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Preliminary communication

How to broaden the light reflection band in cholesteric liquid crystals? A new approach based on polymorphism

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Cholesteric liquid crystals (CLCs) may selectively reflect light when the helicoidal pitch is of the order of the wavelength of the incident beam propagating along the helix axis. The reflection bandwidth is dependent on the birefringence and is limited to a few tens of nanometers, which is insufficient for applications such as white-on-black reflective displays. Recent studies have shown that CLC polymer networks with a pitch gradient induce a broadening of the reflection bandwidth over several hundreds of nanometers. Most related processes rely on photocrosslinking reactions with a UV-gradient in a mixture made of chiral and achiral monomers with different UV-reactivities. Here a new experimental route exploiting the polymorphism of the mixture is presented. The basic concept lies in a thermally-induced pitch variation simultaneously carried out with the UV-crosslinking reaction. The optical behaviour is investigated in parallel with the cross-sectional microstructure as observed by transmission electron microscopy.

Cholesteric liquid crystals (CLCs) exhibit many remarkable properties due to the existence of a macroscopic helicoidal structure [1, 2]. The most striking features are the exceptionally large optical rotatory power and the iridescent colours due to the selective reflection displayed by a uniformly oriented Grandjean planar texture when the helix axis is perpendicular to the observation plane. In a small wavelength range about λ_o, an incident light beam parallel to the helix axis is split 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:

$$\lambda = \lambda_o = np$$

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 is the CLC pitch.

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

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

where $\Delta n = n_e - n_o$ is the birefringence. An incident beam with a wavelength out of the $\Delta\lambda$ region is simply transmitted.

We now consider how to broaden the light reflection band in CLCs and the problems involved. However huge the choice is for pitch values, Δn is typically limited to values below 0.3 for colourless organic materials. As a consequence, $\Delta\lambda$ is commonly less than 100 nm in the visible spectrum and is more often equal to 50 nm. This selectivity of range is desirable for several families of applications—optical filters, thermal imaging, laser or paint technologies, etc.—but a drawback lies in the fact that known CLC filters have too limited a reflection bandwidth for specific purposes like full-colour or white-on-black reflective displays, broadband (BB) circular polarizers or 'smart' windows in buildings where control over sunlight is required.

The goal of this paper is to present a new experimental process which transforms a CLC structure reflecting light inside a narrow wavelength band into a CLC superstructure with a non-monotonous helicoidal pitch which involves a broadening of $\Delta\lambda$. Intrinsically, the

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novelty of the present process depends on the occurrence of a photocrosslinking reaction during a thermally-induced pitch variation in a CLC mixture including a network-forming material.

In the current state of the art, most studies deal with a CLC polymer network with a pitch gradient in the visible spectrum and require an *illumination gradient* during a UV-crosslinking reaction [3–7]. As a consequence, $\Delta\lambda$ is greater than 300 nm. In the pioneering work done by the Philips group [3, 4], the pitch gradient is due to a photoinduced diffusion during a photopolymerization reaction in a blend of chiral and nematic monomers. A UV absorbing dye is required and 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 monomer and the helix-unwinding monomer. Such BB reflectors greatly improve the light yield (by 40% in [5]) and energy efficiency of LC devices by recycling wrongly-polarized light in the backlight system [5, 6].

Reflection band broadening and polarized backlight output enhancement have been studied for two types of CLC films [8–13]: (i) a stack of red-, green- and blue-reflecting films [8–10]; and (ii) a single layer BB CLC [11–13] '*that achieves its wide selective reflection band because of its engineered pitch distribution*' [12].

We then found an alternative route for increasing $\Delta\lambda$ which leads to a novel BB CLC with a pitch gradient [14, 15]. In contradistinction to previous studies, the process depends on a thermal diffusion between two CLC oligomer films with different chiralities and the pitch gradient is a consequence of an *initial concentration gradient*. Neither a polymerization reaction nor photo-induced phase separation was involved. Furthermore, the BB reflector is a single-layer CLC film in the glassy state. $\Delta\lambda$ may simply be tuned by the annealing time, and different optical properties (like tunable bandwidths) are made available [16]. The pitch gradient has been demonstrated and evaluated by transmission electron microscopy (TEM) investigations made on cross-sections [17]. The true glassy state of the reflector is discussed as offering new opportunities for optical data storage. Spatially modulated photoracemization in glassy chiral nematic films can also generate a pitch gradient in the CLC structure [18].

Other studies on polymer-stabilized LCs (PSLCs) have correlated the influence of the chemical structure of one or several components of the LC mixture with the $\Delta\lambda$ increase [19–21]. Combining chiral tolane mesogenic side-on additives into the mixture yields an improvement in the birefringence and consequently increases $\Delta\lambda$ [19]. Due to a greater chiral concentration in the vicinity of the polymer network than in the bulk of a PSCLC material containing specific chiral additives, a distribution of two areas with different pitches is evoked to explain reflection broadening (overlap in the reflection spectra from these two areas) [20]. The position and stereochemical configuration of the chiral centres in the side groups of functionalized polymers with respect to the backbone have an integral role in determining the observed reflection spectra [21].

A $\Delta\lambda$ increase in PSCLCs can also occur when compounds referred to as excited-state quenchers are added to monomeric mixtures [22, 23]. Such quenchers work by transferring the energy of the excited state of the initiator to themselves and by absorbing UV light. A phase separation leading to concentration fluctuations corresponding to different pitches is then expected.

In summary, three material designs based on a gradient and leading to CLC BB reflectors have been reported:

(1) For most of the studies: a UV-illumination gradient in polymeric materials is used [3–7].
(2) A concentration gradient is generated between two CLC glassy materials [14–17].
(3) A temperature gradient has also been proposed as a potential way to create a pitch gradient in a CLC cell [24]; the two substrates would have to be maintained at different temperatures to create a CLC structure with helicities differing from the top to the bottom of the cell. However, due to the small thickness of the optically active layer (from a few to several tens of micrometers), this approach has been described as leading to problems caused by the required slope of such a temperature gradient.

We now present here an alternative route in which UV curing occurs during the thermally-induced pitch variation due to the polymorphism of the mixture and not as a consequence of the above-mentioned gradients.

A blend of a photocrosslinkable CLC substance RM9 (from Wacker Chemie Ltd.) with the conventional nematic low molar mass LC 5CB (from Merck Ltd.) is made. RM9 is a modified siloxane compound suitable for the production of optical filters [25] and consists of a mixture of reactive monomers and side group LC polymers with a siloxane backbone. The RM9 concentration is 80 wt %. Here neither a photoinitiator nor a UV-absorbing dye is added. From texture investigations by polarized light microscopy, the smectic A–cholesteric transition is at about 50°C. Then, when the temperature is increased in the cholesteric temperature range, selective light reflections occur ranging from the near-infrared to the blue end of the spectrum via a large variety of visible colours: red, yellow, green. In principle, the polymorphism is the relevant feature of the present process.

A 20 μm thick cell is made with glass plates. In order to induce a planar orientation, these substrates are treated with polyvinyl alcohol (PVA 15 000, ref. 81381 from Fluka) in solution in water. The mixture is introduced into the cell at 80°C by capillarity. The sample is UV-cured at 365 nm with a power of 0.4 mW cm^{-2} measured with a UV radiometer (UVR-365 from Prolabo). Spectral characteristics are obtained by unpolarized UV-visible-NIR spectrophotometry (UV-3100 Shimadzu) in the transmittance mode and at ambient temperature; it is checked that negative peaks are due to reflection and not to absorbance. For subsequent TEM investigations, the sample is cooled by contact with liquid nitrogen to minimize plastic disturbances when it is taken from the plates. The material is then embedded in a resin and a cross-section (perpendicular to the observation plane, i.e. parallel to the helicoidal axis) is obtained by ultramicrotomy (Reichert Ultracut). A 90 nm thick slice was then observed using a Philips CM12 TEM operating at 120 kV.

The feasibility of the thermal process is demonstrated when the pitch varies from green to blue, i.e. from 62 to 95°C. In order to position the reflection band in the visible spectrum, it is necessary to evaluate the reflection wavelengths at 62 and 95°C. Two different samples are photocrosslinked at 62 and 95°C during 30 and 20 min, respectively. These times were selected in order to store durably the reflection colours from the crosslinking temperature down to ambient temperature without recovering the smectic phase which was thermodynamically stable at room temperature before UV curing. As seen from figures 1 (*a*) and 1 (*b*), the mean reflection wavelengths are 563 and 474 nm for curing temperatures of 62 and 95°C, respectively. These values are only indications about the position of the reflection band since the latter depends on the crosslinking characteristics. Indeed, as a consequence of polymerization-induced volume shrinkage, the reflection peak is currently found to be shifted towards a smaller wavelength. Volume contraction upon polymerization is generally considered to be mainly due to changes in the van der Waals volume of the molecules and their better packing as a result of decreased entropy within the system [26]; the preservation of the order and, as a consequence, of the helicoidal pitch, are thus influenced.

The UV-illumination is carried out during the thermally-induced pitch variation. In this preliminary communication we present the case of a continuous thermal ramp from 62 to 95°C during 2 h. Figure 1 (*c*) shows the variation of transmitted light intensity with wavelength after these thermal and UV curings. Let us mention that the cut-off wavelength for the glass cell is between 350 and 360 nm, involving a decrease in transmitted light intensity from 380 nm and towards smaller wavelengths; during that decrease, we can also observe light scattering which varies in relationship to the thermal and UV curings.

It is clear that the peak is now enlarged and that a polarization band-pass from 385 to 570 nm was obtained ($\Delta\lambda > 180$ nm) with an average transmission approaching 40% for an unpolarized measuring beam. By comparison, the broad reflection peak now includes the two distinct peaks stemming from the UV-cured samples for two different single temperatures and corresponding to the initial and final orders for the ramp, see figures 1 (*a*) and 1 (*b*). However, it is important to remark that supplementary reflections of weaker intensity occur at wavelengths above 600 nm (between about 600 and 850 nm). Work is in progress to elucidate the origin of these reflections situated out of the main band, but a UV-illumination gradient through the sample thickness is suspected as a possible supplementary source of creation of pitch gradient.

How is the CLC pitch distribution related to the $\Delta\lambda$ increase? TEM investigations can give answers to this question. Figure 2 shows the TEM micrograph of a cross-section, obtained perpendicularly to the cell surfaces. The picture exhibits dark and bright lines due to the

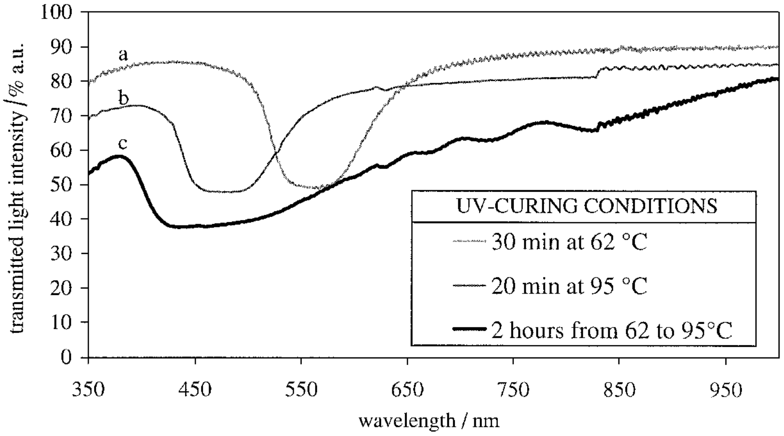

Figure 1. Transmitted light intensity as a function of wavelength when the sample is UV cured during: (*a*) 30 min at 62°C; (*b*) 20 min at 95°C; (*c*) 2 h from 62 to 95°C (thermal ramp).

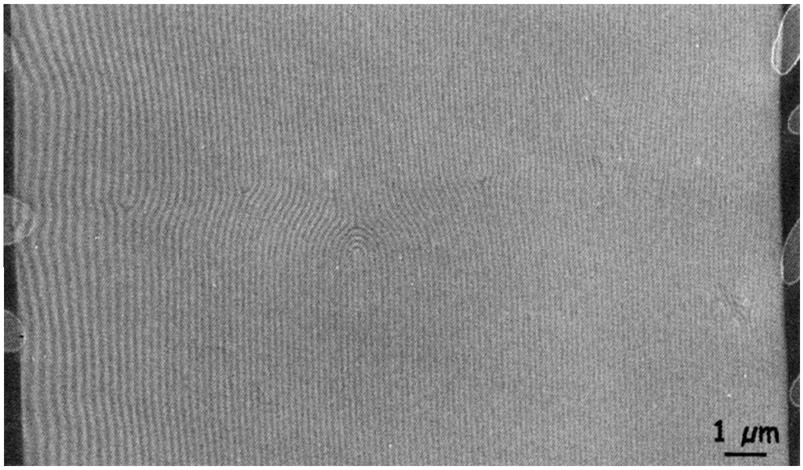

Figure 2. TEM micrograph of a cross-section when the sample was UV cured during 2 h from 62 to 95°C (thermal ramp).

real helicoidal structure [27]; the distance between two dark (or bright) lines is about a half-pitch. The existence of a pitch gradation from one side to the other of the sample and correlated to the range of visible spectrum wavelengths is clearly visible. The longer pitches (left part of figure 2) are situated in the neighbourhood of the surface which was close to the incoming UV beam. The TEM microstructure also confirms the existence of supplementary periodicities for which the correlated reflection wavelengths are situated out of the main reflection band from 385 to 570 nm. Different periodicities occur at different thicknesses in the cross-section. This observation could explain the different intensity levels observed in figure 1 (*c*); let us indeed recall that reflectance usually approaches maximum values when the number of turns in the cholesteric helix is of the order of ten. A quantitative analysis in close agreeement with the spectral behaviour is currently in progress and will be presented in a subsequent paper.

At each moment of the thermal procedure, the aim was to create a memory effect brought about by the very crosslinking which involves a phase separation in the mixture by creating a 'solid' phase in a fluid phase. In the long run, it was expected that the optical properties of the material would derive from the association of a variety of CLC pitches occurring during the crosslinking. If an efficient balance between crosslinking speed and pitch variation is obtained and if the number of helix turns is sufficient to generate reflections in the part of spectrum related to the pitch range, a $\Delta\lambda$ increase as well as a light intensity increase might be obtained. In a forthcoming paper, different thermal processes will be reported and the effect of ramp speed will be considered. The spectrum shape inherent to the variation of the flux of transmitted light with the wavelength/CLC periodicity will also be discussed.

In conclusion, to broaden the light reflection band, a novel experimental process based on polymorphism of the CLC has been presented. It combines a thermally-induced pitch variation simultaneously with a UV cross-linking reaction. The role of the UV curing is probably to preserve a memory of the pitch variation history during the thermal process. As shown by TEM investigations, the broadening of the reflection band is correlated with a CLC structure with a pitch gradient. Further work will focus on different scenarios for the thermal treatment, and optical performances will again be collated with the TEM microstructure.

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