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Bragg Reflections in Cholesteric Liquid Crystals: From Selectivity to Broadening and Reciprocally

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Due to the existence of a macroscopic helicoidal structure, cholesteric liquid crystals exhibit many remarkable properties like selective light reflections. Bragg reflections occur when the helix pitch is of the order of the wavelength of the incident light propagating along the helix axis. The wavelength bandwidth is due to the medium birefringence and is typically limited to 50 nm, which is insufficient for some applications (full-colors displays, for example). The purpose of this paper is to show that, by favoring a pitch gradient in the helix during a novel experimental process, it is possible to get a cholesteric glassy material whose spectral characteristics evolve from a selective to a broad-band filter. Light reflection occurs on several hundreds of nanometers and several intermediary optical states are available during a thermal treatment. From a reciprocal viewpoint, the inverse transition, from a broad- to a narrow-band filter, is also demonstrated. Such a process is driven by one parameter: the annealing temperature. 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. Different possible stages occurring during the thermal history of the sample are discussed. The very glassy state of these reflectors would give new opportunities for optical data storage.

Keywords: cholesteric liquid crystals; pitch gradient; optical properties; Bragg selective light reflections; broad-band light reflections; glassy state

I. INTRODUCTION

Well before Reinitzer reported unexplained color phenomena in cholesteryl esters [1] and research in optical properties of liquid crystals started, Reusch had observed a rotation of the polarization plane of linearly polarized light on a stack

of twisted mica lamellae [2, 3]. Such a system is reminiscent of the helicoidal structure of the cholesteric phase, elucidated by Mauguin [4], Oseen [5] and de Vries [6].

Cholesteric liquid crystals exhibit many remarkable properties due to the existence of a macroscopic helicoidal structure [7–10]. The most striking features are the exceptionally large optical rotatory power and the iridescent colors due to the selective reflection displayed by an uniformly oriented cholesteric Grandjean planar texture, when the helix axis is perpendicular to the observation plane. In a small wavelength range about λ_0 , an incident light beam parallel to the helix axis is splitted into its two circularly polarized components, one of which is simply transmitted whereas the other is totally reflected; the rotation of the reflected circularly polarized light agrees with the screw sense of the structure. At normal incidence, maximum reflection occurs when the incident wavelength λ matches the following Bragg law:

$$\lambda = \lambda_0 = n.p,$$

where $n = (n_o + n_e)/2$ is the average of the ordinary (n_o) and extraordinary (n_e) refractive indices of the locally uniaxial structure and p the cholesteric pitch. The wavelength which does not verify $\lambda = \lambda_0$ is simply transmitted.

It is in the region $\Delta\lambda$ of the pitch band that most of the previous optical investigations of cholesterics have concentrated. $\Delta\lambda$ is given by the following relation :

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

where $\Delta n = n_e - n_o$ is the birefringence.

Therefore, $\Delta\lambda$ is mainly determined by Δn , which is typically limited to values below 0.3 for colorless organic materials. As a consequence, the reflection bandwidth is limited to $\Delta\lambda < 100$ nm and is typically equal to 50 nm. If the selectivity is desired for several families of applications (optical filters, thermal imaging, laser or paint technologies), a drawback lies in the fact that the known cholesteric filters have a too limited reflection bandwidth for some specific purposes (full-color displays, for example).

The goal of this paper is to show that it is possible to get a cholesteric glassy material whose spectral characteristics evolve from a selective to a broad-band film exhibiting light reflection on several hundreds of nanometers. Several intermediary optical states are available. The inverse transition, from a broad- to a narrow-band filter, is also demonstrated. Such a process is driven by one parameter: the annealing temperature.

II. MATERIALS

Our choice of cholesteric liquid crystalline oligomers [11] is motivated by the chirality characteristics of such materials and the easy achievement of the glassy state. The molecule is a siloxane cyclic chain with two types of side-chains attached via spacers: a non-chiral mesogen and a chiral one (Figure 1). On a glass or plastic plate, the compound shows typical iridescent colors ranging from blue to red simply tuned by the molar percentage of chiral mesogens in the oligomer molecule: from 50 to 31%. The cholesteric phase appears between 180/210°C (isotropic transition) and 40/50°C (glass transition temperature). As an advantage with regard to the process and properties we describe, these materials can be very easily quenched at room temperature and the cholesteric order with its color properties are permanently stored within a solid film.

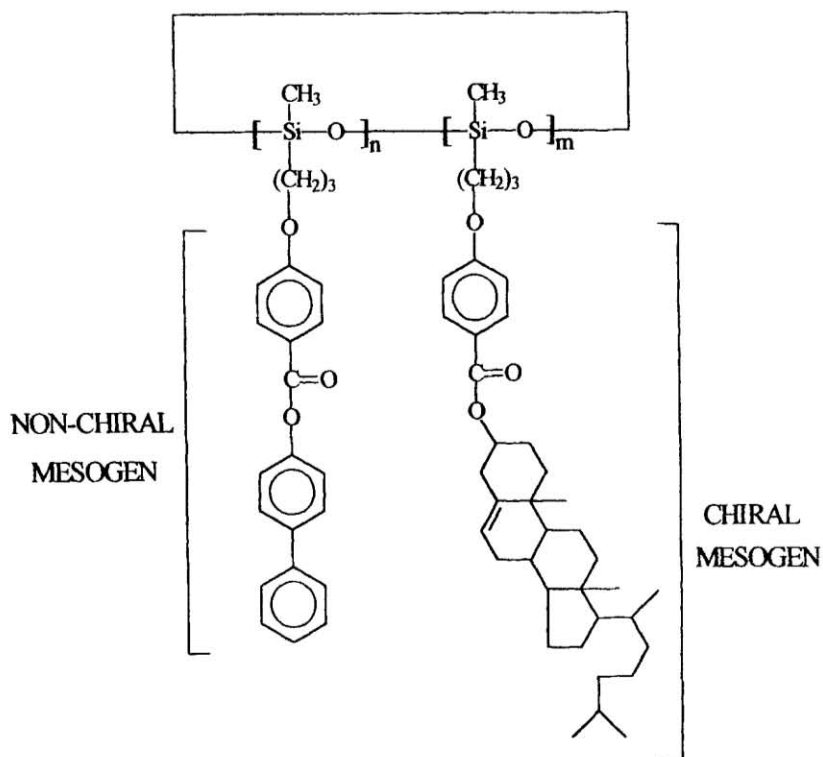


FIGURE 1 General chemical structure of cholesteric polysiloxane oligomers

III. CHOLESTERIC MATERIAL DESIGN

In a previous note [12], we presented the material design leading to a cholesteric glassy system exhibiting a broad-band light reflection. The route is summarized in Figure 2 and is intrinsically associated to the idea of an anisotropic diffusion between two compounds with different chiralities. The experimental procedure is simple. *Step 1.*-40 μm thick films of blue and red compounds are spread with a handcoater on two distinct glass plates without any alignment layer. *Step 2.*- A sandwich-cell is made with these blue and red films separated with 19 μm calibrated spacers. *Step 3.*- The cell is sealed and kept at 85°C. This temperature corresponds to a stable cholesteric phase for which the materials are equally rather fluid. Consequently, a diffusion process between the red and blue compounds – and, therefore, a chirality gradient – may occur in a direction perpendicular to the plane of films. Since these materials belong to the same molecule family, a high miscibility is expected. *Step 4.*- After such an annealing process, the cell is quickly put on a metallic substrate at room temperature: it is the quenching step. The macroscopic characteristics of the film evolve from a viscous to a glassy state. Such a cooling prevents crystallization and preserves the cholesteric structure.

IV. OPTICAL PROPERTIES

The spectral characteristics of materials are obtained by unpolarized UV-visible light spectroscopy at ambient temperature.

IV.1. From a two-peak selective reflection to a broad-band one

Figure 3 shows the variation of transmitted light intensity with respect to the wavelength in the case of a plain glass substrate (a), the blue (b) and the red (c) films. The mean reflection wavelengths exhibited by the blue and red selective films are respectively about $\lambda_B = 444$ nm and $\lambda_R = 711$ nm with the dispersions $\Delta\lambda_B = 50$ nm and $\Delta\lambda_R = 85$ nm. These values are consistent with spectral characteristics of common cholesterics. The negative peak for each film is due to the reflectivity of about 50% which corresponds well to the theoretically predicted value [7].

Then, we make a sandwich-cell from these blue and red films and put it on a heating stage at 85°C. Figure 4 shows the variation of light intensity transmitted by the system with respect to the wavelength for annealing times equal to 5 and 25 minutes. The curve corresponding to 5 minutes simply consists in the sum of the curves intrinsic to the blue and the red films (to be compared to Fig.3.b & c).

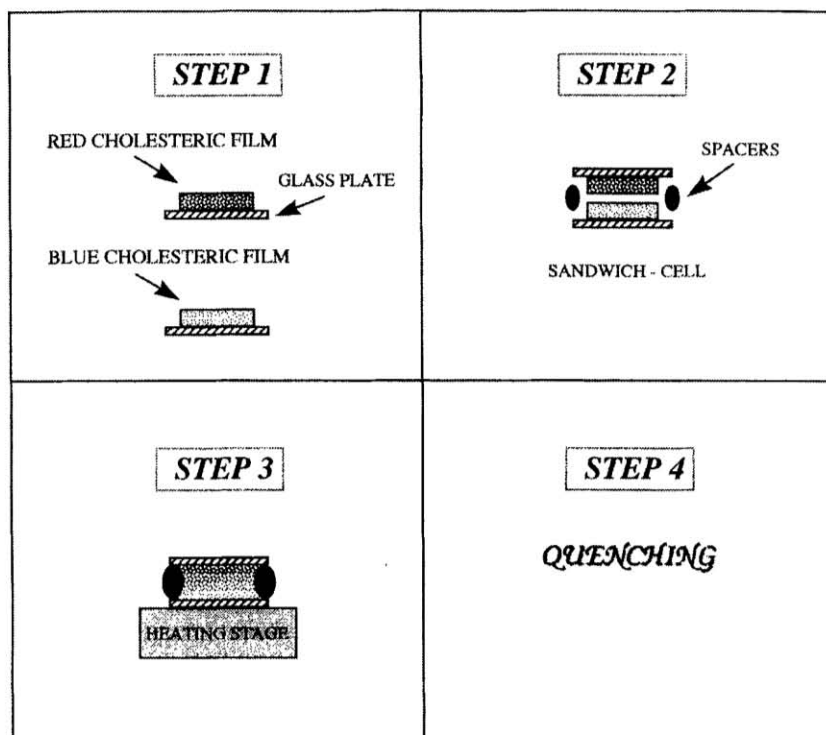


FIGURE 2 Different steps of the material design leading to a cholesteric glass with a pitch gradient. *Step 1*: two cholesteric films exhibiting red and blue reflection colors are spread on distinct glass plates. *Step 2*: a sandwich-cell is made with these plates. *Step 3*: the cell is put on a heating stage to create a diffusion between red and blue compounds. *Step 4*: the cell is quenched at room temperature

We may expect that the diffusion between the chiral films is not relevant: the cholesteric material is a bi-selective film, with two peaks, in the blue and red regions. But as soon as the annealing time reaches 25 minutes, the curve is flat and enlarged on more than 300 nm (about 306 nm): the bi-selective film becomes a broad-band filter as an expected consequence of the establishment of a pitch gradient in the cholesteric superstructure. To the naked eye, the film is colourless with a metallic aspect since it reflects 50% of the light over the visible spectrum.

The behaviour of the curves corresponding to 1 h 05 min. and 2 h 05 min., as shown on Figure 5, are similar to the previous one with, however, a slightly narrower plateau: 258 nm for 1 h 05 min. (which corresponds to a reduction of about 16% compared to 25 min.) and 206 nm for 2 h 05 min. (a new reduction of about 20% compared to 1 h 05 min.).

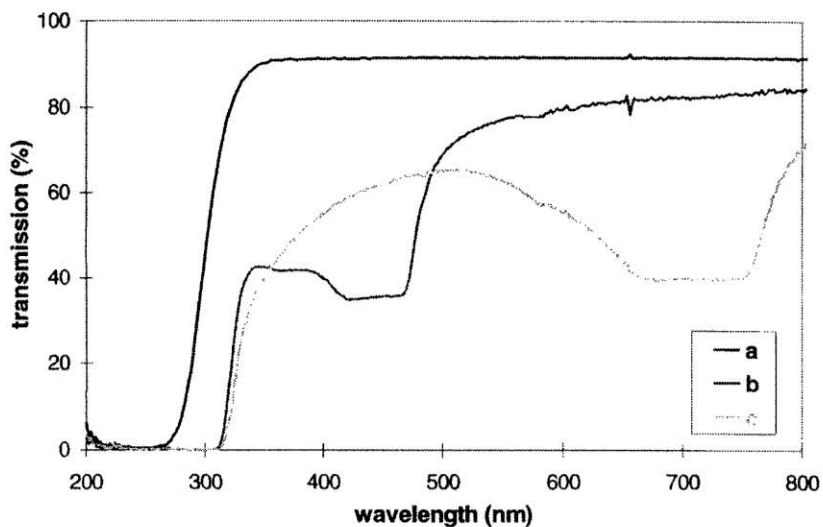


FIGURE 3 Transmission spectra as a function of wavelength for: (a) A glass substrate, (b) The blue cholesteric film and (c) The red cholesteric film

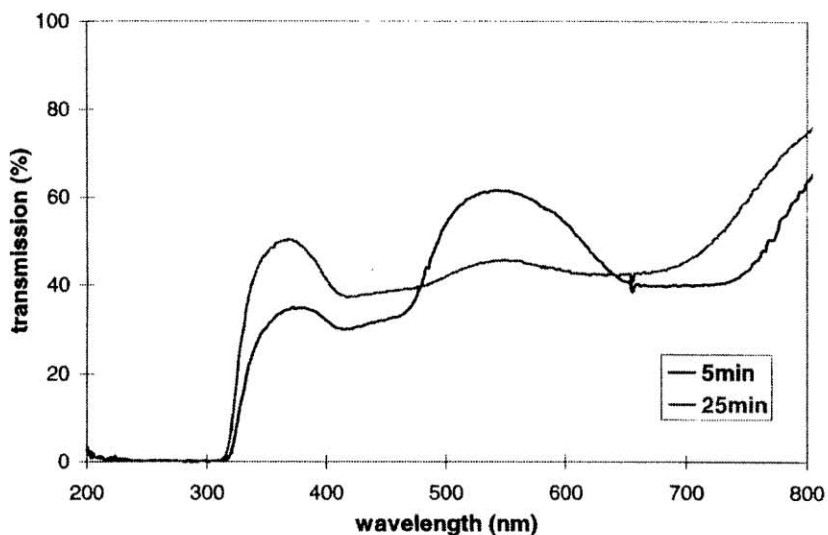


FIGURE 4 Transmission spectra as a function of wavelength for the sandwich-cell after annealing times equal to 5 and 25 minutes

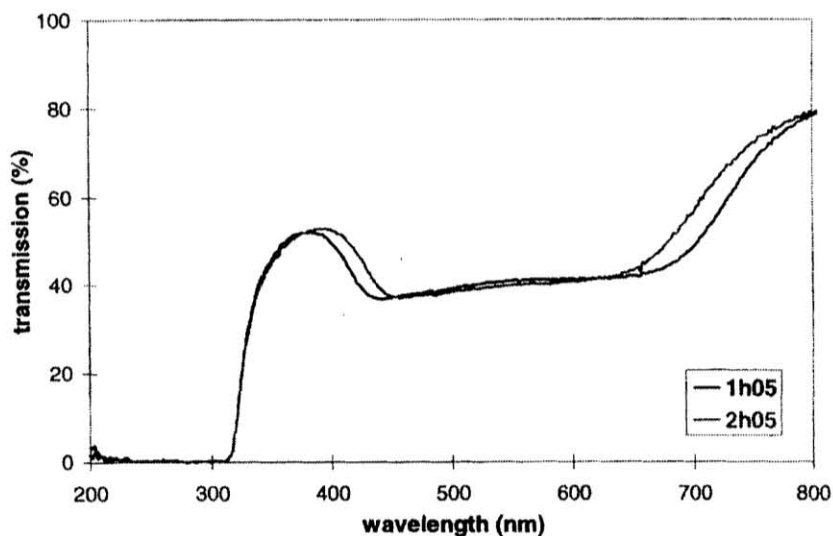


FIGURE 5 Transmission spectra as a function of wavelength for the sandwich-cell after annealing times equal to 1 h 05 and 2 h 05 minutes

Previous investigations by scanning electron microscopy of cross-sections microstructure (after an annealing time equal to 1 hour) have given the following results [12]: (i) the former bilayer film becomes a homogeneous single-layer film, probably due to the efficiency of the diffusion process; (ii) there exists a continuous pitch gradient along the direction perpendicular to the observation plane, which confirms the concept of a cholesteric structure with a gradient pitch.

IV.2. Reciprocally: from a broad- to a narrow-band reflection

The analysis of the spectral behaviour of the sandwich-cell with respect to the annealing time is carried out (Figure 6).

The curve inherent to 4 h 25 min. is flat but the plateau width is smaller than the plateau width corresponding to 2 h 05 min.: 178 nm against 206 nm (about 13% less). The phenomenon is still more spectacular when the annealing time reaches 14 h 25 min.: the plateau width is now equal to 96 nm, which corresponds to a supplementary reduction of about 46%. Although the plateau width is again reduced after 21 hours of further annealing – 82 nm against 96 nm - the reduction is far less sensitive: 14%. The phenomenon of plateau reduction appears to be now stabilized: it is a common narrow-band filter which is recov-

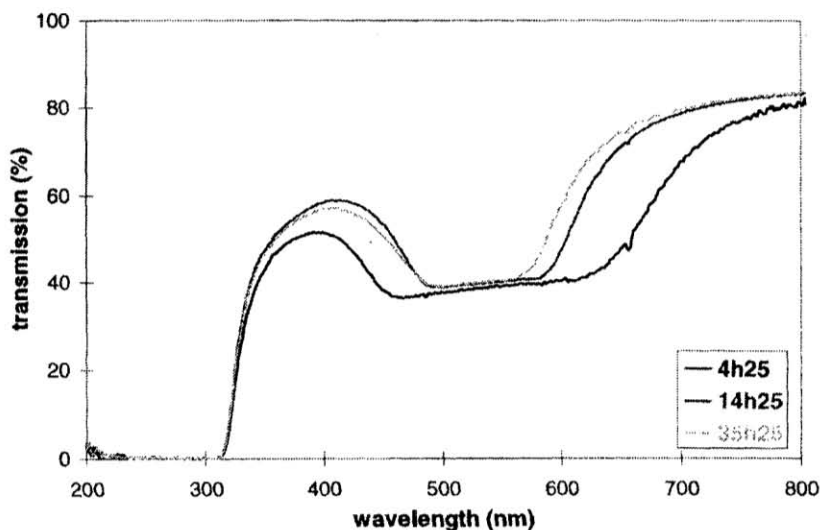


FIGURE 6 Transmission spectra as a function of wavelength for the sandwich-cell after annealing times equal to 4 h 25, 14 h 25 and 35 h 25 minutes

ered, consecutively to the progressive building of a cholesteric structure with an homogeneous pitch whose the associated reflection wavelength is between blue and red reflections (“green region”).

In order to validate such an hypothesis, we prepared a $19\ \mu\text{m}$ thick cell with a 50% homogeneous blend of blue and red compounds. This sample macroscopically gives rise to green reflections. Figure 7 shows the transmission spectra with respect to wavelength for this cell and the sandwich-cell with annealing times equal to 35 hours 25 min.. The mean wavelengths are in the same region – they are respectively equal to 530 and 531 nm – and the bandwidths are highly comparable, since they are respectively about equal to 82 and 87 nm.

V. DISCUSSION

During the mechanism we describe, there are two physical sources of the reflection bandwidth $\Delta\lambda$ around the maximum reflection wavelength λ_0 : (i) the well-known optical anisotropy or birefringence Δn (since $\Delta\lambda = p \cdot \Delta n$); (ii) the existence of a pitch gradient Δp . Therefore, we may expect that these two sources are constantly present during the annealing process but take place with different weights depending on the step of the thermal process taken into consideration:

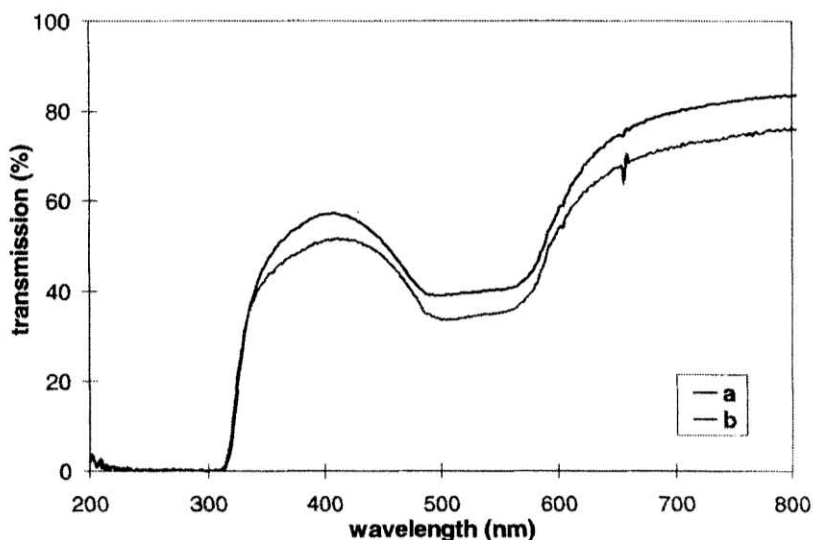


FIGURE 7 Transmission spectra as a function of wavelength after 35 hours 25 minutes of annealing for: (a) the sandwich-cell and (b) the 50% homogeneous blend of blue and red compounds

$\Delta\lambda$ is the result of the roles played by Δn and Δp . Figure 8 schematically describes different stages the system would know during the annealing process. (*1st stage*) The gradient is being 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, we get a plateau intrinsic to a broad-band system filtering light on more than 300 nm: Δp is recognized as responsible for such a reflection bandwidth broadening. At this step, if a broad-band filter in a glassy state is desired, the annealing process may be simply stopped by quenching the cell. (*2nd stage*) The pitch gradient still exists – since $\Delta\lambda$ is clearly greater than 100 nm – but $\Delta\lambda$ progressively decreases. Due to the diffusion, the system is on the way to evolve to a cholesteric structure with a 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 the optical anisotropy Δn .

In the pioneering work of Broer *et al.* dealing with pitch gradients in polymer cholesteric networks [13], the wavelength band position can be varied by changing composition of a mixture of chiral and achiral monomers with different UV-reactivities as well as the polymerization conditions. It is also necessary to add some dye molecules with an absorption close to that of the photoinitiator and

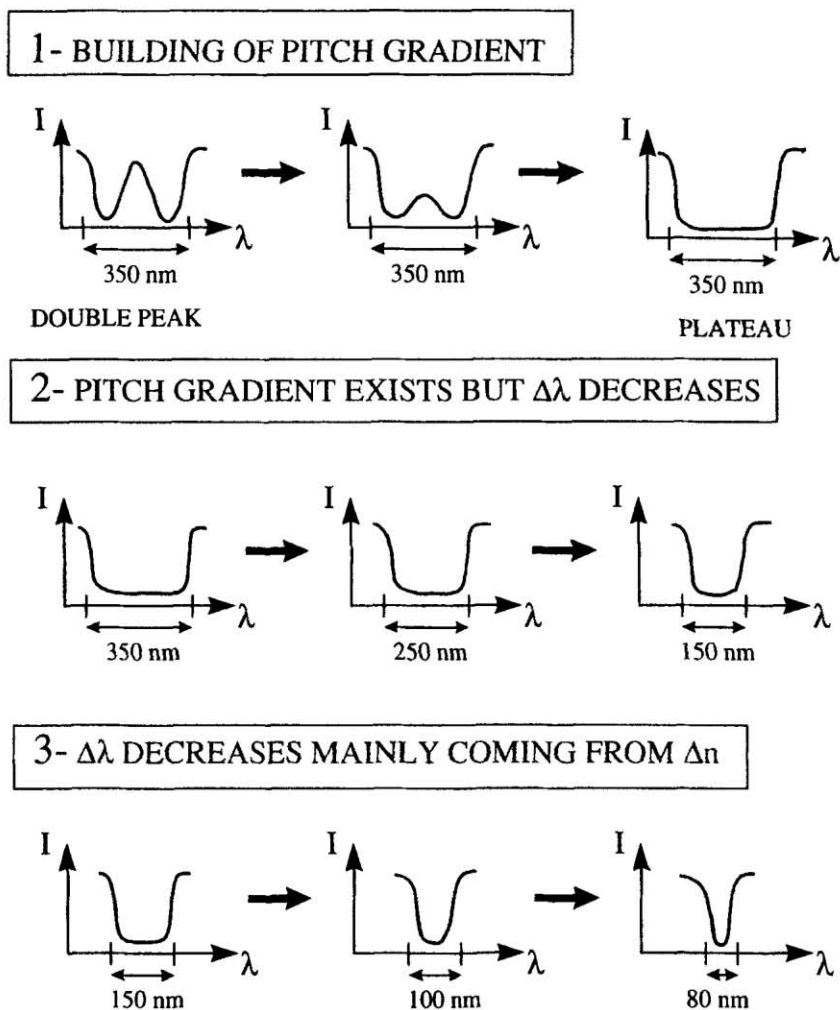


FIGURE 8 Different stages of a possible scenario occurring during the thermal annealing

an extinction coefficient two orders of magnitude larger in order to get a gradient in UV intensity over the thickness of the sample. Here, the pitch gradient is completely controlled by the annealing time. Whereas the photopolymerization rate had to be constantly balanced by the monomer diffusion rate [13], the two steps of pitch gradient building and film hardening are separately driven here (no phase separation mechanism is involved).

Two relevant questions about cholesterics are how to adjust the pitch and how to keep it constant once the right value is reached [14]. Our approach is quite general since the wavelength band amplitude $\lambda_2 - \lambda_1$ may be easily tuned by a convenient choice of the wavelength values λ_1 and λ_2 of the initial cholesteric films and a thermal treatment above 50°C. Besides, after annealing, the film is no longer a stack of blue and red films but a single-layer film. In contrast to the common solution to an optical filtering broadening where several films are put on top of each other, this is an important fact because a single-layer system is far less sensitive to optical defects and additional scattering or reflection losses at the interfaces.

As previously claimed from a technological viewpoint by Philips Research group [13], such broad-band reflectors would greatly improve the light yield (by 40% in Ref. 13) and energy efficiency of liquid crystal devices by recycling wrongly-polarized light in the back-light system. Merck R&D group transferred the concept of a broad-band cholesteric filter from a glass-based to a foil-based technology which consists of a wide-band cholesteric film and a quarter-wave retardation plate laminated together [15, 16]; in such a way, brightness gain was improved from 40% to approximately 80%.

Reveo Group studied polarized backlight output enhancement for two types of cholesteric films: one, a stack of red-, green- and blue-reflecting cholesteric films, and the other, a single layer broad-band cholesteric 'that achieves its wide selective reflection band because of its engineered pitch distribution' [17]; in the absence of more experimental details about the material nature as well as material design we will not discuss the last type comparatively to our system.

Although all these techniques have great potential for display applications, all the methods of locking the pitch by polymerization [13, 15-19] or by use of a polymer network to stabilize the cholesteric structure [20-22] are not suitable for rewritable recording by altering the pitch because of their irreversibility. A reversible fast switching of the cholesteric color, desired for applications as rewritable memory [23] or recording media [24], is impossible to achieve with polymeric materials. Due to the very nature of glassy materials we describe, further potential advantages might be found in high density memory media that use the full spectrum of light and thermo-sensitive full-color recording materials. For example, it is possible to address the material by using laser heating due to absorption. As previously reported for narrow-band cholesterics [23] and now possible for cholesterics with a tunable reflection bandwidth, another potential application of room temperature cholesteric glasses is in optical elements for high power laser systems. While elements in use today confine the liquid crystal between glass plates, optical elements made of a cholesteric solid could be set on a rigid or even flexible (plastic) single substrate to overcome this problem.

How the front between the two cholesteric materials propagate during the diffusion process? Work is in progress about this question by investigating fingerprint cholesteric textures observed by transmission electron microscopy in cross-sections of sandwich-cells corresponding to different annealing times [25].

VI. CONCLUSION

A broadening of the light reflection bandwidth can be realized by a simple thermal treatment in a cholesteric glassy film with a reduced number of independent driving parameters. The position of the wavelength band in the light spectrum depends on the choice of two compounds differing only by their chirality. The bandwidth is simply tuned by the annealing time. The inverse transition, from a broad- to a narrow-band optical filtering, has also been demonstrated. Three main possible stages occurring during the thermal process have been discussed. The unique glassy state of these novel broad-band reflectors provides additional flexibility in the design of optical data-storage media.

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