Broadening of light reflection in glassy cholesteric materials and switchable polymer-stabilized cholesteric liquid crystals

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ABSTRACT

A planar oriented cholesteric liquid crystal (CLC) may selectively reflect light. The reflection wavelength is related to the helix pitch and the wavelength bandwidth depends on the birefringence which is typically less than 0.3. In the visible spectrum, the bandwidth is often limited to 100 nm which is not suitable for specific purposes such as white-on-black polarizer-free reflective displays. Here we present two novel designs of CLC materials exhibiting light reflections on several hundreds of nanometers in the visible spectrum. The first type of broadband reflector is a glassy non-polymeric CLC with a pitch gradient which developed during a thermal annealing. The second kind of approach leads to a Polymer-Stabilized CLC which is switchable when an electric field is applied. Here the material has been UV-cured under out-of-equilibrium conditions *i.e.* when the CLC helicoidal pitch was varying during a thermal process. The elaboration processes are investigated in relationship with the optical properties and the microstructure as observed by transmission electron microscopy.

Keywords: cholesteric liquid crystals, Polymer-Stabilized Cholesteric Liquid Crystals, glassy state, pitch gradient, light reflection, broadband filters, switching process, TEM

1. THE REFLECTION BAND IN CHOLESTERIC LCs

The spatially periodic twisted structure of the cholesteric liquid crystal (CLC) phase gives rise to remarkable physical properties [1, 2]. The most symbolic optical property is the strong selective Bragg reflection exhibited by an uniformly oriented Grandjean planar texture [3]. At normal incidence, the reflection wavelength λ_0 is related to the cholesteric pitch p and the mean refraction index n [4] by:

$$\lambda_0 = n.p.$$

The reflection occurs in a band of wavelengths $\Delta\lambda$:

$$\Delta\lambda = p.\Delta n$$

where Δn is the birefringence (or optical anisotropy) [5].

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Within $\Delta\lambda$, an incident unpolarized or linearly polarized light beam parallel to the helix axis is split into two opposite circularly polarized components, one of which is transmitted whereas the other is totally reflected. The sense of rotation of the latter one agrees with the helix screw sense. A wavelength out of $\Delta\lambda$ is simply transmitted.

Therefore $\Delta\lambda$ depends on Δn. Since Δn is typically limited to 0.3 for colorless organic compounds, $\Delta\lambda$ is often less than 100 nm in the visible spectrum, which is convenient for a great number of applications of CLCs like selective optical notch- or band-pass filters, polarizers, thermal imaging, laser or paint technologies... [6-8]. However, this limit has to be exceeded for other applications like full-colors or white-on-black polarizer-free reflective displays.

Here two novel experimental methods to enlarge the reflection bandwidth in CLC materials in the visible spectrum are investigated. **(i)** The first process leads to glassy CLCs which reflect light on several hundreds of nanometers. The broadband filter was manufactured in the process of a thermal annealing by putting in contact two CLCs layers with different chiralities. **(ii)** The second process deals with Polymer-Stabilized CLCs. The UV-crosslinking of a polymer-forming CLC material blended with a low molar mass LC occurs when the temperature – and therefore the CLC pitch – is changing. Due to this choice of out-of-equilibrium conditions, the optical characteristics of Bragg reflections are modified and the reflection bandwidth is broadened.

2. BROADENING OF REFLECTION BAND IN GLASSY CHOLESTERIC LCs

2.1. Experimental

Materials

The molecule is an oligomer with two types of side-chains attached to a siloxane cyclic chain *via* spacers: a non-chiral mesogen and a chiral one [9]. On a glass or plastic plate, the material shows typical iridescent colors ranging from blue to red simply by tuning the molar percentage of chiral mesogens from 50 to 31%. The CLC phase appears between 180/210°C (isotropic transition) and 40/50°C (glassy transition). As an advantage for our purpose, the materials can be very easily quenched at room temperature and the mesomorphic order with its color properties are permanently stored within a solid film.

Spectrophotometry

The spectral characteristics are obtained by unpolarized spectrophotometry (UV-3100 Shimadzu) in transmittance mode and at ambient temperature. It is checked that negative peaks are due to reflectance and not to absorbance.

Transmission electron microscopy (TEM)

Materials are embedded in epoxy resin cured at 40°C. 150 nm thick slices are obtained with an ultramicrotome (Reichert Ultracut) in a direction perpendicular to the surface (cross-sections) and retrieved on carbon-coated grids. The observations are carried out in a TEM Philips CM12 performed at room temperature and in normal conditions. This means that the dose of electrons received by the specimen is well higher than the critical dose deleting the diffraction contrast, and that the images are produced by a thickness diffusion contrast subsequent to irradiation [10].

2.2. Results

Material design

The material design is based on an anisotropic diffusion between two CLCs with different chiralities. The procedure is summarized in four steps. **1.** 40 μm thick films of blue and red CLCs are spread with an handcoater on two distinct glass plates without any alignment layer. **2.** A 19 μm thick sandwich-cell is made with the two films. **3.** The cell is kept for different annealing times at 85°C. This temperature corresponds to a stable CLC phase for which the materials are equally rather fluid. A diffusion process between the red and blue films — and therefore a concentration gradient between the chiral substances —, occurs in a direction perpendicular to the plane of films (it is why the diffusion between the CLC layers is said anisotropic). **4.** The cell is quickly put on a metallic substrate at room temperature: it is the quenching step. The macroscopic characteristics of the sandwich-film evolve from a viscous state to a glassy one. Such a cooling prevents crystallization and preserves the CLC phase with its colors.

Optical properties and microstructure

Figure 1 shows the variation of transmitted light intensity with the wavelength after different annealing times. The curve intrinsic to a glass plate is also displayed because the cut-off wavelength for glass below 350 nm has some influence on the shape of curves. The negative peaks are due to the reflection of about 50% — as a consequence of circular polarization discrimination induced by a CLC structure —, which corresponds to the theoretically predicted value [1].

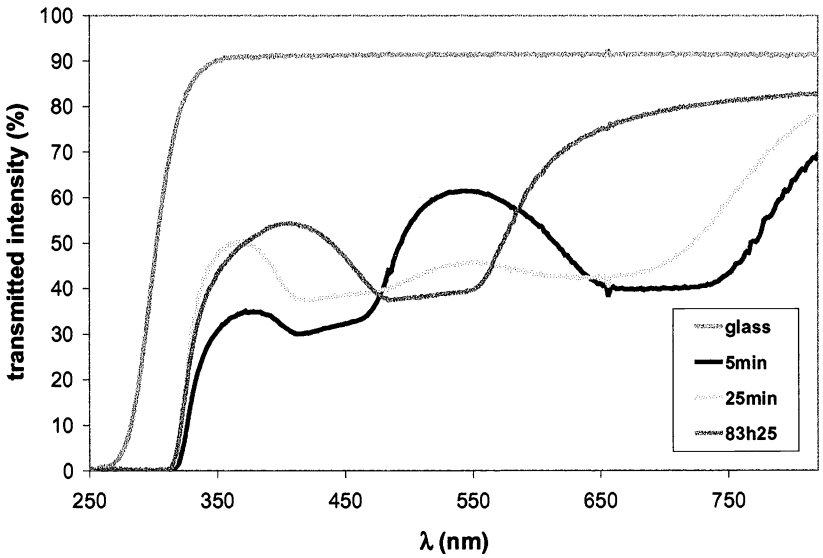

Figure 1: Transmitted light intensity as a function of wavelength for a plain glass plate and for the sandwich-cell after 5 minutes, 25 minutes and 83 hours 25 minutes of annealing.

When the annealing time is equal to 5 minutes, the spectrum is the sum of two peaks intrinsic to the selective reflections of blue and red films. In the following, we will call $\Delta\lambda^{PLA}$ the wavelength bandwidth which corresponds to the plateau, when the level of light transmission stays rather constant. The mean reflection wavelengths are respectively about $\lambda_B = 444$ nm and $\lambda_R = 711$ nm with the dispersions $\Delta\lambda_B^{PLA} = 50$ nm and $\Delta\lambda_R^{PLA} = 85$ nm. In the case of such a short annealing time, the diffusion between the chiral films is not effective and the CLC material is a bi-selective reflector as a simple stack of blue and red CLC slabs.

As soon as the annealing time reaches 25 minutes, the curve becomes flat and enlarged on more than 300 nm: the bi-selective film becomes a broadband filter as an expected consequence of the establishment of a pitch gradient in the CLC superstructure. To the naked eye, the film has a metallic aspect since it reflects 50% of the light over the visible spectrum.

TEM investigations of cross-sections give the status of the helicoidal pitch along the helix axis. Figure 2 is the TEM micrograph of the sample with an annealing time equal to 25 minutes. Alternative dark and bright lines are observed. These periodic lines are intimately associated to the very helical structure of a CLC structure when observed in a direction perpendicular to the helix axis [10]. The periodicity — the distance between two dark or bright lines — is about the half-pitch. No interface is visible. The film is like a monolithic single-layer material. The line contrast is clearly related to a helical structure with a continuous pitch gradient. The two original parts, with their small and large periodicities, can still be distinguished but, between the two extremities, all a set of periodicities intermediate between 'red' and 'blue' CLC periodicities is present.

If the annealing stage is continued, the wavelength bandwidth is more and more reduced until narrow-band reflections are recovered for long annealing times. For example, after 83 hours and 25 minutes, $\Delta\lambda^{PLA}$ is equal to about 75 nm and is centered around 516 nm (Figure 1). The phenomenon of $\Delta\lambda$ reduction appears to be stabilized: a common narrow-band filter is recovered and corresponds to a CLC structure with an homogeneous pitch whose the associated reflection is between 'blue' and 'red', *i.e.* the 'green region'. The reflection is similar to the case of an equimolar blend of 'blue' and 'red' materials [11]. Spectral characteristics for further annealing times are investigated elsewhere [11] and the TEM contrast is discussed in reference [12].

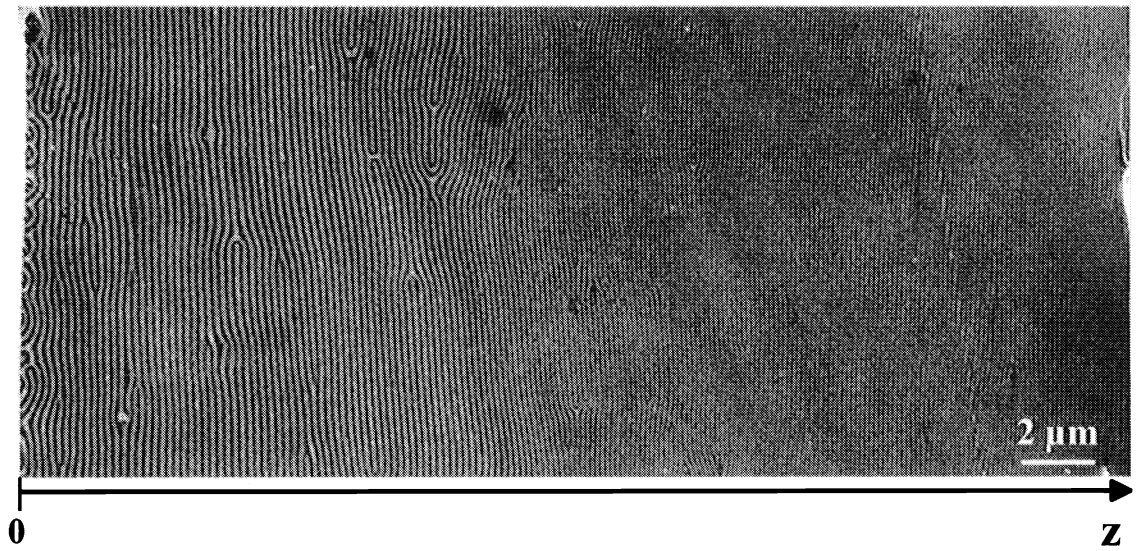

Figure 2: TEM micrograph of a cross-section of a sandwich-cell after 25 minutes of annealing.

From Figure 2 the CLC pitch has been measured as a function of the position z in the cross-sectional view where the measurement was done. The z-axis is taken perpendicular to the film surfaces and the origin is chosen at the side with the largest periodicities. In order to establish a parallel between the periodicities and the related reflection wavelengths, we considered approximated values of λ_R from the Bragg law at normal incidence and by taking n as equal to 1.5. These data are collected in Figure 3 from cross-sectional views as investigated by TEM for annealing times equal to 5 minutes [12], 25 minutes (Figure 2) and 83 hours 25 minutes [12]. The lines are guides for the eye. First, we remark that the curves are progressively reduced when the annealing time increases. Indeed the thickness of sandwich-cell decreases during the diffusion process between the two films since the matter is spreading out in a plane perpendicular to the cholesteric axis.

When the annealing time is equal to 5 minutes, two constant periocities are measured in the sample. The approximated reflection wavelengths which are correlated to them are mainly dispersed between 750 – 850 nm and 350 – 450 nm. These values are coherent with the data issue from the spectrophotometry (Figure 1) and correspond to reflections in the 'red' and 'blue' regions of the visible spectrum. The transition between the two periodicities is very abrupt since there is no region in which the two layers have mixed when the annealing is so short.

When the annealing time is equal to 25 minutes, the periodicity varies smoothly and continuously from around 400 nm to 270 nm by presenting all a set of intermediate periodicities. The curve gives a quantitative analysis of pitch gradient.

The periodicity is finally constant for an annealing time of 83 hours 25 minutes and is centered around 320 nm with a correlated reflection wavelength above 450 nm.

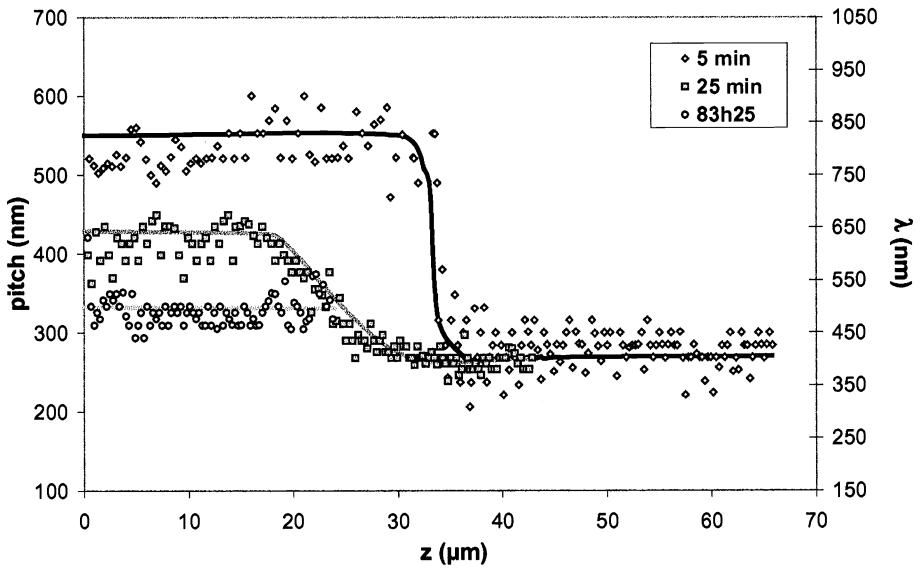

Figure 3: Relationship between the cholesteric pitch (as measured from TEM micrographs) and the position of the measurement in the z-direction perpendicular to the surfaces of the films. Annealing times are equal to 5 min., 25 min. and 83 h. 25 min. On the right ordinate axis the correlated reflection wavelength is represented as deduced from the Bragg relation at normal incidence when n is taken as equal to 1.5. The lines are guides for the eye.

3. BROADENING OF REFLECTION BAND IN SWITCHABLE POLYMER-STABILIZED CHOLESTERIC LCs

Here we present another experimental process to modify and to increase the reflection band. In contrast to the previous one, the elaboration of a material exhibiting an enlarged reflection band is here *in situ* and does not associate two individual CLC slabs. The process is based on a thermally-induced pitch variation occurring during the UV-irradiation of a blend made of a low molar mass LC mixture and a network-forming material. In a previous work, we investigated under these experimental conditions the case of a high concentration in polymer network (80 wt.%) [13]. Here the material is a Polymer-Stabilized CLC (PSCLC) with a concentration in polymer network equal to 3.9 wt.%.

3.1. Experimental

A blend of a photocrosslinkable CLC substance RM9 (from Wacker Chemie Ltd.) with a low molar mass CLC mixture is made. RM9 is a modified siloxane compound suited for the production of optical filters and consists of a mixture of reactive monomers and side groups LC polymers with a siloxane backbone [9]. The RM9 concentration is 3.9 wt.%. An amount of 2 wt.% (compared to the RM9 concentration) of photoinitiator Irgacure 907 (from Ciba-Geigy) is added. The CLC mixture is the following blend: 82 wt.% BL088 + 18 wt.% CB15 (BL088 and CB 15 come from Merck Ltd.).

The mixture is introduced in the isotropic phase at 105°C by capillarity in a 5 µm thick ITO-glass cell (from Linkam Ltd.). The surfaces were treated in order to induce a planar orientation.

From Grandjean planar textures investigations by polarized-light microscopy when the temperature is increased in the cholesteric temperature range from the room temperature, selective light reflections occur from blue to green. The isotropic transition is between 71.5 and 72.5°C.

The sample is UV-cured at 365 nm with a power of 0.1 $mW.cm^{-2}$ (measured with a UV-radiometer UVR-365 from Prolabo) during a thermal ramp of 3 hours from 24.5 to 69.5°C.

The experimental conditions for the spectrophotometry are the same as in section 2.1. The voltage is a sinusoidal signal and the frequency is equal to 1 kHz.

3.2. Optical properties

Figure 4 represents the variation of the transmitted light intensity with the wavelength for the sandwich-cell before and after curing, *i.e.* a UV-irradiation and a thermal ramp occurring together.

Before the curing the reflection peak is centered around 455 nm with a bandwidth measured at half-height [14] equal to 65 nm. After the curing, the peak is slightly shifted until about 435 nm and the bandwidth is now almost of 150 nm. Therefore it appears that the band has been broadened by a factor greater that two as a consequence of a UV-curing occurring when the cholesteric pitch changes. We can think that this broadening is the result of memory effects introduced by the polymer network which has been built in a CLC medium for which a major structural characteristic such as the helical pitch was changing.

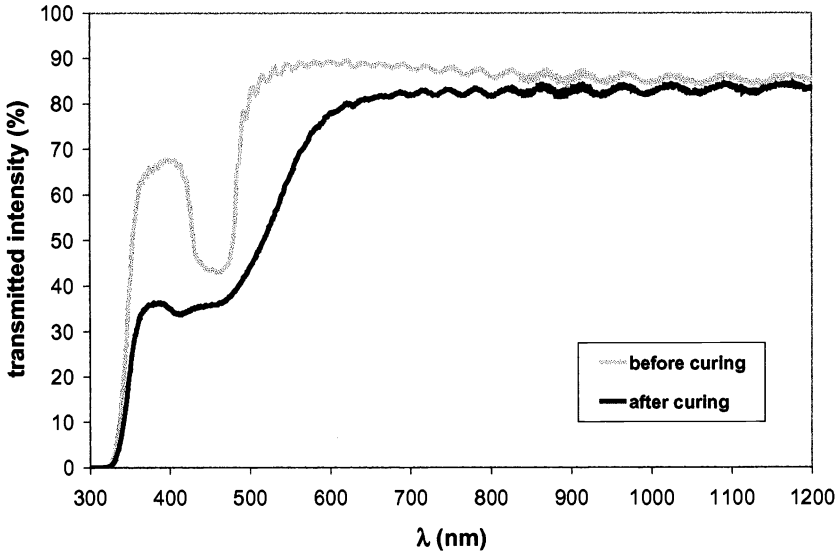

Figure 4: Transmitted light intensity as a function of wavelength before and after curing meaning that the CLC cell has been irradiated with UV-light during the thermally-induced pitch variation.

3.3. Electro-optical properties

The ability and the characteristics of the sample switchability when subjected to an electric field are investigated. Figure 5 represents the variation of transmitted light with the wavelength without voltage and for an increasing voltage.

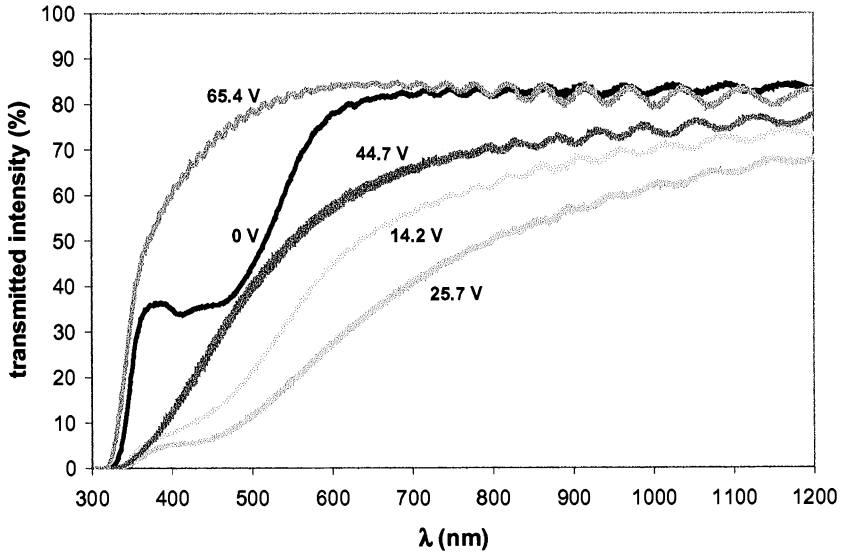

Figure 5: Transmitted light intensity as a function of wavelength for the CLC cell cured under out-of-equilibrium conditions without voltage and when a voltage is applied and progressively increased. The frequency is 1 kHz.

The reflection peak progressively vanishes between 0 and 14.2 V. The progressive decrease of light transmittance (until the voltage reaches 25.7 V in the Figure 5) is due to light scattering. As in PSCLCs with a narrow band for reflection, the light scattering is due to a focal conic texture exhibiting polydomains [15]. This is the result of a competition between LC molecules close to the polymer network which have a tendency to contribute to a stable planar reflecting texture and the electric field effect which is to destroy this order by untwisting the helix. Finally and for higher voltages, the cell becomes progressively transparent (until the voltage reaches 65.4 V) when the structure is untwisted and free LC molecules are perpendicular to the electrodes.

4. DISCUSSION

In the pioneering work done by the Philips research group, a CLC polymer network with a pitch gradient offers the possibility to broaden $\Delta\lambda$ on more than 300 nm [16, 17]. The pitch gradient is due to a photo-induced diffusion during a photopolymerization reaction in a blend of chiral and nematic monomers. The driving force for the diffusion is the combination of a UV-intensity gradient over the film thickness and a difference in reactivity between the helix-winding chiral monomer and the helix-unwinding nematic one. The blend compounds are: a chiral diacrylate, a nematic monoacrylate, a photoinitiator and a dye which absorbs in the same region as the photoinitiator and with an extinction coefficient two orders of magnitude larger. From a structural viewpoint, the film is a CLC polymer network exhibiting a pitch gradient as a consequence of a concentration gradient between chiral and achiral chemical species. Such broadband reflectors greatly improve the light yield (by 40% in reference [17]) and energy efficiency of LC devices by recycling wrongly-polarized light in the back-light system.

The Merck R&D group transferred the concept of a brodband CLC from a glass- to a foil-based technology by laminating together the polymer film with a quarter-wave retardation plate [18, 19]; the brightness gain was then improved from 40 to 80%.

The Reveo group studied the $\Delta\lambda$ broadening and the polarized backlight output enhancement for two types of CLC films [20-25]: *(i)* a stack of red-, green- and blue-reflecting films [21, 23, 24]; and *(ii)* a single layer broadband CLC [20, 22, 25].

Two main features proper to the present work realized in the case of CLC glasses are as follows:

(i) the novel process lies in a thermal diffusion between two CLC oligomer films with different chiralities. Neither polymerization reaction nor photo-induced phase separation is involved; **(ii)** the broadband reflector is a single-layer CLC in the glassy state. On this characteristic, we evoked in a previous paper potential applications in the field of optical storage [26].

In the case of PSCLCs we chose the original case of a photopolymerization and a photocrosslinking of a CLC material mixed with a low molar mass CLC when the helical pitch of the mixture varies because the temperature varies. This choice is different from the idea of creating a temperature gradient as quoted in reference [27] since there is no temperature gradient in the cell during the UV-curing: the temperature changes in the time but not from one side of the cell to the other one. From the point of view of the technological realization, out-of-equilibrium conditions could be preferred to the tuning of a temperature gradient since it is difficult to control the existence of a transverse temperature gradient in a several microns thick slab of LC in agreement with the variation profile of the helical pitch.

5. CONCLUSION

The cholesteric liquid crystal (CLC) phase may selectively reflect light. The wavelength bandwidth $\Delta\lambda$ depends on the birefringence. Recent studies have aimed to broaden $\Delta\lambda$ from several tens of nanometers — an order of magnitude usually encountered in literature — to several hundreds of nanometers. The latter case would especially be relevant for specific applications such as full-colors displays.

First we presented a novel experimental process to elaborate a CLC structure reflecting light on more than 300 nm. The basic idea lies in a thermal diffusion between two CLC films with different colors which is anisotropic because the diffusion happens in a direction perpendicular to the surfaces of films. A concentration gradient between the chiral films and thus a pitch gradient occurs in the material which becomes a single-layer above a critical annealing time. As a novelty, this broadband reflector is a glassy solid.

Then we settled an other experimental process to broaden the reflection bandwidth in a PSCLC. With the set of experimental conditions we chose here, the bandwidth is increased by a factor greater than two as a consequence of a UV-curing happening when the CLC pitch changes because the temperature varies. We previously studied the polymerization and the crosslinking of a polymer–LC composite in out-of-equilibrium conditions when the concentration in polymer is high [13]. Here we focus our interest on a weak concentration (3.9 wt.% in polymer). The reflection band is clearly enlarged and the material presents the possibility to switch between reflective, scattering and transparent states when subjected to an electric field. Further work will present the effect of ramp time and UV-power on the characteristics and the amplitude of the reflection band.

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3. In a Grandjean planar texture, the helix axis is perpendicular to the observation plane.

4. n is the average of the ordinary (n_o) and extraordinary (n_e) refractive indices of the locally uniaxial structure: $n = (n_o + n_e)/2$.

5. $\Delta n = n_e - n_o$.

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