued cooling. The picture at 80°C in figure 8 (*a*) represents the coexistence of two nematics ($N_1 + N_2$), as predicted by the FH/MS theory for the low temperature region, which is considerably different from the single nematic phase of the s-SCLCP/E48 system.

During the course of heating at 0.5°C $\min^{-1}$ from 75 to 100°C, one of the two phase-separated nematics becomes isotropic in the reverse sequence of the cooling process, figure 8 (*b*). The thread-like structure reappears. At this point, the system has gained sufficient mobility to flow. The thread-like structure transforms to large domain textures while exhibiting line disclinations with strength of ± 1 [9]. Some colours can be discerned in the microscopic view before the mixture eventually becomes isotropic. It is interesting to see that the evolution of mesophase structures follows a slightly different route indicating that the kinetic path is somewhat different, although the phase transition is thermally reversible in a thermodynamic sense.

The observed iridescent colours (101 ~ 102°C) may be attributed to birefringence change associated with LC director tilting with temperature. To confirm this mechanism further, several temperature quench experiments were performed from 120 to 100, 98, and 95°C. In the case of a 100°C quench, multiple droplets form spontaneously and grow rapidly through coalescence while bipolar structure develops within these growing droplets, figure 9 (*a*). Upon quenching to 98°C, multiple droplets appear first, followed by coalescence, figure 9 (*b*). The bipolar structure transforms into line disclinations as droplets coalesce. The colour is predominantly rose but tinted with some green. When quenching is undertaken to a slightly lower temperature of 95°C, the coalescence process is so fast that the thread-like structures appear instantaneously while showing annihilation of the defects, figure 9 (*c*). The heterogeneous nematic structures suggest phase separation between the constituent nematics. The colour development associated with the appearance and disappearance of the inversion walls may be attributed to birefringence resulting from the distribution of director tilt angles.

Next, structure evolution of the 70/30 s-SCLCP/E44 composition was investigated to verify the pure nematic phase in the high s-SCLCP regime. A temperature quench experiment was performed from 120°C into a single nematic region of the 70/30 s-SCLCP/E44. Schlieren textures with a strength of ± 1 develop predominantly and subsequently annihilate with elapsed time (figure 10). The growth process is clearly discernible but it is extremely difficult, if not impossible, to quantify the exponent of

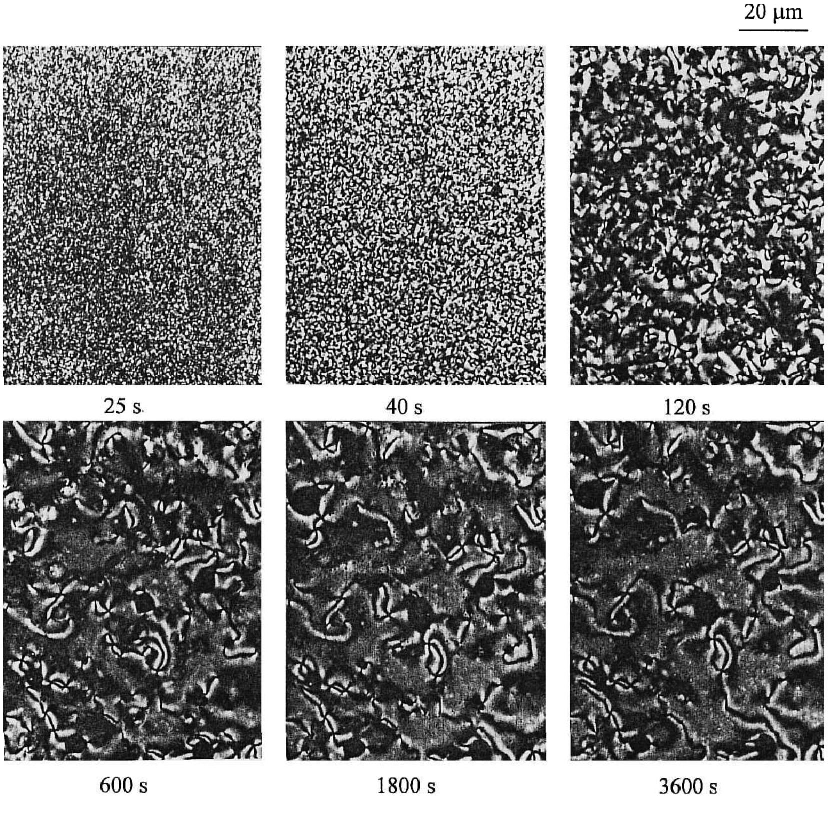

Figure 10. Time evolution of mesophase structure following temperature quenches from 120°C to 95°C at the off-critical 70/30 (v/v) s-SCLCP/E44 mixture.

defect dynamics. Nevertheless, the single phase nematic structure is clearly identifiable, as it is strikingly similar to the single nematic phase of s-SCLCP/E48; it is certainly different from the structure of the two phase nematics in figure 8.

5. Conclusions

We have demonstrated that the combined FH/MS theory having two orientational order parameters and two clearing transition temperatures is capable of predicting various phase diagrams for nematic mixtures containing a side-on side chain liquid crystalline polymer as one component. The FH/MS theory is capable of explaining the nematic coexistence curve of the experimental phase diagram remarkably well. The phase diagram of the s-SCLCP/E48 is relatively straightforward, exhibiting the isotropic, isotropic + nematic, and a single nematic region. The phase diagram consists of liquid + liquid, liquid + nematics and nematic + nematic regions in the intermediate compositions, and a single nematic phase in the s-SCLCP-rich or E44-rich regions. The nematic phase diagram, exhibiting the two nematic coexistence region, is considerably different from a simpler nematic phase diagram of the s-SCLCP/E48 system where the constituent nematics are miscible.

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