Investigations of the structure of a cholesteric phase with a temperature induced helix inversion and of the succeeding S_C^* phase in thin liquid crystal cells

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Investigations of 4-[(S,S)-2,3 epoxyhexyloxy]-phenyl-4-(decyloxy)-benzoate by polarizing microscopy, the Cano-Grandjean method, optical rotation dispersion and UV-VIS spectroscopy reveal a cholesteric phase with temperature induced reversal of the helical twist. Switching time experiments in the S_C^* phase show that the intrinsic helix can be unwound reversibly and irreversibly by application of electric fields of different strengths.

1. Introduction

A cholesteric phase may be described by a continuously twisted nematic director, which forms a supermolecular helicoidal structure with pitch P, corresponding to a 2π twist of the nematic director. The helix axis of the structure represents the optical axis of the system. Such a structure causes a selective reflection for a wavelength λ_0 related to the pitch P by [1]

$$\frac{\lambda_0}{\bar{n}} = P \qquad (1)$$

with $\bar{n}$ a mean refractive index, and assuming the incident light beam parallel to the helix axis. If cholesteric material is placed between a glass plate and a lense with a sufficiently large radius or a wedge (Cano [2], Grandjean [3]) a homeotropic texture may be formed and concentric rings or lines appear with a distance which is related to the geometry of the device and the cholesteric pitch. With a known geometry the pitch can be determined.

A homeotropic texture in thin cells may also lead to the determination of the pitch, if the number of 2π twists, Z, which fit in between a cell of thickness d is known, since

$$Z = \frac{d}{P} = \frac{d\bar{n}}{\lambda_0}. \qquad (2)$$

In the following study the evaluation of equation (2) will be shown in an unusual case of a helix twist inversion of a cholesteric structure on varying the temperature of a pure

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compound and the data compared to those of the Cano–Grandjean method. Furthermore, this compound also exhibits a chiral smectic C phase of which the helicoidal structure can be reversibly or irreversibly unwound by an electric field in thin cells.

In general, the phenomenon of a helix inversion normally depends on the concentration of the two components of a binary system [4] and may occur after adding a nematic liquid crystal to a cholesteric [5, 6] or even in a mixture of two cholesteric liquid crystals with the same helical sense [7]. Compensation of the helicoidal structure also may take place in the simplest case of mixing a left handed with a right handed cholesteric phase [8]. Recently, an inversion of the twist of a cholesteric helix with change in the temperature was observed for the first time in two cellulose derivatives [9] and a cholesteryl compound [10]. An inversion of the helical twist in a chiral smectic C (S_C^*) phase was first observed by Martinot-Lagarde *et al.* [11].

2. Experimental

Polarizing microscopic observations on 4-[(*S,S*)-2,3-epoxyhexyloxy]-phenyl-4-(decyloxy)-benzoate [12]
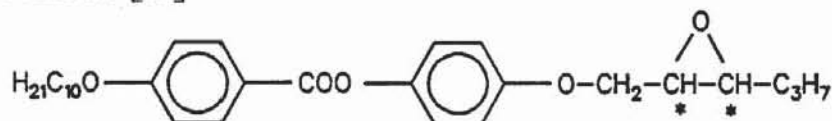
((*S,S*)-EPHDBPE) suggest that the phase sequence in thin liquid crystal cells on heating is

C 77°C N* 95·7°C I

and on cooling

I 95·7°C N* (78·6°C S_C^*) (57·2°C S_1) 57°C C

which do not agree with previously published data [12]. The compound is commercially available from Aldrich Chemical Company with a purity of 98 per cent, according to the producer. Investigations in the cholesteric phase were carried out with commercially available cells (E.H.C. Co. Ltd.) of 4·35 and 10·35 μm thickness (ITO electrodes, polyimide orientation layer), which was determined by a corrected interference spectrum [13] in the UV-VIS range (Bruins Instruments OMEGA10). The polarizing microscopic study concerning the temperature dependence of the pitch was performed by placing the cell in a hot stage (Mettler FP 52) between the crossed polars of the microscope (Olympus BH-2). A polarimeter (Perkin–Elmer 241C), equipped with a home made temperature controller, served for the characterization of the handedness of the cholesteric structure. The pitch of the cholesteric structure was evaluated using the Cano–Grandjean method and verified by IR spectroscopy. The

Figure 1.   Various characteristic cholesteric textures. (*a*) Oily streaks texture (see plate 21 in [15]), (*b*) bundle of oily streaks (see plate 22 in [15]), (*c*) cholesteric fan shaped texture (see plate 28 in [15]) and (*d*) cholesteric polygonal texture (see plate 27 in [15]). Textures (*a*) and (*b*) were obtained in thin liquid crystal cells, textures (*c*) and (*d*) can be observed by preparation on a slide without surface alignment layers.

Figure 2.   Colour changes observed between crossed polars in the cholesteric phase with homeotropic orientation for different temperatures in the 10·35 μm cell, the numbers indicate the temperature in °C.
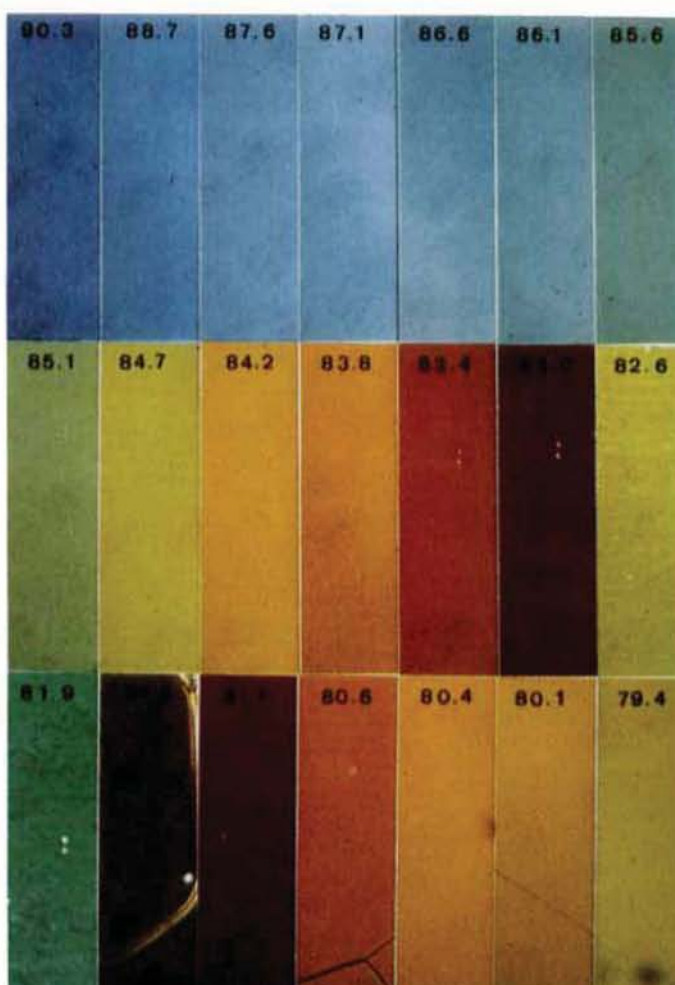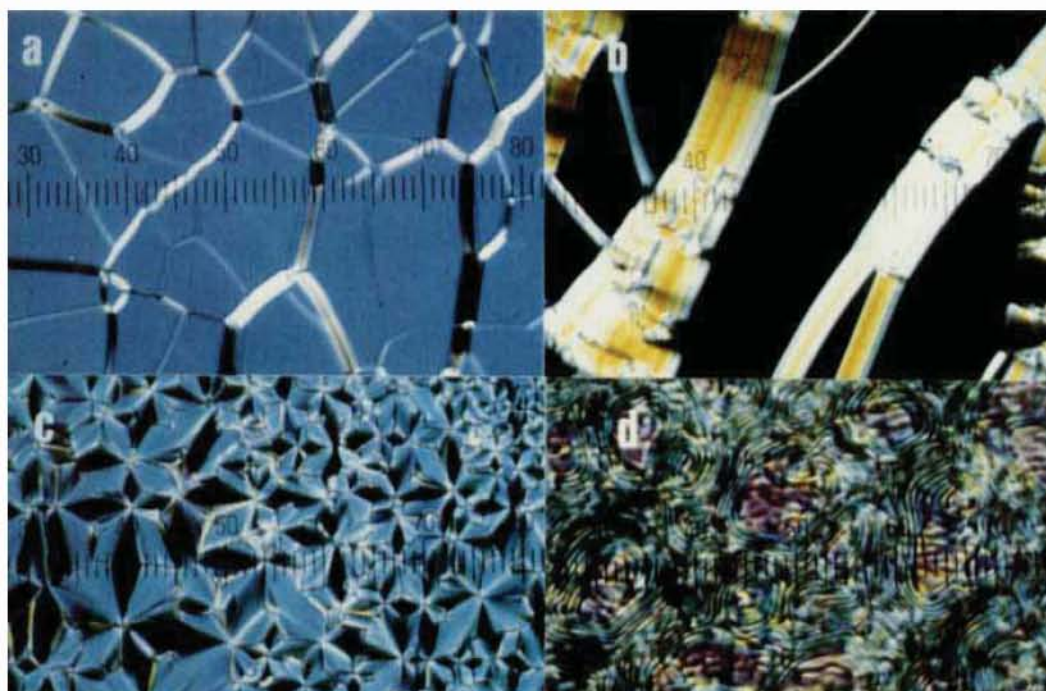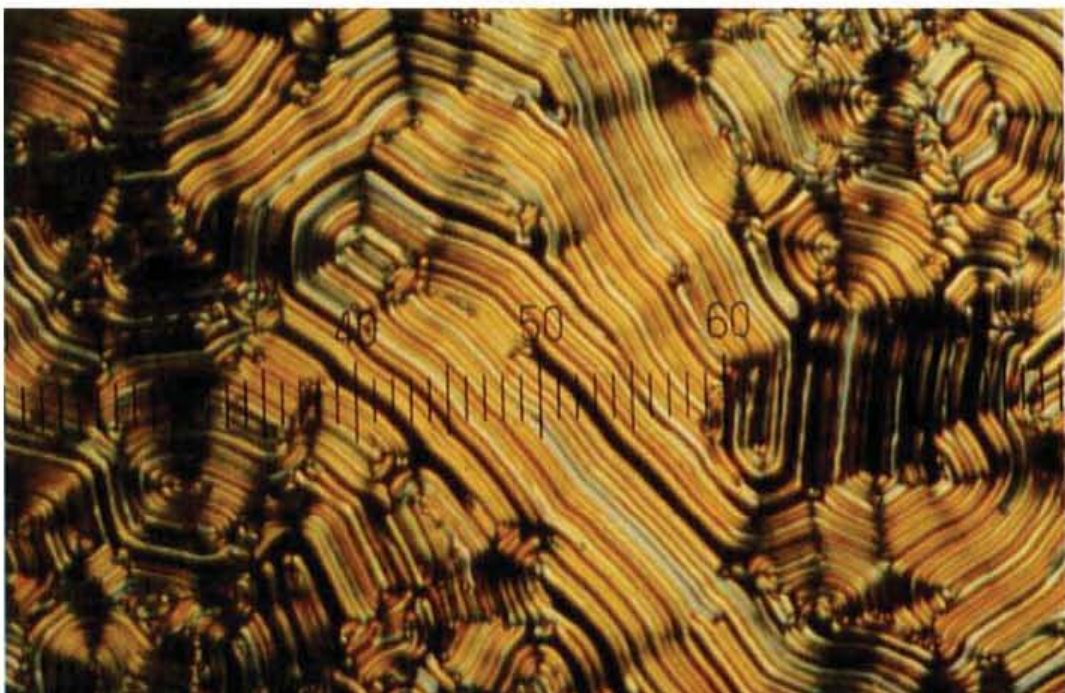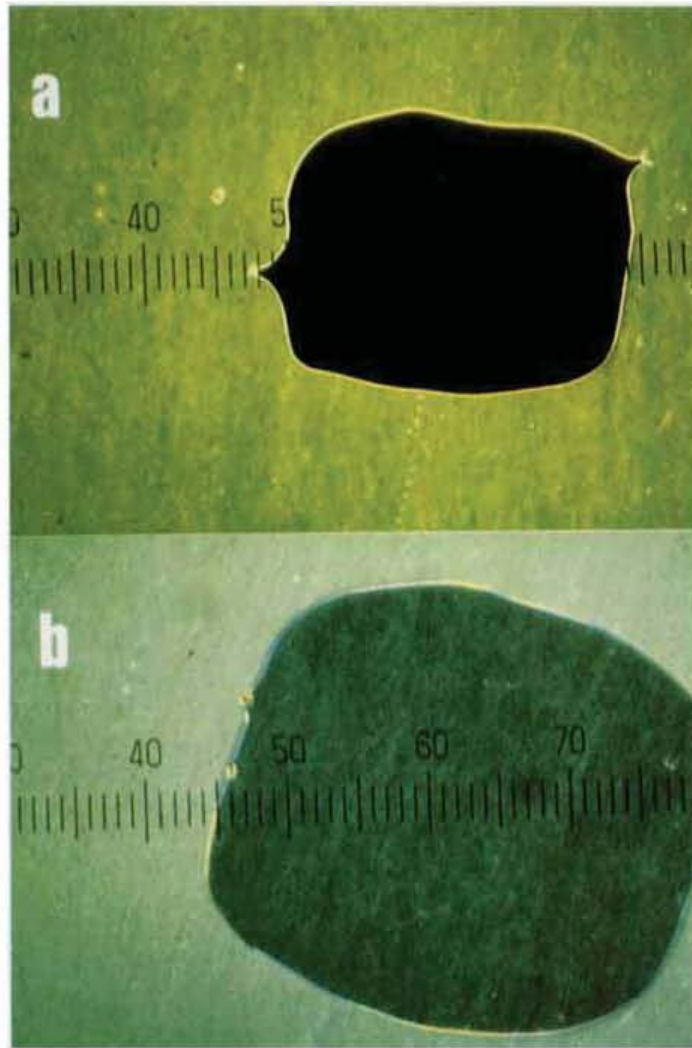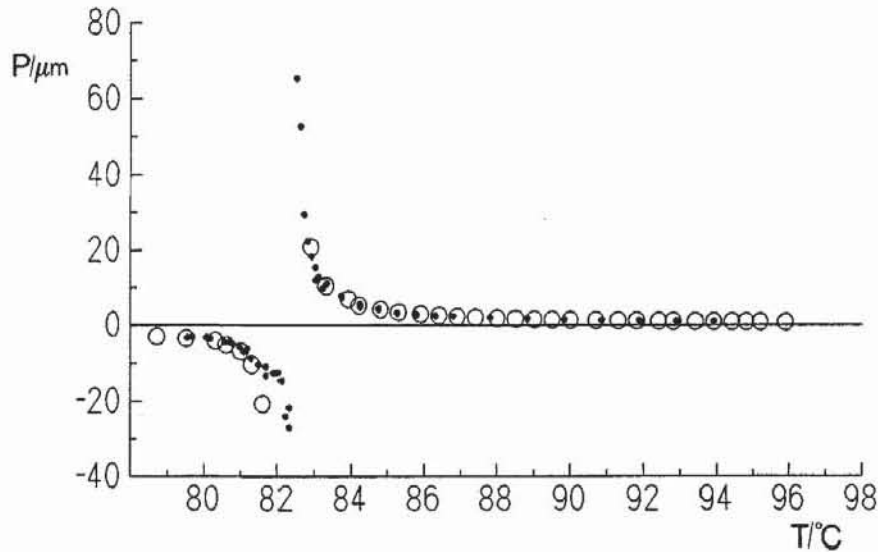
Figure 4. Temperature dependence of the cholesteric pitch *P*. (●) Measured by the Cano–Grandjean method, (○) calculated from equation (2). Positive pitch ≙ right handed, negative pitch ≙ left handed helicoidal structure.

transmission spectra between crossed polarizers were measured for surface aligned samples with a homeotropic texture and the optical axes placed parallel to the light beam in a polarizing microscope equipped with a spectrograph (EG & G Princeton Applied Research Model 1235 Digital Triple Grating Spectrograph) connected by a light pipe and processed with an optical multichannel analyser (EG & G Optical Multi-channel Analyser Parc 1420). The determination of the switching times in the ferroelectric S_C^* phase was carried out with an experimental apparatus described elsewhere [14]. A pulse of 5 ms duration and 10 Hz repetition rate at variable electric field strength served for the evaluation of this time in a 4 μm cell. 64 single measurements were averaged to surpress the statistical noise. The actual transmission curves were then converted to relative transmission values and the switching time taken as the change in relative transmission from 0 per cent to 90 per cent.

3. Experimental results and discussion

In the cholesteric phase a whole series of characteristic textures [15] was obtained under various conditions and these are shown in figure 1. Polarizing microscopic observation of the 10·35 μm cell in the cholesteric phase revealed that the complete visible spectrum is discontinously covered step by step (see figure 2) from blue, blue–green, green, yellow–green, yellow, orange and red on decreasing the temperature from 96 to 83°C. At 82·5–81·6°C the cholesteric pitch diverges, a nematic state is formed and an extinguishing orientation of the cell between crossed polars was found (see figure 3). Further, the typical nematic flickering was observed in the nematic state. This nematic state cannot be regarded as a separate phase, since measurements by differential scanning calorimetry do not exhibit peaks or steps in the thermograms at respective

Figure 3. Polarizing microscopic observation of the nematic state and the cholesteric phase next to it between crossed polars at a polarization angle (*a*) 0° and (*b*) 20° with enlarged nematic area, 10 scales ≙ 60 μm.

Figure 5. Typical fingerprint texture with equidistant stripes, which may be used to evaluate the cholesteric pitch. 10 scales ≙ 60 μm.

temperatures of the change from the cholesteric to the nematic structure. Only, slight changes in intensity were observed in the cholesteric structures next to the nematic state (see figure 2, 82·6°C and 81·5°C) if the sample on the hot stage is rotated between fixed crossed polars. No change in intensity or colour is found in all other cholesteric states. On decreasing the temperature further from 81 to 79°C the cholesteric state reforms with colour changes from red, orange, yellow, to green (see figure 2).

The number of colour changes in the visible range of the spectrum depends on the cell thickness as demonstrated by equation (2). The number of changes observed at temperatures above the nematic state are 10, 25 for the 4·35, 10·35 μm cell and 3, 7 below the nematic state, respectively. Some colour changes may be seen indirectly by light scattering at the interface between regions with different twist states.

The Cano–Grandjean method leads to the temperature dependence of the pitch which is represented in figure 4 (filled circles). In the vicinity of the change from the cholesteric to the nematic state, the pitch can also be evaluated from a typical fingerprint texture obtained by planar orientation (helix axis parallel to the substrate plane) as shown in figure 5. The pitches obtained with this method agree quite well with those determined by the Cano–Grandjean method. The handedness of the cholesteric structure was determined by optical rotation measurements in the visible range of the spectrum for which the wavelength λ is smaller than the selective reflection wavelength λ_0 and, according to de Vries, different signs of the optical rotation verify an inversion of the handedness from right handed above the nematic state (see figure 6, upper curve, $T = 87$°C) to left handed below the nematic state (see figure 6, lower curve, $T = 79\cdot5$°C). This inversion of the helicoidal handedness with temperature variation was also confirmed with the method introduced in [16].

The pitch for thin cells can be calculated with equation (2) assuming $Z = \frac{1}{2}$ for the cholesteric structures next to the nematic state and that every discontinuous colour change adds $\frac{1}{2}$ to Z. These calculated values for the pitch are plotted in figure 4 as open circles, and they agree well with those measured directly. A more detailed evaluation of the colours observed using thin cells results in excellent agreement with observed spectra and may lead to a determination of the pitch by experiments in thin cells. The polarization plane of the incident wave with wavelength λ is rotated by a homeotropic texture according to de Vries by an angle α

$$\alpha = \frac{\pi P \Delta n_{\text{nem}}^2}{4\lambda^2} \frac{1}{1 - (\lambda/\lambda_0)^2} d \tag{3}$$

with Δn_{nem} the birefringence of a nematic sheet of the cholesteric structure. The transmitted light passing through the analyser has the colour or maximum intensity of the rotated polarization plane by 90° or $90° + k \cdot 180°$ ($k = 0, 1, 2, \ldots$) denoted by λ_{90}. The relative transmission $T(\lambda)$ through the analyser as a function of wavelength is then given by

$$T(\lambda) = 100 \sin^2 \alpha. \tag{4}$$

The experimentally determined transmission curves in the visible spectrum range are shown in figure 7. Extinction caused by interference by the cell gap is clearly visible. The curves can be fitted to equation (4), if the dispersion of the birefringence is considered in a simple approximation [17]

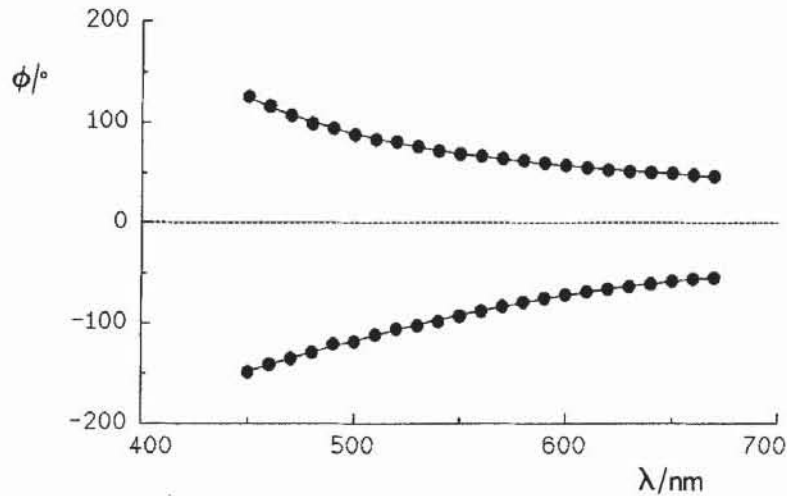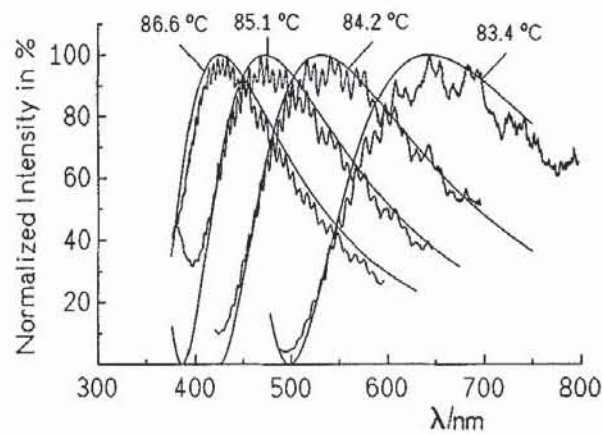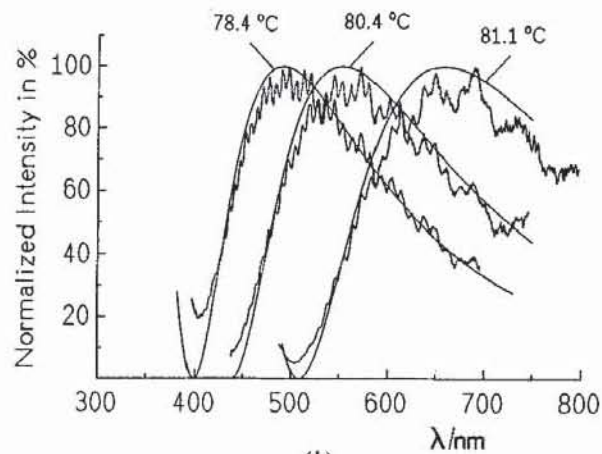$$\Delta n(\lambda) = G \frac{\lambda^2 \lambda^{*2}}{\lambda^2 - \lambda^{*2}}, \tag{5}$$

Figure 6. Optical rotation dispersion measurements of (*S,S*)-EPHDBPE in the $10.35\,\mu$m cell above ($T \approx 87°$C, upper curve) and below ($T \approx 79.5°$C, lower curve) the nematic state, indicating a temperature induced reversal of the helicoidal twist from right handed to left handed.

(*a*)

(*b*)

Figure 7. Some of the measured and normalized transmission spectra with superimposed cell interference between crossed polars and calculated transmission (without cell interference), according to the de Vries equation, for the $10.35\,\mu$m cell above (*a*) and below (*b*) the nematic state.

where G is a temperature dependent quantity related to the order parameter and λ^* a mean wavelength of the UV absorption band. The dispersion of Δn plays a considerable role. Best fits were obtained for Δn between 0·095 and 0·144 over the wavelength region from 350 to 750 nm, and the variation with temperature results in 0·09 at 83·4°C to 0·11 at 87·6°C for $\lambda = 589$ nm. The calculated curves agree quite well with those determined by transmission spectroscopy.

A general correlation between the absolute configuration of the molecule and the macroscopic properties of the cholesteric helix is not yet known [10]. A helix inversion of a single compound with temperature might be explained by the presence of two chiral centres with twisting powers of opposite sense and different strength and temperature dependence [10, 18]. A linear dependence of the twisting power P^{-1} as a function of temperature (see figure 8) supports these arguments.

In the S_C^* phase, line textures were observed as depicted in figure 9. They appear when the intrinsic helicoidal S_C^* structure is homogeneously oriented [19] (helix axis parallel to the substrate planes), not surpressed by the cell geometry and surface stabilization [20] does not occur. The pitch of this structure can be estimated from the distance between two dark lines [19] to be about 3·1 μm, which is slightly smaller than the cell thickness.

It should be noted, if a compound or mixture exhibits a cholesteric phase above a S_C^* phase, knowledge of the helicoidal handedness of the cholesteric structure does not provide a guideline for the handedness of the ferroelectric chiral smectic C structure [16, 21, 22].

If an electric field is applied, the intrinsic helix of the S_C^* phase can be reversibly or irreversibly unwound depending on the strength of the electric field and a ferroelectric surface stabilized structure [20] may occur. This behaviour is probably due to the fact that the pitch of the S_C^* helix is approximately equal to the cell thickness.

The optical τ switching time of the material in the S_C^* phase by application of a square pulse field up to 2 MV m^{-1} is described by [23] $\tau \sim 1/E^2$ and depicted in figure 10 ($T = 65$°C). This dielectric relationship corresponds to an induced polarization P_{ind}
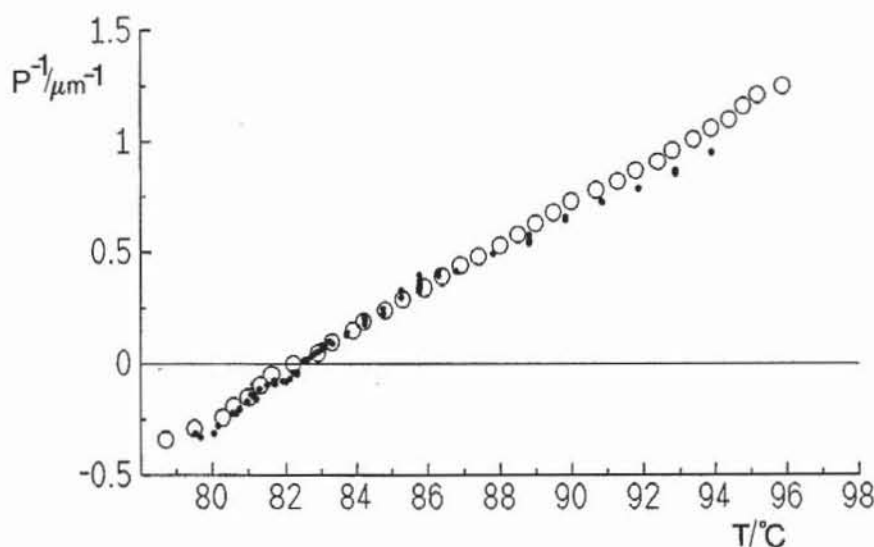

Figure 8. Twisting power, P^{-1}, as a function of temperature for a 10·35 μm cell. Negative values indicate a left handed and positive values a right handed helicoidal structure (●) by the Cano method; (○) by calculation as explained in the text).
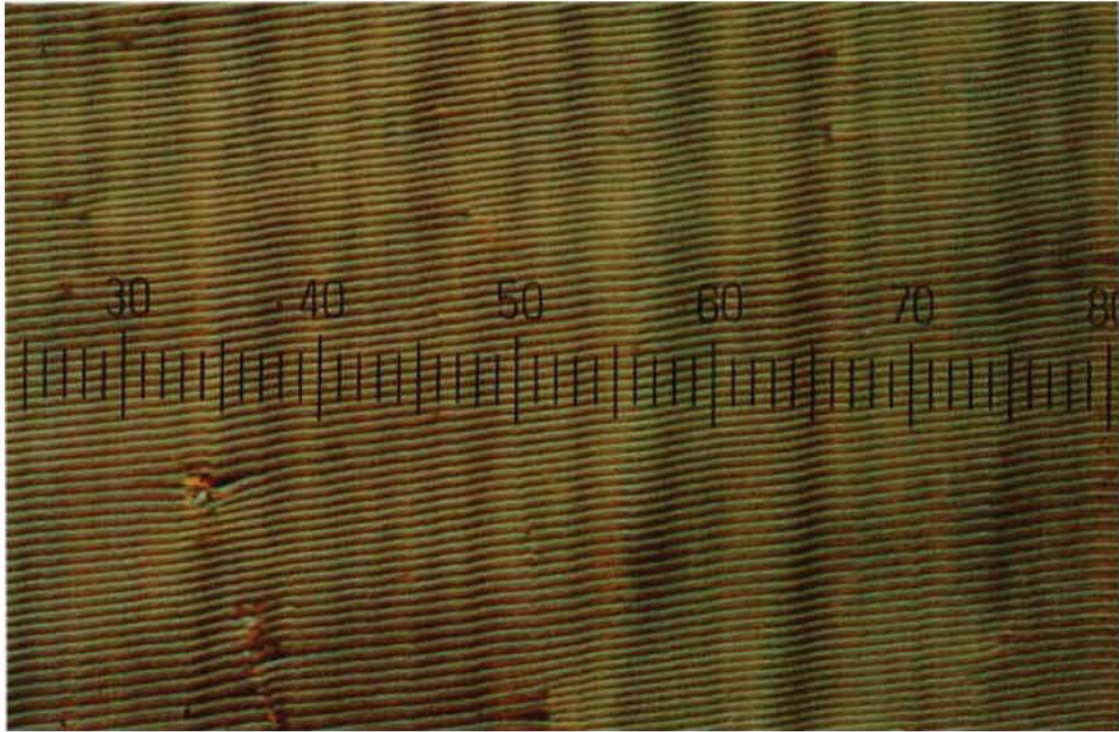
Figure 9. Typical line texture due to the intrinsic helix of the S_C^* phase in homogeneous orientation with the helicoidal axis parallel to the substrate planes observed with the polarizing microscope. 10 scales ≙ 60 μm.
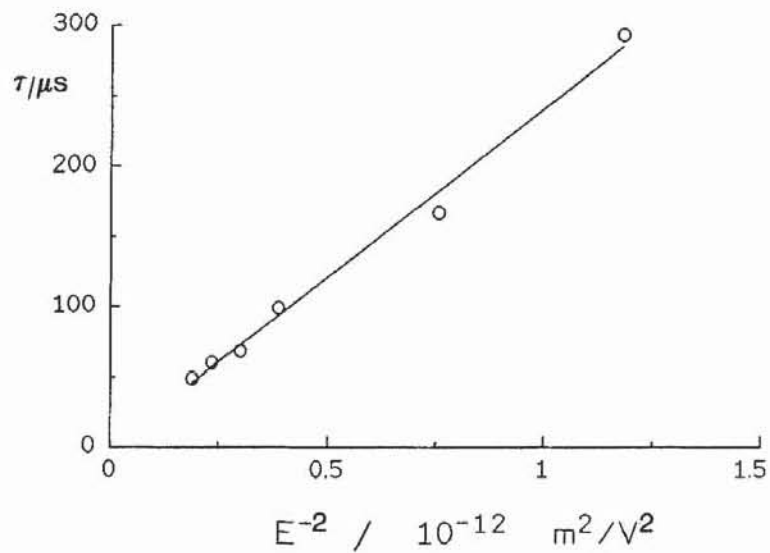

Figure 10. Switching time, τ, versus the applied electric field strength, E, for the dielectric process of reversibly deforming the S_C^* helix.
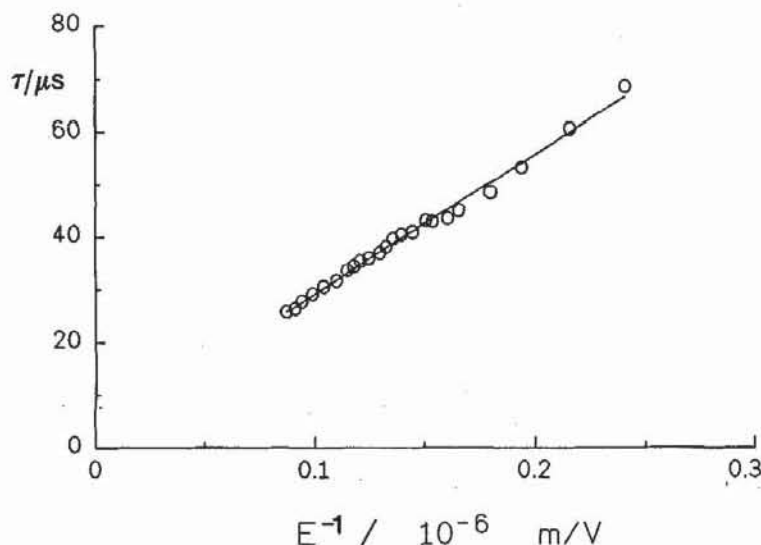
Figure 11. Switching time, τ, versus the applied electric field strength, E, after irreversibly unwinding the S_C^* helix, suggesting ferroelectric interactions.

interaction with the electric field E, and the helix is reversibly deformed. A change is noticed already in the texture, if a higher field is applied. The switching time τ shows a proportionality to $1/E$ suggesting a ferroelectric interaction between the spontaneous polarization P_S and the electric field [24], and the helix is unwound irreversibly, probably caused by an irreversible change of the orientation of the director at the substrate surface. The switching time as a function of the inverse electric field is depicted in figure 11 ($T = 65°C$).

4. Conclusion

In contrast to previously published work [12] the phase sequence of (S,S)-EPHDBPE is given by

$$C \ (57°C \ S_I) \ (57 \cdot 2°C \ S_C^*) \ 78 \cdot 1°C \ N^* \ 95 \cdot 7°C \ I.$$

and a helix inversion of this one component material is detected in the cholesteric state. A smectic A phase was not detected by the polarizing microscopic study, and is not supported by DSC measurements. This phase sequence can be exploited to produce well oriented textures for investigations in the S_C^* phase. The cholesteric helix can easily be unwound by an appropriate electric field, and passing the S_C^*–N^* transition, the ferroelectric irreversible S_C^* state is obtained with a nearly perfect texture.

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