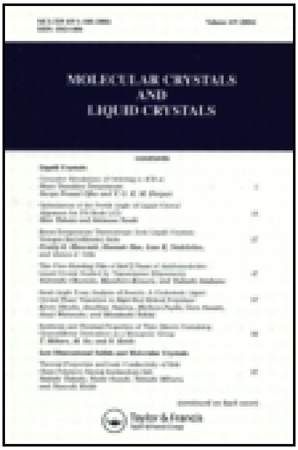

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Dielectric Study of Ferroelectric Properties in Chiral Smectic C

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Version of record first published: 19 Oct 2010.

To cite this article: J. Hoffmann , W. Kuczyński & J. Maĕki (1978): Dielectric Study of Ferroelectric Properties in Chiral Smectic C, Molecular Crystals and Liquid Crystals, 44:3-4, 287-300

To link to this article: http://dx.doi.org/10.1080/00268947808084986

Mol. Cryst. Liq. Cryst., 1978, Vol. 44, pp. 287–300
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Printed in Holland

Dielectric Study of Ferroelectric Properties in Chiral Smectic C

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(*Received May 20, 1977; in final form September 9, 1977*)

Measurements of electric permittivity, and polarization are reported for chiral liquid crystal DOBAMBC. Dielectric hysteresis was found. Temperature-variations of spontaneous polarization and relaxation time are studied. The dielectric properties of chiral smectic C and those of crystalline ferroelectrics are compared.

1 INTRODUCTION

The possibility of finding ferroelectric properties in liquid crystals has long been a subject of interest. Among the earliest experimental papers are those of Kapustin and Vistin[1] and Williams and Heilmeier.[2] However, the effects reported therein were later found to be unrelated with ferroelectricity. In 1973, W. L. McMillan[3] suggested that smectics of type C can exhibit concordant ordering of the permanent dipole moments of the molecules in the liquid crystal. Soon after that, R. B. Meyer *et al.*[4,5] carried out investigations on a new liquid crystal which, in the phases C and H, had properties accessible to explication on the assumption of a concordant ordering of the dipoles in smectic layers.

Meyer and his co-workers showed that the polarization direction rotates with a pitch of several μm about an axis perpendicular to the smectic layers thus causing the effective polarization of the sample as a whole to vanish. If an external agent perturbs the helicoidal distribution of the directions of polarization of the layers, the smectic specimen as a whole exhibits a non-zero polarization.

Detection of this perturbation process can be carried out indirectly, observing optically the deformation in conoscopic figure due to an applied electric field[5] or shear,[7] or directly measuring the charge corresponding to the effective polarization of the specimen.[6] The considerations concerning the symmetry properties leading to ferroelectricity in chiral smectics were convincingly supported by observations of pyroelectricity.[8]

Hitherto, experiments[5–7] have shown that permanent dipole order of the ferroelectric type is present in chiral smectics. The following question arises: Does such ordering in liquid crystals lead to the emergence of properties, specific to classical crystalline ferroelectrics?

Ferroelectrics are generally defined as bodies exhibiting a zero-field spontaneous polarization, subject to reversal by an external electric field, and then exhibiting polarization vs. field hysteresis.[9,10] Moreover, they typically obey a Curie-Weiss law above the temperature of transition from the ordered to the disordered phase.

The question whether chiral smectics possess properties typical for ferroelectrics was answered in part in a series of studies, reported by us in January 1976 at Halle.[11] Our results, at the time, consisted in recordings of hysteresis loops (permitting the evaluation of spontaneous polarization and coercive field values) and measurements of electric permittivity vs. temperature at 1 MHz and 1.5 kHz. The present paper is a continuation and extension of our earlier work.

2 METHOD OF MEASUREMENT

Our work bears on *p*-decyloxy-benzylidene-*p*-amino-2-methyl-butyl-cinnamate (DOBAMBC), synthesized by L. Liebert, L. Strzelecki and P. Keller at Orsay.[5]

Our dielectric measurements were performed in a plane condenser, with gold-coated electrodes of area 2.0 cm^2 distant by 0.32 mm, and thermostatized with an accuracy better than 0.1°C by an electronic circuit, supplying the heater coiled over the bulk of the condenser.

Hysteresis loops were observed using a Diamant bridge.[12] Electric permittivity was measured using an Ulrich 941 type bridge connected to a selective nanovoltmeter. ac voltage, ranging in frequency from 5 Hz to 20 kHz, was applied to the bridge. No dependence of the permittivity on the measuring voltage was found from 0.5 to 10 V_{pp}; all measurements were performed at 2 V_{pp}. The temperature T_c of transition from the phase C to A of the freshly prepared sample was 94°C; it then decreased gradually during several days, to become constant at 87°C after about 1 week.

Nonetheless the experimental results, recorded at a given distance from T_c, proved independent of the age of the sample. Accordingly, in all our measurements vs. temperature, we adopted the $T - T_c$ scale, as done by Martinot-Lagarde.[13]

The samples for dielectric measurements were not oriented; nor did the construction of the condenser permit observations of their texture. However, identically prepared samples, when in the condenser with semi-transparent electrodes used for optical measurements, exhibited focal conic texture. Observation of fringes, related with the helicoidal structure in phases C and H showed, that, throughout almost the entire bulk of the sample, the axis of the helix was parallel (or almost so) to the electrodes. This suggests that the situation was similar in the condenser for dielectric measurements, i.e. that the measuring field was parallel to the smectic layers.

For observations of conoscopic figures, we used samples ranging in thickness from 0.1 to 0.3 mm oriented in their entire bulk. The optical axis was perpendicular to the surface of the glass plates, treated with hexadecyl trimethyl ammonium bromide (HTAB) to induce orientation. Two parallel silver wires, playing the role of electrodes and spacers, were placed between the glass plates. The wires were distant by about 1.5 mm. The conoscopic figures were observed with a polarization-interference microscope and using a He–Ne laser with appropriate optical system.

3 EXPERIMENTAL RESULTS

3.1 Electric polarization hysteresis

Our electric polarization vs. electric field strength measurements applying the Diamant bridge[12] revealed a hysteresis loop in the smectic phases C and H. The loop vanished on heating upwards of the temperature of transition to the smectic phase A (Figure 1). The hysteresis loops presented in Figure 1 were obtained by compensating the phase shift connected with the complex conductivity of the sample. Thus the inevitable conclusion must be drawn that the net polarization revealed by the experiment has a life-time longer (or at least comparable) with the period of the applied field. Due to the fluidity of the sample the life time should be shorter by several orders of magnitude than that observed in the case of solid ferroelectrics.

The loop was observed at various amplitudes (up to 90 kV/cm) and frequencies (7–250 Hz) of the sine electric field, and at various temperatures. The range of field strengths applied was limited by the breakdown voltage (about 100 kV/cm) and the range of frequencies—by the possibilities of compensating the dielectric losses, and conductivity.

Observations of parameters of the hysteresis loop, spontaneous polarization P_s i.e. polarization at zero field strength, and coercive field E_c made

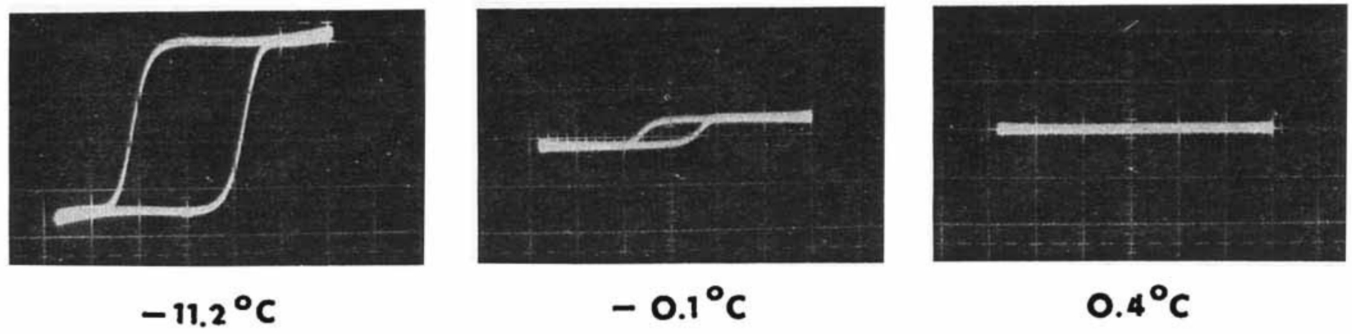

FIGURE 1 Polarization versus electric field recorded at $f = 30$ Hz, 1 div $= 6.2$ nc/cm^2 and 17.4 kV/cm respectively.

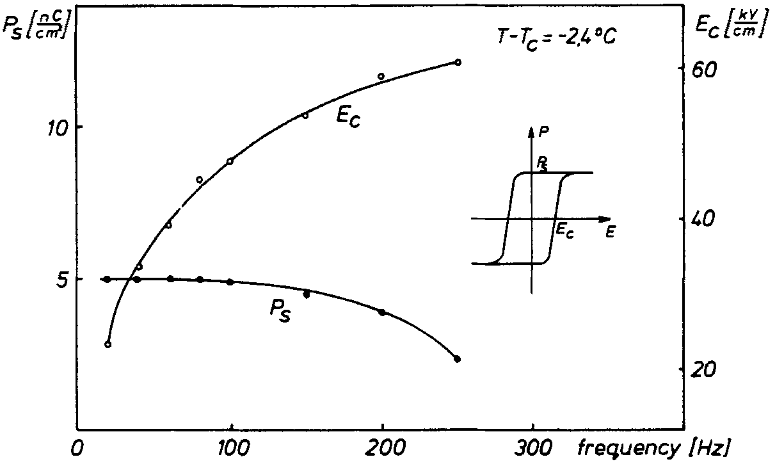

FIGURE 2 Spontaneous polarization P_s and coercive field E_c vs. the frequency of the applied electric field of strength 70 kV/cm, $T - T_c = -2.4°C$.

apparent an increase in E_c and a decrease in P_s with increasing frequency f of the field (Figure 2).

Measurements of P_s and E_c vs. temperature were performed at $f = 30$ Hz and a field strength of 70 kV/cm (Figure 3). Both P_s and E_c decreased with increasing temperature tending to zero at the Sm C–Sm A transition temperature. E_c is larger in the smectic phase H than in C.

Since for technical reasons it was not possible to measure P_s at frequencies less than 7 Hz, we proceeded to observations of the deformation in helicoidal

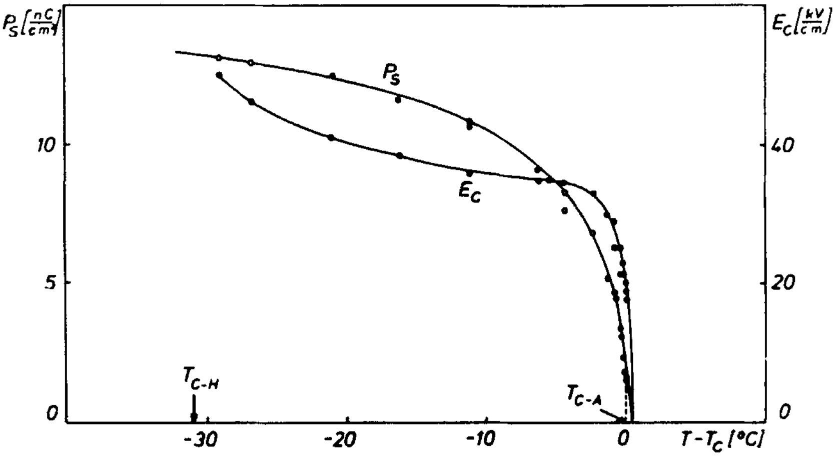

FIGURE 3 Spontaneous polarization P_s and coercive field E_c vs. temperature difference $T - T_c$, at frequency 30 Hz.

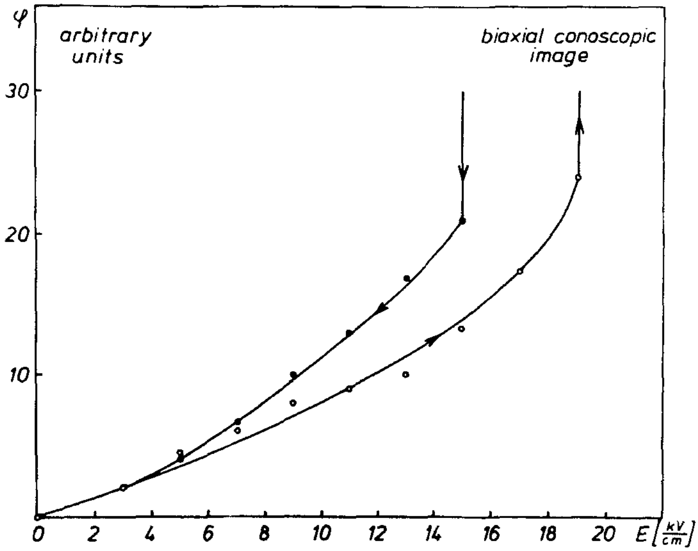

FIGURE 4 Inclination angle φ of the optical axis vs. the electric field strength; $T - T_c = -4°C$.

structure in the smectic phase C due to a dc electric field, applied parallel to the smectic layers, taking the degree of deformation of the helix as a measure of the polarization after Meyer *et al.*[5] We used samples of two kinds: oriented—with optical axis perpendicular to the glass surfaces (for conoscopic figure observations), and unoriented—with confocal texture for observation of the fringes related with the presence of the helix.

In the former case at observation perpendicular to the field, the conoscopic figure shifted as the field strength increased to a value E_k, when the figure became that of a bi-axial crystal pointing to complete unwinding of the helix and attainment of maximal polarization. As the field strength decreased, the figure of the uniaxial crystal reappeared at a field about 20% weaker than E_k (Figure 4). A similar effect was apparent at observation parallel to the field. Here, fringes corresponding to the pitch of the helix were the object of observation. At a given field strength the fringes vanished, to reappear in a field by 20% weaker than that in which they had disappeared.

3.2 Electric permittivity

In order to determine the frequency at which the mechanism responsible for hysteresis of polarization is eliminated, we carried out measurements of the electric permittivity ε as a function of temperature throughout the frequency range from 5 Hz to 1 MHz. Our results are shown in Figure 5, where ε in the

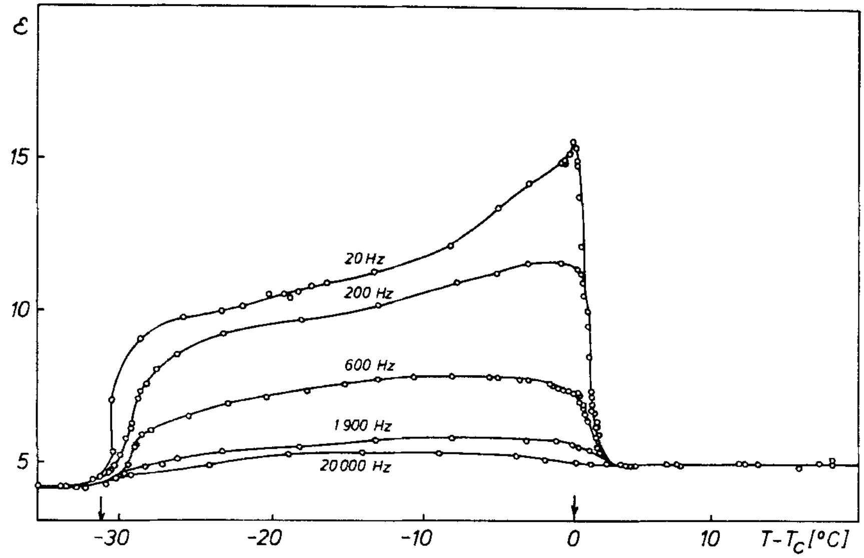

FIGURE 5 Electric permittivity of DOBAMBC vs. temperature, at various field frequencies. Arrows indicate phase transition temperatures.

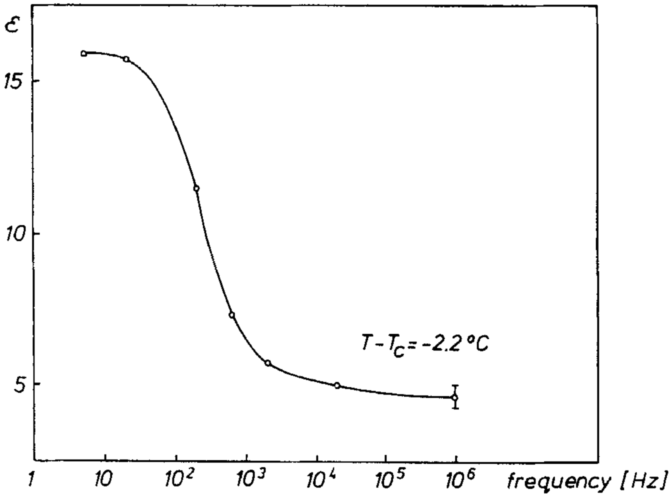

FIGURE 6 Typical plot of electric permittivity of DOBAMBC vs. frequency.

phase C is found to depend strongly on the frequency f between 20 Hz and 20 kHz; below and above this range, the frequency dependence vanishes. Figure 6 shows a typical $\varepsilon(f)$-dependence.

4 DISCUSSION

4.1 Spontaneous polarization

The shape of P_s vs. $T - T_c$ is of the kind typical for ferroelectric crystals and strongly resembles the molecular tilt angle dependence $\theta(T - T_c)$.[13,14] Accordingly, the temperature-dependence of P_s too can be expected to fulfil the relationship:

$$P_s = A(T - T_c)^{\beta} \tag{1}$$

where A is a constant. To determine numerically the exponent β we plotted $\log P_s$ vs. $\log(T - T_c)$ (Figure 7). The slope of the straight line yielded $\beta = 0.30 \pm 0.03$. The value determined for P_s is in good agreement with the analogical value, determined for θ, the tilt angle of the molecules (0.40 from Ref. 13, 0.35 ± 0.05 from Ref. 14).

The good numerical agreement between β from P_s and measurements corroborates the proportionality between P_s and θ, predicted on the basis of symmetry conditions[3,6,15]

$$P_s \sim \theta. \tag{2}$$

It is worth noting that P_s does not vanish in the point of transition to the phase A but rather maintains itself at a level measurable in our experiment

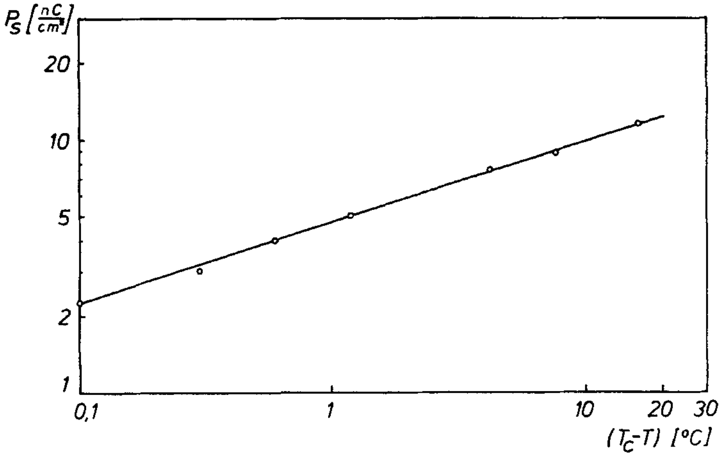

FIGURE 7 Log P_s versus $\log(T - T_c)$, $f = 30$ Hz.

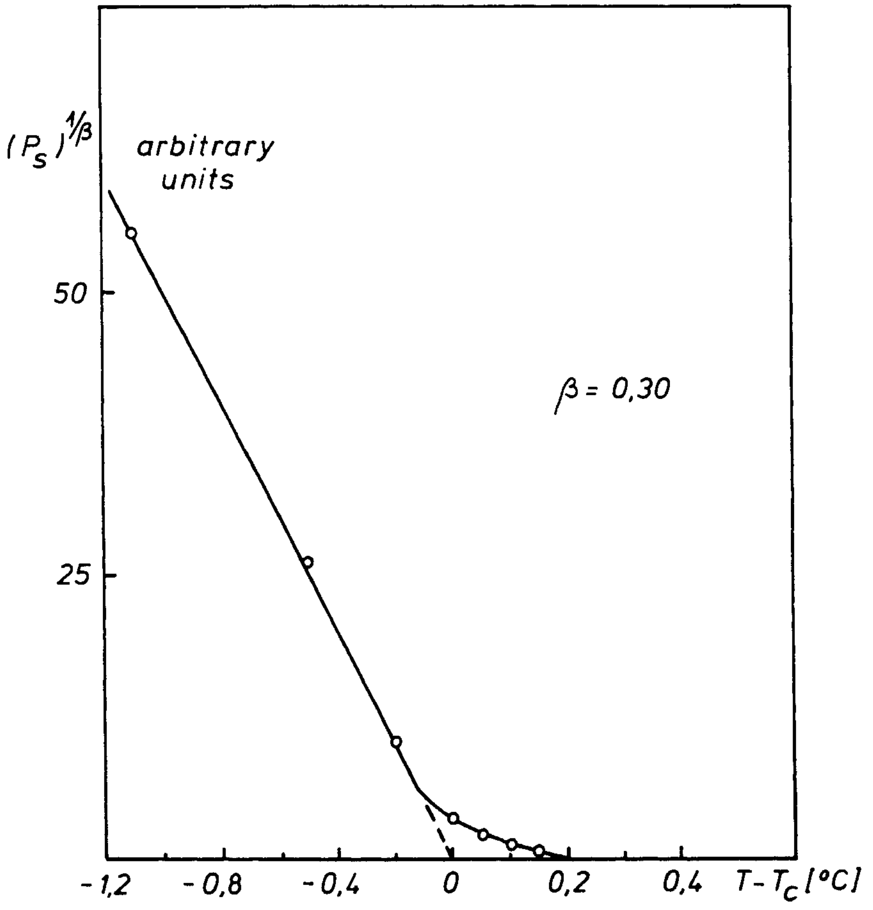

FIGURE 8 $P_s^{1/\beta}$ as a function of $T - T_c, f = 30$ Hz.

up to 0.2°C above the transition temperature. This is clearly apparent in Figure 8, showing $P_s^{1/\beta}$ as a function of temperature close to the phase transition. The non-vanishing of P_s in the phase A is, presumably, due to pretransitional effects; phase A, too, exhibits motions of the conoscopic figure when an electric field is applied.[16] The non-zero values of P_s we observed above the transition temperature T_c could be caused as well by a smearing out of the transition itself due to the inhomogeneouity of the samples used.

Our P_s-values (though too low by about 20% as a result of incompletely defined orientation of the sample) are very small compared with typical P_s-values of ferroelectric crystals. This divergence stimulated us to attempt an evaluation of the dipole moment, contributed to the polarization of the sample by each molecule. Since no data concerning the density of DOBAMBC are available, this could be but an attempt to determine the dipole moment participating in polarization.

The spontaneous polarization, representing the dipole moment per unit volume, is approximately:

$$P_s = \frac{\mu_{\text{eff}} N_A d}{M} \cdot S \tag{3}$$

with: μ_{eff}—the effective dipole moment per molecule; N_A—Avogadro's number; d—density of the sample; M—molecular weight; and $S = \theta$—order parameter.[17] We have:

$$\mu_{\text{eff}} = \frac{P_s M}{N_A d\theta}. \tag{4}$$

Putting $P_s = 12\text{nC/cm}^2$ at a temperature by 10°C lower than T_c, and $d = 1\ \text{g/cm}^3$, $M = 477$ g, $\theta = 17°$,[13] we arrive at $\mu_{\text{eff}} = 0{,}1$ D.

When assessing the dipole moment of the individual molecule we assumed that, owing to intramolecular rotation, the predominant contribution is due to the ester group (Figure 9), whose moment amounts to 1.7 D.[18] Its component perpendicular to the long axis of the molecule amounts to about 1.5 D—a value approximately 15 times larger than that of the effective dipole moment of the molecule determined from spontaneous polarization measurements.

Two explanations of this divergence suggest themselves:

1) Hindered rotation of either the C=O bond about the chiral group or the whole molecule around its long axis.

2) Some small angle between the dipole moment and the tilt plane of the molecules. The moment μ_{eff}, contributing to spontaneous polarization, is

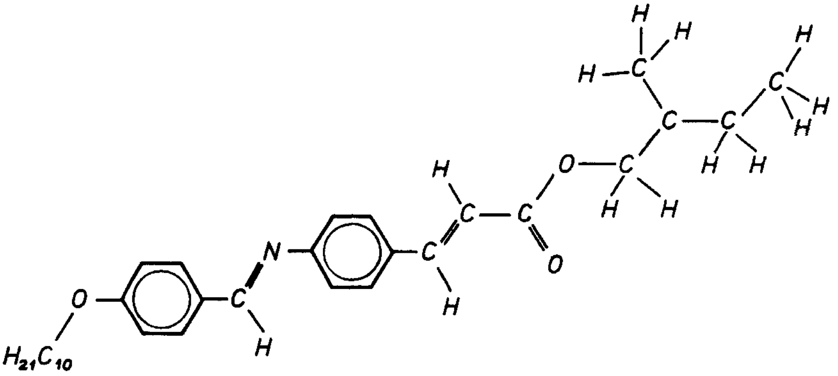

FIGURE 9 Structure of the DOBAMBC molecule.

dependent on the angle α between the tilt plane of the molecules in the smectic layer and the direction of the dipole moment related with the chiral group:

$$\mu_{\text{eff}} = \mu \sin \alpha \tag{5}$$

whence, with the above assessed values, we obtain $\alpha \approx 4°$.

Presumably, in the case of the DOBAMBC molecule, both mechanisms abating μ_{eff} are active simultaneously. The question of the part played by either remains, for the time being, unanswered.

4.2 Coercive field

From Figure 3, which shows the coercive field E_c vs. $T - T_c$, we note that E_c increases with decreasing T, especially strongly near the transition to Sm H. This behaviour is due, in part, to changes in viscosity. The marked rise in viscosity accompanying the transition from phase C to H causes an increase in reorientational relaxation time of the molecules due to unwinding of the helix. Accordingly, at the same frequency, a stronger field is required to achieve polarization reversal. The preceding interpretation is corroborated by the experimental E_c vs. frequency dependence of Figure 2, where E_c tends to zero as f decreases. This behaviour is confirmed by optical measurements in a static electric field in which we observed neither coercion or spontaneous polarization. The facts lead us to presume that the hysteresis loop observed by us appeared due to the circumstance that the measuring frequency was comparable to the inverse relaxation time of the helix. This is also in agreement with Meyer's model, according to which the sample as a whole should not exhibit polarization in the absence of an electric field due to mutual compensation of the spontaneous polarizations of the twisted smectic layers. An analogy suggests itself between smectic layers and ferroelectric domains in crystals, though the association is rather loose since there is no way to obtain a single-domain liquid crystal sample in the absence of an external agent.

4.3 Dielectric relaxation

From the frequency-dependence of ε (Figure 6) measured at various temperatures, we calculated the collective reorientation time of molecules in the individual smectic layers. The results are given in Figure 10, where the relaxation time exhibits maxima for the transitions Sm A → Sm C and Sm C → Sm H. As stated, the increase in relaxation time in the C → H transition is due to the increase in viscosity, whereas that in the C → A transition can be interpreted as due to the increase in pitch of the helix

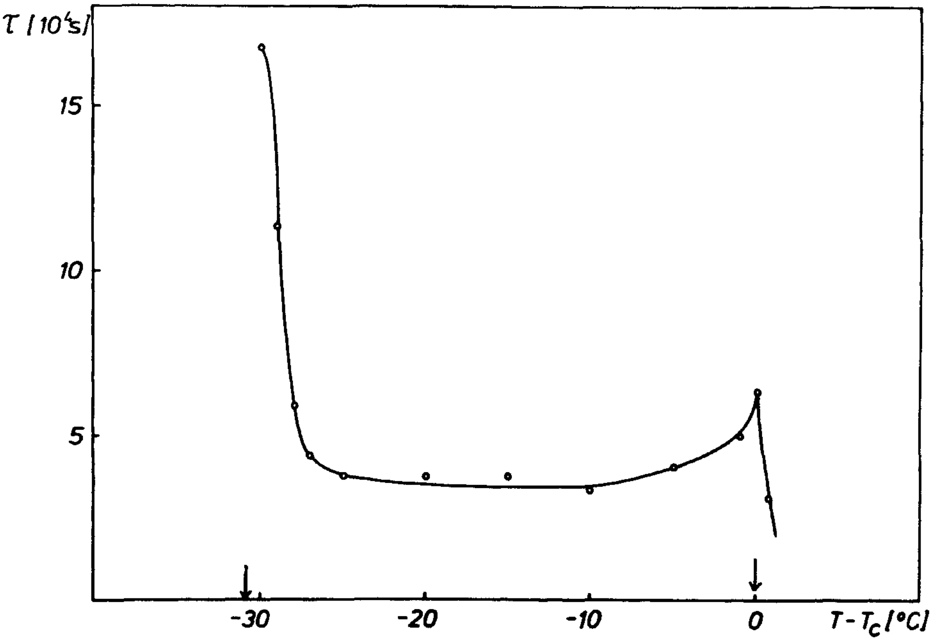

FIGURE 10 Relaxation time as a function of temperature. Phase transition temperatures are indicated by arrows.

immediately preceding the phase transition[13] since, as shown earlier,[7] the relaxation time is proportional to the second power of the pitch. In the phase A the relaxation time falls steeply to very small values.

4.4 Curie–Weiss law

In ferroelectric solids, the Curie–Weiss law:

$$\varepsilon = \frac{C}{T - T_c} \tag{6}$$

is fulfilled in a wide range of temperatures above the order-disorder phase transition. According to predictions of Blinc,[15] the range of applicability of the Curie–Weiss law to chiral smectics has to be much narrower (of the order of 1°C). Our measurements confirmed this (Figure 11).

With regard to the rather small values of ε, only the contribution from the ferroelectric mechanisms $\varepsilon_f = \varepsilon - \varepsilon_A$ (where ε_A is the permittivity in phase A) was taken into account.

It is worth noting that the linear $1/\varepsilon_f$ vs. temperature dependence is fulfilled in phase C also.

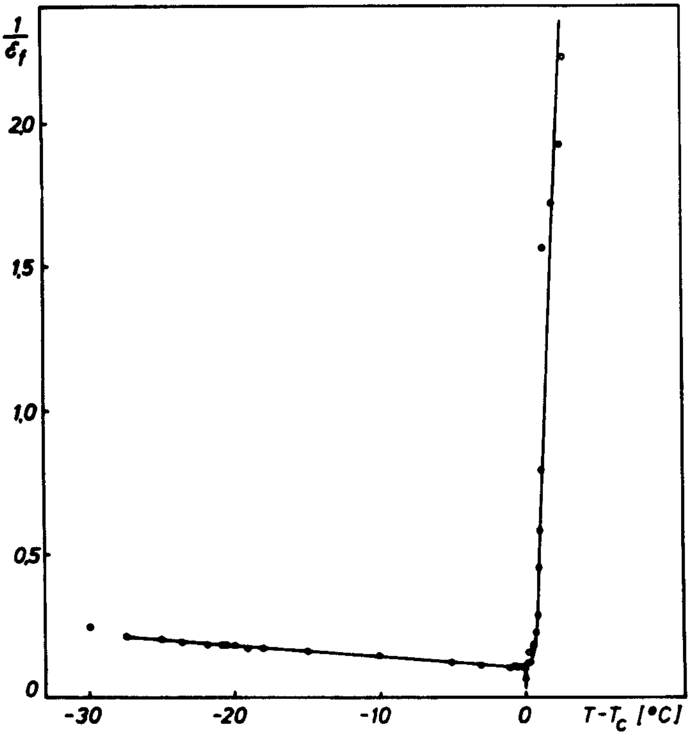

FIGURE 11 $1/\varepsilon_f$ as a function of temperature, f = 20 Hz.

5 CONCLUSIONS

The present measurements show that, in the phases C and H, the chiral smectic DOBAMBC possesses a number of properties specific to ferroelectrics, thus dielectric hysteresis, temperature-dependent spontaneous polarization and Curie–Weiss behaviour of the dielectric permittivity. The loops observed are, however, due to the dynamics of the polarization reversal process and are by no means proof of a stable polarization in the absence of an electric field. The meaning of the term "spontaneous polarization," applied to a chiral liquid crystals, is not quite the same as in the case of a crystalline ferroelectric: if the field decreases sufficiently slowly, the spontaneous polarization of a chiral liquid crystal sample is zero. In this consists one of essential differences between a liquid-crystalline and a crystalline ferroelectric.

Acknowledgements

The authors are indebted to the Orsay Liquid Crystal Group for making available a sample of DOBAMC. Thanks are due to Mrs. Dr. B. Hilczerowa for her very helpful remarks.

References

1. A. P. Kapustin and L. K. Vistin, *Kristall.*, **10**, 118 (1965).
2. R. Williams, G. Heilmeier, *J. Chem. Phys.*, **44**, 638 (1966).
3. W. L. McMillan, *Phys. Rev.*, **A8**, 1921 (1973).
4. R. B. Meyer *et al.*, Fifth International L. C. Conf., Stockholm (1974).
5. R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. Lett.*, **36**, L-69 (1975).
6. P. Pierański, E. Guyon, and P. Keller, *J. Phys.*, **36**, 1005 (1975).
7. P. Pierański, E. Guyon, P. Keller, L. Liebert, W. Kuczyński, and P. Pierański, *Mol. Cryst. Liquid Cryst.*, **38**, 275 (1977).
8. L. J. Yu, H. Lee, C. S. Bak, and M. M. Labes, *Phys. Rev. Lett.*, **36**, 388 (1976).
9. G. A. Smoleński and co-authors, *Segnietoelektriki i antisegnietoelektriki*, Nauka, Leningrad, 1971.
10. E. Fatuzzo and W. Merz, *Ferroelectrics*, North-Holland Publishing Company, Amsterdam, 1967.
11. W. Kuczyński, J. Hoffmann, and P. Pierański, First International L. C. Conf. Social. Counts., Halle, DDR, January 1976.
12. H. Diamant, K. Drenck, and R. Pepinsky, *Rev. Sci. Instr.*, **28**, 30 (1957).
13. Ph. Martinot-Lagarde, *J. de Phys.*, **37**, C3-129 (1976) and *J. de Phys. Lett.*, **38**, L-17 (1977).
14. R. Duke, G. Durand, P. Keller, L. Liebert, and R. B. Meyer, *J. Phys.* in press.
15. R. Blinc, *Phys. Stat. Sol.*, (b) **70**, K-29 (1975).
16. S. Garoff and R. B. Meyer, *Phys. Rev. Lett.*, **38**, 848 (1977).
17. P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1974.
18. O. Exner, *Dipole Moments in Organic Chemistry*, Georg Thieme Publishers, Stuttgart, 1975.