Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Germano S. Iannacchione, Sihai Qian, Monique Wittebrood & Daniele Finotello (1997): The Effect of Chirality on the Phase Transitions of Chiral/8CB Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 302:1, 1-11

To link to this article: http://dx.doi.org/10.1080/10587259708041803

Mol. Cryst. Liq. Cryst., 1997, Vol. 302, pp. 1-11
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THE EFFECT OF CHIRALITY ON THE PHASE TRANSITIONS OF CHIRAL/8CB MIXTURES

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Abstract We report on a study of mixtures of octylcyanobiphenyl (8CB) and equal amounts of two chiral agents (CE2 and CB15) as a function of chiral pitch (concentration). Bulk studies reveal a widening cholesteric temperature range with increasing chirality. The first order cholesteric-isotropic (Ch-I) transition shifts marginally to lower temperature with increasing chirality while exhibiting a pre-transition feature near its C_p maximum. The smectic-A-cholesteric (SmA-Ch) C_p anomaly becomes smaller and continuously shifts to lower temperatures with increasing chirality while exhibiting the unique feature of a discontinuous jump on the *low* temperature side of the C_p peak. The increased chirality suppresses the smectic formation through twist elastic distortion. Upon Anopore confinement, the C_p maximum of the Ch-I transition increases as compared to bulk with the disappearance of the pre-transition feature; the SmA-Ch transition becomes extremely rounded and suppressed. The transitions shift to lower temperatures while retaining the bulk cholesteric temperature range.

INTRODUCTION

The study of liquid crystal ordering continues to stimulate considerable research effort due to the wide range of phenomena accessible. One particular venue that consistently generates activity is the smectic-A to nematic (SmA-N) phase transition. Ever since the analogy made by de Gennes in 1972 between the SmA-N phase transition in liquid crystals and the superconducting to normal transition in metals [1], our understanding of this phenomena has greatly advanced. In this analogy, a twist distortion in a smectic is the equivalent of an applied external magnetic field to a superconductor. Here, a distinction can be made between two types of behavior as the SmA-N transition is approached from the nematic phase. For type I systems, the twist distortion will be completely expelled at the transition, T_c, which is the analogue of the Meisner effect [2]. For type II systems, at a temperature above the expulsion of all twist, a regular array of disclinations can form; in liquid crystals this is the Twisted Grain Boundary (TGB) phase [3] which is the analogue of the Abrikosov phase [4]. For this reason, type II behavior has been the focus of much of the recent research effort.

In de Gennes' landmark paper [1], it was suggested that these distinct types of behavior could be investigated by studying the smectic-A to cholesteric (SmA-Ch) transition of chiral mixtures which has an intrinsic, easily controllable, pitch (or twist deformation). This is considered superior to mechanically imposing twist deformation since the chirality of mixtures is a bulk property and surface effects are unimportant. Theoretically, the SmA-Ch transition should be first order [5], however, previous studies at atmospheric pressure have found it to be an extremely weak first order transition [6-8].

In this work, we report a high resolution ac-calorimetric study on chiral mixtures of octylcyanobiphenyl (8CB) liquid crystal with equal parts of 4 - (2 - methylbutyl) - 4' - cyanobiphenyl (CB15) and 4"-(2-methylbutylphenyl) - 4' - (2-methylbutyl) - 4 -biphenyl carboxylate (CE2) as a function of chirality (concentration). The pitch was varied in five samples from 1.82 to 0.40 μm. Here, results for the 1.82 μm pitch sample will be discussed in detail. The C_p feature of the continuous SmA-N transition of pure 8CB loses its symmetric appearance. It is suppressed and shifts to lower temperatures, consistent with type I behavior. The C_p feature of the cholesteric to isotropic (Ch-I) transition marginally shifts down and retains the pretransitional C_p temperature dependence in the ordered phase of the N-I transition for pure 8CB. However, the Ch-I transition is proceeded by a C_p feature over a 0.5 K wide two-phase region. Since the pitches employed are larger than the pitch typically needed for the onset of Blue phases [2] (< 0.5 μm), this feature may represent the establishment of chirality by a nucleation process in a nematic-like phase. Finally, preliminary specific heat studies of these mixtures confined to the non-interconnected uniform cylindrical pores (0.2 μm diam) of Anopore membranes find a SmA-Ch transition greatly rounded and suppressed while the Ch-I transition is greatly enhanced and devoid of the pre-cholesteric C_p feature.

EXPERIMENTAL DETAILS

Chiral mixtures have been used extensively for studies on TGB and blue phases as well as for applications where CB15 and CE2 are popular agents. The chiral material CB15 melts at 277.2 K with a monotropic Ch-I transition at 243.2 °C with a pitch of p_{CB15} = 0.15 μm while CE2 has a melting point of 376.2 K and a Ch-I transition at 388.65 K having a pitch of p_{CE2} = 0.10 μm. The 8CB used in this study is non-chiral and has been checked for purity to be better than 99.9 %. This liquid crystal has three phase transitions, a first order crystal to smectic-A (K-SmA) at ~ 294 K, a continuous SmA-N at 307.0 K, and a weakly first order nematic to isotropic (N-I) transition at 314.0 K, with latent heats of $l_{K\text{-}A}$ = 97.1 J/g, $l_{SmA\text{-}N}$ = 0.00137 J/g, and $l_{N\text{-}I}$ = 2.1 J/g respectively [9]. The resulting pitch, p, of mixtures of these compounds can be calculated as [10]

$$\frac{1}{p} = \left(\frac{C_{CE2}}{p_{CE2}}\right) + \left(\frac{C_{CB15}}{p_{CB15}}\right) , \tag{1}$$

where C_{CE2} (C_{CB15}) is the weight fractional concentration of CE2 (CB15). Equal concentrations of CB15 and CE2 were chosen to control the pitch and to maintain the clearing temperature. Five concentrations were studied ranging from 6.17 to 28 % chiral content having corresponding pitches ranging from 1.82 to 0.4 μm.

High resolution heat capacity measurements were performed using an AC calorimetric technique. This consists of applying heat sinusoidally to a sample and measuring the amplitude of the resulting thermal oscillations which are inversely proportional to its heat capacity. Under the proper experimental conditions [11], the heat capacity can be obtained from

$$C = \frac{P_o}{2\omega T_{ac}} , \tag{2}$$

where P_o is the applied power and ω is the angular frequency of the temperature oscillations. Temperature oscillations lag behind P_o by a phase shift, Φ, which can contain important information regarding the dynamics of a phase transition. If a sample possesses slow relaxation mechanisms either due to sluggish fluctuation modes of a particular phase or slow phase conversion at a phase transition, then the sample's heat capacity can be thought of as a dynamic response function [12]. The real and imaginary components are calculated as [13]

$$Re(C_p) = C\cos(\phi) \ , \tag{3a}$$

$$Im(C_p) = C\sin(\phi) - \frac{1}{\omega R} \ , \tag{3b}$$

where $\Phi = \phi - 90^\circ$, and R is the thermal conductance linking the sample to an external temperature controlled bath. The real part represents the static heat capacity while the imaginary part is the dispersive component. For a simple fluid away from any phase transition [12,13], $Re(C_p) \approx C$ and $Im(C_p) \approx 0$.

In the present experiments, the values are $T_{ac} \sim 2$ mK, $\omega = 0.6912$ rad/sec, and ϕ = 0.1 to 0.2 rad with data taken in discrete temperature steps spaced by 20 mK and the average temperature controlled to better than 100 μK. Further details of our implementation of this technique can be found elsewhere [14]. Bulk samples consisted of a ~ 6 mg droplet of the chiral mixture while the Anopore confined sample contained ~ 2 mg of the same mixture, all at atmospheric pressure.

RESULTS AND DISCUSSION

The excess specific heat ΔC_p (real component) and $Im(C_p)$ component about the Ch-I transition of the 6.17 % chiral/8CB mixture is presented in Figure 1. This concentration possess a pitch of 1.82 μm. Several striking features are evident at this transition which are characteristic of all mixtures studied. Cooling from the isotropic phase, the Ch-I transition with a 0.5 K wide two-phase coexistence region, is preceded by a C_p anomaly (shown by the arrow in Fig. 1) within the two-phase region. Below the C_p maximum, the behavior is quite similar to that of pure 8CB. This indicates that the fluctuations of the cholesteric phase just below the clearing point are nearly the same as those for the nematic phase. This is not unexpected since the cholesteric phase is generally thought of as simply a nematic phase with a single wavelength twisting director. The Ch-I transition temperature decreases ~ 2 K with decreasing pitch from 1.82 to 0.40 μm. The

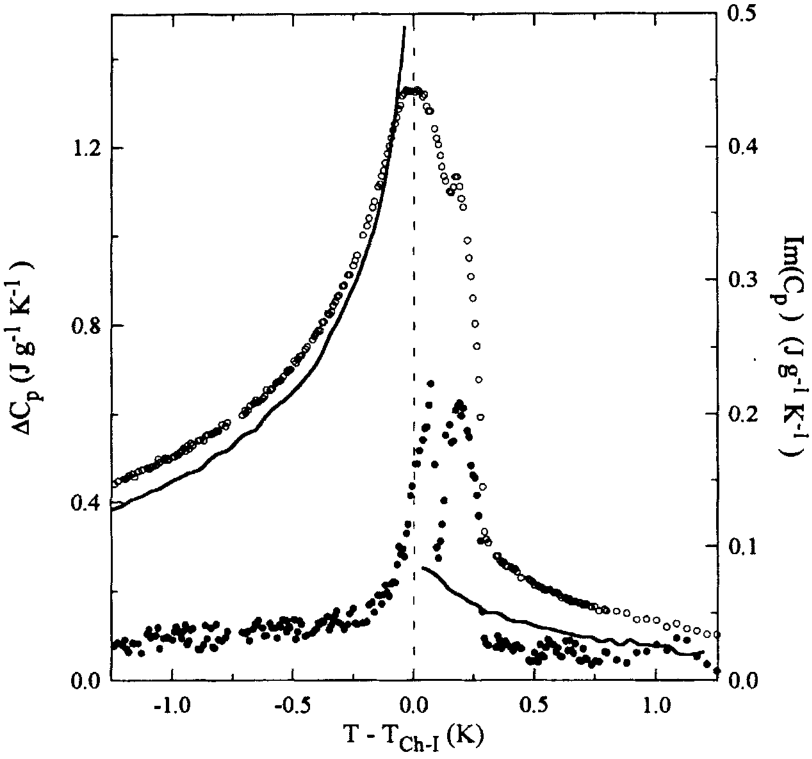

FIGURE 1 Excess specific heat, ΔC_p, (O) and Im(C_p) (●) about the Ch-I phase transition for the 6.17 % chiral/8CB mixture. The solid line represents the pure 8CB ΔC_p behavior at the N-I transition. Note that the Im(C_p) scale is 1/3 of the ΔC_p scale.

change of T_{Ch-I} with inverse pitch is shown in the top panel of Figure 3. This constancy is also expected from the choice of mixture composition which is intended to maintain the clearing temperature.

The imaginary C_p component reveals *two*, sharp, peaks in the two-phase coexistence region, indicating the presence of considerable dynamics in the phase conversion. The higher temperature peak is exactly coincident with the pre-transitional C_p anomaly while the lower temperature peak is ~ 0.08 K *above* T_{Ch-I}. This behavior is found in all mixtures studied; however, the distinction between the two Im(C_p) features becomes progressively less with decreasing pitch. Both ΔC_p and Im(C_p) features represent first order behavior. The low temperature feature is most likely the first order Ch-I transition while the origin of the higher temperature pre-transitional anomaly is yet unclear. It

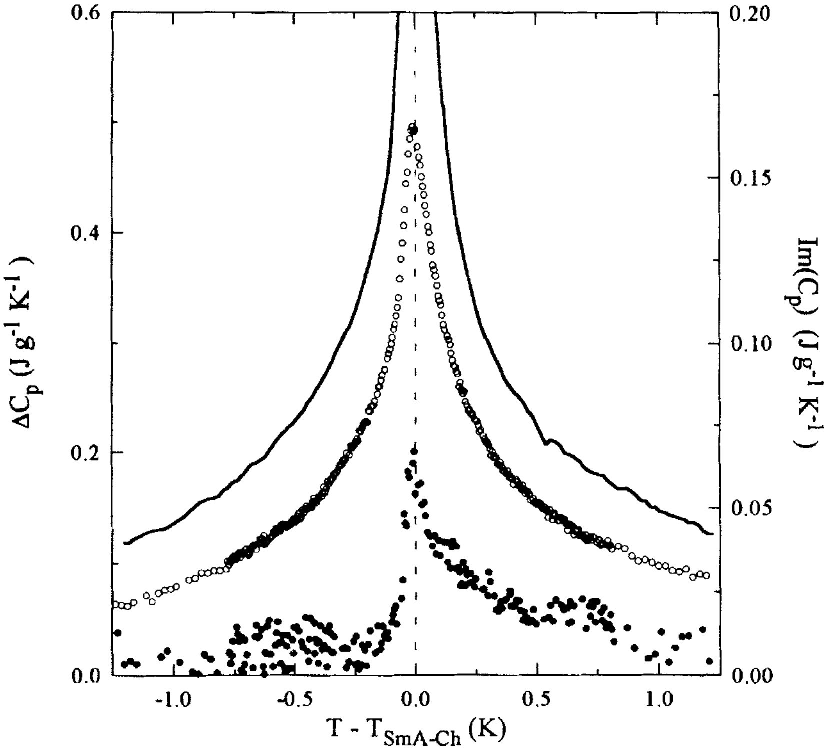

FIGURE 2 Excess specific heat, ΔC_p, (O) and Im(C_p), (●), about the SmA-Ch phase transition for the 6.17 % chiral/8CB mixture. The solid line indicates the pure 8CB ΔC_p behavior at the SmA-N transition. Note that the Im(C_p) scale is 1/3 of the ΔC_p scale.

may signal the onset of some nucleation process of small nematic domains prior to the formation of the cholesteric, similar to a slight phase separation of chiral and non-chiral components during the phase conversion of the transition.

Equally remarkable behavior is observed at the SmA-Ch transition shown in Figure 2. The ΔC_p feature becomes suppressed with increasing chirality (compared to the pure 8CB SmA-N transition) although it retains a sharp appearance. Another distinguishing feature is the asymmetric nature of the ΔC_p peak having a sharper decline on the *low* temperature side of the transition. Again, this behavior is observed for all mixtures studied. $T_{SmA\text{-}Ch}$ considerably shifts to lower temperature with chirality as shown in the top panel of Figure 3.

As in the Ch-I transition, the imaginary component of C_p (see Fig. 2) shows interesting dynamics effects at the SmA-Ch transition. Specifically, Im(C_p) diverges upon approaching $T_{SmA\text{-}Ch}$ from the Ch phase and reaches a maximum at $T_{SmA\text{-}Ch}$. It then abruptly goes to zero below the transition. This behavior may reflect the unwinding of the cholesteric phase as the twist distortion is expelled. Assuming a Debye behavior, a characteristic relaxation time may be estimated by $\tau_R = \mathrm{Im}(C_p)_{max}/(\omega \Delta C_p^{max})$ [13] where the designation *max* refers to the maximum values at the SmA-Ch transition. For the 1.82 μm pitch sample, $\tau_R \approx 0.20$ sec/rad or ≈ 0.80 Hz indicating a very slow relaxation mode connected with the liquid crystal "Meisner" effect.

The effect of chirality (twist deformation) on the SmA-Ch transition is analogous to the application of an external magnetic field on the superconducting to normal transition in metals [1]. As mentioned earlier, for type I smectics, approaching from the Ch (normal) phase, the twist (magnetic field) is expelled at $T_{SmA\text{-}Ch}$ from the sample. For type II smectics, prior to the expulsion of twist, an intermediate phase of a regular array of disclinations known as TGB phase (analogous to the Abrikosov phase) [3] may form. For type I smectics, the transition temperature is given by [1,15,16]

$$T_c(p) = T_c(0) - lT_c(0)\left|\vec{\nabla} \times \hat{n}\right| , \qquad (4)$$

where $T_c(p)$ is the SmA-Ch transition for a given imposed twist, $T_c(0)$ is the SmA-N (untwisted) transition temperature, l is a relevant length scale, and $|\nabla\times\mathbf{n}|$ is the imposed twist distortion which is given by $\delta\theta/\delta x$, the change of director orientation with distance. For a cholesteric, the pitch, p, is the distance the director rotates from 0 to π, hence $|\nabla\times\mathbf{n}| = \delta\theta/\delta x = \pi/p$. Since the clearing temperature varies somewhat with chirality, an equivalent expression of Eq. (4) is [1,15]

$$\Delta T_c(p) = \Delta T_c(0) + lT_c(0)\left|\vec{\nabla} \times \hat{n}\right| , \qquad (5)$$

where $\Delta T_c(p) = T_{Ch\text{-}I} - T_{SmA\text{-}Ch}$ and $\Delta T_c(0) = T_{N\text{-}I} - T_{SmA\text{-}N}$. The plus sign of the second term comes from the rescaling of the transition temperature.

Figure 3 shows the transition temperatures, $T_{Ch\text{-}I}$ and $T_{SmA\text{-}Ch}$, as well as $\Delta T_c(p) = T_{Ch\text{-}I} - T_{SmA\text{-}Ch}$ as a function of π/p for the five concentrations studied. Although $T_{SmA\text{-}Ch}$ decreases nearly linearly, the deviations in $T_{SmA\text{-}Ch}$, are highly correlated with the

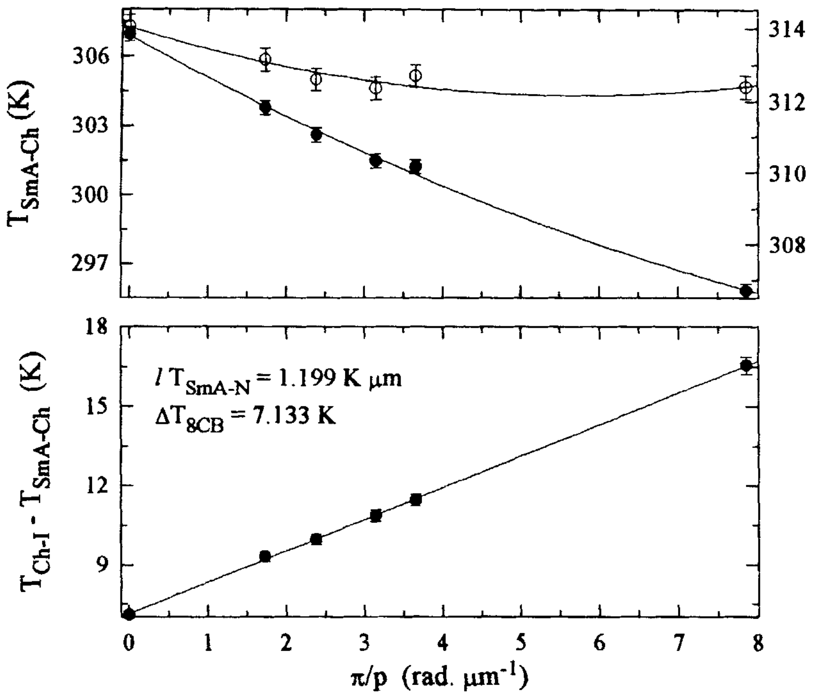

FIGURE 3 Transition temperature shifts as a function of π/p. Top panel: $T_{SmA\text{-}Ch}$ (●) and $T_{Ch\text{-}I}$ (O) where the solid lines are guides to the eye. Bottom panel: $T_{Ch\text{-}I}$ - $T_{SmA\text{-}Ch}$ where the solid line is a linear fit. Inset of bottom panel; slope and intercept.

deviation of $T_{Ch\text{-}I}$ with decreasing pitch. Replotting $T_{Ch\text{-}I}$-$T_{SmA\text{-}Ch}$ verses π/p yields a perfectly linear behavior (bottom panel of Figure 3), justifying the use of Eq. (5) to analyze the shifts. This is characteristic of type I behavior for this material. The resulting intercept matches very well with the literature value [9] and our own measurements [18] of $\Delta T_{8CB} = T_{N\text{-}I}$-$T_{SmA\text{-}N}$ for pure 8CB of 7.133 K. The parameter l can be calculated from the slope of 1.199 K μm using 307 K for $T_{SmA\text{-}N}$, it yields l = 39 Å which represents the smectic interaction length scale. The smectic layer spacing of these mixtures is not known, however, the layer spacing for 8CB is ~ 31.7 Å [17]. Thus, l represents a short ranged coupling between the smectic layers.

Finally, we also studied the effects of cylindrical confinement on these two transitions. Preliminary results of confining the mixtures in the 0.2 μm diameter cylindrical pores of Anopore membranes reveal interesting and unexpected behavior. Anopore

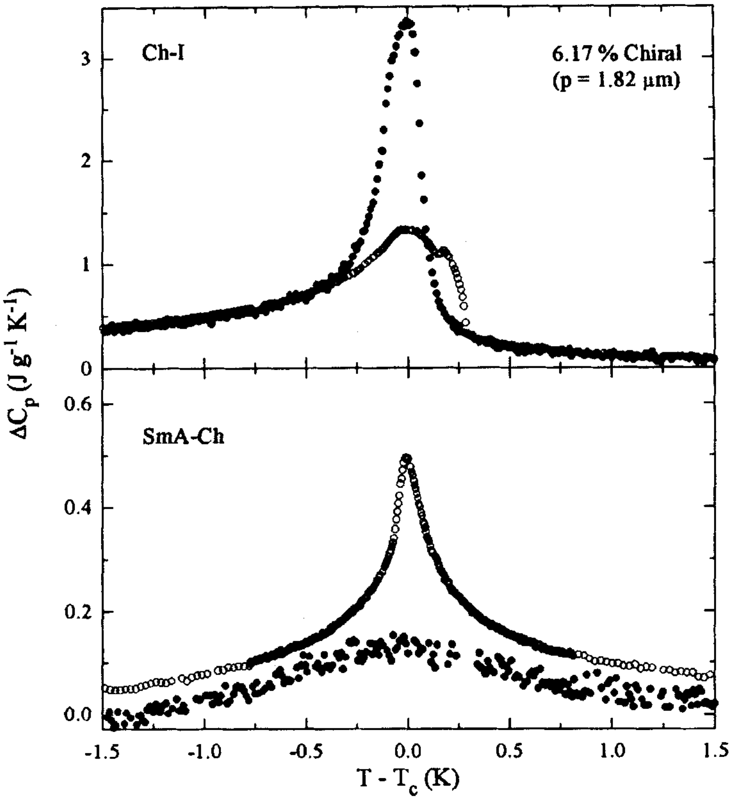

FIGURE 4 Excess specific heat, ΔC_p, of bulk (O) and Anopore confined (●) 6.17 % chiral/8CB mixture about the Ch-I (top panel) and SmA-Ch (bottom panel) phase transition.

confined samples were constructed without any pore surface treatment using a previously published method [18]. The ΔC_p for the Ch-I and SmA-Ch transition are presented in Figure 4 for both the bulk and Anopore confined 6.17 % chiral/8CB mixture. The Ch-I transition becomes greatly enhanced compared to the bulk, appearing quite smooth and with no indications of the pre-transitional C_p anomaly. In comparison, the pure 8CB N-I transition C_p becomes broad and suppressed from bulk under Anopore confinement [18]. For the chiral mixture, this likely reflects the sluggish phase conversion (hence sluggish release of the latent heat) of this first order transition induced by the Anopore confinement modifying the two-phase coexistence region and hence the twist nucleation process. In stark contrast, the SmA-Ch transition appears extremely suppressed and broadened by the confinement. This is similar to previous results of the SmA-N transition for pure 8CB in Anopore [18] and reflects the difficulty of the smectic phase to form layers which uniformly span and fill the cylindrical pores. In general, the transition temperatures for both transitions are shifted ~ 1 K below the bulk.

CONCLUSIONS

We have discussed results from a high resolution ac calorimetric study of chiral mixtures of 8CB, CE2, and CB15 as a function of chirality. The pitch was varied in five samples from 1.82 to 0.40 μm with the 6.17 % (1.82 μm pitch) mixture discussed in detail. The continuous SmA-N transition of pure 8CB loses its symmetric appearance. The resulting SmA-Ch transition is suppressed and shifts to lower temperatures with increasing chirality. The increasing asymmetric nature results from the increased thermal fluctuations of the Meisner effect on the high temperature side of the transition. In fact, the relative shift of $T_{SmA\text{-}Ch}$ is well modeled by type I behavior. The Ch-I transition only shifts marginally to lower temperatures since the choice of mixture was intended to roughly maintain the clearing point. It retains the pretransitional C_p temperature dependence in the ordered phase of the N-I transition for pure 8CB. However, the Ch-I transition is proceeded by a C_p feature in a 0.5 K wide two-phase region. It is speculated that this feature reflects a nucleation process of the establishment of the cholesteric phase in fluctuation driven nematic domains within the biphasic region.

Further work is needed to better characterize the smectic phase of the chiral mixtures as well as extending the studies to higher chirality (smaller pitches). For the SmA-Ch transition, this would explore the possibility of a cross-over to type II behavior with the advent of an intermediate TGB-like (Abrisokov) phase. For the Ch-I transition, at some critical pitch there should form blue phases which typically form below ~ 0.5 μm. Our studies stopped at 0.4 μm and have not yet observed any blue phase behavior. Preliminary Anopore confinement studies reveal interesting suppression of the SmA-Ch and enhancement of the Ch-I transitions. Extending the cylindrical confinement studies using higher chirality would probe possible director configurational transition driven by the cholesteric pitch.

ACKNOWLEDGMENTS

Our thanks go to Prof. C. W. Garland, Dr. Z. Kutnjak, and Dr. H. Haga for many enlightening and helpful discussions. This work at KSU was supported by the NSF-STC ALCOM grant No. DMR 89-20147.

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