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Glassy Cholesteric Broadband Reflectors with a Pitch Gradient: Material Design, Optical Properties and Microstructure

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The cholesteric liquid crystal (CLC) phase may selectively reflect light. The reflection wavelength is correlated with the CLC helical pitch and the wavelength bandwidth $\Delta\lambda$ with the birefringence. Recent studies have aimed to broaden $\Delta\lambda$ from several tens – 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. Our purpose is to present a novel experimental process to design a CLC with a pitch gradient reflecting light on more than 300 nm. As a novelty, this broadband reflector is a glassy solid. The spectral behaviour is analyzed in parallel to the reflector microstructure which is investigated by transmission electron microscopy for the first time.

Keywords: cholesteric liquid crystals; glassy state; light reflection; pitch gradient; TEM

I. GENERALITIES

I.1. Problematics

The spatially periodic twisted structure of the cholesteric liquid crystal (CLC) phase gives rise to remarkable physical properties [1, 2]. The probably 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_R is related to the cholesteric pitch p and the mean refraction index n [4] by:

$$\lambda_R = n.p.$$

The reflection occurs in a band of wavelengths:

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

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

Within $\Delta\lambda$, an incident unpolarized or linearly polarized light beam parallel to the helix axis is splitted 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.

$\Delta\lambda$ is thus mainly determined by Δn . Since Δn is typically limited to 0.3, $\Delta\lambda$ is less than 100 nm, 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, for other applications like full-colors or white-on-black displays, this limit has to be exceeded.

The present study focuses on the physical sources of $\Delta\lambda$ and the possibilities to change its order of magnitude from usual values — several tens of nm — to much larger ones —, more than 300 nm.

I.2. State of the art

In the pioneering work of Philips group, a CLC polymer network with a pitch gradient offers the possibility to broaden $\Delta\lambda$ on more than 300 nm ([9, 10] and [11] for a synthesis). The pitch gradient is due to a photo-induced diffusion during a photopolymerization reaction in a chiral and nematic monomers blend. The driving force for 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's compounds are: a chiral diacrylate, a nematic monoacrylate, a photoinitiator and a dye which absorbs in the same region as photoinitiator and with an extinction coefficient two orders of magnitude larger. From a structural viewpoint, the film is thus a CLC polymer network exhibiting a pitch gradient as a consequence of a concentration gradient between chiral and achiral chemical species. Such broadband (BB) reflectors greatly improve the light yield (by 40% in [10]) and energy efficiency of LC devices by recycling wrongly-polarized light in the back-light system.

Merck R&D group transferred the concept of a BB CLC from a glass- to a foil-based technology by laminating together the BB CLC polymer film with a quarter-wave retardation plate [12, 13]; the brightness gain was then improved from 40 to 80%.

Reveo group studied $\Delta\lambda$ broadening and polarized backlight output enhancement for two types of CLC films [14-19]: (i) a stack of red-, green- and blue-reflecting films [15, 17, 18]; and (ii) a single layer BB CLC [14, 16, 19] 'that achieves its wide selective reflection band because of its engineered pitch distribution' [16].

At CEMES, we experienced an other route for broadening $\Delta\lambda$, which leads to a novel CLC material with a pitch gradient [20].

Two main features of the present work are as follows:

- the new process lies in a thermal diffusion between two CLC oligomer films with different chiralities. Neither polymerization reaction nor photo-induced phase separation is involved;
- the BB reflector is a single-layer CLC in a glassy state.

In the following, after a section devoted to the experimental conditions, the material characteristics will be presented under three aspects:

- about the material design: the different steps leading to a BB CLC reflector are summarized;
- the optical properties : the light reflection evolves from a selective to a BB reflector (reflection on several hundreds of nanometers) with different intermediary optical states. The inverse transition — from a BB to a narrow-band filter — is also demonstrated;
- the transmission electron microscopy (TEM) permits to image the microstructure and the very pitch gradient of glassy CLCs due to cross-sections investigations. Up to now, only the surface of CLC films with a pitch gradient had been observed by scanning electron microscopy (SEM) [10, 20] or atomic force microscopy (AFM) [14].

II. EXPERIMENTAL CONDITIONS

II.1. 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 (Figure 1) [21]. 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, these materials can be very easily quenched at room temperature and the mesomorphic order with its color properties are permanently stored within a solid film.

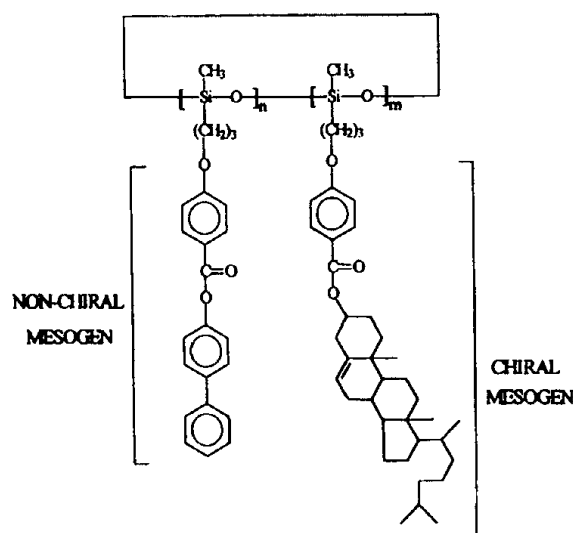


FIGURE 1 General chemical structure of CLC polysiloxanes

II.2. Spectroscopy

The spectral characteristics of materials are obtained at room temperature by unpolarized UV-visible light spectroscopy (UV-3100 Shimadzu spectrophotometer).

II.3. Transmission electron microscopy (TEM)

Materials are embedded in epoxy resin cured at 40°C. 150 nm thin 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 [22].

III. RESULTS

III.1. Material design

The material design is based on an anisotropic diffusion between CLCs with different chiralities. The procedure is here summarized in four steps. **1.** 40 μm thick films of blue and red CLCs are spread with a 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 sealed and 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 chirality gradient —, may occur in a direction perpendicular to the plane of films. 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 to a glassy state. Such a cooling prevents crystallization and preserves the CLC phase.

III.2. Optical properties and microstructure

Figure 2 shows the variation of transmitted light intensity with respect to the wavelength after 5 min of annealing; the curve intrinsic to a glass plate is also displayed. The negative peaks are due to the reflection of about 50% — as a consequence of circular polarization discrimination induced by a CLC structure (see §.I.1) —, which corresponds well to the theoretically predicted value [1].

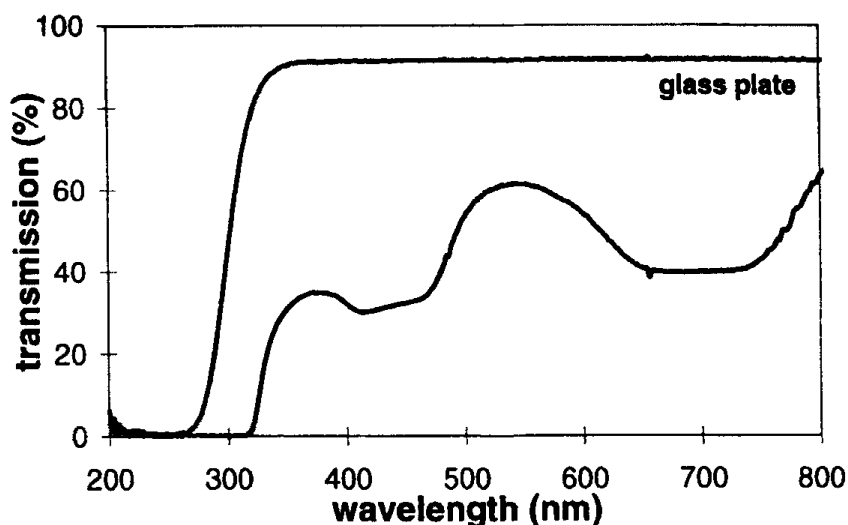


FIGURE 2 Transmitted light spectrum as a function of wavelength for a plain glass plate and a sandwich-cell after 5 min of annealing

The spectrum is the sum of two peaks intrinsic to the selective reflections of blue and red films. The mean reflection wavelengths are respectively about $\lambda_B = 444 \text{ nm}$ and $\lambda_R = 711 \text{ nm}$ with the dispersions $\Delta\lambda_B = 50 \text{ nm}$ and $\Delta\lambda_R = 85 \text{ nm}$. These values are consistent with spectral characteristics of common CLCs. In this case of a short annealing time, the diffusion between the chiral films is not relevant and the CLC material is a bi-selective reflector —, as a simple stack of blue and red layers.

The TEM micrograph of a cross-section (Figure 3) gives the opportunity to visualize the microstructure of the glassy CLC along a direction perpendicular to the observation plane which was also the plane giving rise to light reflections.



FIGURE 3 TEM micrograph of a cross-section of a sandwich-cell after 5 min of annealing

Alternative dark and bright lines are observed. These periodic lines are intimately associated to the very helical structure of a CLC sample when observed in a direction perpendicular to the helix axis [22], which is presently the case. The periodicity — the distance between two dark or bright lines — is about the half-pitch. Two regions with two different periodicities and separated by an interface may be distinguished. The left and right regions show a periodicity equal to – respectively – about 240 and 150 nm; these values are coherent with a periodicity intrinsic to

– respectively – the 'red' and the 'blue' films. The interface — clearly showing a demarcation between the two regions — testifies that the diffusion between the 'red' and 'blue' films is not effective at such a low annealing time (5 min). In this light, the microstructure is consistent with the spectral behaviour which presents two clearly separated reflection peaks (Figure 2).

As soon as the annealing time reaches 25 minutes, the curve is flat and enlarged on more than 300 nm, as shown in Figure 4: the bi-selective film becomes a BB 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.

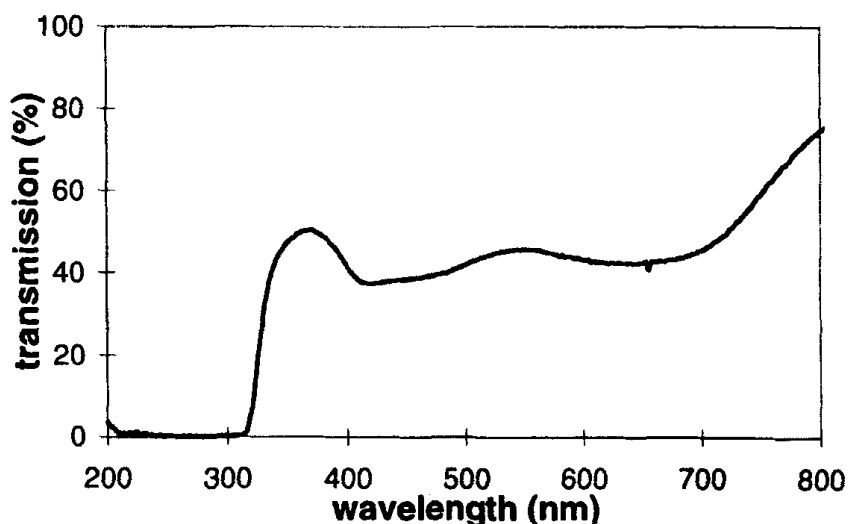


FIGURE 4 Transmitted light spectrum as a function of wavelength for the sandwich-cell after 25 min of annealing

Again, the TEM investigations give the status of the helicoidal pitch along the helix axis (Figure 5). Now, 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 collection of periodicities intermediate between 'red' and 'blue' CLC periodicities is present.



FIGURE 5 TEM micrograph of a cross-section of a sandwich-cell after 25 min of annealing

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 h 25 min, the bandwidth is equal to about 75 nm and is centered around 516 nm (Figure 6).

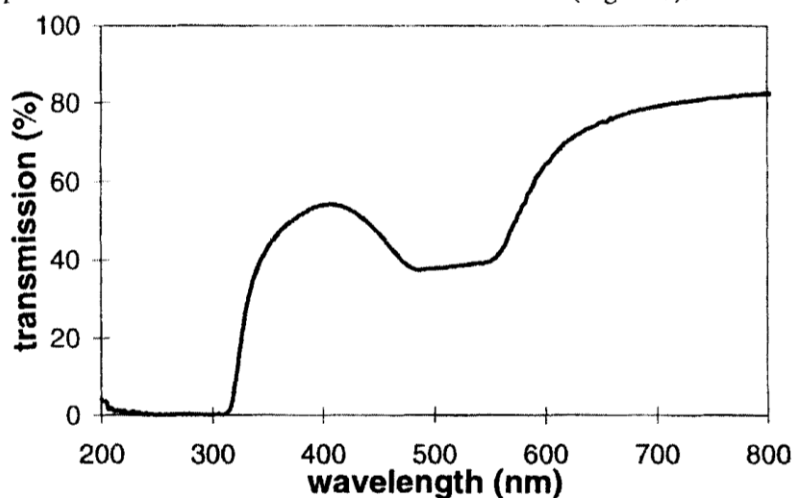


FIGURE 6 Transmitted light spectrum as a function of wavelength for a sandwich-cell after 83 h 25 min of annealing

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 [23].

Spectral characteristics for further annealing times are investigated elsewhere [23] and the TEM contrast will be discussed in a next work [24].

IV. DISCUSSION

Figure 7 proposes different stages that we might distinguish in the evolution of spectral characteristics during the annealing process.

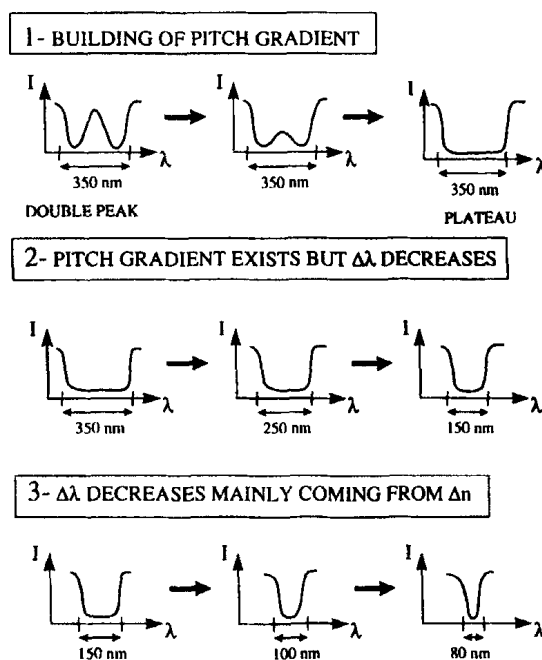


FIGURE 7 Different stages of a possible scenario occurring during the thermal process

1st stage.- The pitch gradient Δp is on the way to be built. The spectral characteristics start from a two-peak selective filter with two distinct $\Delta\lambda$ due to Δn ; then, the limit between peaks becomes significantly less marked and, finally, a plateau intrinsic to a BB reflector is got: Δp is recognized as responsible for such a reflection bandwidth broadening (on more than 300 nm). If desired, the annealing process may be simply stopped by quenching the cell and a solid BB reflector is then available.

2nd stage.- The pitch gradient still exists since $\Delta\lambda$ is clearly greater than 100 nm —, a value that we liken to the $\Delta\lambda$ limit for common CLCs. However, $\Delta\lambda$ progressively decreases. Due to the diffusion, the system is on the way to be progressively transformed into a CLC structure with an uniform pitch.

3rd stage.- $\Delta\lambda$ continues to decrease and has now an order of magnitude — typically less than 150 nm — which suggests that the origin of $\Delta\lambda$ has to be mainly imputed to Δn .

Compared to previous works [9-19], the pitch gradient is here completely controlled only by one parameter, — the annealing time. Besides, whereas the photopolymerization rate had to be constantly balanced by the monomer diffusion rate [9-11], the two steps of pitch gradient building and film hardening are here separately driven (no phase separation mechanism is involved).

On the position of $\Delta\lambda$ in the light spectrum as well as its amplitude, our approach is quite general since $\Delta\lambda \sim \lambda_2 - \lambda_1$ may be easily tuned by a convenient choice of the wavelength λ_1 and λ_2 of the initial films and a thermal treatment above 50°C. After annealing, the film is no longer a stack of blue and red films but a single-layer film, which is important for the optics because a single-layer system is far less sensitive to optical defects and additional scattering or reflection losses at the interfaces.

Finally, we would like to stress the novelty of a BB reflector in a glassy state. All the methods of locking the pitch by polymerization or by use of a polymer network to stabilize the helix are not suitable for rewritable recording by altering the pitch because of their irreversibility. Due to the glassy state, further potential advantages might be found in high density memory media that use the full spectrum of light and thermo-sensitive full-colors recording materials. For example, it is possible to address the material by using laser heating due to absorption. As previously reported for narrow-band CLCs [25, 26] and now possible for CLCs with a tunable reflection bandwidth, another potential application of room-temperature glasses is in optical elements for high power laser systems. While elements in use today confine the LC between glass plates, optical elements made of a CLC solid could be set on a rigid or even flexible single substrate to overcome this problem.

As shown in the case of narrow-band CLCs [27], this glassy BB reflector might also be broken into flakes to be embedded in a carrier such as resin in order to become a polarizing paint or ink with original reflection properties.

V. CONCLUSION

By favoring a pitch gradient in the helix during a novel two-step process with a reduced number of independent driving parameters, it is possible to get a CLC glassy material evolving from a selective to a BB filter. The material design lies in an anisotropic diffusion between two CLCs with slightly different chiralities. First, the reflection bandwidth is adjusted by thermal annealing. Then, the optical properties are permanently stored by quenching the viscous material to a glass at room temperature. The two steps — pitch gradient establishment and film

hardening — are independently controlled. Reflection occurs on several hundreds of nanometers and different intermediary optical states are available if the thermal treatment is stopped by quenching the material. The inverse transition – from a broad to a narrow-band filter – is also demonstrated. First investigations of cross-sections by TEM for different annealing times clearly show that the reflection broadening is due to a transverse helical pitch.

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