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Macroscopic properties of mixed chiral smectic liquid crystals

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Binary mixtures of chiral and non-chiral smectogens, DOBAMBC and DBHP respectively, exhibit a chiral smectic C phase in two separated concentration regions (about 0–20 and 60–100 mol per cent of DOBAMBC) and a chiral smectic I phase in the region of 60–100 mol per cent of DOBAMBC. For the S_C^* phase, the temperature and the concentration dependences of the spontaneous polarization, the tilt angle and the helical pitch were determined. The electric field switching properties of the S_I^* phase have been studied. For higher concentrations, the switching is similar to that of the S_I^* phase of pure DOBAMBC. When the concentration of DOBAMBC is lowered, bistable switching is observed.

1. Introduction

Chiral smectics are layered liquid-crystalline structures with molecules rotating along the layer normal making a constant tilt angle θ with the layer normal. They are of a considerable interest now, because they promise a new generation of electro-optic liquid crystal devices [1]. For the technical realization of novel electro-optic concepts based on the properties of chiral smectics, namely bistability and fast switching [1], it is necessary to optimize certain characteristic parameters of the chiral smectic phase employed. The value of θ is a critical parameter for the electro-optic response, the value of spontaneous polarization, P, influences the switching properties, and the pitch length, p, of the helicoidally modulated structure determines a critical thickness for the electro-optic device [2]. The sequence of mesophases on cooling from the isotropic phase is very important for aligning possibilities of the liquid crystal device. Moreoever, it is rather useful to employ a chiral smectic existing at room temperature.

Up to now only the chiral smectic C (S_C^*) phase has been considered for new chiral liquid crystal devices. There are other chiral smectics with a molecular ordering within the smectic layers, which also promise technical applications. The switching rate of these phases is lower, but they can yield a macroscopic spontaneous polarization even with rather thick cells [3, 4]. This property results in an optical memory similar to solid ferroelectrics.

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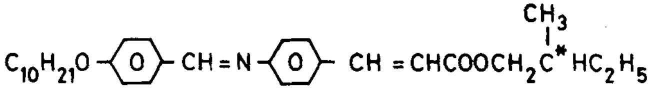
The phase transitions of chiral smectics as well as their macroscopic properties can be governed either by the engineering of the new chiral smectogens, or, very efficiently, by mixing different mesogens. There are several principal ways to obtain new chiral smectics by mixing:

(i) Inducing the chiral smectic phase in a smectic matrix by admixing a cholesteric [5] or a chiral non-mesogenic [6] compound. In both ways the S_C^* phases were obtained with p depending on concentration. In the former case p varied from 3 to 20 μm, in the latter $p \approx 100\,\mu$m.

(ii) Mixing two mesogens with S_C^* phases [7]. The mixture can exhibit a S_C^* phase at lower temperatures than that of the starting compound and moreover, compensation effects can occur. Combining S_C^*s′ exhibiting opposite handedness of the helices, the helicoidal structure can be supressed for a defined concentration ratio, P, of the mixture remaining non-zero [7].

(iii) Mixing chiral and non-chiral smectogens. The chiral properties are weakened, but the new chiral low temperature phases can appear. This attempt, first used in [8], is investigated in the present contribution. We have used



well-known as DOBAMBC, with S_C^* and S_I^* phases and a chiral substance

denoted here as DBHP; this exhibits S_C and S_B phases [9].

We have studied the phase diagram of the mixture, measured the dependence of P, θ and p on concentration in the resulting S_C^* phase and we have studied switching properties in the low temperature smectic phase.

2. Experimental results

2.1. *The phase diagram*

The phases and their transitions have been identified by textural observations under the polarizing microscope, by conoscopical investigations, calorimetric methods (Perkin-Elmer DSC 26) and X-ray diffraction. The X-ray studies have been performed using Guinier equipment. The samples were melted in flat Beryllium cells. The patterns observed for concentrations 86, 65, 48 and 20 mol per cent of DOBAMBC were investigated as a function of temperature. The results of the investigations are shown in figure 1. The S_A phase was observed over the whole concentration range. The cholesteric phase, N*, could be detected for small concentrations of DOBAMBC only. The S_C^* phase of DOBAMBC is not connected by a region of complete miscibility with the S_C phase of DBHP. At concentrations of 48 and 20 mol per cent direct transitions of the S_A phase into the S_B phase were observed by textural observations. The conoscopic investigations revealed uniaxial images from the clearing temperature down to room temperature at these concentrations. The phase designation is supported by the Guinier pattern which exhibits one sharp outer reflection at temperatures below 47°C in both cases. The phase transitions smectic A–isotropic and smectic B–smectic A in a preparation of 48 mol per cent were also confirmed by calorimetric peaks. The

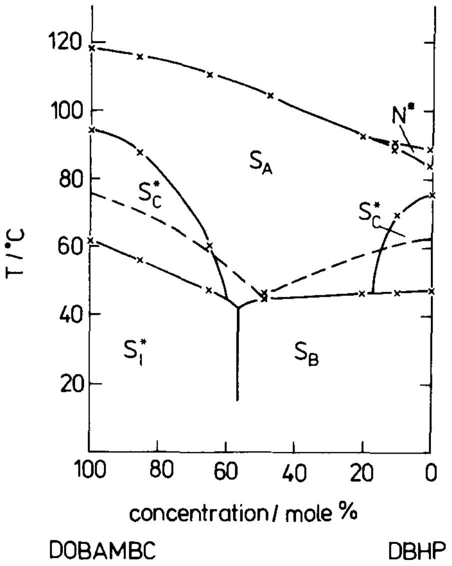


Figure 1. The phase diagram for the mixture of DOBAMBC and DBHP. The dashed lines indicate the melting curves obtained on heating only. The concentration is expressed in mol per cent of DOBAMBC.

thermogram does not give any hint, however, for the existence of the S_C^* phase at 48 mol per cent. In a concentration region above 60 mol per cent a polymorphism S_A, S_C^*, S_I^* was observed. In non-oriented samples of 86 and 65 mol per cent we obtained, by X-ray investigation, patterns with one outer reflection which would be compatible with S_I^* and S_F^* phases. Since pure DOBAMBC exhibits the S_I^* phase we transferred this designation also to the mixed, low temperature smectic phase existing at high concentrations. In a preparation of 65 mol per cent the chiral smectic C–smectic A transition was indicated by a diffuse step at 59–60°C in the D.S.C. curve.

2.2. *Macroscopic properties of the* S_C^* *phase*

The temperature-concentration range of S_C^* existence reveals two separated parts differing in properties. In the left part, for higher concentrations of DOBAMBC, the helicoidal S_C^* structure exists with p decreasing slightly with decreasing concentration. The temperature dependence of p is similar to that of DOBAMBC [10] and it is shown in figure 2 for three concentrations. For concentrations lower than 20 mol per cent of DOBAMBC, samples appear to be unwound.

The temperature dependence of P was measured by the switching method [11] in the high concentration region of DOBAMBC (see figure 3). For the same concentrations, the values of θ (see figure 4) were measured from the difference between crossed-polarizers-extinction positions of two opposite unwound states. For concentrations lower than 60 mol per cent neither θ nor P could be measured, because the structure could not be switched with an electric field up to 50 kV/cm, the limiting field of our experimental set-up. The maximum values of P and θ reached in the S_C^* phase for different concentrations (saturated values P_s and θ_s) are shown in figure 5. Both decrease with decreasing concentration of the chiral compound.

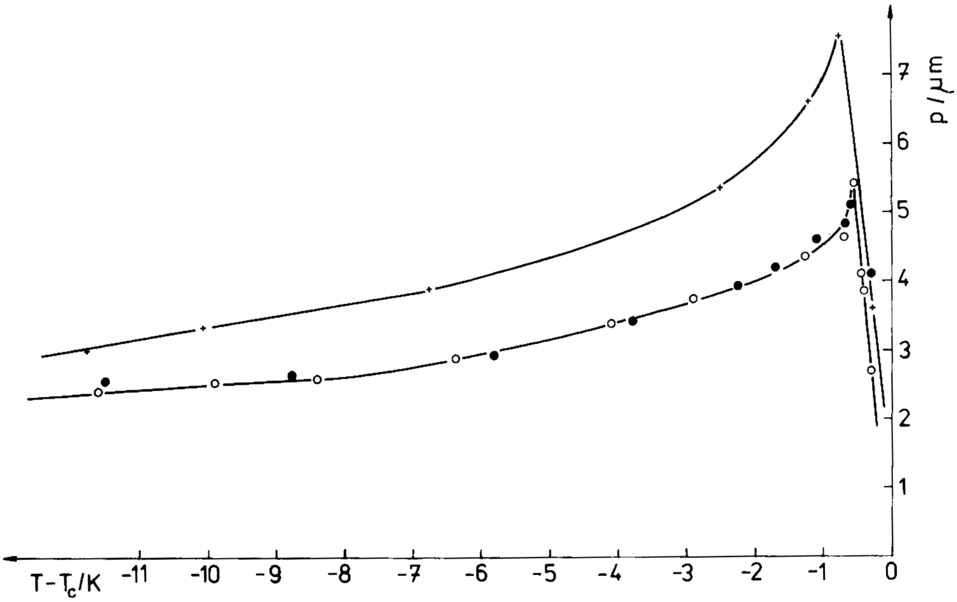


Figure 2. Temperature dependence of the helicoidal pitch, *p*, in the S_C^* phase for three concentrations. One common curve joins the measured points for 80 mol per cent (open circles) and 90 mol per cent (full circles). The other curve is for 70 mol per cent.

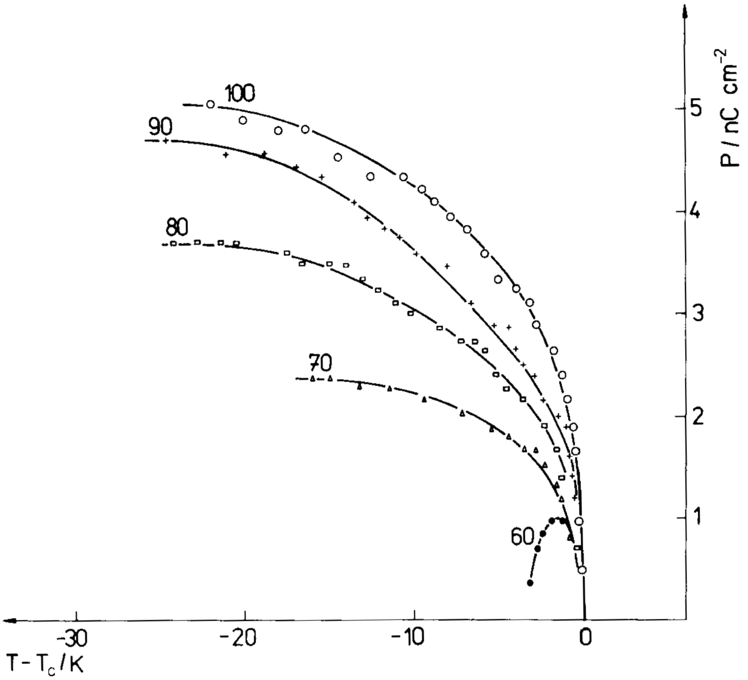


Figure 3. Temperature dependence of *P* in S_C^* phases of denoted concentrations measured at 50 Hz. The decrease for 60 mol per cent is due to an incomplete switching at temperatures lower than $(T_c - 1)$ K.

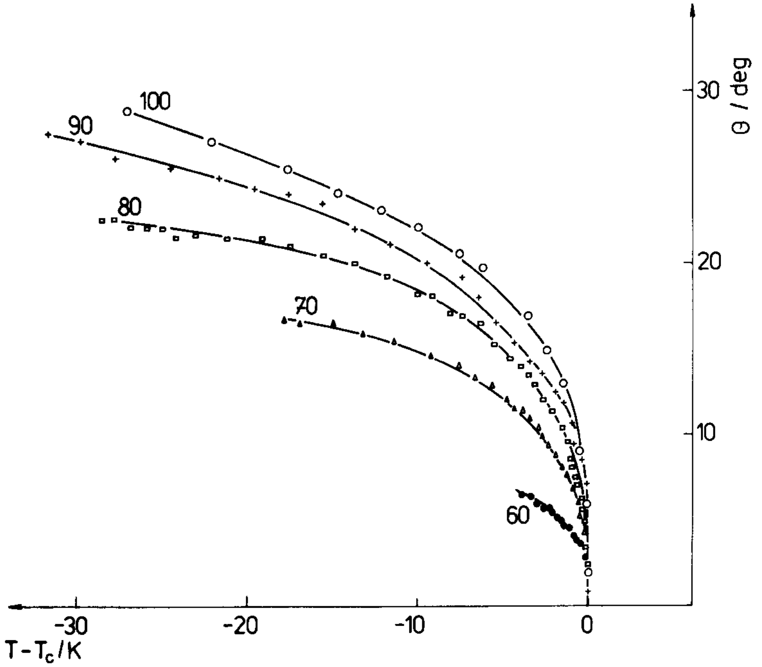


Figure 4. Temperature dependence of θ in the S_C^* phase for the given concentrations.

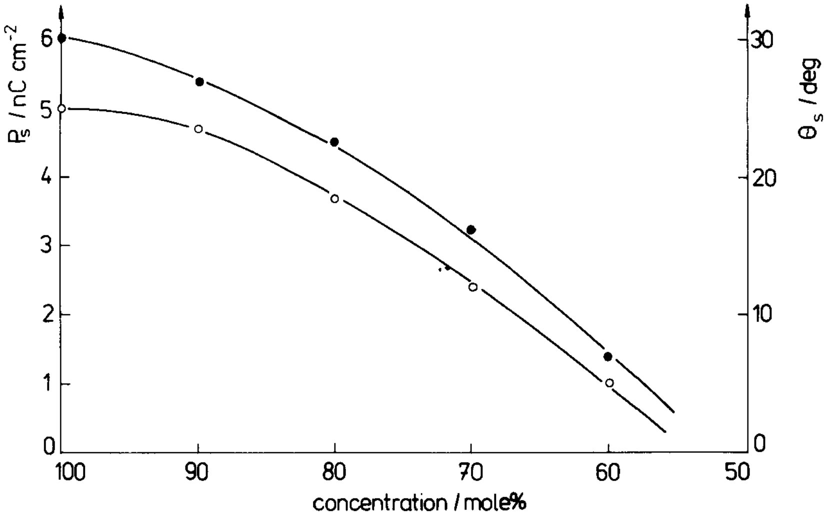


Figure 5. The dependence of the saturated values of P and θ on concentration.

2.3. *The textures of low temperature smectic phases and their behaviour in an electric field*

2.3.1. S_I^* *phase*

The properties of the S_I^* phase in high concentrations (e.g. 86 mol per cent) are very similar to those of pure DOBAMBC. The sample texture consists of parallel, linear defects, showing the existence of a helicoidal structure. The defects are 2π-twist

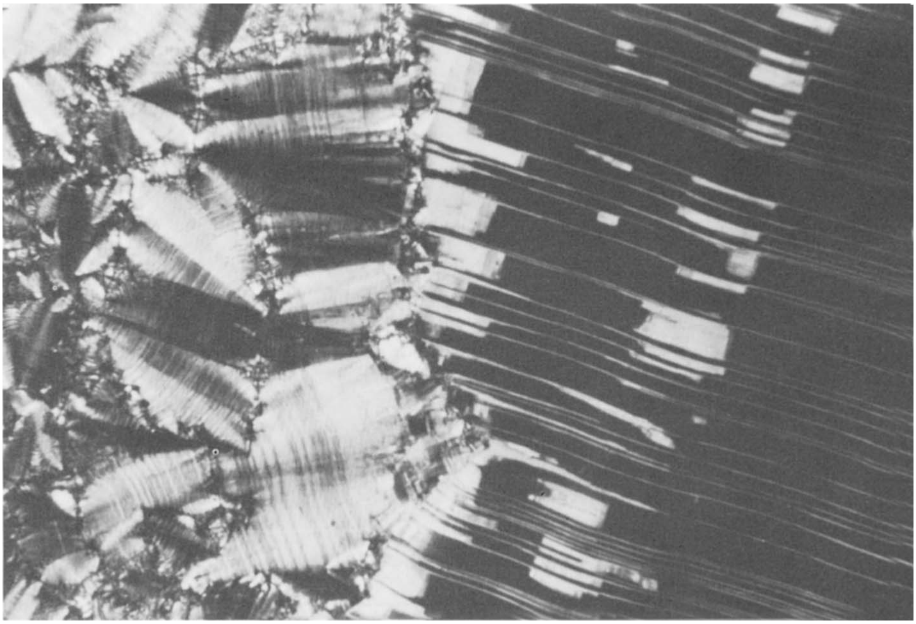


Figure 6. The texture of a plate-like sample in the S_I^* phase, concentration 70 mol per cent, thickness 25 μm. The left side was without electrodes, on the right side an electric field 0·1 Hz was applied for 5 min about 1 hour before the picture was taken.

disclinations mediating the helicoidal structure in the bulk sample with the structure on the surface which is unwound by planar surface anchoring [12]. In an electric field the helicoidal structure is unwound to a uniform state. The unwinding mechanism (via the annihilation of 2π-twist disclinations) is similar to that explained in [13] for the S_C^* phase of DOBAMBC. After the field is removed, the uniform structure relaxes to a helicoidal one within a few seconds. At frequencies higher than 1 Hz, direct switching between two saturated unwound states with the opposite **P** orientations is observed.

For concentrations approaching 60 mol per cent other properties are found. The helicoidal structure, characterized by typical disclination lines, exists only in a sample unaligned by a d.c. electric field (see the left side of figure 6). After unwinding the helicoidal structure with an electric field, the helix does not appear within hours. This fact is demonstrated in figure 6. The part of the sample without electrodes reveals a texture typical of a helicoidal structure. In the adjacent part, where the electric field has been applied, the helicoidal modulation is not seen. Dark and bright areas are observed there. The boundaries between them, preferentially parallel to the smectic layers, can be shifted by an electric field, which means that the areas represent regions with different directions of **P**. Under the electric field the sample can be switched between two monodomains, saturated states with opposite **P** polarity. If the field is removed at any stage of sample switching, the sample state remains stable. Figure 7 shows the sample with 70 mol per cent concentration partly switched from one polarity of **P** to the opposite one (bright and dark areas in figure 7 (*a*)). When the sample is rotated by 22° between crossed polarizers the optical contrast is interchanged (see figure 7 (*b*)). This fact indicates that the tilt angle θ is 11°. In figure 7 (*c*) transient regions near the boundaries of both polarities are revealed. They are in

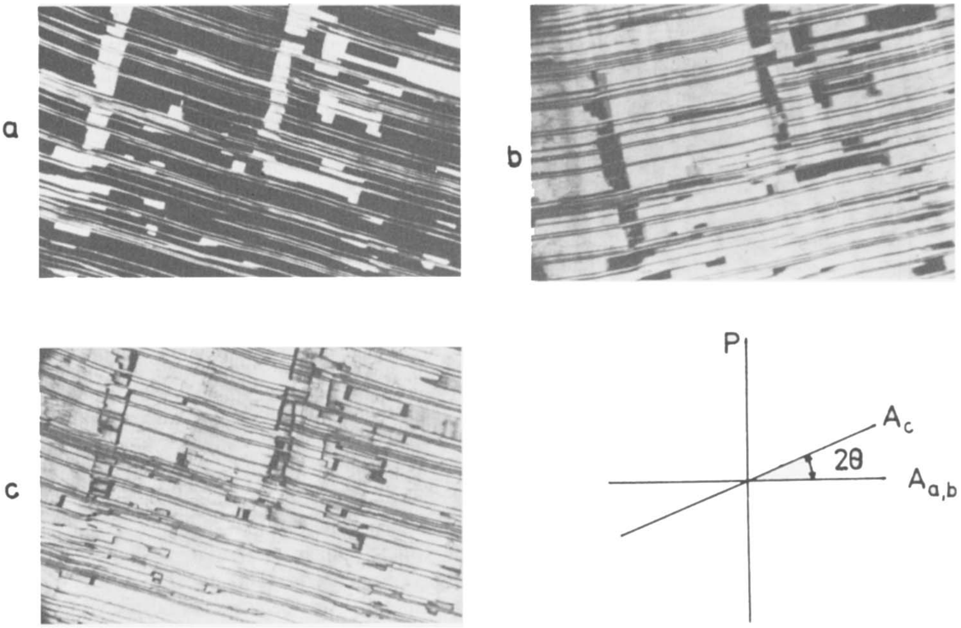


Figure 7. A sample in the S_I^* phase, concentration 70 mol per cent, thickness 25 μm, switched in parts. The position of the polarizer (P) and those of the analyser for (a), (b) ($A_{a,b}$) and for (c) (A_c) are shown.

extinction between polarizers making an angle of 68°, which indicates a structure twisted by 22° between lower and upper glass plates. When a d.c. electric field directed down (or up) is applied to switch the sample state, the switched area boundaries are focused near the upper (or lower) glass plate. This observation determines the location of surface disclinations limiting the switched areas.

On the basis of our optical investigation of the switching process (see figure 7) we can understand its mechanism; a model is described in figure 8. The switching starts from saturated state with **P** oriented in one direction within the whole sample, when the opposite field is applied. First, the surface layer with **P** pointing out of the sample starts to switch to the planar orientation with **P** directed along the field. The switched parts of the surface layer are surrounded by $\pm\pi$-twist disclination lines. The switched parts grow in both the thickness and lateral directions. The places with the switched and non-switched surfaces overlapped, are twisted (see figure 8) and reveal rotation of the plane of polarization by 2θ which is 22°. When the d.c. electric field is increased continuously, the switching starts at the surface which prefers the opposite surface layer polarity. From focusing the surface $\pm\pi$-twist disclination line we can deduce that the surface **P** orientation towards the sample bulk is preferred, i.e. it has a smaller anchoring energy than the opposite one. The same result was established for pure DOBAMBC [12].

The slow switching and bistability which have been observed in S_I^* phase of low concentrations are analogous to S_G^* or S_J^* phases of HOBACPC [15, 16], H_xOBAMBC and 8SI* [4]. On the other hand the continuously degenerated tilt direction which exists in samples, not subject to a d.c. electric field and in twisted states is characteristic of the S_I^* phase.

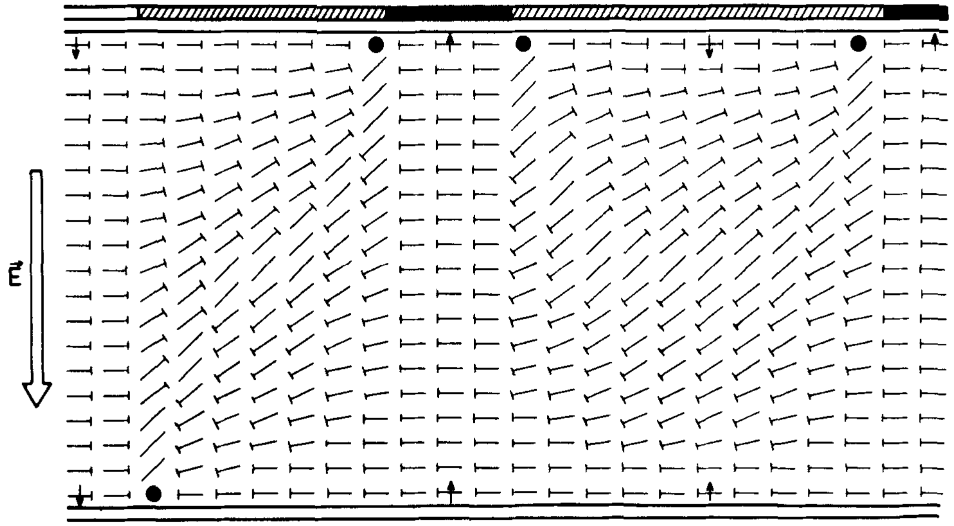


Figure 8. *An intermediate state of switching in the* S_I^* *phase shown in a section of the* plate-like planar sample with the smectic layers perpendicular to the paper. Local directors are represented schematically by the nails, the tips of which are directed toward the observer, the local dipole moments (in the surface layers only) by the arrows, the electric field direction by the thick arrow. The full dots represent sections of $\pm\pi$-twist disclinations. The bars above the upper surface represents sections through domains of different contrast. Dark, white and dashed bars represent unswitched, switched and twisted areas, respectively.

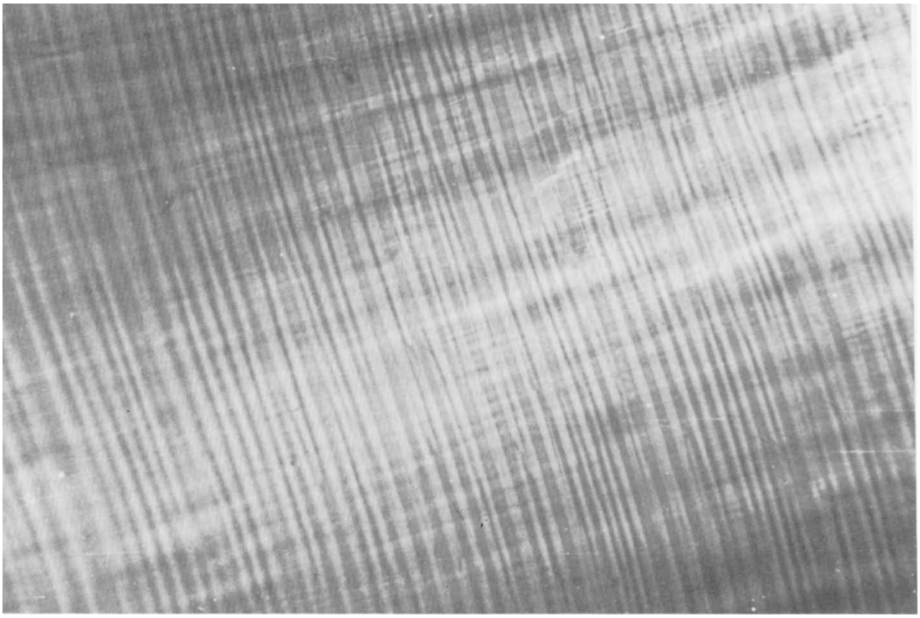


Figure 9. The texture of a plate-like sample, concentration 30 mol per cent, thickness 25 μm, which appeared at the phase transition from S_A to S_B. The largest width of the bands is about 10 μm.

The slow switching can be caused by an increase of the viscosity, γ, and a decrease of P_s with mixture of low concentration. An apparent bistability appears if the relaxation time for reaching an equilibrium state $\tau \sim \gamma/K$ (where K is a Frank elastic constant) becomes very long. With mixtures of low concentration a stable state was observed for several hours after the electric field was removed. Thus, we formally encounter here τ which is three orders of magnitude greater than in mixtures of high concentration. Another, possibly more probable, cause of bistability is an increase of the correlation range between the smectic layers when the concentration approaches 60 mol per cent of DOBAMBC. Then the unwound structure is an equilibrium state and a true bistability takes place as for S_G^* and S_J^* phases.

2.3.2. S_B *phase*

At the phase transition from either S_A or S_C^* phases to the S_B^* phase a texture consisting of bands appears (see figure 9). On further cooling the width of the bands grows and simultaneously their optical contrast disappears. The observed texture probably represents a coexistence of phases; a similar effect is described in [17].

No effect of the electric field up to an intensity of about 50 kV/cm has been observed in any state of temperature evolution of the texture. This finding is in agreement with the X-ray data identifying the phase as a smectic B.

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