

# Asymmetric electrooptic response in a nematic liquid crystal

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An asymmetric electrooptic response in nematic liquid crystal (LC) has been obtained. The liquid crystal hybrid cell was made by using a standard configuration. One of the ITO (Indium Tin Oxide) electrodes was covered with a surfactant, which induces a homeotropic alignment. The second of the indium tin oxide electrodes was covered by a thin layer of photopolymer, which was previously mixed with an acid, which favours a process of release of protons. Such cations are responsible of electrochemical process in the LC leading to an asymmetric electrooptic response, which depend on the polarity of the applied electric field. This fact is due to an internal field, which change the effective voltage thresholds for the reorientation of the liquid crystal. During the anodic polarisation, the optical switching is inhibited because the effective field decreases below the threshold value. On contrary for the opposite polarisation the effective field is enough to determine a homeotropic alignment.

*Keywords:* Liquid crystal; photopolymer; electrooptical response

Se ha obtenido una respuesta electro-óptica asimétrica en cristales líquidos nemáticos. La célula híbrida de cristal líquido fue construida utilizando una configuración estándar. Uno de los electrodos ITO fue cubierto con una película delgada de material orgánico para inducir una alineación homeótropa. El otro electrodo ITO fue cubierto con una película delgada de fotopolímero anteriormente mezclada con un ácido para favorecer la emisión de protones. Estos cationes son responsables del proceso electroquímico en LC, conduciendo a una respuesta electro-óptica asimétrica que depende de la polaridad del campo eléctrico aplicado. Este efecto es originado por un campo interno que cambia el umbral efectivo del voltaje para la reorientación del cristal líquido. Durante la polarización anódica, la conmutación óptica se inhibe debido a que el campo efectivo disminuye abajo del valor del umbral. Por el contrario, para la polarización opuesta el campo efectivo es suficiente para determinar un alineamiento homeótropo.

*Descriptores:* Cristal líquido; fotopolímero; respuesta electroóptica

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## 1. Introduction

The liquid crystal state is a state of matter in which the elongated (typically cigar-shaped) molecules have orientational order (like crystal) but lack positional order (like liquid). The liquid crystals (LC) already occupy a permanent place as electrooptical materials for the display of information, such as digital watches and clocks, pocket calculators, measurement instruments, etc. The liquid crystals are widely recognised as one of the best electrooptical materials for the screens of personal computers in their compact, "Lap-Top" version. The liquid crystals can be applied in field controllable light guides [1, 2]. The switching times of liquid crystal wave guides, based on nematic liquid crystals, are in the range of hundreds of microseconds to milliseconds, since the thickness of the film are chosen to be less than 10  $\mu\text{m}$ . Further progress depends on the development of new electrooptical effects and optimal liquid crystal materials.

Because of their anisotropic nature, the liquid crystals can be arranged to serve as wave retarders, or polarization rotators. Liquid crystals can be therefore used as electrically controlled optical wave retarders, modulators, and switchers. These devices are particularly useful in display technology.

Electrooptic effects in LC are either odd (mainly linear) or even (mainly quadratic) with respect to the external electric field [3]. The nematic liquid crystals are centrosymmetric

and nematic cell with symmetric boundary condition has the same symmetry. Such cells exhibit only the quadratic aspect in field electrooptic effects. In the special case of a hybrid cell with asymmetric boundary conditions (the planar orientation on the plate and homeotropic on the other limiting plate), the flexoelectric polarization [4] and linear electrooptic effects [5, 6], typical of polar structure, may be observed. But the electrooptical response is too weak to be used in practical application.

Recently [7] an interesting polarity sensitive electrooptical effect has been observed in nematic liquid crystal-photopolymer mixture where a gradient of polymer network density is created by strong absorbed ultraviolet light.

In the present work, we show another possible way of creating strong electrooptical asymmetry in the liquid crystal cell in a special nematic liquid crystal hybrid cell. A thin layer of photopolymer, which was previously mixed with an acid, covered one of the ITO electrodes. The second ITO electrode was covered with a surfactant, which induces a homeotropic alignment. The cell was oriented in such a way that has maximum transmitted light on a microscope stage between cross polarizers. When a square electric field is applied with  $E > E_{th}$ , the transition to homeotropic alignment occurs in the LC cell, but only in the case of cathodic polarization of photopolimer layer side of cell. When an anodic polarization is applied a maximum transmission of light occurs. In the

case of anodic polarization a process of intercalation of positive hydrogen ions (protons) will inhibit the switching to the homeotropic state (from now on we will consider the polarization with respect to polymer side of the cell). The strong dependence of the response on the sign of  $\mathbf{E}$  represents the main difference of the new NLC cell as compared with the usual NLC cells, where the switching depends on  $E^2$ .

## 2. Theoretical considerations

The liquid crystals are anisotropic fluids. In the nematic liquid crystals, the molecular positions show only short-range order in all directions, but the molecules possess a long-range orientational order of their long axes, which tend to be parallel to a common axis called the director  $\mathbf{n}$ .

In smectic liquid crystals the molecules are parallel, but their centres are stacked in parallel layers within they have random position, so that they have position order in only one dimension. The cholesteric phase is a distorted form of the nematic phase in which the orientation undergoes helical rotation about an axis.

In order to investigate the anisotropy of the properties of LC and the character of their electrooptical behavior, it is essential to assign a definite orientation to their molecules at the boundary walls of the cell.

The orientation of the molecules on the surface is characterised by two parameters: the average angle  $\theta_o$  of the molecules to the plane of the surface and the anchoring energy  $W^s$ . Using the angle  $\theta_o$  we can distinguish various orientations: homeotropic ( $\theta_o = 0$ ), planar ( $\theta_o = \pi/2$ ) and tilted ( $0 < \theta_o < \pi/2$ ).

Mechanical rubbing of the surface of polymer thin layer, which covered the electrode plate, produces a planar orientation [8]. A good planar orientation of the NLC was obtained by UV-illumination of photopolymer coated substrates without mechanical treatment [9].

The most popular technique for the homeotropic orientation is utilisation of surfactants, an orienting monolayer from the solution, by polymerisation of the organosilicon films directly onto the surface. The treatment of the walls with organometallic complex also produces a stable homeotropic orientation in nematic LC.

The orientation of the molecules at a given angle to the surface is achieved using layers of SiO produced by oblique evaporation at a very large angle ( $80^\circ - 90^\circ$ ) between the normal to the surface and the direction to the source [10].

The liquid crystals used to make electrooptic devices are usually of sufficiently high resistivity that they can be regarded as ideal dielectric materials. Because of the elongated shape of the constituent molecules, and their ordered orientation, the liquid crystals have anisotropic dielectric properties with uniaxial symmetry. The electric permittivity is  $\epsilon_{\parallel}$  for electric field pointing in the direction of the molecules and  $\epsilon_{\perp}$  is the electric permittivity in the perpendicular direction LC for which  $\epsilon_{\parallel} > \epsilon_{\perp}$  (positive uniaxial), are usually selected for electrooptic applications.

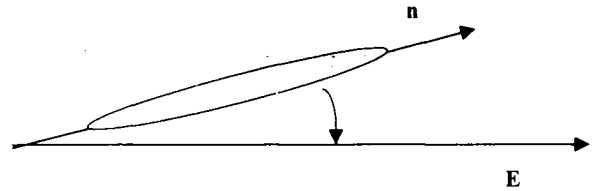


FIGURE 1. The molecule of a positive uniaxial liquid crystal rotates and is aligned with the electric field.

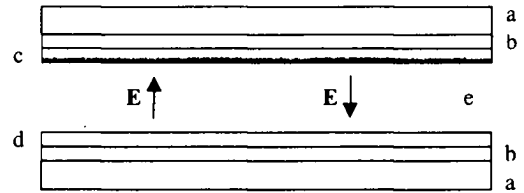


FIGURE 2. Scheme of the cell: (a) BK7 glass; (b) ITO electrodes; (c) photopolymer film; (d) surfactant for homeotropic align; (e) liquid crystal (5CB) layer.

When a steady (a low frequency) electric field is applied, electric dipoles are induced and as the result the electric forces exert torque on the molecules. The molecules rotate in a direction such that the free electrostatic energy,  $-\frac{1}{2}\vec{E}\vec{D} = -\frac{1}{2}\{\epsilon_{\parallel}E_1^2 + \epsilon_{\perp}E_2^2 + \epsilon_{\perp}E_3^2\}$ , is minimized, (here  $E_1, E_2$ , and  $E_3$  are components of  $\mathbf{E}$  in the direction of the principal axes). Since  $\epsilon_{\parallel} > \epsilon_{\perp}$ , for a given direction of the electric field, the minimum energy is achieved when the molecules are aligned with the field, so that  $E_1 = E_2 = 0$ ,  $\mathbf{E} = (0, 0, E)$ , and the energy is then  $\frac{1}{2}\epsilon_{\parallel}E^2$ . When the alignment is complete the molecules axis points in the direction of the electric field (Fig. 1). Evidently, a reversal of the electric field produces the same molecular rotation. An alternative electric field generated by an ac voltage also has the same effect.

In most practical applications and when examining liquid crystals, sandwich-type cells are used. A flat capillary with a thickness of (8–30  $\mu\text{m}$ ) is formed from two glass plates with conductive transparent electrodes coating ( $\text{In}_2\text{O}_3$  or ITO).

## 3. Experiment and results

As it is shown in Fig. 2, in our investigation special hybrid aligned nematic liquid crystal cells have been used. In the hybrid cell, the molecules have homeotropic order on one boundary and planar order on the second boundary. The homeotropic alignment on the one boundary was obtained with a solution (1:1000) of octadecyltrimethoxysilane.

The second boundary plate was covered by spin coating with a solution comprised a 90/10 mixture of prepolymer acrilat de butyl and acid itacomic. The mixture was doped with 1% wt. of a photoinitiator. After spin coating the prepolymer film was irradiated for 20 minute by nonfiltered xenon UV light. The distance between the lamp and plate was 60 cm.

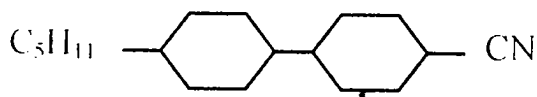


FIGURE 3. Liquid Crystal 5CB [K 24 N 35.3 I] provided by Merck, where K, N, I represent crystalline, nematic and isotropic phase respectively.

We made the hybrid cell with a thickness of  $10\ \mu\text{m}$  (using Mayler spacers), and a standard sandwich configuration [11]. The liquid crystal 5CB (see Fig. 3) provided by Merck has been used.

The dielectric anisotropy,  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} = +9.9$  (at room temperature,  $20^{\circ}\text{C}$ ), being  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  the dielectric constants parallel and perpendicular to the director  $\mathbf{n}$ , respectively. The

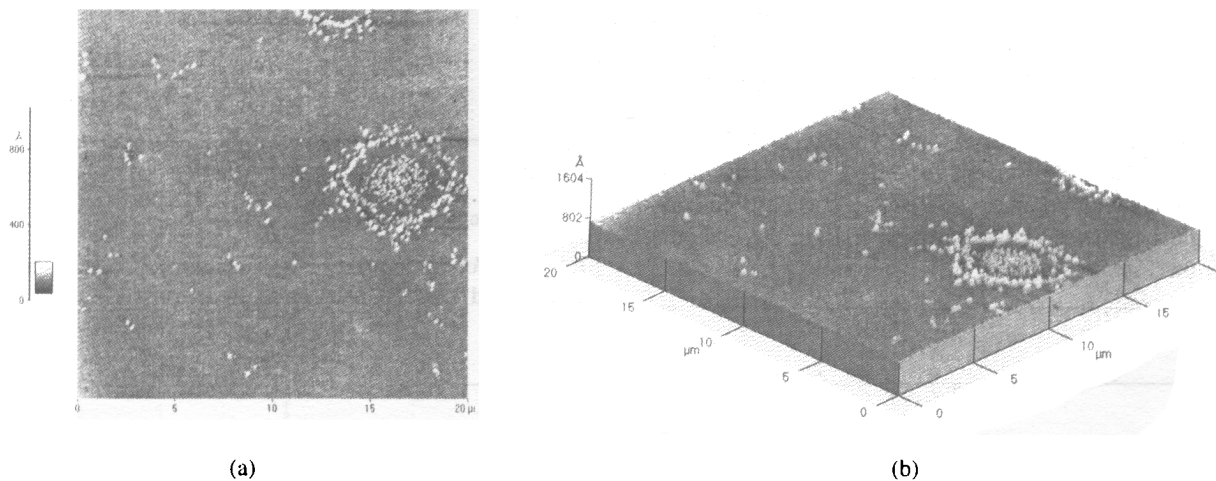


FIGURE 4. Typical AFM image of the photopolymer layer surface. (a) Top view; (b) isometric view.

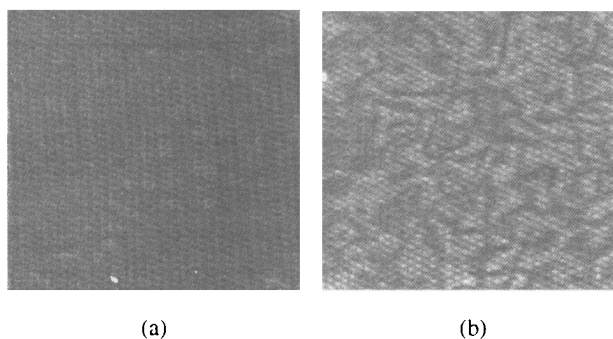


FIGURE 5. Images observed to CCD camera: (a) anodic polarization of photopolymer layer; (b) cathodic polarization of the photopolymer layer.

cell was filled with 5CB in its isotropic phase. Since no orienting procedure was applied to the plate with the polymer layer and the other plate can induce a homeotropic orientation, between cross polarizers we can see a degenerate planar orientation.

The optical observation was made by using a polarising microscope (Axioskop, Zeiss) to observe the alignment of the LC between cross polarizers. The polarising microscope was equipped with an image acquisition system consisting of a CCD Colour Camera connected to a PC and a videorecorder. A function generator provided square wave voltage pulses of amplitude between 0–10 V and various frequencies. The measurements of the discharge electric current in the cell have been made.

By using AFM (Atomic Force Microscopy) technique the structure of photopolymer surface layer have been analysed. As can be seen in Fig. 4 the surface of photopolymer layer shows a quasiplanar character on a small scale explored (up to  $5\ \mu\text{m}$ ). For that, the liquid crystal molecules will be having a degenerate planar alignment at the interface LC-photopolymer layer.

The application of a low frequency electric field (square wave shape) perpendicular to the electrode surfaces induces an asymmetric optical switching as it can be seen directly in the video-microscope images shown in Fig. 5. Initially, the cell was oriented in such a way to have maximum transmitted light on a microscope stage between cross polarizers. In Fig. 5a, when the cathodic polarization of the square electric field is applied of the photopolymer layer side of cell, the black image shows a homeotropic alignment of the molecules inside of the cell. The image is black, because the optical observation is made between the cross polarizers, and the transmission through a homeotropic alignment cell goes practically to zero.

In Fig. 5b. when the anodic polarisation of the square electric field is applied of the photopolymer layer side of cell, for a very short time one can see a strong diffusion of the optical field and a decrease of the electric field in the bulk below the threshold force the image to become bright. The degenerated planar texture in the video image is due to an internal field, which change the effective voltage threshold for the reorientation of the LC. This internal field appears becau-

se the external positive field will push out the protons which were released by photopolymer layer into the LC. This behavior was obtain for frequencies in the range 50 mHz–1 kHz, and for square electric voltage in the range, 3–9 V.

From the electric measurements we can see that the asymmetric electrooptic behavior of our cell is connected with asymmetry of discharge electric current. If the amplitude of the square electric voltage is low, for example 2 V (Fig. 6), the cell exhibits a homeotropic texture for both, anodic and cathodic polarization. The discharge current have the same amplitude which means that the electric field lied is to low to extract a significant number of the protons from photopolymer layer.

With the increase of the electric voltage to 3 V over, (Fig. 7b), the discharge current following the anodic polarization of plate with photopolymer, is larger (in absolute values) than the discharge current which follows the cathodic polarization (Fig. 7a).

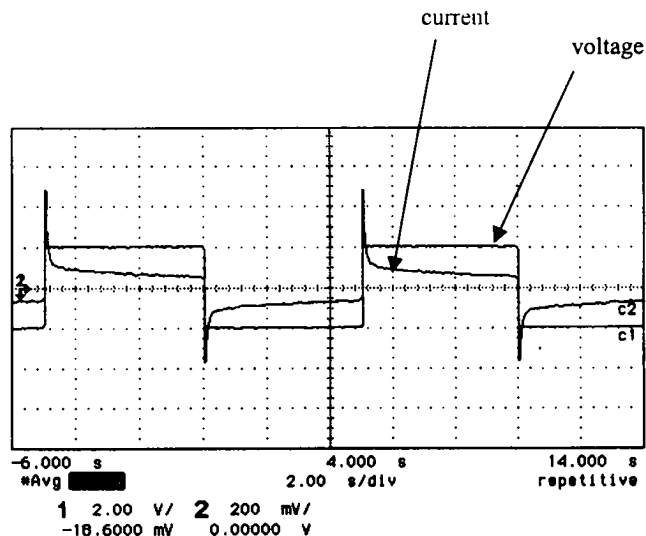
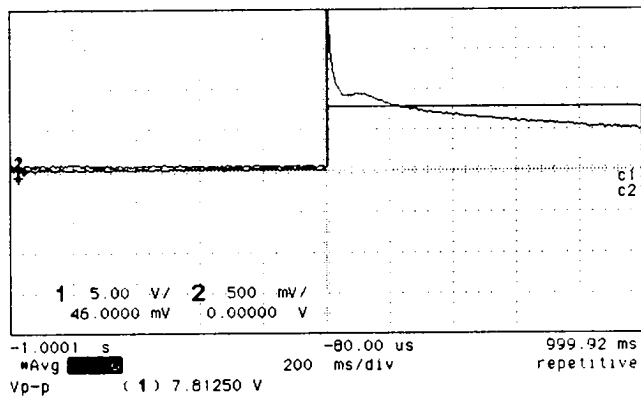
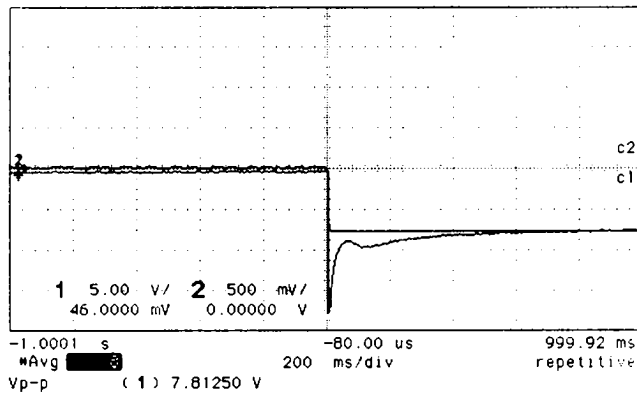


FIGURE 6. Voltage form and current oscillograms taken at the voltage amplitud 2 V (100 mHz) for an 10  $\mu\text{m}$  cell (5CB).



(a)



(b)

FIGURE 7. Voltage form and current oscillograms taken at the voltage amplitud 8 V (100 mHz) for an 10  $\mu\text{m}$  cell (5CB): (a) polarity (-) at photopolymer layer; (b) polarity (+) at photopolymer layer.

In the case of anodic polarization the electric field inside of cell is positive, oriented from photopolymer layer toward the liquid crystal interface, whereas for the cathodic polarization it is negative. The positive field will tend to attract electrons from the ITO-liquid crystal interface and also to push protons from the photopolymer layer into the liquid crystal. Both currents having the same direction give birth to a rather strong current, which inhibits the homeotropic alignment.

If we now have the cathodic polarization, the electric field will tend to attract electrons from photopolymer layer but these cannot be found in it, also ITO cannot inject positive charges into the liquid crystal because ITO is *n*-type semiconductor. The electric field will induce a homeotropic alignment into the cell. Such a homeotropic texture is black between the crossed polarizers.

Similar measurements made with a hybrid cell filled with 5CB but where the photopolymer was not mixed with an acid

before the UV exposure, shown, of course, a complete symmetrical optical and electrical response with respect to the polarity of electric field.

#### 4. Conclusions

We have examined the asymmetric electrooptic response of a LC layer in a hybrid cell. One of the electrodes was covered with a thin film of photopolymer mixed with an acid, a material that releases protons. Such cations are responsible of electrochemical process in the LC leading to an asymmetric electrooptic response, which depend on the polarity of the applied electric field. This fact is due to an internal field, which change the effective voltage thresholds for the reorientation of the liquid crystal. During the anodic polarisation, the optical switching is inhibited because the effective field

decreases below the threshold value. On contrary for the opposite polarisation the effective field is enough to determine a homeotropic alignment.

In the similar liquid crystal cell, but where the photopolymer is not mixed with the acid, the optical response is qua-

dratic *versus* the exciting field and no asymmetric behavior was observed.

Further studies are planned, involving other mixtures of photopolymer and acid to optimise the interaction with the liquid crystal films.

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