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First observation of electromechanical effects in a chiral ferroelectric columnar liquid crystal

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Electromechanical (converse piezoelectric) responses of an electrically switchable chiral ferroelectric columnar liquid crystal 1,2,5,6,8,9,12,13-octakis[(S)-2-heptyloxy] dibenzo [*e*, *l*] pyrene, were studied under a.c. electric fields. The liquid crystal phase has a C_2 rotational symmetry, the same as that of SmC* liquid crystals or of Rochelle Salt, but the responses are orders of magnitude weaker. The possible physical reasons for the observed weak mechanical responses and, in view of the results, the switching mechanism are discussed.

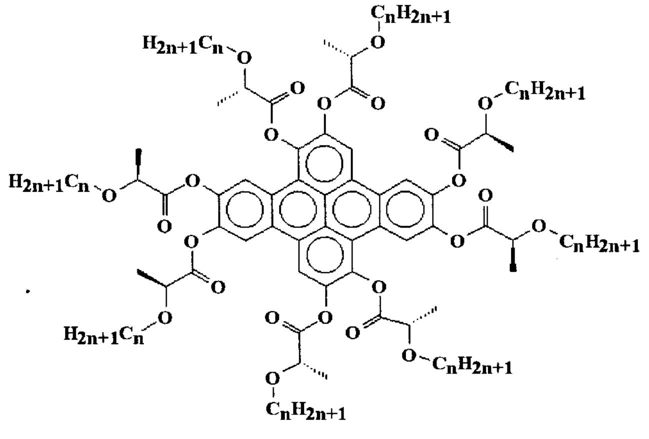
1. Introduction

Columnar liquid crystals [1] are one-dimensional fluids where disc or pyramidal shaped molecules form columns. There is a short range translational order along the columnar axis and a long range hexagonal or rectangular order in the direction normal to it. Depending on the structures of the molecules (disc or pyramidal shaped, chiral or non-chiral), on their orientation with respect to the columnar axis (orthogonal or tilted) and on the lattice structure (rectangular or hexagonal) a number of different columnar phases are distinguished. Among them quite a few are pyroelectric (i.e. possess an electric polarization, $\mathbf{P}_o$). Such phases were first considered by Prose [2], who realized that chiral tilted columnar phases have the same C_2 symmetry as that of chiral smectic C* liquid crystals or of the 3D crystal, Rochelle Salt. Inspired by the studies on SmC* phases, it was suggested that such a columnar phase is also ferroelectric, i.e. it can be switched by electric fields. Experimentally this suggestion was first realized by Bock and Helfrich [3]. Similar linear electro-optical effects were then observed on other compounds by Scherowsky and Chen [4] and Heppke *et al.* [5].

As every pyroelectric material is also piezoelectric, there should also be phases that possess a linear coupling between electric field and mechanical stress. In the case of a 3D crystal, the mechanical stress results in a purely elastic response, whereas for SmC* liquid crystals the stress produces mainly viscous flows [6]. It is an interesting question, therefore, how the electric field induced mechanical responses of 2D crystals, such as lumnar liquid crystals, differ from materials with a different number of crystal-like dimensions, but otherwise with the same symmetry. In addition our studies enabled us to refine the picture of the electro-optical switching of the columnar phases with C_2 symmetry.

2. Experimental

We studied the mechanical deformations of the ferroelectric columnar liquid crystal of 1,2,5,6,8,9,12,13-octakis[(*S*)-2-heptyloxy]dibenzo[*e*,*l*]pyrene (D8m*10) [7] in the form of films under periodic electric fields.



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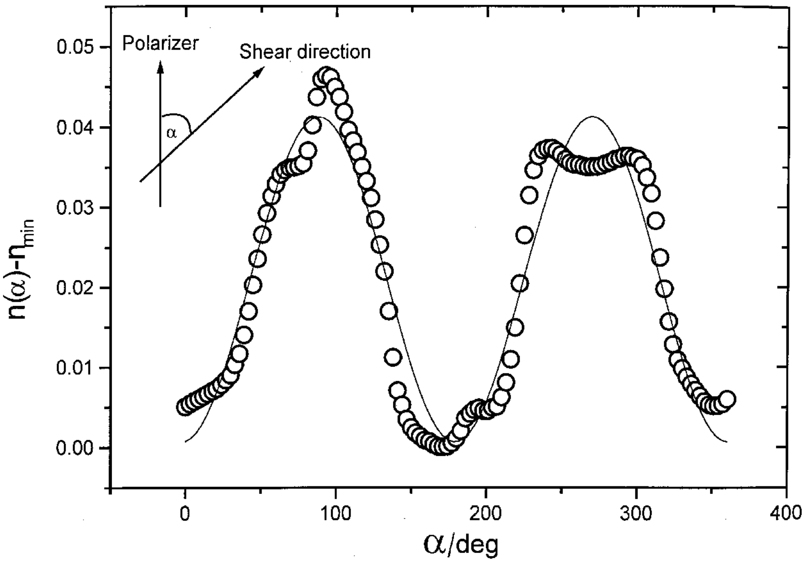


Figure 1. Study of the shear-induced alignment by measuring refractive index as a function of the shear direction with respect to the polarizer.

This is the material in which the electro-optical switching was first detected [3]. The phase sequence of D8m*10 is the following:

glass—columnar—I
70°C 120°C

The columnar phase of the material is tilted and the two-dimensional lattice structure of the columnar axes is nearly hexagonal. The tilt angle of the columnar phase is $\theta = 24{\cdot}5^\circ$ and the electric polarization is $\mathbf{P} = 60\,\mathrm{nC\,cm^{-2}}$ at d.c. fields below $10\,\mathrm{V\,\mu m^{-1}}$, whereas $\theta = 37^\circ$ and $\mathbf{P} = 180\,\mathrm{nC\,cm^{-2}}$ at higher field strengths [8].

We prepared 4-μm-thick films that were aligned by unidirectional shear during cooling from the isotropic to the columnar phase. The glass cover plates were coated by transparent and electrically conductive indium tin oxide (ITO) layers, and no additional surface coating was used. With a spectrometer we measured the refractive index of the aligned columnar phase as a function of the angle between the shear direction and the plane of polarization using one polarizer. We found smaller values for the index if the shear direction was parallel to the plane of polarization and larger values if the shear direction was perpendicular to this plane. Assuming a negative optical anisotropy, we can conclude that the columns are oriented parallel to the shear direction. In figure 1 the refractive index minus the minimum measured value is plotted as a function of the angle (α) between the shear direction and the polarizer. The maximum value of the curve gives the value of the birefringence: $\Delta n = 0{\cdot}045$.

The electric field-induced mechanical deformations were studied by monitoring the acceleration of the cover glass plate in three orthogonal directions. For this purpose three piezoelectric accelerometers (BK 4375 from Bruel & Kjaer) were fixed on the top plate. One was sensitive normal to the film (X), another parallel to the columnar axis (Y), and the third perpendicular to the columns and parallel to the plates (Z). The measurement set-up is represented in figure 2. Electric fields up to $35\,\mathrm{V\,\mu m^{-1}}$ were applied to the sample. The electric field-induced mechanical vibrations of the top plate were measured in the frequency range between 100 Hz and 5 kHz. The voltage was supplied by the internal oscillator of a lock-in amplifier from Stanford Research (SR850) and was applied to the sample after amplification. The first and second Fourier components of the electric signals of the piezoelectric accelerometers were detected by the same lock-in amplifier. The sample was placed in a home-made oven which allowed temperature regulation between room temperature and 120°C with an accuracy of 10 mK.

3. Results

First the optical response was checked under low frequency rectangular fields with amplitudes up to

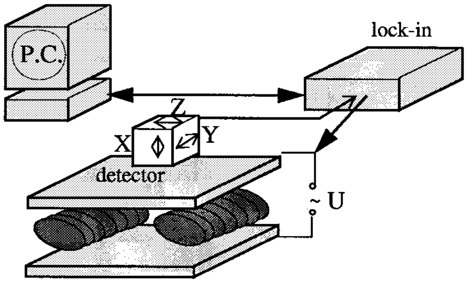


Figure 2. Experimental set-up to measure the electric field-induced vibrations of the top plates of samples containing columnar liquid crystal films.

$35\,\mathrm{V\,\mu m^{-1}}$. No electro-optical switching could be seen below about 70°C. Above 90°C the electro-optical switching reported previously [8] could be observed.

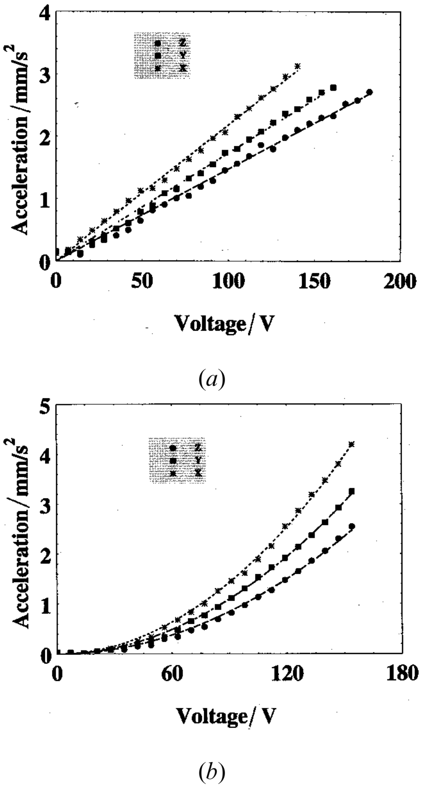
Between room temperature and the transition temperature to the isotropic phase, in the frequency range between 0·1 and 5 kHz, the acceleration of the cover plate is less than $10\,\mathrm{cm\,s^{-2}}$, i.e. the maximum displacement is less than 1 nm. This corresponds to a piezoelectric constant of about $10^{-12}\,\mathrm{C\,N^{-1}}$, which is three orders of magnitude smaller than that usually measured for SmC* ferroelectric liquid crystals [9, 10] and two orders of magnitude smaller than that of the crystal of Rochelle Salt [11], although they have the same symmetry.

In the whole measured frequency range the mechanical response is largest along the surface normal (X) and smallest perpendicular to the columns (Z).

Contrary to the situation with SmC* films, the alignment and piezoelectric responses were insensitive to a moderate external mechanical force (exerted by hand) and the measurements were reproducible within 2%.

Below 70°C, where no electro-optical switching could be observed, the second Fourier component (quadratic response) of the mechanical vibrations is an order of magnitude smaller than the Fourier component (linear response). At higher temperatures the quadratic effect becomes more pronounced: at around 100°C and under $25\,\mathrm{V\,\mu m^{-1}}$ field strength its magnitude is about 50% of the linear response. At constant frequency and temperature the linear (quadratic) effect is a linear (quadratic) function of the applied voltage [see figures 3(*a*) and 3(*b*)]. This indicates that the field-induced rotation of the direction is very small.

The linear electro-mechanical responses are largest in the glassy state where no optical signal could be observed, and smallest in the high temperature range where the optical signal has a maximum. Quadratic electro-mechanical responses, however, behave like electro-optical signals: they are both very small in the glassy state and largest near to the clearing point. The frequency and temperature dependences of the first Fourier component of the acceleration in the X and Y directions are shown in figures 4 and 5, respectively. The spectra contain resonances; two main peaks can be resolved up to 5 kHz (f_1 and f_2). The positions of the peaks do not depend on the applied voltage, but only on the temperature: they decrease by about 50% as the transition to the isotropic phase is approached. The resonance frequencies are comparable with those usually observed for SmC* samples of similar size (where they are connected with the bending modes of the boundary glass plates) and they did not change much with temperature. In the present case the resonance frequency is constant in the glassy state, where the two boundary plates are practically bonded. As the material becomes more fluid-like, the effective thickness gradually drops to half of the previous value. This makes it qualitatively understandable why the resonance frequency decreases as the material becomes more fluid in the columnar phase.



(*a*)

(*b*)

Figure 3. Voltage dependence of the amplitude of the first (*a*) and second (*b*) Fourier components of the field-induced vibrations of the cover plate in three orthogonal directions. $T = 100°\mathrm{C}$, $f = 1\,\mathrm{kHz}$.

The strength of the response vanishes in the isotropic phase. To illustrate the temperature dependences in figure 6 we have plotted (against temperature) the magnitude and the position of the second peak of the linear response measured in the X direction. They are constant below 70°C, then decrease monotonously with increasing temperature. The strength of the response averaged over the measured frequency range also vanishes for the isotropic phase. The frequency dependence of the displacement normal to the film surface (as determined by dividing the first harmonics of the acceleration by the square of the angular frequency) is shown in figure 7. Below the first resonance frequency, f_1, the displacement is nearly constant indicating an elastic response.

4. Discussion

First we consider why the electric field-induced mechanical deformations are so weak compared with

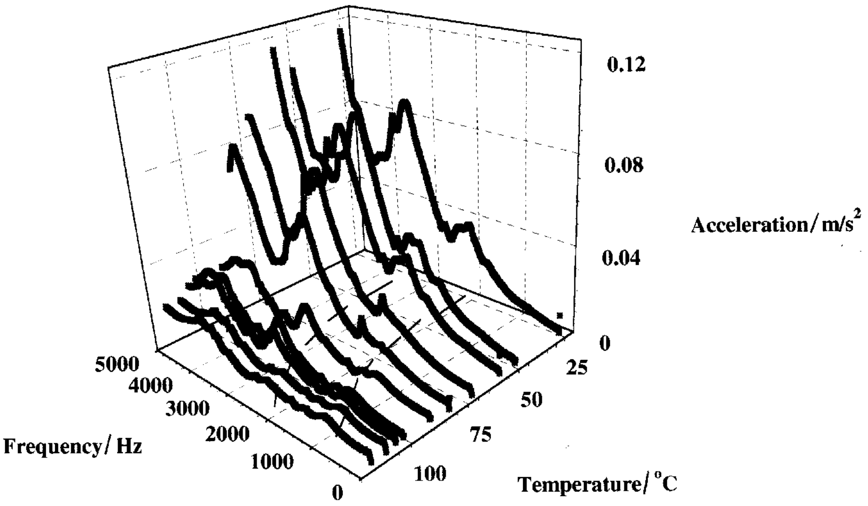


Figure 4. Frequency and temperature dependences of the first Fourier component of the acceleration of the cover plate along the film normal (X).

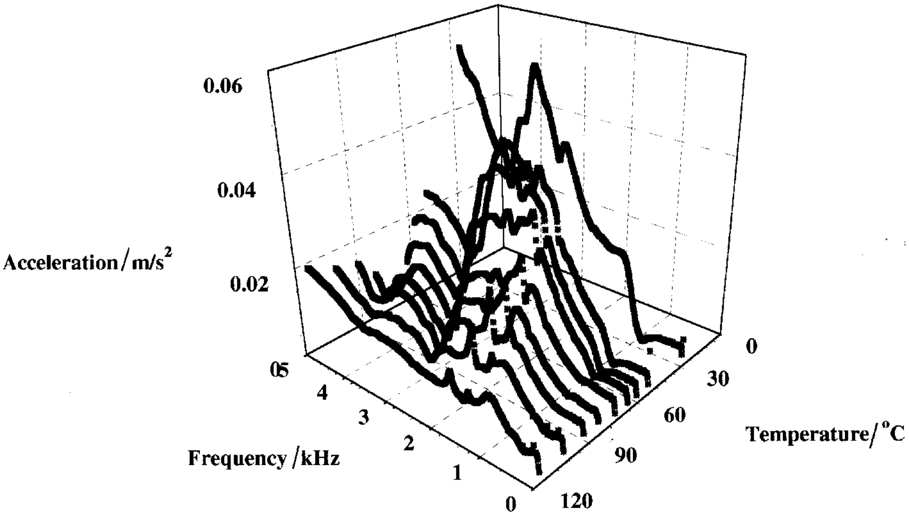


Figure 5. Frequency and temperature dependences of the first Fourier component of the acceleration of the cover plate parallel to the film surface and the columns (Y).

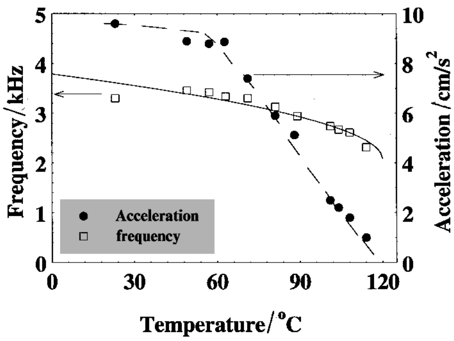


Figure 6. Temperature dependences of the magnitude and the position of the second peak of the linear response measured in the X direction.

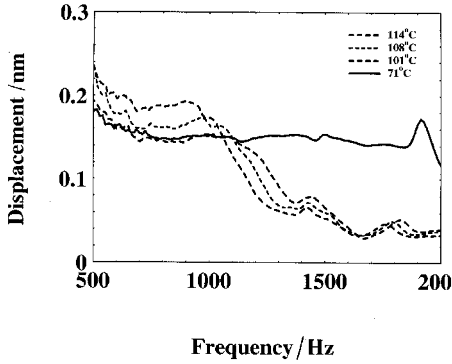


Figure 7. Frequency dependence of the first Fourier component of the field-induced displacement of the cover plate normal to the plates (X direction) at different temperatures. $E = 35\ \mathrm{V\ \mu m^{-1}}$.

materials with the same symmetry but with a one- or three-dimensional lattice structure. We propose that it is the combined consequence of the two-dimensional lattice structure and of the boundary condition. At the surfaces, the anchoring prevents variation of the sample dimensions along the glass plates. We assume incompressibility and that the elastic deformation is in the linear range, i.e. that the displacements inside the film along the plates are less than the sample thickness. Taking into account that the sample is $d = 4\,\mu m$ thick and $L = 2\,cm$ wide, we derive that the displacement normal to the plates cannot exceed a few nanometers. This would explain the observed very small responses. (We note that in SmC* liquid crystals the boundary conditions are similar, but there the viscous nature of the layers allows much larger displacements; in crystal slabs, on the other hand, the free boundary conditions permit larger elastic deformations.)

In view of the strong mechanical constraints imposed by the two-dimensional lattice structure and by the anchoring of the cover plates, the question arises as to how switching can take place at all. Our discussion on this problem is based on Bock and Helfrich's model for the structure [8]. They suggested that the idle state of the material studied has a ferrielectric-like structure as sketched in figure 8 (*a*). The columns have elliptical cross sections and form a quasi-hexagonal lattice (each column has six nearest neighbours). In every second row the polarization makes an angle of 60° with respect to that in every other row with antiferroelectric arrangement.

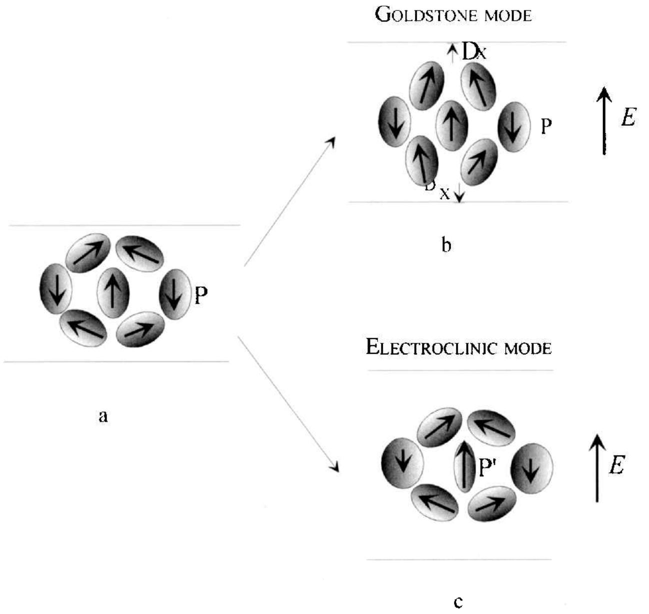


Figure 8. Lattice structures of the columns of the material studied. (*a*) Structure of the idle state as proposed by Bock and Helfrich [8]. The columns have elliptical cross sections and they form quasi-hexagonal lattices (each column has six nearest neighbours). In every second row the polarization makes an angle of 60° with respect to that in every other row having an antiferroelectric arrangement. (*b*) The polarizations of the oblique columns rotate under the electric field. This would result in a deformation of the lattice structure and lead to a variation of the sample thickness proportional to the eccentricity of the ellipses. (*c*) The magnitude of the polarization increases (decreases) in the columns with polarization parallel (anti-parallel) to the field. This results in thinner (thicker) columnar cross sections, respectively.

Unlike tilted smectics, columnar liquid crystals cannot easily change their tilt direction because it would involve distortion of the lattice structure. This is illustrated in figures 8 (*b*) and 8 (*c*), where the mechanical consequences of the possible switching modes are shown. The first switching mode [figure 8 (*b*)] resembles the so-called Goldstone mode, i.e. the polarization vector rotates without altering its magnitude. During this rotation the main axis of the elliptical cross section rotates toward the electric field direction. For uniform switching this should result in a distortion of the lattice structure and would yield a variation of the film thickness (in a first approximation proportional to the eccentricity of the ellipses). For the second switching mode [figure 8 (*c*)] the tilt angle changes, while the magnitude of the polarization varies without altering the direction of the spontaneous polarization (electroclinic mode). As a consequence of this mode the cross section of the columns with polarization parallel (anti-parallel) with the applied

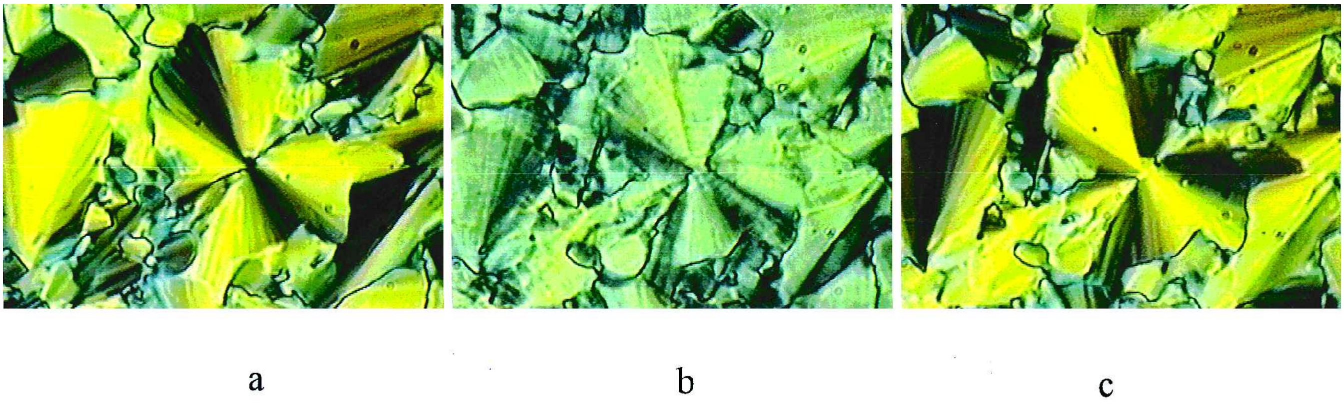


Figure 9. Fan shaped texture after field reversal of $U = 68{\cdot}2$ V at $T = 114{\cdot}5$°C. (*a*) 100 ms (*b*) 270 ms and (*c*) 350 ms after field reversal.

field becomes thinner (thicker). This would also involve a considerable mechanical stress, but would not directly lead to a variation of the sample dimensions. Although the Goldstone type and the electro-clinic modes may occur simultaneously, it can be assumed [8] that at low fields the switching involves only the rotation of the oblique ellipses and the vertical ellipses switch only in the high field range. At high temperatures, and in the low frequency limit of our measurements, the switching is observable, but neither the linear nor the quadratic vibrations exceed an amplitude of 1 nm. This is in accordance with the constraints imposed by the lattice structure and the rigid boundary conditions, but does not fit with a uniform switching model.

The force acting along the film thickness on a unit area can be estimated as $\sigma_{yx} = \mathbf{PE}(L/d)$. Taking that $\mathbf{P} \sim 70\ \mathrm{nC\,cm^{-2}}$ (during the experiments we stayed in the low voltage regime), $\mathbf{E} \leqslant 35\ \mathrm{V\,\mu m^{-1}}$ and $L/d \sim 10^3$, we estimate that the stress imposed on the lattice structure can be more than 20 MPa. Under such large stresses, the lattice structure probably cracks into domains separated by dislocation walls or melted channels. The walls or channels make it possible for the domains to deform individually without leading to a macroscopic deformation. Optical studies seem to confirm this model:

(1) Previous microscopic observations of Bock and Helfrich [7] showed that ‘domains are seen to grow and coalesce during switching, but the rotation of the optical axis is uniform regardless of the local presence or absence of the domain walls’ [8].

(2) Our microscopic observations can also be interpreted accordingly. In figure 9 we present a sequence of pictures of the texture at different time intervals after field reversal. It can be seen that the texture does not change immediately [see figure 9 (*a*)]. After some delay (~100 ms), the birefringence decreases, indicating the decrease of the average order parameter [see figure 9 (*b*)]. This can be due to either a uniform or an inhomogeneous melting. The fine stripes that appear simultaneously with the decrease of the birefringence seem to support the idea of the melted channels. The texture with lower birefringence lasts for about 100 ms. After switching, the texture becomes stable with the same birefringence as before the switching, but with the optical axis rotated by twice the tilt angle [see figure 9 (*c*)].

There are other circumstances that may also facilitate the switching by decreasing the mechanical stresses during director rotation:

(i) The rigid core of dibenzopyrene is elongated (aspect ratio is about 4/3) and, due to the tilted structure, the time average of the molecular shape is not circular. Although this still does not result in a completely circular cross section of the columns, it may reduce the mechanical consequence of the director rotation.

(ii) The long alkyl chains attached to the rigid core are flexible. Accordingly, we can assume that the shape of the cross section of the columns can vary during switching, further decreasing the deformation of the lattice structure.

5. Summary

Converse piezoelectric responses of a chiral ferroelectric columnar liquid crystal with a two-fold symmetry axis were studied under a.c. fields. The responses are orders of magnitude smaller than those observed for chiral ferroelectric smectic liquid crystals or crystals belonging to the same symmetry group. We have proposed a model to explain simultaneously the electro-optical switching reported previously and the weak mechanical deformations observed by us. According to this model, the sample breaks into domains during switching.

There remain, however, a few open questions which require additional measurements that are beyond the scope of the present paper. We plan, for example to study the mechanical responses under quasi d.c. fields, making it possible to study the transition between high and low field phases.

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