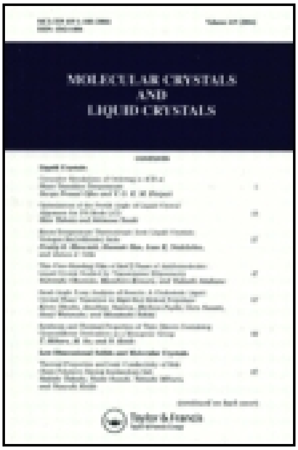

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A. R. Geivandov [a] & S. P. Palto [a]

[a] Institute of Crystallography RAS, Leninsky, Moscow, Russia

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The Influence of Ferroelectric Polymer Alignment Layer on Electrooptical Properties of Nematic LC Cell

A. R. Geivandov
S. P. Palto
Institute of Crystallography RAS, Leninsky, Moscow, Russia

Ferroelectric copolymer of vinylide0ne fluoride and trifluoroethylene (70/30) was used as an alignment layer in nematic liquid crystal cells. The rubbed ferroelectric polymer films produce excellent planar orientation of liquid crystal molecules. We have found that the ferroelectric polymer film at one of LC cell surfaces results in strongly asymmetric electrooptical and electrical response. This fact was qualitatively explained by a model that assumes creating a "p-n" like junction between a liquid crystal and the ferroelectric polymer.

Keywords: alignment; ferroelectric polymer; liquid crystal; PVDF

INTRODUCTION

It is well-known that one can use the LC layer to reveal the domain structure of polarized ferroelectric crystal [1,2]. This phenomenon is associated with the ferroelectric polarization state. The polarization influences the anchoring properties of the alignment surfaces and can even induce a driving electric field in the adjacent dielectric LC layer [3–5]. On the other hand, Belyaev and co-authors [6] showed that the ferroelectric crystal connected in series with the nematic LC cell enables optical bistability that would be a prototype of pixel in the LC matrix with the ferroelectric gate instead of widespread thin film transistor (TFT). But if one has the LC matrix it becomes difficult creating the bulky ferroelectric crystals connected in series with

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Address correspondence to A. R. Geivandov, Institute of Crystallography RAS, Leninsky pr. 59, 119333, Moscow, Russia. E-mail: ageivandov@yandex.ru

corresponding LC pixels [6]. Another case would be using the ferroelectric films as an alignment layers. However, the surfaces of most crystalline ferroelectric films (crystals, oxide films etc.) produce inhomogeneous orientation of the LCs. From this point of view the polymer ferroelectric films are very interesting candidates to solve mentioned "alignment problem" that is so crucial for practical applications.

In this work we present results of investigation of the electrooptical and electrical properties of the LC cells aligned with the rubbed ferroelectric polymer (FP) films of the copolymer of vinylidene fluoride and trifluoroethylene P(VDF/TrFE) (70/30) prepared by spin-coating technique.

EXPERIMENTAL

The LC cells were assembled from ITO covered glass slides with rubbed alignment layers of either the polyimide (PI) or the P(VDF/TrFE). We have used two types of LC materials: (i) classical pentylcianobiphenyl (5CB) and (ii) the mixture NIOPIK ZhKM-1391 (see the Table 1 for its basic parameters). The P(VDF/TrFE) (70/30) is a well-known ferroelectric polymer characterized by high spontaneous polarization $\sim 10\,\mu\mathrm{C/cm}^2$ and dielectric constant of about 10 at room temperature. The first order ferroelectric phase transition in P(VDF/TrFE) (70/30) shows the pronounced hysteresis in a temperature range of 80–110°C [7].

The alignment layers were prepared as follows. The PI films were spin-coated from 1% polyamide acid solution in dimethylformamide and then annealed at 180°C during 1 hour [8]. The P(VDF/TrFE) (70/30) films were spin coated from 3% solution in cyclohexanone

TABLE 1 Parameters of Liquid Crystals ZhKM-1391 и 5CB

	ZhKM-1391	5CB
$\mathrm{Cr}^{-}>\mathrm{N}$ [°C]	-30	$+22.5$
$\mathrm{N}^{-}>\mathrm{I}$ [°C]	$+74$	$+35.5$
$\varepsilon_{\parallel}$	11.9	20.3
$\varepsilon_{\perp}$	3.7	6.4
Dielectric anisotropy $\Delta\varepsilon$ (1 kHz, 20°C)	$+8.2$	$+13.9$
n_e	1.634	1.717
n_o	1.502	1.528
Optical anisotropy Δn	0.132 ($\lambda = 589\,\mathrm{nm}$)	0.189 ($\lambda = 632.8\,\mathrm{nm}$)
Specific resistance [Ohm cm] (20°C)	$\sim 10^{11}$	$\sim 10^{9}$

and softly baked at 70°C for 30 minutes. Both types of the polymer films were rubbed uniaxially to produce planar orientation of the LC.

The polymer films thickness was determined by electrical capacity method. For the cells presented in this work the thickness of the P(VDF/TrFE) films was close to 0.1 μm. The dielectric constant of the PI films was derived from independent measurements of the electric capacity of thick films and their thickness by the microinterferometer (model MII-4). The dielectric constant of the PI films was found to be of 5 ± 0.5. The specific conductivity for the PI and the P(VDF/TrFE) films was $(0.5 \pm 0.3) \times 10^{-10}$ $\mathrm{Ohm}^{-1} \cdot \mathrm{cm}^{-1}$ and $(2 \pm 0.5) \times 10^{-10}$ $\mathrm{Ohm}^{-1} \cdot \mathrm{cm}^{-1}$, respectively.

The gaps in LC cells were produced using 2 μm thick teflon spacers. The gaps of empty cells were measured by electric capacity method. Then the LC material was introduced into the cells at room temperature through capillary action. We have found that the rubbed FP films produce excellent LC orientation competing with traditional polyimide films (see Fig. 1). The LC pretilt angle of I ~2.6° on the rubbed FP films was determined using the set-up described in [9] and the technique based on [10].

The prepared cells with planar LC orientation can be classified as follows: (i) the cells with "symmetric" boundaries where the alignment layers are of the same material (either PI or FP) on the both surfaces, and (ii) the cells with "asymmetric" boundaries, when the alignment layers are different (the PI film is on one of the glass substrates, while the other substrate is coated by FP film).

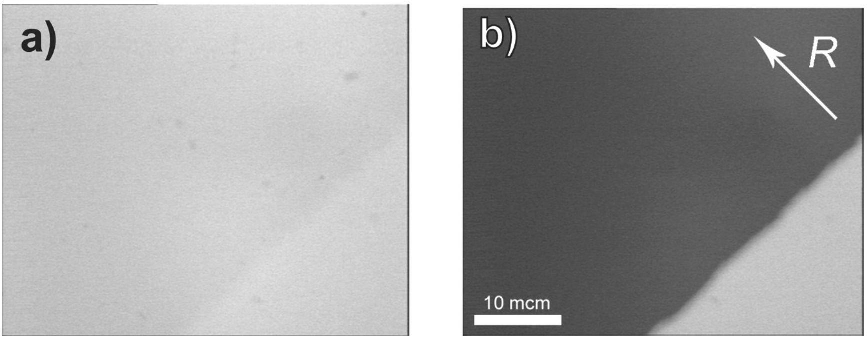

FIGURE 1 Typical textures in the LC cell with FP alignment layer in field-off (a) and field-on (b) states. The LC cell was placed between crossed polarizers and rotated at 45° to the axis of the polarizer. Right lower corner in the Figure contains no electrode. R – rubbing axis direction; a bar width is 10 μm.

We have studied both electrooptical and electrical properties of the LC cells. The electrooptical characteristics were measured using set-up based on the polarizing microscope equipped with photodetector and He-Ne laser (wavelength $\lambda = 632.8\,\text{nm}$). The arbitrary function generator Tectronix AFG 320 connected with amplifier was used to apply voltage pulses to the LC cells. The LC cells were placed between crossed polarizers of the microscope so that their optical axes were at an angle $\varphi = 45^\circ$ with respect to one of the polarizers axis. The electric properties were studied using home-made current to voltage converter producing a sensitivity of 100 V/nA and the arbitrary function generator. In particular, triangular waveforms of different voltage amplitudes (2–10 V) were applied to the LC cell electrodes at a frequency of 0.01 Hz to measure corresponding current and electrooptical responses.

RESULTS AND DISCUSSION

The Figure 2 shows the electrooptical response in the case of different types of the LC cells, when the periodic voltage pulses of opposite polarity are applied. In the case of the symmetric LC cell with polyimide alignment layers the optical response is independent on the pulse polarity, Figure 2(b). This response is typical of the standard symmetric cells with polyimide alignment layers, and it does not depend on the amplitude of the voltage pulses. The last was checked up to amplitudes of 50 V. The electric field interacts quadratically with the dielectric anisotropy of the LC molecules and, a priori, there is no reason for the asymmetry of the electrooptical response.

Quite a different situation takes place in the "asymmetric" cells, where one of the PI alignment layers is replaced by the FP film, figure 2(c). The electrooptical response becomes strongly dependent on both the polarity and amplitude of the applied voltage. After the negative pulse of 20 V is applied, LC director relaxation is extremely slow. Thus, even for the periodical pulses shown in Figure 2(a), the relaxation can not be accomplished during one second between the pulses. For some of similar samples we have observed the relaxation time exceeding a few minutes. In contrary, the positive pulse influences only during its length, while after the pulse is accomplished, the LC director relaxes to the state close to one achieved before this positive pulse was applied. The Maxwell relaxation time estimated using independently measured conductivity of the LC material is

$$\tau \approx \varepsilon\varepsilon_0/\sigma = \frac{10 \times 8.85 \cdot 10^{-12}\,\text{F/m}}{10^{-9}\,\text{Ohm} \cdot \text{m}} \cong 0.1\,s, \tag{1}$$

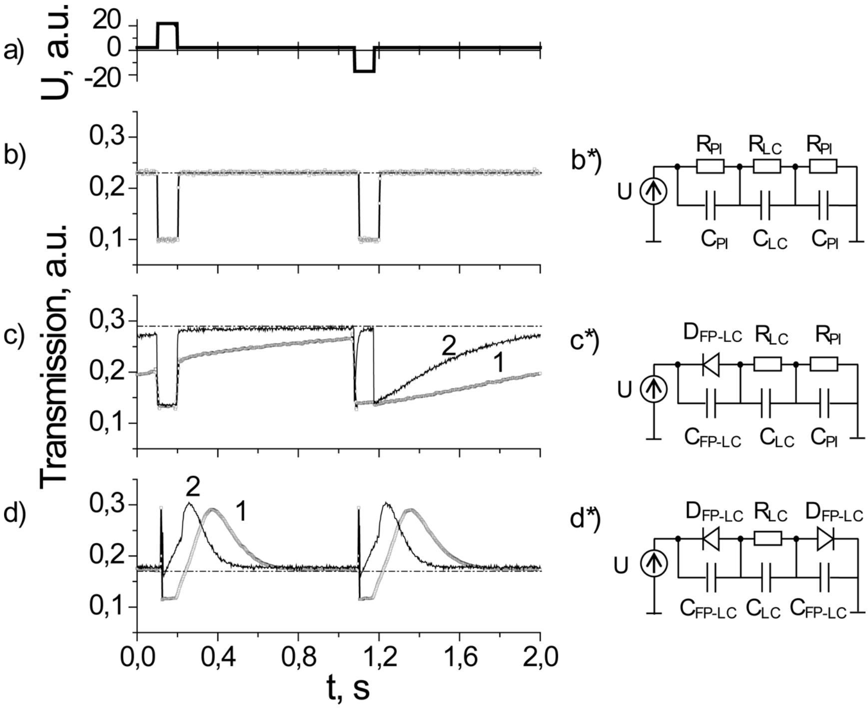

FIGURE 2 Driving waveform (a) and electrooptical response (b, c, d) for different types of the ZhKM-1391 cells modeled by corresponding equivalent electric circuits (b*, c*, d*):(b, b*) are for the symmetric LC cell #1 with a gap of 2 microns and PI alignment layers; (c, c*) are for the asymmetric LC cell #2 with gap of 2.3 μm and FP, PI alignment layers, where the curves 1 and 2 correspond to applied voltage amplitudes of 20 and 10 V, respectively; (d, d*) are for the symmetric LC cell #3 with gap of 2.8 μm and FP alignment layers, where the curves 1 and 2 correspond to applied voltage amplitudes of 20 and 5 V, respectively.

that is of a few orders in magnitude shorter than the relaxation time observed after application the negative pulse. This is one of the surprising results, which is to be explained below by electric processes at the boundary of LC material and ferroelectric film. The other very interesting result is that at the pulse amplitudes lower than 10 V, the LC director relaxes to the field-off state even being under the applied voltage, if the last one is of negative polarity (see the curve 2 in Fig. 2(c)).

The "symmetric" LC cells with two FP alignment layers show the symmetric response, Figure 2(d). However, even in this case the LC director relaxation time is much higher than the elastic relaxation time for a given LC cell thickness of 2.8 μm. This time is comparable, but still higher than the estimated Maxwell relaxation time. Again, at small voltage amplitudes (less than 10 V) the director shows efficient relaxation to the field-off state despite the external voltage is still applied (see the curve 2 in Fig. 2(d)).

The electrooptic responses shown in Figure 2(b–d) for different types of the LC cells can be explained in terms of corresponding equivalent circuits (b^*, c^*, d^*), where in case of using the FP alignment layers we put a diode elements into the circuits. In our model the diode is formed by a part of the LC layer and the FP. It is known that P(VDF/TrFE) can significantly change the electrons work function from electrodes into thin organic films [11]. Our experiments can be explained if the FP is considered as a kind of *n*-type semiconductor or injector of electrons, while the LC material has properties analogous to *p*-type solid state semiconductors. We believe that the electrons from FP layer are injected into the LC that results in creating the depletion area similar to one of *p-n* junction.

Indeed, let us consider in more details the equivalent circuit in Figure 2(c^*), when the negative pulse is applied, and the diode is biased in forward direction. The external pulse voltage is divided between different elements as follows. At the front edge of the pulse the divider is basically formed by electric capacities $C_{\text{FP-LC}}$, C_{LC}, C_{PI} responsible, respectively, for the "*p-n*" junction, some remnant part of the LC layer (closer to PI layer) and PI layer. Both the $C_{\text{FP-LC}}$ and C_{LC} strongly depend on the applied voltage. The higher forward bias (negative voltage) of the "*p-n*" junction results in higher value of $C_{\text{FP-LC}}$ capacity and more narrow depletion area in the LC layer. Namely for this reason at rather small amplitudes of the external driving pulses (less than 10 V), when the depletion region is widest and comparable with the LC layer, only a small part of the external voltage of the negative polarity can be applied to the LC layer, after all the capacities have been charged. Although, the LC molecules can be driven for some time after front edge of the pulse (see the response curve 2 in Fig. 2(c)) until the charge of capacities $C_{\text{FP-LC}}$, C_{LC}, C_{PI} is reached the steady state. If the applied negative voltage is increased the depletion area becomes narrower, while the other part of the LC (with the capacity depicted as C_{LC}) increases and can be driven by the external field. After the capacities are charged by negative pulse, and the external voltage becomes zero at the end edge of the pulse, the charged capacities become "isolated" from the external circuit by the diode, which becomes biased in the inverse direction. For this reason the discharge proceeds very slowly, with the Maxwell relaxation time defined not by the LC material itself, but by the "*p*-*n*" junction. The data in Figure 2(d) are explained in similar manner using an equivalent electric circuit in figure 2(d*).

The experimental data in Figure 3 give an additional strong indication in favor of the proposed "*p*-*n*" junction model. We have

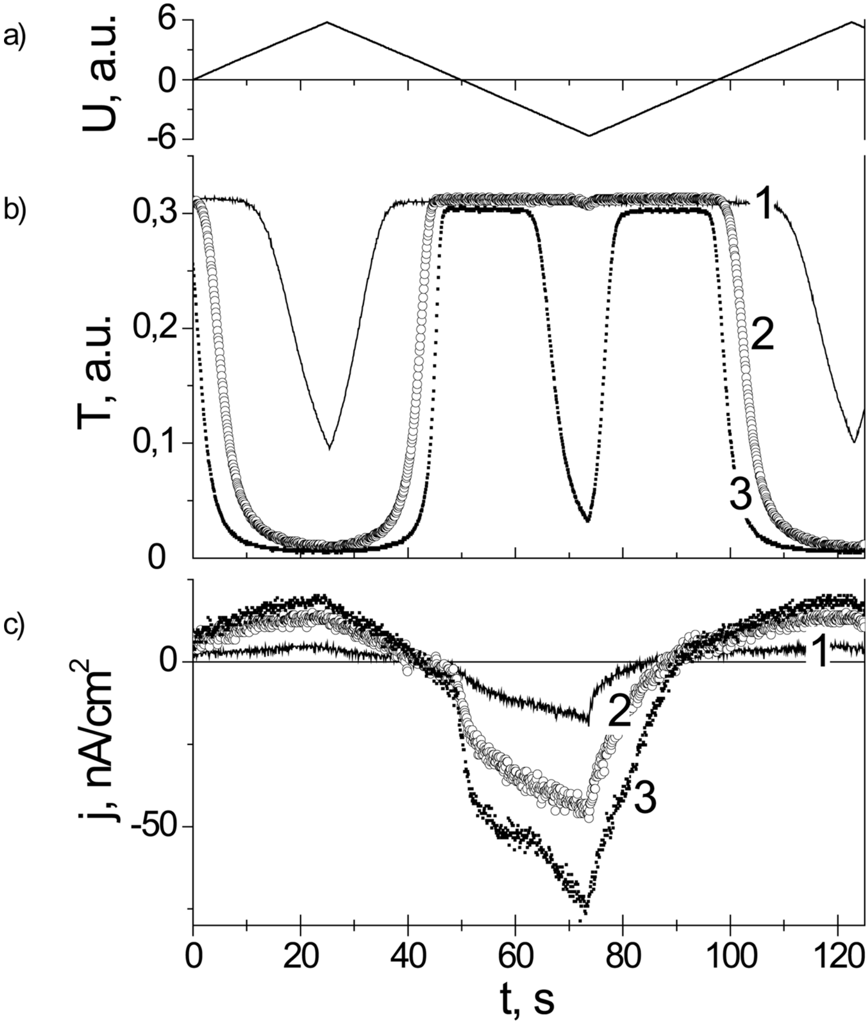

FIGURE 3 Driving waveform (a), the electrooptical (b) and electrical (c) responses of the LC cell with FP and PI alignment layers filled with the ZhKM-1391 (cell gap is 2 μm). The curves 1, 2 and 3 correspond to the applied voltage amplitudes of 2, 6 and 10 V, respectively.

measured both electrooptics and current response in the case of a low frequency (~0.01 Hz) triangular waveform applied to the LC cells with FP alignment layer. Up to external voltage amplitudes of 6 V the electrooptic response is "purely" unipolar (curves 1, 2 in Fig. 3). The LC molecules are driven by positive polarity, but no change in optics is observed if the applied voltage is negative. Only at rather high amplitudes (higher than 8 V) the LC molecules start to be driven by negative

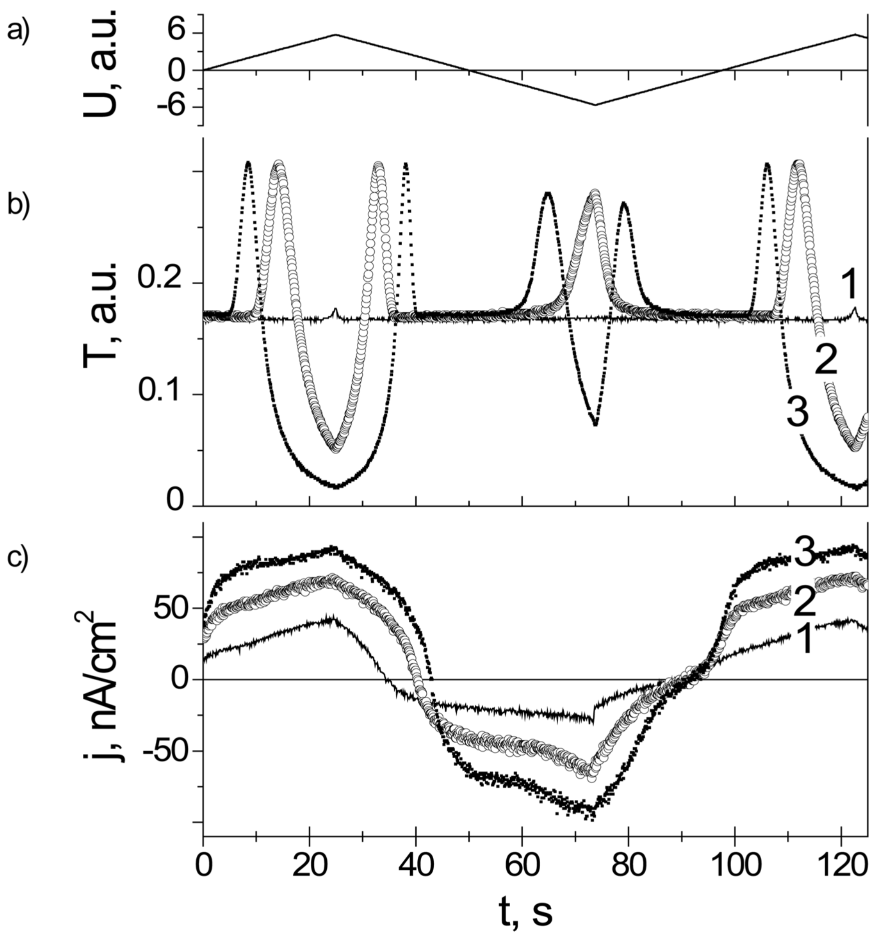

FIGURE 4 Driving waveform (a), the electrooptical (b) and electrical (c) responses of the LC cell with FP and PI alignment layers filled with the 5CB (cell gap is 2.2 µm). The curves 1, 2 and 3 correspond to the applied voltage amplitudes of 2, 4 and 6 V, respectively.

voltage (curve 3 in Fig. 3(b)). The current response in figure 3(c) show the rectification effect and, thus, also supports the discussed model. It is necessary to underline that, despite the frequency is very low, the current response still contains contributions due to the capacitive elements. For instance, by variation of the waveform frequency it was established that the current at positive polarity is basically due to the capacitance.

We have also found that the described effect is significantly influenced by the LC material. For instance, in case of the 5CB the described electrooptical properties are less pronounced (Fig. 4), and the electric rectification effect is also significantly suppressed. We explain this by higher quantity of ionic impurities that result in higher LC conductivity and suppressing the formation of the depletion region that is responsible for the discussed changes in electrooptical properties of the LC cells.

Finally, we want to remind that in this work the ferroelectric films were not subjected to some special procedure of the polarization, while some small remnant polarization can not be excluded. Using the pyroelectric method we have observed, that the ferroelectric polarization of the alignment layers can indeed be switched *in situ*, but it needs applying a rather high external voltage exceeding a value of 80 V, while here we have operated with voltage amplitudes of less than 20 V. The detailed study of LC cells with highly polarized ferroelectric alignment films is out of the scope of this paper.

CONCLUSION

The FP films produce excellent LC alignment. We presume the FP aligned LC systems to have perspectives for a new kind of LC applications. The polymer properties together with ferroelectricity of the P(VDF/TrFE) are ultimately promising for studying new electrical and electrooptical phenomena resulting from contact phenomena at the boundary of the LC and the alignment layers. We have observed the effects of very strong asymmetry in electrooptical switching and changing the director relaxation time in FP aligned nematic LC cells. The results are explained in framework of a model, which assumes creating a "*p-n*" like junction between a liquid crystal and the ferroelectric polymer.

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