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# Microstructure of variable pitch cholesteric films and its relationship with the optical properties

A. Boudet, C. Binet, M. Mitov\*, C. Bourgerette, and E. Boucher

CEMES-CNRS, BP 4347, 31055 Toulouse cedex 4, France

\*Email address: [mitov@cemes.fr](mailto:mitov@cemes.fr)

A way to make cholesteric films reflecting in a broad wavelength band consists in associating different cholesteric pitches in the same film. In two previous papers, we proposed an efficient method to produce variable pitch films, based on a thermal processing, and we studied the optical properties of these films with respect to the time of processing. In the present paper, we study the microstructure of such films with respect to the processing time by means of transmission electron microscopy. The cholesteric phase is shown to be very well ordered. Within a wide range of annealing times, its periodicity is progressive from one face to the other of the film. A description of the evolution of the structure with respect to the processing time is given, and classified in three stages, corresponding to the three stages already stated from the optical properties. The relationship between the evolution of the structure and the optical properties is discussed.

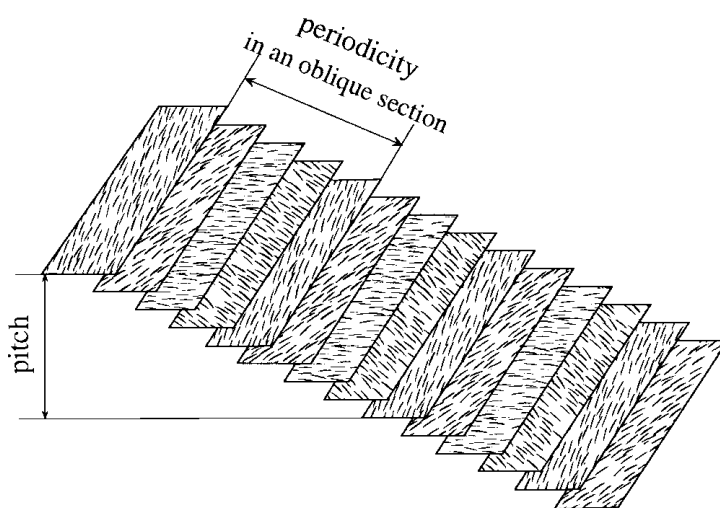
PACS. 61.30.Eb Experimental determinations of smectic, nematic, cholesteric, and other structures – 61.30.-v Liquid crystals – 61.16.Bg Transmission, reflection and scanning electron microscopy (including EBIC)

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## 1 Cholesteric films with extended bandwidth light reflection

This paper is the third of a study devoted to the relationship between the processing, the optical properties and the microstructure of gradually increasing pitch cholesteric films. In two previous articles [1,2], a process was given to produce cholesteric films with an extended bandwidth light reflection. The visible light transmission spectrums from these films stated the efficiency of the process. In the present paper, we demonstrate that this efficiency is related to the particular structure of the cholesteric films, by means of observations by transmission electron microscopy, which was proven to provide well-contrasted images of the cholesteric structure [3].



**Fig. 1.** A sketch of the cholesteric structure.

Cholesteric films are known to exhibit outstanding optical properties especially when they are prepared in such a way that their structure is well ordered. For example, when the cholesteric substance is spread on a substrate like a glass slide, splendid iridescent colours are produced when the axis of the cholesteric helix is preferentially perpendicular to the substrate. These colours take their origin in the selective reflections of the light on the periodic helical planar structure, the pitch of which falls in the visible light wavelength range (Fig. 1) [4]. The reflected light is not monochromatic but, due to the birefringence of the cholesteric structure varies in a narrow range of wavelengths as explained in our previous article [2].

Such optical properties have led many to integrate cholesteric films in devices for colour

displays, optical filters [5], or even energy savings in building windows. But in some of these applications, the use is limited by the narrowness of the wavelength band. For example, windows incorporating such a film exhibit residual colours.

Therefore, several studies have been devoted to find ways to increase the range of reflected wavelengths to a broad band of the light spectrum in cholesteric polymer networks [6–10]. The wavelength band position can be varied by changing the composition of a mixture of chiral and achiral monomers with different UV-reactivities as well as the polymerisation conditions. By recycling wrongly polarised light in the back-light system, such broad band reflectors would greatly improve energy efficiency of liquid crystal devices and brightness gain: by 40% [6] or even 80% when the cholesteric film is laminated with a quarter-wave retardation plate [7,8].

To our knowledge, we present here the first example of a cholesteric structure in a glassy state where thermally controlled low concentration gradients between two chiral substances give birth to a pitch gradient and are turned to good account for light reflection broadening.

In our last study [1,2], we proposed, described and tested a new process to achieve such a goal, based on a simple thermal treatment. It consists in stacking two cholesteric films into a sandwich, one reflecting in the blue range, the other reflecting in the red range, which is subjected to annealing during determined various lengths of time, then rapidly brought back to room temperature to quench its structure. The practical details are recalled in Section 2 below. Then, we characterised the transmitted light spectrum of the samples with respect to their annealing time. The most meaningful results are summed up in Figure 8 (in the discussion section). We could infer that a modification of the sandwich occurred progressively during annealing, and we could distinguish three stages in this evolution. Before any treatment and after a few minutes annealing, the transmission spectrum exhibits two flat extended minima corresponding to the contributions of the blue and red films. During the second stage, these two minima go on broadening until only one extended plateau remains. At this stage, the goal is achieved since the reflection bandwidth almost covers the visible light spectrum. Further annealing gradually reduces the width of the single plateau to a peak centered in the green range, that is, at the mean position between the blue and the red original ranges.

In the present paper, we report a further study, which was intended to understand the relationship between the evolution of the visible light transmission spectrum and the microstructure, with respect to the annealing time. We were especially keen on knowing if the

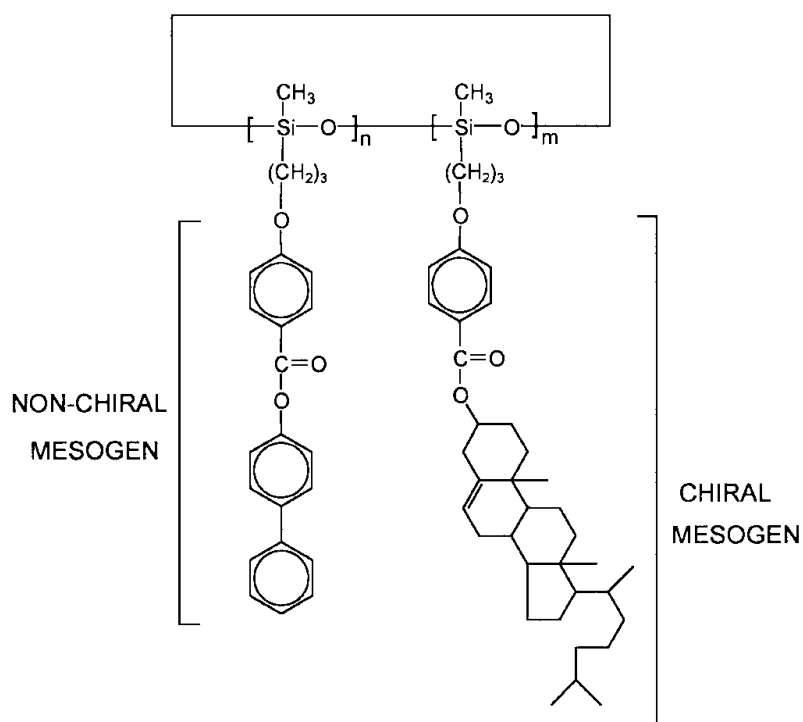
enlargement of the spectrum was related to a texture where numerous domains with different pitches coexisted or if a single well-ordered macrostructure with a gradually increasing pitch had been created. A few previous observations [1] tended to lend credit to the last proposition. In this case, did a mechanism of diffusion or mixing occur at the interface of the two original films and if it did, what was its importance?

The cholesteric microstructure is currently evidenced by polarised light microscopy, with a limitation in resolution down to about 1  $\mu\text{m}$  [11]. This resolution is too crude to allow the periodic structure of our samples to be visible, lower than 1  $\mu\text{m}$ , since there is a direct correspondence between the periodicity  $d$  of the structure, the pitch  $p = 2d$  of the helix, and the wavelength  $\lambda$  of the reflected light (at normal incidence  $\lambda = n \cdot 2d$ , where  $n$ , the mean refractive index, is about 1.5). Therefore, the electron microscope is the necessary instrument to get information on the microstructure, either scanning electron microscope (SEM) or transmission electron microscope (TEM). We have already reported preliminary SEM micrographs in [1], where the cholesteric periodic structure showed up in alternative bright and dark lines. They were evidenced at the surface of fractured specimens. In the subsequent and present study, the observations were conducted in TEM on thin slices regularly sectioned in the specimen by ultramicrotomy. This technique was chosen because it has proven to give excellent images in previous studies, well contrasted and reproducible [3,12,13]. The investigations were carried out on the morphology of liquid-crystal polymers and polymer-dispersed liquid crystals. In reference [3], the origin of the contrast of a cholesteric substance, analogous to that studied here, made of alternated bright and dark lines, was investigated and discussed. Two types of the origin of contrast were analysed, diffraction contrast and irradiation contrast. The first is very sensitive to the radiation damage by the electron beam, and the second takes place when the radiation damage has proceeded and has fixed the structure. In both cases, the bright/dark line alternation was related to the change of orientation of the molecules. The present study fully exploits the bright/dark line alternation in irradiation contrast. Such cholesteric liquid crystals with a pitch gradient have never been observed by TEM to our knowledge. Only their surface has been examined by scanning electron microscopy [1,6] and by atomic force microscopy [9,14].

## 2 Experimental details

### 2.1 Materials

The original films were made of a cholesteric oligomer, the molecule of which is a cyclic siloxane with two types of side-chains attached by a spacer to the main chain (Fig. 2) [15]. One is chiral and the other is not, so that the cholesteric pitch and consequently the reflected colours are tuned simply by the choice of the chiral side-chain percentage. The two films chosen were one reflecting in the blue range named SB, with 50% chiral side-chains, one reflecting in the red range, named SR (31% chiral sidechains). The degree of polymerisation is small ( $n+m \leq 7$ ). 40  $\mu\text{m}$  thick films were made separately on glass slides, then stacked together and put on a heating stage at 85°C during a determined time. At this temperature, the films are both in their cholesteric phase and rather fluid, so that they are able to move and diffuse. The times of annealing varied between 5 min and 83 h 25 min. Then they were quenched to room temperature in a glassy state. More details are given in the previous articles [1,2].



**Fig. 2.** A scheme of the cholesteric molecule.  $n$  and  $m$  are small ( $n + m = 5$  to  $7$ ).

## 2.2 Transmission electron microscopy

The sandwiches were then carefully separated from the glass slides and embedded in epoxy resin cured at 40°C. At this temperature, the film is below its glass transition (around 50°C). 150 nm thin slices were obtained with an ultramicrotome (Reichert Ultracut) in a direction crossing the sandwich perpendicularly to the surface (cross-sections) and retrieved on carbon-coated grids. The observations were carried out in a transmission electron microscope 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 [3]. The contrast was enhanced by a slight defocus.

## 3 Experimental results

### 3.1 Observation of blue and red films

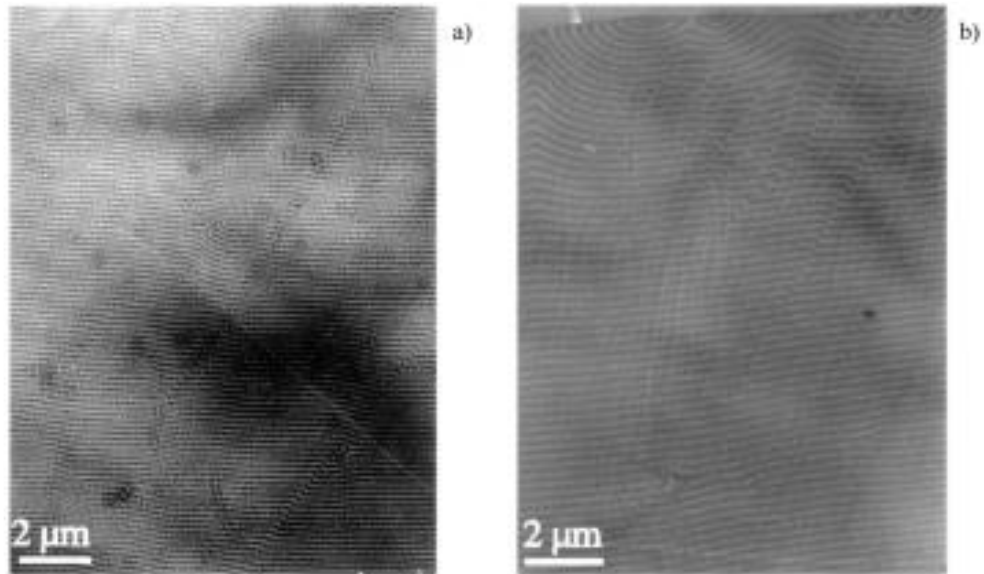
Figure 3 displays the electron micrographs of isolated sections of the SB film (Fig. 3a) and of the SR film (Fig. 3b). The structure shows up as parallel lines alternatively bright and dark, regularly spaced in a periodic arrangement, as already seen in our previous study on bulky SB samples [3]. Here these lines are very well oriented all over the section, parallel to the outer boundary delimited by the glass slide. This order is outstanding considering the mode of annealing, since the parallelism is maintained up to the boundary, with the exception of a few defects. A first class of defects is the presence of some disclinations, but their density is very low. A second class consists in the slightly wavy character of the lines that appears in some areas.

As already stated in reference [3] and in Figure 1, the periodicity of the parallel lines is directly related to the cholesteric pitch of the material, and depends on the relative orientation of the helix axis and the section direction. In diffraction contrast, it was demonstrated that inside the dark lines, the mesogenic rods are parallel to the line, while they are perpendicular to it and to the observation plane in the bright lines, so that the periodicity for a normal sectioning is approximately half of the pitch. Irradiation contrast takes over the diffraction contrast and provides the same periodicity. Measurements of the periodicity then provide evaluations of the pitch and have been performed.

However, several factors bring on a small uncertainty to measurements of this half-pitch. First, note that we are not really dealing with a bimodal contrast, with two distinct categories of lines, one dark and one bright, since there is a soft transition between the two as the molecules are progressively tilted from one position in the centre of the line to the other position in the centre of the other line. Therefore, due to this soft transition and to the slight sinuosity, the distance between two lines cannot be precisely determined. Second, there is no insurance that the sample has been sectioned in a direction exactly along the helix axis or even perpendicular to the outer boundary. The sectioning direction depends on the position of the sample in the embedding medium. Though the samples were carefully positioned in the epoxy resin, a slight deviation is unavoidable. Thirdly, the magnification of the microscope itself is given within a small deviation related to the precision of the height of the sample in the microscope and to the exact focusing of the image. Now, we reported above, that we enhanced the contrast precisely by means of a small defocusing. Thanks to calibrated networks, this deviation was shown to remain low, less than 10%. Obviously, the microscope cannot be used to calibrate precisely the pitch of our samples. Nevertheless, except for the first cause of uncertainty which could not be reduced and was evaluated to a few nanometers, the other two shift the measurement in the same sense all over the image, so that we could collect invaluable information about the relative variation of the pitch inside a given section.

With this precaution, several cross-sections of SB and SR films were observed and analysed, Figure 3 showing an example. The value of the periodicity is the same in the whole section, estimated at  $150 \pm 10$  nm in the blue sample and at  $240 \pm 20$  nm in the red one.

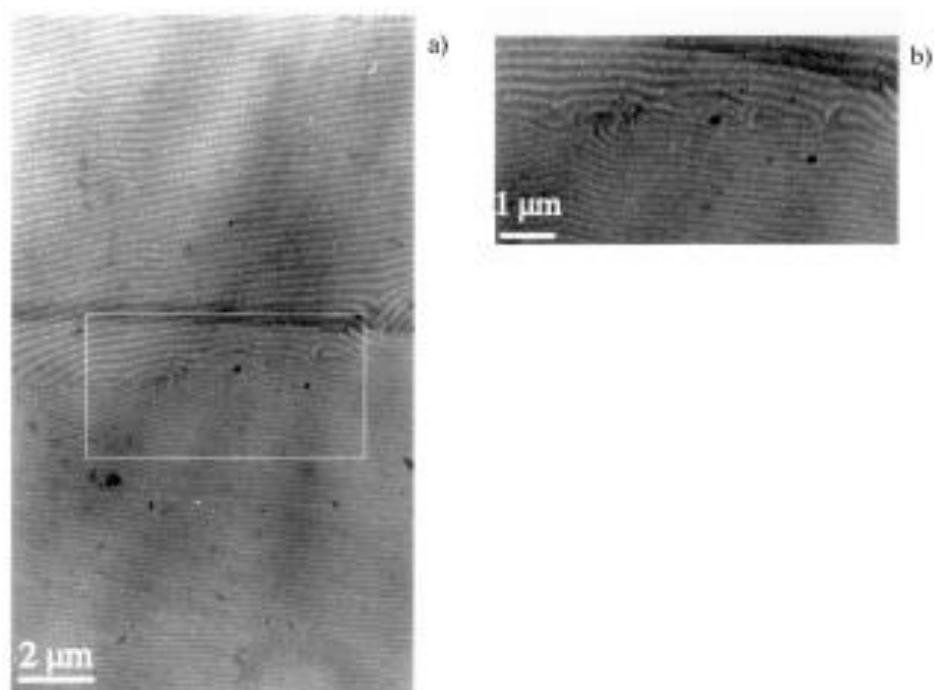




**Fig. 3.** Views of cross-sections of SB (a) and SR (b) non-annealed films. Periodic alternated bright and dark lines. TEM, bright field.

### ***3.2 Observation of sandwiched blue + red films annealed at different lengths of time***

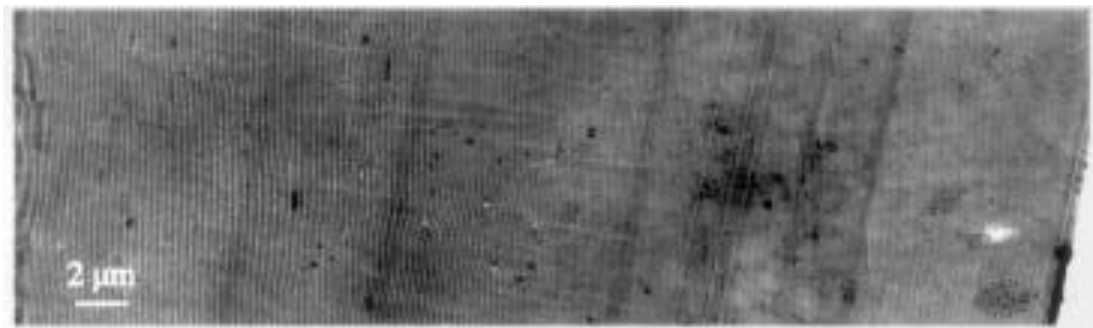
Figure 4 is one of the micrographs obtained from a sandwich annealed for 5 minutes.



**Fig. 4.** Cross-section of a SB + SR sandwich annealed during 5 min. (a) The SB and the SR domains clearly delimited by an interface. (b) Magnified view of the interface in the white frame of image (a).

The two components of the sandwich are clearly visible, the blue film and the red film, due to the different values of the periodicity. This periodicity is constant in each part and has the values of the initial blue-film and red-film periodicity. The original ordered structure has been preserved in spite of the annealing. The interface deserves a special attention and we display an enlarged view of it in Figure 4b. The transition between the two parts is clearly abrupt and sharp. However, there is a perfect matching to each other. It is likely that before annealing, the two parts were distinct with small voids at the interface and that the annealing has realised the connection between them by a good adhesion. Some disclinations can also be seen, likely due to the beginning of mixing, but comparison with micrographs of SB and SR sections (for example Fig. 3b) led us to think that some of them already existed at the glass/material interface before annealing.

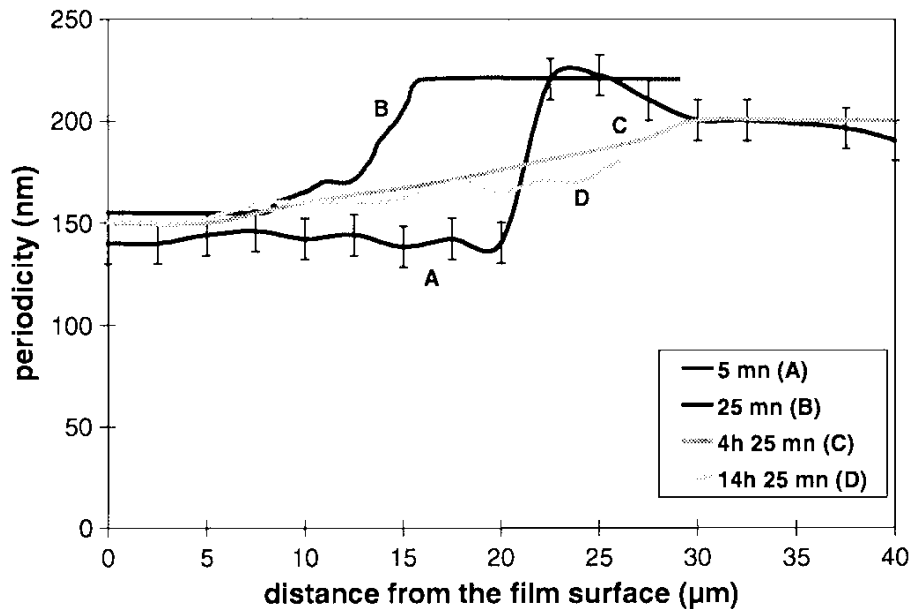
When the annealing is increased to 25 min, the two original parts can still be distinguished with their small and large periodicity, but the interface is no longer visible (Fig. 5). There is now a soft transition between the two parts, taking place over about 8-9  $\mu\text{m}$ . Clearly, the two adjacent surfaces have merged and diffusion has occurred. This question is discussed below.



**Fig. 5.** Cross-section of a SB+SR sandwich annealed for 25min.

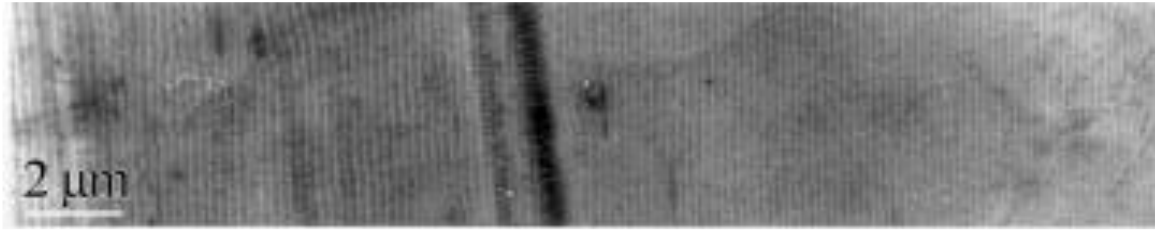
Figure 6 reports the diagram of the evolution of the periodicity versus its distance to the outer surface. It shows up the three parts of the section: blue part, linear transition and red part (Fig. 6, curve B). The error bars have only been reported on the A-curve. They are the same whatever the curve and have been estimated from the two uncertainties discussed in the previous section (broadness of the lines and slight undulation). The curve 6B (as well as 6D)

is shorter since the specimen could not be transferred entirely from the glass slide. Due to this experimental difficulty, the zero reference surface may not be constant from a specimen to the other, and the position of the interface slightly shifted.



**Fig. 6.** Graphics of the variation of the periodicity through the SB + SR specimens. A: 5 min, B: 25 min, C: 4h25 min, D: 14h25 min. Note: the zero reference surface may vary when the specimen is not entirely retrieved from the glass slide as specimen B.

After an annealing of 4 h 25 min, the two parts cannot be distinguished any longer (Fig. 7). Rather we have achieved a continuous linear variation of the periodicity from an edge to the other (Fig. 6, curve C). The range of variation of periodicity has begun to be narrower, since the lower value has increased in the blue edge, and the higher value has decreased in the red edge. This tendency shows up totally for an annealing of 14 h 25 min (Fig. 6, curve D) where the periodicity is now uniform, and stabilised at an intermediary value, within the fluctuations due the defects already mentioned.



**Fig. 7.** Cross-section of a SB + SR sandwich annealed for 4 h 25 min.  
The SB and SR domains have disappeared.

#### 4 Relationship between structure and optical properties

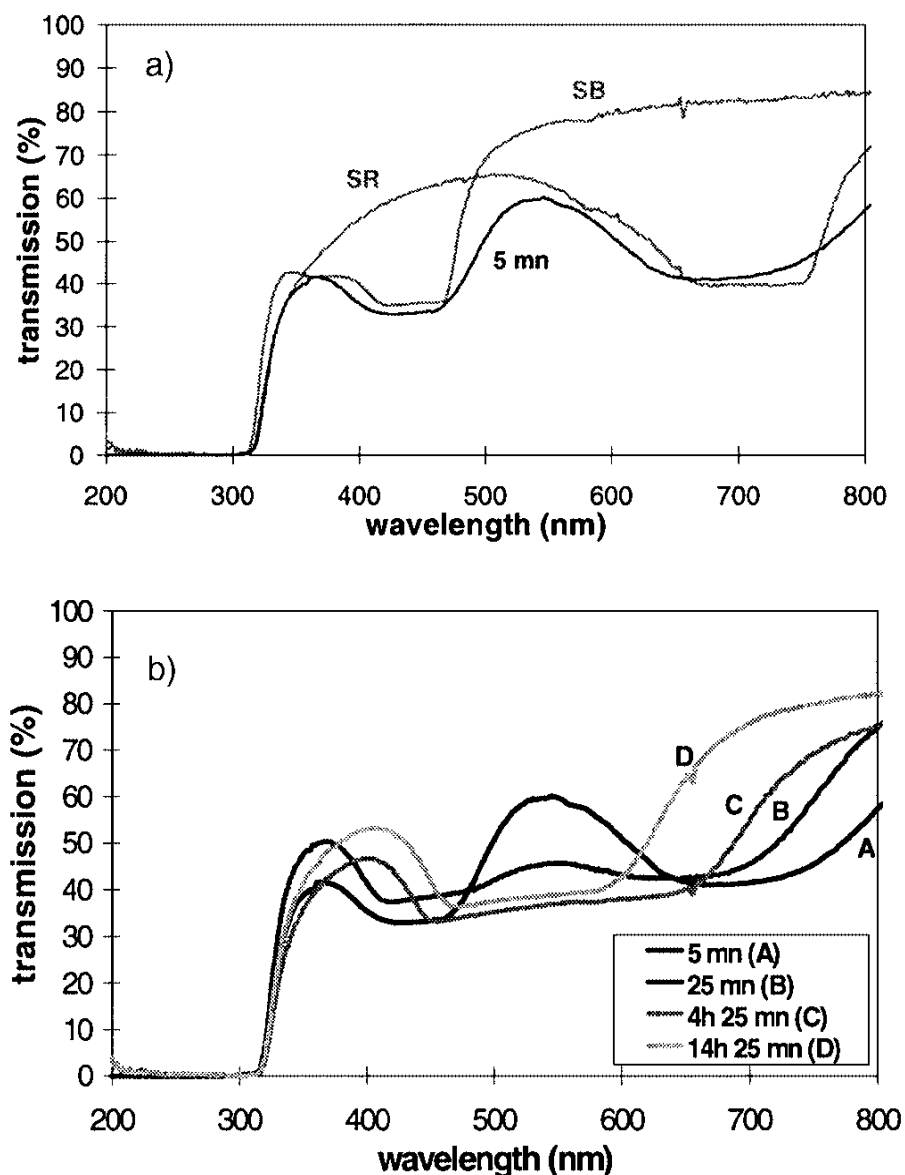
The correspondence between the structures measured in microscopy above (Fig. 6) and the optical spectrums reported in the previous study [2] and reproduced in Figures 8a and b, is quite striking. For a 5 min annealing, the two distinct regions of the periodicity (Fig. 6, curve A) correspond to two minima of transmission—in the form of narrow peaks—one in the blue band, one in the red band (Fig. 8b, curve A). Of course, the mechanism involved to explain this relationship is the selective reflection of the light on the periodic structure.

The three regions of periodicity in the 25 min annealed sample (Fig. 6, curve B) perfectly fit the three areas in the minimum plateau of the corresponding spectrograph (Fig. 8b, curve B). In these, two regions are analogous, though broader, to those of Figure 8b, curve A, that is the blue and the red regions, and the other contained in between is a higher bumpy minimum. It corresponds to the transition region of the interface extending over around 4 μm. In the next sample, annealed for 4 h 25 min (Fig. 8b, curve C), this region has extended to cover the whole section, and the transmission band is now uniform over a spectrum which is a little narrower than the whole visible light spectrum, reflecting the monotonous linear curve of periodicity in Figure 6, curve C. And like it, the bandwidth is a little narrower (207 nm, from 447 to 654 nm).

At last, the uniformity of the periodicity in the 14 h 25 min annealed sample (Fig. 6, curve D) has its correspondence in the reduced width of the spectrum plateau (Fig. 8b, curve D). This plateau is centred around a green wavelength (527 nm) but it is to be noted that it keeps a relatively important width (127 nm, from 463 to 590 nm) which can still become lower for longer annealing as reported below.

These comparisons led us to the conclusion that there is a perfect matching of the optical

properties and the microstructure.



**Fig. 8.** Transmitted light spectrums of SB + SR films. (a) SB: non-annealed SB film. A single minimum with a 50 nm large bandwidth. SR: non-annealed SR film. A single minimum with a 85 nm large bandwidth. 5 mn: SB/SR sandwich annealed for 5 min. Two flat minima, one in the blue range (50 nm wide), the other in the red range (85 nm wide). (b) A: same as 5 min in Figure 3a; B: SB/SR sandwich annealed for 25 min; two minima flanking a low bump; C: SB/SR sandwich annealed for 4 h 25 mn: a single minimum plateau extended to the whole light spectrum; D: SB/SR sandwich annealed for 14 h 25 mn: a single minimum plateau, narrow, centred in the green region.

## 5 Complementary observations

In order to precise this morphological change during annealing, in particular to better analyse the transition between the stages, we made complementary observations at intermediate times of annealing. A question was to determine when the interface between the original films ceases to be distinguished, that is when a merging of the two has succeeded. Samples were prepared at times 10, 15 and 20 min of annealing, optically characterised and observed in TEM. Others were annealed for 45 min and 9 h 25 min, to precise the stage of establishment of the gradual pitch before reaching the full thickness of the sample. Another question was: is it possible to obtain still narrower spectrum in the green for further annealing? Therefore, samples were annealed for 35 h 25 min and 83 h 25 min.

The structure for the 10 min annealed specimen resembles the 5 min one. At 15 min and 20 min, the interface has more or less disappeared but some disclinations keep the memory of its location, in a way analogous to the structure of the 25 min annealed specimen.

At 45 min, the two initial parts cannot be recognised any longer, except in a few small areas. The variation of the periodicity extends over the entire cross-section, like at 4 h 25 min. The difference with the 4 h 25 min annealed specimen appears in their light transmission spectrums. The wavelength bandwidth is larger at 45 min and covers the entire visible light spectrum (297 nm from 407 to 704 nm).

This width has decreased at 4 h 25 min to 207 nm (447– 654 nm). At 9 h 25 min, it reduces to 127 nm (463–590 nm). At last, it was found that the minimum width decreases to 82 and 75 nm for 35 h 25 and 83 h 25 min annealing times, but the images were similar to the 4 h 25 min images.

## 6 Discussion and conclusions

### 6.1 Efficiency of the process

All the observed specimens have shown an excellent oriented structure. The striations were all parallel to the substrate and very few defects were detected, either in pristine specimens, or in annealed sandwiched specimens. Furthermore, within a wide range of annealing time, the periodicity has proven to be progressive from one edge to the other. Let us recall that our intention was to make multiple pitched specimens. This goal has been fully completed and more, since now no discontinuity remains between areas with different pitches. The presence

of such discontinuities would be a drawback, for it is the source of light scattering [1]. Thus it is demonstrated that the process involved is really efficient.

As recalled at the beginning of this article, the periodicity of the structures is closely related to the cholesteric pitches, and consequently to the selective reflected light wavelengths. This relation was clearly checked in the correspondence stated here between the measured periodicity and the transmission spectrums. For example, in the 5 min annealed specimen, the two narrow peaks are located in the blue and the red ranges. The corresponding measured periodicity is around 150 and 240 nm. Now, let us multiply these periodicities by 2 and by the diffraction index (around 1.5) as mentioned above in the introduction, and we find the wavelengths at the blue/violet and red/infrared positions, in close agreement with the transmission spectrum.

The comparison of the microscopic observations with respect to the annealing time (Fig. 6 and complementary observations) allows us to precise the evolution of the structure and the switch between the different stages. For annealing times from 0 to 10 min, the two initial films of the sandwich are still recognisable and their contribution to the spectrums is distinct. From 15 min to 45 min. The interface is no longer visible and has been replaced by an area of progressive pitch that extends until it covers the whole thickness of the sample. This critical situation occurs for about 45 min long annealing. Then, the range of pitch becomes narrower and narrower and uniform throughout the entire sample at 9 h 25 min and more.

## **6.2 Mechanism of diffusion**

The success of the annealing process is mainly due to the disappearance of the initial interface and the establishment of the progressive pitched transitional area. An immediate question arises. How two different substances with well-determined characteristics—that is a known cholesteric pitch—can give birth to a third type of structure with intermediate and gradual characteristics? The customary situation when it happens is the good mixing of the two substances in a gradient of concentration. This is possible only when the two substances have a good miscibility, which is rarely achieved in high molecular weight substances, especially in macromolecular materials. Here, we are in the special case where the two substances are easily miscible, because their molecules though already pretty large (oligomers), have a similar structure, differing only by the rate of chiral side chains. It is easy to imagine that at the interface they diffuse in each other during the annealing, since at the annealing

temperature (85°C), the substances have a good fluidity. The front of diffusion increases with the time of annealing until about 25 min, and a concentration gradient takes place. Thereafter, the diffusion process allows the concentration to become uniform throughout the sample. Indeed, the optical spectrum of a non-annealed 50-50% homogeneous mixture of SB and SR compounds is quite similar to the spectrum of a 35 h 25 min annealed specimen, as was shown in reference [2].

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