Unique Pitch Evolution in the Smectic-C^*_α Phase

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Employing resonant x-ray diffraction, we observed unique pitch evolutions in the smectic-C^*_α phase in mixtures of two antiferroelectric liquid crystals. Our results show that the pitch in this phase continuously evolves across 4 layers, contradicting a theoretical model that predicts that the smectic-C^*_{FI2} phase intervenes in the smectic-C^*_α phase. The phase sequences we found can be explained by another model that includes one type of long-range interaction among smectic layers.

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Liquid crystals (LC) are mesomorphic phases. Molecules in the LC state are more organized than in the liquid state, yet less organized than in the solid state, exhibiting solid properties in some dimension(s) and liquid nature in the other dimension(s). Rich structures and complex phase transitions are common in LCs. In addition, chiral rodlike molecules can exhibit spontaneous polarization [1]. This group of materials has been known for its ferroelectric (FE) properties since 1975. Antiferroelectric (AF) and ferrielectric (FI) properties were found in compound MHPOBC in 1989 [2]. Since then, many antiferroelectric liquid crystals (AFLCs) have been synthesized and investigated. They provide great opportunities to study the physics of LCs as well as possibilities in electro-optical applications [3]. Structures, properties, and phase transitions of the FE, AF, and FI subphases in AFLCs have become a major focus in liquid crystal physics.

In this Letter, we will discuss our findings from investigating binary mixtures of two AFLC compounds that show unique pitch evolutions in the smectic-C^*_α (SmC^*_α) phase. Molecules in the smectic phases are organized in layers and are liquidlike within the layers. The molecules are not tilted in the smectic-A (SmA) phase and tilted uniformly from the layer normal in the variant smectic-C^* (SmC^*) phases. Spontaneous polarization rises from the broken symmetry of the chiral molecules [1] and couples to the tilt. The variant subphases, with different tilt orientations between neighboring layers, possess FE, AF or FI properties. The SmC^*_α phase has an incommensurate nanoscale helical pitch (INHP) structure. The length of the INHP evolves with temperature. The SmC^* phase has a helical structure with a longer pitch on the order of several hundred layers. Since the SmC^* and the SmC^*_α phases have the same symmetry, the phase transition should be a first-order transition, which ends at a critical point [4]. A long helical pitch is present in all of the following phases. The SmC^*_{FI1} (SmC^*_{FI2}) is FI (AF) with 3- (4-) layer repeat unit [5,6], with distortions [7–9] from a uniform helical structure. The SmC^*_A phase is AF with a 2-layer unit cell. The commonly observed phase sequence upon cooling is SmA-SmC^*_α-SmC^*-SmC^*_{FI2}-SmC^*_{FI1}-SmC^*_A. Many theoretical phase diagrams have been proposed [10–15] to illustrate experimental observations. Two of them [11,15] presented some critical variation of the helical pitch in the SmC^*_α phase relevant to this work.

So far, one of the most successful phenomenological models of the SmC^* variant phases is proposed by Olson *et al.* [11]. This model produces all known variant phases with just five expansion terms, including interactions up to the third-nearest-neighboring layers. The phase diagram calculated from the model shows that two SmC^*_α phases exist, one with an INHP larger than 4 layers (L), namely, the Sm$C^*_{\alpha 1}$ phase, and the other with INHP $<$ 4 L, namely, the Sm$C^*_{\alpha 2}$ phase. The two phases are separated by the SmC^*_{d4} phase, a distorted 4 L phase similar to the SmC^*_{FI2} phase. The Sm$C^*_{\alpha 1}$ phase has been extensively studied since its discovery. The Sm$C^*_{\alpha 2}$ phase was unveiled by a recent optical study [16] on MHPOCBC. Since there has been no report of any compound with INHP evolving near 4 L, two intriguing questions remain unanswered: how the INHP in the SmC^*_α phase evolves near 4 L, and whether the evolution of the INHP is always interrupted by the distorted phase SmC^*_{d4} in the vicinity of 4 L. We decided to address these problems by investigating binary mixtures of R-10OTBBB1M7 (compound A) and R-MHPOCBC (compound B). Their chemical structures are given in Fig. 1. Employing resonant x-ray diffraction (RXRD), we found that the pitch decreased strictly and continuously across 4 L upon cooling, with no evidence that the SmC^*_{d4} phase intervenes in the SmC^*_α phase.

To investigate the nature of the SmC^*_α phase, several binary mixtures were made with A and B. The two compounds, which are very similar in their structures, showed no phase segregation in any of the mixtures we made. Compound A offers the Sm$C^*_{\alpha 1}$ phase, with one sulfur atom in its core part suited for RXRD. Compound B

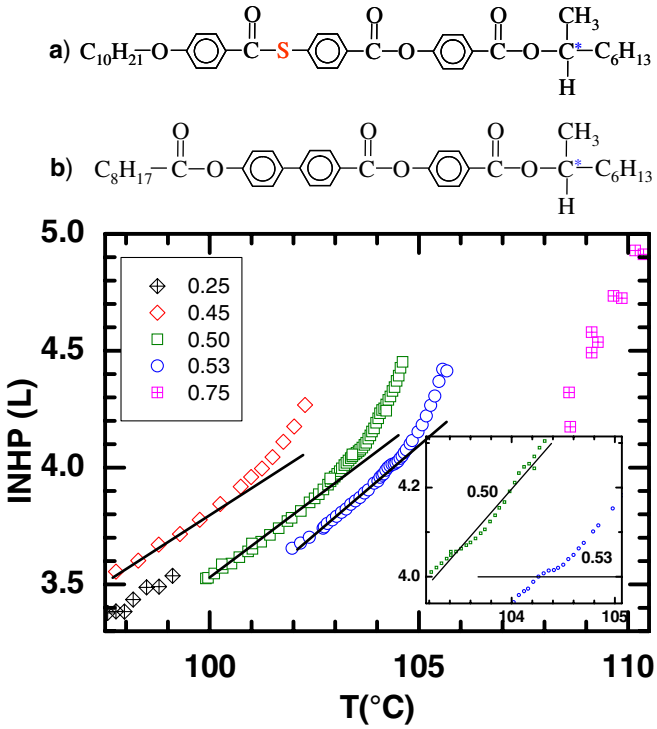

FIG. 1 (color online). INHP temperature evolution obtained from R-10OTBBB1M7 (x)—R-MHPOCBC (1-x) mixtures. Data from five mixtures are included representing three different behaviors of INHP evolutions. The mixture of $x = 0.25$ has the SmC^*_α phase with INHP < 4 L. The mixtures of $x = 0.45$, 0.50, and 0.53 have INHP evolving across INHP $= 4$ L. The mixture of $x = 0.75$ has the SmC^*_α phase with INHP > 4 L. Only data from 3.4 to 5 L are presented in order to emphasize the details around 4 L. The inset shows the INHP evolution around 4 layers for the $x = 0.50$ and 0.53 mixtures. The lines are aids to the eye. (A) and (B) show the molecular structures of R-10OTBBB1M7 and R-MHPOCBC.

provides the Sm$C^*_{\alpha 2}$ phase. Their mixtures permitted us to explore the miscibility of these two phases and the pitch evolution in the vicinity of 4 layers.

In order to unambiguously determine the detailed pitch evolution, we investigated thick freestanding films of the mixtures with RXRD. RXRD is a powerful tool to acquire nanoscale orientational orders in liquid crystals [5]. Samples need to contain heavy elements (Cl, S, or Se) in their core parts. We scan the x-ray energy near the K-absorption edge of the heavy element to find the maximum absorption and tune to that energy. We observe resonant satellite peaks in addition to the layer diffraction peaks, which we also observe at nonresonant energies. These satellite peaks reveal the periodicity of the bonding environment of the heavy elements, which indicates orientational order of the molecules. The orientational periodicity is calculated from the separation between the satellite peaks and their respective layer diffraction peaks. More than ten mixtures of $A(x)$-$B(1\text{-}x)$ (x is weight percentage of A) were made and studied with our in-house tabletop optical probe [17] to select the key mixtures that were studied with RXRD. Figure 1 shows RXRD results of the key mixtures, representing three distinct ranges of the INHP as functions of temperature. All mixtures were investigated with RXRD within 24 h after loading. No noticeable degradation (as studied by Lagerwall *et al.* [18]) was observed. No splitting of Bragg peaks, corresponding to two coexisting layer spacings, was detected.

Upon cooling from T_{AC} (transition temperature between the SmA-SmC^*_α phases), in the $x = 0.75$ mixture, we observed the INHP evolving from 6.07 to 4.17 L, which was followed by a first-order transition to the SmC^*_{FI2} phase. The result was similar to that of the pure A obtained from previous RXRD studies [6], with the INHP range narrowed and value shifted down. In the $x = 0.25$ mixture, we detected the SmC^*_α phase with the INHP evolving from 3.54 to 3.38 L upon cooling from T_{AC}, consistent with the result obtained from pure B in previous optical studies [16]. This was the first time the SmC^*_α phase with INHP $<$ 4 L was observed by RXRD. This result is a solid proof of the existence of a helical phase with INHP < 4 L. It is very encouraging to see that with only 25% sulfur-containing constituent, the mixture offered clear resonant peaks in the incommensurate phase at ± 0.02 L accuracy in pitch measurement. In the $x = 0.53$ mixture, we discovered a SmC^*_α phase with the INHP evolving from 4.41 to 3.65 L upon cooling from T_{AC}. This was the first observation that the INHP evolved from more than 4 L to less than 4 L. High resolution scans on $x = 0.53(0.50)$ mixture at 0.05(0.1) K/step around 4 L showed no discontinuity in the INHP evolution. The SmC^*_{FI2} phase was observed in the $x = 0.53$ mixture below the SmC^*_α phase while it was absent in the $x = 0.50$ mixture. The SmC^*_{FI1} phase was directly below the SmC^*_α phase in this mixture. The $x = 0.45$ mixture confirmed that the INHP is strictly decreasing and continuous upon cooling through 4 L. The $x = 0.62$ mixture showed a tiny window where the INHP evolved below 4 L. A complete list of phase sequences is presented in Table I. Based on the fact that no separate SmC^*_α phases were observed in any mixture, we will refer to this helical phase just as the SmC^*_α phase, rather than retaining the distinction between the Sm$C^*_{\alpha 1}$ phase and the Sm$C^*_{\alpha 2}$ phase.

Instead of splitting the SmC^*_α phase into INHP > 4 L and INHP < 4 L regions, the SmC^*_{FI2} phase appeared at a lower temperature than the SmC^*_α phase in all the mixtures that showed both phases ($x = 0.53$, 0.62 and 0.75). Split resonant peaks were observed in the SmC^*_{FI2} (SmC^*_{FI1}) phase, confirming that the structure was a distorted phase with 4(3) L unit cells. The INHP in all mixtures shows strict decrease and continuous evolution upon cooling, regardless of whether it crosses 4 L or not. Besides that, different mixtures feature different details of the temperature dependence of the INHP. The $x = 0.50$ and 0.53 mixtures showed small features around 4 L (Fig. 1 inset).

TABLE I. Summary of the phases and transition temperatures of the observed SmC^* variant phases. The 1st column is x. The 5th column is the INHP range in the SmC^*_α phase.

1.00[c]	SmA	118.9	SmC^*_α	(7.7–5.4)	114.7	SmC^*_{FI2}	109.7[b]	SmC^*_{FI1}	107.7[b]	SmC^*_A
0.75	SmA	112.5	SmC^*_α	(6.07–4.17)	107.2	SmC^*_{FI2}	102.5	SmC^*_{FI1}	100.9	SmC^*_A
0.62	SmA	106.5	SmC^*_α	(4.63–3.95)	103.5	SmC^*_{FI2}	101.2	SmC^*_{FI1}	99.0	SmC^*_A
0.53	SmA	105.7	SmC^*_α	(4.41–3.65)	101.9	SmC^*_{FI2}	97.6	SmC^*_{FI1}	96.5[a]	SmC^*_A
0.50	SmA	104.6	SmC^*_α	(4.45–3.35)	99.8			SmC^*_{FI1}	98.2	SmC^*_A
0.45	SmA	102.4	SmC^*_α	(4.27–3.47)	96.5			SmC^*_{FI1}	95.3	SmC^*_A
0.25	SmA	99.2	SmC^*_α	(3.54–3.38)	93.9[a]					SmC^*_A
0.00	SmA	96.8[a]	SmC^*_α	(3.0–2.6)[a]	91.4[a]					SmC^*_A

[a]The values were obtained from our optical measurements on freestanding films.
[b]The values were from bulk measurements.
[c]In our optical studies, the SmC^* phase was observed between the SmC^*_α phase and the SmC^*_{FI2} phase, with about 1 K range.

The INHP of the $x = 0.50$ and 0.53 mixtures evolves more slowly in the vicinity of 4 L than the other regions. The INHP of the $x = 0.50$ mixture showed some nonlinear changes. In the $x = 0.53$ mixture, the INHP evolved linearly below 4 L. The slope of the pitch started to increase as the INHP evolved above 4 L and was faster than linear (Fig. 1). This behavior was also observed in the $x = 0.50$ mixture. A rather smooth and faster than linear change of the INHP was observed in the $x = 0.45$ mixture, both above and below 4 L in the SmC^*_α phase. On the other hand, we found that the INHP vs the layer spacing (d) plots are linear for all mixtures.

This linear relation was not observed in other compounds. Some simple relation could exist between the INHP and d. Figure 2 shows such behavior from the $x = 0.50$ mixture. The slope of the INHP vs $(d_{AC}\text{-}d)/d_{AC}$ curves decreases from -133 to -23 when x decreases from 0.75 to 0.25. Since the interlayer tilt orientation change is described as $\Delta\phi = 2\pi/\text{INHP}$, the quantity $\Delta\phi(d - d_0)$ seems to be a constant in a given sample. d_0 is the intercept. It is worth mentioning that the layer spacing of the samples was strictly decreasing upon cooling. Further studies are required to understand the physical meaning of the observed linear correlation between the INHP and the smectic layer spacing.

To further examine Olson's model, we explored a wide range of a_3, the coupling constant between the third-nearest-neighboring layers in Olson's model. We did not find any qualitative change in the INHP behavior that could otherwise explain our data [19]. On the other hand, our new experimental results are consistent with the phase diagram calculated from a recent theory proposed by Hamaneh and Taylor [15]. The proposed free energy included both a short-range interaction term and an effective long-range interaction term due to layer fluctuations. It successfully

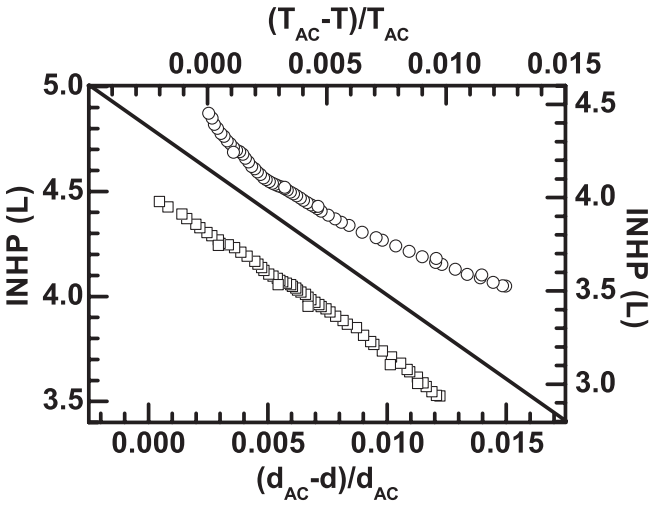

FIG. 2. A comparison between the INHP vs temperature and the INHP vs layer spacing. d_{AC} is the layer spacing at T_{AC}. The data came from the $x = 0.50$ mixture.

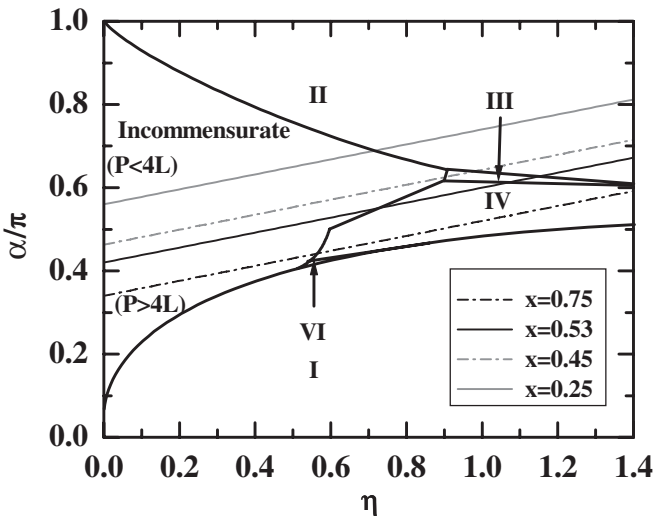

FIG. 3. Phase sequences of the mixtures were qualitatively mapped to Hamaneh and Taylor's phase diagram. Four mixtures were presented, $x = 0.25$, 0.45, 0.53, 0.75. I, II, III, IV, and VI indicate the regions of the SmC^*, SmC^*_A, the SmC^*_{FI1}, the SmC^*_{FI2}, and a phase having a 6-layer structure. The SmC^*_α phase is marked as incommensurate. η is the strength of the long-range interaction. Temperature decreases from bottom left to top right of the phase diagram.

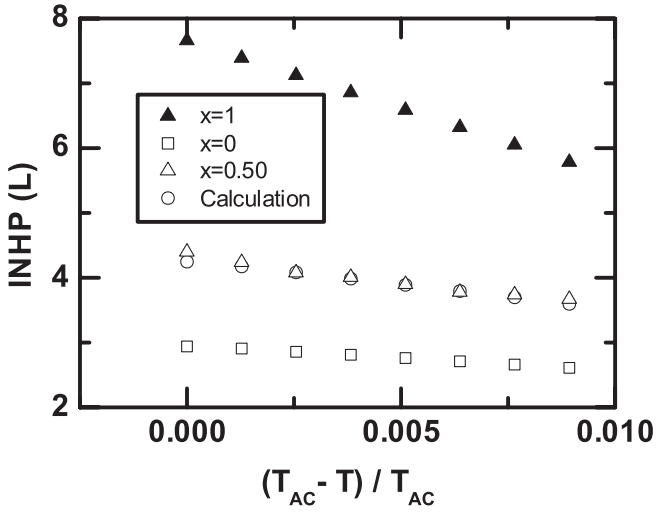

FIG. 4. The empirical method to predict the INHP behavior of the mixtures from the INHP behavior of the pure compounds. The points in the $x = 0$, 0.50, and 1 plots were obtained from interpolating the actual data points so the points are evenly spaced for calculations.

explained common phase sequences, and a recent identification of the SmC^*_{FI2}-SmC^* phase sequence reversal in one pure compound and related mixtures [20]. We qualitatively mapped our results onto their phase diagram (Fig. 3). The straight lines represent traces in the parameter space. As x decreases from 0.75 to 0.25, the starting point of the trace shifts from low to high values at T_{AC}, where $\alpha = 2\pi/\mathrm{INHP}$ and $\theta = 0$. The series of traces make their way across the phase diagram with the exact sequences the mixtures exhibited in the experiments (Table I). Hamaneh-Taylor theory includes both short-range and long-range interactions while Olson's model only includes short-range interactions. The better agreement of our data with Hamaneh and Taylor's theory than with Olson's model suggests that long-range interactions may play an important role in describing the SmC^* variant phases.

We have also compared the INHP temperature evolution in mixed samples with that in the pure samples. We can define a wave vector $Q = 1/\mathrm{INHP}$. We found that the weighted average of the wave vectors of the pure samples is in good agreement with the wave vector of the mixed samples (Fig. 4). Such a simple relation is not applicable to other mixture systems we have studied so far. Further investigations on this behavior are in progress.

Table I summarizes phase sequences of mixed and pure samples from our RXRD experiments and previously published results. In the mixtures, the INHP range shifts downward upon adding MHPOCBC. The $x = 0.75$ samples exhibit SmA-SmC^*_α-SmC^*_{FI2}-SmC^*_{FI1}-SmC^*_A on decreasing temperature. The INHP is above 4 L in the entire SmC^*_α temperature window. The $x = 0.62$ and 0.53 mixtures display SmA-SmC^*_α-SmC^*_{FI2}-SmC^*_{FI1}-SmC^*_A upon cooling. The INHP crosses 4 L smoothly. Further reducing x (0.50 and 0.45) results in the disappearance of the SmC^*_{FI2} phase. The SmC^*_{FI1} phase also disappears between $x = 0.45$ and 0.25. The $x = 0.25$ and 0 samples manifest a simple SmA-SmC^*_α-SmC^*_A phase sequence. The INHP is less than 4 L in this region.

To conclude, we investigated mixtures of R-10OTBBB1M7 and R-MHPOCBC and found that the INHP in the SmC^*_α phase decreases strictly and continuously across 4 L upon cooling. The SmC^*_α phase in this mixture system is one phase, not separate phases. Comparison with a recent theoretical model suggests long-range interactions may be present in the smectics.

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