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Selective reflection and textural studies of free-standing films of a chiral liquid crystal

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We present a detailed study of selective reflection from free-standing films of chiral smectic phases. Free-standing films are drawn of the chiral compound 2-(4-hexyloxyphenyl)-5-[4-(1-chloro-3-methylbutanoyloxy)phenyl]pyrimidine (2f-6) possessing a chiral smectic C and the recently discovered chiral smectic M phase, both phases showing the phenomenon of selective reflection of visible light in a certain temperature range. With linearly polarized incident light two selective reflection maxima are observed which are caused by the presence of π -walls in the film. The wavelength of the selective reflection maxima is independent of the film thickness, whereas the intensity decreases with decreasing film thickness. The dependence of the reflection maxima on temperature and enantiomeric excess is studied.

1. Introduction

If tilted smectic phases without positional molecular order within the layers—such as S_C , S_I , and S_F —consist of chiral molecules, the tilt direction changes continuously by a small amount when going from layer to layer, i.e. a helical superstructure exists with its axis parallel to the smectic layer normal; in some cases even crystalline smectic phases of chiral molecules—such as S_G and S_J —seem to exhibit a helical structure [1]. The helical pitch p can be in the range from some hundred nm up to several μm . Similarly to the cholesteric phase, chiral smectic phases show the phenomenon of selective reflection. If light is incident on a chiral smectic phase in the direction parallel to the helical axis, a certain component of the incident light is selectively reflected by the sample; the reflected light is circularly polarized with the same handedness as the helix of the sample and it possesses a wavelength λ given by

$$\lambda = \bar{n} \cdot p, \quad (1)$$

where \bar{n} is an effective refractive index. Thus, the phenomenon of selective reflection can be used to determine both the handedness and the pitch of chiral smectic phases, provided that the sample can be oriented homeotropically, i.e. the smectic layers must be aligned parallel to the boundary glass plates. Usually, this can be obtained by a suitable surface treatment of the glass, for example, with a diluted lecithin solution.

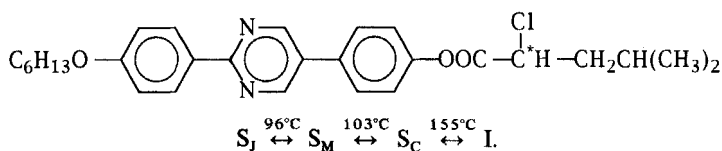
Free-standing films [2] of smectic phases, which can be prepared by drawing the material over an opening in a suitable substrate (glass, metal), provide a perfect homeotropic orientation, because the smectic layers align always parallel to the two free surfaces of the film. Nevertheless, free-standing films apparently have been used very scarcely to study the helical structure of chiral smectic phases. A reason for this may be that we study free-standing films usually near the two dimensional limit, i.e. the films are only a few smectic layers thick, whereas the period of the helical pitch extends

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over at least some hundred smectic layers. On the other hand, Goodby *et al.* [3] recently used the selective reflection of thick free-standing films for the determination of the handedness and qualitative temperature dependence of the helix in chiral S_C and S_{CA} (antiferroelectric) phases. Thus, it was the aim of this study to investigate in detail the possibilities of using free-standing films for selective reflection studies of chiral smectic phases.

2. Experimental

The compound under investigation is 2-(4-hexyloxyphenyl)-5-[4-(1-chloro-3-methylbutanoyloxy)phenyl]pyrimidine (abbreviated in the following as 2f-6), the molecular structure and phase sequence of which are given below:



S_C is the simplest tilted smectic phase, showing no positional order of the molecules within the layers, S_J is a highly ordered smectic phase possessing a three dimensional positional order. S_M designates a recently discovered smectic phase which is tilted and shows no positional order within the layers [4]; presumably it belongs to the group of tilted hexatic phases [5]. Both the S_C and S_M phases of chiral 2f-6 show, in a certain temperature range, selective reflection of visible light [6]. Most measurements are done with the pure *S*-enantiomer, but some mixtures of the *R*- and *S*-enantiomers with different amounts of enantiomeric excess are also studied.

Free-standing films are prepared by spreading a small amount of the material in the smectic C state over a circular opening (4 mm in diameter) in a brass plate. The films are maintained by a Mettler FP 82 heating stage. Selective reflection spectra are recorded in the transmission mode: the films are illuminated in perpendicular incidence by white light which is linearly polarized in front of the film, i.e. we can imagine the incident light to consist of equal parts of left- and right-handed circularly polarized light with zero phase difference. When the light is incident upon a free-standing film with, for example, right-handed helix, the right-handed circularly polarized component of the incident light possessing a wavelength obeying equation (1) is reflected. Thus, the transmitted light is linearly polarized at most wavelengths, but left-handed circularly polarized at the wavelength where selective reflection occurs. A second polarizer, which is placed behind the film and with the azimuthal angle set at 90° with respect to the first polarizer, can be passed only by the component of the transmitted light which is circularly polarized and possesses the selective reflection wavelength. The transmission spectrum behind the second polarizer is recorded using a diode-array-spectrometer (Photo-Research Spectrascan PR-710) with a range of wavelength from 390 to 730 nm. In a few cases, where we use circularly polarized incident light, spectra are not recorded of the transmitted light, but of the light reflected by the film, the angle of incidence then being less than 5° (i.e. nearly perpendicular incidence).

For the textural observation we used a Leitz ortholux polarization microscope.

3. Results

A typical selective reflection spectrum of the S_C phase of a several micron thick free-standing film is shown in figure 1. The transmitted light is left-handed circularly

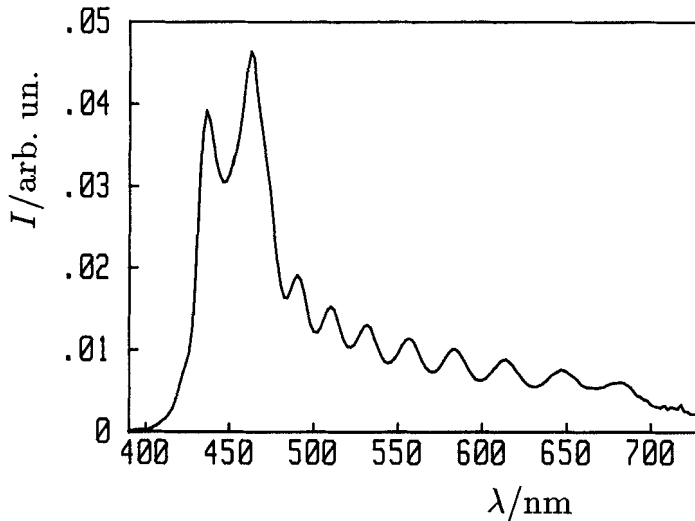


Figure 1. Selective reflection spectrum of a free-standing film of the S_C phase of 2f-6 (thickness: $4 \mu\text{m}$). Besides the double-peaked selective reflection maximum, we can see an interference pattern which may be used to determine the film thickness.

polarized, i.e. there is a right-handed helix. Remarkably, two selective reflection maxima seem to exist. The occurrence of these two maxima can be traced to a certain configuration of the director field of our films. As shown in figure 2, the films exhibit a striped texture indicating the existence of so-called π -walls in which the azimuthal tilt direction changes continuously by π . Such π -walls occur frequently for various reasons in free-standing S_C films [7]. To describe the director field of free-standing S_C films, it is appropriate to use the so-called c -director which is the projection of the director on the smectic layer plane. The c -director field of a linear π -wall array is illustrated in figure 2(d) for one (arbitrary) smectic layer of a film; because of the helical structure all c -directors in an adjacent layer would have to be drawn in the same way but rotated by a small fraction of π .

How does the existence of π -walls lead to the occurrence of two selective reflection maxima? The reason for this has already been found in 1975 by Tur [8] who studied the selective reflection of cholesteric phases for the case in which the refractive indices of the liquid crystal and its ambience are different. (Usually, the ambience of a liquid crystal sample consists of glass boundary plates showing a refractive index relatively similar to that of the liquid crystal; in the case of a free-standing film, however, there will always be a large jump in the refractive index at the film-air-interface.) Tur found that the shape of the selective reflection peak will in general depend on the polarization state of the incident light. For linearly polarized incident light, the wavelength of the selective reflection maximum depends on the polarization direction with respect to the azimuthal position of the director \mathbf{n} at the liquid crystal-ambient boundary: polarization parallel to \mathbf{n} shifts the maximum to larger wavelength values, whereas polarization perpendicular to \mathbf{n} leads to a lower wavelength of selective reflection (provided, that the ambience possesses the smaller refractive index compared to the liquid crystal) [8].

The optical properties of cholesteric and chiral smectic C phases are quite analogous in many aspects, if we replace the nematic director by the c -director and use

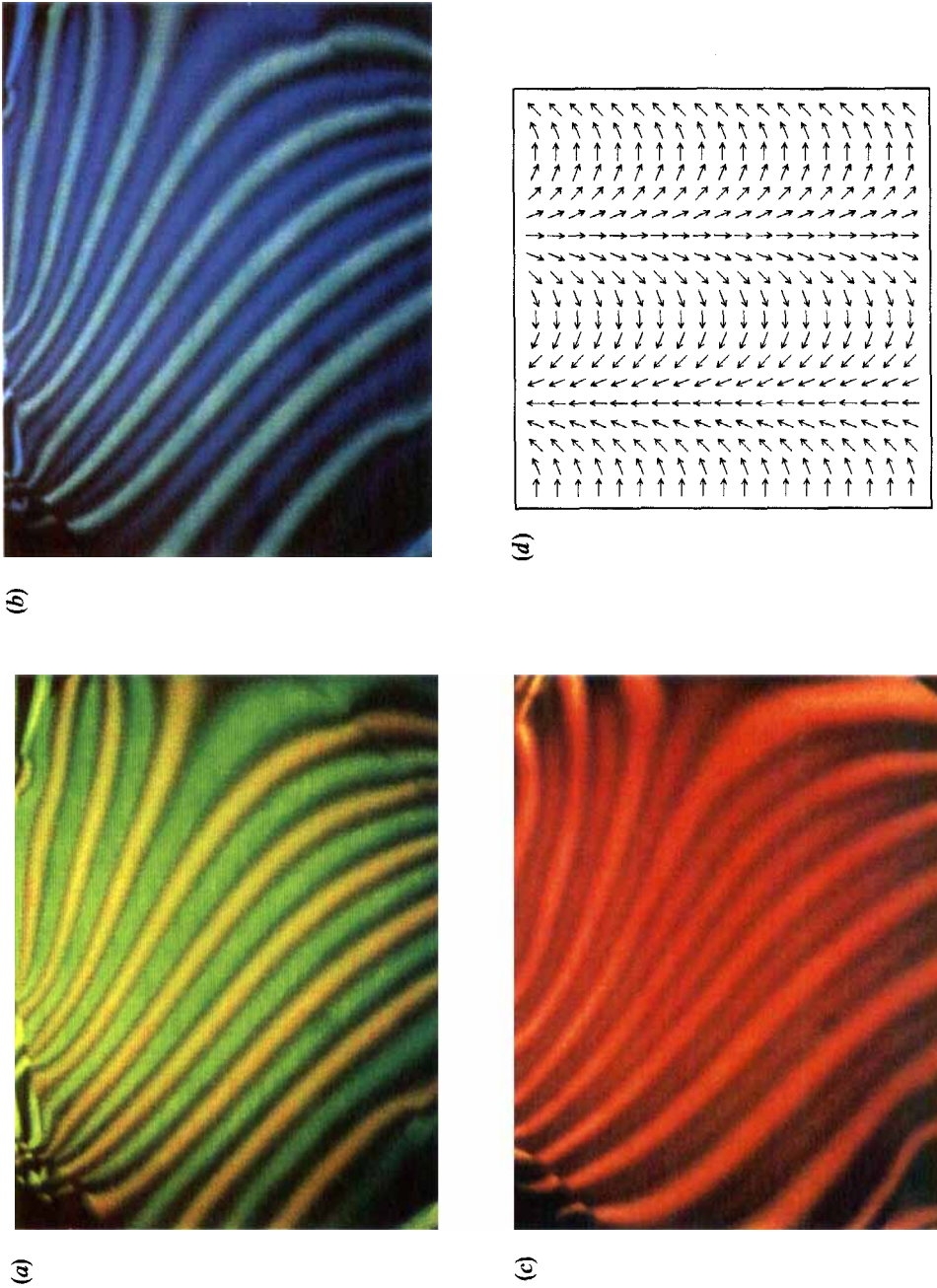


Figure 2. (a)–(c) Photomicrographs (crossed polarizers) of a free-standing film of 2f-6 showing linear π -walls and selective reflection; (a) 110°C, S_C ; (b) 105°C, S_C ; (c) 98°C, S_M . (d) Schematic drawing of the c -director field of linear π -walls.

appropriate values of the effective refractive index \bar{n} [9]. The selective reflection wavelength will depend in the same way on the polarization direction of the incident light with respect to the orientation of the c -director at the film surface, as described above for the cholesteric phase. Since in a π -wall array the orientation of the c -director changes continuously through all possible azimuthal directions, we can expect that the selective reflection peak will split into two maxima. Two experimental observations confirm our assumption described above. First, the two different selective reflection colours, which are simultaneously observable, are clearly correlated with the stripes of the π -walls as can be seen in figure 2. Second, if we use circularly polarized light, the double peak disappears. Figure 3 shows selective reflection spectra of the same sample obtained with linearly, left-handed circularly, and right-handed circularly polarized light: only the linearly polarized light produces two maxima, whereas of the two kinds of circularly polarized light, one is only weakly reflected, while the other shows a distinct and single reflection peak. To summarize, the occurrence of the double peak of selective reflection does not indicate the existence of two different helical pitches, but rather shows that—if the incident light is linearly polarized—regions with different values of the effective refractive index \bar{n} exist in the film.

We now turn to the temperature dependence of the selective reflection of free-standing films of the 2f-6 compound. Figure 4 shows the wavelengths of the two selective reflection maxima as a function of temperature. In the S_C phase, the helical pitch p obviously decreases with decreasing temperature as is usually observed; at the transition to the S_M phase, a pronounced increase of p sets in. Provided that the S_M phase is really a hexatic phase, the increase of p results probably from the increase of the bond orientational order which grows continuously with decreasing temperature in hexatic phases [10]. Because of the coupling between bond orientational order and tilt direction, growing bond orientational order will tend to align the tilt direction

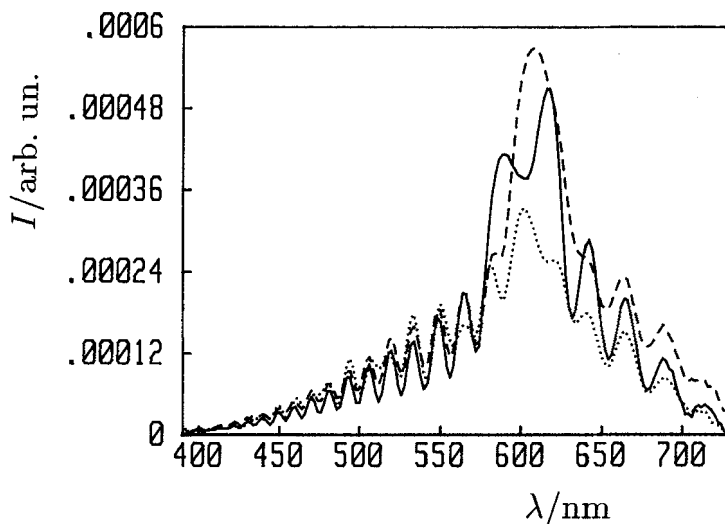


Figure 3. Selective reflection spectra (recorded from the reflected light) of a free-standing film of the S_C phase of S -2f-6 obtained with different polarization states of the incident light; solid line: linearly polarized; dotted line: left-handed circularly polarized; broken line: right-handed circularly polarized.

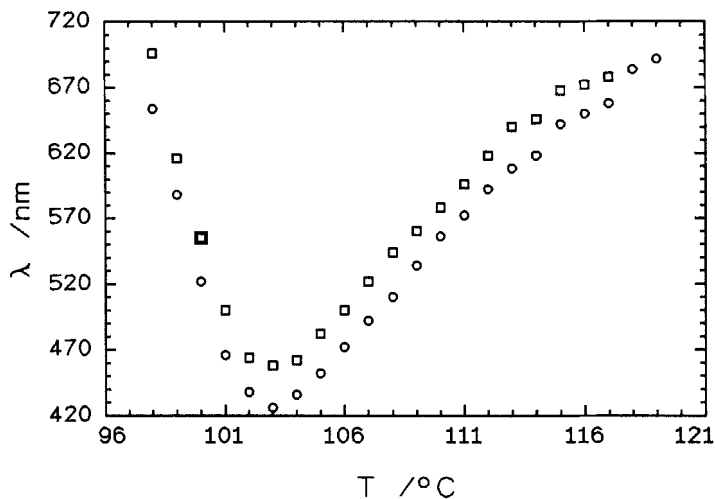


Figure 4. Temperature dependence of the selective reflection wavelength of a free-standing film of 2f-6. The two wavelength values at one temperature value correspond to the two maxima of the selective reflection peaks. At $\approx 103^\circ\text{C}$, the S_M - S_C transition occurs; near the transition to the S_I phase (96°C), the wavelength values move out of the range of our spectrometer.

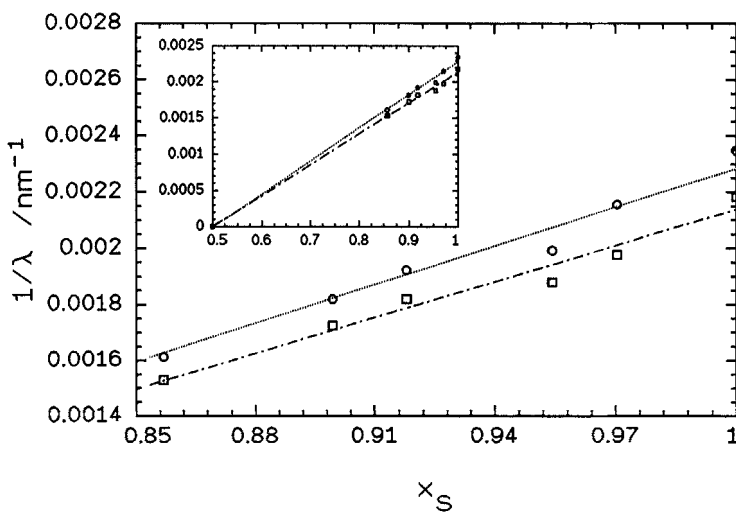


Figure 5. Selective reflection wavelength of free-standing films of various mixtures of *S*-2f-6 with *R*-2f-6 with different amounts of enantiomeric excess ($T = 105^\circ\text{C}$, S_C phase). Inset: extrapolation to the racemic system ($x_S = 0.5$).

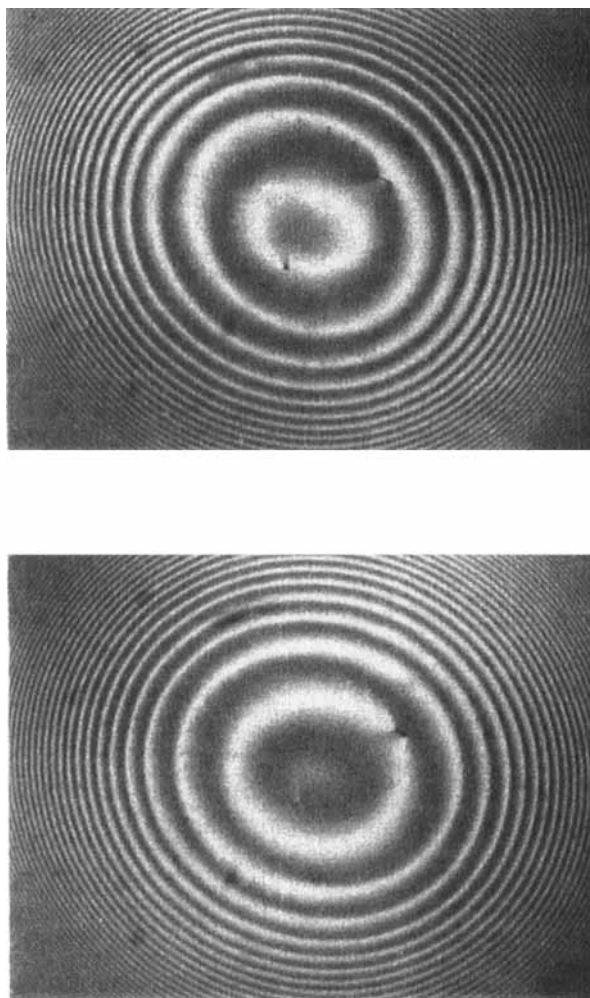


Figure 6. Photomicrographs (crossed polarizers) of a free-standing film of the S_C phase of 2f-6 showing circular π -walls. For the second photomicrograph, the azimuthal angle of both crossed polarizers is changed by $\pi/4$.

homogeneously throughout the sample, thereby increasing more and more the value of the helical pitch.

The mean values of the two wavelength maxima determined here for a free-standing film are the same as measured earlier for a bulk sample of the 2f-6 compound [11]. This is to be expected, since a several micron thick free-standing film is practically a bulk sample, the only difference being the existence of the two free surfaces.

We have also investigated the dependence of the helical pitch on the enantiomeric excess by studying free-standing films of binary mixtures of the two enantiomers of 2f-6. We observe the usual behaviour: in both phases, S_C and S_M , the reciprocal selective reflection wavelength decreases linearly with decreasing enantiomeric excess, as exemplified for the S_C phase in figure 5.

All results reported above are obtained for free-standing films with a thickness of several microns. A decrease in the film thickness leads to a decrease of the intensity of the selective reflection, while the wavelengths of the reflection maxima remain unchanged. For film thicknesses below 1 μm , no selective reflection is observable with our experimental set-up. For these relatively thin films, we observe an interesting phenomenon concerning the configuration of the π -walls of our films: whereas in thick films linear π -wall arrays occur, we find in thinner films a strong tendency to form circular π -walls. These circular π -walls develop easily in the presence of a very slight tangential flow of air [12] which causes a rotation of the central part of the film. Because the edge of the film is fixed at the brass substrate, two π -walls are generated with every rotation of the film centre. This formation of circular π -walls is similar to that in an experiment by Cladis *et al.* [13] who generated circular π -walls by rotating a pin piercing the centre of the film. As shown in figure 6, both the number and the density of the π -walls can become very high, especially in the outer regions of the film; at least some hundred are possible in a 4 mm diameter film. That these structures are really π -walls can be checked easily by a rotation of the two crossed polarizers by $\pi/4$, which leads to an interchange of the dark and bright regions in the film (cf. figure 6).

In conclusion, we have shown that thick free-standing films are suitable systems on which to study the helical structure of chiral smectic phases by selective reflection. When linearly polarized light is used, the large difference between the refractive indices of the film and its ambience can lead to a split of the selective reflection peak if π -walls are present in the film. The quantitative values of the selective reflection maxima do not depend on the film thickness and are the same as in corresponding bulk samples.

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