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Electromechanical Effects in Ferroelectric Liquid Crystalline Polymers

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ABSTRACT

Electric fields can induce mechanical vibrations in planar aligned sandwich cells of ferroelectric liquid crystals. Measurements on a polysiloxane and a polyacrylate side chain polymer proved that the electromechanical effect also exists in ferroelectric liquid crystalline polymers. The main characteristics of the electromechanical responses of these polymers are described and compared to the response of low molecular weight ferroelectric liquid crystals. According to the proposed interpretation, the vibrations in the direction parallel to both the smectic layers and cell substrates are due to coupling between the director rotation and the flow, while the resonances in the vibrations normal to the plates are connected to layer deformations.

KEYWORDS: Electromechanical effect, Ferroelectric liquid crystal, Polymeric liquid crystals

INTRODUCTION

The influence of an electric field on liquid crystals is primarily manifested in changing the orientation of the director and hence the optical properties (e.g., birefringence) of the cell. However, the reorientation of the director is coupled to a viscous flow (e.g., the "backflow" effect in nematics [1]) and in smectics the field may induce layer compressions, which means true piezoelectricity (e.g., the electroclinic effect in the S_A^* phase [2]). In certain geometries either the flow or the layer compression may result in mechanical displacement or vibration of the cell substrates. These phenomena are called electromechanical effects. The inverse of these effects can also occur, i.e., mechanical deformations or flow may induce an electric polarization or current. These are called mechanoelectrical effects. In the majority of liquid crystalline phases these phenomena are expected to be mainly nonlinear, due to the quadratic interaction between the electric field and the induced polarization of the substance. Only flexoelectricity seems to allow some exceptions to this rule [3].

In ferroelectric liquid crystals (FLC), however, the interaction between their spontaneous polarization and the electric field is linear, so that they are sensitive to the polarity of the applied electric field [4] and, as a consequence, they may exhibit various linear electro-optic [5] and electromechanical effects [6]. The shear flow induced electric polarization, i.e., a mechanoelectrical effect, has also been observed in homeotropically aligned [7] as well as in planar S_C^* samples [8].

The electromechanical effects have been widely studied in low molecular weight (LMW) ferroelectric liquid crystals since 1985. These measurements were performed by detecting the a.c. electric field induced mechanical vibrations of the substrates of FLC cells in a geometry where one of the glass plates could move freely with respect to the other one [6, 9–12, 13], and recently in a hermetically sealed surface stabilized FLC cell also [14].

The electromechanical responses were measured both at the fundamental frequencies (the linear effect

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[10, 11]) and at the double frequencies (the quadratic effect [12]). For low voltages the linear effect was proportional to the applied voltage, while the quadratic effect was proportional to the square of it. At higher voltages, when the field caused a considerable distortion of the director configuration, deviations from these proportionalities were observed [12]. The linear response at low voltages followed the temperature dependence of the helical pitch, while the quadratic effect had a maximum at the S_A–S_C^* phase transition. At low frequencies (typically below 1 kHz) the electric field induced motion took place inside the smectic layer, parallel to the substrates, while at higher frequencies the vibration also had a normal component, which exhibited resonance-like maxima [9].

Ferroelectric liquid crystalline polymers (FLCP) are similar to low molecular weight FLC substances in many respects; for example, they may exhibit similar linear electro-optic responses. This leads to the assumption that linear electromechanical and mechanoelectrical effects can also appear in FLCP.

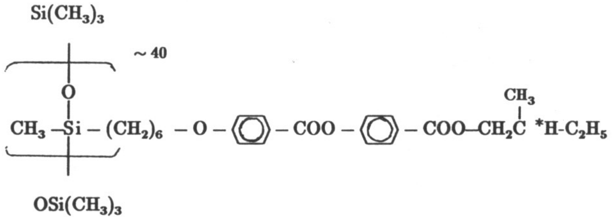
It was recently shown by Meier [15] and Vallerien [16], and explained by Brand [17], that mechanical stresses can induce electrical polarization in liquid crystalline elastomers (where the polymer molecules are crosslinked). According to our definition this is a mechanoelectrical effect.

In this paper we summarize the outcome of the electromechanical investigations on side chain ferroelectric liquid crystalline polymers. The measurements were performed on a room-temperature FLCP with small polarization by Jákli [18, 19] and on a high-temperature FLCP with relatively high polarization by Éber [20]. The experimental results are compared with those on LMW substances.

EXPERIMENTAL

The measurements were carried out using two different side chain polymeric compounds, A and B.

Compound A was a polysiloxane material (LCP1) from BDH:

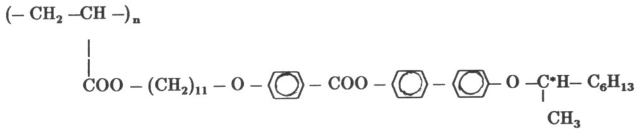


Its phase sequence is the following:

$$\text{Glass} \underset{-11^\circ\text{C}}{\leftrightarrow} S_C^* \underset{69\text{–}79^\circ\text{C}}{\leftrightarrow} \text{I}$$

LCP1 has a relatively small spontaneous polarisation, $P_s = 4 \times 10^{-5}$ C/m^2. Electro-optic effects are not observable in the applied voltage interval of 0–40 V.

Compound B was a polyacrylate side chain polymer [21], having $M_W = 15\ 000$:



The phase sequence of sample B is:

$$\text{Glass} \underset{\sim 50^\circ\text{C}}{\leftrightarrow} S_B^* \underset{\sim 92^\circ\text{C}}{\leftrightarrow} S_X^* \underset{\sim 125^\circ\text{C}}{\leftrightarrow} S_C^* \underset{\sim 142^\circ\text{C}}{\leftrightarrow} S_A^* \underset{\sim 151^\circ\text{C}}{\leftrightarrow} \text{I}$$

As for sample A the phase transitions are broad, and typically are in the range of 10°C. The spontaneous polarization of this compound reached $P_0 = 4 \times 10^{-4}$ C/m^2 at 132°C. The electro-optic response was characterized by a ferroelectric switching in the smectic C* range, while in the S_X^* phase it was very similar to the electroclinic response of a typical S_A^* substance [22].

The geometries of the cells used for studying the electromechanical effect and sample preparation technics were quite similar for both compounds. The experimental set-up and the co-ordinate system used in this paper are shown in Fig. 1. Sandwich cells with thicknesses of 20 μm and 15 μm were prepared from compounds A and B respectively. The bottom glass plates of the cells were fixed inside a thermostat-controlled chamber, while the tops could move. The accelerations of the top plates were detected by accelerometers (BK 4375, sensitivity is 0.314 pc/ms^{-2}, $m = 2.3$ g) which were fixed to them properly. The linear and quadratic contributions to the acceleration were separated by a lock-in amplifier.

In order to obtain planar alignment the samples were sheared along the y axis at the isotropic/smectic phase transition. Unfortunately, instead of the perfect alignment indicated in Fig. 1 we could achieve only partial orientation. The samples contained small elongated focal conic domains with an approximate size of 50 μm, which were generally oriented perpendicular to the shear direction. Nevertheless, for convenience, a co-ordinate system corresponding to the idealized bookshelf geometry will be used.

RESULTS

The measurements revealed that ferroelectric liquid crystal polymers do exhibit linear and quadratic electromechanical effects. Electric field induced mechanical vibrations were detected in the horizontal (y) as well as in the vertical (x) direction.

For both polymers it was found that in the y direction (horizontal, parallel to the layers) the linear electromechanical effect had a maximum in the frequency range of ~3.5–4 kHz. The maximum value varied with the temperature. For compound A the temperature dependence of the vibration amplitudes followed the temperature dependence of the helical pitch (similarly to the findings on LMW FLC materials), while for compound B the maximum response was detected in the middle of the S_X^* phase.

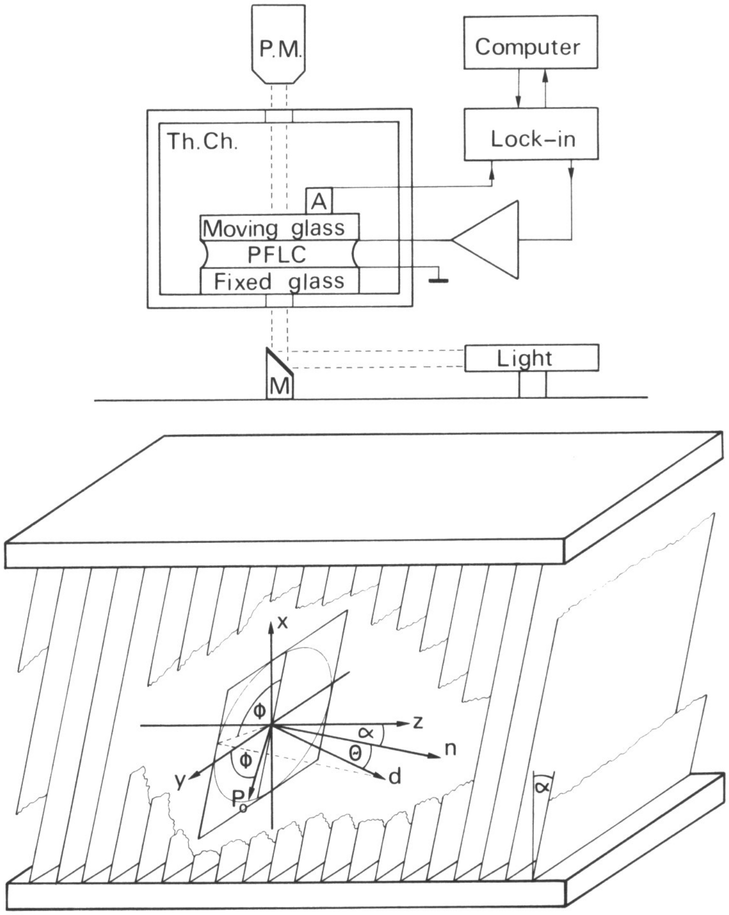


FIGURE 1. Sketch of the experimental set-up: A, accelerometer; Th. Ch., thermostat-controlled chamber; P.M., polarizing microscope; M, mirror. (*b*) Sample geometry with respect to the co-ordinate system used in the measurements of electromechanical responses of ferroelectric liquid crystal polymers.

Measurements on LMW substances have already shown that the electromechanical effect is very sensitive to the alignment. This means that experimental data are reproducible only if irreversible texture changes do not occur. Otherwise the reproducibility fails; e.g., a deterioration of the orientation of the cell results in a significant decrease of the vibration amplitudes. The same effect was found in our polymers. The linear electromechanical responses could be reproduced during subsequent heating–cooling cycles until the compounds stayed in the S_C^* or S_X^* phases. This was not the case when phase transitions into either the isotropic or the S_B^* or glass phases occurred. This is presumably due to the fact that, upon entering into any of these phases, the orientation was at least partially lost, so after returning the recovered texture did not coincide with the original one.

For a rough characterization of the electromechanical properties of an FLC substance one can define the strength S of the linear electromechanical effect as the maximum obtainable displacement induced by a unit electric field. In LMW materials its typical value was found to be in the range of $S = 10^{-16}$–10^{-14} m^2/V. In the case of our polymers we obtained $S(A) = 10^{-17}$ m^2/V and $S(B) = 3 \times 10^{-16}$ m^2/V. Although these are slightly smaller than the typical values for LMW compounds, taking into account the relatively poor alignment of the studied polymers (compared to that of usual LMW cells), one can expect that electromechanical effect of ferroelectric polymers can be almost as strong as in the low molecular weight FLC materials.

It is remarkable that the linear electromechanical effect was also found in the S_X^* phase of compound B. As linear effects are generally not detected in non-ferroelectric phases, we think that the linear electromechanical effect is connected with the presence of spontaneous polarization. Therefore the above-mentioned results indicate that the S_X^* phase should also be a ferroelectric or an antiferroelectric phase.

The vertical motions (vibrations involving changes in the sample thickness) were also measured by Jákli [19] in sample A. In the kHz range the effect was in the same order of magnitude as in the horizontal direction (at low frequencies the vibration was mainly horizontal and parallel to the layers, as was also found for monomers [9]). A typical frequency dependence of the vertical vibrations is shown in Fig. 2. It is seen that the spectrum contains a series of relatively broad resonance-like maxima where, at higher frequencies (overtones), the humps are widening. The frequency ratios of the subsequent overtones are approximately 1:3:5:8.

The quadratic electromechanical effect was also measured on sample A, although it was close to the measuring error. The quadratic response exhibited maxima in the frequency dependence just as the linear one did, but these maxima were situated at one half of the resonance frequencies of the linear response [18].

DISCUSSION

The main difference between ferroelectric side chain polymers and low molecular weight liquid crystals lies in the interaction of the constituents of the smectic layers. In LMW compounds the building blocks of the layers are individual molecules, while in polymers the mesogenic side chains play that role. However, the flexible main chains of the polymer form links between the individual side chains situated within the same or in the neighboring layers. As a result, at low frequencies the motion is still viscous, although the viscosity coefficients of the polymer are probably much larger, and one can predict that at high frequencies the main chain renders viscoelastic properties to the material. However, the rotational viscosity, which is related to the rotation of side chains around a cone, is supposed to be of about the same magnitude in polymers as in LMW materials.

Despite previous efforts, [18, 23, 24], a complete and satisfactory theoretical description of the electromechancial effect is still elusive. Experimental data suggest, however, that the vibrations in the horizontal (y) and in the vertical (x) directions are due to two different mechanisms acting simultaneously.

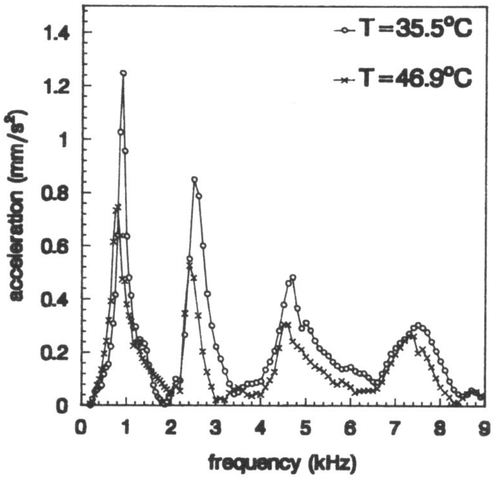


FIGURE 2. Frequency dependence of the acceleration of the cover plate of sample A in the direction normal to the surfaces (along the x axis) corresponding to the linear electromechanical response: $U = 10$ V.

On the one hand, we think that the low-frequency response in the y direction is due to coupling between the director rotation and the viscous flow. Therefore it might be essentially different in polymers and in LMW substances. On the other hand, the vertical vibrations are presumably related to layer compressions, so we do not expect a great difference between LMW and polymer responses. In the following we analyse our results in the light of these predictions, presenting simple models for both mechanisms.

First we focus on horizontal (y) vibrations. We assume that the layers are not deformed by the applied field (piezoelectricity is neglected). Then the director can move on a cone around the layer normal **n**, and the magnitude of the spontaneous polarization $\mathbf{P}_0$ remains constant. The electric field induced "backflow" phenomenon can be calculated [18] if we consider only linear effects, neglecting the dielectric anisotropy, and we approximate the hydrodynamics of S_C^* polymers with those of a uniaxial nematic. According to this calculation the mechanical stress σ_{xy}, i.e., the force per unit area, is

$$\sigma_{xy} = (1/8)\cos\theta \sin 2\alpha(\gamma_2/\gamma_1 - 1)EP_0 \qquad (1)$$

in the case of a helical structure, and

$$\sigma_{xy} = (1/2)\cos\phi(\gamma_2/\gamma_1 + 1)EP_0 \qquad (2)$$

if the helix is suppressed by the surfaces (surface-stabilized structures).

In these equations θ is the tilt angle between the director **d** and the layer normal **n** (see Fig. 1(b)). The layer normal forms an angle α with the z axis, and ϕ denotes the angle between the spontaneous polarization $\mathbf{P}_0$ and the y axis. γ_1 is the rotational viscosity, $\gamma_2 = \eta_\beta - \eta_c$, whee η_c and η_b are the shear viscosities with the director in the direction of the flow gradient and parallel to the flow respectively.

Supposing, as usual, that the flow velocity of the liquid crystal at the cell surface is equal to the speed of the cover plate, v_y, the momentum balance at the surface reads as

$$mv_y = \Omega(\sigma_{xy} - \eta\nabla_x v_y). \qquad (3)$$

Using the approximation that $\nabla_x v_y \approx v_y/d$ (where d is the cell thickness) we obtain, for the magnitude of the velocity of the cover plate, that

$$|v_y| = (\sigma_{xy} d/\eta)/\sqrt{1 + \left(\frac{md\omega}{\eta\Omega}\right)^2}. \qquad (4)$$

Here m and Ω are the mass and the area of the plate, respectively, and η is an effective shear viscosity (if the cone angle θ is small, then the director is almost

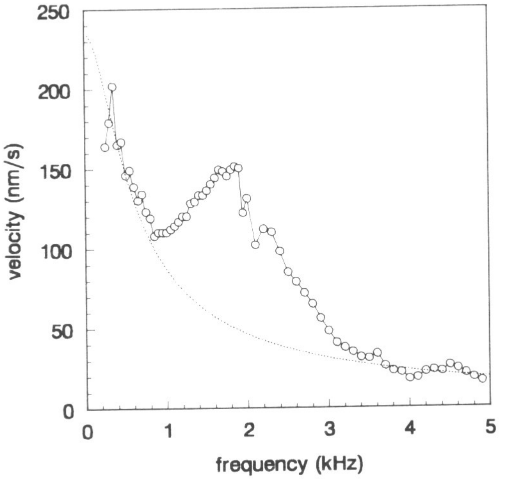


FIGURE 3. Frequency dependence of the velocity of the cover plate measured along the *y* axis on sample A. The magnitude of the applied a.c. voltage was held constant at $U = 10$ V. The dotted line corresponds to a theoretical fit using equation (4).

perpendicular both to the flow and the flow gradient, and $\eta \approx \eta_a$).

Equation (4) is a complicated function of the viscosities, so depending on the ratios of the different viscosities, the effect can be very different from that of the monomers. If $\omega \ll \omega_0 = \eta\Omega/(dm)$ a constant velocity is predicted, while at high frequencies ($\omega \gg \omega_0$) it should decrease with $1/\omega$. With $d = 2 \times 10^{-5}$ m, $\Omega \simeq 10^{-4}$ m^2, $m \simeq 0.01$ kg and taking ~6 Pas for η, we obtain that $\omega_0 = 3000$ s^{-1}.

In Fig. 3 is shown the measured frequency dependence of the horizontal velocity of sample A, as well as the theoretical curve using equation (4) with the estimated value of ω_0 and with $\sigma_{xy} = 0.07$ N/m^2. It is seen that the theoretical fit is satisfactory in the intervals of 300 Hz$<f<$800 Hz and 3.2 kHz$<f<$5 kHz, while there are no experimental data in the very low frequency limit ($\omega < 100$ Hz). In the frequency interval of 1–3 kHz, however, a broad resonance-like peak is sitting on the monotonously decreasing theoretical curve. We think that this disagreement is due to the nonperfect alignment; i.e., the sample is not a monodomain. Then the motion along the *y* direction also involves layer deformations, and resonances can appear either due to the presence of different chevron domains [25] or owing to the second sound resonance, which is described below.

Let us now focus on the vibrations in the *x* direction (see Fig. 2), which possess a sequence of resonance-like maxima. Due to coupling between the magnitude of the spontaneous polarization and the director tilt θ, an a.c. electric field induces an increase of θ (the electroclinic effect) which, in turn, leads to layer compression. This mechanical consequence of the electroclinic effect can be regarded as a piezoelectric response. Since the volume compressibility of the material is typically negligible below 100 kHz, a modulation of the layer thickness requires an oscillatory flow within the layers. Due to the integrating behavior of the cell substrates, this flow mainly yields a vertical (x) vibration of the substrates, indicating that these layer deformations should be responsible for the resonances.

In smectic liquid crystals there is a special acoustic wave called the second sound [1], which also involves oscillation of the layer spacing. In finite samples, as shown in Fig. 1, standing waves of second sound can develop, with a wave vector of $\mathbf{q} = (q_x, q_z) \simeq (m\pi/d, n\pi/L)$. Here m and n are integer and L is the sample size in the z direction ($L = 1$ cm). A homogeneous excitation, such as the application of an a.c. voltage to the cell electrodes, can transfer energy only to standing waves with the fundamental frequency f_r (at $n = m = 1$) and its odd overtones ($3f_r$, $5f_r$, etc.), since at even overtones the increment of the spontaneous polarization integrated over the sample is zero. In LMW smectics the fundamental second sound resonance frequency is in the order of 1 kHz [26], which conforms to the experimental value for polymer A (see Fig. 2, where $f_r = 900$ Hz). This shows that the piezoelectric behavior is essentially the same in polymers and in LMW liquid crystals. The second sound resonance would yield the same 1:3:5:7 sequence of overtones that is generally observable in normal piezoelectric crystals, such as quartz. The observed sequence of 1:3:5:8 of the overtones in the vertical vibration of our polymer sample is close to this rule. We guess that the deviations come from two main sources. First, since the standing waves in the liquid crystal film may cause deformation of the cell substrates, the position and the size of the vibration transducer may be important. At higher overtones the accelerometer, the diameter of which is about a quarter of the cell size, can integrate various nodes together, resulting in wider and less defined resonance peaks. Second, imperfectness of the alignment may have a similar effect.

In summary, we have reviewed the electromechanical effects in ferroelectric liquid crystalline polymers. The electromechanical behavior of polymers were found to be very similar to that of low molecular weight ferroelectric liquid crystals.

We presented two models to interpret our experimental findings. One describes a backflow mechanism causing vibrations horizontally, parallel to the smectic layers. The other is a piezoelectric effect, which leads to sample thickness variations exhibiting resonances in the kilohertz frequency range. In order to obtain better agreement between the theoretical predictions and the experimental results, a cell with a better orientation should be prepared.

As the electromechanical effects may have an impact on the electro-optic characteristics of FLC cells (flow can also modify the director configuration), a full understanding of this phenomenon could help in designing better displays. Moreover, the electromechanical effects can be of interest for practical applications (sensors, electromechanical transducers, speakers, etc.). A successful quantitative description of the experimental results could serve as a powerful tool in studying the physical properties of ferroelectric liquid crystals. Further study of the electromechanical phenomena is thus required.

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