Simultaneous determination of fundamental parameters for ferroelectric liquid crystals

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An analysis of an experimental technique which allows for a simultaneous determination of several parameters with special interest for ferroelectric liquid crystals is presented. These parameters are the spontaneous polarization, the rotational viscosity and the switching time. In addition, the susceptibility associated with the soft mode free of contributions related to the helicoidal structure can also be obtained. The experimental results for these parameters for the ferroelectric liquid crystal HDOBACEEC are reported. A comparison between the switching time values deduced from the rotational viscosity and those obtained by optical measurements is performed.

1. Introduction

Since the discovery by Meyer *et al.* [1] of the presence of ferroelectricity in certain liquid crystals, these materials have attracted a great and increasing interest both from the experimental and theoretical point of view [2]. The great extent of their area of applications and their peculiar properties more than justifies the large amount of work published on this subject in the last decade. These materials are composed of chiral molecules and, among others, have smectic phases. By symmetry arguments it can be demonstrated that there is an in-plane polarization. However, an intrinsic helical structure is present, which results in a macroscopic spontaneous polarization only if this helix is unwound. The unwinding can be produced by electric fields or, in thin cells, by means of surface interactions [3]. The use of these systems as fast electrooptic devices is going to be one of their most important applications. The switching time between the two polarization states is one of the main parameters of the device. It is related to the polarization as well as the rotational viscosity [4–6].

In addition, there is a considerable theoretical interest in these materials [4, 7, 8–10]. It is obvious that if we want to characterize a material and above all, if we want to explain its behaviour in a theoretical frame work the best method is to obtain the maximum number of parameters simultaneously. In this paper we deal with the triangular wave method [11–13] and present an analysis of this technique, its possibilities and performances. We also show that from only one measurement we can obtain the spontaneous polarization, the soft mode contribution to the dielectric permittivity which means that the transition temperature between the smectic A phase, and the ferroelectric phase is obtained directly, together with the rotational viscosity, the switching time and the electrical conductivity. This technique has been applied to the study of the behaviour around the ferro-paraelectric phase transition of 2-hydroxy-4-decyloxybenzilidene-4'-amino-1-carboethoxyethylcinnamate

(HDOBACEEC) [14, 15]. In this paper we show the results obtained for the spontaneous polarization, the soft mode contribution to the dielectric response and the rotational viscosity. Likewise, the switching time deduced from this last parameter has been compared with that obtained by optical techniques. The comparison shows a good agreement which indicates the reliability of the triangular wave method to determine this parameter.

2. The triangular wave method

One of the most relevant parameters in ferroelectric liquid crystals is the spontaneous polarization, thus its accurate measurement is very important. Most of the experimental methods deal with the application to the sample of an electric field sufficiently high to reverse the polarization. This electric field can be a pulse or a periodic signal. The material response has different contributions whose origin is (i) conduction; (ii) linear dielectric response and (iii) non-linear dielectric response, including the reverse of the polarization. All of them contribute to the total current density, J:

$$J = J_c + J_L + J_{NL} = J_c + \varepsilon_0 \frac{dE}{dt} + \frac{dP_L}{dt} + \frac{dP_{NL}}{dt}, \qquad (1)$$

where J_c denotes the direct current density and P_L and P_{NL} are the linear and non-linear parts of the polarization, respectively. The usefulness of the different experimental methods lies in the ability to discriminate the last contribution from the others. The classical methods, Sawyer–Tower circuit [16] and Diamand bridge [17] are integrator circuits. The linear resistive and capacitive contributions are compensated and the resultant polarization-voltage cycles can be visualized on an oscilloscope. In 1981 [11] one of the authors pointed out the convenience of the use of direct methods with an adequate time dependence for the electric field. In this paper the use of the triangular wave method was proposed, and in 1983 it was used for ferroelectric liquid crystals by Miyasato *et al.* [12].

First let us consider the linear terms in equation (1). It can be shown [11] that for a harmonic field the system is equivalent to an RC parallel circuit with

$$\frac{1}{R(\omega)} = \omega C_0 \left(\frac{\sigma_{dc}}{\varepsilon_0 \omega} + \chi''(\omega) \right), \qquad (2\,a)$$

$$C(\omega) = C_0(1 + \chi'(\omega)), \qquad (2\,b)$$

where all the symbols have the usual meaning. If the material is under a triangular wave of maximum voltage V_m and period T, using Fourier analysis we can demonstrate that the intensity-voltage diagram is a rectangle (see figure 1, where we present an experimental cycle and the deconvolution of the different contributions, I_c, I_L, I_{NL}). The values $I(0)$ and $I(T/4)$ are related to the material parameters through

$$I(0) = \frac{2\omega_1 V_m C_0(1 + \chi')}{\pi}, \qquad (3\,a)$$

$$I(T/4) - I(0) = \omega_1 V_m C_0 \left(\frac{\sigma_{dc}}{\varepsilon_0 \omega_1} + \chi'' \right), \qquad (3\,b)$$

where ω_1 is the frequency of the first harmonic. To obtain equations (3 a) and (3 b) we have assumed that there is no noticeable dispersion in the spectral region around ω_1.
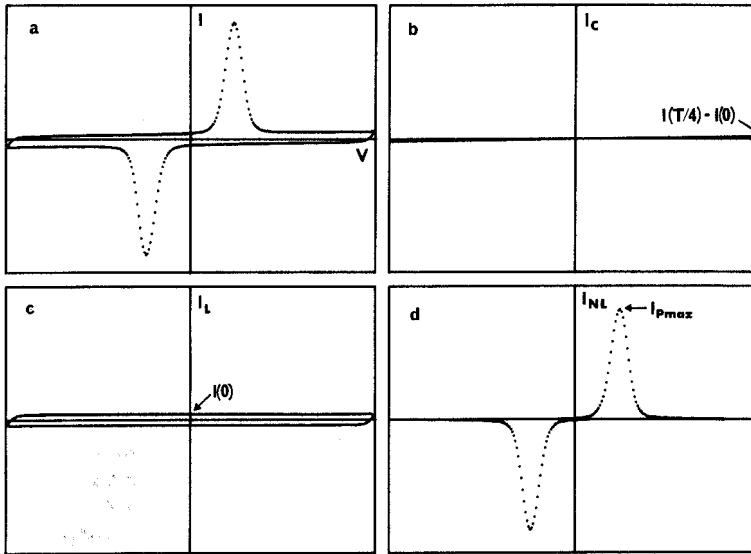
Figure 1. Experimental I–V plot on application of a triangular signal to the sample. The total response includes both linear and non-linear contributions (*a*). Current associated with conduction and losses (*b*). Linear capacitive response: the width of the rectangle is related to the dielectric permittivity (*c*). Non-linear response: the peaks correspond to the polarization reversal (*d*). The symbols are described in the text.

2.1. *Polarization, rotational viscosity and switching time*

We now consider the non-linear contributions assuming ferroelectric behaviour. If the field strength is high enough the spontaneous polarization, P_s, can be reversed and an additional contribution to the current appears. This can be clearly discriminated from the linear contributions allowing us to obtain the spontaneous polarization from the integral of the current. Thus, from the recording of the I–V cycle we can obtain the linear dielectric permittivity (the width of the rectangle), conductivity and losses (the slope) and P_s value (the integral of the non-linear current). Furthermore, with an adequate model for the dynamics of P_s more information from the shape and localization of the current peak can be obtained. We shall deal later with a model proposed by Xue Jiu-Zhi *et al.* [4] and applied by Escher *et al.* [18] to the dynamics of the polarization reversal under a triangular wave. For completeness the main features of their model will be reviewed.

When the applied field is in the smectic layers, the director reorientation, and therefore that of the polarization, takes place by means of a viscous rotation around an axis normal to the layers without any variation of the tilt angle, as shown in figure 2. The helix is considered to be unwound during the whole process, and the reversal takes place uniformly within the sample. As a consequence, the soft and Goldstone mode contributions to the dielectric response do not appear. We shall return to this point later. The model contains neither the elastic forces associated with the helix nor the surface effects.

With these assumptions the current density $J_p(J_p \equiv J_{NL})$ can be written as

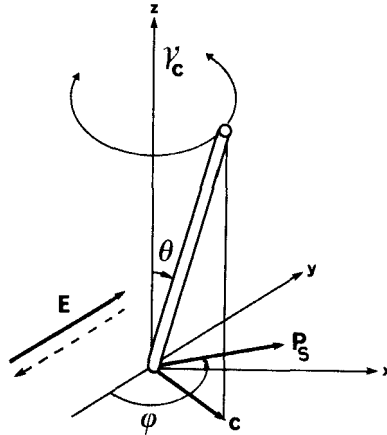$$J_p = \frac{P_s^2 \sin^2 \varphi \, E_0 t}{\gamma_c}, \tag{4}$$

Figure 2. Geometry of the director reorientation. The XY plane coincides with the smectic layers. The spontaneous polarization P_s lies in this plane and is perpendicular to the director c. The z axis defines the layer normal and θ is the tilt angle of the director. The electric field produces a rotation of the director around z. φ is the angle between the field and the polarization.

where φ is given by

$$\text{tg}\,(\varphi/2) \;=\; \text{tg}\,(\varphi_0/2)\,\exp\left(-\,\frac{E_0 P_s t^2}{2\gamma_c}\right) \tag{5}$$

and all of the symbols correspond to those given in figure 2. E_0 is the maximum field amplitude and γ_c is the rotational viscosity of the c director. To obtain equations (4) and (5) we have integrated their equation of motion for the assumed dependence of the field but beginning at zero field and with the condition that at this limit the polarization is still totally unreversed (φ_0 must be taken small but non-zero). The model does not allow a correct description of the current near zero field. If we want to obtain any information of the system dynamics from the current peak it is necessary for this peak to be far from this region. This implies that the frequency of the signal must be sufficiently high, and in addition the maximum field value cannot be very high if the dielectric anisotropy is high [4, 19, 20]. With all of these considerations it is proposed to obtain the rotational viscosity, γ_c, from the parameters of the current peak via

$$\gamma_c \;=\; \frac{P_s^2 A E_{\text{max}}}{I_{\text{p max}}}, \tag{6}$$

where A is the area of the electrodes, E_m is the field at the maximum current and $I_{\text{p max}}$ the maximum current value of the non-linear contribution (see figure 1 (d)).

From the same model [4] we can predict the optical response time, τ, to an applied voltage step. It can be seen that it is related with the rotational viscosity, the spontaneous polarization and the field amplitude through

$$\tau \;=\; K\frac{\gamma_c}{P_s E} \tag{7}$$

In this equation τ is the time required to go from a 10 to a 90 per cent in the transmitted light under crossed polarizers with these arranged to produce extinction

for the initial orientation [4]. The constant K depends on the anisotropy and field values but over a wide region is 1·75 (our case) [19].

The different approximations in the model [4, 18] impose several restrictions to the experimental conditions:

(a) The sample, with planar alignment, has to be sufficiently thick to overcome surface effects.

(b) The field has to be sufficiently high to produce the total reorientation of the polarization but not too high in order to prevent the effect of the dielectric anisotropy.

(c) The frequency mut be sufficiently high to exclude the existence of intermediate helicoidal states during the switching process and to separate the current peaks from the zero-field point.

Conditions (a) and (b) do not cause any trouble. In practice, for a wide variety of materials thicknesses of about 100 μm can be used and well saturated hysteresis loops with voltages of about 100 V are obtained. The last condition could be more problematic because a rise in the frequency needs a rise in the field amplitude in order to saturate the cycles. Therefore, in order to determine the optimum frequency in our case, we have studied the rotational viscosity as a function of frequency at several temperatures. Figure 3 shows the results obtained for HDOBACEEC at two different temperatures $\Delta T = T - T_C = 1°C$, $10°C$; this plot allowed us to decide the best frequency range which is between 50 and 150 Hz.
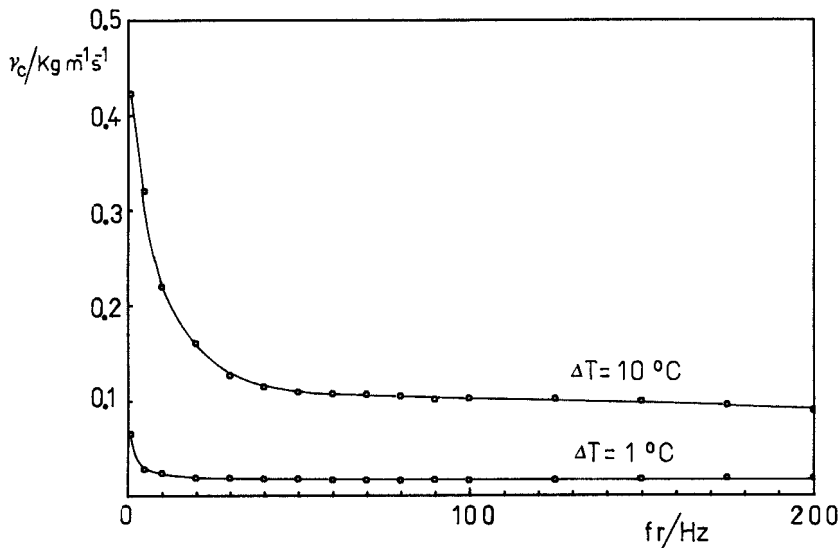

Figure 3.   Rotational viscosity versus frequency of the applied field in HDOBACEEC at two temperatures.

2.2. *Soft mode contribution to the dielectric permittivity*

Now let us return to the linear current. As we have noted the model does not allow for the appearance of the contribution associated with the soft mode, but it is obvious that it appears in the current after reversal of the polarization. In this situation with the helix unwound, two polarization states $+P$ and $-P$ similar to those present in

a uniaxial ferroelectric exist. Thus, the polarization changes induced by the field in these states will only be in the amplitude and so will be related with the soft mode. The amplitude of the susceptibility associated with this mode can be deduced from the width of the rectangle obtained after deconvolution of the signal ($I(0)$ in figure 1 (c)).

3. Experimental

Measurements were carried out on the compound HDOBACEEC which has a crystal-S_I^*-S_A-I phase transition sequence. This material was studied previously by the authors in order to determine its dielectric behaviour and polarization [14].

Cells for measurements were made of two gold plated brass electrodes of diameter 12 mm on which a thin film of polyvinyl alcohol was deposited by evaporating an aqueous solution. Both plates were rubbed so as to achieve a maximum planar alignment. The sample was placed between them with an annular teflon-plus-glass fibre ring of 120 μm as spacer. This thickness was considered sufficiently high to minimize the wall anchoring contribution to the reorientation process. Materials were introduced in the isotropic phase and then slowly cooled down to the S_A phase. The temperature control and stability are described in previous works [14, 22].

The cell was connected in series with a resister and submitted to a triangular wave voltage. If the resistance value of the resister is very small compared with that of the sample, most of the voltage difference will take place across the cell. The cell resistance was higher than 20 MΩ in all cases, so that a 10 KΩ resister was considered low enough to fulfil this condition. The current response was obtained by measuring the voltage difference across the resister. The triangular wave voltage was supplied by a HP3325A function generator and then magnified by a KEPCO amplifier. The current-voltage cycles were recorded by a digital acquisition system HP7090A, and all of the equipment was interfaced to a microcomputer. The whole experimental set-up allows for a voltage range between 5 mV$_{pp}$ and 1000 V$_{pp}$ and a frequency band from DC to 1 kHz, limited by the amplifier response.

In this work two kinds of measurements were made almost simultaneously at two different frequencies, 5 Hz and 64·5 Hz. In both cases, amplitudes were chosen to be high enough to saturate the I–V cycles, i.e., to destroy the helical structure. The P_s values were obtained from the depolarization contribution of the director reorientation to the total current from the 64·5 Hz and 300 V cycles. These measurements were also used to determine the viscosity. On the other hand, the permittivity behaviour of the soft mode was detected by measuring the rectangle width at a fixed voltage for which the reorientation has completely taken place in the 5 Hz measurement.

Really, all the parameters could be attained from a unique frequency recording. Nevertheless, small differences in the rectangle width are due to noticeable changes in the permittivity values and so a high precision is required. This effect is less important if the frequency is decreased, but even for a 5 Hz frequency, the data acquisition scale must be so low that the depolarization peak cannot be totally recorded, so no polarization values can be attained and another measurement is needed. On the other hand viscosity measurements require the frequency not to be extremely low in order to avoid the peak appearing near $V = 0$, as we have already mentioned. This requirement is clearly seen in figure 3 in which the calculated viscosity versus frequency is shown at two different temperatures. At frequencies below 50 Hz γ_c increases very quickly; for higher frequencies it appears to be nearly constant till 150 Hz and then decreases slowly. This later behaviour is probably due to no-saturation effects in the

depolarization processes. Taking this into account, a 64·5 Hz frequency was finally chosen.

For the switching time measurements a different cell was used. It was made with two tin oxide coated glass plates and the planar alignment was achieved by depositing a thin film of nylon 6/6. The cell thickness was 7 μm and the procedure has been described elsewhere [22, 23, 24]. The sample was put under a square wave with amplitude 1·4 V/μm and frequency of 100 Hz. The light intensity transmitted under crossed polarizers was recorded with a digital oscilloscope. We take τ as the time required by the optical transmittance to go from 10 to 90 per cent after field reversal.

4. Results and discussion

Figures 4 and 5 show the results for the spontaneous polarization and the rotational viscosity obtained, for each temperature, from the same 64·5 Hz cycle. The polarization exhibits a small tail in the S_A phase due to field-induced effects. The transition temperature T_c appearing in these plots was determined from the behaviour of the dielectric permittivity as will be explained later. The rotational viscosity can be fitted to a $(T - T_c)$ law. The rotational viscosity of the n director, γ, can be obtained from the one of the c director, γ_c, through [18]

$$\gamma = \frac{\gamma_c}{\sin^2 \theta}, \tag{8}$$

where θ is the tilt angle. We have calculated γ from our experimental results for γ_c and from those for θ reported in [25] and they are plotted versus temperature in figure 6. In [25] θ^2 was found to show a good fit to a $(T_c - T)$ law over a broad temperature range in the S_I^* phase. Thus if we take $\sin^2 \theta \approx \theta^2$ and bear in mind the behaviour of γ_c the horizontal line obtained in this plot need not be surprising in spite of the fact that molecular theories [26] predict some kind of Arrhenius-like behaviour. Nevertheless, we have to point out that in our case the temperature range studied may be too short to detect such behaviour. On the other hand, in the plot of γ_c shown in figure 5, we
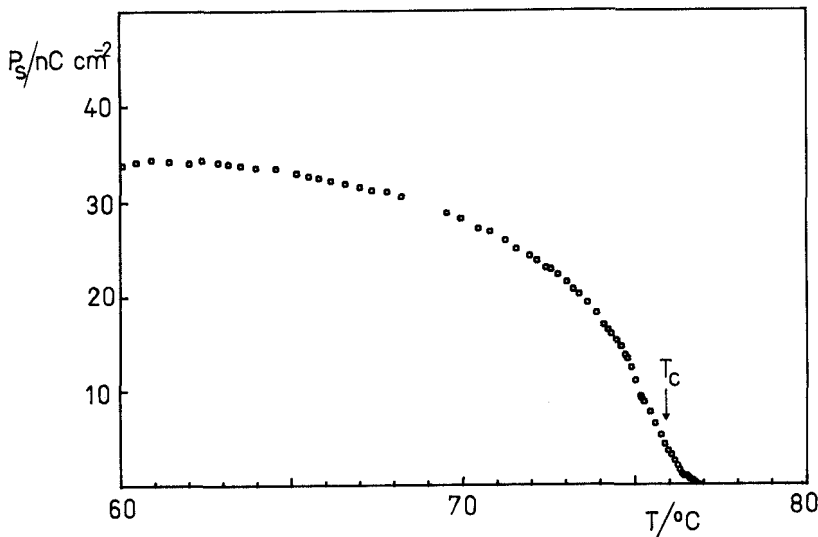

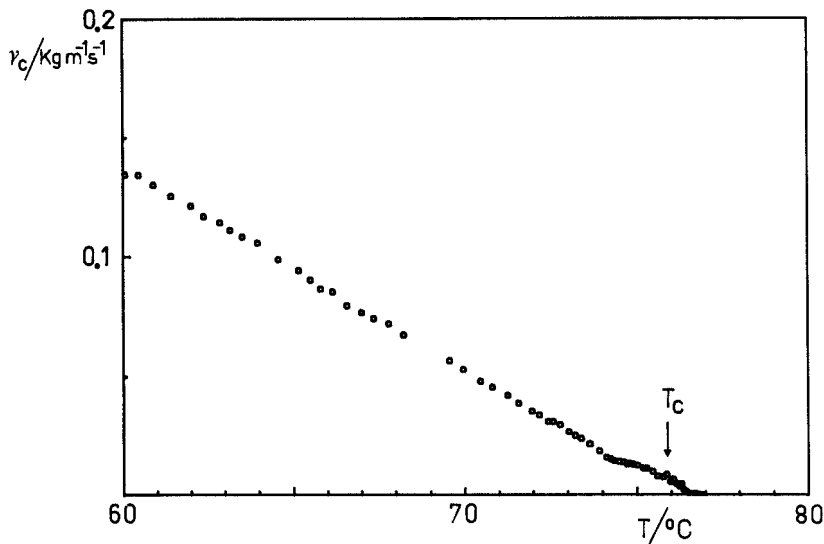Figure 4. Spontaneous polarization versus temperature.

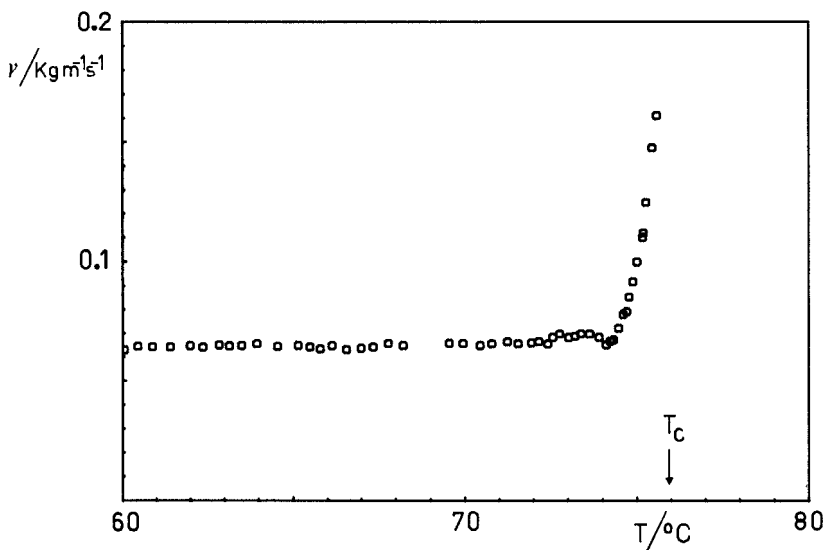Figure 5.   Temperature dependence of the rotational viscosity.

Figure 6.   Rotational viscosity of the director, γ, deduced from the rotational viscosity of the director c, γ_c, and the tilt agle, θ, through equation (8).

can see an anomalous behaviour near T_c. It deviates from the straight line which also produces an anomalous increase in γ. This result is not expected and must be related with the method of measurement. Near the transition temperature the validity of the law in equation (6) is no longer justified because it was obtained under the assumption that the ferroelectric torque is the prominent one in the director reorientation, but in this region the P_s value is small and so the dielectric anisotropy plays an important role [4, 5, 19].

From the viscosity we can predict the switching time if we assume equation (7) to be valid. Thus, in figure 7 we have plotted by open circles the τ evaluated by means
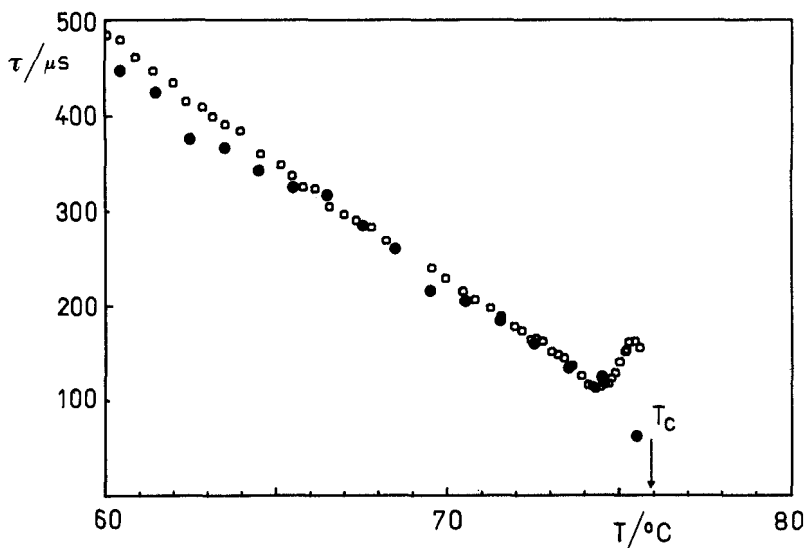
Figure 7. Open circles (O): switching time deduced from equation (7) with $K = 1.75$ and $E = 1.4\,\text{V}/\mu\text{m}$; closed circles (●): experimental switching time measured with an applied square field with amplitude $E = 1.4\,\text{V}/\mu\text{m}$ and frequency 100 Hz.

of equation (7) with out experimental values for γ_c and P_s ($E = 1.4\,\text{V}/\mu\text{m}$). Likewise we have measured τ with a $1.4\,\text{V}/\mu\text{m}$ square wave as described previously, which we have represented by closed circles in figure 7. These plots show good agreement between both results except in the region very near T_c. The origin of this disagreement is, as before, the anomalous behaviour of the viscosity and also the invalidity of the law in equation (7) for these temperatures. The plot of τ as obtained from optical measurements, with a critical slowing down, seems the most plausible. The attempt by Skarp [5] to predict the critical behaviour of the switching time from equation (7) seems not to be very useful at least for our compound in which the variation of the polarization and the tilt as a function of temperature exhibit a significant deviation with respect to the predictions in the mean field models. In addition we have to point out the relatively high value of the switching time: $0.5\,\text{ms}$ for this field at $15°\,\text{C}$ below the transition temperature. This may be related with the structure of the ferroelectric phase, S_I^* in this case, which usually are more viscous than other ferroelectric phases. Nevertheless the nature of the ferroelectric phase in HDOBACEEC is not clear. At present X-ray studies to clarify this point are in progress.

Relation (3 a) is used to evaluate the dielectric permittivity ε' from the 5 Hz cycles. The dielectric permittivity, after the subtraction of an almost temperature independent value ε_∞ [14] represents the soft mode contribution. In figure 8 it is plotted in the form: $(\chi' \text{ soft})^{-1} = (\varepsilon' - \varepsilon_\infty)^{-1}$ versus temperature. There we can see that the plot can be fitted by two straight lines which intersect at zero. This result is the one expected here because with the helix unwound the material behaves as a uniaxial ferroelectric and so χ' soft at T_c must go to infinity. It is worth noticing the difficulty in obtaining this magnitude in the ferroelectric phase due to the large magnitude of the Goldstone mode contribution to the dielectric permittivity. In previous works we have obtained it by other methods: measuring ε' at a frequency high enough to quench the helix or under a bias field high enough to unwind the helix (a procedure also used by other authors) [21].
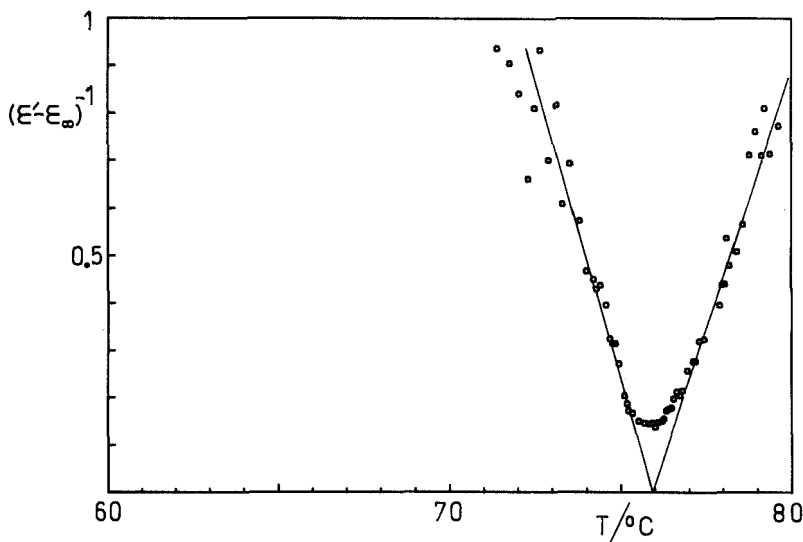
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Figure 8. Inverse of the soft mode contribution to the dielectric permittivity versus temperature. The intersection of the two straight lines determines the transition temperature.

In a previous paper [14] we have reported a dielectric study of the same compound. There the transition temperature was slightly different. This fact is usual for such compounds and contribute to the difficulty of comparing parameters measured with different experimental techniques. In this context the importance of a measurement method which allows for a simultaneous determination of the maximum number of parameters becomes clear. With the triangular wave method we can obtain the spontaneous polarization, the rotational viscosity, the switching time, the conductivity and the soft mode contribution to the dielectric permittivity. Other parameters, such as the tilt, could be obtained with a little more effort using transparent electrodes and the optical technique reported in [27] and extended in [28, 24]. It allows a continuous and direct determination of the tilt angle as a function of temperature by recording the phase of the transmitted light when the sample is driven by an electric field.

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