Phase Diagram and Evolution of Mesophase Structure in Mixtures of a Low Molar Mass Smectic Liquid Crystal and a Nematic Side-on Side-Chain Liquid Crystalline Polymer

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ABSTRACT: Miscibility phase diagrams in mixtures of side-on side-chain liquid crystalline polymers (s-SCLCP) and low molar mass smectic liquid crystals (K36) have been investigated by means of polarized optical microscopy. K36 is a smectic liquid crystal that exhibits a smectic−isotropic transition at 58 °C and a smectic-to-crystal transition (crystallization) at 27 °C. The nematic/smectic phase diagram of the s-SCLCP/K36 has been analyzed by combining the Flory−Huggins (FH) free energy for isotropic demixing and the Maier−Saupe−McMillan (MSM) free energy for smectic ordering of the mesogens. This combined FH/MSM theory compares reasonably well with the observed nematic/smectic phase diagrams composed of isotropic + nematic, smectic + nematic, smectic + isotropic, pure nematic, and pure smectic regions. Several temperature quench experiments have been conducted to confirm various predicted coexistence regions. However, at present, the combined theory does not include any crystallization processes occurring at a lower temperature.

Introduction

In a previous paper,[1] we developed a mean-field theory to predict various phase diagrams of a binary smectic-A mixture based on the combination of Flory−Huggins (FH) theory for isotropic demixing and the Maier−Saupe−McMillan (MSM) theory for smectic ordering. The predictive capability of this combined FH/MSM theory has been favorably demonstrated on the basis of the reported smectic phase boundaries. This theory has been employed to elucidate the occurrence of an induced smectic phase due to the strong mesogenic interactions of the constituent nematic liquid crystals.[2] Again, comparisons with the induced smectic boundaries of the experimental phase diagrams showed remarkable agreement, attesting to the validity of the theory. This smectic theory was further extended in order to predict various coexistence regions involving liquid + liquid, liquid + nematic, pure nematic, smectic + liquid, smectic + nematic, pure nematic, pure smectic, and induced smectic phases in nematic/smectic mixtures.[3]

The purpose of the present paper is to establish an experimental phase diagram for mixtures of s-SCLCP and a smectic liquid crystal (K36) using polarized optical microscopy. The experimental nematic/smectic phase diagram of K36/s-SCLCP has been analyzed in the framework of the combined Flory−Huggins (FH) free energy for isotropic mixing[4,5] and the Maier−Saupe−McMillan (MSM) free energy for smectic ordering of the mesogens.[6−9] It was found that the predicted coexistence curves based on this combined theory conform remarkably well to those observed in the experimental phase diagram of the K36/s-SCLCP system. Several temperature quench experiments have been conducted at several compositions to verify various coexistence regions predicted by the theory.

Experimental Section

The side-on side-chain liquid crystalline polymer was synthesized by grafting polymethacrylate with a 2,5-bis((4-butoxybenzoyl)oxy)benzoate mesogen connected by a butyl group; i.e., the flexible butyl spacer was linked asymmetrically to the middle section of the benzoate mesogen.[10] The s-SCLCP exhibits a nematic−isotropic (NI) transition (T_{NI}) at 114 °C. The dispersing liquid crystal, commercially known as K36, was purchased from EM Industries. K36 is a smectic liquid crystal exhibiting an isotropic−smectic-A ($I-S_{mA}$) transition at 58 °C and a smectic-A to crystal transition ($S_{mA}-K$) at about 27 °C. Various mixtures of s-SCLCP and K36 were prepared by dissolving them together in tetrahydrofuran (THF) at ambient temperature. The solution was poured onto a slide glass and subsequently solvent-cast by evaporation. The resulting thin film (about 10 μm thick) was heated to the isotropic state (130 °C) on a heating block for 2 min and then covered with a cover glass.

A temperature versus composition phase diagram of the s-SCLCP/K36 mixture was established by polarized microscopy using a Nikon optical microscope (Model Optiphot 2-pol). Various coexistence points of nematic + liquid, pure nematic, liquid + smectic, nematic + smectic, and pure smectic regions were determined by monitoring structural changes during heating and cooling cycles. The ramp rate was typically 0.5 °C/min, but a slower rate (0.1−0.2 °C/min) was needed for compositions rich in s-SCLCP due to the high viscosity of the LCP molecules.

Results and Discussion

In general, all liquid crystals undergo phase transitions from nematic to isotropic or from smectic to isotropic directly or through a nematic phase.[6,7] In binary LC mixtures, phase separation may occur in various mesophase regions. When one of the constituents is a liquid crystalline polymer, liquid−liquid phase separation could also take place in isotropic regions. It is therefore essential to consider both isotropic demixing as well as anisotropic ordering of the constituent nematic and smectic LCs.[7] The total free energy density of demixing, g, of a binary nematic and smectic mixture may be expressed by simply adding the free energy density of demixing of isotropic liquids, g^i, and the free energy density of anisotropic ordering of the nematic and smectic liquid crystals, g^a, i.e., $g = g^i + g^a$.[7] However, these isotropic and anisotropic free energy densities are coupled through their volume fractions as described below.

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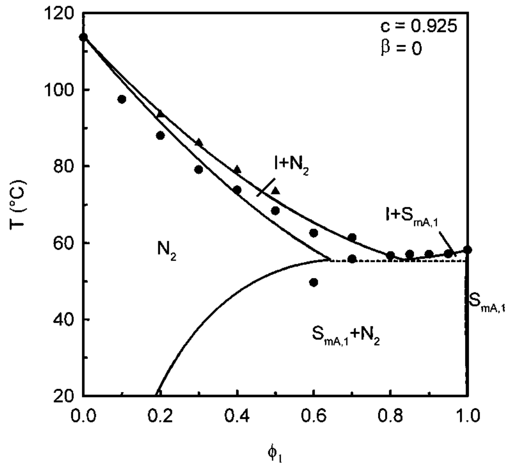


Figure 1. Smectic/nematic phase diagram of the K36/s-SCLCP mixture in comparison with the calculated coexistence curves, showing isotropic + nematic, single nematic, isotropic + smectic, single smectic, and smectic + nematic coexistence regions. The filled circles and the triangle symbols were obtained during the cooling and heating cycles of the optical microscopic investigations, respectively. ϕ_1 represents the volume fraction of K36, assuming the densities of K36 and s-SCLCP are the same, and $\beta = \alpha_{in}$.

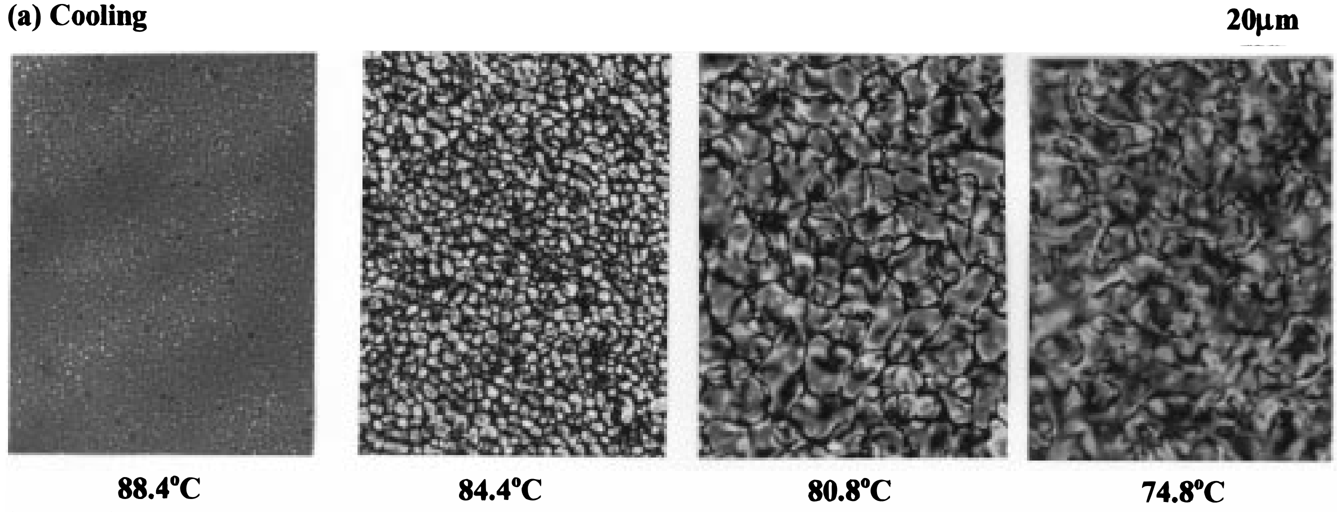
The free energy density of a binary isotropic LC/isotropic SCLCP blend has been customarily described in the context of the Flory–Huggins free energy expression,[4,5] viz.,

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

where k is Boltzmann's constant and T is the absolute temperature. r_1 represents the number of sites occupied by one liquid crystal molecule, whereas r_2 signifies the number of statistical segments or sites occupied by a single polymer chain. ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively, which can be defined as $\phi_1 = n_1r_1/n$, $\phi_2 = n_2r_2/n$, and $n = n_1r_1 + n_2r_2$, where n_1 and n_2 are the numbers of liquid crystal and polymer molecules, respectively. χ is the Flory–Huggins interaction parameter, which is generally assumed to be a function of reciprocal absolute temperature, viz., $\chi = A + B/T$, where A and B are constants.[5]

The anisotropic part of the free energy density for a mixture of nematic and smectic liquid crystals may be described as follows[1,3]

$$g^a = \frac{G^a}{nkT} = -\Sigma_1\phi_1 - \Sigma_2\phi_2 - \frac{1}{2}\nu_{11}({s_1}^2 + \alpha_1{\sigma_1}^2){\phi_1}^2 - \frac{1}{2}\nu_{22}{s_2}^2{\phi_2}^2 - \nu_{12}(s_1s_2 + \alpha_{in}\sigma_1\sigma_2)\phi_1\phi_2 \qquad (2)$$


(a) Cooling

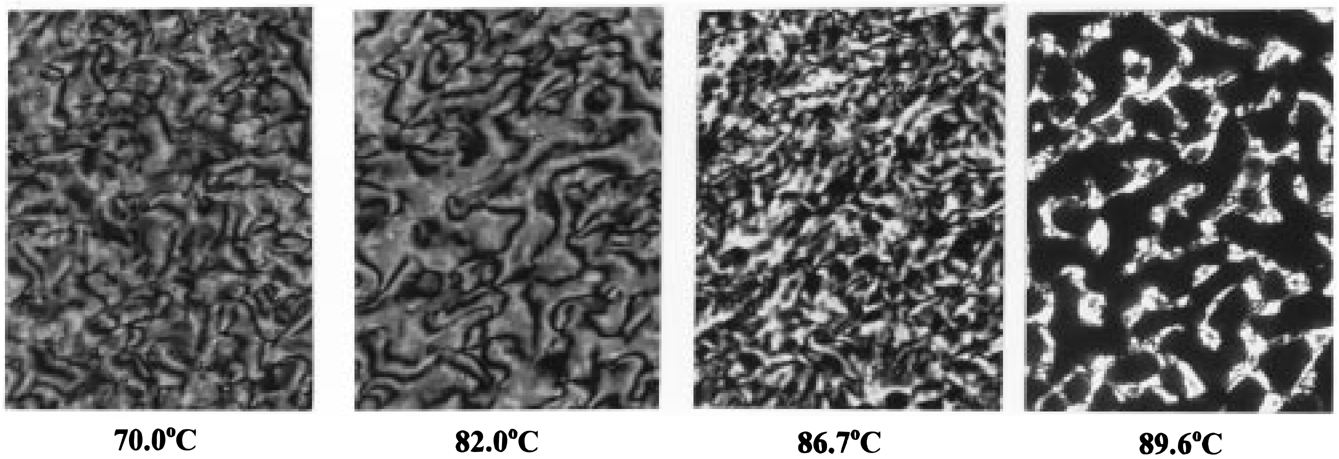
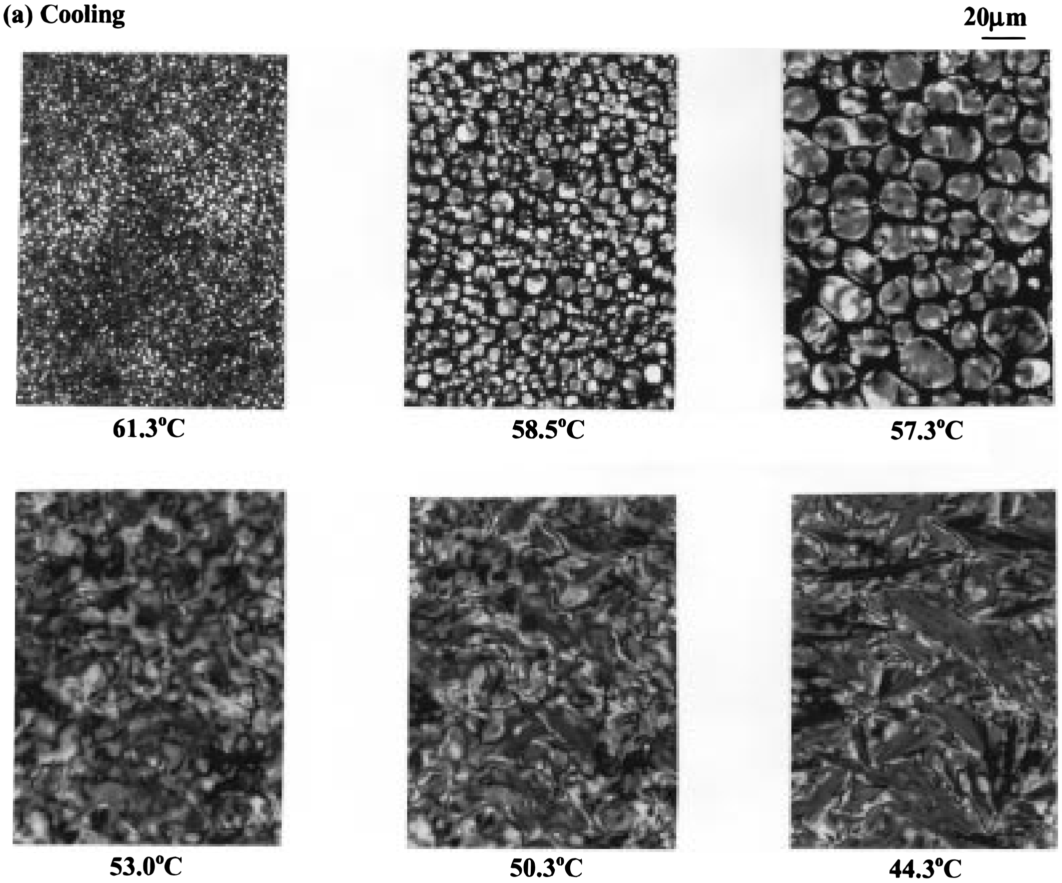

(b) Heating

Figure 2. Evolution of mesophase structure at the 20/80 K36/s-SCLCP composition during the course of (a) cooling and (b) heating cycles, showing a reversible phase change from isotropic, isotropic + nematic, and the pure nematic. The ramp rate was 0.5 °C/min.

(a) Cooling



(b) Heating

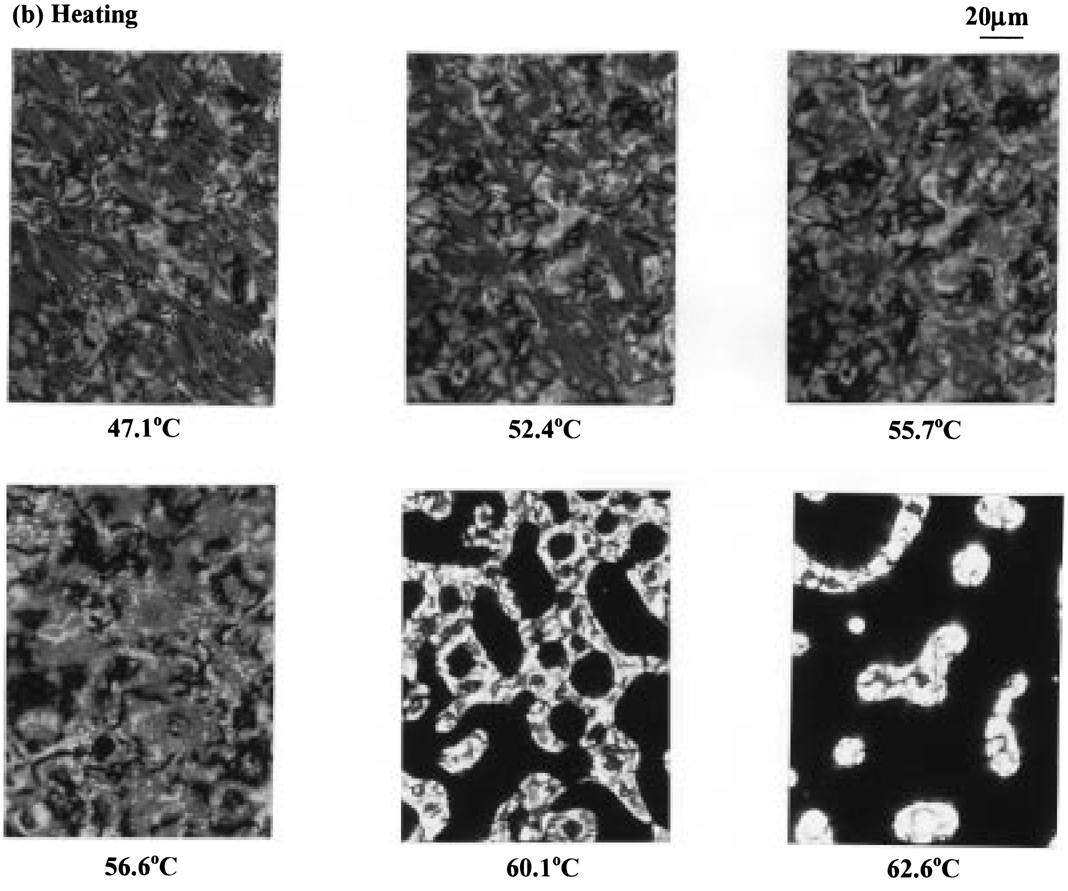
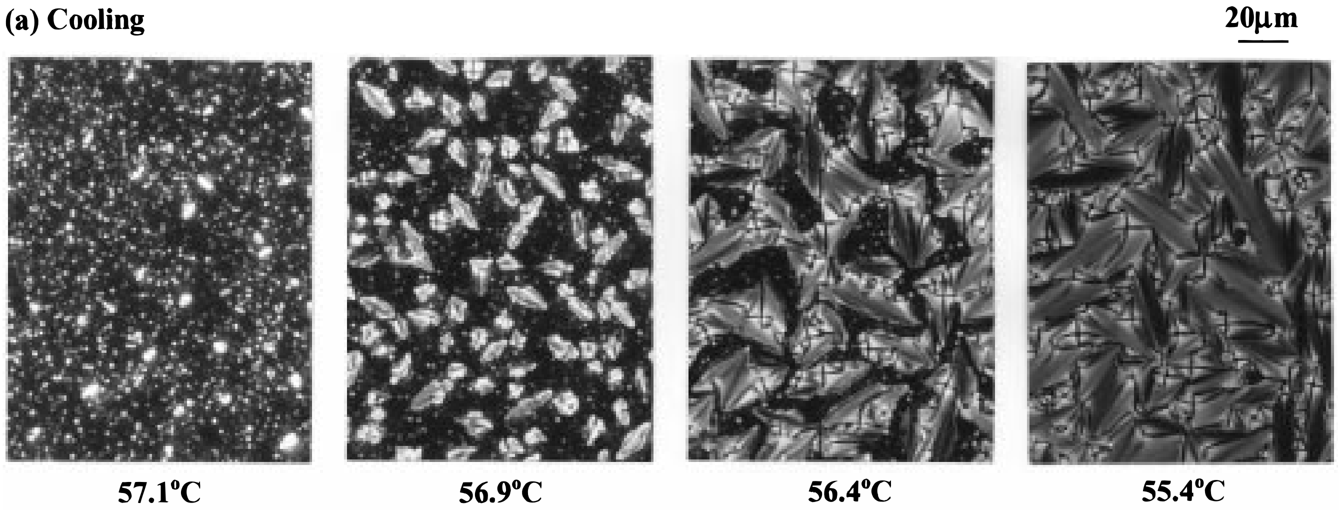


Figure 3. Evolution of mesophase structure at the 60/40 K36/s-SCLCP composition during the course of (a) cooling and (b) heating cycles, showing a reversible phase change from isotropic, isotropic + nematic, the pure nematic, and the smectic + nematic coexistence regions. The ramp rate was 0.5 °C/min.

(a) Cooling



(b) Heating

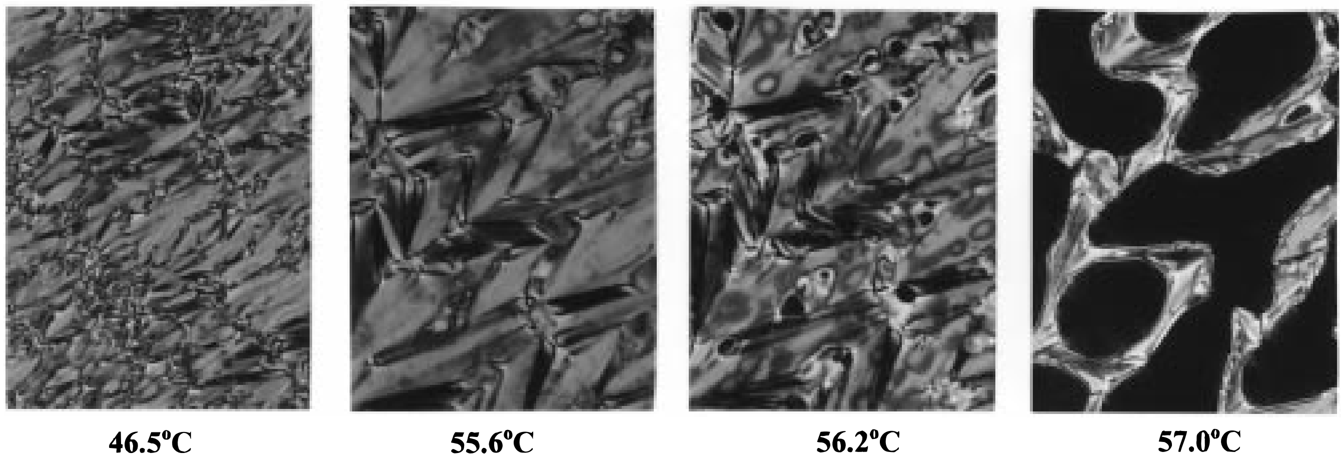


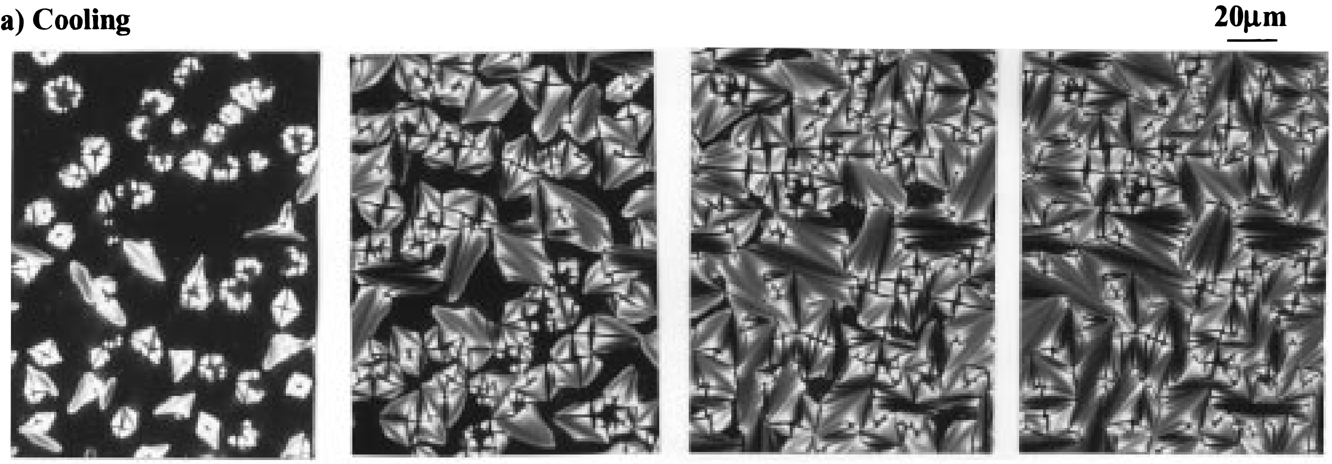
Figure 4. Evolution of mesophase structure at the 85/15 K36/s-SCLCP composition during the course of (a) cooling and (b) heating cycles showing a reversible phase change from isotropic, isotropic + smectic, and smectic + nematic coexistence regions. The ramp rate was 0.5 °C/min.

assuming that the nematic liquid crystal undergoes a nematic−isotropic transition while the smectic LC has only a smectic−isotropic transition. Σ_1 and Σ_2 represent the decrease of entropy due to the alignment of the individual LC molecules of component 1 (K36) and the mesogenic group of component 2 (s-SCLCP), respectively. ν_{11} and ν_{22} are the nematic interaction parameters of the pure components, whereas ν_{12} represents the cross-nematic interaction between the dissimilar mesogens.[11] The relation among these nematic interaction parameters is generally expressed through $\nu_{12} = c\sqrt{\nu_{11}\nu_{22}}$, where c is a parameter that accommodates any departure from their geometric mean (i.e., $c = 1$). Physically, c is a measure of the strength of the cross-nematic interaction between the constituents relative to those in the same mesogens. When $c > 1$, a single nematic phase is induced in the LC mixtures due to the strong cross-mesogenic interaction. However, when $c < 1$, individual nematic phases are favored to form in their own constituents, resulting in two separate nematic phases.[11] s_1 and s_2 are the nematic order parameters, which can be defined according to the Maier−Saupe theory, i.e., $s_j = (1/2)(\langle 3\cos^2\theta_j\rangle - 1)$.[6−9]

On the other hand, σ_1, representing the smectic order parameter of component 1 (LC), is customarily defined as $\sigma_1 = (1/2)\langle\cos(2\pi z/d)(3\cos^2\theta_1 - 1)\rangle$ in the context of the Maier−Saupe−McMillan theory,[6−9] where θ_1 is the orientation angle between the LC director and the reference axis (i.e., the z direction). The smectic order parameter of component 2 (s-SCLCP), σ_2, can exist only in the mixture, as smectic ordering is forbidden in neat s-SCLCP. The smectic layer ordering is taken along the reference axis, z, and d is the interlayer distance. α_1 is the interaction strength for the smectic ordering in component 1 defined as $\alpha_1 = 2\exp[-(\pi d_0/d)^2]$, where d_0 is the molecular length representing the rigid portion of the LC molecules. α_{in} represents an induced smectic interaction parameter.[1,2] The coupling between the nematic and smectic ordering arises through the third and fifth terms of eq 2. In the event that there is no induced smectic phase, the phase diagram may be described by taking into consideration a weak cross-mesogenic interaction, i.e., by choosing a small value of c or by letting $\alpha_{in} = 0$.[2,3] For the detailed theoretical deduction, interested readers are referred to our recent papers.[1,3]

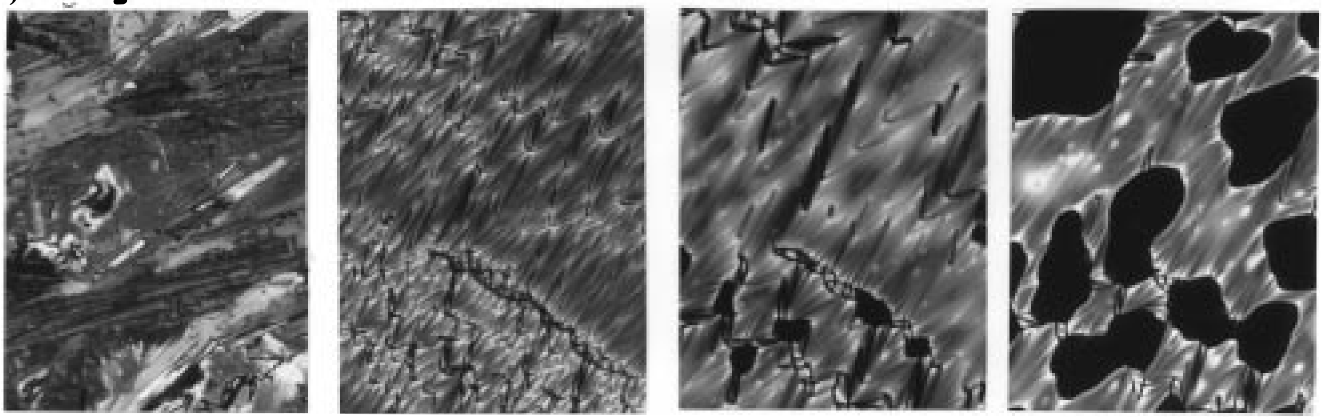
In the present phase diagram calculation, it was assumed that the densities of the s-SCLCP and the low molecular weight LC were comparable. Figure 1 shows the phase transition temperatures of the I + N_2, $S_{mA,1}$ + I, $S_{mA,1}$ + N_2, the pure N_2, and the pure $S_{mA,1}$ regions of the K36/s-SCLCP mixtures in comparison with the calculated coexistence curves (solid lines) of the nematic/smectic phase diagram. At present, phase transitions such as crystallization and the glass transitions were not considered in this combined FH/MSM theory. The

(a) Cooling



57.0°C **56.5°C** **56.1°C** **30.7°C**

(b) Heating



24.0°C **54.3°C** **56.6°C** **57.0°C**

Figure 5. Evolution of mesophase structure at the 95/5 K36/s-SCLCP composition during the course of (a) cooling and (b) heating cycles showing a reversible phase change from isotropic, isotropic + smectic, and smectic + nematic coexistence regions. The ramp rate was 0.5 °C/min.

c parameter, signifying the relative strength of the cross-nematic interaction to that within the same mesogens, was set to be 0.925 along with $\alpha_1 = 1.0575$, $\alpha_{in} = 0$, and $r_2/r_1 = 16/1$. To account for the broadness of the coexistence curve, *A* is taken to be −1.0. The value of *B* in turn has been estimated from the critical point of the liquid + liquid equilibrium, i.e., $B = (\chi_c - A)T_c$, where T_c represents the critical temperature and χ_c the critical interaction parameter.[5] To calculate the temperature dependence of the χ parameter, T_c is taken as 20 °C. The value of *A* is generally dictated by the critical temperature and the broadness of the liquid + liquid coexistence curve, if it exists, but the influence of χ is inconsequential for the nematic + smectic coexistence region. It should be pointed out that the choice of *c* and α_{in} parameters is crucial for predicting the smectic + nematic coexistence phase and/or the induced smectic phase in the smectic/nematic phase diagrams, whereas T_c and χ are important only for describing the liquid + liquid equilibrium.[1]

The calculated phase diagram reveals the coexistence of the I + N_2 region and a pure nematic region at very high concentrations of s-SCLCP (N_2) (Figure 1). The coexistence of the I + $S_{mA,1}$ region was found along with the pure $S_{mA,1}$ at extremely high low molar mass LC (K36) compositions. In the figure, the peritectic line (a dotted line) represents the coexistence of isotropic, nematic, and smectic phases. The theory further predicts a $S_{mA,1}$ + N_2 region at a lower temperature, but in the actual experiment it is often masked by the $S_{mA,1}$-to-K (crystal) transition occurring at a much lower temperature.

To verify these coexistence regions, the evolution of the mesophase structure has been investigated as a function of temperature and composition by means of polarized optical microscopy. Parts a and b of Figure 2 depict the evolution of the mesophase structure at the 20/80 K36/s-SCLCP composition during the cooling and heating cycles at a rate of 0.5 °C/min. When phase separation takes place, modulated textures develop around 88.4 °C. The phase-separated structure transforms into the droplet morphology in the vicinity of 84.4 °C, exhibiting a predominantly bipolar structure. With continued cooling, the droplets coarsen through coalescence, creating a multitude of line disclinations reminiscent of a Schlieren texture at the domain boundaries with a strength of ±1 (e.g., see at 80.8−74.8 °C). The color of the background changes, which may be a consequence of changing tilt angles in the LC directors. During the heating cycle (70−82 °C), the disclinations continue to grow via annihilation. Concurrently, the LC molecules experience thermal motions, which show up as a subtle structural undulation in the background. Eventually, around 86.7 °C, the coexistence of isotropic (I) and nematic (N_2) phases can be noticed. The structural change in this temperature gap, labeled as

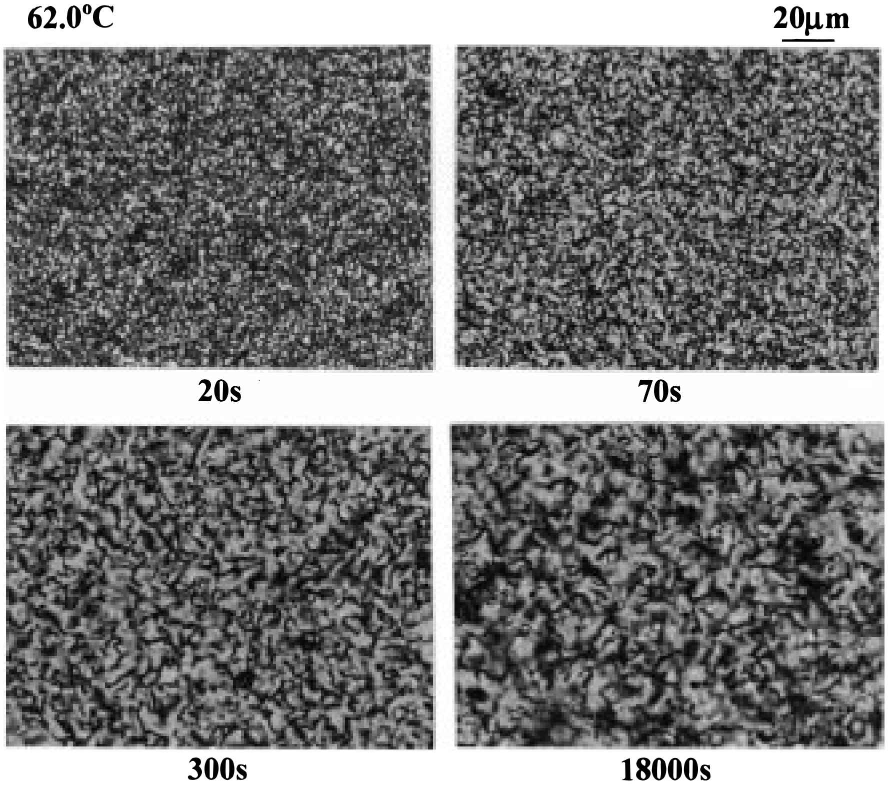
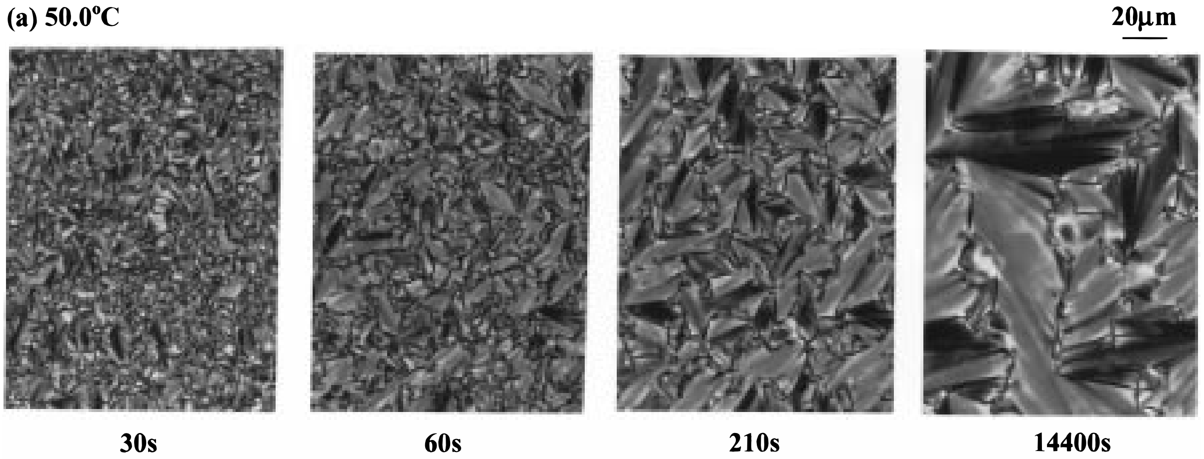


Figure 6. Temporal evolution of mesophase structure following temperature quenches from 130 to 62 °C for the 30/70 K36/s-SCLCP mixture, confirming the phase transition from isotropic to the pure nematic through the isotropic + nematic coexistence region.

(a) 50.0°C



(b) 35.0°C

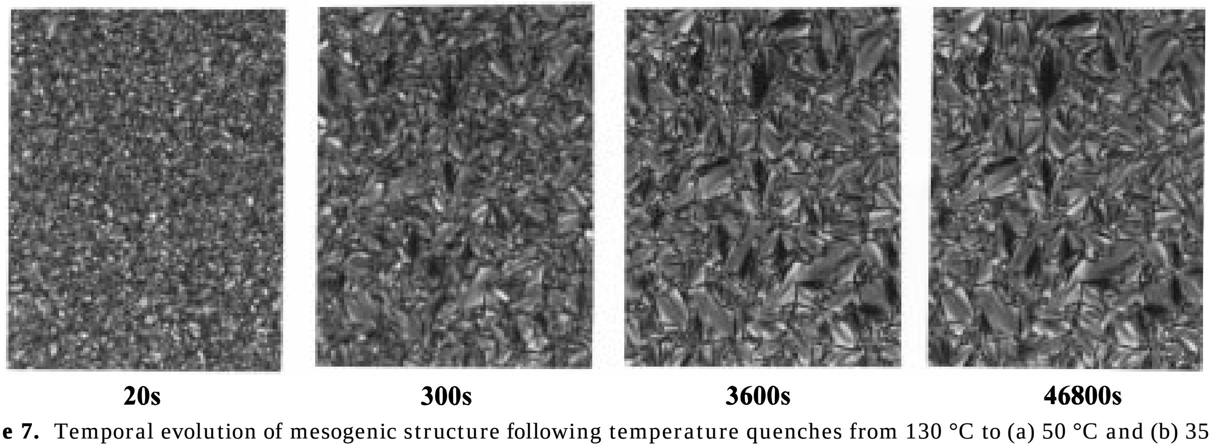
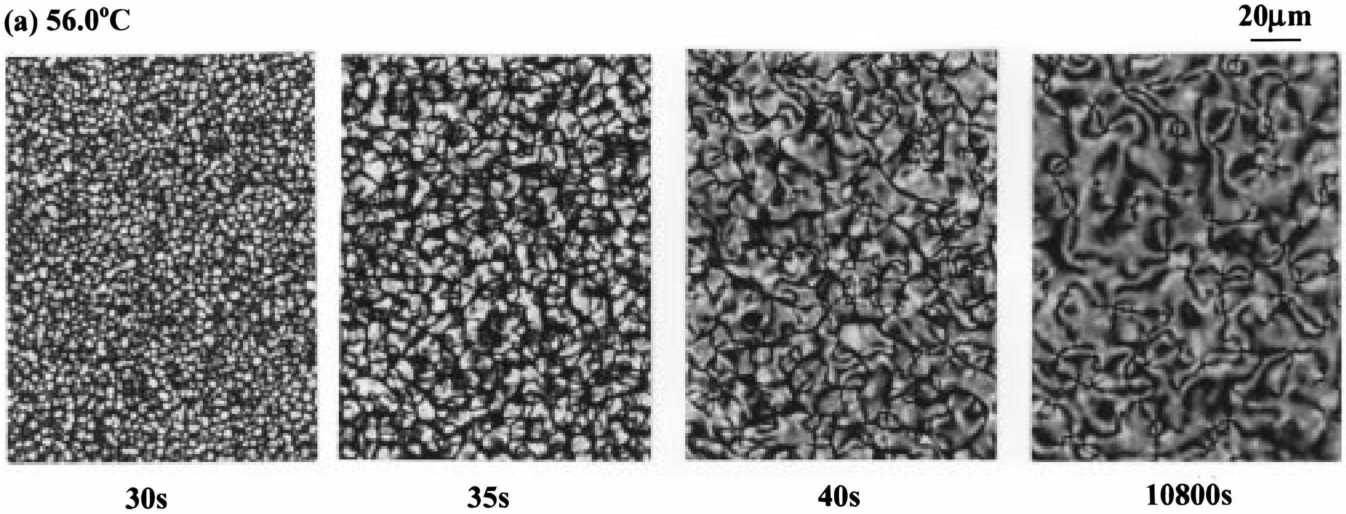


Figure 7. Temporal evolution of mesogenic structure following temperature quenches from 130 °C to (a) 50 °C and (b) 35 °C for the 80/20 K36/s-SCLCP mixture, showing the quench depth dependence of the average size of the focal conic structures in the smectic + nematic coexistence region.

(a) 56.0°C



(b) 43.0°C

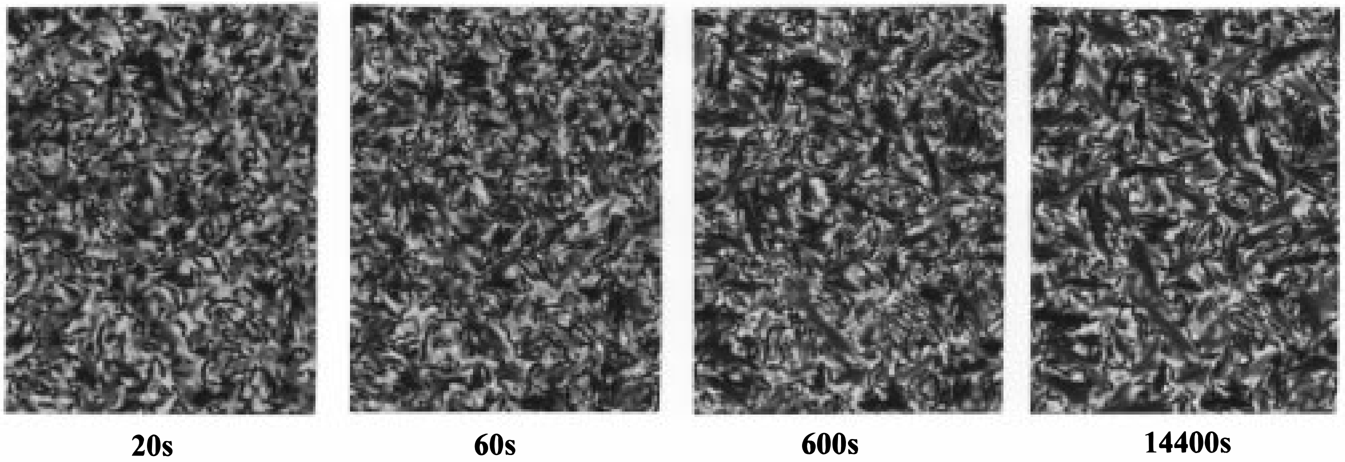


Figure 8. Temporal evolution of mesogenic structure following temperature quenches from 130 °C to (a) 56 °C and (b) 43 °C for the 60/40 K36/s-SCLCP mixture, verifying the single phase nematic and the smectic + nematic coexistence regions, respectively.

the I + N_2 coexistence region, is in good agreement with the predicted coexistence region within a few degrees.

As the K36 content is increased to 60%, the phase transition temperature of the isotropic to nematic region is suppressed considerably, exhibiting the isotropic + nematic region around 62 °C during the cooling run. As shown in Figure 3a,b, the structural transformation of the mesophases occurs in a fashion similar to that in the 20/80 K36/s-SCLCP composition, except that the coarsening process of the multiple tiny structures to larger droplets is more distinct (e.g., at 61.3−57.3 °C). In the vicinity of 55−53 °C, a pure nematic structure is observed (see the picture at 53 °C). At lower temperatures (50.3−44.3 °C), the development of the focal conic texture is discernible, which may be attributed to the smectic-A phase of K36. However, these focal conic textures coexist with the nematic Schlieren texture of s-SCLCP, thereby indicating the S_{mA1} + N_2 coexistence region. During the heating cycle, the nematic + smectic coexistence phase changes to the pure nematic phase around 55.7−56.6 °C, which is exactly what has been predicted by the present theory. With continued heating, the I + N_2 coexistence region is discernible at 60.1−62.6 °C. Again, the observed S_{mA1} + N_2, the pure N_2, and the L_1 + N_2 coexistence phases in ascending order of temperature at the 60/40 K36/s-SCLCP composition conform remarkably well with the predicted phase diagram (Figure 1).

In compositions very rich in K36, such as the 85/15 K36/s-SCLCP, the development of diamond-like (or trapezoidal) textures can be seen in the nematic continuum, suggestive of the $S_{mA,1}$ + N_2 region (57.1−56.4 °C of Figure 4a). Such tiny trapezoidal textures transform into a focal conic texture with continued cooling (56.4−55.4 °C), indicative of smectic-A. In the vicinity of 24 °C, crystallization has taken place in the K36. During the heating cycle, the crystals melt away to a focal conic texture (46.5−55.6 °C) (Figure 4b). Upon further heating, a phase transition takes place from $S_{mA,1}$ to an isotropic phase (I) by passing through a coexistence I + $S_{mA,1}$ region (56.2−57 °C). This observed behavior is in good agreement with the predicted phase diagram.

The phase transition for the 95/5 K36/s-SCLCP composition shows some interesting behavior. As can be seen in Figure 5a during the cooling cycle, the smectic phase develops around 57.0 °C and transforms quickly into the focal conic texture (e.g., at 56.5 °C), which continues to persist until 30.7 °C. Upon further cooling, a phase transition occurs from a smectic to a crystal phase in the K36 rich region. Upon heating, the crystal structure (shown at 24 °C) melts away to become a smectic-A phase with a Chevron texture (around 54.3 °C) and further transforms into an isotropic phase via the I + S_{mA} coexistence region (56.6−57 °C) (Figure 5b). Since only a minute amount of the nematic s-SCLCP is present in such a composition, the nematic phase is no longer identifiable due to the domination of the smectic phase.

To further verify these coexistence regions, several temperature quench experiments were performed from a single-phase temperature of 130 ^{o}C to various temperatures at several compositions. Figure 6 shows the temporal evolution of a typical nematic texture following a T quench from 130 to 62 °C at the 30/70 K36/s-SCLCP composition. The development of the pure N_2 region can be confirmed in conformity with the prediction of the present theory. In the 80/20 K36/s-SCLCP composition, the $S_{mA,1} + N_2$ coexistence region is discernible during the T quenches to 50 and 35 °C, as depicted in Figure 7a,b. As expected, the average length scale of these smectic textures is larger for the smaller quench depth; i.e., the average size of the focal conic structure at 50 °C is greater than that at 35 °C. The T quench experiment at 60/40 K36/s-SCLCP also shows some interesting behavior (Figure 8a); viz., a pure nematic structure develops at 56 °C, which is in good agreement with observations during the cooling and heating cycles (Figure 3a,b). Moreover, the coexistence of nematic + smectic-A is clearly identifiable at a lower temperature of 43 °C (Figures 8b). It is reasonable to conclude that the observed coexistence regions are in excellent agreement with the predicted phase diagram, thereby attesting to the predictive capability of the present theory.

Conclusions

We have demonstrated that the nematic/smectic phase diagram of the K36/s-SCLCP is explicable in the context of the combined Flory−Huggins (FH) free energy for isotropic demixing and the Maier−Saupe−McMillan (MSM) free energy for smectic ordering of the mesogens. However, the theory did not take into consideration the process of crystallization occurring at lower temperatures. This combined FH/MSM predicted the nematic/smectic phase diagrams consisting of isotropic + nematic, smectic + nematic, isotropic smectic, pure nematic, and pure smectic regions. Polarized optical microscopic investigations of the K36/s-SCLCP system revealed various coexistence regions in the phase diagrams that can be verified on the basis of the present combined FH/MSM theory of the nematic/smectic mixture.

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