Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Electrooptic properties of chiral smectic liquid crystals with a dipolar order

M. Glogarová[a]; H. Sverenyák[a]; A. Fukuda[b]; H. Takezoe[b]
[a] Institute of Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia [b] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan

To cite this Article Glogarová, M. , Sverenyák, H. , Fukuda, A. and Takezoe, H.(1993) 'Electrooptic properties of chiral smectic liquid crystals with a dipolar order', Liquid Crystals, 14: 2, 463 — 468
To link to this Article: DOI: 10.1080/02678299308027661
URL: http://dx.doi.org/10.1080/02678299308027661

LIQUID CRYSTALS, 1993, VOL. 14, NO. 2, 463–468

Electrooptic properties of chiral smectic liquid crystals with a dipolar order

by M. GLOGAROVÁ*†, H. SVERENYÁK*†, A. FUKUDA‡ and H. TAKEZOE‡

† Institute of Physics, Czechoslovak Academy of Sciences,
Na Slovance 2, 18040 Prague 8, Czechoslovakia
‡ Tokyo Institute of Technology,
Department of Organic and Polymeric Materials,
O-okayama, Meguro-ku, Tokyo 152, Japan

The compound 4-(1-methylheptyloxycarbonyl)phenol 4′-octyloxy biphenyl-4-carbonate exhibits ferroelectric S_C^*, paraelectric S_A, antiferroelectric $S_{C_A}^*$ and two ferrielectric $S_{C_\alpha}^*$ and $S_{C_\gamma}^*$ phases. From the electrooptic response measured in the frequency range 100 Hz to 100 kHz the soft mode relaxation frequency in the paraelectric phase and the Goldstone mode relaxation frequency in the ferrielectric and ferroelectric phases have been determined. In the $S_{C_\gamma}^*$ phase the shape of the real and imaginary parts of the electrooptic frequency dispersion reflects dipolar disorder. In the ferrielectric, ferroelectric and antiferroelectric phases the temperature dependencies of both the spontaneous polarization and the tilt angle are measured under an electric field high enough to enforce the saturated ferroelectric state. The dependencies are smooth within the entire temperature range studied indicating all the studied phases are indistinguishable under high electric field.

1. Introduction

In tilted chiral smectics a local spontaneous dipole moment appears parallel to the smectic layers due to the hindered rotation of chiral molecules along their long axes and consequently due to the non-compensated molecular dipole [1]. The symmetry of the structure determines the direction of the dipole moment along the polar two-fold axis lying in the smectic layer and perpendicular to the long molecular axis. The dipole arrangement allows either ferroelectric (FE) [1] or antiferroelectric (AF) [2] order, the dipole moments of subsequent smectic layers being parallel or antiparallel (and thus compensated to zero within two layers). Besides these two states, a series of ferrielectric (FI) states can exist with the dipole moment more or less compensated within a few layers [3]. Due to chirality a spiral alignment of molecules along the smectic layer normal arises in all these phases with a macroscopic pitch over thousands of layers [1, 2].

For some materials, all these three types of phases occur in definite temperature regions. The first material where AF and FI behaviour has been found is 4-(1-methylheptyl oxycarbonyl)phenol 4′-octyloxy biphenyl-4-carbonate (MHPOBC) [2] which exhibits paraelectric (PE) S_A, FE S_C^*, AF $S_{C_A}^*$ and two FI $S_{C_\gamma}^*$ and $S_{C_\alpha}^*$ phases with the phase sequence [2, 5]

$$\text{C } 30^\circ\text{C } S_I^* \ 66^\circ\text{C } S_{C_A}^* \ 118{\cdot}3^\circ\text{C } S_{C_\gamma}^* \ 119^\circ\text{C}$$

$$S_C^* \ 120{\cdot}7^\circ \ S_{C_\alpha}^* \ 122^\circ\text{C } S_A \ 156^\circ\text{C I.}$$

* Author for correspondence.

0267–8292/93 $10·00

(Some of the authors (H. T. and A. F.) suggest the $S^*_{C_\alpha}$ phase is ferrielectric only just above the S^*_C–$S^*_{C_\alpha}$ transition. At higher temperatures it has antiferroelectric properties (see [4]). In the following, we will call this phase ferrielectric for simplicity.) The dielectric properties of this material have been studied which give basic information about the vibrational modes responsible for the phase transitions [6]. These modes, known as soft and Goldstone modes, being the vibration of the molecular long axis, can be detected in the frequency dispersion of both the dielectric and the electrooptic response. The dispersion of the electrooptic response has not been performed so far.

The aim of this contribution is to determine the temperature dependencies of the low frequency electrooptic response and of the relaxation frequencies in the temperature region 130–110°C covering both FI phases, FE and AF phases and the PE phase above the S_A–$S^*_{C_\alpha}$ phase transition. In addition, the temperature dependencies of the spontaneous tilt angle θ_s and spontaneous polarization P_s in the two FI, FE and AF phases were determined.

2. Experimental results

All measurements were performed in a cell filled with MHPOBC between two glass slides with a cell gap of 25 or 50 μm and an electrode area of 25 mm^2. The samples were aligned by an electric field of 20 Hz, 40 kV cm^{-1} applied in the PE S_A phase, which resulted in good planar alignment (book shelf geometry). The sample was placed between crossed polarizers with the optical axis in the S_A phase (parallel to the layer normal) making an angle of 22·5° with the polarized light of one of the polarizers. In this position the electrooptic signal is proportional to the vibration angle $\delta\theta$ of the optical axis to the smectic layer normal. The electrooptic response was detected by a PIN photodiode connected to the lock-in amplifier. The typical frequency dependence of the real and imaginary parts of the response $I(f)$ in the S_A phase is shown in figure 1 (*a*). Its form is of the lorentzian type: $I(f) \sim (1 + jf/f_r)^{-1}$ with the relaxation frequency f_r and the real and imaginary parts of I:

$$\mathrm{Re}\, I(f) \sim (1 + f^2/f_r^2)^{-1}, \tag{1a}$$

$$\mathrm{Im}\, I(f) \sim f[f_r(1 + f^2/f_r^2)]^{-1} \tag{1b}$$

The experimental curves (see figure 1 (*a*)) correspond to equations (1 *a*) and (*b*). The relaxation frequency was determined from the maximum of Im $I(f)$.

In the FI, FE and AF phases, in the absence of biased electric field the light passes through a spatially inhomogeneous medium. Nevertheless, an average optical axis is found along the smectic layer normal. Thus the electrooptic effect is detected for the same sample orientation with respect to the crossed polarizers as for the S_A phase. In the FE phase and high temperature FI phase ($S^*_{C_\alpha}$) a single relaxation frequency curve is also found of the same form as in figure 1 (*a*). In the low temperature FI phase ($S^*_{C_\gamma}$) besides the relaxation around 1 kHz, there is also a low frequency contribution to the electrooptic response (see figure 1 (*b*)).

The relaxation frequencies determined from the maxima of Im $I(f)$ are shown in figure 2 and depend on temperature for all the studied phases. The relaxation frequency decreases with decreasing temperature in the S_A phase, whereas in other phases it is temperature independent with downward jumps at every phase transition. In the AF $S^*_{C_A}$ phase the electrooptic effect is non-measurably small, so that no relaxation can be detected.

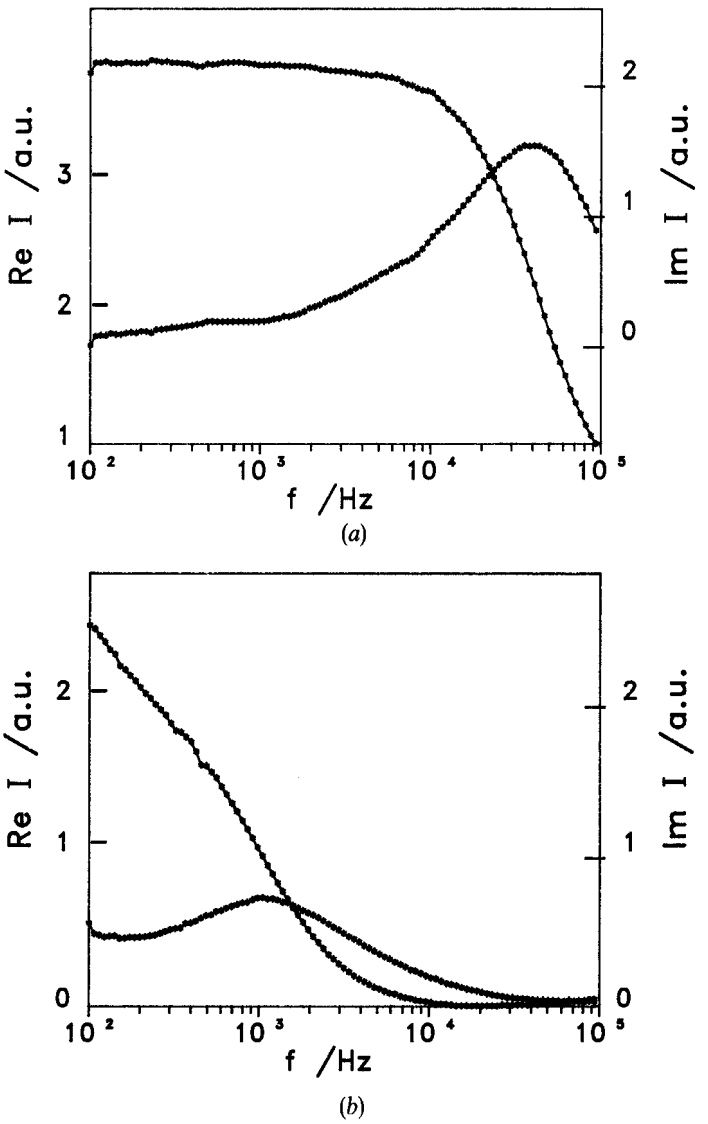

Figure 1. The frequency dispersion of the real and imaginary parts of the electrooptic response. (*a*) in the PE S_A phase, $T = 122{\cdot}5°C$, (*b*) in the FI $S^*_{C_\gamma}$ phase, $T = 118{\cdot}5°C$.

The low frequency electrooptic response was measured during continuous cooling. The result is shown in figure 3. The phase transitions correspond to the distinct points where the character of the curve changes. A similar result has been obtained in [7].

The spontaneous tilt angle θ_s of molecules from the smectic layer normal was calculated from the difference between extinction positions of the sample between crossed polarizers under opposite DC fields $\pm 40\,kV\,cm^{-1}$. The field has to be high enough to unwind the helical structures in the FI, FE and AF phases and also to accomplish the phase transition from the FI or AF phases to the unwound FE phase. The temperature dependence of θ_s (see figure 4) shows no anomalies at the phase transition temperatures between FI and FE or AF phases.

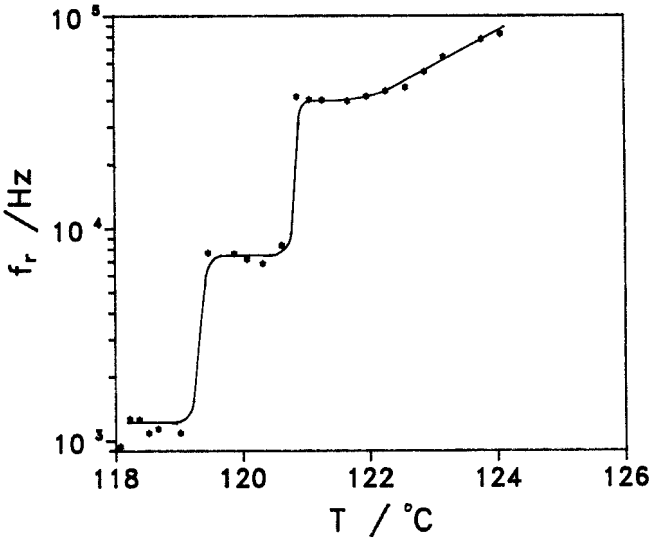

Figure 2. The temperature dependence of the relaxation frequencies of the soft and Goldstone modes in the PE phase and in the FI and FE phases, respectively.

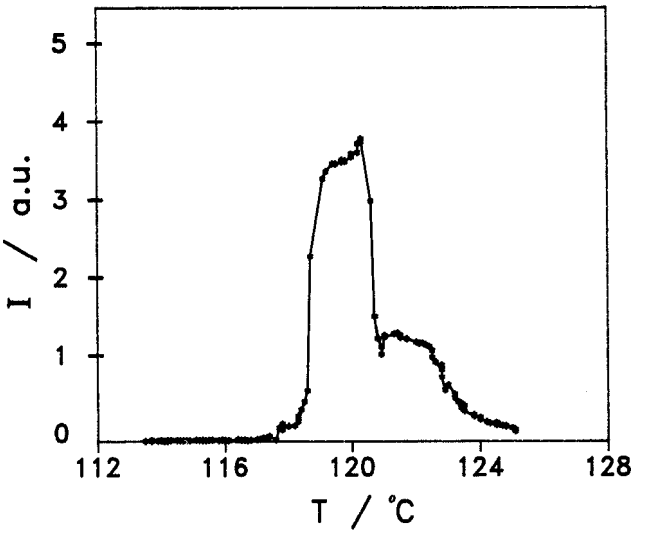

Figure 3. The temperature dependence of the electrooptic response measured at a frequency of 1 kHz.

The spontaneous polarization P_s was determined from the $P(E)$ dependence detected during switching of P_s in an AC field of frequency 50 Hz. At this frequency the $P(E)$ dependence, in the form of a simple hysteresis loop, was obtained for the two FI, and the FE and AF phases. This implies that switching of a ferroelectric type takes place in all phases (direct switching between two saturated states). For this material the double hysteresis loops typical for the AF phase could be obtained only in a quasistatic field [8]. Similarly $\theta_s(T)$, the temperature dependence of P_s (see figure 5), shows no anomalies at the phase transition temperatures. The measured $P_s(T)$ dependence is in accordance with the result obtained in [9], where P_s was determined by integrating the switching current.

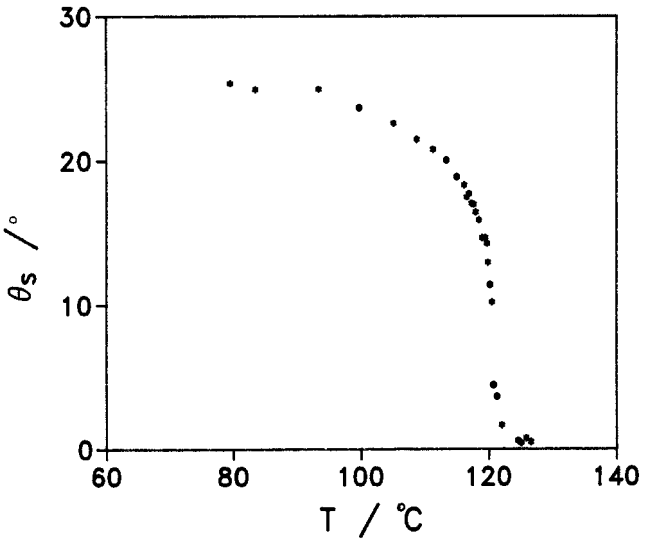

Figure 4. The temperature dependence of the spontaneous tilt angle.

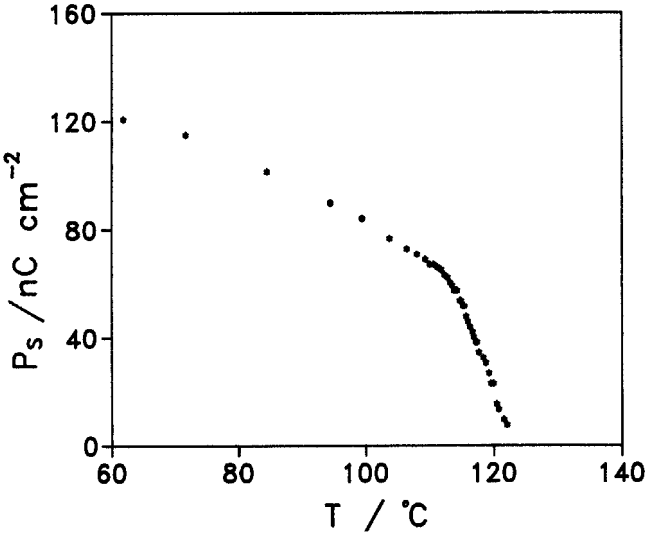

Figure 5. The temperature dependence of the spontaneous polarization.

3. Discussion and conclusions

In the FI, FE and AF phases both the spontaneous polarization and the tilt angle have been measured under an electric field high enough to bring about the parallel alignment of molecules—the saturated FE state. The $P_s(T)$ and $\theta_s(T)$ dependencies are smooth within the entire temperature range studied, no kinks at the temperatures corresponding to the phase transitions (without field) were found. This implies that all the studied phases are indistinguishable under high electric field.

The measurement of the frequency dispersion of the electrooptic response is a useful tool for the study of vibrational modes in chiral smectics with a dipolar order; it gives similar results as for dielectric dispersion, but it is more sensitive since there is a very

low (non-measurable) high frequency component. For dielectric response, on the other hand, the high frequency component can overwhelm the contribution from the relevant mode and make it hardly measurable. The mode detected in the S_A (PE) phase is the soft mode, its relaxation frequency decreases and its amplitude increases hyperbolically on approaching the phase transition to the FI phase. In the FI $S^*_{C_\alpha}$ and $S^*_{C_\gamma}$ phases and the FE S^*_C phase relaxations are detected, the frequencies of which in respective phases are not temperature dependent within the precision limits (see figure 2). These relaxations could be accounted for by the Goldstone mode connected to the structure modulation. The temperature dependence of the low frequency intensity (see figure 3) shows the different strength of the Goldstone mode in these phases. The soft mode should also exist in all these phases, but it is very weak and overwhelmed by the Goldstone mode.

The relaxations in the S_A, $S^*_{C_\alpha}$ and $S^*_{C_\gamma}$ phases can be compared to those determined from dielectric dispersion [6]. Moreover, electrooptic dispersion has yielded the Goldstone mode relaxation in the $S^*_{C_\gamma}$ phase and furthermore, in the $S^*_{C_\gamma}$ phase, a low frequency 'tail' is observed in the electrooptic response (see figure 1 (*b*)) which is not present in other phases so that it can be hardly explained by a conductivity process. One explanation could be a dipolar disorder, similar to that in dipolar glasses [10]. The $S^*_{C_\gamma}$ phase which behaves macroscopically as a FI phase might, therefore, be a mixture of clusters of both neighbouring phases, namely FE and AF phases existing at higher and lower temperatures, respectively. On the other hand, the regular three layer ferrielectric structure as a model for the $S^*_{C_\gamma}$ phase [11] is not excluded being more compatible with results from rotatory power experiments [11]. Other experiments are needed to clarify this idea.

The authors are grateful to Dr J. Petzelt for valuable discussions.

References

[1] MEYER, R. B., LIÉBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett., Paris*, **36,** L69.

[2] CHANDANI, A. D. L., GORECKA, E., TAKEZOE, H., and FUKUDA, A., 1989, *Jap. J. appl. Phys.*, **28,** L1265.

[3] GORECKA, E., CHANDANI, A. D. L., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1990, *Jap. J. appl. Phys.*, **29,** 131.

[4] TAKANISHI, Y., HIRAOKA, K., AGRAWAL, V. K., TAKEZOE, H., FUKUDA, A., and MATSUSHITA, M., 1991, *Jap. J. appl. Phys.*, **30,** 2023.

[5] FUKUI, M., ORIHARA, H., YAMADA, Y., YAMAMOTO, N., and ISHIBASHI, Y., 1989, *Jap. J. appl. Phys.*, **28,** L849.

[6] HIRAOKA, K., TAGUCHI, A., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1989, *Jap. J. appl. Phys.*, **29,** L103.

[7] HIRAOKA, K., TAKANISHI, Y., SKARP, K., TAKEZOE, H., and FUKUDA, A., 1991, *Jap. J. appl. Phys.*, **30,** L1819.

[8] LEE, J., CHANDANI, A. D. L., ITOH, K., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1990, *Jap. J. appl. Phys.*, **29,** 1122.

[9] CHANDANI, A. D. L., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1988, *Jap. J. appl. Phys.*, **27,** L276.

[10] HÖCHLI, U. T., KNORR, K., and LOIDL, A., 1990, *Advances in Physics* (*Orientational Glasses*), **39,** 405.

[11] TAKEZOE, H., LEE, J., OUCHI, Y., and FUKUDA, A., 1991, *Molec. Crystals liq. Crystals*, **202,** 85.