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## Liquid Crystals

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## Electrooptic properties of the ferroelectric smectic C phase induced by chiral dopants in HOBA and OOBA

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A ferroelectric smectic C state was induced in 4-*n*-octyloxybenzoic acid (OOBA) and 4-*n*-heptyloxybenzoic acid (HOBA) by the chiral dopants-cholesteryl benzoate (CB) and DOBAMBC—M<sub>1</sub> and M<sub>2</sub> mixtures respectively. A strong electrooptic effect was found for a DC electric field in the ferroelectric state of the M<sub>1</sub> mixture stabilized by the boundaries. This effect is characterised by six increasing electric field thresholds ( $E_{th}^{(1)}-E_{th}^{(6)}$ ), where drastic textural and colour changes occur. The electrooptic responses in AC electric field for the two mixtures are discussed. A qualitative model to explain the observed phenomenon is presented.

### 1. Introduction

Achiral tilted smectic C phases are not ferroelectrics because of the centre of symmetry existing in these materials [1]. However, the properties of these liquid crystals mixed with optical active dopants are of peculiar interest. The achiral smectic C phases in such binary mixtures serve as a matrix, where parallel molecular dipole orientation of the dissolved chiral molecules is created. A result of this parallel orientation can be the appearance of spontaneous polarization  $\mathbf{p}$  and ferroelectric state induction [2]. One important requirement for this effect is hindered rotation along the whole molecular length of the dopant in the smectic matrix. The hindered rotation provokes partial short molecular axis orientation. The most effective in this respect are the chiral dopants with dipole moments perpendicular to the long molecular axis. As a result the spontaneous polarization is perpendicular to the tilt angle plane (between the normal ( $\mathbf{N}$ ) to the smectic layer and the molecular director  $\mathbf{n}$ ) and lies in the layer-plane [3]. This is a fundamental property in the nature of ferroelectric smectic C phases.

The fastest method for the ferroelectric state identification is the analysis of the optical textural. This analysis is based on the fact that minimization of the free energy of the bulk ferroelectric sample is characterized by a helicoidal structure (spontaneous twist) where  $\mathbf{n}$ , and  $\mathbf{P}$ , precesses from one smectic layer to another around the layer normal  $\mathbf{N}$  and so describes a spiral. At definite boundary conditions (smectic layers normal to the orienting substrates) this spiral can be identified by a regular stripe texture [4]. The helicoidal structure compensates the macroscopic polarization in the bulk at comparatively thick samples. For stimulation of a non-zero volume polarization in the smectic C\* phase, different external excitations were applied as for example an electric field [1, 4], and mechanical layer shearing [5], where the helicoidal structure can be destroyed under control.

The initial electrooptic S\* investigations [4, 6] were related mainly to destroying the helicoidal structure and the stabilization of the ferroelectric state by the electric

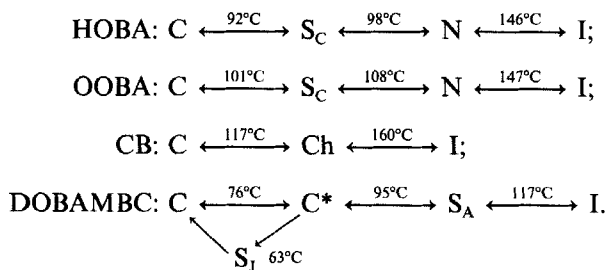
field. In recent years the electrooptic and optic investigations involved very thin cells where the boundary forces destroy the helicoidal structure and the ferroelectric  $S_C^*$  state is stabilized, namely the surface stabilized ferroelectric liquid crystal method [7, 8]. Since the pitch  $P_0$  of the pure ferroelectric smectic C is small (for DOBAMBC  $P_0 \approx 1.5 \mu\text{m}$  [4]), very thin cells might be used (a few microns) to realize this which creates significant technological difficulties. An important advantage of the ferroelectric smectic C state induced in mixtures is that the helix pitch is larger and so the surface stabilised method can be applied for relatively thick cells as well.

A requirement for the ferroelectric smectic C materials, besides the low electrooptic response threshold, is fast switching of the system by the electric field. From recent optic and electrooptic investigations of the achiral smectic C phase [9, 10] we can conclude that some 4-*n*-alkyloxybenzoic acids are suitable as a matrix in which to induce a ferroelectric  $C^*$  because the tilt angle ( $\omega$ ) is comparatively large  $\approx 45^\circ$  (n.b. the spontaneous polarization is proportional to this angle {1}) in this system and is independent of the temperature. Besides, the switching processes of the smectic C phase of these substances are relatively fast in AC and DC electric field (the decay time is 3–5 ms [9]).

The purpose of the present work is to investigate the optic and electrooptic properties of the ferroelectric state induced by a chiral dopant in the smectic C phase of the 7th and 8th homologues of the 4-*n*-alkyloxybenzoic acids—namely HOBA and OOBA, respectively.

## 2. Experimental results

Cholesteryl benzoate (CB) and the classic ferroelectric  $S_C$  DOBAMBC were used as chiral dopants. The transition temperatures of the substances used are:



We have found that CB is an effective dopant to induce a ferroelectric smectic  $C^*$  state in OOBA. It possesses a significant dipole moment  $\mu \approx 2.4 \text{ D}$  perpendicular to the long molecular axis {11}. The chiral dopant concentration in the binary mixtures used was chosen in such a way that the smectic  $C^*$  phase occurred in a temperature interval suitable for investigation. For the mixture of DOBAMBC with HOBA the smectic  $C^*$  and cholesteric (Ch) phases occurred at all concentrations. In the mixtures of OOBA with CB  $S_C^*$  and Ch phases were found for concentrations 2–5.5 wt %. Below 2 wt %, weakly stripped smectic  $C^*$  and Ch phases were observed while above 5.5 wt % of CB, the mixture displayed only a cholesteric phase.

The planar orientation of the sample was achieved by treatment of the substrates with ITO and rubbing in a uniform direction. The liquid crystal cell thickness was fixed by Mylar spacers. The optical textures were investigated with a polarizing microscope.

### 2.1. Experimental investigations of the mixture of OOBA and CB mixture $M$

We have observed different textures in the smectic phase of the binary mixtures at different CB concentrations and electric field strengths. We have found the 3.5 wt % CB concentration to be the most effective in inducing the  $S_C^*$  state. The ferroelectric smectic C phase forms for this concentration on cooling the planar oriented  $30\ \mu\text{m}$  thick sample at  $97^\circ\text{C}$ . The transition  $S_C^*$ -Ch is weak and occurs through battonnets forming an angle approximately  $\pi/4$  with the rubbing direction, see figure 1. The stripped confocal texture typical for the  $S_C^*$  phase, see figure 2, appears on coalescing the battonnets. At  $96^\circ\text{C}$  the helix pitch is approximately  $14\ \mu\text{m}$ . At  $92^\circ\text{C}$  we have observed a transition to a new phase. The texture of this phase is stripped similarly to that of the preceding  $S_C^*$  phase and probably it is a low-temperature ferroelectric smectic. On the basis of the textural analysis, using the notations in [12, 13, 14], we conclude that this phase may be a smectic  $I^*$ . At  $53^\circ\text{C}$  the system forms a stable solid phase.

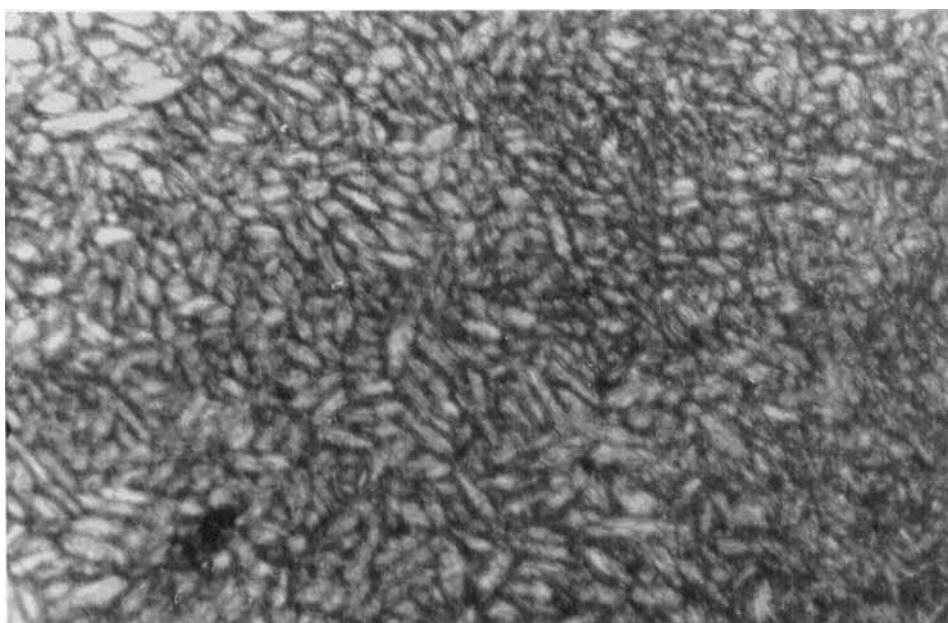


Figure 1. The battonnets at the smectic  $C^*$ -cholesteric transition ( $T_{S_C^*,Ch} = 97^\circ\text{C}$ ) of mixture  $M_1$  (OOBA and 3.5 wt % CB). Magnification  $125\times$ .

A ferroelectric smectic C evidenced by single local monocrystals, see figure 3, forms on cooling in the presence of a high frequency electric field ( $E = 6.8 \times 10^4\ \text{V/cm}$ ,  $\nu = 60\ \text{kHz}$ ). We have succeeded in obtaining comparatively large local  $S_C^*$  monocrystals when the smectic  $I^*$  phase passes to the smectic  $C^*$  phase in the presence of the electric field ( $E = 9 \times 10^4\ \text{V/cm}$ ,  $\nu = 60\ \text{kHz}$ ). The local monocrystals so formed remain after the removal of the field.

The critical field  $E_c$  for unwinding the  $C^*$  helix into a cell of  $30\ \mu\text{m}$  thickness depends on the frequency. For low frequencies in the interval 0–700 Hz its value is constant and is approximately  $0.33 \times 10^4\ \text{V/cm}$ . This value increases several times (up to  $1.6 \times 10^4\ \text{V/cm}$ ) at 700 Hz and reaches saturation. The frequency of 700 Hz can be accepted as a critical frequency.

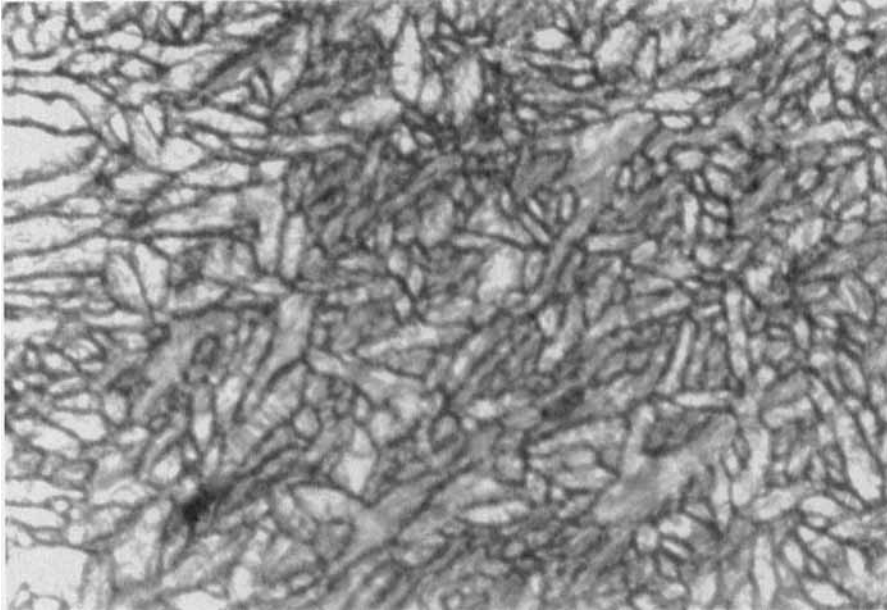


Figure 2. The stripped ferroelectric smectic C\* confocal texture at  $T = 95^{\circ}\text{C}$  of the  $M_1$  mixture. Magnification  $\times 125$ .

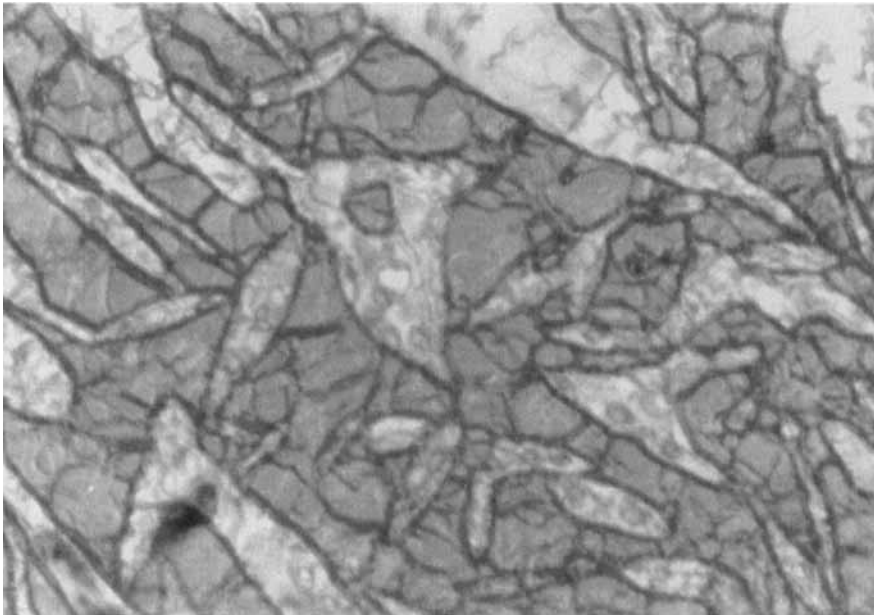


Figure 3. The ferroelectric smectic C local single monocrystals formed on cooling the sample in the presence of an electric field ( $E = 6.8 \times 10^4 \text{ V/cm}$ ,  $\nu = 60 \text{ kHz}$ ). Magnification  $125\times$ .

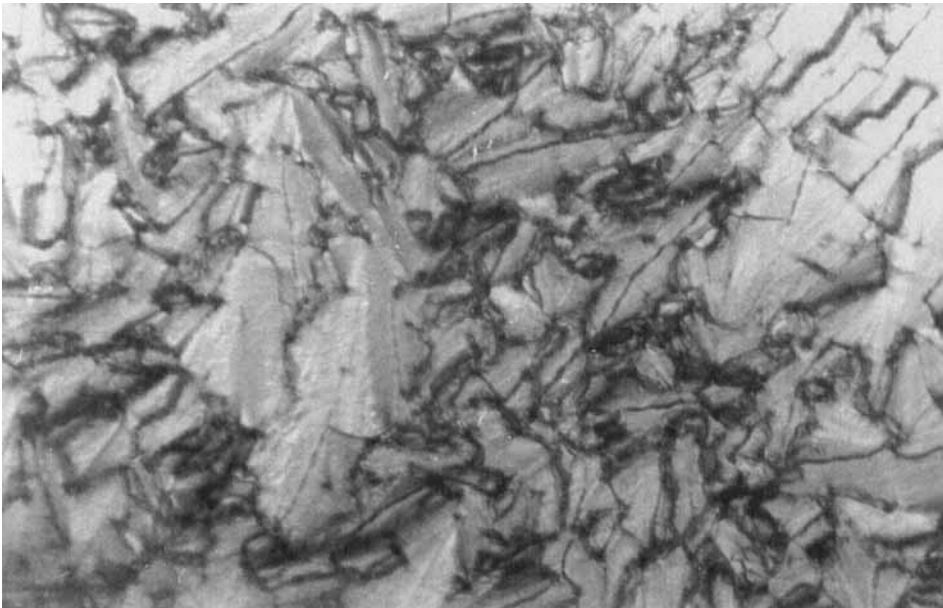


Figure 4. Unwound by the orienting surface the ferroelectric smectic C texture ( $d = 20 \mu\text{m}$ ); mixture  $M_1$ . Magnification  $125 \times$ .

The unwinding action of the orienting surfaces starts at cell thickness  $d \leq 20 \mu\text{m}$  and is accompanied by the formation of colour in the local monocrystals without stripes, see figure 4. By applying a DC electric field normal to the orienting substrates, for  $d = 20 \mu\text{m}$ , we have found a few threshold values at which the local monocrystal texture changes colour with a jump under the crossed polarizers. At the threshold value  $E_{\text{th}}^{(1)}$  of  $0.44 \times 10^3 \text{ V/cm}$ , the texture changes colour drastically from green to red. At the second threshold  $E_{\text{th}}^{(2)} = 1.2 \times 10^3 \text{ V/cm}$  the texture changes from red to green. Increasing the electric field further we can reach the threshold value  $E_{\text{th}}^{(6)} = 8.5 \times 10^3 \text{ V/cm}$  where the texture is yellow in  $P \perp A$  by a cascade of drastic transitions accompanied by a colour change of the texture from red to green and vice versa at  $E_{\text{th}}^{(3)} = 2.2 \times 10^3 \text{ V/cm}$ ,  $E_{\text{th}}^{(4)} = 3.25 \times 10^3 \text{ V/cm}$ ,  $E_{\text{th}}^{(5)} = 4.25 \times 10^3 \text{ V/cm}$ . For  $E > E_{\text{th}}^{(6)}$  the texture does not change colour. As we can see from the data, the threshold value  $E_{\text{th}}^{(6)}$  is approximately two times higher than the  $E_{\text{th}}^{(5)}$  value. In addition, at each higher threshold in the interval  $(E_{\text{th}}^{(1)} - E_{\text{th}}^{(5)})$  the electric field value increases by approximately  $1 \times 10^3 \text{ V/cm}$ .

The threshold of the AC electric action on the system is shown also by a drastic change in the colour of the local monocrystal. The frequency dependence of the threshold is shown in figure 5. As we can see from the figure, the threshold value between 20 Hz and 20 kHz is  $1.3 \times 10^3 \text{ V/cm}$  and does not depend on the frequency;  $E_{\text{th}}$  increases 2–3 times above 20 kHz. Increasing the AC electric field to  $E > 1.37 \times 10^4 \text{ V/cm}$  at constant frequency between 20 Hz and 20 kHz, we have observed a periodical swinging of the texture. The smectic I\* phase is also excited by an AC electric field, as the threshold values found from a drastic colour change of the texture increase with the frequency, shown in figure 6, indicate.

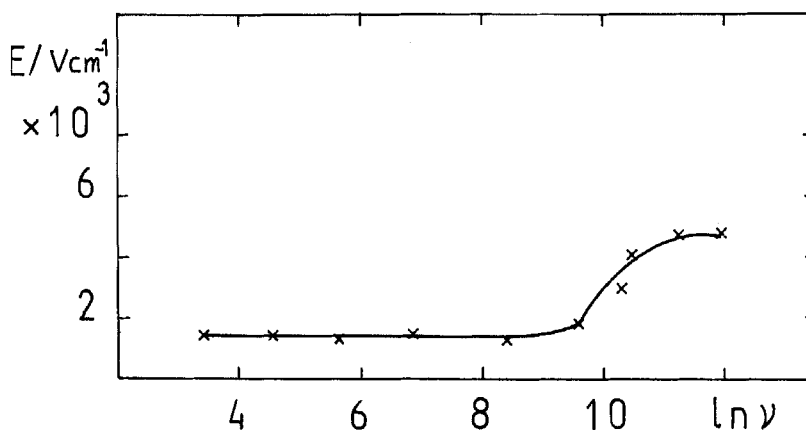


Figure 5. The frequency dependence of the field threshold for the electro-optic response of the ferroelectric smectic C\* state, unwound by the orienting surface in M<sub>1</sub> mixture.

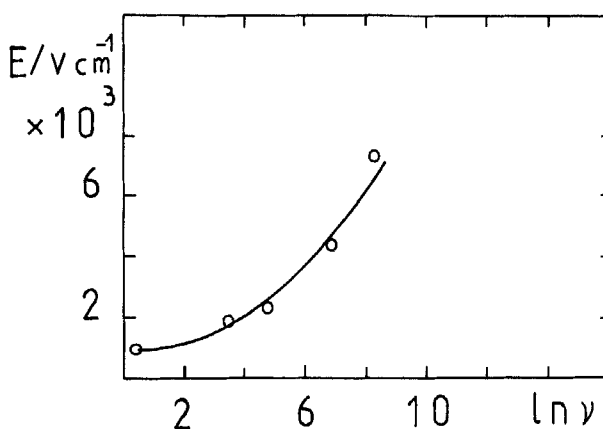


Figure 6. The frequency dependence of the threshold field for electrooptic response of the S<sub>1</sub>\* state.

## 2.2. Experimental investigations of the mixture of HOBA and the ferroelectric liquid crystal DOBAMBC-mixture M<sub>2</sub>

The induced ferroelectric C\* state evidenced by the stripped texture for the M<sub>2</sub> mixture (15 wt % DOBAMBC) in a 30 μm thick non-oriented sample is shown in figure 7.

The transition from cholesteric to smectic C\* in a planar oriented sample occurs through strongly coloured battonets with long axes making an angle of approximately  $\pi/4$  with the rubbing direction. Close to the transition temperature (96°C) the battonets coalesce together. The smectic C\* texture formed without an electric field or in the presence of an electric field below the threshold for the helix unwinding is characterized by confocals. This confocal C\* texture is strongly coloured and stripped. On cooling in the presence of a strong electric field, smectic C\* coloured local monocystals form.

For the confocal stripped texture in the samples with thickness of 30 μm we have found a critical AC electric field to unwind the helix of  $0.83 \times 10^4$  V/cm. This value

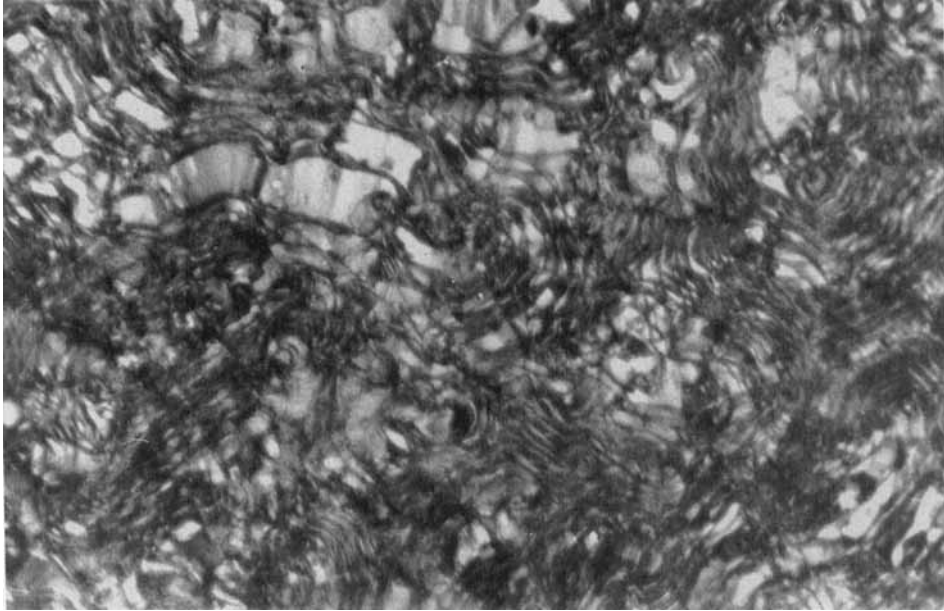


Figure 7. The induced ferroelectric smectic  $C^*$  state evidenced by the stripped texture for a  $30\ \mu\text{m}$  unoriented sample in the  $M_2$  mixture (HOBA and 15 wt % DOBAMBC). Magnification  $125\times$ .



Figure 8. The striped ferroelectric smectic  $C^*$  confocal texture ( $3^\circ\text{C}$  below the  $S_C^*$ -Ch transition— $90^\circ\text{C}$ ) in the planar oriented  $M_1$  mixture at  $E = 0$ . Magnification  $125\times$ .



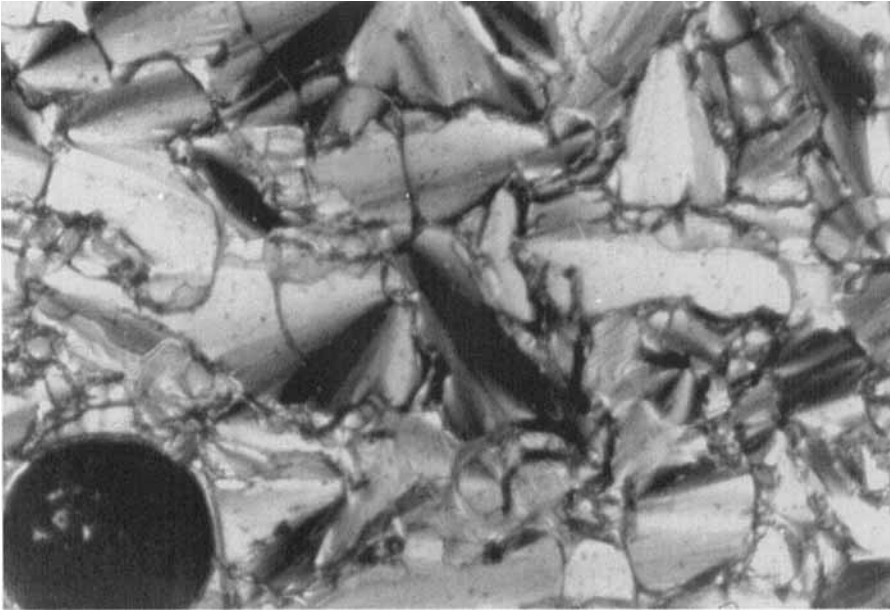


Figure 9. The smectic A-like confocal texture obtained after unwinding the helix and with  $E = 6.8 \times 10^4$  V/cm in a planar oriented  $M_1$  mixture. Magnification  $125 \times$ .

is independent of the frequency in the interval 0–550 Hz. For  $\nu > 550$  Hz, the critical electric field increases to  $4.16 \times 10^4$  V/cm and remains constant on further increasing the frequency. Decreasing the AC electric field, at  $\nu > 550$  Hz, down to  $3.4 \times 10^4$  V/cm, the stripped texture reappears. This hysteresis in the stripped texture is typical for smectic C\* [4].

We fixed the temperature at  $93^\circ\text{C}$  ( $3^\circ\text{C}$  below the  $S_C^* \text{--Ch}$  phase transition) and observed a stripped ferroelectric C\* confocal texture as indicated in figure 8. Increasing the electric field at  $\nu = 60$  kHz, smoothly after the helix has been unwound we found that the colouring of the confocals is conserved to  $6.8 \times 10^4$  V/cm. Above this electric field, the colouring disappears quickly and smectic A-like confocals form, see figure 9.

We observed a pronounced electro-optic response, resembling a Fredericks transition, in the coloured confocals below  $6.8 \times 10^4$  V/cm. Upon increasing the electric field further to  $8 \times 10^4$  V/cm, the battonets, typical for the  $S_A \text{--N}$  transition, appear and finally a homogeneous and very black nematic is established in  $P \perp A$ . The coloured confocal texture reappears upon smoothly decreasing the electric field to  $4.4 \times 10^4$  V/cm. Consequently, we have induced a phase transition  $S_C^* \text{--N}$  through  $S_C$  and  $S_A$  phases by means of the electric field.

### 3. Discussion

Ferroelectric smectic C\* phases like the achiral smectic C phases are the only liquid crystals which allow rotation of the director about the surface normal of the orienting substrates in the homogeneous regime. As demonstrated in [15], in order to obtain bistable or multistable states in this system, boundary conditions are required which constrain the director from being parallel to the plates but allowing several or

continuous orientations about the normal to the plates. As a result, the director at the surfaces can be switched between stable surface orientation states by external forces.

The formation of large single local monocrystals in a smectic  $C^*$  phase, similar to the formation of local monocrystals in achiral smectic  $C$  phases, is a major problem and its solution is very important for practical applications. In these liquid crystal systems the orientation, in a uniform manner, over the entire area of the active liquid crystal cell depends strongly on the coordination of the layer and the director orientations. To achieve a uniform layer orientation, a combination of anisotropic surface treatment (rubbing), cell thickness, cooling rate and external field (electric or magnetic) is required. By this combination we have obtained normal single local monocrystals in the induced  $S_C^*$  phase for electrooptic investigations. The single local  $S_C^*$  monocrystals were formed better in  $M_1$  mixture under these conditions. Circular cone boundary conditions [15] are admissible in the surface stabilised case at non-ideal planar orientation. Under these conditions the director close to the orienting substrates is constrained to lie on a cone coaxial with the surface normal. The director also prefers to lie on the layer cone coaxial with the layer normal. Simultaneous application of these two constraints determines different possibilities for realizing distinctly allowed orientations of the director.

As is known [1, 4], smectic  $C^*$  formation indicated by stripes usually occurs below the  $S_A$  phase with layers disposed normally or slightly tilted [6] towards the substrates and, as a result, only the director inclines. Smectic  $C^*$  formation, however, is more peculiar [17] after a cholesteric phase. The transition from a planar cholesteric to a planar  $S_C^*$  structure without an electric field is obviously connected with the conservation, of the director position but with the transformation of the direction of the spontaneous twist axis from normal to parallel to the orienting substrates. Our experiment demonstrates that the transition of the cholesteric phase into the smectic  $C^*$  performed by generation of battonets, making an angle of approximately  $\pm \pi/4$  with the rubbing direction. The battonets further develop in focal cone domains. However, on cooling in the presence of a strong electric field (higher than the threshold for helix unwinding), we always obtain local single monocrystals. Usually these local monocrystals are elongated. The axis of the elongation direction makes an angle of  $\pm \pi/4$  with the rubbing direction. The angle  $\pi/4$  coincides with that of the tilt angle of the hosts HOBA and OOBBA [18]. As demonstrated in [14, 18], in the local single monocrystals formed below initially planar oriented nematic (or in our case below planar oriented induced cholesteric), the layer planes are vertical and oriented at  $\pm \pi/4$  to the rubbing direction. So far, as we know the local single monocrystals preferably form in smectic  $C$ , and  $C^*$  with a temperature independent tilt angle. So the mutual perpendicular connection between the helix axes in the cholesteric and smectic  $C^*$  phases is not essential on  $S_C^*$  phase formation with an electric field since local single monocrystals with vertical or slightly tilted layers are formed. The sizes, however, of the focal conic domains formed with an electric field depends on the pitch of the cholesteric helix. Recently [17], a method has been demonstrated to obtain planar boundary conditions and smectic  $C^*$  monodomains on cooling a previously oriented thin ( $8 \mu\text{m}$ ) cholesteric sample by means of a rubbed polymer surface. The authors were able to suppress one of the possible layer orientations at an angle of  $\pm \pi/4$  with the rubbing direction. For correctness, in order to use our method for sample preparation, we constrain our interpretation to local single monocrystals.

Let us discuss the electrooptic behaviour of the ferroelectric structure in the two mixtures. We consider two fundamental electrooptic responses: (i) helix structure

unwinding in comparatively thick samples and (ii) electrooptic switching processes in ferroelectric C\* state stabilized by the boundary conditions [7, 8]. First we consider the electrooptic response concerning the helix unwinding by the electric field. As demonstrated in the Experimental section, the critical frequencies, after which the helix unwinding fields increase quickly (5–6 times), are 700 Hz and 550 Hz for M<sub>1</sub> and M<sub>2</sub> mixture, respectively. It is reasonable to accept, [19], that below this critical value ( $\nu_c$ ) a linear coupling between the director and the electric field is the basis of the electrooptic response. Above the critical frequency another mechanism for the electro-optical response is included namely the dielectric coupling of the director and the field which is quadratic in E. Consequently, the linear coupling of  $\mathbf{n}$  and  $\mathbf{E}$  disappears above  $\nu_c$ , since the director rotation around the layer normal cannot follow the higher rate of the field variation. As a result of the static response above  $\nu_c$ , the unwinding electric field increases 5–6 times. Obviously, the dielectric response can be neglected below  $\nu_c$ . The larger critical frequency  $\nu_c = 700$  Hz in the M<sub>1</sub> mixture compared to that for M<sub>2</sub> demonstrates that the director reorientation frequency around the layer normal in M<sub>1</sub> is also larger than that in M<sub>2</sub>. In addition, we can also conclude that the rotational viscosity in M<sub>1</sub> mixture is less than that in M<sub>2</sub>.

We can determine the ratio of the spontaneous polarizations in the two mixtures. For this purpose we use the dependence of the critical electric field for unwinding the helix [3]

$$E_c = \pi^4 K_{22}/4P_0^2 P,$$

where  $K_{22}$  is the twist elastic constant and  $P_0$  is the helix pitch in the unperturbed ferroelectric system. The average pitch  $P_0$  over the S<sub>C</sub>\* range in the M<sub>1</sub> mixture is 15  $\mu\text{m}$  and in the M<sub>2</sub> mixture it is 10  $\mu\text{m}$ . The critical field for M<sub>1</sub> and M<sub>2</sub> below  $\nu_c$  are  $0.33 \times 10^4$  V/cm and  $0.83 \times 10^4$  V/cm, respectively. Assuming that the twist elastic constants are approximately equal in the two mixtures, we find that the ratio of the spontaneous polarizations,  $P_1$  and  $P_2$ , of the mixtures M<sub>1</sub> and M<sub>2</sub> is about 1.15. We shall discuss the electrooptic switching behaviour of the M<sub>1</sub> mixture when the helix is unwound by the boundary forces. Because of the larger helical pitch, it is possible to maintain easily the constant thickness  $d$  in the thicker cells for larger sample areas.

The local monocrystals formed in the smectic C\* phase in the presence of an AC electric field demonstrate that the smectic layers are vertical toward the orienting substrates and are at an angle of  $\pm \pi/4$  to the rubbing direction. On the basis of this initial director and layer geometry with the electric field normal to the orienting surfaces or approximately parallel to the layers, we can adopt the recently proposed model [7, 19, 20] to explain this electrooptic switching process. We have in mind also the model [10, 18] proposed by us for the electrooptic behaviour of the achiral smectic C phase of HOBA and OOBA (with  $\epsilon_a < 0$  where  $\epsilon_a$  is the dielectric anisotropy) as well as the model developed by the Halle group [21] for the Fredericks transition in a smectic C with  $\epsilon_a > 0$ . The basis of these models is the common smectic C property that the energy of the system is minimized for a given external influence by director rotation around the layer normal, as long as the interlayer distance remains constant. It has been demonstrated [22], that the smectic layers can only be destroyed under the influence of a very strong DC or AC electric field in the electrohydrodynamic regime. An important consequence of this property is that the rotational viscosity plays a fundamental role in the dynamic processes related with the electrooptical response. This viscosity is significantly lower than the other liquid crystal viscosities [23]. Having in mind the fundamental structural and elastic properties of the smectic C

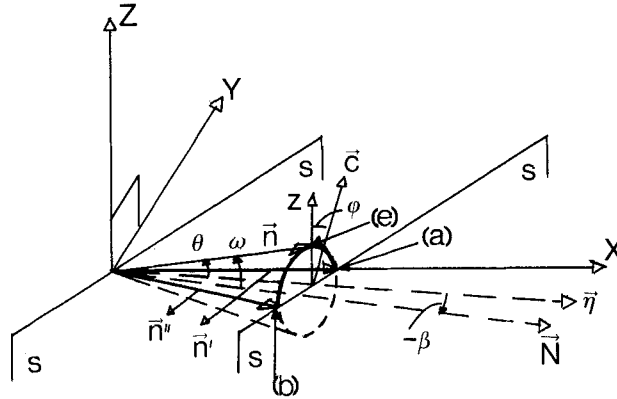


Figure 10. The director ( $\mathbf{n}$ ) and layer(s) representation of the ferroelectric  $C^*$  state stabilized by the boundaries for a planar orientation in laboratory coordinate system  $OXYZ$ . The electric field  $\mathbf{E}$  is normal to the orienting substrates and coincides with the  $Z$  axis. (a) and (b) present the extreme director position in the  $XOY$  plane ( $\mathbf{n}'$  and  $\mathbf{n}''$ ) at a rotation over a cone around the layer normal  $\mathbf{N}$ . (c) is the  $\mathbf{n}$  position corresponding to the middle of the arc ( $ab$ ) and to the maximum value of angle  $\theta$  (between  $\mathbf{n}$  and the  $O\eta$  axis lying in the  $XOY$  plane).  $\Phi$  is the azimuthal angle of the director,  $\omega$  is the tilt angle,  $\mathbf{C}$  is the projection of  $\mathbf{n}$  onto the layer plane or  $\mathbf{C}$  director,  $\beta$  is the angle between the layer normal  $\mathbf{N}$  and the  $XOY$  plane.

phase [23] as well as the smectic  $C^*$  phase [24] we propose in figure 10 a qualitative model to explain the electrooptic effects observed by us. The director  $\mathbf{n}$ , the layer normal  $\mathbf{N}$  and the layer  $S$  close to the low orienting surface are presented in the figure;  $\theta$  is the angle between the director (at some position of  $\mathbf{n}$  on the surface of the cone) and the orienting surface— $XOY$ , i.e. in the figure between the  $O\eta$  axis lying in the  $XOY$  plane and the director. In this case the layer normal  $\mathbf{N}$  does not lie in the plane  $XOY$  but forms angle,  $\beta$ , with this. So the  $XOY$  plane cuts the cone in two parts. For the angle  $+\beta$  ( $\mathbf{N}$  is above the  $XOY$  plane) the arc ( $ab$ ) above  $XOY$  plane is longer than the one below  $XOY$  and vice versa for angle  $-\beta$  that is the arc ( $ab$ ) above  $XOY$  plane is shorter than that below  $XOY$ . The case presented in figure 11 is also possible. Where the section cut from the orienting plane (hatched in figure 12) contains the two extreme positions for the director ( $\mathbf{n}'$  and  $\mathbf{n}''$ ) as well as the layer normal  $\mathbf{N}$ . In this case the angle  $\beta$  is 0 and  $\mathbf{N}$  coincides with  $O\eta$ . The angle  $\theta$  is equal to zero in the positions  $\mathbf{n}'$  and  $\mathbf{n}''$  of the director and is equal to the smectic  $C$  tilt angle ( $\theta = \omega$ ) at the position of  $\mathbf{n}$  corresponding to the middle of the arc ( $ab$ ), i.e. to the position (c) in figure 11.

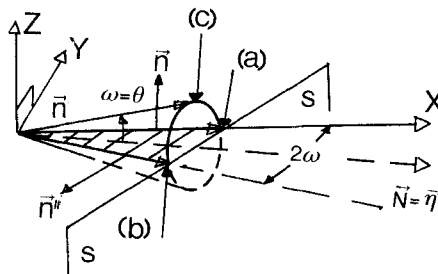


Figure 11. The director  $\mathbf{n}$  and layer representation at a surface stabilised state in a possible case when the director positions  $\mathbf{n}'$ ,  $\mathbf{n}''$  and the layer normal  $\mathbf{N}$  lie in the same plane ( $XOY$  plane); the angle  $\beta = 0$  and  $\theta = \omega$ .

It has been indicated [25] for the induced mixture ferroelectric, oriented by ITO substrates that the spontaneous polarization vector  $\mathbf{P}$  points to the sample volume. Since the spontaneous polarization  $\mathbf{P}$  is perpendicular to the tilt plane for planar orientation, its possible directions in positions (a) and (b) are along  $+Z$  and  $-Z$  respectively, here we adopt  $\mathbf{n}$  rotation from initial (a) to (b) position.

The electric field in the geometry of our experiment is applied along the  $Z$  axis, see figure 10. Consequently, two torques will act on the director in positions (a) or (b), (i) the ferroelectric torque on unit azimuthal angle  $\Phi$  (see figure 11) [19]

$$\mathbf{M}^F = \mathbf{P}E$$

and (ii) the dielectric torque [23]

$$M_e = -1/2\epsilon_a E^2.$$

The balance between these torques determines the resultant torque, which depends on the frequency and the strength of the field. As follows from our experiment, there is a frequency interval where the two torques become equal since below and above this interval one of the torques predominates. The resultant torque at the undisturbed layers (for the comparatively weak electric influence applied in our case) induces a rotation of  $\mathbf{n}$  over a cone around  $\mathbf{N}$  from one position to another for example (a)  $\rightarrow$  (e) or (e)  $\rightarrow$  (b) in figure 10. The  $\mathbf{n}$  rotation induced by the electric field is set against the liquid crystal reaction, strongly depending on the rotational viscosity  $\gamma$ . Obviously, at zero or at low frequencies the torque  $M^F$  will dominate. Naturally, at high electric frequencies  $\mathbf{n}$  does not react to the two directions of the AC electric field, but only to its absolute value  $\langle E^2 \rangle$ . As a result, only the induced polarization with a smaller efficiency than the permanent one will act.

On the basis of the model proposed let us discuss the effect of the discontinuous change of the texture and the colours from  $E_{th}^{(1)}$  to  $E_{th}^{(6)}$  for DC electric fields. The effect probably reflects a discontinuous change of the azimuthal orientation of  $\mathbf{n}$  measured by the angle  $\Phi$ . We found that increasing the field in steps of  $1 \times 10^3$  V/cm from  $E_{th}^{(1)}$  to  $E_{th}^{(5)}$  only two colours change drastically. This probably indicates that on increasing the electric field the director (or its projection  $C$ ) consecutively takes strictly defined positions between (a) and (b) where optically stable distinct states are established. It is reasonable to accept that at lower thresholds for the interval  $E_{th}^{(1)}$  to  $E_{th}^{(6)}$  the torque  $M_e$  can be neglected and the torque  $M^F$  predominates. Consequently, the spontaneous polarization vector  $\mathbf{P}$  changes its direction into the opposite direction going from position (a) to (b) for  $E$  applied to  $-Z$ . This may be the case if our assumption, that  $\mathbf{P}$  points inside the sample for the ITO treated substrates used by us, is correct. In position (e)  $M^F$  is a maximum; the threshold value  $E_{th}^{(6)}$  is twice as high as  $E_{th}^{(5)}$ . We assume that this happens because the dielectric torque stabilizing positions (a) and (b) of the director (since  $\epsilon_a < 0$  for the  $M_1$  mixture) starts to dominate in the resultant torque  $M^F + M_e$  above  $E_{th}^{(5)}$ . The action of the  $M_e$  torque on the director is in general less effective, leading to a significant increase of the threshold. Besides the torque,  $M_e$  acts (because of  $\epsilon_a < 0$ ) in a direction opposite to that of  $M^F$ .

For  $\beta = 0$  (see figure 11) the deformation of the system by the field increases continuously accompanied by permanent (without jump) colour changes from (a) to (b). We have observed this electrooptic effect in thinner samples. Thus the effects described here and found in the  $M_1$  mixture are a typical switching process reflecting the rotation of the director about the layer's normal through twice the tilt angle.

As has been shown [15, 16] the director near the surface is under two constraints: it should lie on the surface circular cone of angle  $\pi/2 - \theta$ , coaxial to the surface normal and it should lie on the layer cone of angle  $\omega$  as well, see figure 10. Simultaneous application of these two constraints and for  $\pi/2 - \omega < \theta < \pi/2$ , in general, determines four allowed values of  $\Phi$  at each of the orienting substrate surfaces. This means also that four allowed states with a different direction of the polarization are possible at each surface. The number of the allowed states, consequently, depends strongly on the boundary conditions. So, the degree of intersection of the two cones is very important in this case. At  $\theta = 0$  (ideal planar orientation) the surface cone collapses to a plane and the four allowed states reduce to two. This is the original surface stabilised ferroelectric liquid crystal geometry [7] with  $\mathbf{P}$  perpendicular to the substrate surfaces. As  $\theta$  increases,  $\mathbf{P}$  rotates in the various states further away from being normal to the surface. So, different positions including also a spontaneous polarization parallel to the surface are possible. Therefore, for a non-ideal planar orientation, mainly in a thick cell, more than four states can be stabilized. The coupling of the ferroelectric dipole to the applied electric field results in first order transitions between the various surface stabilized states.

For comparatively thicker samples of DOBAMBC, regions have been observed [16] which exhibit six field-induced states going from large negative to large positive  $E$ . Depending on the boundary conditions, some of the induced stabilized states can be non-uniform. For example, significant bending of the director in the bulk in combination with ferroelectric polar surface interaction can stabilize the non-uniform state of splayed polarization [16]. The multiple switching states (four, six or more) consequently could be a combination of uniform and non-uniform states. For our geometry and boundary conditions we assume that the stable uniform states are realized at  $E = 0$  and at  $E = E_{th}^{(6)}$  where a yellow colour is established. The difference in the strength of the anchoring forces on the two orienting substrates can also exert an influence on the induction of uniform or non-uniform states as well as the number of switching processes. In addition in the smectic  $C^*$  phase, the optical switching effect has also been observed in other low temperature phases. According to [13] the low temperature phases  $S_f^*$  and  $S_j^*$  (non-chiral ferroelectric) of HOBACPC are really bistable, i.e. have two or more stable states analogous to those of solid ferroelectrics. These authors have observed four switching states in the  $S_j^*$  phase and present a switching mechanism different from that known for smectic  $S_C^*$  phases.

We have observed a well pronounced swinging of the texture in the  $M_1$  mixture at a fixed frequency  $\nu < 20$  kHz and  $E > E_{th} = 1.37 \times 10^3$  V/cm. The frequency of the swinging increases with the AC field increasing at constant  $\nu$ . In our geometry and probably  $\beta = 0$  at frequencies  $\nu < 20$  kHz the torque  $M^F$  dominates. As a result, for one period of the AC electric field the director manages to pass from (a) to (b) stable positions and vice versa and this we have observed as swinging. The frequency 20 kHz seems surprisingly high as a critical frequency for the relaxation of the director over the cone. However, this frequency may indicate that the director does not describe the full arc (ab) but only a small arc or vibrates around position (c) (see figure 11) succeeding to follow the AC field variations.

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