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A New Method for High Accuracy Tilt Angle Measurements in Ferroelectric Liquid Crystals

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A new method for measuring the tilt angle between the long molecular axes and the normal to the layer planes in ferroelectric liquid crystals is described. This technique provides a direct and continuous determination of the tilt angle as a function of temperature in contrast to existing techniques. Therefore, it is specially well-suited to studies of phase transition phenomena. The method is applied to the particular case of the smectic A(SmA) to chiral smectic C(SmC*) phase transition in *p*-(n-decyloxybenzylidene)-*p*-amino-(2-methyl-butyl) cinnamate (DOBAMBC). The tilt was found to exhibit a behaviour that can only be explained within a mean-field model if new terms are included in the free-energy expansion, as has been recently proposed.

Keywords: ferroelectric liquid crystals, tilt angle measurements

I. INTRODUCTION

The optical properties of ferroelectric liquid crystals have attracted significant attention since their discovery by Meyer *et al.*,[1] due to their potential importance in several technical applications such as high speed modulation devices, microsecond optical switches, etc.[2,3]

The most relevant physical parameters characterizing the performance of these devices are the birefringence Δn, the tilt angle θ, and the spontaneous polarization. Among these, and from a more fun-

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damental point of view, the tilt angle plays a special role in the sense that it behaves like the order parameter modulus in the most common phase transition leading to a ferroelectric mesophase, the SmA–SmC* phase transition. It is surprising however, that even for the most studied ferroelectric liquid crystal material, namely DOBAMBC, large differences exist among the results published by several authors.[4–9] The reasons for these discrepancies may be mainly attributed to 1) degradation problems when the compounds are subjected to dc electric fields, 2) changes in some of their physical parameters when they remain for a long time in their liquid crystal phases, and 3) the influence of sample thickness and orientation on their physical properties.

Up to now, three different techniques have been used for measuring the tilt angle; one is an X-ray diffraction method[4,5] and two are optical methods.[1,4,6] The former method is based on the fact that the interlayer distance between the smectic planes is related to θ and the molecular length. Nevertheless, this method is inadequate for molecules possessing long-end chains.[10] The two optical methods differ from each other in the sample alignment. For homeotropically aligned cells, the θ value is determined by finding the direction which gives rise to the symmetric conoscopic pattern when a strong dc electric field is applied parallel to the glass plates. For homogeneously aligned cells, the molecular tilt can be measured by determining the extinction angles when the sample is placed between crossed polarizers and two opposite dc fields perpendicular to the glass plates are successively applied. Usually, if proper homogeneous alignment can be achieved, the second procedure is preferred, because it is easier to perform and more accurate results are attained. However, both methods suffer from a number of disadvantages derived from the fact that only manual point by point measurements are possible, and dc electric fields must inevitably be employed. In this paper we propose another optical method for tilt angle determinations in which neither of these two difficulties arise. This method produces either point by point or continuous tilt angle values as a function of temperature and is, therefore, specially well-suited for phase transition studies. Furthermore, dc fields are no longer needed, and can be replaced by ac fields.

II. EXPERIMENTAL TECHNIQUE

The present technique (see Figure 1) takes advantage of the Wood and Glazer rotating analyser method for birefringence measure-

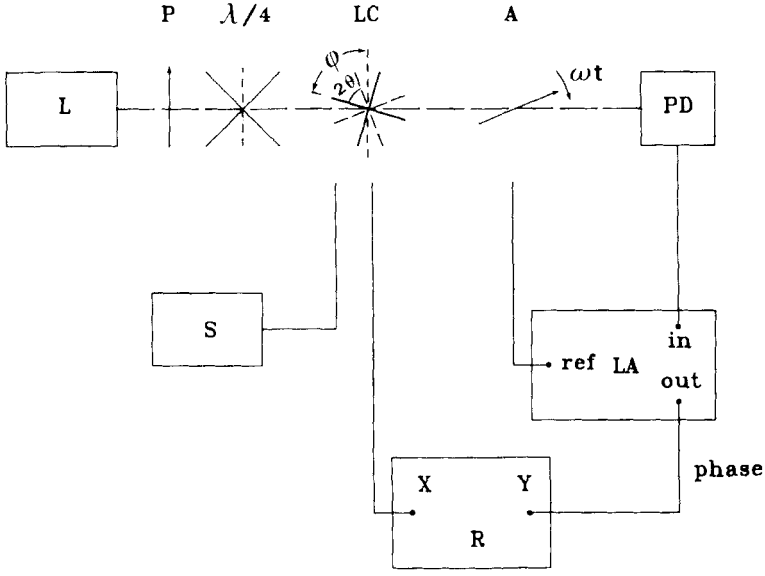

FIGURE 1 Block diagram of the experimental equipment for tilt angle measurements. L = laser, P = polarizer, λ/4 = quarter-wave plate, LC = homogeneously aligned liquid crystal, A = rotating analyser, PD = photo-diode, LA = lock-in amplifier, S = square-wave source, R = recorder.

ments,[11] together with the strong linear coupling of the molecular director to the applied field in ferroelectric liquid crystals. The optical part of the present device is exactly the same as that in Wood and Glazer's set-up and the only difference lies in what is actually measured and in the necessity of incorporating a low frequency driving ac field to the sample perpendicular to the glass plates. The principle of operation is as follows: The initial polarizer P and the λ/4 plate set at 45° to the polarizer produces circularly polarized light which is incident on a homogeneously aligned sample. The amplitude of the electric field is chosen to be high enough to suppress the helicoidal structure. Under these conditions, the sample has two principal directions over its entire surface, and if the optical indicatrix makes an angle φ with the direction of P, the light intensity passing through the rotating analyser is given by

$$I = Io/4 \left[1 - \sin \left(\frac{2\pi}{\lambda} \Delta nd \right) \sin (2\omega t - 2\varphi) \right]$$

where Io is the incident light intensity, λ the wavelength of the light, d the cell thickness, and ω the angular frequency of the rotating

analyser. Now, if the sample is driven by a low frequency electric field, the optical indicatrix is forced to rotate back and forth by an angle 2θ. Therefore, the phase angle of the resulting ac signal oscillates with the frequency of the exciting field and has a peak-to-peak amplitude equal to 4θ. These oscillations can be recorded through the phase output of a two channel, lock-in amplifier and monitored as a function of temperature in a continuous way. The resulting curve is shown schematically in Figure 2 for a typical case of a SmA–SmC* phase transition. Finally, the θ value is obtained from the envelope curve as indicated in Figure 2. It must be noted that the number of experimental points can be increased at will by using higher field frequencies or by decreasing the temperature scanning rate.

The main improvement introduced by this method is the ease of the measuring process, providing (virtually) continuous and direct data, allowing for a quick achievement of the experiment, and avoiding sample degradation problems. The experimental system can also be interfaced to a microcomputer, offering improvements in data recording and analysis for operator convenience.

Several modifications and complementary components may be introduced in the arrangement. For example, dc fields can be applied

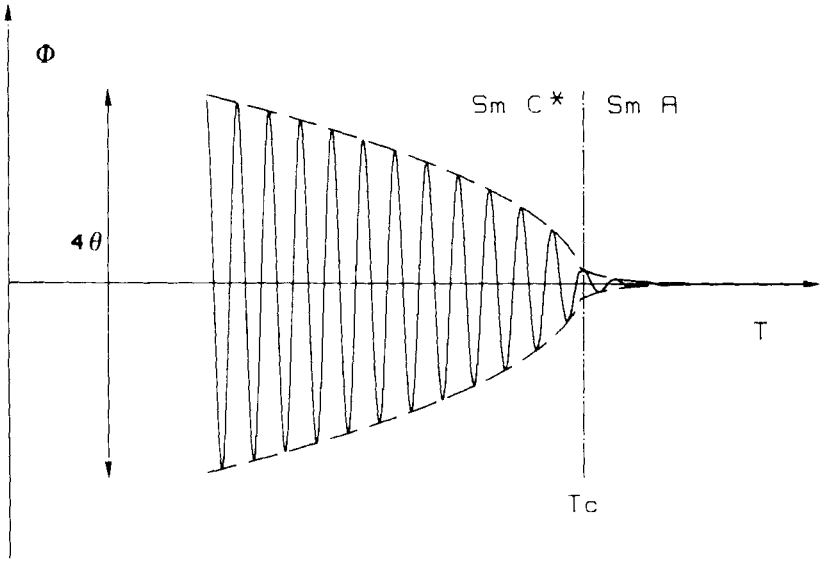

FIGURE 2 Schematic diagram for the phase angle as a function of temperature at a SmA–SmC* phase transition. The distance between the two dashed lines represents four times the tilt angle.

instead of ac fields. In this case the dashed lines in Figure 2 are obtained instead of the sinusoidal curve and, moreover, the amplitude channel of the lock-in can be used to get the birefringence from the sinus of the optical path difference. This last point is the basis in Wood and Glazer's set-up for measuring Δn in (solid) crystals. However, we think that it is not particularly advantageous in the case of liquid crystals and has the disadvantage of producing possible degradation problems in the sample as it is subjected to dc electric fields.

III. APPLICATION TO DOBAMBC

The performance of our experimental arrangement has been tested by determining the tilt angle behaviour at the SmA–SmC* phase transition of DOBAMBC. Cells were fabricated by depositing a thin film of poly(hexamethylene nonanediamide) (nylon 6/9) onto tin oxide coated glass plates as described in Reference 12. Only one side of the cell was rubbed in order to get maximum alignment.[12,13] The cell gap was maintained without spacers simply by use of glue at the edges. The sample was introduced by capillarity in the isotropic phase and cooled slowly (12°C/h) into the SmA phase. The cell thickness was 10 μm, being uniform to within less than 1 μm over most of the sample area. The measurements were performed with heating and cooling rates of 40°C/h and no significant differences were found between them. The frequency of the driving field was fixed at 0.1 Hz, and the lock-in integration time was set at 100 ms, which is short enough for the lock-in to follow the signal changes in this case. The measurements were carried out at fields larger than 5 kV/cm. Figure 3 shows the tilt angle data for an electric field of 7 kV/cm. If smaller fields were applied, a lack of symmetry between the upper and lower part of Figure 2 was observed; this effect became greater the lower the temperature. Since a perfectly symmetrical bipolar square wave was used, this implies a difference in the field required for the formation of the complete SmC structure depending on the field polarity. For the present, the cause of this phenomenon remains unclear, although the strong surface anchoring conditions imposed by the aligning agent, as well as the asymmetric treatment of the cell plates may be the origin of the effect.

As can be seen in Figure 3, a small tilt is observed in the high temperature phase (SmA). This is in agreement with the results found in References 14–16. The tail effect is due to the hindered rotation of the molecules produced by the electric field and to the coupling

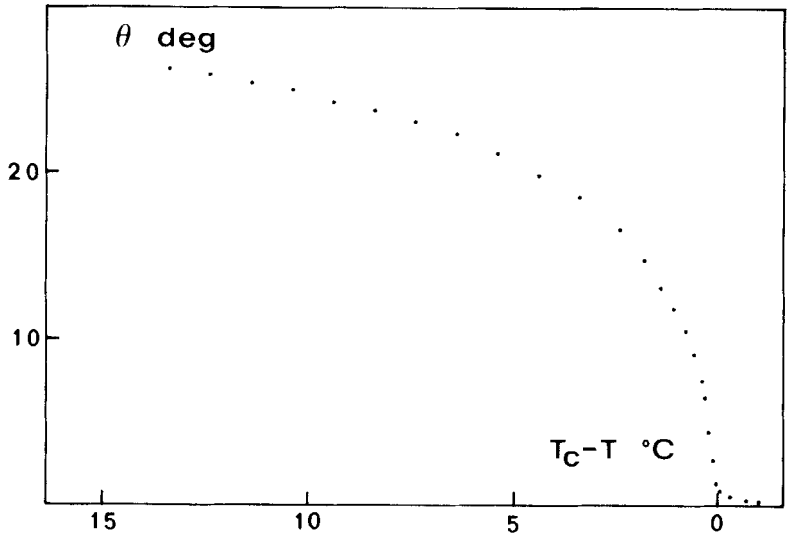

FIGURE 3 Tilt angle values in DOBAMBC for an applied electric field of 7 kV/cm.

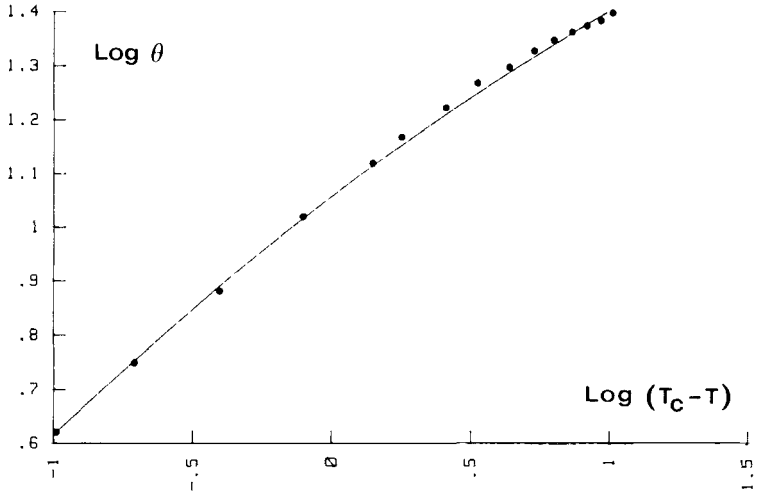

FIGURE 4 Zero-field limit tilt data *vs* Tc–T for DOBAMBC.

between the polarization and the tilt angle. It must be noted that measurements of the tail size as a function of the applied field could give important information about the microscopic mechanisms in liquid crystals. More theoretical and experimental work along the lines pointed out in References 14 and 15 is necessary. In order to avoid this tail, a zero-field tilt was obtained by extrapolation for several fields. The results are very similar to those in Figure 3 except in the vicinity of the phase transition, and agree quite well with the measurements by Dumrongrattana and Huang.[8] Figure 4 shows the log–log plot of the finite-field corrected data versus Tc−T. A simple power law fails to fit the results obtained over the entire temperature range, whereas the extended mean-field model developed by Zeks[17] and by Dumrongrattana and Huang[8] (continuous curve) accounts for them much better as is also the case for the experimental results of Reference 8. These new measurements strengthen the relative importance of the additional terms, suggested in References 8 and 17, which must necessarily be included in the free-energy expansion for explaining the SmA–SmC* phase transition for this compound.

Acknowledgment

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