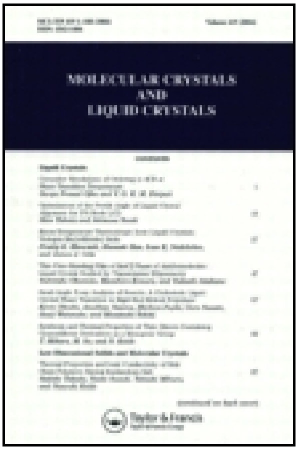

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Polarization and Viscosity Measurements in a Ferroelectric Liquid Crystal by the Field Reversal Method

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POLARIZATION AND VISCOSITY MEASUREMENTS IN A FERROELECTRIC LIQUID CRYSTAL BY THE FIELD REVERSAL METHOD

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With the aim to develop a standard method for measurements of the polarization of ferroelectric chiral smectic C liquid crystalline materials, we have studied thin, well-aligned samples of MBRA-8 using the field-reversal method. The method also provides an estimate for the rotational viscosity and for the response times.

INTRODUCTION

Although ferroelectricity was discovered in the chiral smectic C phase about ten years ago[1], it is only in the last few years that the application potential of ferroelectric liquid crystals has come to be fully recognized. This has brought renewed and strong interest in synthesizing tilted chiral smectics. Also the possibility to induce ferroelectricity by doping smectic C materials with chiral dopants has begun to be explored[2]. With ferroelectric liquid crystals much higher switching speeds can be obtained than those common in other liquid crystals[3] and interesting bistability effects also await exploration. In this situation it is important to characterize new ferroelectric substances by measuring the most important physical parameters, such as spontaneous polarization, rotational viscosity, pitch and tilt angle.

The present work is primarily concerned with measurements of the polarization. Such measurements have been achieved in the past by various techniques: pyroelectric effect[4], shearflow[5], capacitance bridge method[6] and light scattering on a thin film[7].

We have chosen the method of measuring the transient current obtained when making a polarization reversal in the sample by changing the polarity of the applied electric field. The experimental method involves applying a step function electric field to the sample and measuring the displacement current density J = dP/dt as a function of time. This type of experiment was first carried out on solid state ferroelectrics in 1954[8], and was introduced for ferroelectric liquid crystals by Martinot-Lagarde in 1977[9]. It is still probably the most direct method for studying the switching behaviour for ferroelectric crystals of low conductivity, and furthermore allows a simultaneous study of the electrical and optical properties during switching. However, different contributions to the current make both measurements and interpretation of data non-trivial. The prime intention behind the work presented here was to test if polarization reversal can be developed into a useful standard method of measurement. (Very precise measurements near phase transitions seem to require further improvement of the method).

By using thin cells we unwind the helix that otherwise cancels the spontaneous polarization, and we also avoid the defects that can be introduced by the interaction between the helix and the boundaries in thicker samples. Since we achieve very good alignment, we can expect to get representative values for the polarization. A further benefit of using thin samples is that the measurements are done on samples which have electro-optical properties that should prove very useful in future applications.

EXPERIMENTAL METHOD

The experimental set-up is shown in Figure 1. A function generator delivers a sine, square or triangular wave which is amplified to maximum 120 V with about 1 microsecond rise time. In the present work we use a one Hz square wave of 20 V peak-to-peak amplitude. The square-wave voltage, when applied to the sample, causes a reversal of the dipoles in the ferroelectric liquid crystal. The current associated with this process is measured as the voltage drop over a series resistor, and the signal is read into a memory oscilloscope. Data are subsequently transferred to a MINC computer for processing.

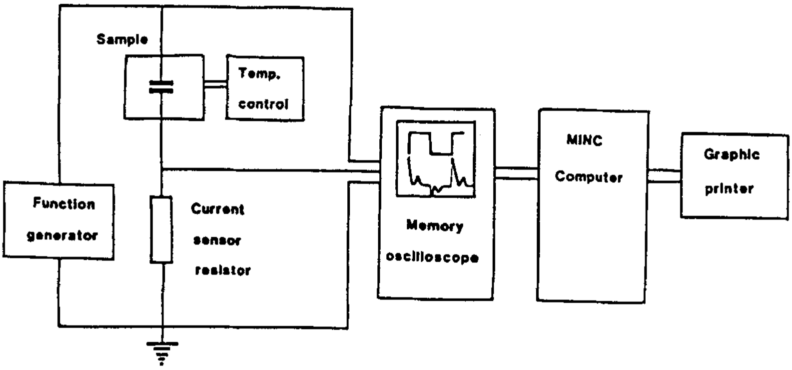
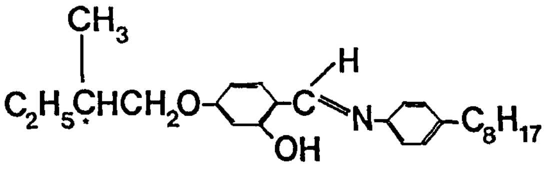


Figure 1. Set-up for polarization measurements.

Experiments were carried out on the Schiff-base substance MBRA-8(2-hydroxy-4(2-methyl-butyloxy)-benzylidene-4-p-n-octyl-aniline).[10] Between the crystal phase (X) and the isotropic liquid phase (L) this material exhibits smectic-A and smectic-C liquid-crystalline phases as indicated in Figure 2.



MBRA-8 X 36° C^* 50° A 57° L

Figure 2. MBRA-8 structure formula and phases.

The material supercooles to room-temperature in the C-phase and is therefore easy to work with. It also seems to be more stable than e.g. HOBACPC.

Cells for polarization measurements are made of two glass plates, one of which has 2 μm thick SiO-spacers evaporated on it to obtain a uniformly thick liquid crystal layer. Tin oxide conductive coating is etched to obtain an approximately 20 mm^2 active overlapping area. After filling in a vacuum oven, the cell is sheared in a specially designed shear apparatus to obtain homogenous "bookshelf" orientation (smectic layers stand perpendicular to glass plates), thus making it possible to switch between two welldefined (spin up and spin down) states of polarization with the applied field. During the measurements, the cell is observed in a polarizing microscope. It is kept in an electrically heated temperature chamber with a temperature variation of less than 0.1 °C during the measurements. However, in the present temperature chamber construction it has not been possible to measure the temperature gradient along the sample.

The current measured through the sample when applying a voltage step is determined by several factors. To be able to extract the polarization from the observed current, we make a model of the sample in the absence of ferroelectric behaviour. Our model is shown in Figure 3. We assume that the sample can be represented by a capacitor C (of the order of 1 nF) in parallel with a resistor R_p. The parallel resistance represents the internal resistance of the sample, and should be rather high, of the order of 10 MΩ, otherwise the polarization reversal current will be short circuited. In series with these two components we place another resistor R_s (of the order of 10 kΩ) that will represent the resistance in the connections and in the conductive coatings. The current sensor resistor (5 kΩ) is also included in the series resistor; thus we do not need a differential amplifier for the voltage measurement.

Our equivalent circuit implies that the background current I obeys the equation

$$CR_s \frac{dI}{dt} + \frac{R_s + R_p}{R_p} I = \frac{U}{R_p} + C\frac{dU}{dt}$$

where U is the applied voltage.

This equation is easily solved numerically for any applied voltage. We can then subtract the background current from the measured current to get the polarization current. The polarization current can then be integrated to give the polarization charge. By using this procedure, we are free to choose an arbitrary curve shape of the applied voltage, and can even use this method to study differences between the switching behaviour for different types of voltage curves. To get the contribution from the dU/dt term under control, one method is to use a slowly varying voltage. If a sinus wave is chosen, the method becomes equivalent to the use of a Diamant bridge (assuming $R_s = 0$). If a triangular wave is chosen, we get the method discussed by Miyasato et al[11]. We have instead chosen, as in Ref. 9, to apply a square wave voltage and have obtained a separation in time between the different current contributions. The ionic currents can be represented by the resistor R_p only as long as they are linear in the applied field. According to our experience, the ionic current, very often, displays nonlinear behaviour. A big contribution to the ionic current seems to come from chemically stable ions, which under the influence of the applied voltage can move from one of the electrodes to the other. This can give a current peak very similar to the current peak from polarization reversal. For MBRA-8 the ionic current peak is seen most easily at much higher voltages than required for polarization reversal. This ionic current peak remains in the smectic-A phase. With square wave voltage applied, the polarization reversal is so fast, and the applied voltage can be kept so low, that the ionic current can be assumed to be constant and low during the polarization reversal. We have also checked that the electrooptical switching coincides in time with the polarization reversal current peak.

The equivalent circuit gives a response to a square wave voltage as shown to the right in Figure 3. It is a single exponential curve raised to a level of $U/(R_s + R_p)$ above the x-axis. It is important that the series resistance R_s is kept low, in order to get the time constant for the exponential decay considerably shorter than the polarization reversal time.

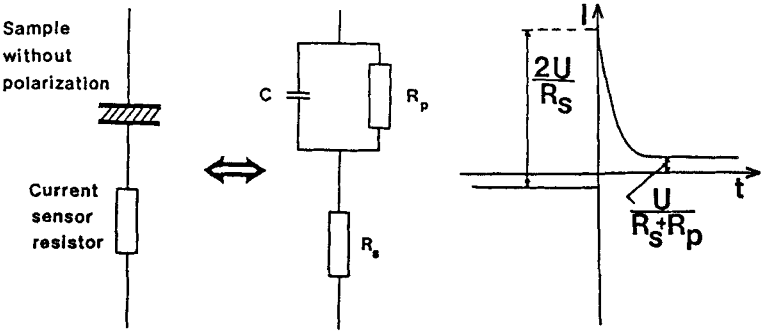


Figure 3. Equivalent circuit and its response to a square wave voltage step 2U applied at t = 0.

The transient exponential does not truly represent the properties of the liquid-crystal cell in our present set-up. The transient overload recovery characteristics of the memory oscilloscope will also affect the curve. Still, an exponential curve with a time constant of 6 μs represents the immediate response well.

Two typical oscilloscope traces are shown in Figure 4, one at T = 36.7 °C, the other at T = 47.3 °C near the SmC-SmA transition. The current peak due to polarization reversal is well separated from the capacitive current (the transient exponential), and also from the conductive current peak coming later. Thus it is possible to obtain a good fit to the experimental points for making a background curve according to our model described above. The general trend is that the background level rises with temperature because of increasing conductivity.

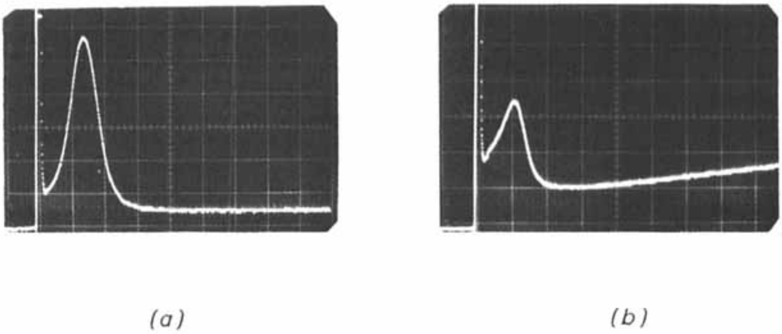

(a) (b)

Figure 4. Oscilloscope traces at T = 36.7 °C and T = 47.3 °C. Horizontal axis: 200 µs/div. Vertical axis: 1 µA/div. The effect of the ionic current is seen in (b) as a shifted baseline.

The numerical computation of the background curve and the integration of the current peak is made in the computer. Such an integration is shown in Figure 5. The area under the polarization current peak is $2 \cdot a \cdot P$, where a is the area of the sample. Thus the step in the charge curve in Figure 5b gives the polarization P directly. The contribution from the ionic current is much less disturbing at lower temperatures, where the current curve coincides with the background also in the long-time "tail" of the curve (cf. Figure 4a).

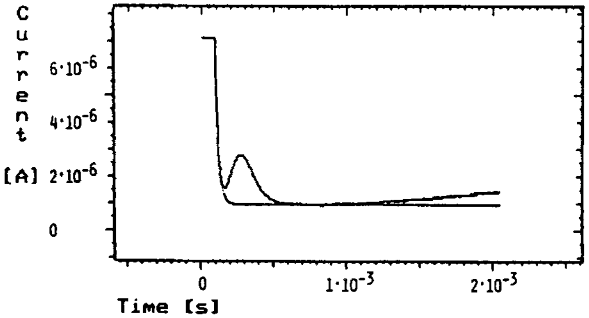


Figure 5a. Current curve at T = 46.4 °C with computed background curve.

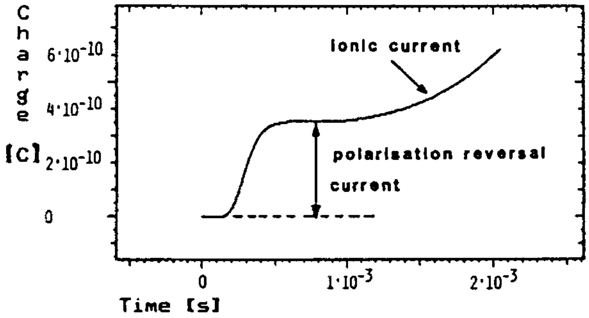


Figure 5b. Integration of the current curve in (a) with background subtracted.

RESULTS

An important point to check when making the polarization measurements is that the applied voltage is sufficient to induce polarization saturation, i.e. to align the dipoles in one of the two states up or down. In Figure 6 is shown polarization versus applied field at T = 33.0 °C. It is seen that at about U = 5 V polarization saturation is obtained, confirming that the voltage actually used in the measurements (U = 9.80 V) is sufficient.

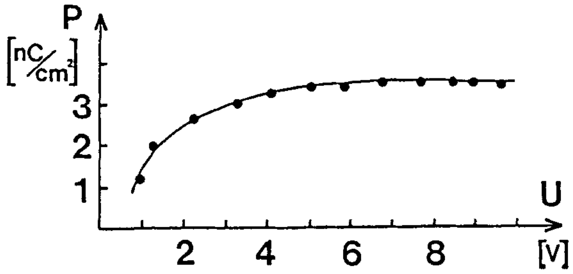


Figure 6. Polarization versus applied voltage at T = 33.0 °C.

The spontaneous polarization as a function of temperature is shown in Figure 7. A least-squares fit of the experimental points to the relation $P = A \cdot (T_c - T)^\beta$ gives $T_c = 48.6$ °C and $\beta = 0.51 \pm 0.02$, compatible with a mean-field exponent of 0.5. The detailed behaviour of P near T_c was not possible to elucidate with set-up used for temperature control.

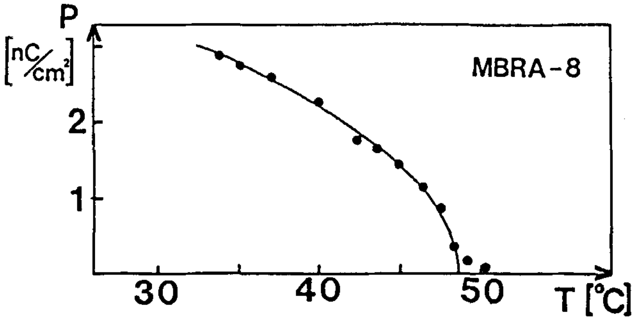


Figure 7. Temperature dependence of the spontaneous polarization for MBRA-8, experimental points and fitted curve.

The main source of error for the polarization seems to be the quality of alignment obtained by shearing. For very well aligned samples higher values of P are obtained than when defects are frequent.

Our values given in Figure 7 are slightly (20%) higher than those obtained by Loseva et al[10]. This difference is comparable to the experimental uncertainties. The polarization for MBRA-8 is about one-third of that reported for HOBACPC [12].

SIGN OF POLARIZATION

An important point to discuss and to study experimentally is the orientation of the polarization vector $\underline{P}$ relative to the smectic C-vector $\hat{c}$ and the smectic layer normal $\hat{k}$ (cf. Figure 8), or, otherwise expressed, the sign of P according to the convention by Clark and Lagerwall[13].

The observation is made near T_c, where θ is small. The orientation of the smectic layers is known since they orient along the direction of the shear. The direction of $\underline{P}$ is given by the direction of the DC electric field.

If we set $\underline{P} = P\,\hat{k} \times \hat{c}$ we can determine the sign of P by observing the direction of $\hat{n}$ (and thereby also $\hat{c}$) relative to $\hat{k}$. This is done in a polarizing microscope. We find that for MBRA-8 $P < 0$ as for DOBAMBC and HOBACPC[14].

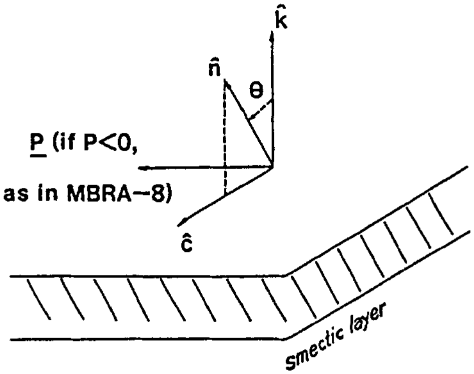


Figure 8. Relation between the vectors $\underline{P}$, $\hat{n}$, $\hat{c}$ and $\hat{k}$. In MBRA-8, which is a "minus" substance, $\underline{P}$ has the direction given in the figure.

RESPONSE TIME AND VISCOSITY

The experimental set-up does not only provide information about the polarization. We can also study the position of the current peak on the time axis. If we define a response time τ as the time between the square pulse edge and the current peak, a simple model (without considering the switching mechanism) would imply $\tau = \eta/P\cdot E$, where η is some effective viscosity. In Figure 9 is shown the temperature dependence of τ for square wave applied voltage of constant amplitude (9.80 V).

Also shown (dashed curve) is the viscosity η obtained from a straightforward use of this formula.

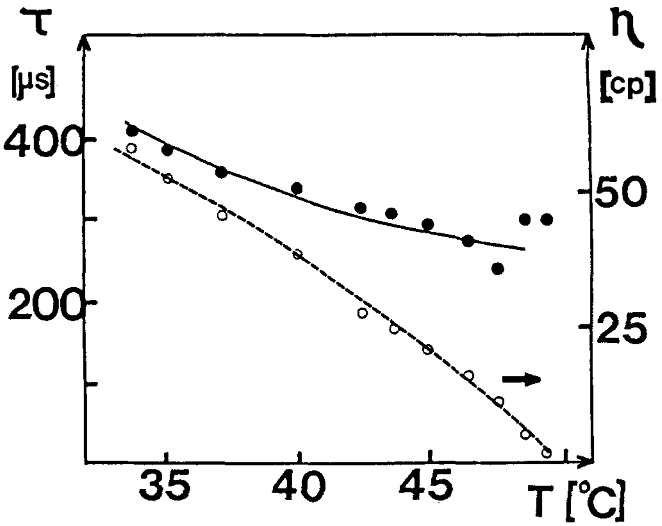


Figure 9. Response time τ *(●) and effective viscosity* η *(○) as a function of temperature.*

The simple model implies that the response time is proportional to E^{-1}. However, this seems not to be the case in the voltage regime we have studied. See Figure 10, which is a log-log plot of τ versus E. Nevertheless, it is of interest to estimate an effective viscosity η from our experimental . data, since very few measurements of viscosities in the SmC-phase have been reported. 'The viscosity values given in Figure 9 are comparable to those found in Ref. 15 for a non-chiral SmC-material, while the values in Refs. 16 and 17 are about one order of magnitude smaller.

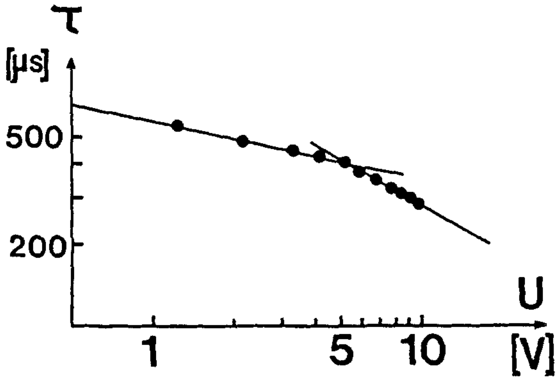


Figure 10. A log-log plot of response time τ versus applied voltage U.

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REFERENCES

1. R. B. Meyer, L. Liébert, L.Strzelecki and P. Keller, J. Phys. (France) 36, L-69 (1975).
2. W. Kuczyński and H. Stegemeyer, Chem. Phys. Lett. 70, 123 (1980).
3. N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett., 36, 899 (1980).

4. L. A. Beresnev, L. M. Blinov and Z. M. Elashvili, Pis'ma v zh. Tekh. Fiz. 4, 225 (1978).
5. P. Pieranski, E. Guyon and P. Keller. J. Phys. (France), 36, 1005 (1975).
6. J. Hoffman, W. Kuczyński and J. Malecki, Mol. Cryst. Liq. Cryst., 44, 287 (1978).
7. C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett., 42, 1220 (1979).
8. W. J. Merz, Phys. Rev., 95, 690 (1954).
9. Ph. Martinot - Lagarde, J. Phys. (France), 38, L - 17 (1977).
10. M. V. Loseva, B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin and N. I. Chernova, Fiz. Tverd. Tela, 22, 938 (1980).
11. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, Jpn. J . Appl. Phys. Part 2, 22, L 661, (1983).
12. T. Uemoto, K. Yoshino, Y. Inuishi, Mol. Cryst. Liq.Cryst. 67, 137 (1981).
13. N. A. Clark and S. T. Lagerwall, Ferroelectrics (1984), in press.
14. Ph. Martinot - Lagarde, R. Duke and G. Durand, Mol. Cryst. Liq. Cryst., 75, 249 (1981).
15. S. Meiboom and R. C. Hewitt, Phys. Rev. Lett. 34. 1146 (1975).
16. W. Kuczyński, Ber. Bunsenges. Phys. Chem. 85, 234 (1981).
17. C. S. Rosenblatt, R. Pindak. R. B. Meyer, N. A. Clark, Phys. Rev. A21, 140 (1980).