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Investigations on the Flexoelectric and Electroclinic Effect in a Cholesteric Phase with Twist Inversion

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The linear flexoelectrooptic effect in short-pitch cholesterics was investigated for four configurations of a compound with two chiral centers. One of the four compounds, the (S,S) configuration, is a single component twist inversion cholesteric and we were able to study the electroclinic effect of the compound in the unwound state around the twist inversion point. This made it possible to separate the electroclinic from the flexoelectric electro-optic response and our results show that the electroclinic deflection of the optical axis is about 100 times smaller and 100 times faster than the flexoelectric one. Moreover, this is the first investigation of the electroclinic effect, far from the N*-SmC* transition, in a single component N* liquid crystal.

Keywords: liquid crystal, cholesteric phase, flexoelectric effect, electroclinic effect

Introduction

In the cholesteric phase (N*), two linear electrooptic effects can be observed, depending on the director configuration. A very general effect in liquid crystals is the flexoelectric effect [1,2] which is the linear coupling between splay and bend deformations and electric polarization and is not related to chirality. The flexoelectric linear electro-optic effect in cholesteric liquid crystals was first reported by PATEL and MEYER [3] in 1987 and has since been investigated mainly in short pitch cholesterics [3-9]. The samples used are uniformly oriented cholesteric phases with the helical axis (which is the macroscopic optical axis of the system) lying in the plane of the cell (Uniform Lying Helix (ULH) texture). Application of an electric field perpendicular to the helix axis causes the formation of a periodic splay-bend deformation, due to the coupling of the flexoelectric polarization with the electric field E. The accompanying rotation of the molecules in the cell plane causes a macroscopic rotation of the optical axis $\phi(E)$, which in first approximation, for small

electric fields below the dielectric helix unwinding, is determined by an average flexoelectric coefficient e_f and the ratio of the cholesteric pitch P and the average elastic constant K [3]:

$$\phi(E) = \arctan\left(\frac{e_f E P}{2\pi K}\right) \quad (1)$$

The characteristic time τ of the electrooptic response is determined by [4]:

$$\tau \approx \left(\frac{\gamma P^2}{4\pi^2 K}\right) \quad (2)$$

The flexoelectric effect displays a linear optical response when the cell is placed between crossed polarizers cf. fig. 1.

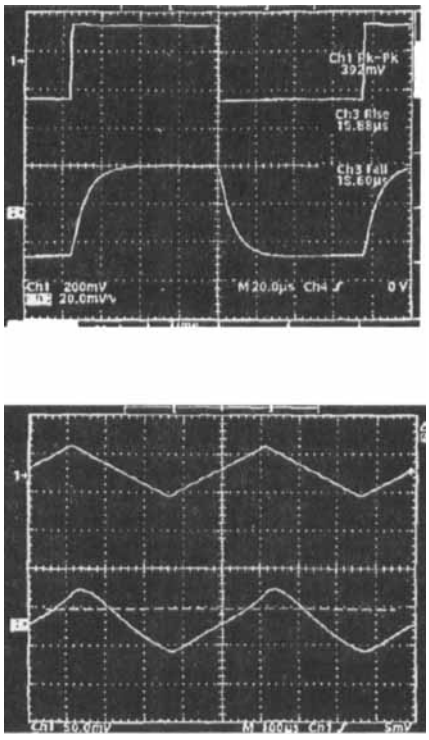


FIGURE 1 Flexoelectric response of (S,R)-M96 at T=150°C for square wave (top) and triangular (bottom) electric field application. The electrooptic response is linear up to reasonable high frequencies and fast response times in the µs range are observed (one unit of scale = 20 µs).

Response times are in the μs range and induced deviation angles $\phi \leq 10^{\circ}$, lower than the values up to 30° which have been measured in certain materials [7]. The sign of the induced deviation of the optical axis for given electric field direction and handedness of the helicoidal structure is determined by the sign of the flexoelectric coefficient. As e_f does not depend on the helicity of the system, the electrooptic response of the flexoelectric effect below and above the inversion temperature T_{inv} in the cholesteric twist inversion compound (S,S)-M96, should display a phase shift of 180°, being in phase with the applied electric field for a certain handedness and out of phase after its inversion [8]. This behaviour is in fact observed, as depicted in fig. 2.

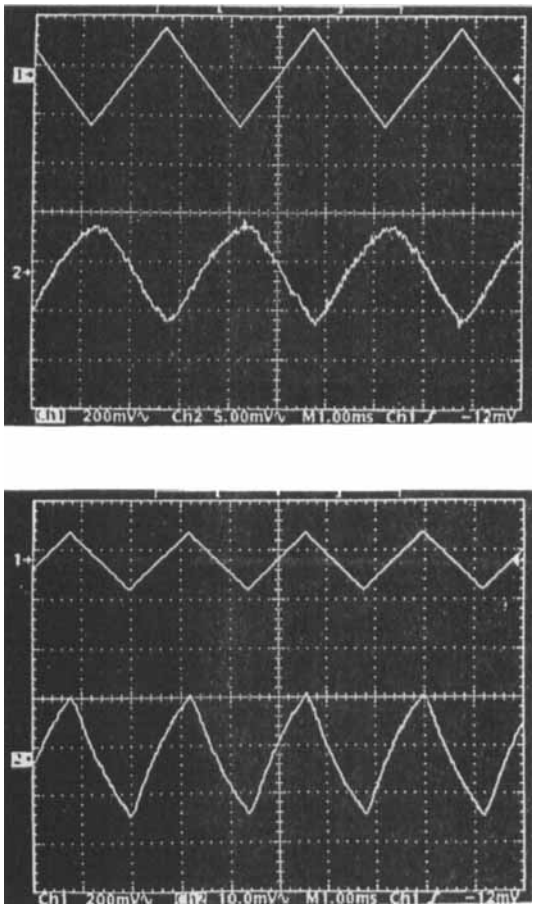


FIGURE 2 Flexoelectric response of (S,S)-M96 at T=115°C below (top) and T=155°C above (bottom) the twist inversion temperature, demonstrating the phase change of the signal when the helicoidal structure changes from left- to right-handed.

Liquid crystal phases comprised of chiral molecules exhibit the electroclinic effect, which was first reported by GAROFF and MEYER [10] in 1977 for the orthorgonal chiral smectic A (S_A^*) phase, near the transition to the smectic C* phase. Experimental data of the electroclinic effect in the chiral nematic phase [11,12] are rather rare and limited to measurements in the vicinity of the transition to the smectic phase [11-17], where the cholesteric pitch tends to diverge. Of vital importance for the observation of the N* electroclinic effect is a helix-free sample, i.e. an unwound chiral nematic. The induced deviation angles of the optical axis ϕ are very small ($\phi \leq 0.2^\circ$). The response time of the N* electroclinic effect is fast [13,14], being in the upper ns range and the electrooptic response is linear with the applied electric field, as demonstrated in fig. 3.

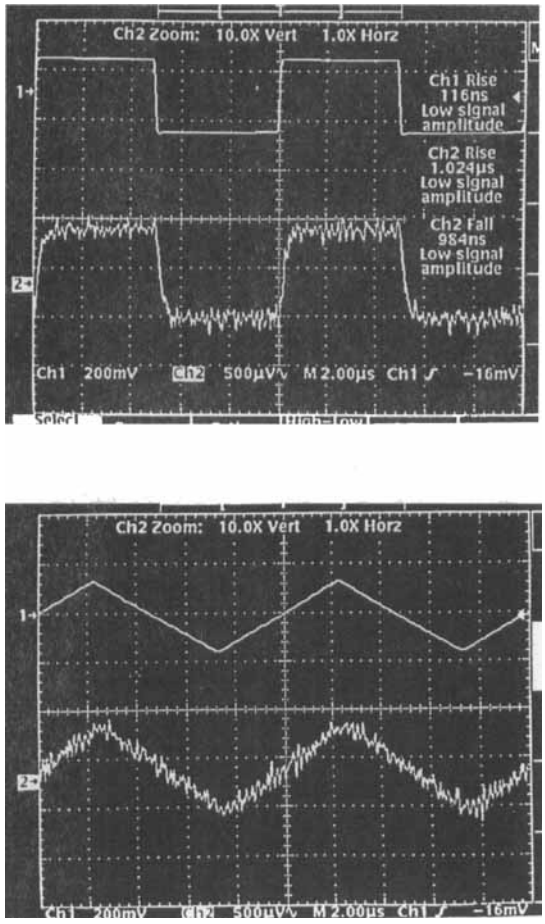
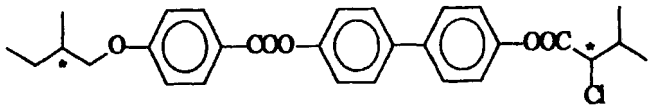


FIGURE 3 Electroclinic response of (S,S)-M96 at the twist inversion temperature T_{inv}=122°C for square wave (top) and triangular (bottom) applied electric field. The electrooptic response is linear and fast, response times being in the upper ns range (one unit of scale = 2µs).

Experimental

A benzoic acid biphenyl ester M96



was investigated for four different configurations of the two chiral centers: (S,S), (S,R), (Rac,S) and (S,Rac). The characterization and material properties of these compounds were reported and discussed elsewhere [18-20], together with the verification and an explaination of the inversion of the handedness of the cholesteric structure with temperature for the (S,S)-configured system [19]. The temperature dependence of the cholesteric pitch P was determined by the color change method [21,22]. For the electrooptic measurements, samples were placed in a polarizing microscope (Zeiss) with the temperature controlled by a Mettler FP 52 hot stage. For the application of electric fields a Leader LFG-1300 function generator in combination with an amplifier (x10) was used. The electrooptic response was detected with a photodiode detector and monitored on a Tektronix TDS 540 digital storage oscilloscope. For measurements of the fast response times of the electroclinic effect ($\tau \approx 400$ ns), the experimental setup had to be modified in a way, that the electronic equipment (amplifier, detector) did not represent the limit of resolution. For field application, a HP model 214A pulse function generator with rise time $\tau_{rise} \approx 15$ ns was used. The detector system was changed to allow the detection of rise times $\tau_{rise} < 50$ ns. Special attention should be payed to the cell preparation, as the boundary conditions essentially determine the quality of the director configuration neccessary for the respective measurements. For investigations of the flexoelectric effect for the (S,R), (Rac,S) and (S,Rac)-configured systems, shear cells were prepared with ITO electrodes and a normally evaporated SiO layer. The unidirectional lying helix texture was then obtained by shearing the sample, while applying a low frequency electric field (f≈1 kHz). For the measurements, samples of d=2 μm cell gap were used with a E=7.5 MVm^{-1} square wave electric field applied. The frequency had to be varied between 400 Hz and 7 kHz, to suppress the dielectric influence and to maintain a stable, well aligned texture for all temperatures. Due to the rather large pitch values of the (S,S)- configured system, which are naturally strongly increasing when approaching the inversion temperature, cell preparation and measuring conditions had to be adjusted to obtain unidirectionally oriented texture. For measurements of the temperature dependence of the induced tilt angle $\phi(T)$, 2 μm cells of the previous type were treated with SURFASIL, strongly promoting homeotropic boundary conditions. The electric field amplitude applied was E=0.6 MVm^{-1} at a frequency of f=200 Hz. The electric field dependence of the induced tilt angle $\phi(E)$ was determined with same conditions for different temperatures.

For measurements of the electroclinic effect of (S,S)-M96, two cells of cell gap d=2 μm and d=12 μm were used. For promoting the neccessary planar boundary conditions, a polyimide layer was brought on the substrate by spin coating and subsequent unidirectional rubbing with a velvet cloth. With this treatment an optically uniaxial unwound chiral nematic layer was obtained

within the temperature range of surface induced helix unwinding in the vicinity of the twist inversion temperature. Naturally this temperature range is enlarged for thinner cells. For temperature dependent measurements in the unwound state, an electric square wave field of E=15 MVm^{-1} and frequency f=100 kHz was used.

Due to the necessity of obtaining and maintaining well aligned samples for the two effects under investigation, some measurements had to be performed for different conditions as applied to samples they are compared with. In these cases, measured values were linearly extrapolated to the respective electric field strengths. The validity of such an extrapolation is discussed below for the respective cases.

Experimental results and discussion

The flexoelectric effect

As the flexoelectric response of the cholesteric phase with respect to the induced rotation of the optical axis (ϕ) and the switching time (τ) is strongly dependent on the pitch P (eq. (1) and (2)), the temperature dependence of the cholesteric pitch ist depicted in fig. 4 for the four configuration of M96 under investigation [19]. For reasons of comparability only absolute values are displayed, disregarding the handedness of the helical superstructure.

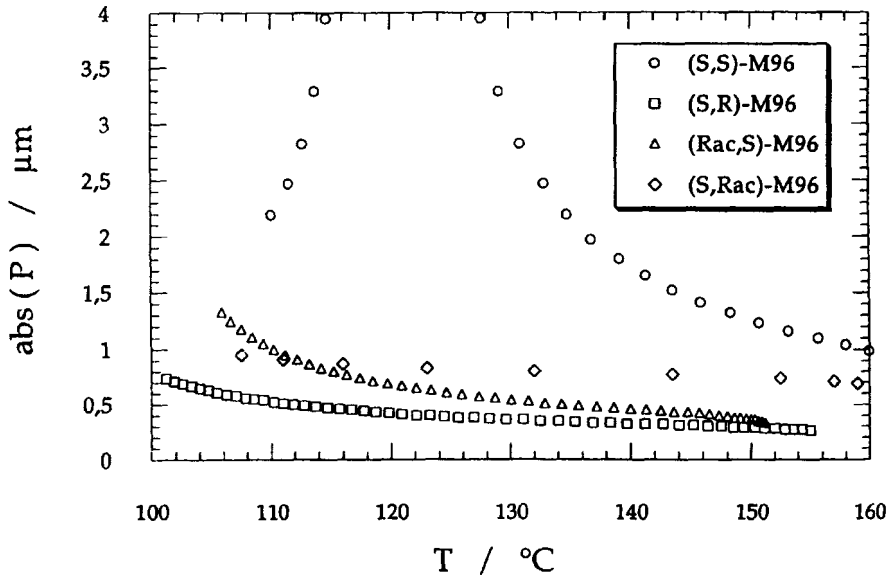


FIGURE 4 Temperature dependence of the cholesteric pitch P for the different configurations of M96 under investigation. For reasons of comparability, only absolute values are depicted.

Comparing the phase shift of the flexoelectric response and the helical screw sense, we find that the flexoelectric coefficient has the same sign for all compounds under investigation, especially, that it does not change while passing the twist inversion temperature of (S,S)-M96. Fig. 5 shows the temperature dependence of the induced deviation of the optical axis for all four configurations of M96. Note that the values for (S,S)-M96 are linearly extrapolated for an applied field strength of E=7.5 MV m^{-1}, in order to compare the tilt per unit field for all four compounds in the same diagram. In reality, such high fields destroy the ULH texture for (S,S)-M96 because of its longer pitch which gives a much lower threshold field for dielectrically unwinding the helix.

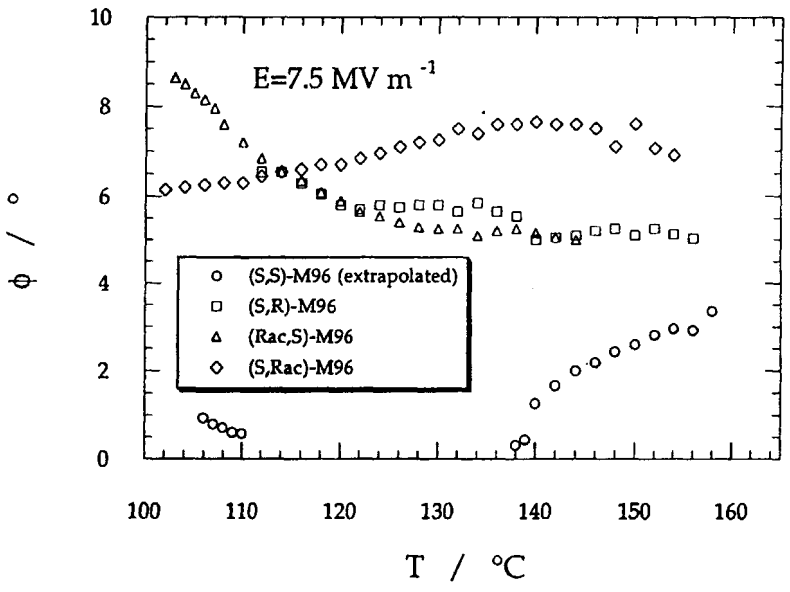


FIGURE 5 Temperature dependence of the flexoelectrically induced rotation of the optical axis for the different configurations of M96. The values for (S,S)-M96 are linearly extrapolated, to account for different experimental conditions.

In fact a linear field extrapolation is adequate for a comparison, as demonstrated in fig. 6 for (S,S)-M96 at various temperatures. There seems to be a limit for the induced tilt angle above which the tilt is no longer linear with the applied field, i.e. there is a saturation for $\phi(E) \geq 0.5°$, cf. fig. 6.

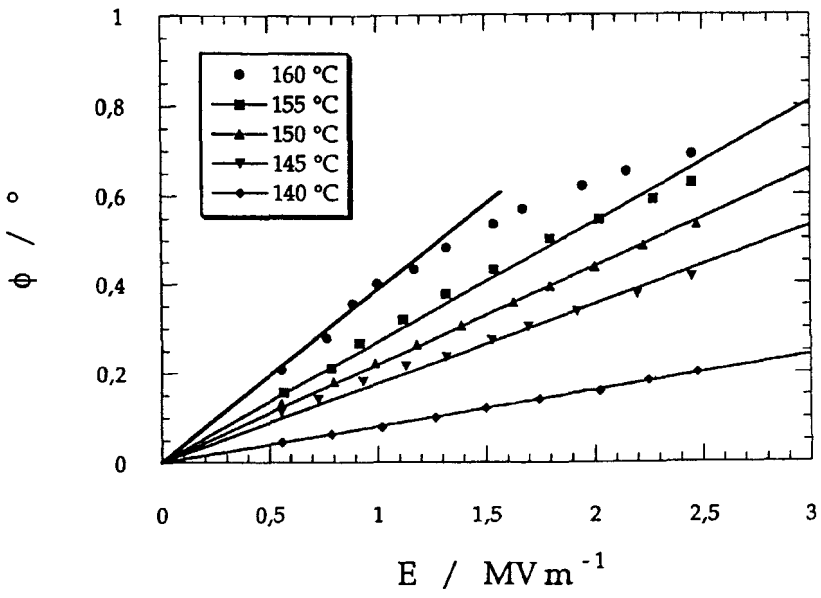


FIGURE 6 Electric field dependence of the flexoelectrically induced tilt angle for (S,S)-M96, demonstrating a linear relationship for most temperatures. Above T≈155°C a saturation behaviour can be observed.

This angle of saturation seems to be thickness dependent and will be discussed elsewhere. From fig. 5, it can be observed, that the $\phi(T)$ behaviour for the configurations (S,R)-M96 and (Rac,S)-M96 is basically governed by the temperature behaviour of the pitch, i.e. $\phi \sim P$. For (S,S)-M96, but also to some extent for (S,Rac)-M96, the situation is different and $\phi(T)$ decreases with diverging pitch, both on approaching the SmC* phase and around the twist inversion point for (S,S)- M96. However, for (S,S)-M96 and (S,Rac)-M96 the value of the pitch exeeds the cell thickness in a d=2μm cell and we can not expect the bulk theory to be strictly valid since the ULH texture should be strongly distorted when P/d>1. For (S,R)-M96 and (Rac,S)-M96 P/d≈0.5 and 0.7, respectively, while for (S,S)-M96 and (S,Rac)-M96 P/d≈1-2 and ≈1, respectively. Moreover, the longer the pitch, the less valid is the simple spatial averaging of the optical tensor making the macroscopic optical axis coincide with the helix axis and the preferred condition for utilizing the flexoelectrooptic effect is $P<\lambda$. In contrast to the temperature behaviour of the field induced deviation of the optical axis $\phi(T)$, the response time of the flexoelectric effect $\tau(T)$, which is also expected to be strongly influenced by the temperature dependence of the cholesteric pitch (eq. 2), does not exhibit any peculiarities (fig. 7).

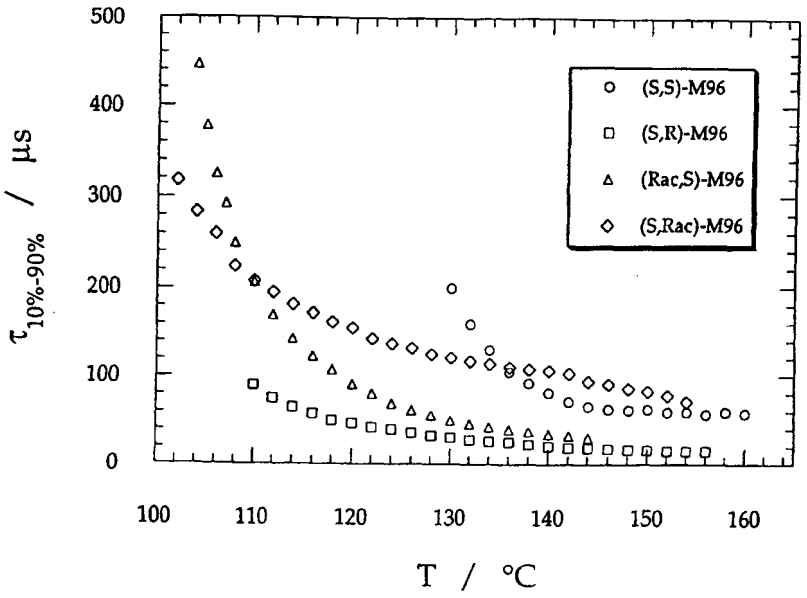


FIGURE 7 Temperature dependence of the flexoelectric response time for the different configurations of M96.

The switching time increases with increasing pitch and decreasing temperature. Even the stronger increase of the pitch for (Rac,S)-M96 as compared to (S,Rac)-M96 on approaching the transition to the smectic C* phase, can be observed from the response time measurements. The general relation of short pitch and fast switching, long pitch and slow optical response, is well reflected by fig. 7. The response times are essentially independent of the applied electric field strength, as demonstrated in fig. 8 for (S,S)-M96 at a temperature of T=150 °C. This behaviour was also observed for the other configurations at constant temperature. With response times of about 15 µs for (S,R)-M96 and induced tilt angles of $\phi \leq 10°$, a fast, linear electrooptic response with well observable transmitted light variation can be achieved.

Electroclinic effect

In the vicinity of the twist inversion temperature T_{inv} for (S,S)-M96, a temperature region can be observed, in which a non-twisted director configuration is formed by chiral molecules, if they are subjected to unidirectional planar boundary conditions. In this temperature range the electroclinic effect of the chiral nematic phase can be observed. The width of this region is dependent on the cell gap d. As the non-helical director configuration is formed for $d<P(T)/2$, its temperature region is enlarged by reduction of the cell gap. Fig. 9 depicts the linear relationship between applied electric field strength and induced tilt angle ϕ at the twist inversion temperature for two different cell gaps.

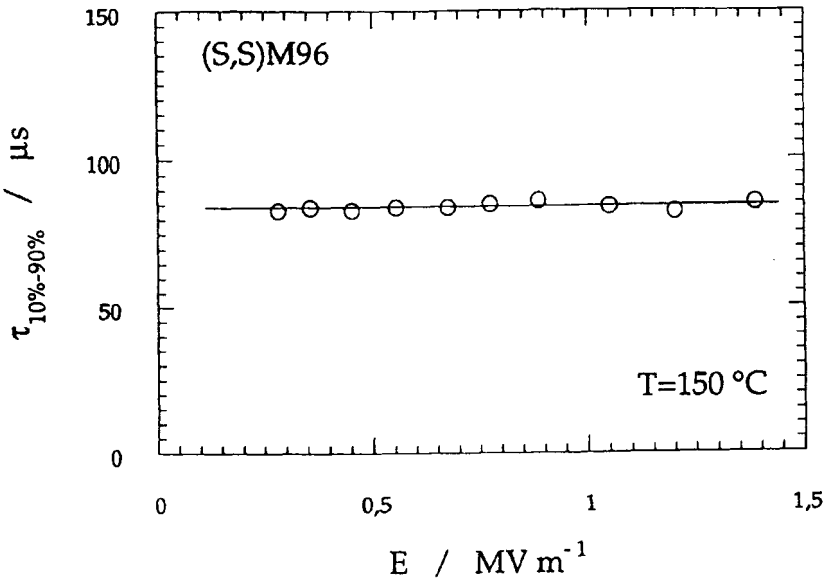


FIGURE 8 Electric field dependence of the flexoelectric response time for (S,S)-M96 at temperature T=150°C.

The induced tilt angles are about equal and independent of d. Slight deviations might be accounted for by a stronger influence of the orientation layer for thin cells, hindering the induction of the deviation of the optical axis from its position without an electric field applied. The observed behaviour gives a hint on the origin of the N* electroclinic effect as a volume effect, i.e. the driving force is of molecular character and not due to the surface. A further piece of evidence for an interpretation according to Li et al.[11,12], can be found from the fall time behaviour after pulse application. If the relaxation would be governed by a restoring torque due to liquid crystal-surface interactions, a dependence of the switching time on the cell gap should be observed, $\tau_{fall} \sim d^2$. In our investigations we observed no change of the relaxation after pulse application for cells of gap d=2,4 and 12 µm. For a cell gap of d=2 µm the temperature region of the non-twisted director configuration can be extended to about 8 K, still being well above the transition temperature to the smectic C* phase. We see that the electroclinic deflection is about two orders of magnitude smaller than the flexoelectric one and any contribution from the electroclinic effect on the flexoelectric effect is negligible in this case. In fig. 10 the temperature dependence of the induced tilt angle is depicted for the region of the non-helical state and displays a behaviour, which shows slightly decreasing values for increasing temperatures.

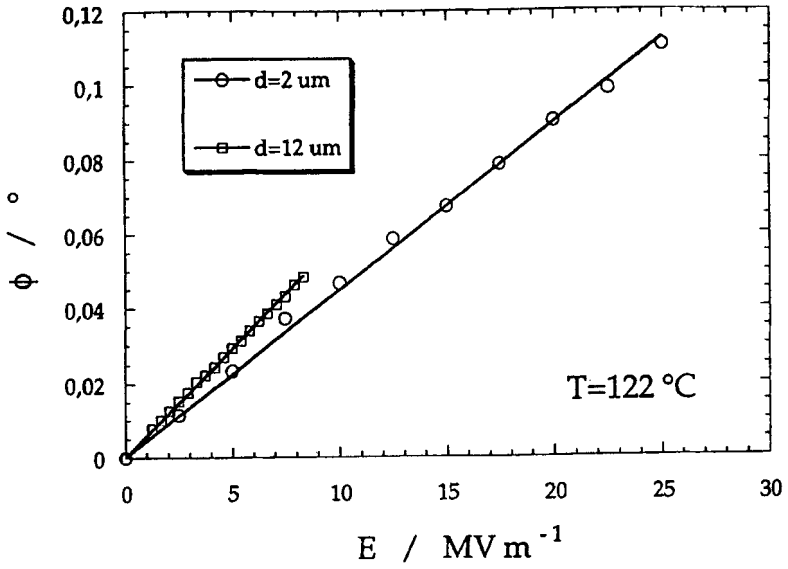


FIGURE 9 Electric field dependence of the electroclinically induced tilt angle for (S,S)-M96 at the twist inversion temperature T_{inv}=122°C for different cell gaps of d=2 and 12 μm.

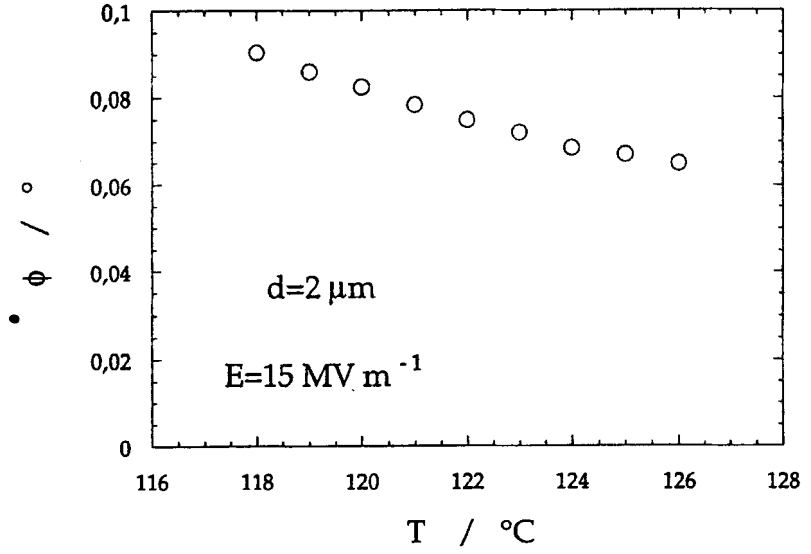


FIGURE 10 Temperature dependence of the electroclinic effect for (S,S)-M96 in the unwound chiral nematic state.

Within experimental error, the switching times in this rather narrow temperature interval are found to be independent of temperature (fig. 11). The response may be very fast, with characteristic times down to 400 ns, but the achievable light modulation is small, due to the small induced tilt.

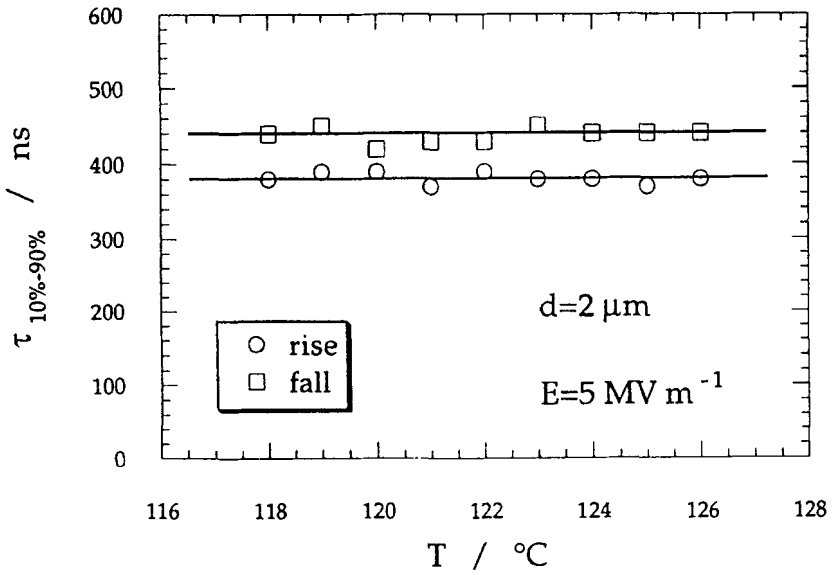


FIGURE 11 Temperature dependence of the electroclinic response time for (S,S)-M96 in the unwound chiral nematic state by pulse field application.

Conclusions

Measurements of the flexoelectric and electroclinic effect of the chiral nematic phase were presented. For a compound, which exhibits a twist inversion with temperature, we succeeded to separate both linear electrooptic effects. Fig. 12 elucidates the behaviour observed.

The induced deviation of the optical axis ϕ for the flexoelectric effect is about 50-100 times larger than the induced tilt angle due to the electroclinic effect. Hence, we do not have to consider an eventual influence from the electroclinic effect on the flexoelectric effect. On the other hand, it is not a priori clear that what we have observed as electroclinic effect might not in reality be a residue of the flexoelectric effect in the unwound state, due to present twist fluctuations in the chiral medium. Anyway this can not be excluded from symmetry. However, the dynamics of the two observed effects strongly speaks against this. Because $\tau \sim k^{-2}$ ($k=2\pi/P$) for the flexoelectric effect, the characteristic wavevectors for these twist fluctuations would have to lie at least one order of magnitude higher than corresponding to the natural pitch of the material and it is hard to see why these larger pitch values would not also dominate the fluctuations (the amplitudes going as k^{-2}). We thus conclude that the small effect observed in the unwound state is a true

electroclinic effect, rather connected to the smectic fluctuations in the material. For this reason, an observable influence of the electroclinic effect on the flexoelectric behaviour of the cholesteric phase can not be detected within experimental error. The electroclinic effect in the N* phase can only be observed for a completely unwound (P=∞) chiral nematic. In so far, twist inversion compounds represent interesting materials for experimental investigations of this effect, avoiding the vicinity of a transition into a smectic phase. Regarding the response times of the two effects under investigation, it can be concluded, that the slow flexoelectric effect of the N* phase anyway exhibits switching times, which are approaching the order of values observed for ferroelectric S_C^* materials. The induced tilt angles of $2\phi \approx 15^\circ$ allow quite reasonable modulation depth with linear electrooptic response. Achieved response times for the electroclinic effect in the cholesteric phase are by about two orders of magnitude faster, but the very small induced tilt angles limit the use for applicational devices.

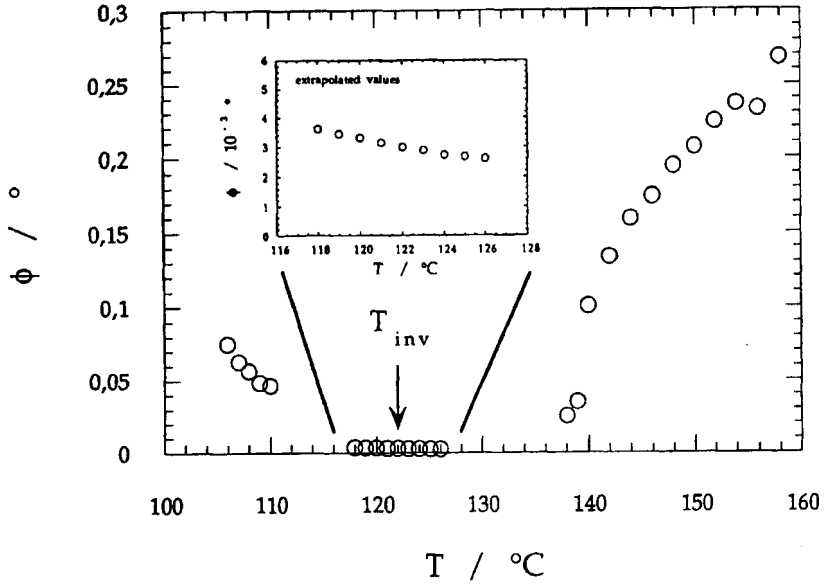


FIGURE 12 Comparison of the flexoelectrically and electroclinically induced tilt angles for (S,S)-M96. The electroclinic effect is about two orders of magnitude smaller than the flexoelectric effect, if compared for the same experimentall conditions. The values determined for the electroclinic effect (inlet) are extrapolated to applied field conditions for measurements of the flexoelectric behaviour.

Acknowledgements

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