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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Wróbel, S. , Hiller, S. , Pfeiffer, M. , Marzec, M. , Haase, W. , Twieg, R. and Betterton, K.(1995) 'Collective and molecular processes in a new class of ferroelectric liquid crystals', *Liquid Crystals*, 18: 1, 21 – 29

To link to this Article: DOI: 10.1080/02678299508036586

URL: <http://dx.doi.org/10.1080/02678299508036586>

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Collective and molecular processes in a new class of ferroelectric liquid crystals

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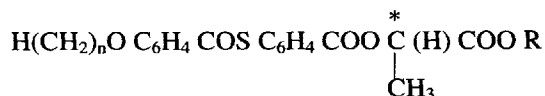
(Received 15 November 1993; accepted 5 May 1994)

Electro-optic and dielectric studies have been performed for a thioester (with a chiral chain incorporating the lactic acid ester moiety), which exhibits a monotropic room temperature ferroelectric S_C^* phase. Moreover, there are some hints that this substance also shows the recently discovered helicoidal S_A^* phase. The dielectric and electro-optic measurements have been carried out using ITO coated glass plates ($d = 10 \mu\text{m}$). Planar alignment was obtained by means of an AC electric field ($\nu = 1 \text{ Hz}$ and $V_{p-p} = 70 \text{ V}$). The tilt angle and spontaneous polarization temperature dependences show that the $S_A^* - S_C^*$ transition is of second order. Soft mode behaviour in the pretransitional region also confirms this result. The monotropic S_C^* phase exhibits a rather strong Goldstone mode (GM) with pronounced temperature dependence of the dielectric parameters. The molecular reorientation about the long axis has been found for both principal alignments. The homeotropic effective alignment was obtained by applying a magnetic field of 1.2 T to a thick sample ($c. 100 \mu\text{m}$) placed in a specially designed cell for anisotropic high frequency measurements. The reorientation about the long axis gives a broad spectrum centred at $c. 100 \text{ MHz}$. This spectrum shows minor changes at the $S_A^* - S_C^*$ transition.

1. Introduction

Ferroelectricity in liquid crystals was discovered in 1975 for the S_C^* phase of DOBAMBC [1-3] which shows rather weak ferroelectric properties. Due to some possibilities for very important display applications of ferroelectric liquid crystals (FLCs) [4], a great number of new ferroelectric liquid crystalline materials have been designed recently and investigated by different methods [5-7]. Strong ferroelectric properties have been found for substances and mixtures exhibiting S_C^* , S_A^* and S_A^* phases, which possess either liquid-like or hexatic order within the layers. Highly ordered tilted crystal smectics (G^* , J^* , H^* and K^*) show only minor ferroelectric properties [8]. As far as practical applications are concerned, many ferroelectric mixtures [9-12] have been designed showing extended room temperature ferroelectric phases.

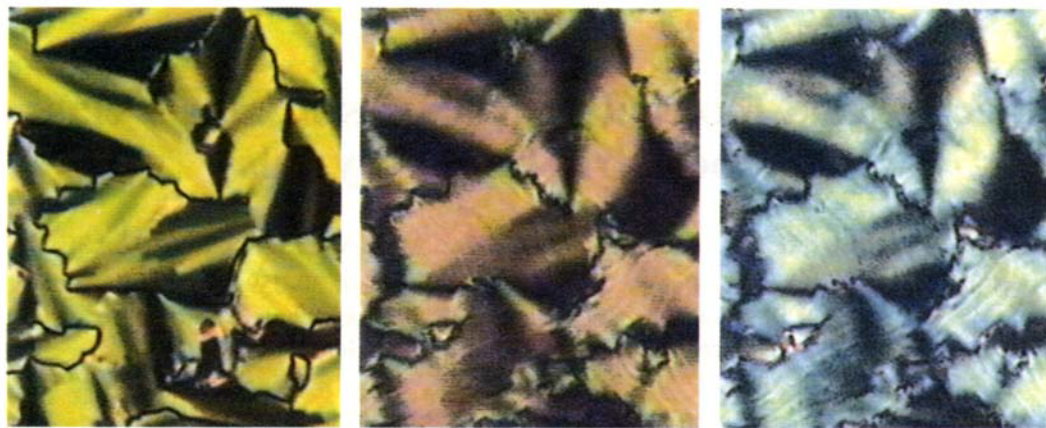
In this paper the electro-optic and dielectric properties of materials with a thioester core are discussed [13, 14]. The chemical formula for the homologous series is



Previously, the substance with $n = 12$ and $R = \text{ethyl}$ was studied [14]. This paper is devoted to another homologue of this series with $n = 11$ and $R = \text{isopropyl}$. It is known that such materials exhibit ferroelectric phases with enhanced stability in relation to their oxygen counterparts (carboxylic esters) [15 (a)]. It was also found that the terminal chiral lactate moiety gives rise to pronounced ferroelectric properties. An interesting point is that they show monotropic S_C^* phases which are stable for a few days, and so give ferroelectric properties at room temperature. Besides these phenomena, other very interesting ferroelectric and electro-optic properties are observed:

- (1) They are easily uniformly aligned by means of an AC electric field.

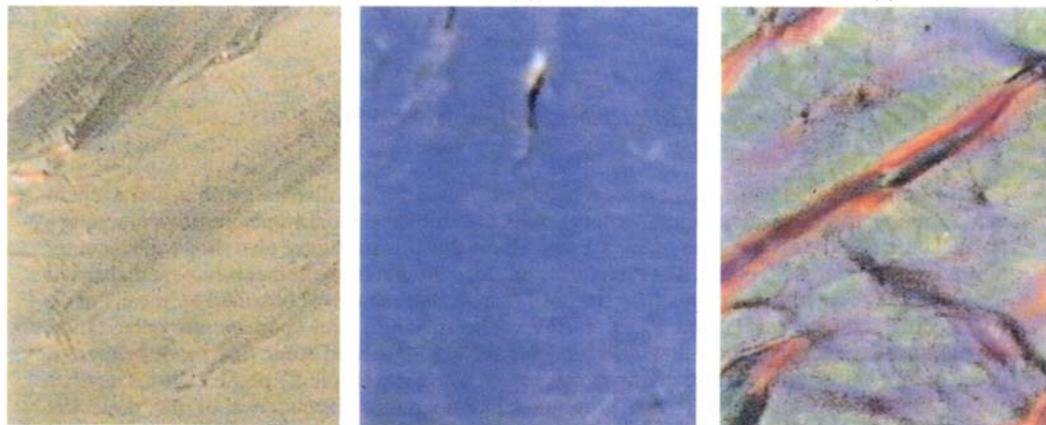
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(a)

(b)

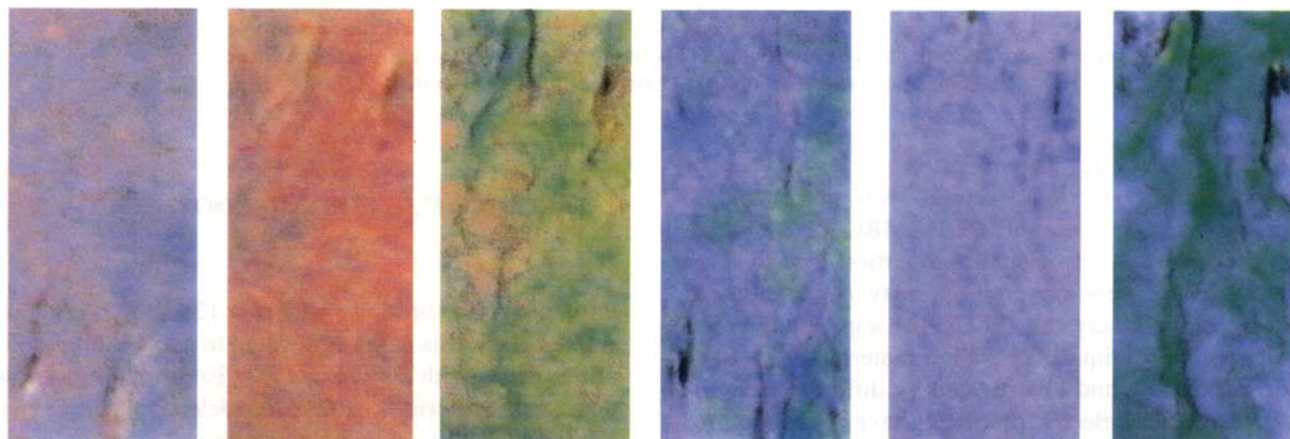
(c)



(d)

(e)

(f)



(g)



(h)

transition from the isotropic phase. (b) Appearance of dechiralization lines 2.5 K below the clearing point. (c) The application of an electric DC field ($10 \text{ V } \mu\text{m}^{-1}$) leads to a change in the colours of the focal-conics. (d) S_C^* phase oriented by means of an AC field of $70 \text{ V}_p - p 10 \mu\text{m}$. (e) Uniform texture after heating from the ferroelectric S_C^* to the S_A^* phase. (f) About 2.5 K below the clearing point, a filament texture is visible. (g) Drastic change of colour of the texture within a very narrow temperature interval. The colour changes from blue through orange, green and purple to dark green with crossed polarizers. (h) 1.5 K below the transition to the isotropic phase an applied A.C. field ($7 \text{ V } \mu\text{m}^{-1}$) influences the uniform texture. A focal-conic structure with a lot of defects becomes visible.

- (2) In the S_A^* phase they show a tendency to form the so-called 'Twist grain boundary' (TGB) deformations [16].
- (3) The spontaneous polarization is rather high ($P_s > 100 \text{ nC cm}^{-2}$).

The dielectric and to a degree the electro-optic behaviour of FLCs can be qualitatively described by the extended mean-field theory [17]. One of the fundamental assumptions of this theory is that the spontaneous polarization (P_s) is proportional to the tilt angle (θ),

$$P_s \sim \theta. \quad (1)$$

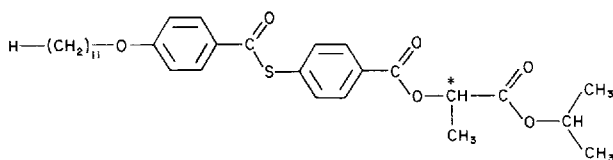
However, it has been demonstrated [5] that there is a second contribution to the spontaneous polarization of the S_C^* phase that is proportional to the third power of θ ,

$$P_t \sim \theta^3. \quad (2)$$

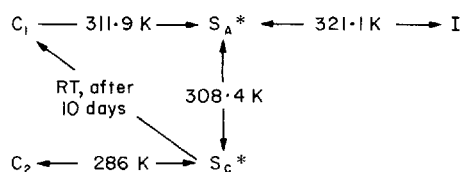
It is known that the relaxation time for the latter contribution is, for some materials, smaller than 10^{-8} s, which is remarkably shorter than the soft mode relaxation time. For the thioester core materials, the second contribution becomes of great importance.

2. Experimental

The substance investigated possesses the following chemical structure:



and it exhibits the following phase diagram:



The thermodynamic properties of the substance under investigation were determined using a polarizing microscope (Leitz orthoplan) with an attached high resolution CCD-camera (Panasonic VW-CL-500HR), a video recording system (Panasonic AG 7330) and a video printer (Sony WP-300 P).

The room temperature S_C^* phase aligns very well in AC fields. Typical textures observed for the S_A^* and S_C^* phases are shown in figure 1.

The dielectric relaxation spectra of the substance have been studied in the frequency range from 10 Hz to 1 GHz. The low frequency dielectric measurements (10 Hz–13 MHz) of the perpendicular component of the complex electric permittivity ($\epsilon_{\perp}^* = \epsilon'_{\perp} - i\epsilon''_{\perp}$) have been

carried out using ITO coated cells (EHC Company, Tokyo, thickness = $10 \mu\text{m}$) attached to the HP 4192A impedance analyser. The measurements were temperature controlled and fully automated as described elsewhere [18].

The high frequency dielectric spectra were measured in the frequency range from 1 MHz–500 MHz by means of a 4191A impedance analyser equipped with a newly designed parallel plate capacitor [19] electrically connected by the end of a coaxial waveguide.

The cell allows dielectric measurements to be made for both principal alignments up to 500 MHz. For the frequency range between 500 MHz and 1 GHz only unoriented measurements were possible. However, in the case of the thioester material, one was able to obtain planar alignment for the electro-optic studies in the same way as that used for the texture investigations. The effective homeotropic alignment was obtained by means of a magnetic field of 1.5 T.

For the electro-optic experiments, a Philips frequency generator (PM5138) and a Philips oscilloscope (PM3305) were connected to the EHC cell. The spontaneous polarization and the tilt angle of the substance under investigation were measured by the reversal current method described elsewhere [20, 21].

3. Results and discussion

3.1. Texture observations

There is a suggestion that the thioester materials show a tendency to form a TGB phase at the transition $I-S_A^*$. Upon cooling from the I phase to the S_A^* phase, a focal-conic texture (see figure 1(a)) appears with a large number of defects. On cooling, this texture changes—dechiralization lines' become visible at about 2.5 K below the clearing point (see figure 1(b)). This texture looks similar to an unoriented S_C^* phase. Applying a DC field of about 100 V_{p-p} ($\equiv 10 \text{ V } \mu\text{m}^{-1}$), the colour of the focal-conics changes from red to green (see figure 1(c)) with crossed polarizers. It should be pointed out that this phase is not a S_C^* phase, because it is not switchable even on application of field strengths higher than $10 \text{ V } \mu\text{m}^{-1}$. A further argument against the existence of a S_C^* phase at this temperature is the absence of the Goldstone mode relaxation in the dielectric spectrum. After switching off the DC field, the colour changes to red again. On further cooling this texture remains unchanged until the transition to the ferroelectric phase.

In the S_C^* phase, the sample is switchable on application of a field strength of at least $1 \text{ V } \mu\text{m}^{-1}$ and could easily be oriented by applying an AC electric field ($\nu = 1 \text{ Hz}$; $U = 70 \text{ V}_{p-p}$). In figure 1(d) we show the oriented sample 3 K below T_c .

On heating up the sample oriented in this way, a quite different texture was observed. This texture looks intensively blue with crossed polarizers (see figure 1(e)) and

reminds one of a planar oriented cholesteric texture. No response to electric fields was observed. A further increase in temperature had no influence on the texture over a broad temperature range. About 2.5 K below the clearing point, filaments become visible (see figure 1 (f)). This filament texture looks similar to the textures observed by Bouchta *et al.* [16(b)], and Patel *et al.* [16(c)]. The resulting colour of the texture in this temperature regime now changes drastically from blue through orange, green, and purple to dark green (see figure 1 (g)) with crossed polarizers. A further argument for the formation of a TGBA phase is given by the atomic force microscopic investigations made on this compound by Terris *et al.* [16(e)], where the tendency for the formation of a helicoidal S_A^* phase was noted. In order to prove whether the observed, unusual texture really is connected with the existence of a TGBA phase precise DSC and more detailed electro-optic measurements would have to be performed. This was not the objective of this contribution and will be considered in a future article.

The application of an AC electric field ($\nu = 1$ Hz; $U = 70$ V_{p-p}) now has an influence on the texture. The single-coloured texture breaks up and a defect structure with the commencement of formation of focal-conics becomes visible. This texture is shown in figure 1 (h). Without an applied electric field, the uniform texture remains unchanged until reaching the clearing point.

Upon cooling to the S_C^* phase, the planar alignment can be renewed easily leading to well-defined Clark–Lagerwall states which show up under the low frequency square wave. At room temperature, the cell remains switchable for a few days before the sample transforms into the stable solid phase (C_1).

3.2. Spontaneous polarization measurements and electro-optic studies

The spontaneous polarization and tilt angle measurements were done simultaneously on the planar oriented sample. Figure 2 shows the temperature dependence of P_s versus relative temperature. Upon approaching T_c the spontaneous polarization goes smoothly down to zero. By fitting the power law

$$P_s(T) = P_0(T_c - T)^\beta, \quad (3)$$

the following parameters have been obtained: $P_0 = (35.6 + 0.6) \text{ nC cm}^{-2}$ and $\beta = 0.43 + 0.01$. The critical exponent β is distinctly lower than the mean-field value of 0.5.

The spontaneous polarization of the thioester core substances is high (almost one order of magnitude higher than for DOBAMBC), which is mainly due to the direct coupling of the two ester groups (COO) to the chiral centre. The chiral centre in this case is also strongly

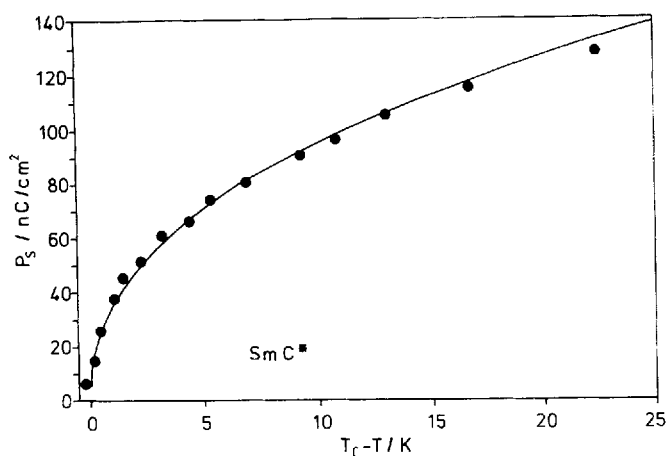


Figure 2. Spontaneous polarization versus temperature. The solid line is a power law fit (see equation (3)) with the following parameters: $P_0 = 35.6 \text{ nC cm}^{-2}$, $\beta = 0.43$.

coupled to the molecular core in which the sulphur bridge may also influence the effective perpendicular component of the permanent molecular dipole moment (μ_\perp) responsible for the spontaneous polarization at the microscopic level.

The tilt angle has been measured by applying a low frequency square wave slowly switching the aligned sample between the two Clark–Lagerwall states. Figure 3 presents the tilt angle θ_0 for different temperatures. A power-law fitted to the experimental points leads to the following fitting parameters $\theta_0(0) = 15.9^\circ$ and $\beta = 0.19$. Such a drastic disagreement with the mean-field model might be due to a temperature dependent coupling between the molecular dipole and the optically polarizable molecular core [5].

Figure 4 demonstrates that the relation between the spontaneous polarization and the tilt angle θ_0 also contains the θ_0^3 term.

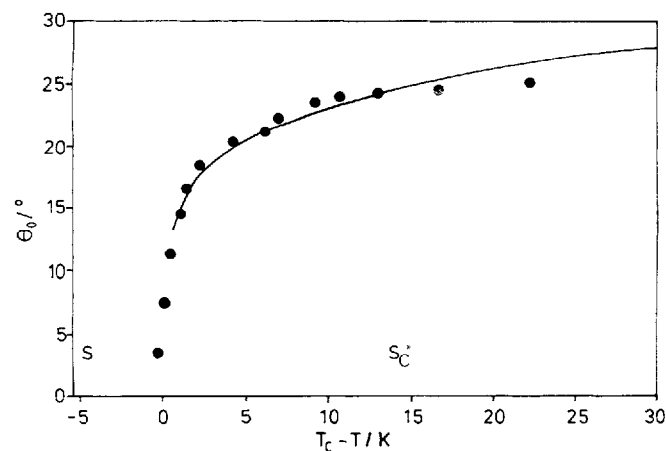


Figure 3. Tilt angle versus temperature for the S_C^* phase. The solid line is a power law fit with the fitting parameters: $\theta_0(0) = 15.9^\circ$ and $\beta = 0.17$.

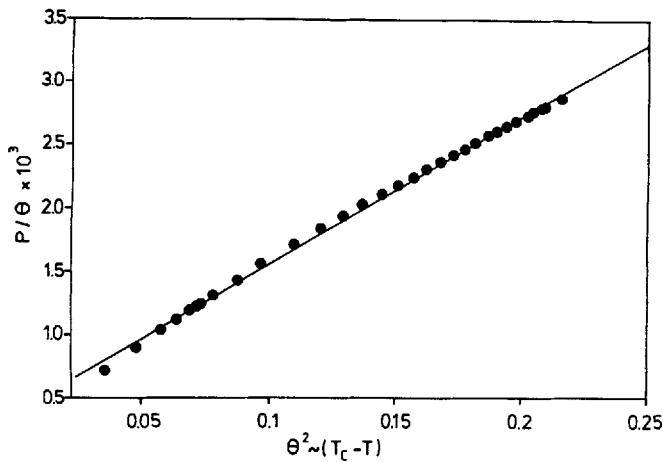


Figure 4. P_s/θ as a function of θ^2 —a test for applicability of the mean-field model. The least-square fit gives the following relation between P_s and θ : $P_s = 0.00043\theta + 0.012\theta^3$.

3.3. Dielectric spectra in a broad frequency range

The dielectric spectra of the thioester core material show a pronounced soft mode in the vicinity of the $S_A^* - S_C^*$ phase transition. The soft mode spectrum was observed up to 1.5 K below T_c and can only be measured after suppressing the Goldstone mode by means of sufficiently strong DC or magnetic field. The spectrum is very pronounced and its dielectric parameters show distinct temperature dependences. The Goldstone mode spectrum shows up at T_c and becomes very large in the S_C^* phase. Figure 5 (a), (b), (c) and (d) show representative dielectric spectra obtained for the substance studied. In particular, figure 5 (a) presents an exemplary fit of the first term of the sum of two Cole–Cole functions

$$\begin{aligned} \varepsilon_{\perp}^* &= \varepsilon_{\perp}' - i\varepsilon_{\perp}'' \\ &= \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_S}{1 + (i\omega\tau_S)^{1-\alpha_S}} + \frac{\Delta\varepsilon_G}{1 + (i\omega\tau_G)^{1-\alpha_G}} \end{aligned} \quad (4)$$

to the soft mode dielectric spectrum obtained for the S_C^* phase. In equation (4) $\Delta\varepsilon$, τ and α are, respectively, the dielectric strength, relaxation time and distribution parameter for a particular relaxation process. Indices ‘S’ and ‘G’ stand for the soft mode and Goldstone mode, respectively. $\varepsilon_{\perp\infty}$ denotes the high frequency limit of the dielectric permittivity originating from the electronic and atomic polarization and fast inter- and intra-molecular dipolar reorientations. The soft mode dielectric spectrum in the S_A^* phase is almost a single Debye-type process (see figure 5 (a)). However, the α_S parameter is not zero and this might be due either to some anisotropy of the tilt fluctuations in the pretransitional region or to overlapping of the soft mode spectrum with some molecular relaxation processes. The latter option is more probable, as on the high frequency side some points deviate from the circular

arch fit. In figure 5 (b) one can see a typical dielectric spectrum acquired in the S_C^* phase close to T_c . In this region the soft mode and Goldstone mode spectra overlap. Fitting the sum of two Cole–Cole functions (equation (4)) to the experimental points gives the possibility of obtaining separately the dielectric parameters for both the Goldstone mode and the soft mode.

It is worth noting that the Goldstone mode spectrum is broad ($\alpha_G = 0.22$) in this range, which may be due to soft mode or domain mode [22–26] contribution. Further cooling leads to a pronounced Goldstone mode spectrum (see figure 5 (c)) which is almost a pure Debye-type spectrum with $\alpha_G = 0.03$.

Below T_c one can see the soft mode dielectric relaxation spectrum only by applying a bias field of 15 V ($\equiv 1.5 \text{ V } \mu\text{m}^{-1}$) (see figure 5 (d)). The spectrum which, under the influence of the BIAS field, overlaps the soft mode is no longer a Goldstone mode. This effect, contributing to the domain mode has been discussed in several papers [22–26]. In this article we would like to point out that this mode exists for many substances exhibiting high P_s values and one has to do a careful data analysis to isolate the soft mode dielectric spectrum from the experimental spectrum below T_c . In figure 5 (d), the solid line represents a least-square fit of the equation

$$\begin{aligned} \varepsilon_{\perp}^*(\omega, E > E_C) &= \\ \varepsilon_{\perp\infty} &+ \frac{\Delta\varepsilon_S(E)}{1 + (i\omega\tau_S)^{1-\alpha_S}} + \frac{\Delta\varepsilon_D(E)}{1 + (i\omega\tau_D)^{1-\alpha_D}} \end{aligned} \quad (5)$$

to the experimental points. The new term in equation (5) corresponds to the so-called domain mode relaxation, which overlaps the soft mode spectrum below T_c . At lower temperatures in the S_C^* phase, a pure domain mode dielectric spectrum shows up after suppressing the Goldstone mode. The intensity of the domain mode for this substance is rather weak compared to our previous results [22–26].

Using the fitting procedures presented above, it was possible to find the dielectric parameters of the soft mode and Goldstone mode as functions of temperature. Figures 6 (a) and (b) present, respectively, the relaxation frequencies and the inverses of the dielectric increments for these two collective modes versus temperature. The characteristic ‘V’ shape of the soft mode behaviour in the vicinity of the $S_A^* - S_C^*$ transition is clearly seen. However, the ratios of the slopes of the straight line fits are equal to -0.33 for the relaxation frequency and -1.17 for the inverse of the dielectric strength. Both these values differ very much from the mean-field value (-2.0). This may be caused by strong positive dipole–dipole correlations within the smectic layers.

It is worth noting here that for one of the ferroelectric mixtures [12], a fairly good agreement with the extended

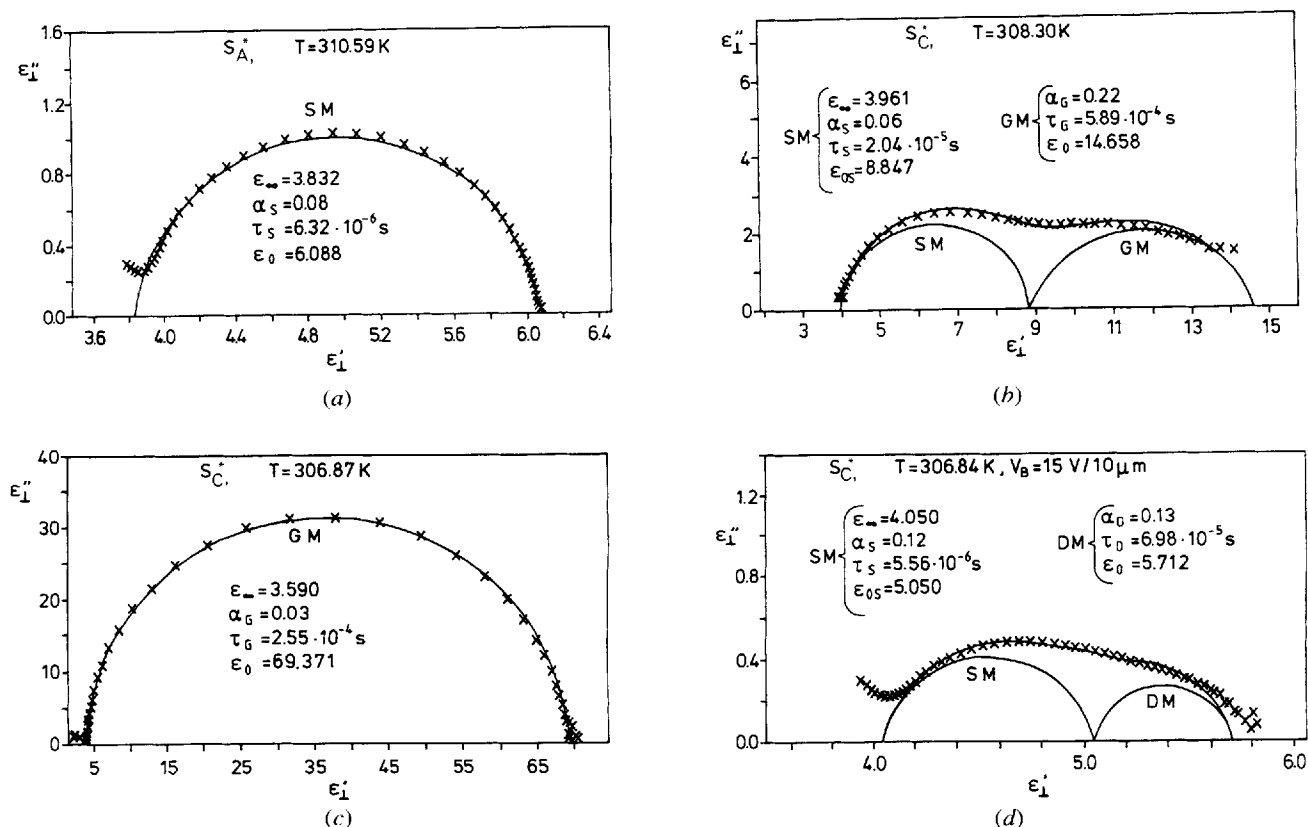


Figure 5. Low frequency dielectric spectra in the vicinity of the $S_A^*-S_C^*$ transition and in the S_C^* phase. (a) Soft mode (SM) dielectric relaxation spectrum in the S_A^* phase. This solid line represents the least-square fit of the first term of equation (4) to the experimental data. (b) Merged soft mode (SM) and Goldstone mode (GM) dielectric relaxation spectrum at the transition $S_A^*-S_C^*$. The solid line is a least-square fit of experimental points. The two semicircles represent the soft mode (SM) and the Goldstone mode (GM) contributions (see equation (4)) and they result from the fitting procedure. (c) Pure Goldstone mode (GM) spectrum obtained below T_c . The solid line is a least-square fit of the second term of equation (4) to the experimental points. (d) Soft mode (SM) and domain mode (DM) dielectric relaxation spectrum in the S_C^* phase after suppression of the Goldstone mode (GM) by means of an applied BIAS field of 15 V.

mean-field model has been obtained. Thus a smaller concentration of dipoles may favour a model behaviour. The relaxation strengths, as well as the critical frequencies of the Goldstone mode and the soft mode relaxation, are in good agreement with the values obtained for a homologous thioester reported earlier [14]. Using the electro-optic and dielectric parameters, the rotational viscosity γ_ϕ has been calculated for different temperatures (see figure 7) for the substance under discussion. For this purpose the following formula was used [27]:

$$\gamma_\phi = \frac{\tau_G}{2\epsilon_0\Delta\epsilon_G} \left(\frac{P_S}{\theta_0} \right)^2 \quad (6)$$

where ϵ_0 is the electric permittivity of free space. There are some divergences in the Arrhenius plot of γ_ϕ in the pretransitional regions, but in the S_C^* phase, it obeys the Arrhenius behaviour and the least-square fit gives an activation energy of $(91 \pm 4) \text{ kJ mol}^{-1}$. The values of γ_ϕ ,

as well as the activation energies, agree quite well with the respective values found earlier for other single component systems [28, 29] and with the results obtained for the homologous substance [14]. Of course, γ_ϕ is high for pure thioester core materials and it is almost two orders of magnitude higher than the value found for one of the ferroelectric mixtures [12].

The dielectric spectra measured for the planar alignment in the high frequency range are very broad with a distribution parameter of 0.3–0.4. There is no distinguishable change in the spectrum at the $S_A^*-S_C^*$ transition. Figure 8 shows an average critical frequency versus temperature for the high frequency molecular modes. In the S_C^* phase, the activation energy for the high frequency process is 10 per cent higher (55 kJ mol^{-1}) than the value found for the S_A^* phase (49 kJ mol^{-1}). This difference in the activation energies in the S_C^* and in the S_A^* phase is not so pronounced as that observed for the previously investigated thioester [14].

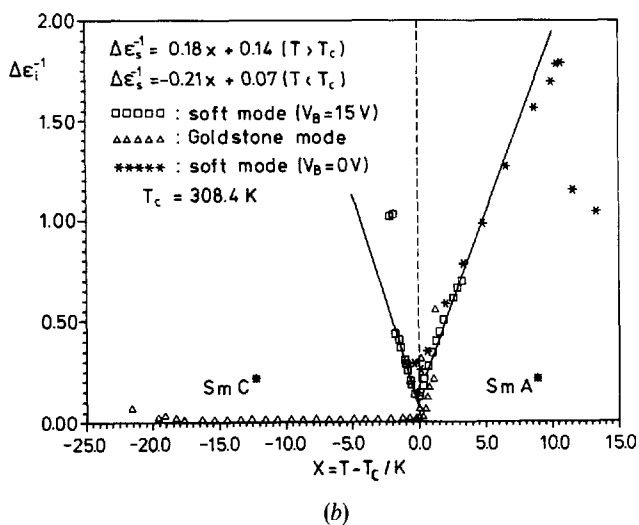
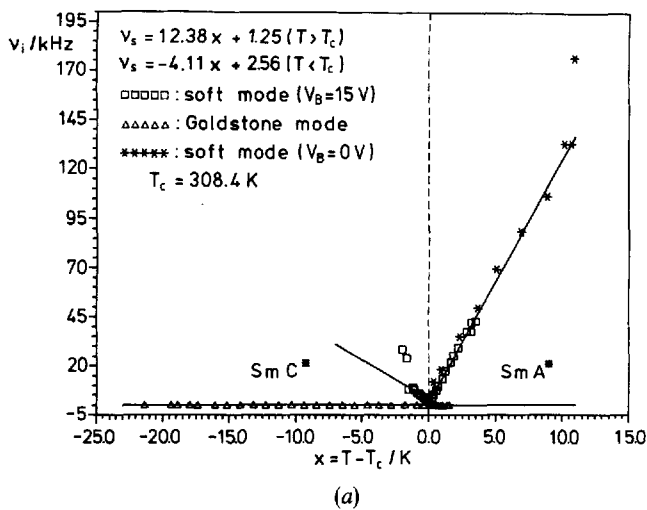


Figure 6. (a) Curie-Weiss plot for the relaxation frequency of the soft mode (SM). Goldstone mode (GM) frequencies are also included. (b) Curie-Weiss plot for the inverses of the dielectric increments.

For one temperature below T_c , a least-square fit of two Cole-Cole functions has been made

$$\begin{aligned} \varepsilon_{\perp}^* &= \varepsilon_{\perp}' - i\varepsilon_{\perp}'' \\ &= \varepsilon_{\perp\infty} + \frac{\Delta\varepsilon_C}{1 + (i\omega\tau_C)^{1-\alpha_C}} + \frac{\Delta\varepsilon_M}{1 + (i\omega\tau_M)^{1-\alpha_M}} \quad (7) \end{aligned}$$

where indices 'C' and 'M' designate the collective and molecular processes. $\varepsilon_{\perp\infty}$ is, for this case, influenced only by electronic and atomic polarizations and should agree to 5 per cent with the n_0^2 value for such materials. It was one of the boundary conditions for our fit. The following fitting parameters have been obtained:

$$\begin{aligned} \Delta\varepsilon_C &= 1.0546, \quad \tau_C = 8.91 \times 10^{-9} \text{ s } (\nu_C = 17.9 \text{ MHz}), \\ \alpha_C &= 0.15; \end{aligned}$$

$$\begin{aligned} \Delta\varepsilon_M &= 0.93, \quad \tau_M = 1.32 \times 10^{-8} \text{ s } (\nu_M = 120.2 \text{ MHz}), \\ \alpha_M &= 0.1. \end{aligned}$$

One may try to make a further analysis of the spectrum, as the two relaxation regions obtained are not single processes. Such a procedure is not adequately substantiated and does not ensure a unique solution. However, such a breakdown has been made for another single component material [30].

A recent careful high frequency study on a low mass FLC material [19] and its racemic mixture, as well as on a side chain polymeric system containing the same mesogenic chiral groups [31], shows that the molecular dynamic parameters do not change distinctly at the $S_A^* - S_C^*$ transitions in all three cases.

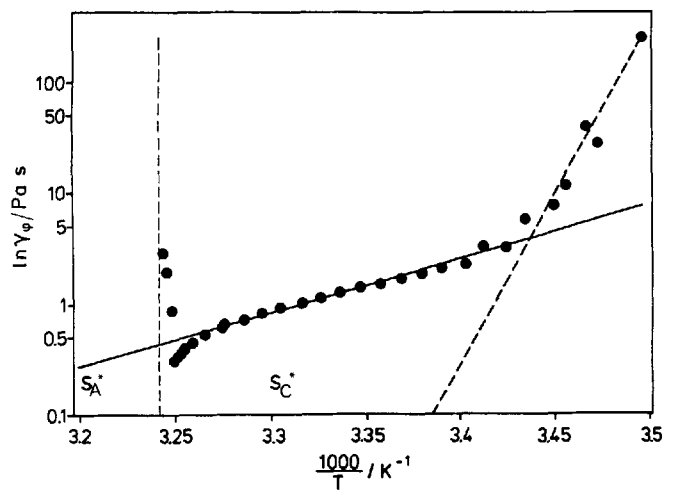


Figure 7. Temperature dependence of the rotational viscosity, γ_{ϕ} .

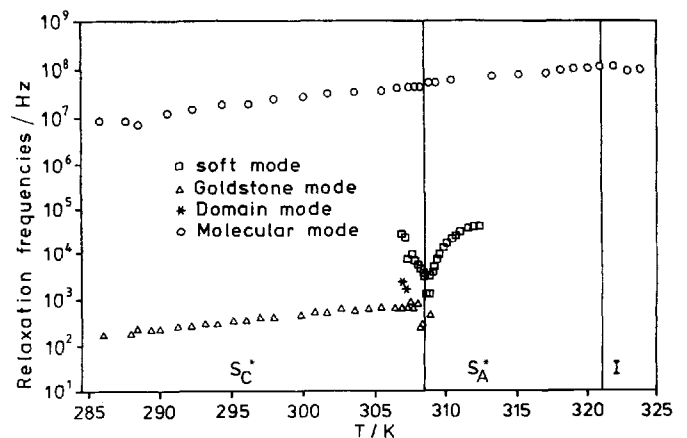


Figure 8. Relaxation frequencies acquired for the collective (Goldstone mode (GM), soft mode (SM) and domain mode (DM)) and molecular processes in the planar aligned S_C^* and S_A^* phases.

The high frequency dielectric spectrum is influenced by a few collective and molecular processes:

- (1) the reorientation of molecules about their long axes;
- (2) some intramolecular out-of-phase fluctuations of θ which according to the extended mean-field model, applied to the dynamics of the S_C^* phase, should give some contribution to the dielectric spectrum in a broad frequency range from 1 MHz to 1 GHz.

Following the arguments used in the discussion of the high frequency dielectric results for ZLI3654 mixture [32], one can only say that the broad, high frequency spectrum cannot be split uniquely to receive all relaxation times and dielectric increments for different modes.

A detailed analysis of molecular dynamics in FLCs, in relation to the composed high frequency dielectric spectrum, can be made by applying different experimental techniques to study various intra- and inter-molecular, as well as collective processes [33]; NMR, NQR, dielectric relaxation, analysis of the Poley absorption band, QNS and other methods may be helpful in order to answer some of these questions.

4. Conclusions

- (i) The tilt angle and spontaneous polarization measurements show that the $S_C^*-S_A^*$ transition is of second order. The critical exponent for the P_s temperature dependence is: $\beta = 0.43$, which is in fairly good agreement with the mean-field value of 0.5. On the other hand the tilt angle varies with T according to the power law, with $\beta = 0.19$.
- (ii) The thioester core material exhibits an unusually strong contribution to P_s coming from the θ^3 term. It was found that the relation between P_s and θ is: $P_s = 4.26E - 4\theta + 1.17E - 2\theta^3$.
- (iii) The dielectric spectra of the substance studied show the existence of the soft mode strongly in the vicinity of the $S_A^*-S_C^*$ transition. The soft mode dielectric parameters do not obey the extended mean-field model. The ratio of the slopes of the straight lines describing the temperature dependences of the inverse of the soft mode dielectric increment is equal to -1.17 . The corresponding value for the relaxation frequencies amounts to -0.33 . Both values differ distinctly from the mean field value (-2).
- (iv) The Goldstone mode dielectric relaxation spectrum is influenced by the soft mode close to T_c , but far away from the transition it becomes a single Debye-type process. However, its dielectric parameters behave critically upon approaching the glassy state.

- (v) The rotational viscosity γ_ϕ shows an Arrhenius behaviour in the S_C^* phase, with an activation energy of 91.3 kJ mol^{-1} .
- (vi) In the planar oriented S_C^* phase, the following distinguishable relaxation processes were observed:
 - (1) the Goldstone mode ($\nu_G \sim 500 \text{ Hz}$);
 - (2) the Domain mode with $\nu_D \sim 30 \text{ kHz}$;
 - (3) the soft mode coming from in-phase fluctuations of the tilt angle in the vicinity of the $S_C^*-S_A^*$ transition ($\nu_S \sim 10^4\text{--}10^5 \text{ Hz}$);
 - (4) the molecular mode originating from the reorientation around the long axis ($\nu_M \sim 10^7 \text{ Hz}$).

One should stress that the last process exhibits a distribution of the relaxation times. This means that it consists of at least two different intramolecular processes—of the Boulder Model [15] which proposes that there might be some intramolecular contribution.

The DFG is gratefully acknowledge for the grant support. One of us (S.W.) acknowledges personal support via the German–Polish research project (X087.8–I) and two of us (M.M. and S.W.) are indebted to the KBN for financial support under grant No. 20082911. We would like to thank L. A. Beresnev for discussions.

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