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Abstract. — Temperature variations of heat capacity, optical tilt angle, polarization, and helical pitch have been measured in the vicinity of the smectic-A (SmA)-chiral-smectic-C (SmC*) transition of one liquid-crystal compound which exhibits an unusual reversal behavior in polarization at about 25 °C while the SmA-SmC* transition occurs at 50 °C. Unexpectedly, from our detailed calorimetric and optical microscopy studies, we have found that the recrystallization also occurs around 25 °C during a reasonably slow cooling experimental run.

Ferroelectric liquid-crystalline mesophases, in particular, the chiral-smectic-C (SmC*) phase have been demonstrated as potentially useful operating media in electro-optical applications with switching speeds in the microsecond range [1]. Compared to conventional liquid-crystal devices employing nematic materials, electro-optical devices based on the ferroelectric liquid-crystal materials have, at least, one important new feature. Namely, the switching speed can be much faster. Numerous new homologous series of liquid-crystal compounds have been synthesized to explore the various physical properties related to device applications. Meanwhile, the interplay of the polarization and other molecular properties has created very rich and interesting physical phenomena, e.g., polarization reversal [2, 3]. In this paper, we report our detailed thermal and electro-optical investigations on one liquid-crystal compound which exhibits this unusual behavior near room temperature.

The smectic-A (SmA) and smectic-C (SmC) liquid-crystal mesophases can be characterized as orientationally ordered fluids with a layer structure. The layer normal is along the long axis of the molecule (molecular director) in the SmA phase or at an angle to it in the SmC phase. The order parameter characterizing the SmA-SmC transition is the tilt angle. The inclusion of a chiral center within the molecular structure will break the mirror symmetry in the SmC phase and create a new mesophase, namely, the SmC* phase [4]. In the SmC* phase, the molecular director precesses around the layer normal and forms a helicoidal structure with a pitch about several microns. The breaking of the mirror symmetry allows for a spontaneous polarization to be generated along the two-fold rotational axis which is perpendicular to the plane containing both the layer normal and the molecular director. The existence of a

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spontaneous polarization within each smectic layer leads us to call the SmC* phase a ferroelectric liquid-crystal mesophase. Thus in addition to the molecular tilt angle, both polarization and helical pitch are essential macroscopic quantities to describe the nature of the SmC* phase or the SmA-SmC* transition. Experimentally, it has been demonstrated that the primary order parameter for the SmA-SmC* transition of the well-characterized DOBAMBC compound is the tilt angle [5, 6]. Here DOBAMBC refers to p-(n-decyloxybenzylidene)-p-amino-(2-methylbutyl) cinnamate.

Much of our knowledge concerning the SmA-SmC* transition has been acquired from the experimental work on the renowned DOBAMBC compound [7, 8]. Recently, Mikami et al. [2] and Goodby et al. [3] have reported an unusual polarization reversal behavior in the SmC* phase of (S)-2''-methylbutyl 4'-n-alkylcarbonyloxy-(1,1'-biphenyl)-1-carboxylate (2MBnCBC). For example, the polarization of 2MB8CBC increases from zero at the SmA-SmC* transition temperature (42 °C), reaches a maximum value around 37 °C, gradually approaches zero around 22 °C and reverses the sign of the polarization. The tilt-angle measured by an optical technique on 2MB9CBC also displays reversal behavior [2]. Subsequently, Skarp et al. [9] have carried out several electro-optical measurements on 2MB9CBC to investigate the nature of the SmC* phase. In addition, employing two sample cells with different thicknesses, the thicker one in the presence of the helix and the other one without the helix, Eidenschink et al. [10] obtained different temperature variations of tilt-angle near the reversal temperature of 2MB8CBC. Later Musevic et al. [11] obtained the temperature dependence of tilt angle from both measurements of rotatory power and x-ray diffraction on 2MB8CBC. Both results gave a tricritical-like behavior without any anomaly near the polarization reversal temperature. To get a better understanding of this family of homologous compounds with unusual reversal behavior in polarization, we have carried out high-resolution measurements on the heat capacity, tilt angle, polarization and helical pitch in the vicinity of the SmA-SmC* transition of (S)-2''-methylbutyl 4'-n-decylcarbonyloxybiphenyl-1-carboxylate (2MB(10)CBC). Its chemical formula is

\[
\text{C}_{10}\text{H}_{21}\text{COO-}-(\text{C}_6\text{H}_4)-(\text{C}_6\text{H}_4)-\text{COOCH}_2\text{C}^*\text{H}(\text{CH}_3)\text{C}_2\text{H}_5
\]

and transition sequence is

Isotropic (62 °C) SmA (51 °C) SmC* (29 °C) Crystal.

The details of our measurement techniques for heat capacity and electro-optical properties have been described in references [7, 12] respectively. The thickness of our well-aligned sample in the planar configuration for electro-optical investigations is 25 μm. Separations between the laser diffraction spots from dechiralization lines in the SmC* phase are employed to determine the helical pitch. The tilt angles are obtained from the extrapolation of « apparent » tilt-angles measured at several applied electrical fields. Due to the existence of the pretilt angle between the liquid crystal and the substrate and the possible chevron structure inside the sample [13, 14], some concerns have been raised in this approach in determining the tilt angle. However, the justification for this approach has been demonstrated nicely by the work of Seppen et al. [15]. In the case of DOBAMBC, the tilt-angle obtained by our research group [6] from such an extrapolation scheme is in excellent agreement with the one from the measured rotatory power [15]. Our experimental measurements required to unwind the helical pitch and the rotatory power measurements did not. Three typical sets of data are shown in figure 1. Except in the vicinity of the transition temperature (see Fig. 1c), the field dependent apparent tilt-angle exhibits a nonlinear effect (see Figs. 1a and b). This nonlinear effect is enhanced as the sample temperature is decreased. It is plausible that the deviation in the low field region, which is still larger than the critical electric field \(E_c\), may be due to either strange temperature dependence of the polarization in the low
temperature region or the surface anchoring effect, e.g., the well known chevron structured smectic layers [13]. The chevron structure tends to reduce the measure tilt-angle. The deviations of the apparent tilt angle from the linear extrapolation were not seen in our measurements of two other ferroelectric liquid-crystal compounds which have moderate size in polarization with well-behaved temperature variations. As a result, the tilt-angle data reported in this paper are determined from high-field extrapolation if nonlinear behavior exists. Here $E_c (\approx 8 \times 10^5 \text{ V/m})$ is the electrical field required to unwind the helical pitch. Moreover, Takezoe et al. [16] have argued that the tilt fluctuations are a plausible cause for the non linearity in the apparent tilt angle. We believe that the deviation of the apparent tilt angle in the low field and low temperature region should not be due to the fluctuation effect of the tilt angle. This kind of fluctuation should be much stronger near the transition temperature range than in the low temperature region. Finally, the polarization was also measured as a function of the applied field. The polarization remains constant for the field strength larger than twice the critical field.

In the neighborhood of the SmA-SmC* transition of 2MB(10)CBC temperature variations of heat capacity, helical pitch, tilt angle, and polarization are displayed in figures 2-5,
respectively. While both heat capacity and helical pitch behave similar to the SmA-SmC* transition of DOBAMBC (Refs. [7, 17], the polarization acts very differently. Similar to 2MB8CBC, the polarization increases from zero at the SmA-SmC* transition temperature (about 50 °C), reaches a maximum value around 42 °C and exhibits a reversal behavior around 25 °C.

Our heat-capacity data (Fig. 2a) demonstrated that there exists another transition near 25 °C which is in the neighborhood of the polarization reversal temperature (see Fig. 5). The melting point of 2MB(10)CBC is 46 °C and reported recrystallization temperature is – 6.6 °C (Ref. [3]). In order to investigate the nature of this transition just above room temperature, we have employed a polarizing optical microscope equipped with a Mettler hot stage. The sample can be quickly supercooled from any high temperature phase to room temperature without crystallization. Upon cooling from the SmA phase to 30.5 °C, the sample was kept at 30.5 °C. It remained in the SmC* phase for more than three days without any sign of crystallization. Cooling further to and monitoring at 29.2 °C, the sample crystallized in about 5Hr. Another quick cooling run from the isotropic phase down to 29.2 °C directly gave the same result. Namely, the sample crystallized within 5Hr at 29.2 °C. Consequently, the recrystallization is the primary cause of the second transition in our heat-capacity result.

Fig. 2. — Temperature variation of heat capacity over a wide temperature range (a) and in the vicinity of the SmA-SmC* transition (b). The solid line in the part (b) is the fitting result to equation (3).
Because the peak position of the polarization is about 10 K above the crystallization temperature, it is highly unlikely that the crystallization will have any effect on the polarization reversal behavior. Without any further direct experimental evidence, we can not entirely rule out this possibility.

On the basis of their high-resolution heat-capacity measurements on another liquid-crystal compound, Huang and Viner [18] proposed the following free energy expansion to describe the temperature variations of the heat capacity and tilt angle near the SmA-SmC* transition:

$$ G = G_0 + a t \Phi^2 + b \Phi^4 + c \Phi^6. $$

By minimizing this free energy, the temperature dependence of the tilt angle and heat capacity near the transition temperature can be obtained and are

$$ \Phi = \left( \frac{b}{c} \right) \left( 1 - \frac{3 t}{t_0} \right)^{1/2}, \quad T < T_c $$

and

$$ C = \begin{cases} B + D t, & T > T_c \\ A (T_m - T)^{-1/2} + B + D t, & T < T_c \end{cases} $$

respectively. Here $A = a^{3/2} / (2(3 c)^{1/2} T_c^{3/2})$, $T_m = T_c(1 + t_0/3)$ and $B + D t$ is the background heat capacity obtained from the non-singular part of the free energy $G_0$. We have also defined a dimensionless quantity $t_0 = b^2/(ac)$ which characterizes the cross-over from the ordinary meanfield region ($|t| < t_0$) with $(b \Phi^4) > (c \Phi^6)$ and $\Phi = \Phi_0 |t|^{1/2}$ to the meanfield tricritical region ($|t| > t_0$) with $(b \Phi^4) < (c \Phi^6)$ and $\Phi = \Phi_0 |t|^{1/4}$. The coefficients $a$, $b$, and $c$ are positive constants for a continuous transition, $\Phi$ is the magnitude of the order parameter and $t = (T - T_c)/T_c$ is the reduced temperature. The fitting of our heat-capacity data to equation (3) is shown as the solid line in figure 2b over the temperature range from 35 °C to 53 °C. The important dimensionless parameter obtained from this fitting is found to be $t_0 = 3.37 \times 10^{-3}$. The reported tilt-angle data on 2MB9CBC with tricritical-like behavior by Musevic et al. [11] agree with this small value in $t_0$. Thermodynamically, in a mean-field phase
transition, the anomalous part of heat capacity \((\Delta C)\) and the order parameter \((\Phi)\) are related by [19]

\[
\Phi = \left[ \frac{1}{a} \int_{T}^{T_c} \frac{\Delta C}{T} \, dT \right]^{1/2}.
\]

Here \(\Delta C = C - B -Dt\). The solid line in figure 4 displays the calculated result from our heat-capacity data except for an overall constant factor. They are in reasonable good agreement except the drop in tilt angle for \(T_c - T > 20\) K. We believe that this drop is caused by the great reduction in the polarization near the reversal temperature. In the case of DOBAMBC (Ref. [6]) and DOBA-1-MPC (Ref. [20]), we have demonstrated that \(\Delta C\) and tilt angle satisfy equation (4) and concluded that the tilt angle is the primary order parameter for the SmA-SmC* transition of these two compounds. In the immediate vicinity of the SmA-SmC* transition, the helical pitch exhibits a sharp drop and reaches a finite value at the transition temperature. Correspondingly, the ratio of the polarization to tilt angle exhibits a pronounced drop and reaches a finite value in the immediately vicinity of the transition temperature. This agrees with the prediction based on the generalized mean-field model proposed by Zeks [21] and Dumrongrattana and Huang [22]. However, detailed descriptions of both polarization and tilt angle data within one theoretical model are not available, because we do not truly understand the origin of the reversal behavior in the polarization. In the following paragraph, we will present two preliminary attempts in fitting the temperature dependence of polarization.

After discovering the polarization reversal phenomena in two liquid-crystal homologous series, Goodby and co-workers [3] tried to describe the polarization data by the following empirical form

\[
P = [P_A \exp(-\Delta/T) + P_B(1 - \exp(-\Delta/T))] |t|^{-\beta},
\]

with four adjustable parameters \(P_A\), \(P_B\), \(\Delta\) and \(\beta\). The basic idea is that among numerous confirmational configurations of the given liquid-crystal molecule, two of them dominate all of the others. They are separated by an energy barrier \(\Delta\) and have polarization \(P_A\) and \(P_B\), respectively. So the Boltzmann factor accounts for the probability that a molecule will be in confirmational configuration with polarization \(P_A\) which has an opposite sign from \(P_B\). In this argument, the different sign for \(P_A\) and \(P_B\) is the major source of the polarization reversal behavior. Fitting results, based on equation (5), are shown in figure 5a as solid line and lead to \(P_A = 397\) \(\mu\)C/\(m^2\), \(P_B = -42.4\) \(\mu\)C/\(m^2\), \(\Delta = 670\) K, and \(\beta = 0.53\) which qualitatively agree with the results reported before [23]. However, it has been clearly demonstrated that a simple power-law expression is not sufficient to describe the temperature dependence of either tilt angle or polarization near the SmA-SmC* transition of ordinary liquid-crystal compounds [6]. Temperature variations of both tilt angle and polarization experience evolution from one value of the critical exponent near the transition temperature region \((T_c - T < 1\) K) to another value away from the transition temperature. For example, the temperature dependence of the tilt angle has an ordinary mean-field critical exponent \((\beta = 1/2)\) just below \(T_c\) and a tricritical-like exponent \((\beta = 1/4)\) away from \(T_c\) \((T_c - T > t_0 \times T_c)\). A tricritical-like behavior in the temperature dependence of tilt-angle has been reported by Musevic et al. [11]. Thus the value of \(\beta\) obtained from the fitting of equation (5) may not be realistic. Our high-resolution heat-capacity measurements give the value of the important parameter \(t_0\) to be \(3.37 \times 10^{-3}\). This means that the cross-over from the ordinary mean-field behavior to the tricritical one occurs around \(T_c - T = 1\) K. (Note: majority of the tilt angle data reported in reference [11] are in the range \(T_c - T > 1\) K).
Consequently, simple power-law description for either tilt angle or polarization with \( \beta = 1/2 \) is not appropriate. The temperature dependence of the primary order parameter \( (\Phi) \) is known from equation (2). Assuming that polarization is proportional to \( \Phi \), we tried to fit our polarization data to equation (5) using the expression for \( \Phi \) in equation (2), instead of \( |r|^{-\beta} \). No reasonable fitting results can be obtained. Instead, the following expression gives a fairly good description of our polarization data:

\[
P = [P_C \exp(\Delta'/T) + P_D] \Phi,
\]

Our fitting results are displayed in figure 3b as the solid line and give \( P_C = -2.23 \times 10^{-10} \) \( \mu \)C/m\(^2\), \( P_D = 10.3 \) \( \mu \)C/m\(^2\), \( \Delta' = 7380 \) K. Again an opposite sign for \( P_C \) and \( P_D \) is responsible for the reversal behavior. Obviously, both equations (5) and (6) give fairly good fit to the polarization data. However, in equation (6), there exist only three adjustable parameters, instead of four as in equation (5). Although we do not precisely know the microscopic origins for the activation energy term in equation (6), several physical quantities (e.g., viscosity) exhibit an activation energy form in liquid-crystal mesophases. The magnitude of the spontaneous polarization in the SmC\(^*\) phase is closely related to damping of the molecular rotation around its long axis. A trend similar to the reversal polarization phenomenon has been observed in recent NMR studies of the temperature dependence of the polar order parameter of the C=O group in 2MB8CBC (Ref. [24]). Furthermore, while investigating the diverging behavior of the twist viscosity near the nematic-SmA transition of another liquid-crystal compound, Huang et al. [25] have found that the non-divergent part of the twist viscosity has an activation energy form with activation energy \( B = 5.3 \times 10^3 \) K. This value of \( B \) is comparable to the activation energy \( \Delta' \) obtained from data fitting to equation (6). On the basis of these facts and our current knowledge on the nature of the SmA-SmC\(^*\) transition, we believe that equation (6) with only three adjustable parameters may be a more realistic model to describe the polarization reversal behavior.

Here we assume that both \( \Delta \) in equation (5) and \( \Delta' \) in equation (6) are temperature independent variables. These quantities are related to the phase transition and are in the argument of the exponent. Any small temperature dependence will have a dramatic effect on the temperature variation of the polarization. At this moment, we do not have any appropriate theoretical model to describe the possible temperature variation of these two important parameters. Furthermore, the existing data fitting can’t rule out these two parameters being completely independent of temperature. Further experimental work and

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Fig. 5. — Temperature variation of polarization in the SmC\(^*\) phase. The solid lines in (a) and (b) are fitting results from equations (5) and (6), respectively.
theoretical advances are essential to understand the physical origin of this unusual polarization reversal phenomenon.

In conclusion, we have investigated the temperature variation of heat capacity, polarization, tilt angle and pitch for one liquid-crystal compound with reversal polarization behavior. In the vicinity of the polarization reversal temperature, the sample exhibits a phase transition from the SmC* phase to the crystalline phase, provided that the sample is cooled slowly enough. However, the recrystallization can not be fully responsible for the polarization reversal phenomenon. The microscopic origin of this reversal phenomenon is still lacking. Without a satisfactory microscopic explanation or a proper free energy expansion for the temperature variation of polarization, fitting our experimental data to equation (5) and (6) is rather tentative. Further experimental information is needed to unfold this unusual phenomenon in polarization.

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