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## Liquid Crystals

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## Electro-optical cells using a cellulose derivative and cholesteric liquid crystals

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A cellulose derivative/liquid crystal composite-type electro-optical cell using a commercial cholesteric liquid crystal (CLC) was investigated. The electro-optical properties of the system were examined, i.e. the dependence on applied voltage of the reflected wavelength and the minimum and maximum transmissions. A thin film of the CLC was dispersed with a cross-linked cellulose film of 25  $\mu\text{m}$  thickness. In the voltage dependence of the reflected wavelength it was verified that there is a hysteresis in the reflected wavelength. The variation of the reflected wavelength with temperature was also determined. The results are analysed in the framework of similar systems described in the literature for CLC dispersed in a polymer matrix.

**Keywords:** cellulose derivative; cholesteric liquid crystal; electro-optical cell; temperature effect; pitch

### 1. Introduction

The historic discovery of polymer-dispersed liquid crystal (PDLC) materials for electro-optic devices opened a new direction for LC research and interest in confined LCs flourished. Much work has been done on these topics, starting from the surface effect of the nematic to isotropic phase transition to the development of light valve applications. The mechanism of light scattering in PDLC materials was addressed by Zumer and Doane (1) for sub-micron droplet structures and refractive index matching. The above mentioned studies of PDLC with nematic LC materials led the researchers to test the chiral nematic LC under confinement. For materials with negative dielectric anisotropy and short pitch, Yang and Crooker (2) showed that it is possible to achieve texture showing bright selective reflection by employing an electric field. Later, the alignment of ferroelectric and antiferroelectric LC droplets was controlled by the mechanical shearing technique during the photopolymerisation process. Since they are easily available at low cost and have good optical properties, cellulose and cellulose derivatives have become interesting to researchers of applications in this field.

Hydroxypropylcellulose (HPC) is readily available at low cost and exhibits a good stability toward UV light (3). Recently, it was found that solid films of HPC and HPC cross-linked with diisocyanates can be used as the matrix of a polymer/LC composite system with application in the production of electro-optical

displays (4). The electro-optical behaviour of such cells depends on the nature of the cellulose derivative used, the nematic LC, the preparation conditions of the cells and the ruggedness of the film's surface (4–7). It was pointed out that one of the advantages of this kind of system over the conventional PDLC-type systems (8) is the possibility of preparing the polymer film in absence of the LC component. Cellulose-dispersed liquid crystal (CDLC)-type cells have been widely studied and improved (4–7) and as PDLCs they are switchable from an opaque to a transparent state by an applied electrical field. These systems have shown relevant electro-optical properties along with good temporal stability and acceptable contrast ratios that may challenge usual PDLC systems for window applications.

Nematic and cholesteric PDLC materials have been widely studied. Theoretical predictions, taking into account the shape of the droplets (9–11), indicated that electro-optical properties could be improved by modification of droplet shape (12, 13). Polymer-dispersed cholesteric liquid crystals (PDCLCs) have been used in electro-optical displays (14–18). Oriented chiral nematics confined in elliptic droplets dispersed in an organic monomer matrix have also been described in literature. In these systems colour diffusion processes can be hindered by the shape of the cholesteric droplets (19).

In this paper, results are presented for PDCLCs where the cholesteric LC is not confined in droplets but placed in layers covering a polymeric thin film. The textures exhibited by the LC, as well as the wavelength

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of the reflected light at several temperatures and applied voltages, were observed and measured using polarising optical microscopy (POM).

## 2. Experimental

In the preparation of the solid films, HPC (commercial reagent grade, Aldrich,  $M_w = 100\,000\text{ g mol}^{-1}$ ), acetone (Aldrich, without further purification) and 1, 4-diisocyanatobutane (BDI, Aldrich) as a cross-linking agent were used. The preparation of the HPC solution in acetone with the BDI cross-linking agent was performed according to a procedure described previously (4). The reaction with BDI (7% w/w) was performed under nitrogen atmosphere for 3 h. The HPC percentage in the solution was 12% w/w.

The solution with the cross-linked HPC was spread on a flat Teflon film by means of a calibrated ruler (0.5 mm), moving at a constant speed of  $5\text{ mm s}^{-1}$ . After the spreading of the solution, the solvent was allowed to evaporate for 2 days in a laboratory atmosphere ( $25^\circ\text{C}$ ), and a cross-linked HPC solid film was obtained ( $\approx 25\text{ }\mu\text{m}$  thick).

The cholesteric LC used in the cell preparation was the commercial cholesteric LC TI 511 from Merck. The cells were obtained by covering the rough surface of the HPC solid film, with a  $10\text{ }\mu\text{m}$  thick layer of the cholesteric LC TI 511. The thickness of the LC was controlled by  $10\text{ }\mu\text{m}$  silica spherical spacers. The set was then placed in between two transparent conducting glasses substrates (ITO coated glass). Figure 1 shows a schematic illustration of the cell preparation procedure. Subsequent measurements were performed 24 h after the film had been covered with the LC, to allow stabilisation.

The LC textures were observed using a polarising optical microscope (Olympus BH2-UMA) equipped with a camera. The POM observations were performed between cross polarisers.

The wavelengths,  $\lambda_o$  ( $\lambda_o = \bar{n}P$ , where  $\bar{n}$  is the average refractive index and  $P$  the pitch of the cholesteric structure), of the maximum selective reflection peaks were recorded with a Jobin-Yvon H10-VIS monochromator, mounted on the microscope stage, equipped with a photomultiplier and a data recorder (Jobin-Yvon Data Link) (20).

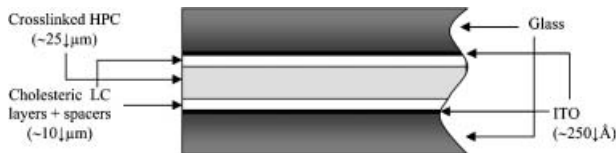


Figure 1. Schematic representation of the celluloptic/liquid crystal electro-optical cell.

The temperature variation was achieved using a Mettler FP 82 HT hot stage coupled to the Olympus microscope.

The measurements performed with applied voltage were made using a controllable ac wave generator and an amplifier.

## 3. Results and discussion

Macroscopically, the cells had a red appearance, as observed from the visible light reflection in the OFF state. On application of an electric field, the cells lost their colour because of the cholesteric LC alignment under the applied field. Figure 2 shows the macroscopic appearance of the cells with and without an applied electrical field.

Looking at the cells under the microscope in reflection mode, with the same degree of excitation by application of an electric field, a shift of colour due to a shift of the wavelength of the reflected light was clearly observed. Figure 3 shows the reflection optical microscopy photographs of the cells with and without an applied electrical field.

When observing the cells through the optical microscope in transmission mode for three states of electrical excitation, the LC textures formed in each state could be visualized. Figure 4 shows different cholesteric LC textures for three different levels of electrical excitation.

The dependence on temperature of the wavelength of the reflected light was also studied for this

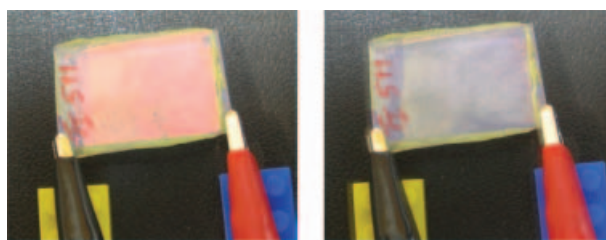


Figure 2. Macroscopic photographs of the OFF (on the left side, showing a red colour) and ON (on the right side, showing no colour) states.

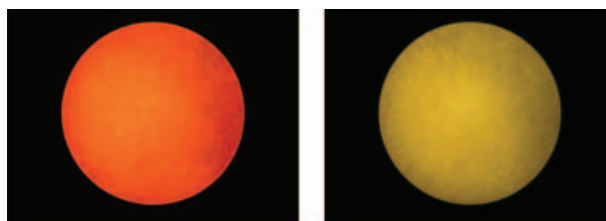


Figure 3. Optical microscopy in reflection: OFF state on the left (reflecting orange colour) and ON state on the right (reflecting yellow colour).

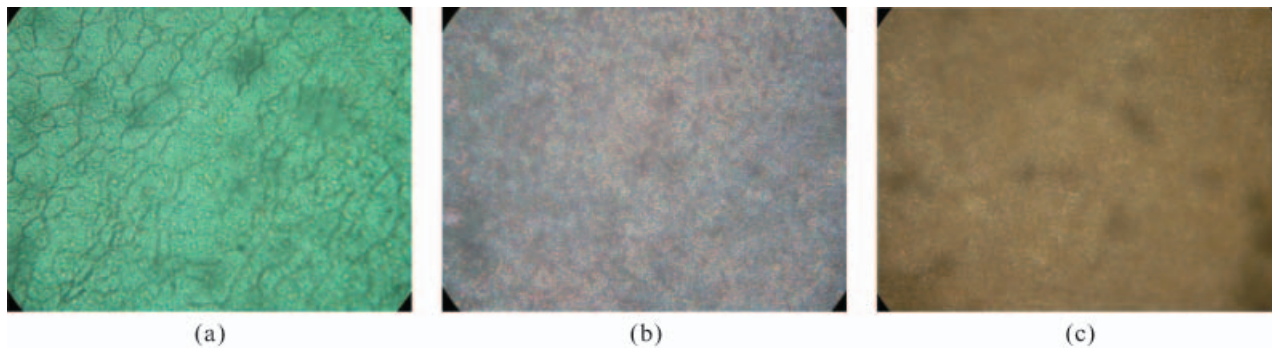


Figure 4. Optical microscopy in transmission; without applied voltage (a), with 95 V of applied voltage (b) and with 200 V of applied voltage (c).

system. The study was performed for both the pure cholesteric LC and the composite system with the LC and the cellulose derivative film. Figures 5 and 6 show the variation with temperature of the reflection spectra and of the wavelength of maximum intensity of the reflected light. The study was performed between 22°C and 48°C.

The dependence on the applied voltage of the spectra and the wavelength of the reflected light was also investigated for the composite system. Figures 7–9 show the variation with the applied voltage of the spectra and wavelength of maximum intensity of the reflected light at 22°C, 28°C and 40°C, respectively.

The hysteresis exhibited by the wavelength of maximum intensity of the reflected light when the

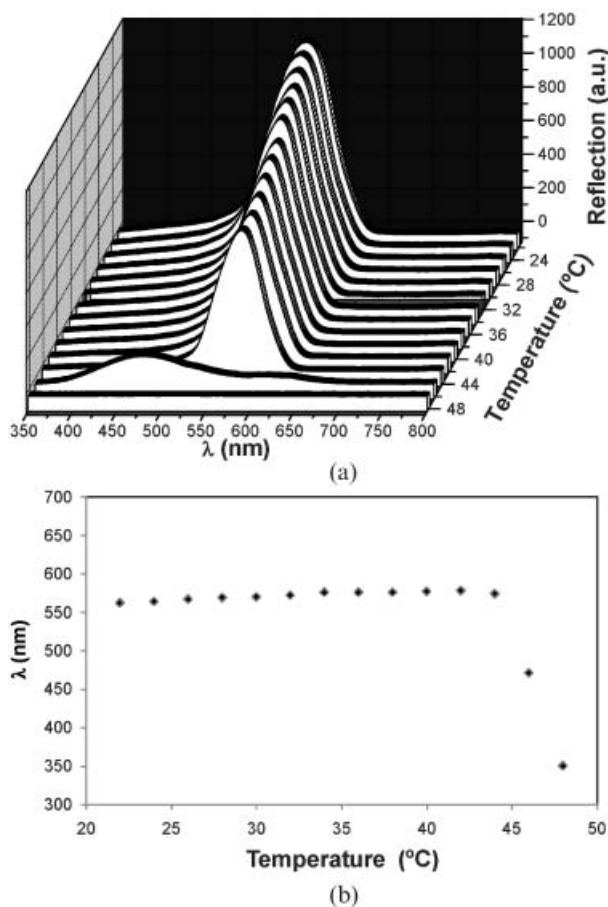


Figure 5. Dependence on temperature of the spectra (a) and wavelength of maximum intensity (b) for the pure cholesteric liquid crystal TI 511.

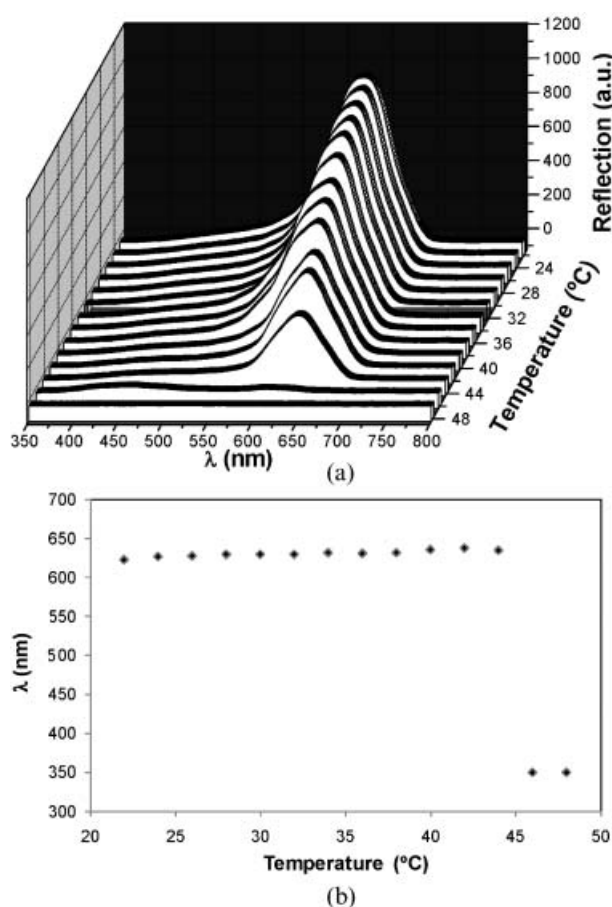


Figure 6. Dependence on temperature of the spectra (a) and wavelength of maximum intensity (b) for the cell with HPC and cholesteric TI 511.



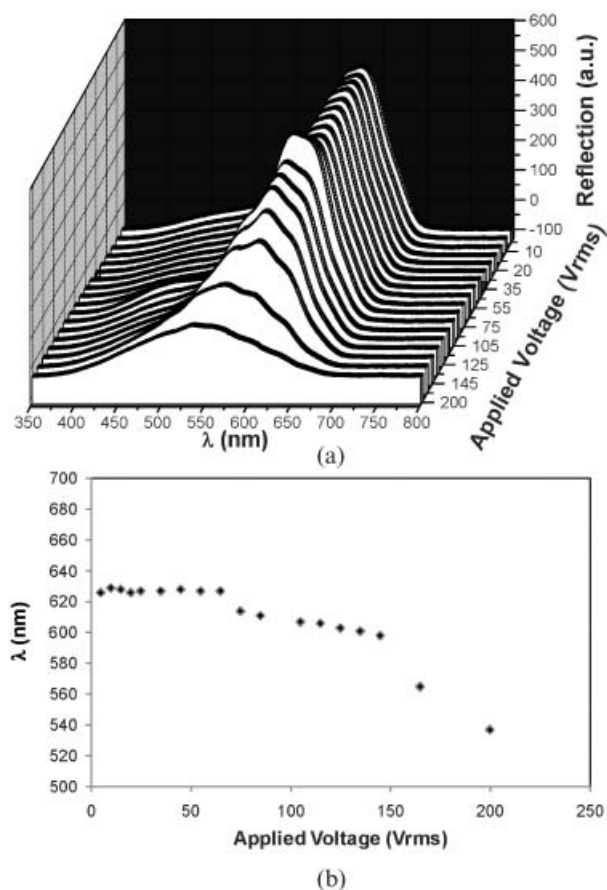


Figure 7. Dependence on the applied voltage of the spectra (a) and wavelength of maximum intensity (b) for the cell with HPC and TI 511 at 22°C.

applied voltage was cycled up to a high value and back was also investigated. The wavelength of the maximum intensity of the reflected light was measured when the applied voltage was being increased, and later decreased after having reached the maximum applied voltage for the test. The test was performed at 22°C and the results are shown in Figure 10.

Selective light reflection of cholesteric LCs is a well known fact and the reflection wavelength depends on the temperature and applied field as the pitch length changes. In this study, we have shown that both the temperature and the applied electric field can change the reflection wavelength of a cholesteric LC interacting with a cellulosic film. The voltage dependence of reflection has been studied at three different temperatures, revealing noticeable differences. The HPC film promotes the planar alignment of the adjacent LC layer according to its surface morphology, inducing the pitch axis to align normally to the cell surface. The voltage applied to the cell disrupts this alignment, promoting at intermediate voltage values the

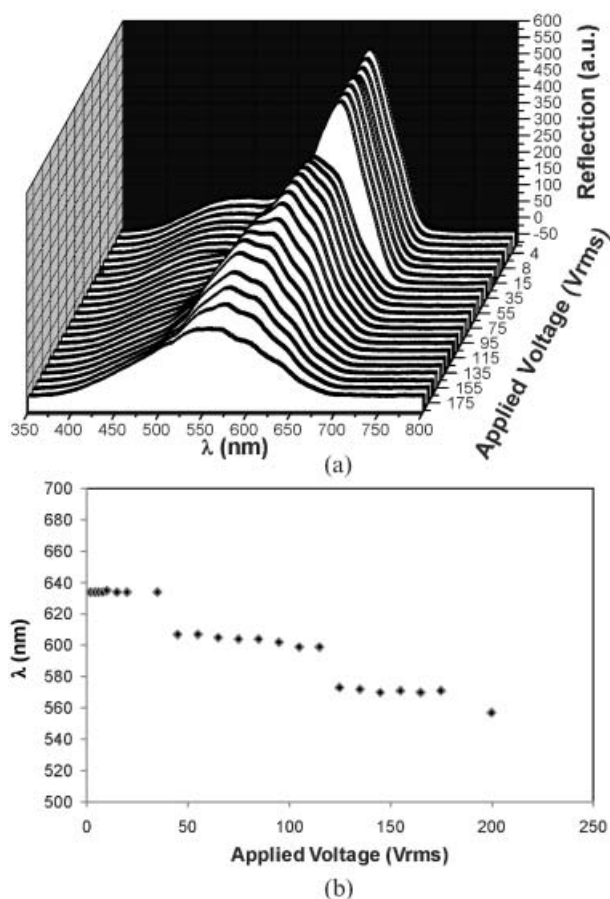


Figure 8. Dependence on the applied voltage of the spectra (a) and wavelength of maximum intensity (b) for the cell with HPC and TI 511 at 28°C.

appearance of focal conic structures and at high voltage values the tendency for homeotropic alignment of the LC molecules with direct impact over the reflection spectra. The steps appearing in the voltage dependence of the wavelength of the maximum reflected light intensity are thus linked to the transition between the different director structures in the sample; planar structure to focal conics structure and focal conics structure to tendentially homeotropic structure.

The hysteresis reported in Figure 10 indicates that when the voltage is lowered from the tendentially homeotropic structure, the focal conics structure is stabilised and does not evolve to the planar structure in a short time interval when the electric field is removed.

Thus, the device is working as a reflection phase modulator, which can be controlled by changing temperature as well as the applied voltage. The system behaves similarly to the cholesteric/polymer dispersed materials reported by Doane and co-workers (14–18).

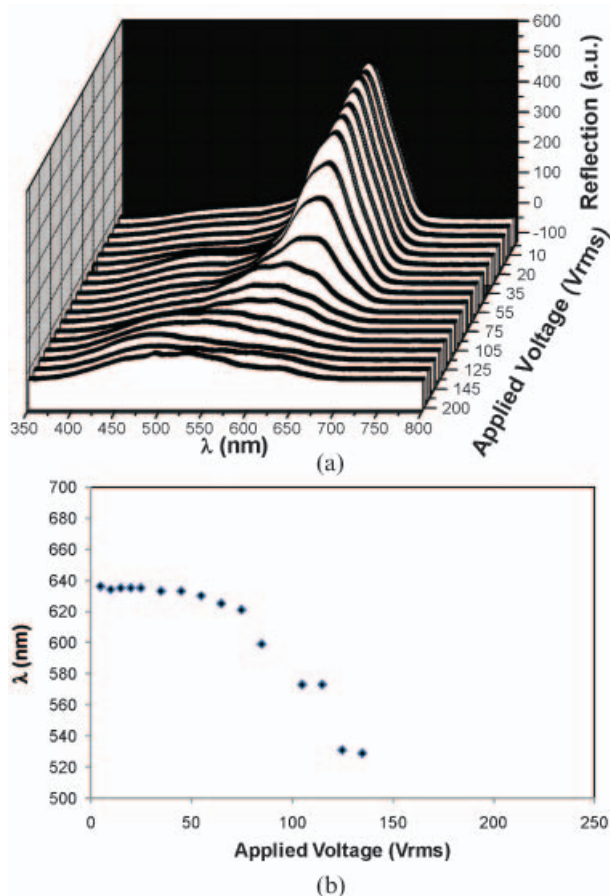


Figure 9. Dependence on the applied voltage of the spectra (a) and wavelength of maximum intensity (b) for the cell with HPC and TI 511 at 40°C.

#### 4. Conclusions

The textures with oily streaks (see photo in Figure 4) exhibited by the sample in light transmission under crossed polarisers and the voltage dependence of the

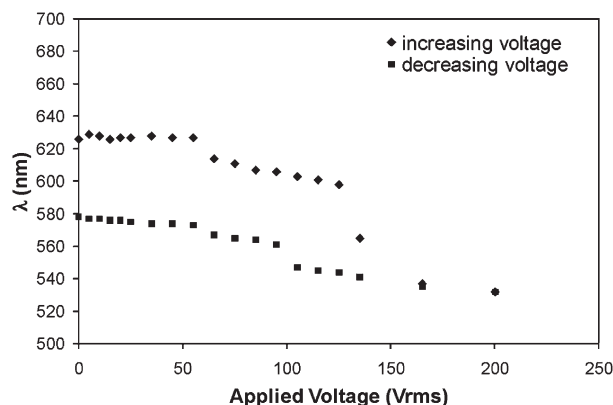


Figure 10. Hysteresis in the voltage dependence of the wavelength of maximum intensity of the reflected light at a temperature of 22°C.

wavelength of the reflected light indicate that the cellulosic matrix induces a planar anchoring of the liquid crystal and therefore the cholesteric helix aligns perpendicular to the glass substrates (the sample shows a reflected red colour, which corresponds to the characteristic selective reflection of the helix structure of cholesterics).

The applied voltage promotes the director to align parallel to the imposed electric field, which in the case of the highest electric fields correspond to a suppression of the helix and the sample becomes colourless.

For intermediate values of the applied electric field the LC is in a polydomain focal conics structure with the helices distributed randomly, giving rise to lower values of the intensity of the reflected light. The structure evolution in the cell with the applied field is apparently made in steps (as we can see in the plotted charts of the wavelength of the maximum intensity of reflected light versus applied voltage), each step corresponding to a transition, starting on increasing the voltage from the planar texture (oily streaks) to the texture with focal conics (see photo in Figure 4) and at higher voltages to the tendentially homeotropic aligned cell.

The existence of hysteresis indicates that there are two accessible states of orientation without the applied field, corresponding the initial state of a planar orientation of the director (before the application of the electric field), and the second one to the focal conics structure.

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