

# New cellulose derivatives composites for electro-optical sensors

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Received 11 November 2005; accepted 24 July 2006

Available online 18 September 2006

## Abstract

In this work we used hydroxypropylcellulose (HPC) and acetoxypopylcellulose (APC) to produce free standing solid films ( $\sim 60\ \mu\text{m}$ ) for electro-optical devices. Cellulose derivatives films were prepared from crosslinked both HPC and APC isotropic and liquid crystalline solutions without and with a low molecular weight nematic liquid crystal mixture (LC) E7.

Films prepared from anisotropic solutions presented a band texture and E7 droplets of micron and submicron size were found to coexist with the band texture in the films prepared with E7.

The optical cells were composed by the cellulose derivatives films covered on both free surfaces by a layer of the LC E7 and placed between two transparent conducting substrates. All the electro-optical cells prepared showed switching times in the range of some milliseconds to hundreds of milliseconds. The on-voltage ( $V_{\text{on}}$ ) is lowered for cells prepared with the ester derivative film obtained from isotropic solutions. The maximum transmission values show a clearly tendency to decrease for the cellulosic matrix prepared from anisotropic solutions with and without nematic liquid crystal droplets.

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**Keywords:** Ester and ether cellulose derivatives; Liquid crystals; Electro-optical cells; Electro-optical properties

## 1. Introduction

Hydroxypropylcellulose (HPC) and HPC esters can generate lyotropic and thermotropic mesophases (Bianchi, Marsano, Picasso, Matassini, & Costa, 2003; Gray, 1994). Due to the ability of their molecules to spontaneous self-assemble in helicoidal arrangements light can be reflected selectively (Giasson, Revol, Gray, & Stpierr, 1991; Hou, Reuning, Wendorff, & Greiner, 2000; Sato, Nakamura, Teramoto, & Green, 1998; Tseng, Valente, & Gray, 1981).

Bulk aliphatic esters can exhibit cholesteric reflections in the visible range of the spectrum. The selective reflection depends on several parameters including the degree of esterification (Bhadani & Gray, 1983) and on the temperature (Rusig et al., 1994). The pitch of the cholesteric

helix can also be locked by using different procedures among them by photoinitiated crosslinking of pendant acrylate groups (Muller & Zentel, 2000). One of the most studied thermotropic cellulose esters is Acetoxypopylcellulose (APC), it is cholesteric from below room temperature up to  $180\ ^\circ\text{C}$  (Tseng et al., 1981) and can originate lyotropic phases in some common solvents (Laivins & Gray, 1985a; Laivins & Gray, 1985b). Rheo-optical and rheological studies (Riti, Cidade, Godinho, Martins, & Navard, 1997) were also performed in APC in order to better understand the relationship between the textures observed in optical microscopy and the light scattering patterns.

The study of composite materials making use of cellulose layers and liquid crystals for electro-optical applications opened new horizons for using cellulose derivatives (Godinho, Martins, & Figueirinhas, 1996; Graighead, Cheng, & Hackwood, 1982). Electro-optical cells were produced by enclosing a cellulose derivative film, obtained

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from an isotropic solution, with two E7 nematic liquid crystal layers and the set placed between two transparent conducting substrates. These cells show electro-optical properties similar to those reported for polymer dispersed liquid crystals (PDLCs) but the polymer matrix and the liquid crystal component are arranged in a diverse fashion that enables the modification of the polymer surface in order to optimize the optical properties of the cell (Figueirinhas, Almeida, & Godinho, 2004).

It was found that a fine tuning of the surface properties of the solid cellulosic matrix can be achieved by varying their preparation conditions (Godinho, Fonseca, Ribeiro, Melo, & Brogueira, 2002). The influence of different matrix parameters upon the electro-optical behaviour of the cells was studied (Almeida et al., 2002; Sebastião et al., 2002). In order to optimize and understand the electro-optical characteristics presented by these kinds of cells the study of the anchoring properties of the LC on the solid cellulosic films was also performed (Fonseca, Godinho, & Ribeiro, 2005).

Some cellulose derivatives were used as matrix materials for preparation of PDLC films. The influence of the curing temperature on the morphology of the films prepared from ethyl cyanoethyl cellulose/poly(acrylic acid)/4'-*n*-pentyl-4-cyanobiphenyl was analysed (Zhou & Huang, 2002). It was reported that the size of the dispersed droplets and the uniformity of their diameter depends on the curing temperature of the composite material.

There have also been several basic studies of liquid crystal alignment in spherical and elliptical droplets in elastomeric matrices (Aphonin, Panina, Pradin, & Yakolev, 1993). It is also known that polymer chains align during the PDLC film stretching process and this promotes subtle changes in the liquid crystal alignment in the droplets as a result of the polymer alignment induced by the tensile strain (Amimori, Priezjev, Pelvovits, & Crawford, 2003). Uniaxially stretched anisotropic phase separated polymer films were recently obtained from APC and their optical (Filip, Costa, Figueirinhas, & Godinho, 2006a) and mechanical properties (Filip, Costa, Figueirinhas, & Godinho, 2006b) have been studied.

In this work we have studied the electro-optical behaviour of several cells assembled with APC and HPC films crosslinked with a diisocyanate obtained from isotropic and anisotropic solutions with and without dispersed liquid crystal droplets/LC composite systems. The influence upon the electro-optical properties of the acetylated cellulose matrix was studied and compared with the results obtained for the ether derivative. A qualitative relationship between the structure of the matrix and the electro-optical behaviour of the cells was also established.

## 2. Experimental

### 2.1. Materials

Hydroxypropylcellulose (HPC) ( $M_w = 100,000 \text{ g mol}^{-1}$ ) was purchased from Aldrich and dried in vacuum at  $50^\circ\text{C}$

for about 48 h before use. Acetic anhydride (Merck), acetic acid (Merck) and 1,6-Hexamethylenediisocyanate (HDI) (Aldrich) were used without further purification. N,N-dimethylacetamide (DMAC) (Merck) was used as received.

The nematic liquid crystal mixture used was the commercially available mixture E7 (Merck Ltd., UK).

### 2.2. Synthesis of acetylated polymer and cross linked reactions

The synthesis of acetoxypropylcellulose was performed according to the procedure described in literature (Tseng et al., 1981). For this work the acetylation of (hydroxypropyl)cellulose (Aldrich, nominal  $M_w = 100,000$ ) (molar substitution equal to 4 determined by NMR  $^1\text{H}$ ) (50 g) was performed by adding the HPC to acetic anhydride (160 g) to give a viscous solution on standing. Acetic acid (15 g) was added to initiate esterification, and the mixture was allowed to stand for one week, with stirring. The polymer was washed with water and purified by solution in acetone and reprecipitation in water. The final product was dried in an oven at  $60^\circ\text{C}$ , the final yield was around 75%. The number of acetyl groups per residue was evaluated by NMR  $^1\text{H}$  and is 2.0.

Isotropic (30% by weight) and nematic chiral (60% by weight) solutions were obtained, in 5 ml glass containers, by adding APC and HPC to dimethylacetamide (DMAC), at room temperature, the contents were allowed to mix for several weeks.

The HPC and APC were lightly cross linked with HDI, under nitrogen atmosphere, and to the anisotropic solutions the commercial low molecular liquid crystal E7 (12% wt) was also added. The polymers idealised structures along the chemical steps involved are shown in Fig. 1.

### 2.3. Preparation of solid films

After homogenization the solutions were cast onto a Teflon plate at room temperature with a calibrated Gardner knife moving with a controlled rate,  $v = 5 \text{ mm/s}$ . The films were cured at room temperature and then carefully peeled from the substrate. The film average thickness was approximately  $60 \mu\text{m}$ .

### 2.4. Preparation of electro-optical cells and measurements

The cells, with the four kinds of cellulosic matrices obtained, were prepared from the cellulose derivative film surrounded by two nematic liquid crystal layers placed in between two transparent conducting glasses substrates. In Fig. 2, we illustrate the cell preparation.

Five distinct cells were prepared, APC films were used in three of them and HPC films in the other two. Two of the three APC film samples used in the cells were prepared from anisotropic solutions with (APCaniE7) and without (APCani) added E7, respectively. The third APC film sample was prepared from an isotropic solution (APCiso). The

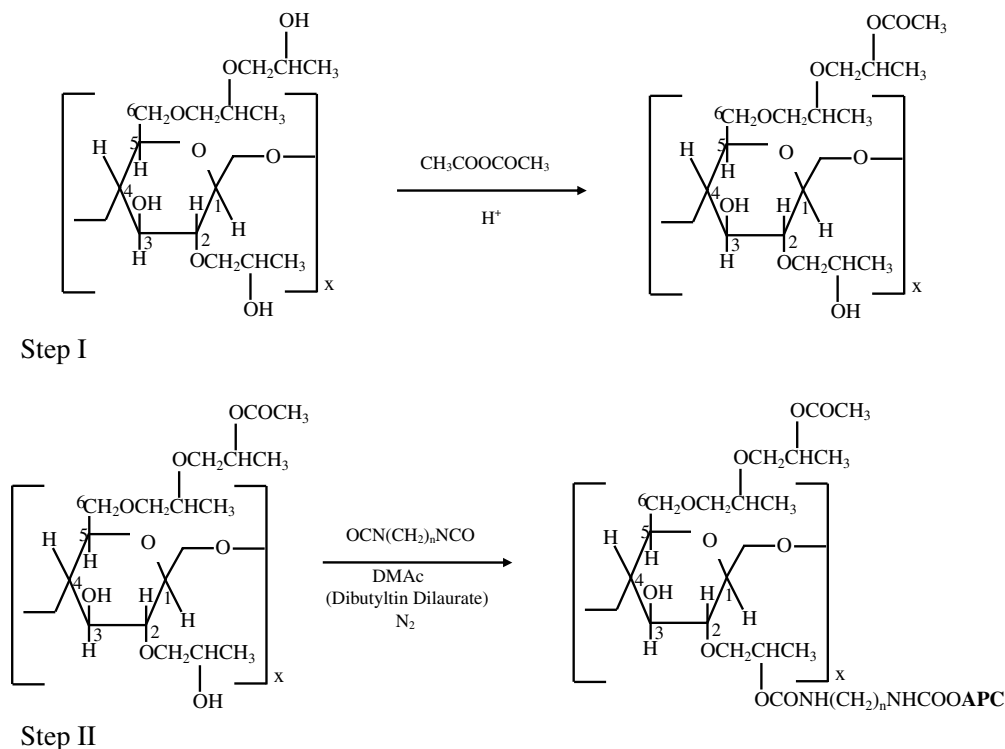


Fig. 1. Chemical steps involved in the synthesis of the polymer matrix. (Step I) Modification of hydroxypropylcellulose (HPC) (DS = 2; MS = 3; DP = 236) to give the ester acetoxypolypropylcellulose (APC) (ME = 2; MS = 3). (Step II) Crosslink reaction between the free unreacted hydroxyl groups from APC and the diisocyanate to give urethane links.

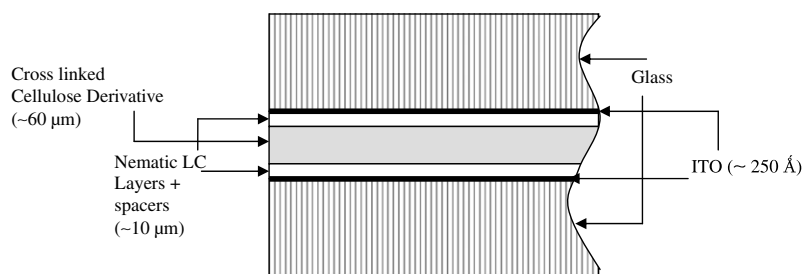


Fig. 2. Schematic representation of the cellulosic/liquid crystal electro-optical cell.

HPC cells were prepared with films prepared isotropic (HPCiso) and anisotropic plus E7 (HPCaniE7) HPC solutions, respectively.

The electro-optical characterization of the cells was carried out using a helium–neon laser-equipped optical bench in association with a function generator, a voltage amplifier and a diode detector. To measure the sample switching times, AC voltage pulses were used. All the electro-optical results were obtained for normal sample incidence, at room temperature ( $\sim 25^\circ\text{C}$ ).

### 2.5. Optical microscopy

Optical microphotographs were taken using an Olympus microscope equipped with a camera and cross polarizers.

## 3. Results and discussion

The electro-optic switching in these cellulose matrix/liquid crystal composites resulting from a controllable light scattering process is shown in Fig. 3.

The nematic liquid crystal layers are characterized by a molecular organization where the density function is that of an isotropic liquid but the molecules are on average oriented, defining a unit vector called the director. The director field in the liquid crystal layers is determined by a balance between the bulk elastic distortion energy that favors a uniform director field, the electrical energy that for positive dielectric anisotropy tends to align the director with the field and the constraints imposed by the anchoring of the director at the interfaces with the polymer and the conducting substrates. The

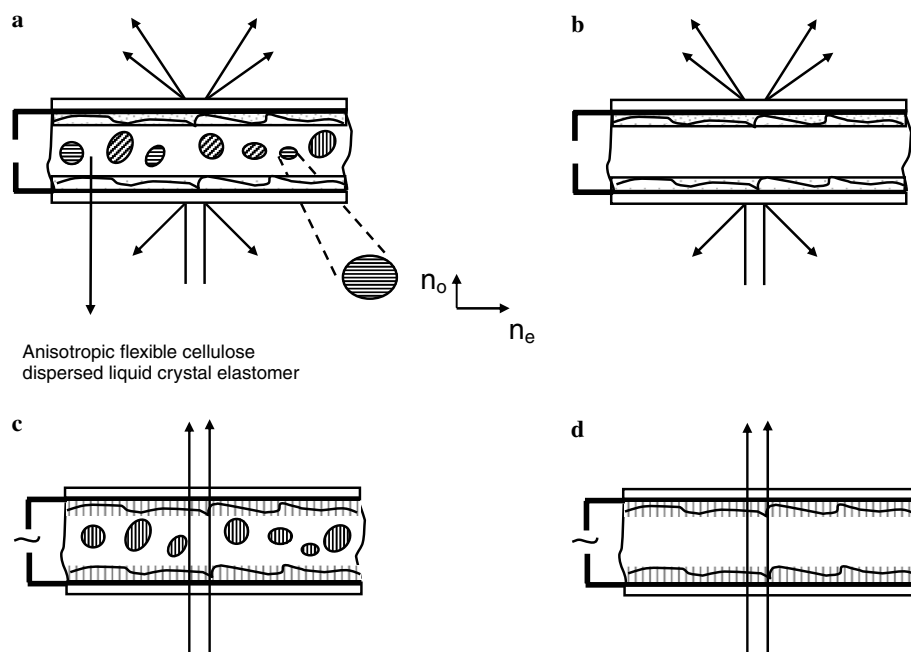


Fig. 3. Liquid crystal cellulose composite principle of the electro-optical effect. (a) and (b) the electric field is off, the cell is scattering; (c) and (d) the electric field is on, the cell is transparent. (a) and (b) the matrix consists of a flexible cellulose anisotropic elastomer in which randomly oriented liquid crystal domains are dispersed. (b) and (d) the matrix is a flexible isotropic or anisotropic cellulose derivative. In both cases (a) and (b) the cellulose matrix is surrounded by two nematic liquid crystal layers (see Fig. 2).

cellulosic matrices impose a planar alignment of the liquid crystal at their surfaces that extends to all liquid crystal volume in the absence of the electric field. When light rays propagating in the medium encounter different optical paths caused by the polymer surface rugosity and the mismatch between cellulose derivative refraction index and the liquid crystal extraordinary index, produce a destructive interference pattern scattering light, the sample is in the off state. When an electric field of adequate strength is applied to the optical cell, the nematic director aligns with the field, and the differences between optical paths are strongly reduced, suppressing the destructive interference and the cell transmits light, the cell is in the on state. In Fig. 4 is presented the voltage dependence of the light transmission coefficient for the five samples analysed. From these results the maximum transmission of the sample, the contrast given by the ratio between maximum and minimum transmissions and the on-voltage were determined and are shown in Table 1.

The liquid crystal–polymer surface interaction energy is crucial for the functioning of these cells and several characteristics of the films influencing this interaction were considered in this work. The polymer–liquid crystal surface interaction was changed by the use of a different cellulose derivative (HPC and APC), by the preparation of the polymer film both from isotropic and anisotropic solutions and by adding nematic E7 to the anisotropic solutions producing also E7 droplets dispersed in the polymer film. These droplets introduced an additional scattering effect unaffected

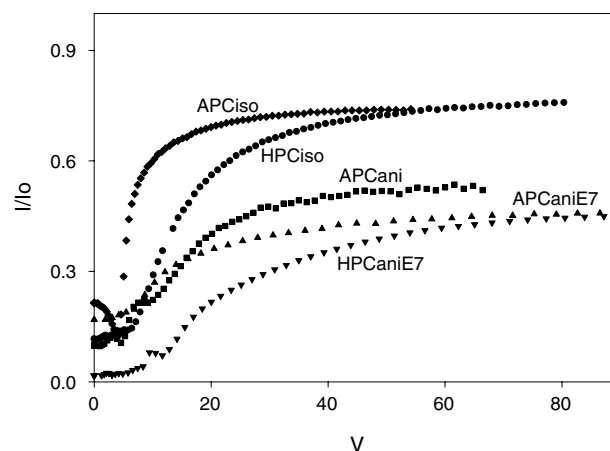


Fig. 4. Voltage dependence of the light intensity transmission coefficient obtained for the five samples analysed.

by the switching field of the optical cells lowering their maximum transparency

The modification of the polymer surface, from water soluble cellulose ether to an ester gave rise to a different electro-optical behaviour, the  $V_{on}$  decreases as the affinity of the liquid crystal to the polymer substrate decreases.

The anisotropy of the matrices also affects the electro-optical properties of the cells, the contrast is lowered as is  $V_{on}$ . In the anisotropic matrices the molecules of the liquid crystal were found to be aligned along shear direction, the zenithal anchoring was found to be planar and rather strong (Fonseca et al., 2005) increasing the  $V_{on}$  voltage.



Table 1  
Summary of the electro-optical results obtained for the five different cells studied

Sample	Maximum transmission/ percent	Maximum contrast	$V_{on}/V_{rms}$
APCiso	74.6	6.12	18.5
HPCiso	75.9	6.59	38.0
APCaniE7	48.3	2.87	67.6
HPCaniE7	48.0	28.9	69.4
APCanis	54.2	5.64	38.6

The contrast of the cells was obtained from the ratio (maximum transmission)/(minimum transmission).  $V_{on}$  was calculated from the voltage dependence of the transmission coefficient and represents the applied rms voltage necessary to reach 95 per cent of the maximum transmission of the sample.

The optical anisotropy of the cells prepared can be detected by placing them between crossed polarizers. In Figs. 5(a) and 6(a) representative images obtained from polarized light transmission microscopy are shown by the cells prepared from anisotropic films without and with dispersed liquid crystal droplets, respectively. We observed the presence of several multidomains that when the electric field ( $\sim 1.1 \text{ V } \mu\text{m}^{-1}$ ) was applied changed to the pattern shown in Figs. 5(b) and 6(b).

In Figs. 5(c) and 6(c) we present the pictures obtained for the initial ester anisotropic cellulose derivative free standing films without and with droplets of liquid crystal, respectively, before preparing the electro-optical cells.

The anisotropic cellulosic matrices studied in this work show three types of periodic structures with different average wave lengths and different average orientations relative to the shear direction, those periodicities were also found

and some of them evaluated by atomic force microscopy in hydroxypropylcellulose solid films (Godinho et al., 2002). The periodicity found at approximately  $\sim 90 \text{ } \mu\text{m}$  in APCani is in agreement with the stripe behaviour along the shear direction found in the cell prepared from this matrix where each wavelength is split in half in two stripes of different LC (E7) orientation (see Fig. 5). The stripes are separated by LC orientation defects. The matrix imposed alignment is translated in the LC orientation pattern observed. The bands structure response to the electric field can be seen in Figs. 5(a) and (b). The LC response to the electric field, in the matrices with E7 droplets (Fig. 6(c)), is shown in Figs. 6(a) and (b) where the alignment of the director in the droplets with the electric field is observable.

#### 4. Conclusions

In this work it was found that chemical differences in the polymeric matrix produce significant changes in the electro-optical behaviour of the cells stressing the importance of the liquid crystal–polymer surface interaction for the electro-optical behaviour of these systems. These observations are in agreement with the working principle thought to be behind these optical cells which is based on the existence of different optical paths that can be equalized through the application of an electric field to the nematic liquid crystal as described before, but the differences in optical paths are not only determined by polymer rugosity but also by the nematic director alignment at the polymer surface.

The presence of liquid crystal droplets in the polymer matrix in these systems brings additional light scattering

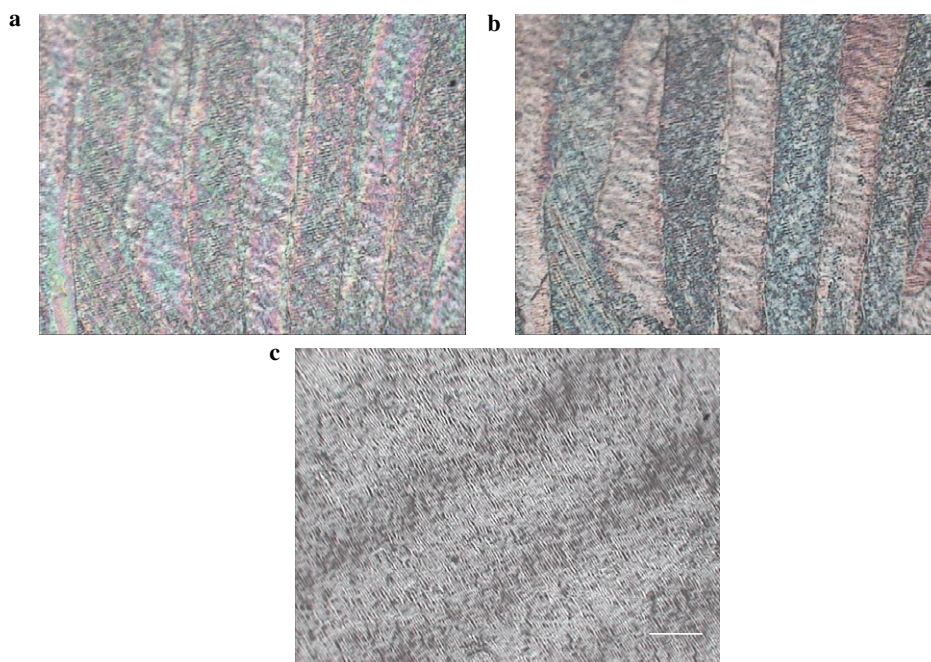


Fig. 5. (a) Stripes microdomains at room temperature of cell prepared from APC cross linked anisotropic matrix containing the liquid crystal before electric field is applied. (b) as for (a) at the time electric field was applied. (c) Initial cellulose anisotropic matrix without liquid crystal. All with crossed polarizers. Bar indicates  $50 \text{ } \mu\text{m}$ .

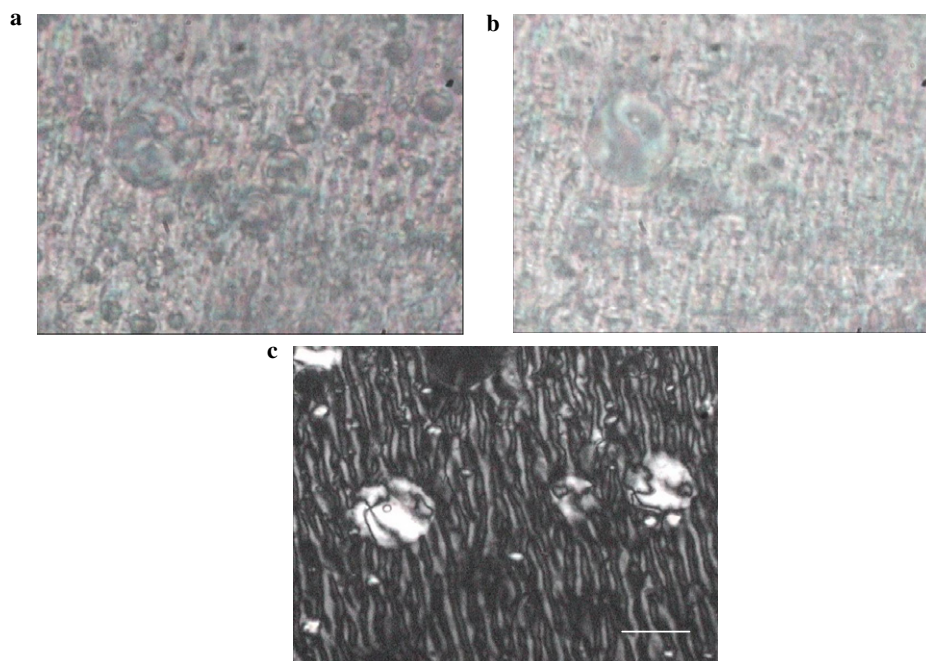


Fig. 6. (a) Texture observed, at room temperature, for cell prepared from APC cross linked anisotropic matrix with dispersed nematic liquid crystal droplets and containing the liquid crystal before electric field is applied. (b) as for (a) at the time electric field was applied. (c) Initial cellulose anisotropic matrix with dispersed nematic liquid crystal droplets. All with crossed polarizers. Bar indicates 10  $\mu\text{m}$ .

part of which is not electrically switchable as desired in an optical valve.

### Acknowledgments

This work was supported by projects POCTI/CTM/56382/2004 and POCTI/CTM/37435/2001 by the Portuguese Science Foundation (FCT) through Pluriannual contracts with CENIMAT. D. Filip gratefully acknowledges FCT for Grant SFRH/BPD/19722/2004.

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