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Temperature Dependence of Molecular Tilt Angle and Rotatory Power in a Ferroelectric Liquid Crystal with Polarization Sign Reversal

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The molecular tilt angle of the ferroelectric liquid crystal IS-2424 monotonously increases in the smectic C* phase with decreasing temperature from zero at the smectic A–smectic C* transition to about $\theta = 15°$. It can be described by a critical exponent $\beta = 0.26 \pm 0.02$. The temperature dependence of the tilt angle is definitely not proportional to the temperature dependence of the spontaneous polarization which shows a sign reversal.

1. INTRODUCTION

The smectic C* phase is ferroelectric[1] if the molecules are chiral and have a permanent dipole moment transverse to their molecular long axis. In the high temperature smectic A phase the molecules rotate freely around their long axes which are on average oriented perpendicular to the smectic layers ($n_z = 1$, $n_x = n_y = 0$). The point symmetry of each layer corresponds to the group D_∞. At the transition to the ferroelectric smectic C* phase the point symmetry of the layers is reduced to C_2. The order parameters of the transition are the molecular tilt with respect to the layer normals, i.e. the quadratic combinations

$$\xi_1 = n_z n_x = \theta \cos \phi \quad \text{and } \xi_2 = n_z n_y = \theta \sin \phi \tag{1a}$$

and the components

$$P_x = -P \sin \phi, \quad P_y = P \cos \phi \tag{1b}$$

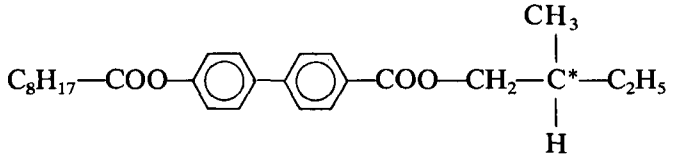
of the in-plane spontaneous polarization. Here $\phi = q \cdot z$ with q being the wave vector of the Sm C* helix.

It is generally assumed[2] that the tilt θ is the primary and the spontaneous polarization P the secondary order parameter and that these two quantities are proportional to each other:

$$P \propto \theta \tag{2}$$

Only recently, deviations from this behavior have been observed and a Landau theory[3,4] has been proposed which explains the fact that the ratio between the polarization P and the tilt θ is not always constant, but may vary with temperature.

In this connection it is interesting to note that the compound



(IS-2424)

shows the unusual behavior of sign reversal in the spontaneous polarization P *versus* temperature plot.[5,6] The compound is isotropic above 60°C and undergoes a smectic A–smectic C* (SmA → SmC*) transition around 43°C. The polarization first increases, reaches a maximum around 35°C and then decreases with decreasing temperature. It passes through zero around 20°C, and then changes sign. Crystallization may start well below 20°C on cooling, and depends upon the rate of cooling. Differential scanning calorimetry shows supercooling and superheating of the SmC*–crystal transition. The crystalline–SmC* transition is always 37°C irrespective of the rate of heating.

The question is what is the exact relation between the polarization and the tilt in this system? Is P still proportional to θ or is the proportionality factor temperature dependent, as expressed by the equation below?

$$P = \mu(T)\theta \tag{3}$$

If the proportionality factor μ in the above equation is indeed temperature dependent, as suggested by recent studies,[5,6,8] the question is what is the origin of this behavior? One possibility is that there are at least two species with opposite dipole moments which are interconvertible *via* a rotation about the carbon–carbon bond adjacent to the chiral carbon atom.[5] Still another possibility is the interplay between polar and bipolar ordering.[3,4] To solve this problem, which is quite important for the theory of ferroelectric liquid crystals, high resolution and high precision measurements of the tilt and the polarization are clearly needed. Whereas high precision measurements of the spontaneous polarization are now available,[5,6] this is not the case with tilt angle measurements.

The standard, but indirect, electro-optic method of measuring tilt angles is to take angular readings of the two switching positions of the optic axis on the cone in an applied external electric field. This method of measurement yields a tilt angle

which goes to zero at the same temperature at which the polarization changes sign.[6,7] Microscopy, ^{13}C NMR and other studies,[5,6,8] on the other hand, indicate a regular behavior and a non-vanishing tilt angle in this temperature range.

In order to resolve this discrepancy, we decided to determine the temperature dependence of the tilt angle *via* high resolution X-ray measurements of the layer thickness and molecular tilt angle as a function of temperature. Additionally, we have made high resolution measurements of the optical rotatory power which—together with a measurement of the helical pitch—allow for an independent determination of the tilt in an unperturbed smectic C* phase, i.e., without unwinding of the helix.

2. RESULTS AND DISCUSSION

The measured temperature dependence of the rotatory power ρ in the smectic C* phase is presented in Figure 1 for a laser light wavelength λ = 476.5 nm. The rotatory power monotonously increases with decreasing temperature. Since we are only interested in the optical activity due to the long range helical structure present in the smectic C* phase, and not in the background optical activity due to the chirality of the molecules, all results are presented relative to that at the SmA–SmC* transition temperature, T_c. The experimental set-up was the one used pre-

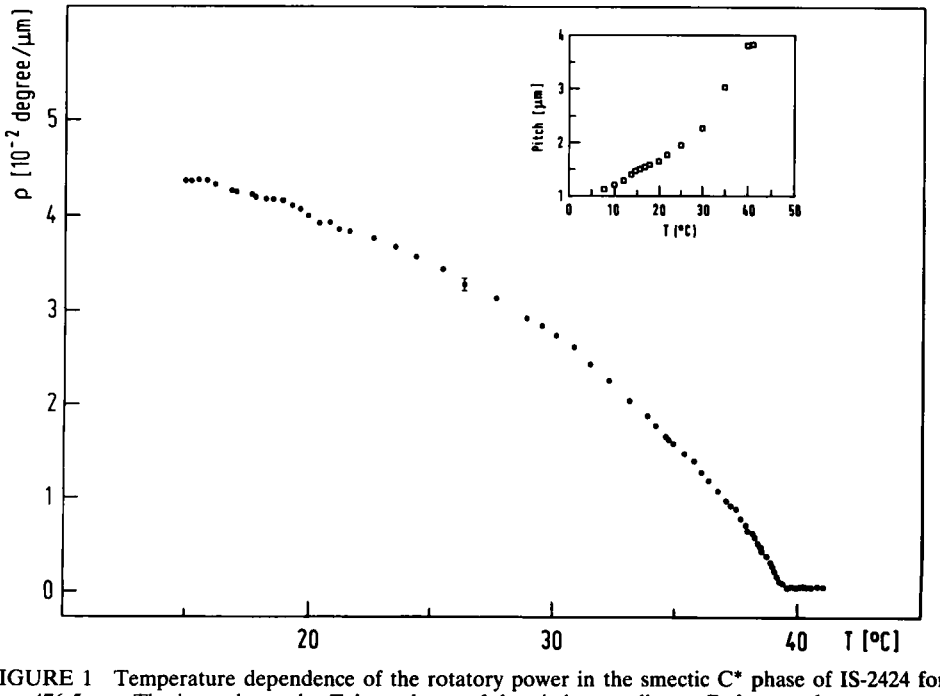


FIGURE 1 Temperature dependence of the rotatory power in the smectic C* phase of IS-2424 for λ = 476.5 nm. The inset shows the *T*-dependence of the pitch according to Reference 6.

viously.[9] The samples were prepared in a homeotropic alignment and spaced with two strips of 75 μm thick Mylar film. The helical axis was perpendicular to the glass surface. The angular resolution was about 5×10^{-4} rad.

As shown in Reference (9), the tilt angle is related to the optical rotatory power ρ, helical pitch p and the principal values of the refractive index tensor n_1, n_2, n_3 at the wavelength λ as:

$$\theta = \arcsin \left\{ \left[-\rho \frac{8}{\pi p} \frac{(n_1^2 + n_2^2)}{(n_3^2 - n_1^2)^2 \frac{n_1^4}{n_3^4}} \right] \lambda^2 \left[1 - \frac{2\lambda^2}{p^2(n_1^2 + n_2^2)} \right] \right\}^{1/4} . \quad (4)$$

Here the reference frame is chosen in such a way that the 3-axis of the refractive index tensor makes a tilt angle θ with both the wave vector of the helix and the wave vector of the light, whereas the 2-axis is normal to the tilt plane and the 1-axis is perpendicular to both the 2- and the 3-axis.

The temperature dependence of the tilt angle is largely determined by the temperature dependences of the rotatory power ρ and the helical pitch p. Since the pitch is finite at the temperature of the polarization sign reversal, the rotatory power would go to zero if the tilt angle were zero at this temperature. Since this is obviously not the case (Figure 1), it is clear that the tilt angle does not vanish

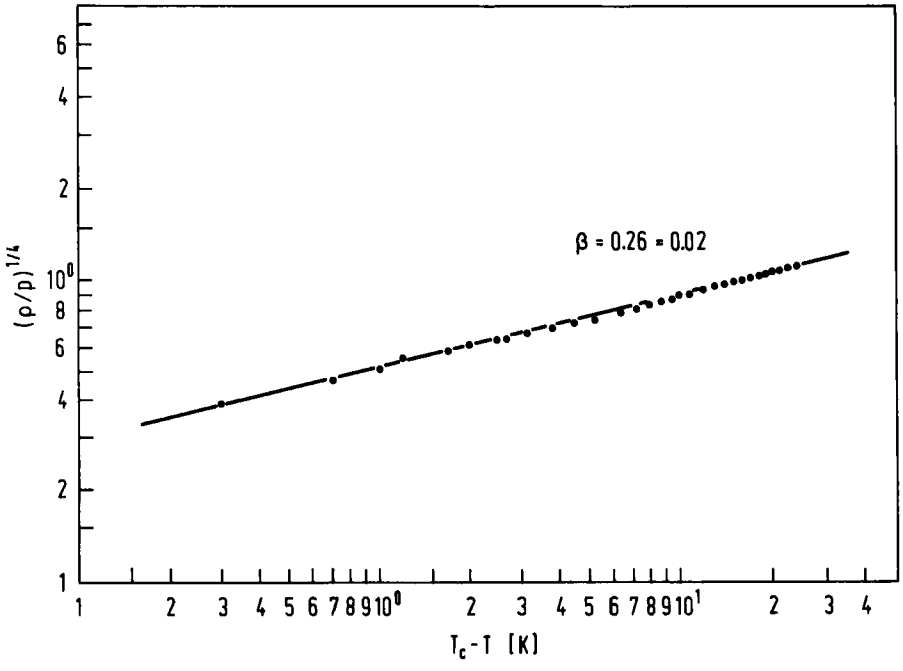


FIGURE 2 Log–log plot of the tilt angle—which is proportional to $(\rho/p)^{1/4}$ *versus* $T_c - T$.

at the temperature of the polarization sign reversal. The tilt is thus not simply proportional to the polarization in this compound.

Since the pitch p is finite and nearly constant at the SmA–SmC* transition, and since $\arcsin x \approx x$ for $x \to 0$, the rotatory power ρ is, close to T_c, proportional to the fourth power of the tilt angle:

$$\rho \propto \theta^4 = \theta_o^4 (T_c - T)^{4z} \tag{5}$$

From the measured T-dependence of ρ, we obtain—after correcting for the non-critical T-dependence of p—the critical exponent for the temperature dependence of the tilt angle as $\beta = 0.26 \pm 0.02$ (Figure 2). The value of the exponent indicates that the system is close to a tri-critical point.

The temperature dependence of the smectic layer thickness near the SmA–SmC* transition determined by X-ray scattering is shown in Figure 3. Whereas the layer thickness increases with decreasing temperature in the SmA phase, it decreases with decreasing temperature in the SmC* phase, due to the tilting of the molecules with respect to the smectic layer normals. The data again show no sign of a tilt angle reversal in the SmC* phase.

The results of the optical rotation data agree rather well with the direct measurement of the molecular tilt angle by high resolution X-ray scattering (Figure 4). The tilt angle monotonously increases with decreasing temperature in the SmC* phase up to $\theta = 15°$. In the crystalline phase, the tilt angle is T-independent and

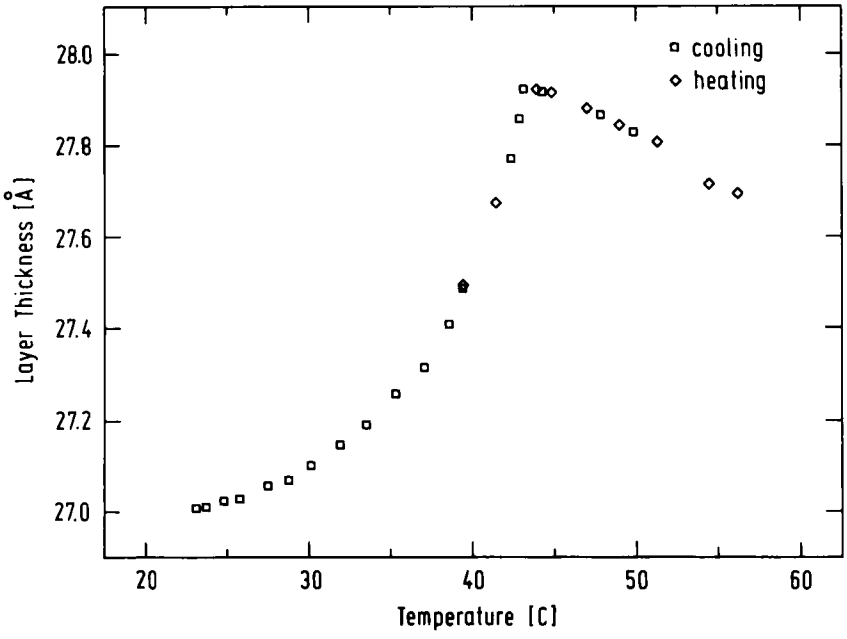


FIGURE 3 Temperature dependence of the smectic layer thickness near the smectic A–smectic C* transition. The errors (± 0.01 Å) are smaller than the size of the points on this graph.

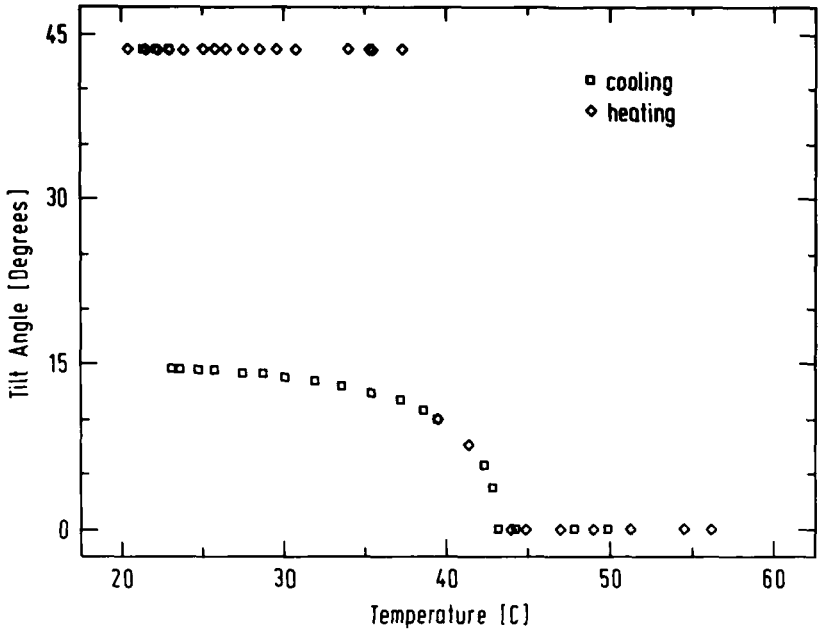


FIGURE 4 Temperature dependence of the molecular tilt angle as determined by high resolution X-ray scattering.

equals about 45°. On further heating, the crystal-SmC* transition takes place and the tilt angle discontinuously drops to the value found in the SmC* phase when one cools down from the SmA phase. The above high resolution data on the temperature dependence of the molecular tilt angle in IS-2424 thus show not only that the temperature dependence of the tilt is not proportional to the temperature dependence of the spontaneous polarization,[5] but also that the temperature dependence of the tilt angle can be described by a critical exponent $\beta = 0.26 \pm 0.02$ over nearly two decades in $\varepsilon = (T_c - T)/T_c$.

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