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Viscoelastic director rotation of a low molecular mass liquid crystal

A. JÁKLI* and A. SAUPE

Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

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We show evidence for a viscoelastic rotation of the spontaneous polarization in a low molecular mass chiral ferroelectric smectic liquid crystal (SmC*). A weak elastic modulus of $\sim 10^2$ Pa is sufficient to cause a unique effect: the polarization turns perpendicular to sufficiently strong a.c. electric fields. Viscoelasticity is unusual for low molecular mass materials. We suggest that it is connected to the anisotropy of the positional order. This is an inherent property of liquid crystals, but has never been taken into account in macroscopic descriptions.

1. Introduction

Our earlier studies on SmC* liquid crystal films with quasi-antiferroelectric arrangements [1] showed that under a.c. electric fields the electric polarization may turn perpendicular to the electric field. The threshold field for the transition increases strongly in the kHz frequency range indicating that the effect cannot be attributed to a proper dielectric relaxation. Although the interplay of strong symmetric boundary conditions and the nematic-like curvature elasticity can give rise to splayed states with polarization partially parallel to the surfaces, for materials with low polarization such a state could be present only in the ground state [2]. Under strong fields the electric polarization usually follows the electric field direction, so a uniform director structure forms. Our observations indicate just the opposite situation: the director field is uniform in the ground state and becomes splayed under strong electric fields.

In this paper we give a detailed description of the a.c. field-induced reorientation process and consider different models for explanation. We show that the observations are caused by a viscoelastic director rotation. This result is surprising, because no corresponding viscoelasticity has been observed in low molecular mass materials.

2. Experimental

We prepared 5 μm thick films with unidirectionally rubbed polyimide coatings using the mixture ZLI-4237-000 (E. Merck). It has a ferroelectric SmC* phase between −20 and 63°C, and a long helical pitch (> 40 μm) over the whole SmC* range. At room temperature the director tilt angle is $\theta = 26°$ and the spontaneous polarization is $\mathbf{P}_0 = 7$ nC cm^{-2}. We studied the textures, the linear electromechanical responses [3] and the complex impedance under various electric fields at room temperature.

On cooling the samples to room temperature, a bookshelf texture appeared, consisting of 50 μm wide stripes parallel to the rubbing direction [1]. In the subsequent stripes the polarization alternated between nearly up and down directions (see figure 1). At zero fields the extinction directions made angles $\alpha = \pm 5°$ to the rubbing

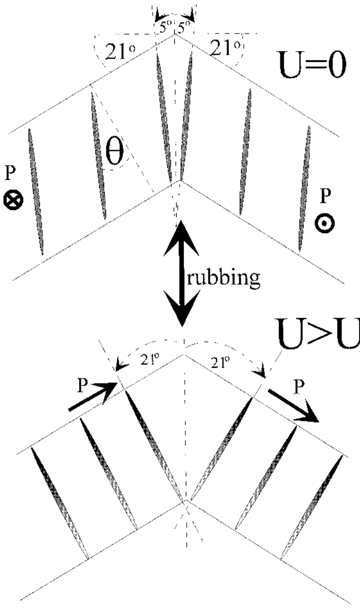

Figure 1. Sketch of the director and layer structures in the equilibrium ground state and under sufficiently fast and strong periodic voltages. Shading of the molecules indicates director tilt with respect to the plane of the page (darker parts are further away from the reader).

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*Author for correspondence; e-mail: jakli@lci.kent.edu

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direction. When a.c. voltages of $f > 50$ Hz and $U > U_{th}(f)$ were applied, the extinction directions became $\alpha = \pm 21°$ directions in a few ms. The frequency dependence of U_{th} is shown in figure 2. After removing the voltage the polarization relaxed to the original position in $\tau = 12$ ms.

Vibrations of the cover-glass plate with the frequency of the field were monitored both parallel (Y) and perpendicular (X) to the glass plates. Voltage dependences of the displacement s_Y and s_X are shown in figure 3. The vibration perpendicular to the plates is connected with the electroclinic effect and is strongest when the polarization is parallel to the fields [3]. A vibration along the plates is due to the coupling between the rotation of the electric polarization and flow [3]. For small fields $s_Y \propto \sin \psi_0$ and $s_X \propto \cos \psi_0$ where ψ_0 is the angle between the electric field and the average direction of the polarization. In figure 4 we plot $\sin \psi_0(U)$ as calculated from $s_Y(U)$. It shows that the change in extinction direction observed optically corresponds to a reorientation of the polarization from a nearly vertical to a horizontal direction.

Voltage dependences of the complex impedance also show distinct changes at U_{th}: the capacitance increases, whereas the resistance decreases when the reorientation occurs (see figure 5).

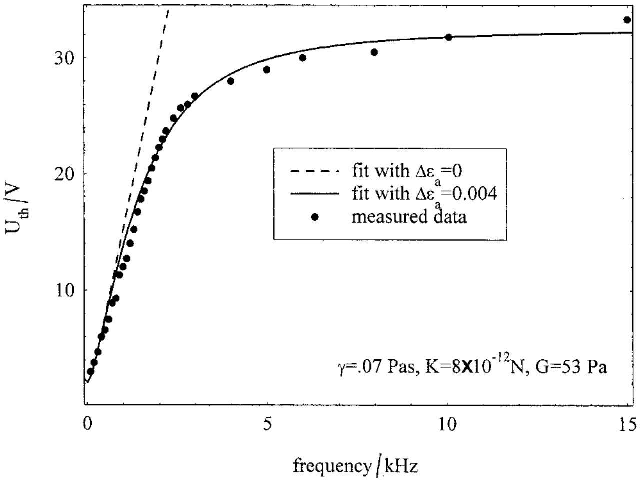

Figure 2. Frequency dependence of the threshold voltage U_{th} for the a.c. field-induced director reorientation process: ● = data determined by polarizing microscopy; solid line = fit with $\Delta\varepsilon_a = 0.004$; dashed line = fit with $\Delta\varepsilon_a = 0$.

3. Theory

The frequency dependence of the threshold voltage indicates that (at least below a few kHz), the electroclinic effect and the dielectric anisotropy do not play an important role in the reorientation process. The in-plane dielectric anisotropy contains terms arising only from differences in molecular rotations, and is not supposed to have significant frequency dependence below a few MHz. Similarly, the contribution of electroclinic $\Delta\varepsilon_{ec}$ is constant below a few hundred kHz.

There remains to consider the contribution from the rotation of the director with constant tilt angle, i.e. the rotation of the spontaneous polarization $\mathbf{P}_0$. As the width of the stripes is much larger than the sample thickness we take into account only one stripe, i.e. a uniform texture. We assume that at the threshold the amplitude of the oscillation ψ_1 is smaller than $\psi_0 \sim 5°$. The coupling between the director rotation and flow (backflow) is neglected, as are the inertial terms. The electric conductivity and its anisotropy are not considered here†. The electric field inside the sample is

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† The calculations were also carried out by incorporating the anisotropy of the conductivity, but this does not alter the main conclusions we draw here.

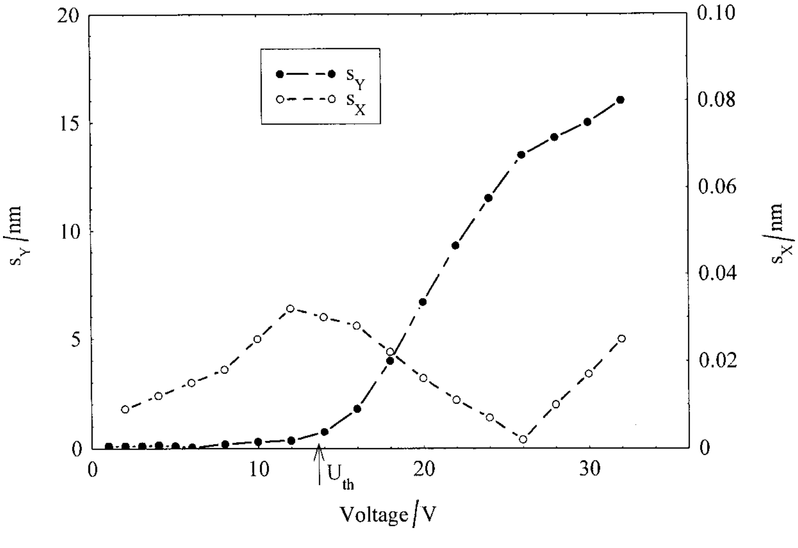

Figure 3. Electric field-induced displacement of the cover-glass plate parallel (s_Y) and perpendicular (s_X) to the glass plates at $f = 700$ Hz. Measurements were carried out using piezoelectric accelerometers from Bruel & Kjaer.

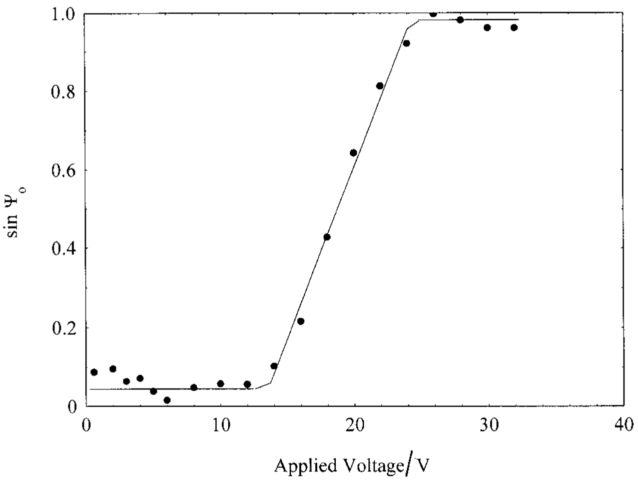

Figure 4. Voltage dependence of sin ψ_0 as calculated from the voltage dependence of s_Y shown in figure 3.

constant and periodic: $\mathbf{E}(t) = \mathbf{E}_0 \sin(\omega t)$. Assuming that the rotation of the polarization is purely viscous and the sample reacts as a uniform slab, the torque balance equation reads $\mathbf{P}_0\mathbf{E}\sin\psi = -\gamma\dot{\psi}$ (γ is the rotational viscosity). This gives to the first order that

$$\psi_1(t) \approx \frac{2\mathbf{P}_0\mathbf{E}_0}{\omega\gamma}\sin\psi_0\cos(\omega t)$$

consequently the time average of the ferroelectric torque $\Gamma_{\mathrm{FE}} = \mathbf{P}_0\langle \mathbf{E}(t)\sin\psi(t)\rangle = 0$ and ψ_0 remains constant.

Next we consider viscoelastic [4] director rotation. A viscoelastic rotation can be described by a complex rotational viscosity $\gamma = \gamma' + \mathrm{i}\gamma''$. For an ideal fluid $\gamma = \gamma'$ is real, whereas for an elastic material $\gamma = \gamma''$ is purely imaginary and $\gamma'' = G/\omega$, where G is the elastic modulus. From the torque balance equation in the limit of small fields we obtain

$$\psi_1(t) = -\mathbf{P}_0\mathbf{E}_0\sin\psi_0\frac{\gamma''\sin(\omega t) - \gamma'\cos(\omega t)}{\omega(\gamma'^2 + \gamma''^2)}. \qquad (1)$$

This gives that the time average of the ferroelectric torque is

$$\Gamma_{\mathrm{FE}} = -\frac{1}{4}\frac{(\mathbf{P}_0\mathbf{E}_0)^2\sin(2\psi_0)}{G}\frac{1}{1+(\tau\omega)^2}. \qquad (2)$$

Here $\tau = \gamma'/G$ is the relaxation time from the viscoelastic deformation. Γ_{FE} derives the polarization away from the equilibrium position. It has maximum when $\psi_0 = 45°$, and reduces to zero as ψ_0 reaches 90°. The dielectric torque is $\Gamma_{\mathrm{DI}} = -1/2\Delta\varepsilon_{\mathrm{a}}\mathbf{E}_0^2$, where $\Delta\varepsilon_{\mathrm{a}}$ is the in-plane dielectric anisotropy. As the polarization rotates away from its original direction a director deformation occurs due to the strong anchoring at the surfaces. This builds up an elastic torque $\Gamma_{\mathrm{EL}} = 1/2Kq^2$, where K is the curvature elastic constant and q is the wave number of the curvature. At the threshold $q = \pi/d$ (d is the sample thickness) and the threshold field is:

$$\mathbf{E}_{\mathrm{th}} = \frac{\pi}{d}\left[\frac{K}{\Delta\varepsilon_{\mathrm{a}} + \dfrac{\mathbf{P}_0^2\sin 2\psi_0}{2G}\dfrac{1}{1+(\tau\omega)^2}}\right]^{1/2}. \qquad (3)$$

This equation shows that the threshold voltage $U_{\mathrm{th}} = \mathbf{E}_{\mathrm{th}}d$ is independent of the sample thickness, just as for the so-called Fréedericksz transition in nematics. We note that Fréedericksz-type transitions were predicted theoretically for antiferroelectric cells of moderate thickness [5] and were recently observed experimentally [6] on antiferroelectric smectic phases of achiral banana-shaped molecules [7].

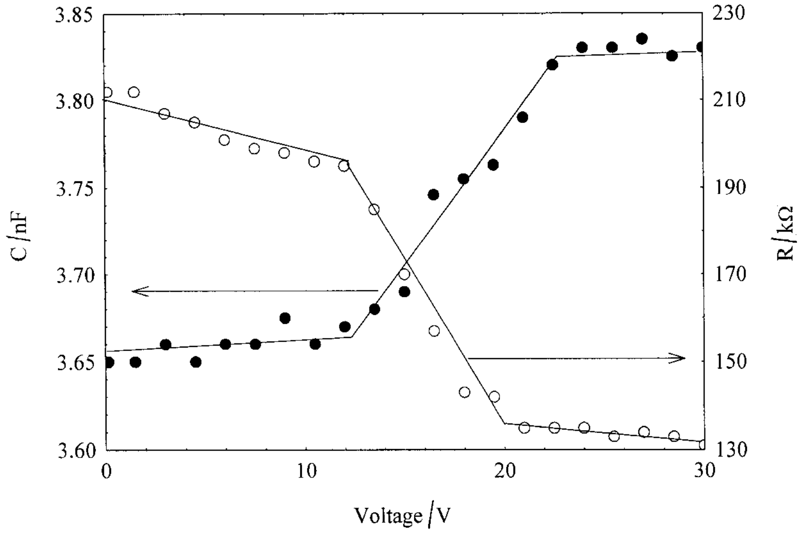

Figure 5. Voltage dependence of the capacitance (C) and the resistance (R) at $f = 700$ Hz as measured by a HP 4824A impedance analyser.

Knowing $\mathbf{P}_0$, ψ_0 and assuming that G is constant (this is valid only at sufficiently high frequencies), equation (3) gives an excellent fit to the measured frequency dependence of the threshold voltage. Taking the value for viscosity from Merck data ($\gamma = 0.07$ Pa s) the best fit gives $K = 8 \times 10^{-12}$ N, which is typical for conventional SmC* materials. For the in-plane dielectric anisotropy we obtain $\Delta\varepsilon_a = 0.004\varepsilon_0$. It is very small, but becomes important at high frequencies. This can be seen on the dashed line of figure 2, which corresponds to the parameters of the best fit but with $\Delta\varepsilon_a = 0$. We see therefore that at low frequencies ($f < 2$ kHz) the viscoelastic rotation of the permanent polarization is responsible for the observed director reorientation, whereas above 5 kHz it is due to the small positive in-plane dielectric anisotropy. For the elastic constant associated with the viscoelastic director rotation the best-fit gives $G = 53$ Pa. This is comparable to dilute polymer solutions of liquids [8], and is about three orders of magnitude smaller than the elastic constant associated with the distortion of the antiferroelectric order in banana-shaped liquid crystals [9].

The contribution of a viscoelastic rotation of the spontaneous polarization to the capacitance of the cell can be expressed as

$$C_P = \left|\frac{\Omega \Delta P}{dU}\right|$$

where U is the applied voltage, $\Omega \sim 5\,\mathrm{cm}^2$ is the sample area and

$$\Delta P \cong P_0 \psi_1 \sin\psi_0 = \mathbf{P}_0^2 \mathbf{E}_0 \frac{\sin^2\psi_0[\gamma'' \sin(\omega t) + \gamma' \cos(\omega t)]}{\omega(\gamma'^2 + \gamma''^2)}$$

is the contribution of the rotation of the polarization to the surface charge density. This gives

$$\Delta C_P = \mathbf{P}_0^2 \frac{\gamma'' \sin^2\psi_0}{\omega(\gamma'^2 + \gamma''^2)}.$$

Substituting here the parameters obtained from the fit shown in figure 3, we obtain reasonably good agreement with the experimentally observed increment in the capacitance (see figure 4). We can also calculate the angle and frequency dependence of the resistance $\Delta R = U/I_R$, where $I_R = \mathrm{d}\mathbf{P}/\mathrm{d}t$ is the polarization current in-phase with the voltage U. Using the expression for $\Delta\mathbf{P}$ we obtain

$$\Delta R = \frac{Gd[1 + (\tau\omega)^2]}{\Omega \mathbf{P}_0^2 \gamma \omega^2 \sin^2\psi_0}.$$

Experimentally we observed that above a few kHz ΔR was independent of the frequency, below it decreased. This is in accordance with the calculated $\Delta R(\omega)$.

4. Discussion

The calculations presented above clearly show that all the experimental observations can be consistently explained by the concept that the rotation of the spontaneous polarization is viscoelastic. We note that in the liquid crystal literature the expression 'viscoelasticity' is often used just to refer to the combination of the curvature elasticity and viscous director rotations. This is different from our case.

Although, to our knowledge, viscoelastic director rotations have never been observed in low molecular mass materials, viscoelasticity is an inherent property of liquid crystals. Due to the anisotropic shape of the molecules and the long range orientation order, the pair correlation function is anisotropic.

In SmC materials the macroscopic director tilt ordering breaks the rotational symmetry about the layer normal [10] and the distribution of the centre of masses is anisotropic along the smectic layers. The orientation order of vectors connecting the nearest neighbour molecules determines the bond order. This is strongly coupled with the tilt direction of the molecules, which determines the *c*-director. As the *c*-director rotates during switching the direction of the bond order rotates, too. They however have a different dynamics, resulting in a small phase difference between the direction of the bond order and the *c*-director. This leads to the viscoelastic nature of the director rotation and may account for the unique effect, that the polarization turns perpendicular to a sufficiently strong and fast electric field.

The phase difference between the direction of the bond order and the *c*-director has not yet been considered in current theories of the rotational viscosities of SmC* phases [11]. We suggest that the incorporation of this into continuum theories would lead to a complex rotation viscosity, i.e. to viscoelastic rotation of the spontaneous polarization.

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