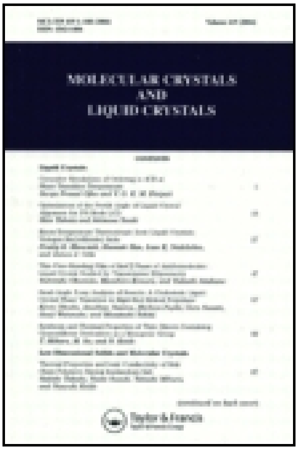

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# A Heat Capacity Study of Phase Transitions in the Ferroelectric Liquid Crystal ($R^-$) Hexyloxybenzylidene *p′*-amino-2-chloropropyl cinnamate (HOBACPC)

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The heat capacity of the ferroelectric liquid crystal ($R^-$) hexyloxybenzylidene $p'$-amino-2-chloropropyl cinnamate (HOBACPC) has been measured between 64 and 88 °C. In this temperature range HOBACPC has three phase transitions. The smectic A–chiral smectic C transition is found to be mean-field like which is similar to other smectic A–smectic C transitions. The chiral smectic C–chiral smectic I transition has a large heat capacity anomaly. A large hysteresis between the heating and cooling experimental runs is found for the chiral smectic I–chiral smectic G transition.

A variety of organic compounds exhibit the smectic A (SmA) and, at lower temperatures, the smectic C (SmC) liquid crystal phases characterized by a one dimensional density wave whose wave vector is along (A) or tilted with respect to (C) the average long molecular axis (director). Upon further cooling some of these compounds show tilted smectic phases with additional degrees of translational ordering (SmF, I, G, H, etc.). An important subclass of any of these tilted smectic phases is the corresponding chiral smectic phase (SmC*, SmF*, ...), obtained if the constituent molecules are chirally asymmetric (nonenantiomorphic). In the SmC*, SmF* and SmI* phases, as a consequence of the molecular chiral asymmetry, the director exhibits a helicoidal structure, precessing around the direction perpendicular to the layers. An additional by-product of molecular chirality in a tilted smectic phase is ferroelectricity, with the bulk ferroelectric dipole moment locally normal to the director and in the layer planes.[1] In recent years there has been considerable interest in the structure of the various tilted smectic phases as well as in the phase transitions between them.[2-6]

In this paper we will present a detailed heat capacity study of the chiral compound ($R^-$) hexyloxybenzylidene $p'$-amino-2-chloropropyl cinnamate[7] (HOBACPC) which is of interest since it exhibits, over the temperature range studied ($64 < T < 88\,^\circ$C), three tilted smectic phases, as follows:

$$\text{SmG*} \xrightarrow[67\,^\circ\text{C}]{} \text{SmI*} \xrightarrow[74\,^\circ\text{C}]{} \text{SmC*} \xrightarrow[80\,^\circ\text{C}]{} \text{SmA}.$$

In addition, because of its large ferroelectric polarization density arising from a large transverse molecular dipole moment at its chlorine-chiral carbon bond, HOBACPC has been studied for the purpose of realizing a fast switching electro-optic device.[8] Consequently, it is a technologically important material.

A quasi-adiabatic ac calorimetric technique[9] was used to measure the heat capacity of HOBACPC as a function of temperature. The liquid crystal was contained in a sample cell[10] consisting of two chemically etched cover glass slides, a thin-film heater and thermocouple temperature sensing elements. An ac current $I$ (rms) at angular frequency $\omega$ passing through a gold-film heater of resistance $R$ and area $A$ periodically heated the liquid crystal and produced a temperature oscillation of amplitude $\Delta T$ (rms) at the ac thermocouple temperature sensor. $\Delta T$ typically had a value of 3 mK. The total measured heat capacity per unit area was then given by $(I^2R/A)/(\sqrt{2}\,\omega\,\Delta T)$. Figures 1 and 2 show the total heat capacity per unit area of the HOBACPC sample: the SmA–SmC* transition has a sharp heat capacity jump, the SmC*–SmI* transition has a large heat capacity anomaly and the SmI*–SmG*[11] transition a small anomaly. A more detailed discussion of the above phase transitions follows.

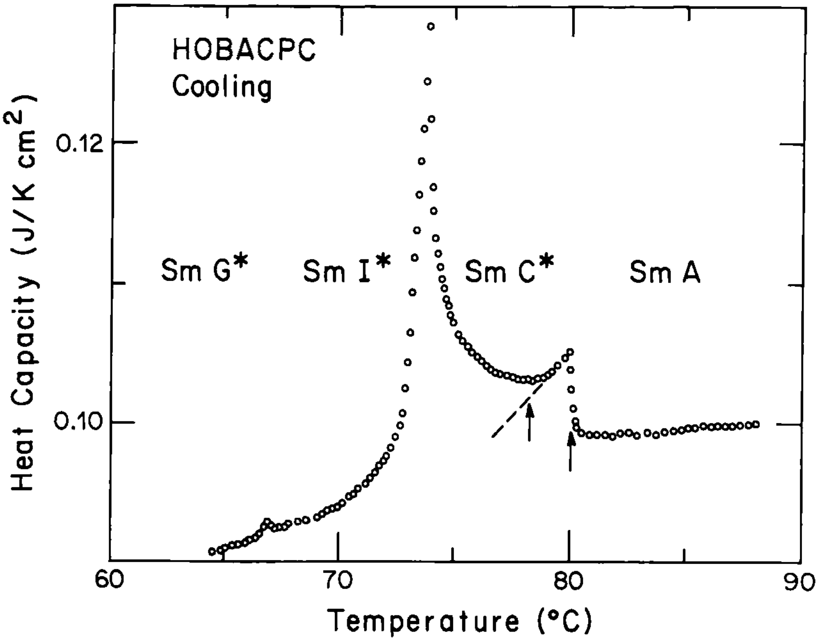

FIGURE 1 Temperature dependence of the total heat capacity (sample and sample cell) per unit area of HOBACPC between 64 and 88 °C. The data were acquired in a cooling run. The dashed line is the extrapolation of the data just below the SmA-SmC* transition for the purpose of roughly estimating the full width at half height of this heat capacity anomaly. Two arrows indicate the size of this full width at half height. The important parameter $t_0$ deduced from this procedure is about $5 \times 10^{-3}$.

*SmA-SmC* Transition*. Meyer *et al.*[1] have observed a rather small difference in the SmA-SmC transition temperatures between the nonchiral and chiral versions of one liquid crystal compound. This indicates that the transition is mainly driven by intermolecular forces producing the tilted SmC phase and not by ferroelectric coupling between permanent dipoles. The spontaneous polarization is thus a secondary rather than a primary order parameter. Consequently, one can use a complex scalar order parameter $\Psi = \psi e^{i\phi}$ in the vicinity of the SmA-SmC* transition. Here $\psi$ and $\phi$ are, respectively, the tilt and azimuthal angles of the nematic director in the SmC* phase. The symmetry of the order parameter allows the SmA-SmC* transition to be continuous and places this transition in the *XY* universality class. In order to determine the nature of the SmA-SmC* transition in HOBACPC, both x-ray and optical techniques have been employed to measure the temperature dependence of the tilt angle.[3] The associated critical exponent ($\beta$) has been obtained from a simple power law

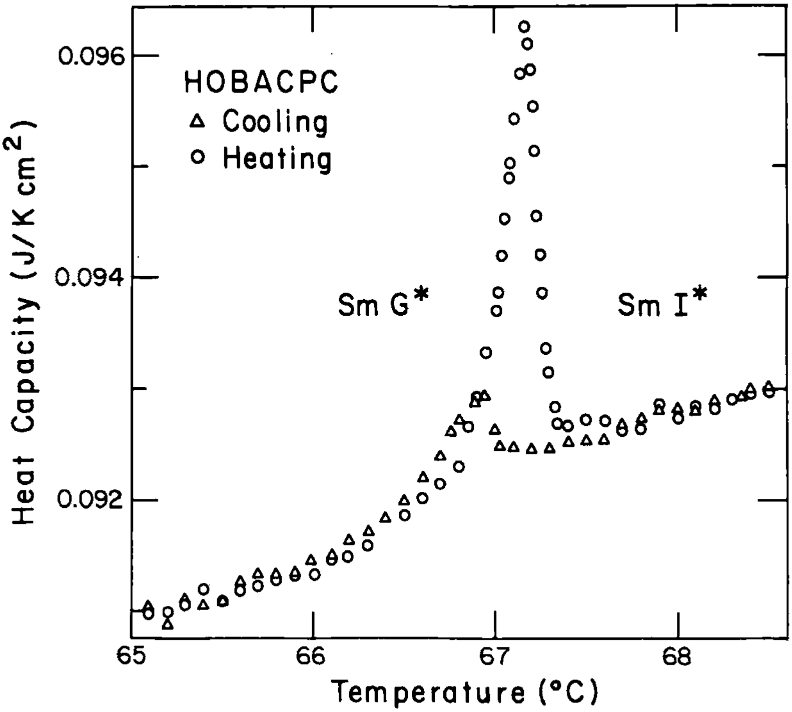

FIGURE 2 The total heat capacity of HOBACPC in the vicinity of the SmI*-SmG* transition. The data, taken in a cooling as well as a heating run, are shown here.

fitting, i.e., $\psi = B|t|^{\beta}$. Here $t = (T - T_c)/T_c$ is the reduced temperature for the SmA-SmC* transition with transition temperature $T_c$. For HOBACPC two values were obtained for the exponent $\beta$ corresponding to two different sample preparations, i.e., $\beta = 0.43$ in the planar configuration and 0.37 in the homeotropic configuration. These critical exponents fall between the mean-field value ($\beta = 0.5$) and the tricritical exponent ($\beta = 0.25$).

In the course of investigating the nature of SmA-SmC transitions in both pure[12] and mixture systems,[13] we have found that in the vicinity of the SmA-SmC transition, the singular part of the free energy can be written as[14]

$$F_s = a\left[t|\Psi|^2 + b|\Psi|^4 + c|\Psi|^6\right]$$

Here $a$, $b$ and $c$ are positive constants for a continuous transition. This free energy results in an important dimensionless parameter ($t_0 = b^2/c$) which determines the relative importance of the $|\Psi|^4$ and $|\Psi|^6$ terms. In the case of $t_0 = 0$, i.e., $b = 0$, one has a mean field tricritical point ($\beta = 0.25$) instead of an ordinary mean-field critical point ($\beta = 0.5$) with $c$ very small. Consequently, if a small $t_0$ is found in a given system, one expects to have crossover from mean-field to tricritical behavior.[12,13] Thus far, several heat capacity measurements have been made on the SmA–SmC transition of different liquid-crystal compounds. All of them have very small values for $t_0$ in comparison with other systems showing a mean-field transition.[12]

In the case of HOBACPC, because of the small temperature range for the SmC* phase (approximately 6 K), the large heat capacity anomaly associated with the SmC*–SmI* transition makes a detailed analysis of the SmA–SmC* heat-capacity anomaly impossible. Nevertheless, a sharp drop in the heat-capacity anomaly on the high-temperature side accompanied by a linear temperature-dependent heat-capacity in the SmA phase is similar to other measured SmA–SmC transitions and suggests a mean-field like transition. The size of the heat capacity jump calculated from the measured heat-capacity jump per unit area and the sample thickness (87 $\mu$) is about 0.67 J/K-cm$^3$ which is larger than the corresponding heat-capacity jumps of the other measured SmA–SmC transitions. Although the heat capacity data did not allow us to determine the important parameter ($t_0$) unambiguously, an approximate scheme was used. Linearly extrapolating the data just below the SmA–SmC* transition temperature (shown as a dashed line in Figure 1), then the full width at half height in the reduced temperature is roughly equal to $t_0$. In this way we obtained $5 \times 10^{-3}$ for $t_0$ which is comparable to the $t_0$ of other SmA–SmC transitions.[12] Consequently, the reason that different $\beta$ values were obtained by Martinot-Lagarde *et al.*[3] is that the SmA–SmC* transition in HOBACPC is also mean-field like with a small value of $t_0$. The crossover[12] between the ordinary mean-field region ($t \ll t_0$) and the tricritical region ($t \gg t_0$) makes the simple power law fitting to the measured tilt angle inconclusive. The critical exponent $\beta$ determined in this way will strongly depend on the fitting-temperature range.

*SmC*–SmI* Transition.* X-ray studies[15] have shown that the SmI* phase is characterized by smectic layers with almost no interlayer correlation and a pseudohexagonal order within the layers with the molecular director tilting toward the corner of the hexagon. From optical observations,[15] the SmI* phase appears to be helicoidal just as with the SmC* phase. As a consequence the SmI* phase can be described as a stacked-tilted-hexatic phase with the molecular director precessing along the normal to the smectic layers. Bond-orientational order is the relevant symmetry breaking order parameter.[16] Thus far all high-resolution x-ray measurements have demonstrated that the molecular tilt angle does not remain constant through the SmC–SmI or SmC–smectic F (SmF) transition. Either a jump[17] or a significant variation[18] in the molecular-tilt angle was found. A jump in the molecular-tilt angle leads to a first order SmC–SmI or SmC–SmF transition. Theoretically it has been shown that a change in the tilt angle will induce a change in the bond-orientational order.[16] This is one of the plausible explanations for the observed asymmetric heat capacity anomaly in the SmC–SmI transition of racemic 4-(2′-methylbutyl)phenyl 4′-*n*-nonyloxybiphenyl-4-carboxylate (2M4P9OBC).[19] In the immediate vicinity of the SmC*–SmI* transition the data show a stronger heat capacity variation with respect to temperature in the region $T > T_p$ than in $T < T_p$. Here $T_p$ is the temperature which corresponds to the peak of the SmC*–SmI* heat capacity anomaly. The SmC–SmI transition in 2M4P9OBC has the same behavior.[19] Consequently, the asymmetry in the heat capacity anomaly may result from the fact that the molecular-tilt angle does not stay constant through this SmC*–SmI* transition as well.

*SmI*–SmG* Transition.* As the temperature was lowered through the SmI*–SmG* transition of HOBACPC, x-ray measurements[15] have shown that the symmetry of the diffraction spots remained the same with increasing long-range order. Interlayer ordering also increased which corresponds to a transformation from two-dimensional to three-dimensional order. The SmG* phase does not exhibit a spontaneous helical direction rotation. Despite the large increase in the helix pitch through the SmI*–SmG* transition,[20] the measured heat capacity anomaly (see Figure 2) is quite similar to the SmI–SmG transition anomaly of 2M4P9OBC.[19] The difference in heat capacity, heating and cooling, indicates hysteresis and suggests a first order phase transition. Kumar *et al.*[21] have observed a similar behavior in their study of the SmF–SmG[11] transition of *N*-(4-*n*-heptyloxybenzylidene)-4-hexylaniline (HBHA) and have suggested that this type of hysteresis is a characteristic of defect mediated transitions.

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