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# A hybrid-aligned polymer network liquid crystal: optical and electro-optical properties

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We have studied the influence of polymer network liquid crystal alignment on optical and electro-optical properties. Composite alignment (parallel/homeotropic) was investigated in comparison with symmetric parallel/parallel and homeotropic/homeotropic alignments. The applied voltage leads to a reflective wavelength shift towards low wavelengths according to two modes in the case of symmetric planar alignment. Depending on polymerization conditions, a band broadening can be obtained, but a total reversibility of the optical properties is not recovered after application of a high voltage to the samples. The layer thickness appears to be a fundamental parameter in the case of a hybrid-aligned active layer and a wide band is obtained after measurements (*I–V*) using increasing voltages.

## 1. Introduction

Reflective wavelengths strongly depend on the orientation of cholesteric liquid crystal molecules, and consequently, most electro-optical applications of such liquid crystals (LCs) require a high level of LC molecular orientation. Various methods have been developed to produce unidirectional LC alignment such as exposure of polymers to polarized ultraviolet light (PUV) [1]. This last technique also allows one to generate desired pre-tilt angles according to polyimide (PI) composition, UV exposure time and UV exposure angles [2]. However, parallel alignment is generally obtained by using mechanically rubbed polyimide [3]. In a similar way, several methods are used to generate tilted or non-tilted homeotropic alignments according to the material composition coated on the conductive glass substrate [4–7].

In this work, we set out to study the optical behaviour of a hybrid-aligned polymer network liquid crystal (parallel/homeotropic alignments) in comparison with the parallel and homeotropic symmetric alignments. A preliminary study was made using a hybrid-aligned passive layer leading to a strongly reflective side in the case of parallel alignment and to a dull side in the case of homeotropic alignment [8]. With one parallel and one homeotropic alignment, the cholesteric pitches are gradually aligned from the parallel state to the perpendicular, and the optical properties express this phenomenon. We then studied the influence of layer thickness and applied voltage on the optical properties. Finally, a polymerization under an applied voltage was carried out and the results were assessed.

## 2. Experimental

The conductive glass substrates were treated by coating and rubbing a polyimide layer in order to obtain a parallel alignment. Homeotropic alignment was achieved by coating an ultra-thin layer of *N*-octadecyldimethyl-3-trimethoxysilylpropylammonium chloride (DMOAP) from aqueous solution. The empty cells were made by assembling two conductive glass substrates, and spacers were used to maintain a constant cell gap of about 8.6 µm, which was controlled by reflection measurements.

The polymer network liquid crystal (PNLC) contained a small amount of CM14 cholesteric monomer (3%) and a liquid crystal mixture composed of BN5 nematic liquid crystal and right chiral agents (NXL and CML), whose concentration allows the reflective wavelength to be modified. The characteristics of the cholesteric polymer and chiral dopant have been described in [9].

The cells were filled by capillary action with the LC mixture at room temperature for homeotropic and composite alignments and at the temperature of the isotropic phase (~90°C) for parallel alignment. A previous study had indicated that, in the case of homeotropic- and hybrid-aligned cells, any increase of temperature during

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the filling favoured an inhomogeneous, parallel alignment in spite of homeotropic treatment. Finally, the passive layer was photopolymerized using an UV lamp at 6 mW cm$^{-2}$ during 20 min.

Three kinds of sample were used to obtain the best understanding of the results: a sample with two parallel alignments, another with two homeotropic alignments and finally a hybrid sample with both kinds of alignment. We then studied the influence of polymerization kinetics, with or without an applied voltage, and the influence of the cell thickness.

## 3. Results and discussion

It is important to note that, as previously observed in the case of a hybrid-aligned passive layer [8], a clear difference appears between both kinds of alignment: for parallel alignment, the surface looks very bright and very reflective, whereas for homeotropic alignment, it appears clearly dull.

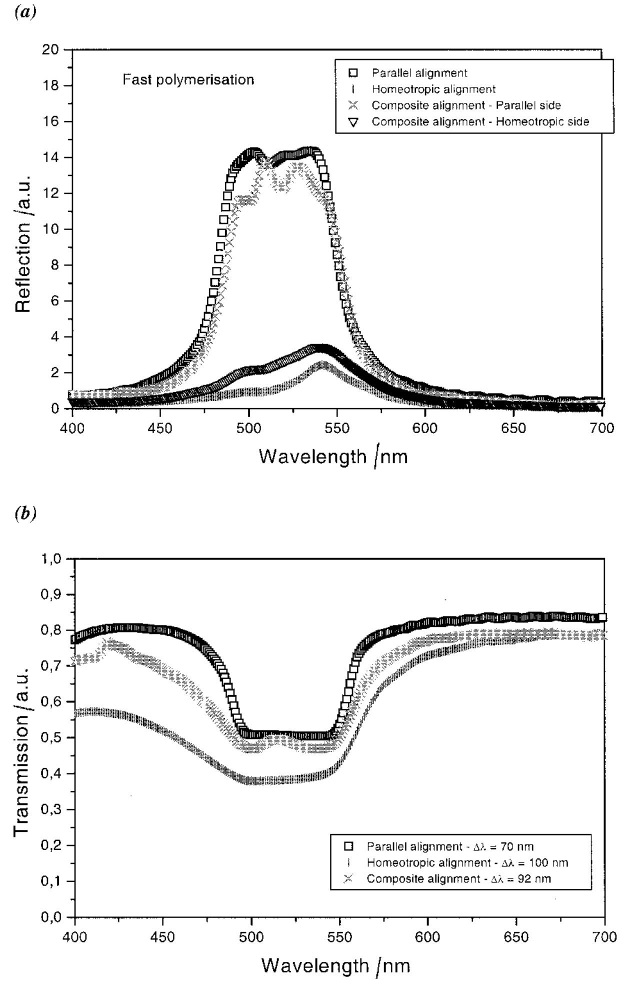

Figure 1. Influence of liquid crystal alignment on the optical properties in the case of fast polymerization: (*a*) reflection measurements, (*b*) transmission measurements.

### 3.1. *Fast polymerization without applied voltage*

Figure 1 shows the influence of alignment on the reflection and transmission properties. The measurements were effected in the so-called 'direct–direct configuration'; that is, when the incident and reflected beams are perpendicular to the sample plane. As expected, the reflection measurements show that the reflective intensity is very weak for homeotropic alignment, due to the molecular orientation. A slight broadening of the band is observed for transmission measurements on hybrid- and homeotropic-aligned samples. The same result was also observed for a passive layer, which is attributed

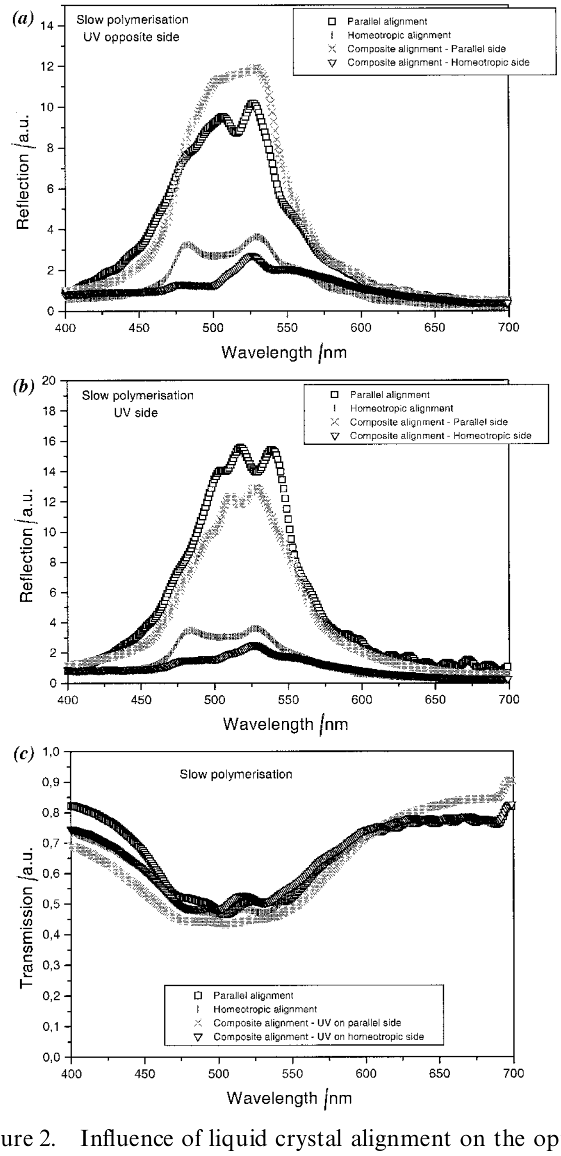

Figure 2. Influence of liquid crystal alignment on the optical properties in the case of slow polymerization: (*a*) reflection measurements on the opposite side to UV treated side, (*b*) reflection measurements on the UV side, (*c*) transmission measurements.

either to disorientation of the liquid crystal cholesteric axes or to a distortion of the cholesteric pitches due to the high material viscosity. However, this last factor does not apply in the case of the PNLC material and the broad band can be ascribed to a distribution of the liquid crystal cholesteric axes

### 3.2. *Slow polymerization without applied voltage*

It is well known that slow polymerization leads to a polymer gradient with a polymer concentration decrease from the UV-irradiated side to the opposite side [10]. Therefore we examined four different samples with: parallel or homeotropic symmetric alignments, and composite alignments with UV irradiation either on the parallel side or on the homeotropic side.

Figure 2 presents the influence of alignment on the reflection and transmission properties. As already mentioned, reflective measurements show a very weak reflective intensity for homeotropic alignment. In comparison with the fast polymerized samples, the reflection and transmission spectra show a band broadening, whatever the alignment conditions. This broadening is

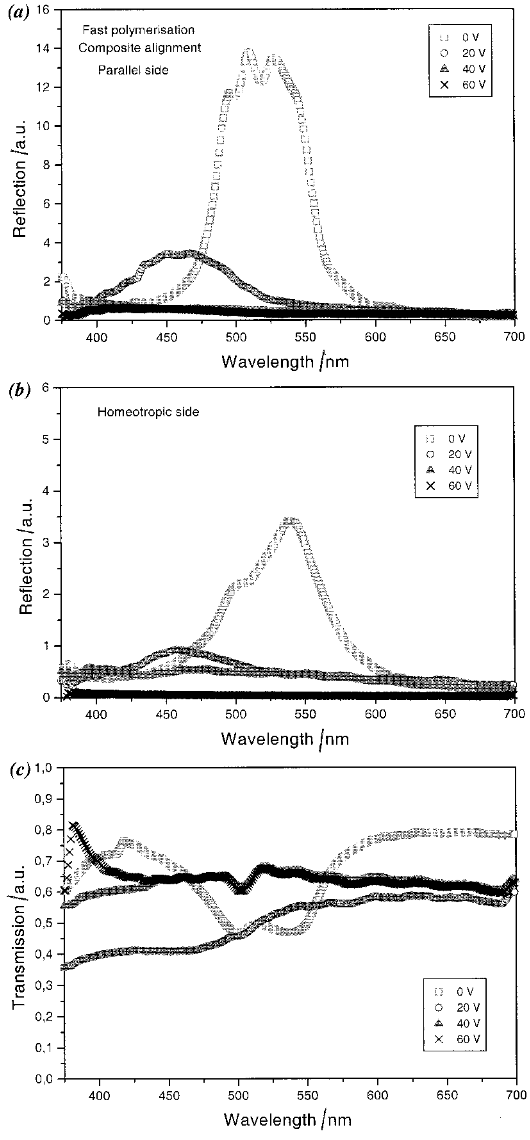

Figure 3. Optical properties of hybrid-aligned liquid crystal cells under applied voltage in the case of fast polymerization: (*a*) reflection measurements on the parallel aligned side, (*b*) reflection measurements on the homeotropic side, (*c*) transmission measurements.

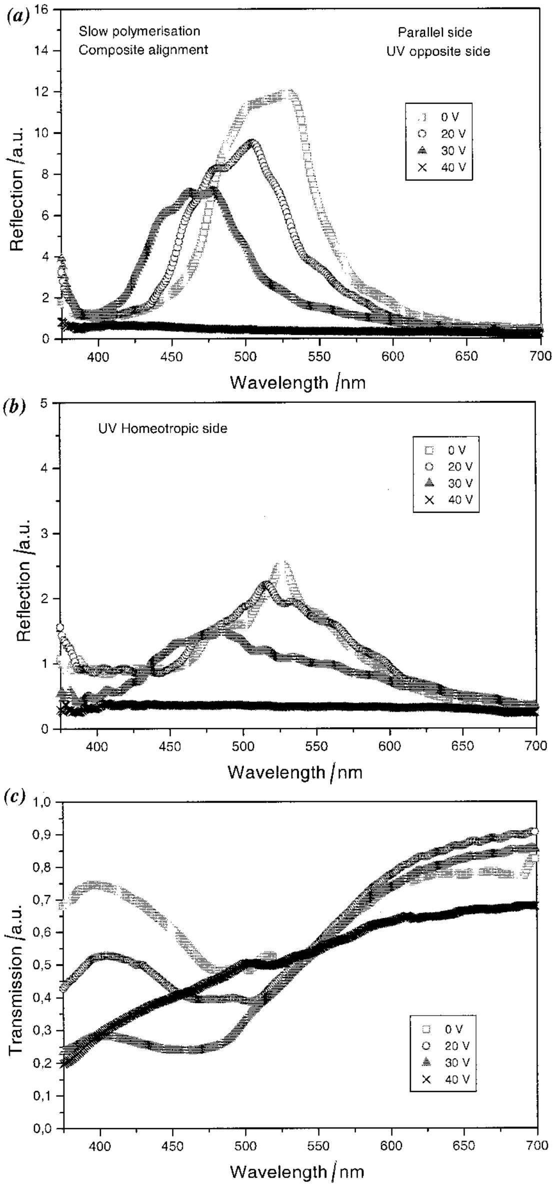

Figure 4. Optical properties of hybrid-aligned liquid crystal cells under applied voltage in the case of slow polymerization: (*a*) reflection measurements on the parallel aligned side, (*b*) reflection measurements on the homeotropic side, (*c*) transmission measurements.

interesting in all cases, and particularly in the composite alignment sample with UV irradiation on the parallel side; here the broadening amounts to about 150 nm.

### 3.3. *Influence of applied voltage*

In each case, whatever the polymerization kinetics, the electric field induces the same behaviour corresponding to a general change in the liquid crystal that leads to a shift towards low reflective wavelengths; see figures 3 and 4. This phenomenon is accompanied by a decrease in the reflective intensities. The transmitted intensities decrease for low voltages and increase for higher voltages. Semi-quantitative analyses show a linear decrease of the reflective intensity with increase in applied voltage. However, the reflective wavelength decreases slowly up to a threshold voltage and strongly beyond this value, suggesting two different modes of molecular orientation under the applied field; see figure 5 (*a*). This result can be associated with the process reported by Hikmet and Kemperman in the case of planar alignment [11]. The first mode could be connected with tilting of the cholesteric helix and the second mode could be attributed to its unwinding; see figure 5 (*b*). The variation in transmitted intensity is also in agreement with this interpretation. This threshold voltage is higher in the case of slow polymerization (20 $V_{rms}$) than in the case of fast polymerization (10 $V_{rms}$).

An interesting behaviour is also observed in the case of composite alignments: the shift towards low wavelengths is greater on the parallel side than on the homeotropic side, particularly for slow polymerization on the parallel side. This result suggests that homeotropic anchoring is stronger when the polymer concentration is lower and therefore that the applied voltage has a very low influence on molecular orientation. This phenomenon could be put forward to explain a band broadening by polymerization with an electric field. Concerning the full width half-maxima (FWHM), these

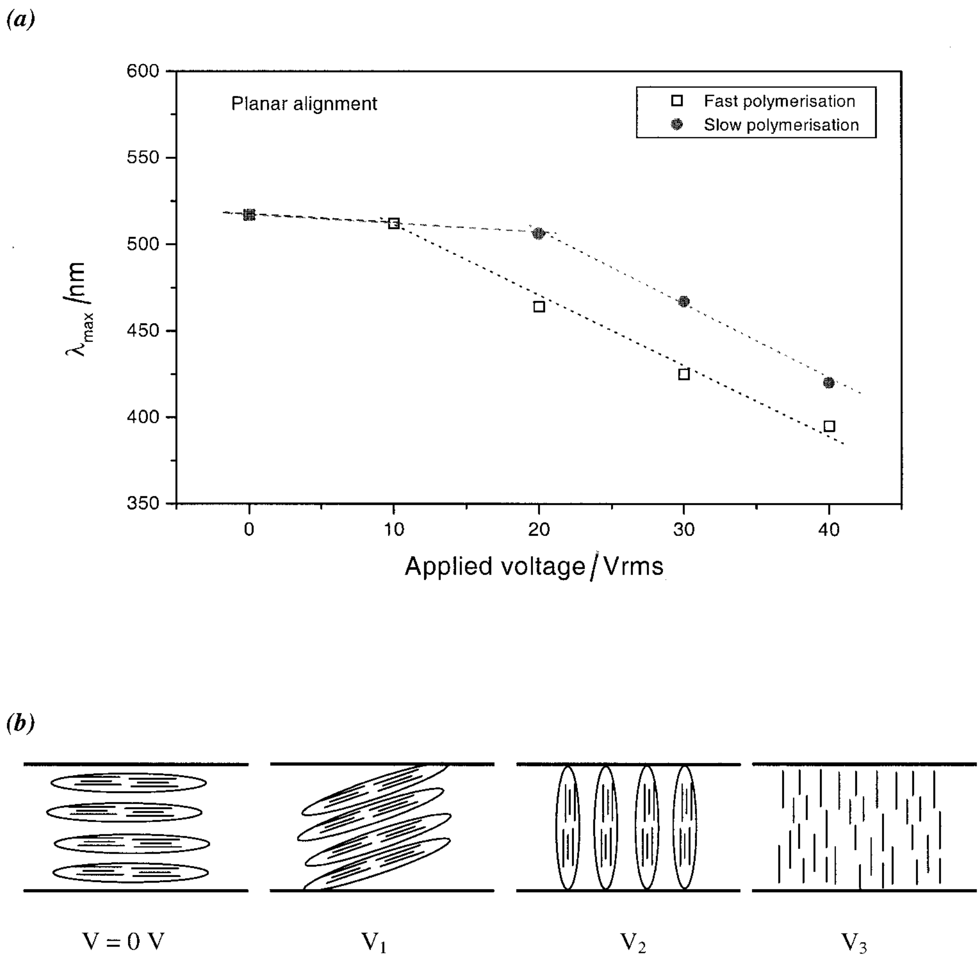

Figure 5. (*a*) Variation of maximum wavelength with applied voltage in the case of planar alignment; (*b*) schematic representation of processes taking place within the PNLC in the case of symmetric parallel alignment during switching at various applied voltages (0, $V_1$, $V_2$, $V_3$) from reference [10].

tend to decrease with the applied voltage, except in the case of composite alignment, for which a strong increase is observed.

### 3.4. *Influence of I–V measurements*

In the preceding experiment, a fixed voltage was applied. Now an increasing voltage from 0 to 100 V was applied and the reflected and transmitted intensities were measured as a function of voltage (*I–V* measurements). The reflected and transmitted spectra at zero volts were again measured and compared with the same spectra before the *I–V* measurements. In the case of fast polymerization, the optical properties are barely modified by the *I–V* measurements, for the reflective and transmitted intensities. This can be shown by comparing figure 6 (fast polymerization after *I–V* measurements) with figure 1 (fast polymerization before *I–V* measurements). The most important modification concerns the *shape* of the band broadening in the transmission spectrum. However evaluation of the band broadening before and after *I–V* measurements does not show significant modification. Regarding the slow polymerization, in the case of symmetric planar alignment, the reflection spectra are not modified by the *I–V* measurements; see figure 7. In the other cases, the reflective intensities and FWHM decreased strongly after *I–V* measurements (see also figure 2 for comparison). However, the transmission spectra become similar in the four cases, without any difference between the various alignments. Moreover, the transmitted intensities are clearly weaker in comparison with the intensities measured before voltage application; this is due to the sample opacity and indicates that the liquid crystal molecules do not completely return to their initial alignment state. Consequently, slow polymerization allows the best band broadening to be reached in comparison with fast polymerization, but the active layers do not completely return to their initial state.

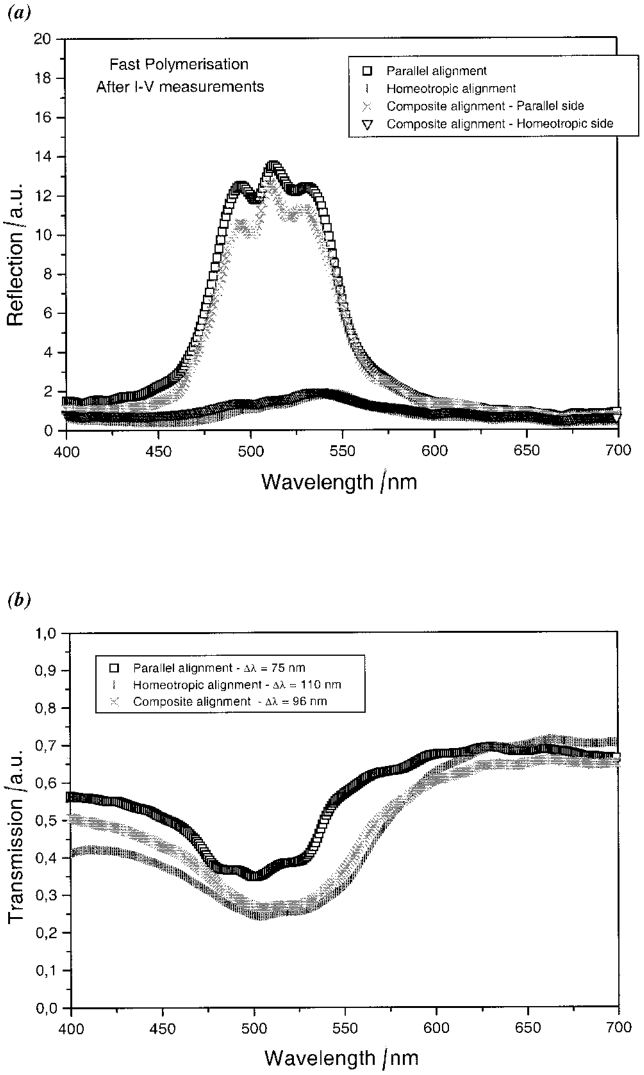

Figure 6. Influence of *I–V* measurements on the optical properties in the case of fast polymerization: (*a*) reflection measurements, (*b*) transmission measurements.

### 3.5. *Influence of the cell gap*

The influence of cell gap on optical and electro-optical properties for a fast polymerized, hybrid-aligned active layer was then studied next. An active layer thickness increase, corresponding to an increase in cholesteric pitch number, leads to an increase in the reflective intensity. This phenomenon is verified in reflection spectra recorded on the planar alignment side (figure 8), whereas the reflective intensity recorded on the homeotropic side is not modified. Optical measurements also show a shift in maximum wavelength towards low wavelengths, an effect that is stronger in the case of the parallel side than the homeotropic side, when the cell gap increases. Explanation of this phenomenon would need the elaboration of a model taking into account the sample thickness, the elastic constants of the liquid crystal and the strength of the two anchorings. The spectrum modification can be roughly associated with the orientational distribution of the direction of the cholesteric axis in the sample. On the first substrate, the planar anchorage (polyimide) is strong. On the second substrate, the homeotropic anchorage is relatively weak. When the thickness is low (5 μm), the cholesteric layers located in the sample depth are practically parallel to the polyimide substrate, except very near to the second substrate treated for homeotropic anchorage. The observed mean reflected wavelength for this sample and for a perfect planar sample are close. When the sample has a greater thickness (20 μm for example), the effect of the polyimide anchorage is lost in the sample depth and a large

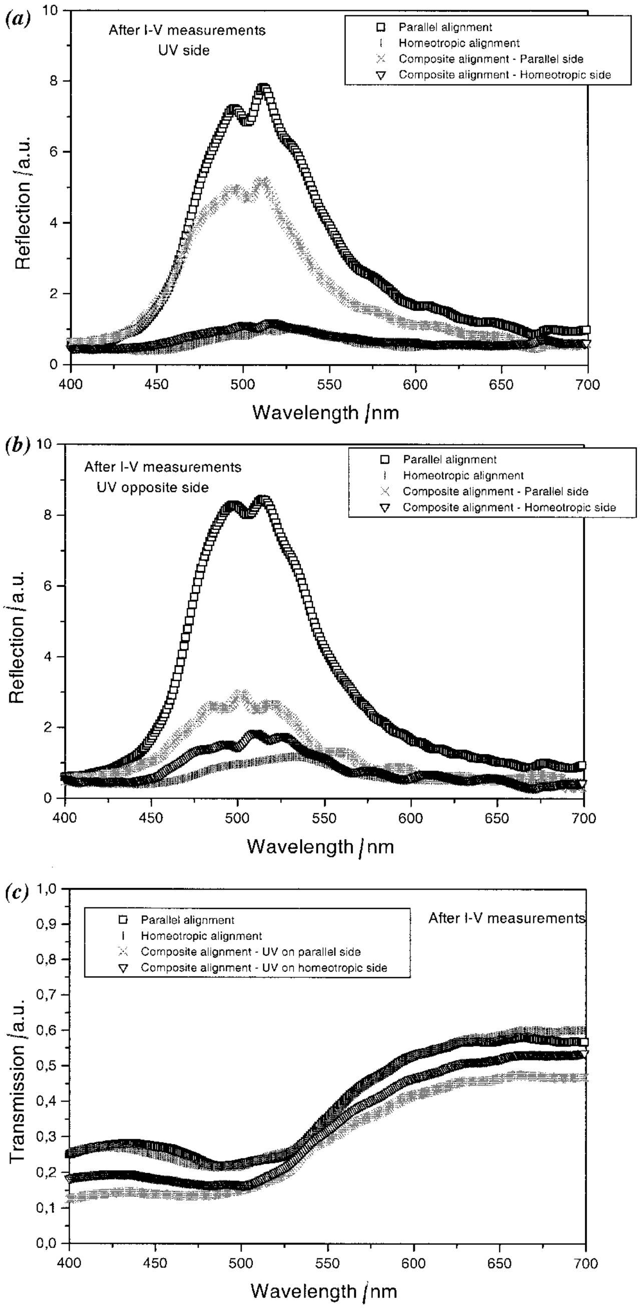

Figure 7. Influence of *I–V* measurements on the optical properties in the case of slow polymerization: (*a*) reflection measurements on UV side, (*b*) reflection measurements on the opposite side to UV treatment, (*c*) transmission measurements.

distribution of the cholesteric axis is obtained. The tilted cholesteric axis orientations (comparatively to the planar orientations) give a 'blue shift' contribution to the reflection intensity. For each case it can also be noticed that the band broadening is not strongly dependent on the thickness (FWHM about 100 nm for each case).

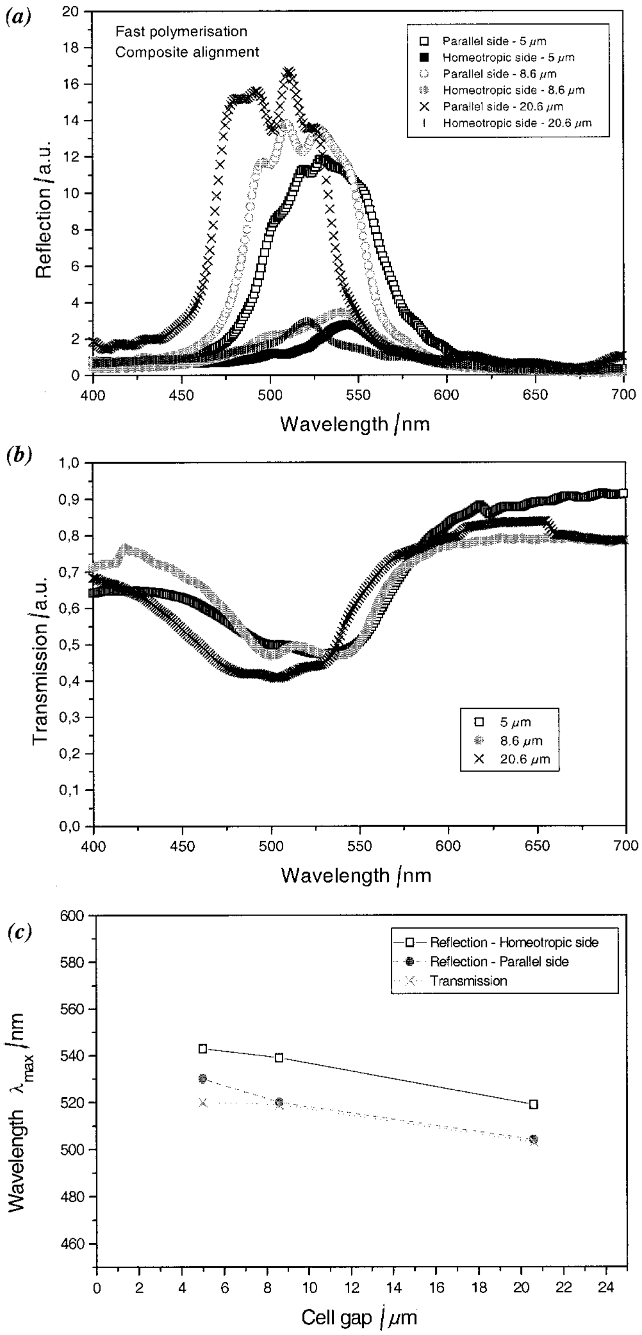

Figure 8. Influence of cell gap on the optical properties in the case of fast polymerized hybrid-aligned PNLC: (*a*) reflection measurements, (*b*) transmission measurements, (*c*) variation of maximum wavelength versus cell gap.

Figure 9 shows the optical properties of a 20.6 μm fast polymerized hybrid-aligned active layer before and after *I–V* measurements. Reflection measurements reveal few differences between the spectra recorded before and after *I–V* characterization. However, a clear difference is observed in transmission measurements concerning the

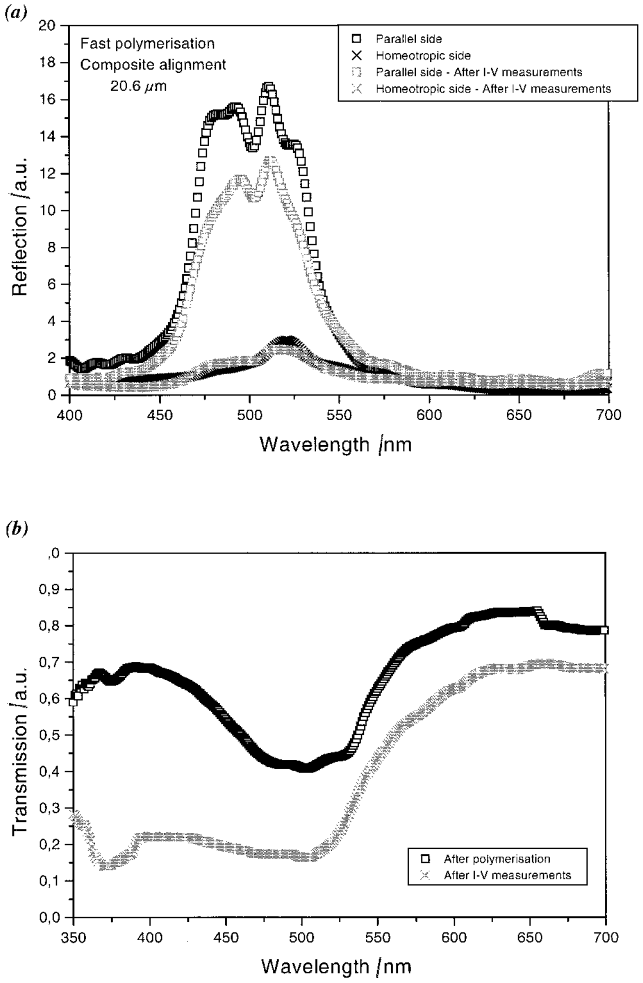

Figure 9. Optical properties in the case of fast polymerized hybrid-aligned PNLC before and after *I–V* measurements for a cell gap of about 20.6 μm: (*a*) reflection measurements, (*b*) transmission measurements.

full width half-maxima, which strongly increase after the *I–V* measurements from 120 to 200 nm towards lower wavelengths. This result tells us that the molecules in the vicinity of the substrate with planar orientation return partially to their initial state. The modification of the transmission transparency proves that this return is not obtained in the bulk where the anchorage strength has a lower effect.

## 4. Conclusion

We have studied the influence of thickness and various alignments on the optical and electro-optical properties of an active layer containing PNLC. The results reveal that the hybrid-alignment offers great interest for a broadband layer because it allows the reflective wavelength and the band broadening to be chosen by modifying, respectively, the chiral agent concentration and the cell gap. Moreover, the active layer prepared with composite alignment is of great interest because of its double property corresponding to one reflective side and one dull side.

## References

[1] Gibbons, W. M., Shannon, P. J., Sun, S. T., and Swetlin, B. J., 1991, *Nature*, **351,** 49.
[2] Nishikawa, M., and West, J. L., 1999, *Mol. Cryst. liq. Cryst.*, **329,** 579.
[3] Nishikawa, M., Miyamoto, T., Kawamura, S., Tsuda, Y., and Bessho, N., 1992, *Proc. Japan Display'92*, 819.
[4] Vithana, H., Johnson, D., and Bos, P., 1996, *Jpn. J. appl. Phys.*, **35,** L320.
[5] Chen, L.-Y., and Chen, S.-H., 1999, *Appl. Phys. Lett.*, **74,** 3779.
[6] Marinov, Y., Shonova, N., Versace, C., and Petrov, A. G., 1999, *Mol. Cryst. liq. Cryst.*, **329,** 533.
[7] Shang, W., and Labes, M. M., 1994, *Mol. Cryst. liq. Cryst.*, **239,** 55.
[8] Guillard, H., and Sixou, P., 2001, *Liq. Cryst.*, **28,** 831.
[9] Sixou, P., Gautier, C., and Guillard, H., 2001, *Mol. Cryst. liq. Cryst.*, **364,** 665.
[10] Li, L., and Faris, S. M., 1996, *Proc. SPIE*, **2873,** 202.
[11] Hikmet, R. A. M., and Kemperman, H., 1998, *Nature*, **392,** 476.