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Rapid Note

From selective to wide-band light reflection: a simple thermal diffusion in a glassy cholesteric liquid crystal

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Due to their helicoidal structure, cholesteric liquid crystals exhibit remarkable optical properties. Selective light reflection occurs when the pitch (repeat distance) is of the order of the wavelength of incident light propagating along the helix axis. The wavelength bandwidth, due to the optical anisotropy, is typically limited to 50 nm which is insufficient for some applications (full-colors displays, for example). By introducing a pitch gradient in the helix during a novel two-step process in a cholesteric glass, we show that reflection may occur over a wavelength bandwidth greater than 300 nm. 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. The present process exhibits some reversibility and properties intrinsic to the glassy state are gained: laser-writing high resolution full-color images on solid films for image recording or high-density optical data-storage are indeed conceivable.

PACS. 61.30.-v Liquid crystals – 78.20.-e Optical properties of bulk materials and thin films – 81.40.Tv Optical and dielectric properties (related to treatment conditions)

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1 Introduction

A planar oriented cholesteric liquid crystal reflects circularly polarized light of which the handedness corresponds to the sense of the cholesteric helix [1]. The reflection wavelength λ_0 is related to the helix pitch p by the Bragg relation (at normal incidence):

$$\lambda_0 = np,$$

where $n = (n_0 + n_e)/2$ is the average of the ordinary (n_0)and extraordinary (n_e) refractive indices of the locally uniaxial structure. The rest of the light is transmitted.

Cholesterics have been subjected to different applications such as optical filters for selective reflection and large optical rotation, thermal imaging, flat-panel displays, laser or paint technologies [2]. However, for some specific purposes, a drawback lies in the fact that the known cholesteric filters have a limited reflection bandwidth $\Delta\lambda$: $\Delta\lambda = p\Delta n$, where $\Delta n = n_e - n_0$ is the birefringence. Therefore, $\Delta\lambda$ is mainly determined by Δn – limited to values below 0.3 for colourless organic materials – which limits the bandwidth to $\Delta\lambda < 100$ nm.

It has previously been shown that by creating a pitch gradient in the cholesteric helix during a photopolymerization process, reflection could occur over the entire visible spectrum [3]. By keeping almost constant these optical performances, we show that $\Delta\lambda$ can be extended to more than 300 nm by using a simpler, new experimental procedure with the added advantage of specific properties linked to the glassy non-polymeric solid state of this novel wide-band reflector.

2 Materials

Our choice of cholesteric liquid crystalline oligomers [4] 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 (Fig. 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.

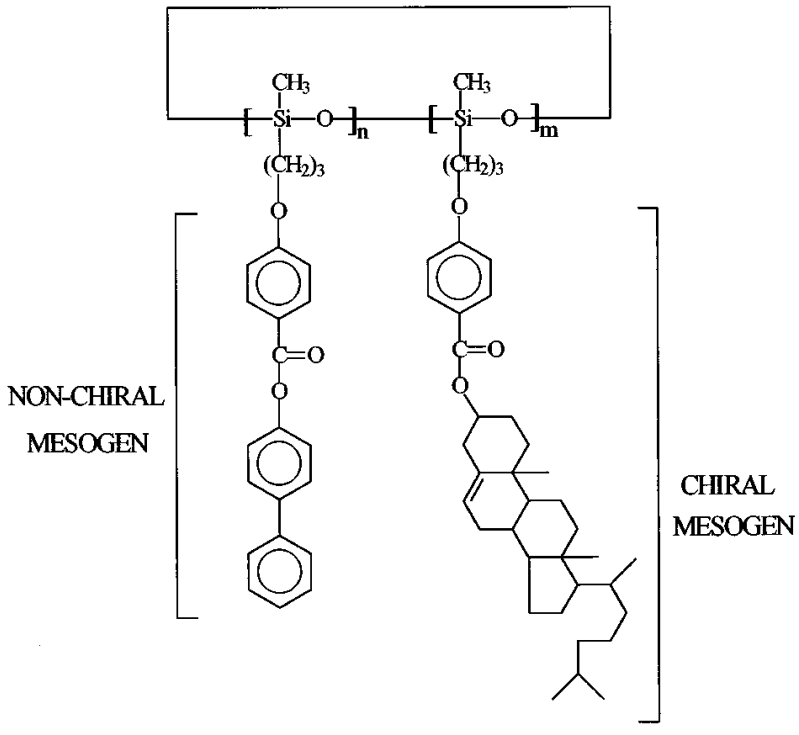

Fig. 1. General formula of cholesteric polysiloxane oligomer.

3 Results

3.1 Optical properties

The experimental procedure is simple. 40 μm thick films of blue and red compounds are spread on two distinct glass plates. Their spectral characteristics are obtained by unpolarized UV-visible light spectroscopy at ambient temperature. Figure 2 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.

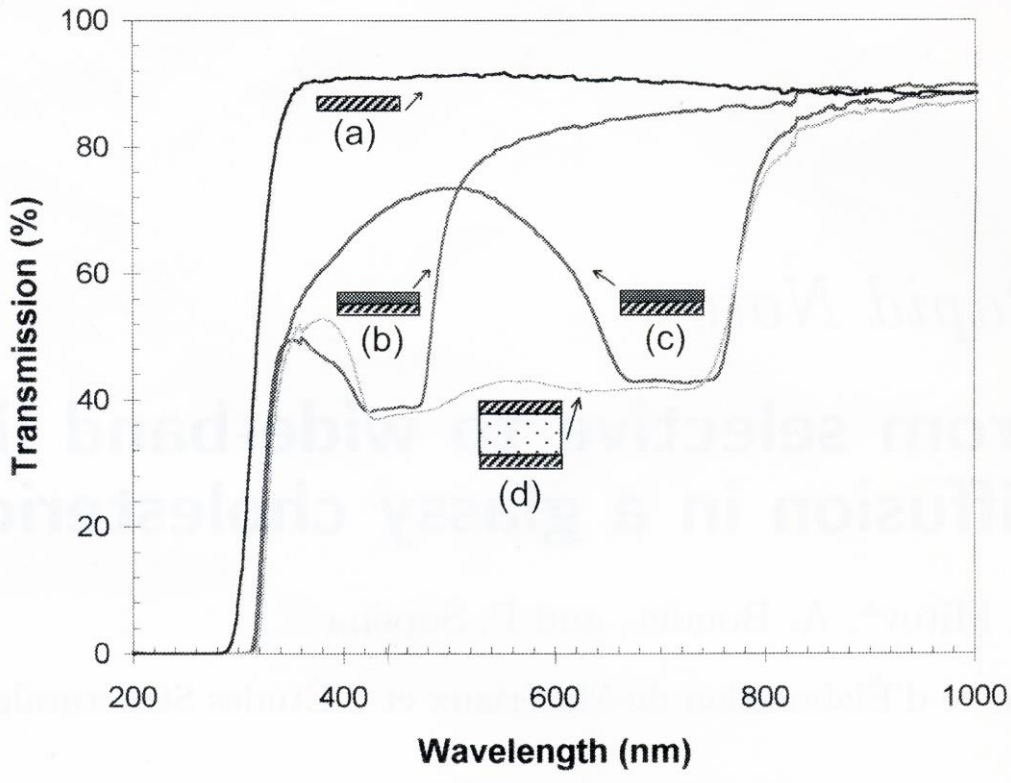

Fig. 2. Transmission spectra as a function of wavelength: (a) Glass substrate, (b) Blue cholesteric film, (c) Red cholesteric film and (d) Sandwich-cell made of blue and red films after one hour of annealing.

The mean reflection wavelengths exhibited by the blue and red films are, respectively, λ_B = 445 nm and λ_R = 710 nm with the dispersions $\Delta\lambda_B$ =50 nm and $\Delta\lambda_R$ =80 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 [1]. Then, a sandwich-cell is made with the blue and red films spread on glass plates separated with 20 μm calibrated spacers. The cell is sealed and kept during one hour 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. After such an annealing process, the cell is quickly put on a metallic substrate at room temperature. The

macroscopic characteristics of the film evolve from a viscous to a glassy state. Such a cooling prevents crystallization and preserves the cholesteric structure. The reflection now occurs between about 430 and 740 nm which corresponds to a wavelength band greater than 300 nm (Fig. 2 (d)). To the naked eye, the film is colourless with a metallic aspect since it reflects 50% of the light over the visible spectrum.

3.2 Cholesteric glass microstructure

Is this spectral behaviour due to a continuous pitch gradient along the direction perpendicular to the observation plane? A cholesteric observed in a direction perpendicular to the helicoidal axis presents a contrast displaying alternative dark and bright stripes (due to the periodic variation of the molecules director according to the helicoidal axis) with periodicity of about the half-pitch [1]. A cross-section of the material is investigated by scanning electron microscopy and pictures are taken at different heights in this section (Fig. 3, top). Preliminarily, we report that a hypothetical interface between the blue and the red films is not localized, although a bilayer system has been established: the former bilayer film became a homogeneous single-layer film, probably due to the efficiency of the diffusion process. 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. Then, stripes are observed from the top ("red" region) to the bottom ("blue" region) of the sample. It clearly appears that the periodicity continuously decreases during the observation. As shown in Figure 3 (bottom), the double periodicity goes from about 450 to 250 nm with different intermediate values.

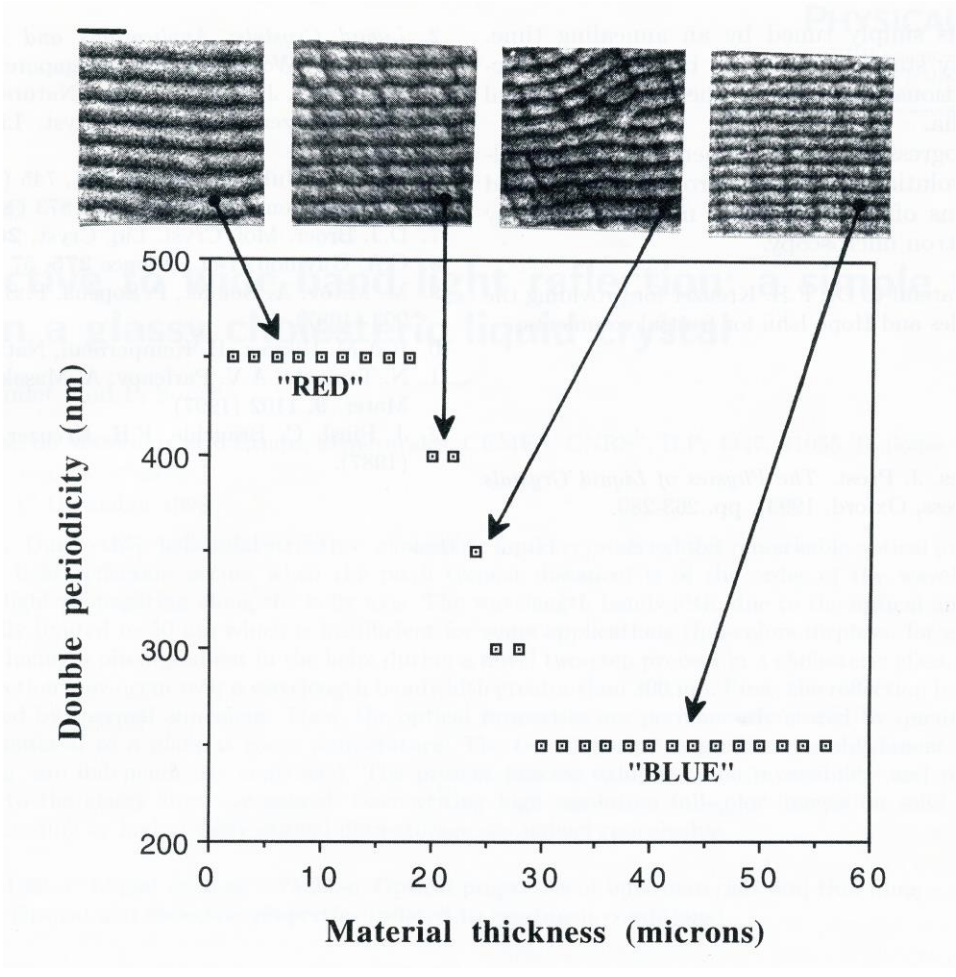

Fig. 3. Top: scanning electron microscopy micrographs of a cross-section of the gradient-pitch cell at different heights (bar scale = 500 nm). Bottom: periodicity (distance between two dark or bright stripes) as a function of the considered height in the cross-section.

4 Discussion

Two relevant questions about cholesterics are how to adjust the pitch and how to keep it constant once the right value is reached [5]. 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. In the case of a polymer cholesteric network [3], the 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 (like a stranger host in the liquid crystalline material) with an absorption close to that of the photoinitiator and 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 [3], the two steps of pitch gradient building and film hardening are separately driven here (no phase separation mechanism is involved). We also mention that the manufacture of the reflective film takes just a few tens of minutes, is inexpensive, highly reproducible and does not require exotic liquid crystalline materials.

As previously claimed from a technological viewpoint [3], such broad-band reflectors would greatly improve the light yield and energy efficiency of liquid crystal devices by recycling wrongly-polarized light in the back-light system. Although this technique has great potential for display applications, all the methods of locking the pitch by polymerization [6,7] or by use of a polymer network to stabilize the cholesteric structure [8–10] 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 [11] or recording media [12], is impossible to achieve with polymeric materials. Since the process described here is reversible, 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 [11] and now possible for cholesterics with a tunable reflection band-width, 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.

5 Conclusion

We have shown that a broadening of the light reflection bandwidth can be realized by a simple thermal process in a cholesteric solid film with a reduced number of independent driving

parameters. The position of the wavelength band in the light spectrum depends on the choice of the two compounds differing only by their chirality. The bandwidth is simply tuned by an annealing time. The unique glassy state of this novel broad-band reflector provides additional flexibility in the design of optical data-storage media. Work is in progress about the influence of the annealing time on the evolution of reflection properties connected with investigations of the cholesteric microstructure by transmission electron microscopy.

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