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Optical and dielectric investigations on the electroclinic effect exhibited by a ferroelectric liquid crystal with high spontaneous polarization

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The electroclinic effect in the smectic A phase of 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxybiphenyl has been investigated. Values up to 10° are obtained for the induced tilt angle, which is proportional to the applied d.c. field. The amplitude of the tilt angle modulation shows exactly the same dependence on temperature and frequency as the dielectric constant which indicates a linear coupling between the tilt angle and the polarization. The relaxation frequency increases linearly with temperature from 0·4 MHz at the S_A–S_C^* transition to 3·5 MHz near the S_A–I clearing point. Optical switching times below 0·5 μs were established.

1. Introduction

Tilted smectic phases consisting of chiral molecules are known to show ferroelectric properties. They can be treated as pseudoproper ferroelectrics, i.e. the polarization is coupled linearly to the order parameter of the ferroelectric phase, which is the tilt angle between the director and the smectic layer normal. This leads to a spontaneous polarization, perpendicular to the director and to the layer normal in tilted smectic phases such as S_C. In orthogonal smectics such as S_A the coupling between the tilt and the polarization should result in the induction of a molecular tilt when the material is polarized by an external electric field. This electroclinic effect was found in 1977 by Garoff and Meyer [1, 2], who used it to study the pretransitional behaviour in the smectic A phase of the ferroelectric liquid crystal DOBAMBC. However, because of the weak coupling between tilt and polarization in DOBAMBC the effects are small and no further investigations on this subject have been performed.

Recently new ferroelectric liquid crystals have been prepared which show a spontaneous polarization two orders of magnitude higher than that of DOBAMBC [3, 4], i.e. the tilt–polarization coupling constant is in the range of 10 nC/cm^2 per degree tilt angle compared to 0·15 nC/cm^2 per degree tilt angle in DOBAMBC. Thus, it seemed of interest to study the electroclinic effect in the smectic A phase of such materials.

2. Experimental

The compound studied was 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxybiphenyl with its structural formula

The substance exhibits smectic A, C*, G and H phases: C 72°C (S_H 64°C S_G 71°C) S_C^* 73·4°C S_A 81·6°C I. The spontaneous polarization in the S_C^* phase is in the range 80 nC/cm^2 to 150 nC/cm^2 [4].

The sample was placed in a glass cell (thickness 9 μm and 14 μm) with a planar orientation (i.e. in the bookshelf geometry, as for the usual SSFLC devices [5]). This allows an electric field to be applied parallel to the smectic layers thus inducing a tilt perpendicular to the electric field vector.

The induced tilt angle was measured optically with a Leitz Lux Pol polarization microscope and an RCA 1P28 photomultiplier. Two methods were used: a static method applying a large d.c. field at constant temperature and a modulation method applying a small a.c. field in order to measure the temperature and frequency dependence of the effect.

2.1. *Static method*

The sample was rotated between crossed polarizers while the intensity of transmitted light was measured by the photomultiplier. The signal voltage of the multiplier varies as $\sin^2(2\varphi)$ where φ is the angle between the director (i.e. the optical axis) of the liquid crystal and the polarization direction of one of the polarizers. When a d.c. electric field is applied the phase of the curve is shifted by the amount of the induced tilt angle. For the determination of the tilt angle the transmission curves for both positive and negative d.c. voltages were recorded, the phase shift between the curves corresponding to twice the amount of induced tilt (cf. figure 1).

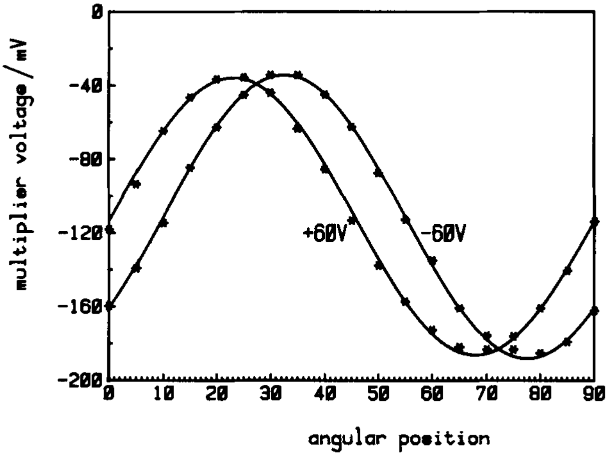

Figure 1. Photomultiplier voltage (corresponding to the transmission of the sample) versus the angular position of the cell between crossed polarizers kept at fixed position. The phase shift between the curves obtained with + 60 V and − 60 V applied at the 9 μm thick sample is equal to twice the amount of the induced tilt angle.

2.2. *Modulation method*

The temperature and frequency dependence of the field induced tilt was determined by a modulation method which also allows us to measure, simultaneously, the dielectric constant. For this the cell was connected to a Hewlett-Packard 4192 LF impedance analyser, which provides a voltage of 1 V in the frequency range from 100 Hz to 13 MHz. The sample was rotated in a position where the angle between the smectic layer normal (i.e. the director at zero field) and the polarization direction of one of the polarizers was equal to 22·5°. In this position the signal voltage of the multiplier varies nearly linearly with the induced tilt angle. The temperature dependence of the effect was investigated at a frequency of 1 kHz allowing us to use a PAR 126 lock-in amplifier for sensitive detection of the multiplier signal, which is proportional to the optical modulation. The temperature was varied at a constant rate of 0·1 K/min and the values of the lock-in signal voltage, the capacitance of the cell and the temperature were stored every 10 s on a Hewlett-Packard 85 computer as described in [6]. The frequency dependence of the optical modulation amplitude was determined by measuring the multiplier signal with a Gould 4050 digital storage oscilloscope using the average mode facility provided by the wave-form processor Gould 135.

3. Results

To analyse the experimental results a linear coupling between the polarization P and the tilt angle θ is assumed [1, 2],

$$P = \kappa\theta. \tag{1}$$

The smectic A phase of a chiral compound exhibits an additional contribution (the soft mode contribution) to the dielectric constant, as compared to the corresponding racemate [7]. Thus, the amount of the polarization which is coupled to the induced tilt angle is given by

$$P = (\varepsilon_\perp^* - \varepsilon_\perp^0)\,\varepsilon_0 E. \tag{2}$$

Here $\varepsilon_\perp^*$ is the dielectric constant of the optically active compound, $\varepsilon_\perp^0$ is the dielectric constant of the corresponding racemate, ε_0 is the vacuum permittivity and E the strength of the applied electric field. In consequence, a simple proportionality between the induced tilt angle and the applied field strength is expected:

$$\theta = \frac{(\varepsilon_\perp^* - \varepsilon_\perp^0)}{\kappa}\,\varepsilon_0 E \tag{3}$$

As figure 2 shows, this relationship is clearly established by the experimental results obtained for the compound under investigation. The slopes of the θ versus E curves

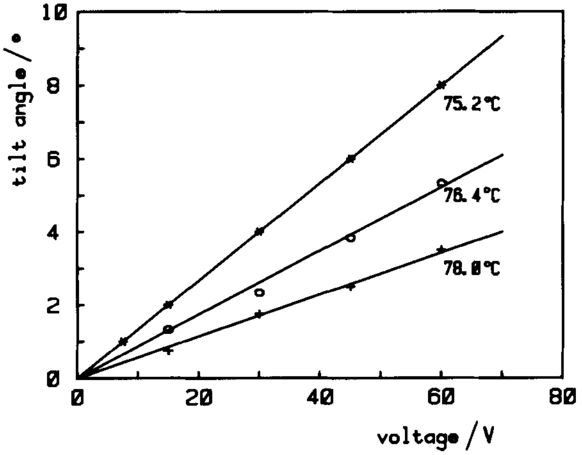

Figure 2. Induced tilt angle versus d.c. field at different temperatures (cell thickness 9 μm).

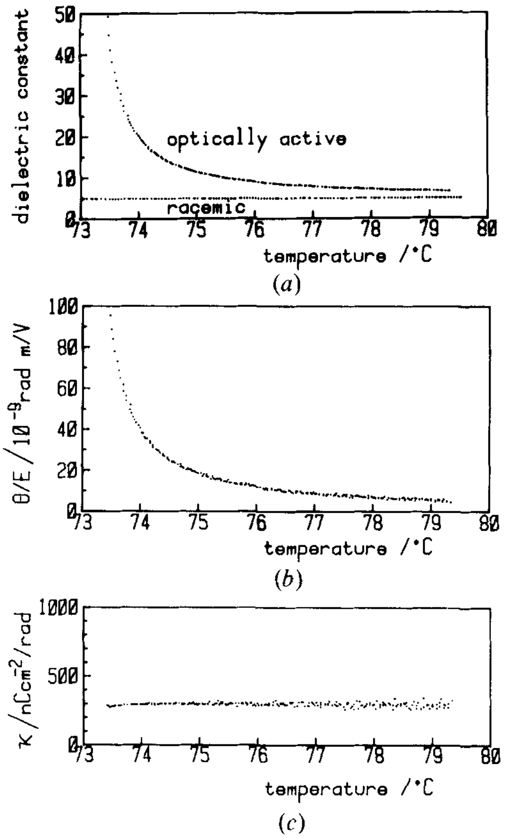

Figure 3. (*a*) Temperature dependence of the dielectric constant of the optically active compound and the racemate. (*b*) Temperature dependence of the electroclinic effect θ/E. (*c*) Plot of the ratio between $(\varepsilon_{\perp}^{*} - \varepsilon_{\perp}^{0})\,\varepsilon_0$ and θ/E $(=\kappa)$ versus temperature.

increase when the temperature approaches the S_A–S_C^* transition, a behaviour, which is also to be observed in the temperature dependence of the dielectric constant [6]. In figure 3 the temperature dependence of the dielectric constant $\varepsilon_{\perp}$ of the optically active compound and the corresponding racemate are given and compared with the electroclinic coefficient θ/E measured simultaneously by the lock-in method (see § 2). The ratio between $(\varepsilon_{\perp}^{*} - \varepsilon_{\perp}^{0})$ and θ/E, which (multiplied by ε_0) is plotted in figure 3 (*c*), shows almost no temperature dependence. This demonstrates that the coupling constant κ,

$$\kappa = \frac{(\varepsilon_{\perp}^{*} - \varepsilon_{\perp}^{0})}{\theta/E}\,\varepsilon_0 = \frac{P}{\theta}, \tag{4}$$

is temperature independent in the S_A phase as is usually assumed when applying Landau theory to the S_A–S_C^* transition. As shown recently for the same compound, the inverse of $(\varepsilon_{\perp}^{*} - \varepsilon_{\perp}^{0})$ varies nearly linearly with temperature [6]. When plotting the inverse of the electroclinic coefficient θ/E versus temperature, the corresponding critical behaviour is obtained giving a critical exponent equal to 1 within the limit of the experimental accuracy [8].

The coupling constant $\kappa = 300\,\mathrm{nC\,cm^{-2}/rad}$ as determined in the S_A phase (cf. figure 3 (*c*)) can be compared with the ratio between the spontaneous polarization and the tilt angle in the S_C^* phase. Using the values of the tilt angle obtained by X-ray measurements and the spontaneous polarization values determined with a Diamant bridge [9], a ratio of 440 nC cm^{-2}/rad is calculated. However, from this observation an increase of the coupling constant when passing the transition from the S_A to the S_C^* phase cannot be concluded definitely so far because both values are based on different methods of tilt angle measurement. Obviously, further investigations of this point are required.

The dielectric constant is found to depend on frequency according to a simple Debye law, indicating that only a single relaxation mechanism is involved. At frequencies above 10 MHz the value found at low frequency for the racemate is approached. As shown in figure 4, the amplitude of the electroclinic effect exhibits almost the same frequency dependence. This, as well as the measurements of the temperature dependence, clearly demonstrates that the described behaviour of the dielectric and optical properties is caused by the same physical phenomenon, i.e. the modulation of the tilt magnitude corresponding to the soft mode.

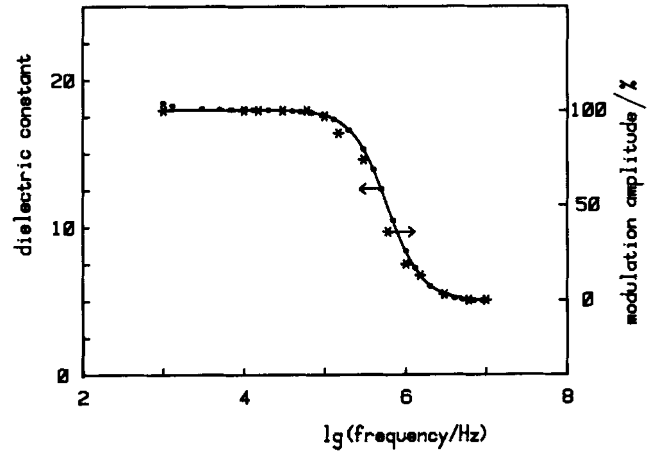

Figure 4. Frequency dependence of the optical modulation amplitude (crosses, right-hand scale) and the dielectric constant (small dots, left-hand scale) measured simultaneously. The solid line is calculated according to the relation

$$\varepsilon = \varepsilon(hf) + \frac{\varepsilon(lf) - \varepsilon(hf)}{1 + (f/f_{1/2})^2},$$

assuming a single Debye relaxation.

The relaxation frequencies determined by the dielectric measurements vary linearly with temperature. As figure 5 shows, the values decrease from 3·3 MHz at 2 K below the S_A–I clearing temperature to a limited value of about 0·4 MHz at the S_A–S_C^* transition. Such behaviour is in accord with theoretical predictions concerning the soft mode contribution to the dielectric constant [10–12].

The electroclinic effect with ferroelectric compounds exhibiting high spontaneous polarization shows promising features for electro-optical applications. The difference in the electro-optical response of the same material in its chiral smectic C and smectic A phases is demonstrated in figure 6: for the S_C^* phase application of a 1 kHz sine-voltage leads to a switching between two states, whereas in the S_A phase the transmission of the cell follows exactly the applied voltage. The high values of the relaxation frequency should permit optical switching times below 500 ns, which could

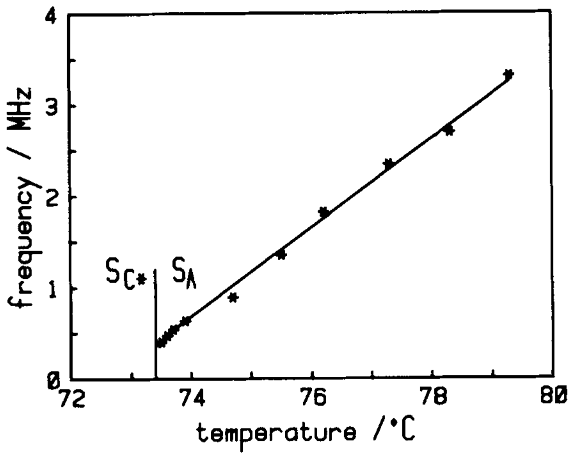

Figure 5. Temperature dependence of the relaxation frequency.

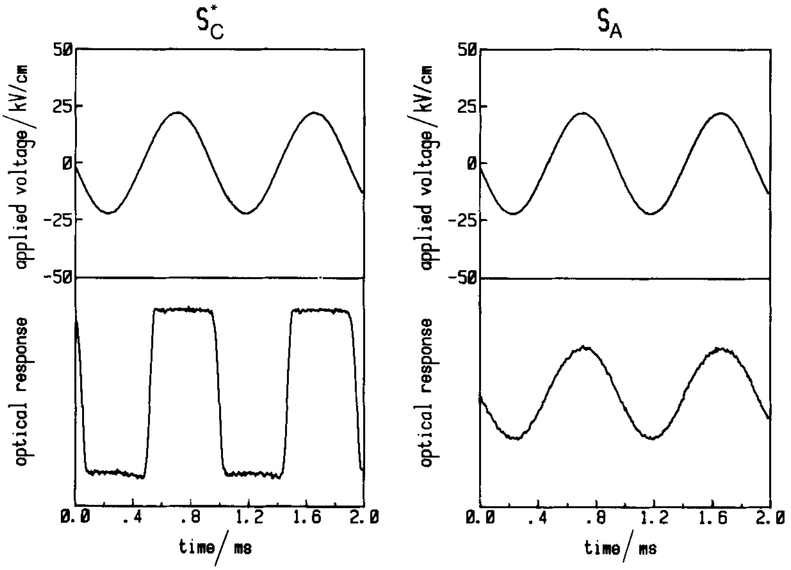

Figure 6. Electro-optic response in the S_C^* and S_A phase of the compound under investigation.

indeed be observed experimentally. Thus, the electroclinic effect can be used in fast modulator devices.

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