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Light Control of Cholesteric Liquid Crystals Using Azoxy-Based Host Materials

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The characteristics of cholesteric liquid crystals can be controlled by light irradiation if conformationally photo-active molecules are present. Recently, control of the selective reflection band (spiral pitch) in nemato-chiral mixtures was demonstrated when photosensitive molecules, namely nematic azoxy-based compounds, were used as the host material. In this report, the investigation of light induced effects in cholesterics with azoxy-based host materials is continued to highlight the mechanisms of the response. Different non-photosensitive chiral materials were added to different azoxy-nematic liquid crystals and the pitch change caused by UV irradiation was investigated. A change in the pitch of 50–210 nm was observed depending on the exposure time and the intensity of the light. This effect is reversible: under illumination at wavelengths greater than 410 nm, the pitch shifts in the opposite direction. The dependence of the selective reflection band and the full-width-at-half-maximum of the band on the exposure time and the temperature dependence of the selective reflection band were investigated. The lowering of the phase transition temperature and narrowing of the width of the selective reflection band can be explained by a decrease in the orientational

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order parameter. The blue shift of the selective reflection band is due to a decrease in both the order parameter and the concentration of linear nematogenic molecules.

Keywords: cholesteric mixtures; light sensitive materials; liquid crystals

INTRODUCTION

Cholesteric liquid crystals (CLCs) possess unique properties: a self-organized, supramolecular, helicoidal structure (the period can vary over a wide range, from 100 nm up to infinity); reflection of 100% of circularly polarized light in a band of wavelengths; and shifts of the selective reflection band due to external factors (electric, magnetic, acoustic fields, temperature, and light irradiation) [1,2]. In CLCs the period of the helicoidal structure is equal to half the pitch P, and for light propagating along the helical axis, $P = \lambda_o/n$, where λ_o is the wavelength of the maximum reflection or the middle of selective reflection band (depending on the shape of the band) and n is the average refractive index $n = (n_e^2 + n_o^2)^{1/2}$. The extraordinary and ordinary indices of refraction are denoted by n_e and n_o, respectively. The full-width-at-half-maximum of the selective reflection band ($\Delta\lambda$) is equal to $P\Delta n$, where $\Delta n = n_e - n_o$ is the birefringence of a nematic layer perpendicular to the helix axis. A change of the characteristics of CLCs can be achieved by light illumination when the CLC contains conformationally photo-active molecules. Changes in the structure or stereochemistry of these molecules can produce a significant change in the structural organization of the CLC. As was shown previously in low molecular mass (weight) CLC mixtures, the photo-induced changes lead to reversible and irreversible color changes, cholesteric-nematic and cholesteric-isotropic phase transitions due to photochemical decomposition, and racemization or transformation of conformationally active components [3–8]. More recent investigations have concentrated on photo-control applications for optoelectronic devices. Most of the studied systems consist of conformationally active molecules that are capable of *trans-cis* (E-Z) isomerization. Typically an elongated rod-like molecule (*trans* isomer) transforms under the influence of UV radiation to a bent or fractured form (*cis* isomer). A shift of the wavelength of selective reflection (colour) is observed in the following cases: a) when a photoisomerizable chiral or non-chiral, mesogenic or non-mesogenic compound is added to a cholesteric mixture already possessing a pitch in the visible range, b) when a photo-isomerizable chiral compound is added to a non-photosensitive nematic liquid crystal, and c) when a photoisomerizable nematic component is used in mixtures with photo-inactive chiral components.

Photosensitive chiral compounds based on azobenzene, menthone, stilbene or binaphtyl derivatives were used as a chiral dopant in induced cholesteric mixtures. [9–14]. Recently, for the well-known chiral dopant ZLI-811, a change of pitch under UV irradiation was discovered. This effect could be explained by Fries photo-rearrangement of ZLI-811 which is observed in aromatic esters. The remarkable photosensitivity of the cholesteric mixtures with ZLI-811 makes this chiral dopant very promising in experiments and applications where control of the helical pitch is important [15,16].

Shift of the selective reflection band due to UV irradiation was reported for induced cholesteric systems (nematic host with an optically active dopant) doped with ergosterol (provitamin D_2) or 7-dehydrocholesterol (provitamin D_3). This effect is based on the photo-induced conversion of ergosterol into vitamin D_2 and 7-dehydrocholesterol into vitamin D_3, with the vitamins and provitamins having helical twisting power of opposite signs [17–19].

The majority of investigations were devoted to *trans-cis* transformations observed in different chiral or achiral azobenzene derivatives [20–30]. Recently, the use of a photo-isomerizable nematic component in induced cholesteric mixtures was proposed [31,32]. Various nematic liquid crystals with different conformationally active moieties, such as azo-, azoxy-, and cinnamic acid (thus with different absorption wavelengths) were investigated. The possibility of creating cholesteric mixtures sensitive to the UV A, B, and C parts of solar spectrum was demonstrated [33]. For the mixtures based on nematic azoxy-compounds, strong photo-control was obtained in the blue phases [34]. In this report, the investigation of light-induced effects in CLCs with azoxy-based host materials is continued in order to highlight the mechanisms behind the response.

MATERIALS

The chemical formulas of the materials used in this study are shown in Figure 1. The different azoxy-compounds used as the nematic host were:

1. p-n-ethyl-p-pentylazoxybenzene (EPAOB) with a nematic temperature range between 5°C and 40.5°C.
2. ZhK-440 (NIOPIK) – a mixture of 2/3 p-n-butyl-p-methoxyazoxybenzene (BMAOB) and 1/3 p-n-butyl-p-heptonoiloxyazoxybenzene

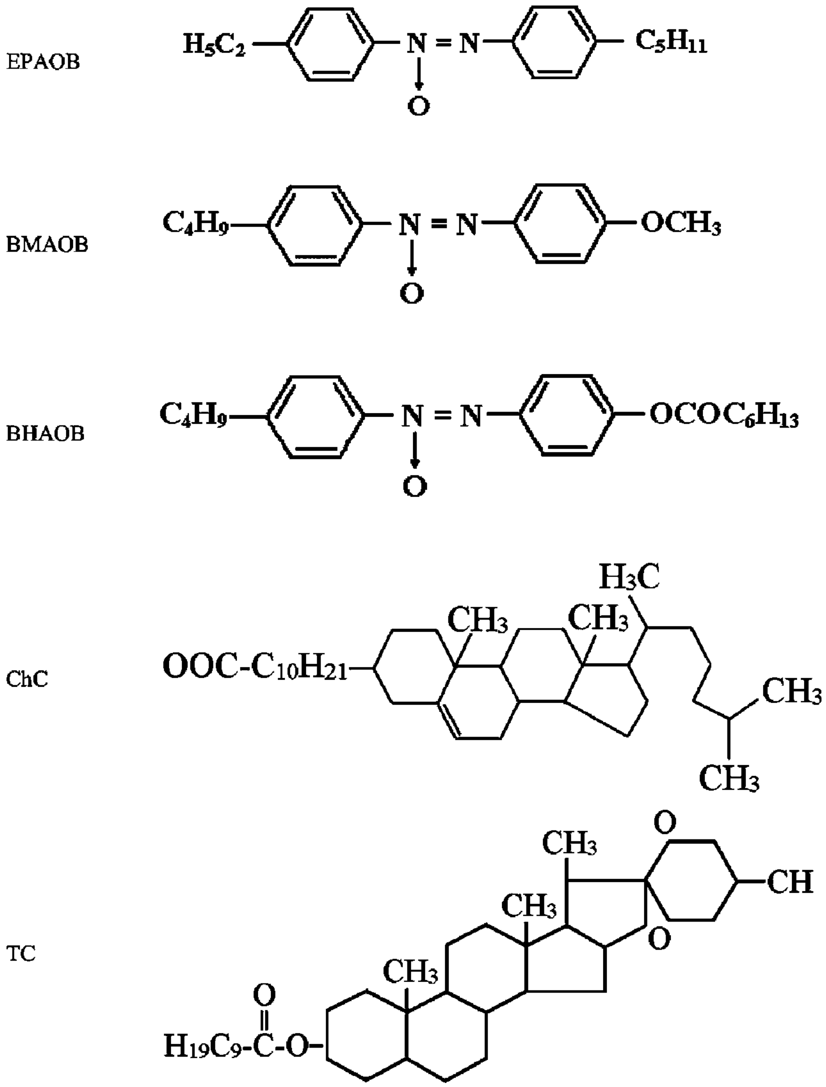


FIGURE 1 Compounds used in this investigation.

(BHAOB) with a nematic temperature range between −5°C and 75°C.

To investigate the dependence of photosensitivity on the concentration of the azoxy-compound, mixtures of ZhK-440 with different amounts of the non photo-isomerizable and UV/vis transparent nematic liquid crystal MLC-6815 (Merck) were prepared in the proportions 75:25%, 50:50%, and 25:75%.

3. ZhK-999, a mixture of ZhK-440 with 2 non-photoisomerizable compounds (NIOPIK) with a nematic temperature range between 0°C and 77.5°C. This mixture possesses a low dielectric relaxation time: at 20°C the dielectric anisotropy $\Delta\varepsilon$ is $+2.2 \pm 0.2$ at 200 Hz and -2.1 ± 0.2 at 40 kHz.

The following chiral dopants were used:

1. MLC-6248 (2011 R, Merck),
2. Cholesteryl Caprinate (ChC),
3. Tigogenin Caprate (TC) [34].

EXPERIMENTAL RESULTS AND DISCUSSIONS

All experiments were carried out in cells of 10 μm thickness. The transmission spectra measurements were made at room temperature using a fiber-optics Avantes spectrophotometer. A 100 W Mercury lamp and appropriate filters were used as the light source for illumination. The distance from the lamp to the cell was approximately 20 cm. For investigating the *trans-cis* and *cis-trans* conversions, two types of interference filters were used, 365 nm (F_1) and 436 nm (F_2), along with two types of band pass filters, 240–390 nm (F_3) and 410–500 nm (F_4). The intensity of UV light at the sample varied from 0.1 to 1 mW/cm^2 depending on the filter.

The *trans* form of azoxy-compounds absorbs in UV-violet region of spectrum up to about 400 nm, and as shown Refs. [30–33], the cholesteric pitch decreases with exposure to irradiation that has a wavelength between 330 and 400 nm. Thus during UV irradiation, the color of the cholesteric film changes from red to blue. This effect is reversible: the pitch returns to its initial state when the irradiating light has a wavelength greater than 410 nm.

Figures 2 and 3 show the exposure time dependences of the wavelength of the selective reflection peak (λ_o) for a mixture of EPAOB with TC using filter F_1 or with ChC using filter F_1. For the mixture of EPAOB and TC, the pitch shifted by 210 nm during 50 minutes of irradiation.

A more detailed investigation was carried out with the mixture ZhK-440. Figures 4–6 show the results for a mixture of 75% ZhK-440 and 25% ZLI-2011, including the dependence of λ_o on temperature and exposure time, and the dependence of the full-width-at-half maximum of the selective reflection band on exposure time. As shown in Figure 5, after 120 minutes of irradiation using the interference filter, λ_o shifted to shorter wavelengths by 160 nm. After irradiation with 436 nm light, a shift in the opposite direction was observed due to *cis-trans* conversion, but not to its initial value. This indicated that not all of the *cis* molecules transform back to the *trans* form. A return to the initial state was observed after waiting several days or upon re-heating to the isotropic phase. To obtain a faster shift and to understand the effect of different concentrations of azoxybenzene compounds

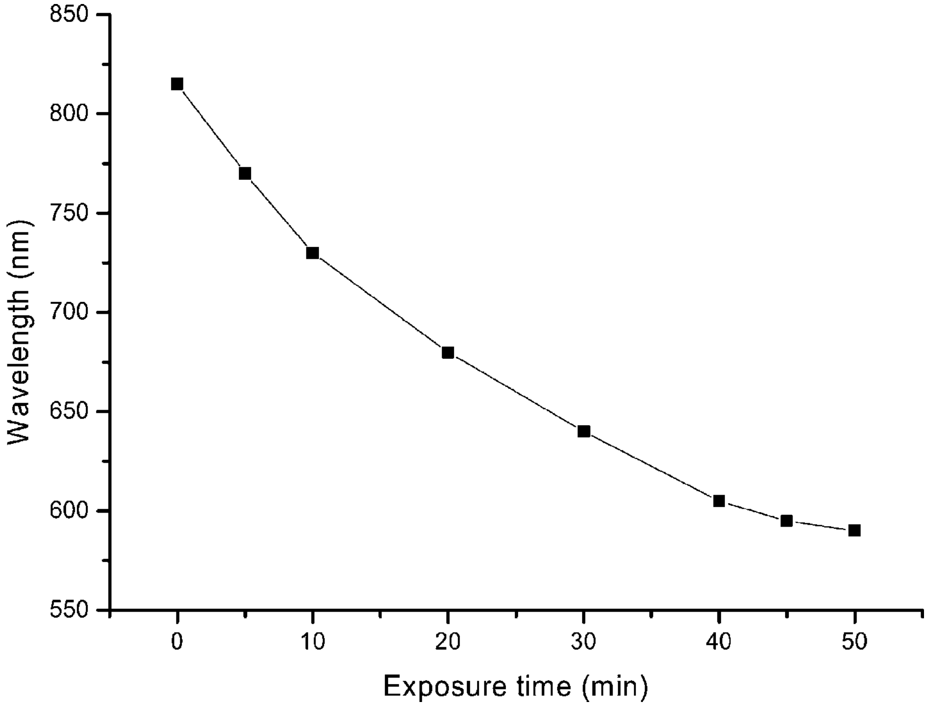


FIGURE 2 Dependence of λ_o for a mixture of 90% EPAOB and 10% TC on exposure time using filter F_1.

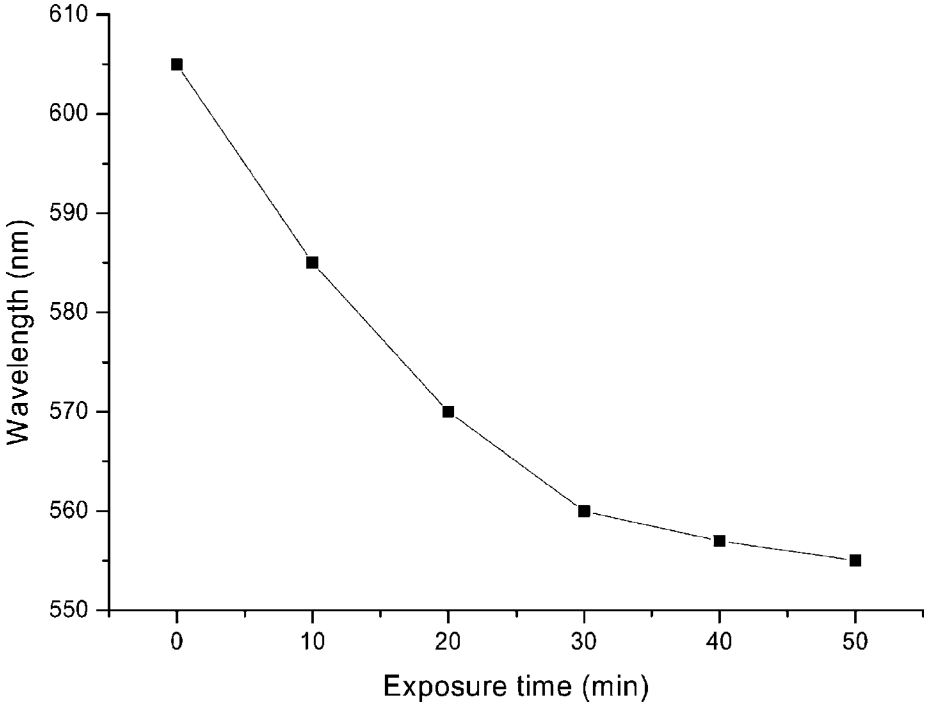


FIGURE 3 Dependence of λ_o for a mixture of 72% EPAOB and 28% ChC on exposure time using filter F_3.

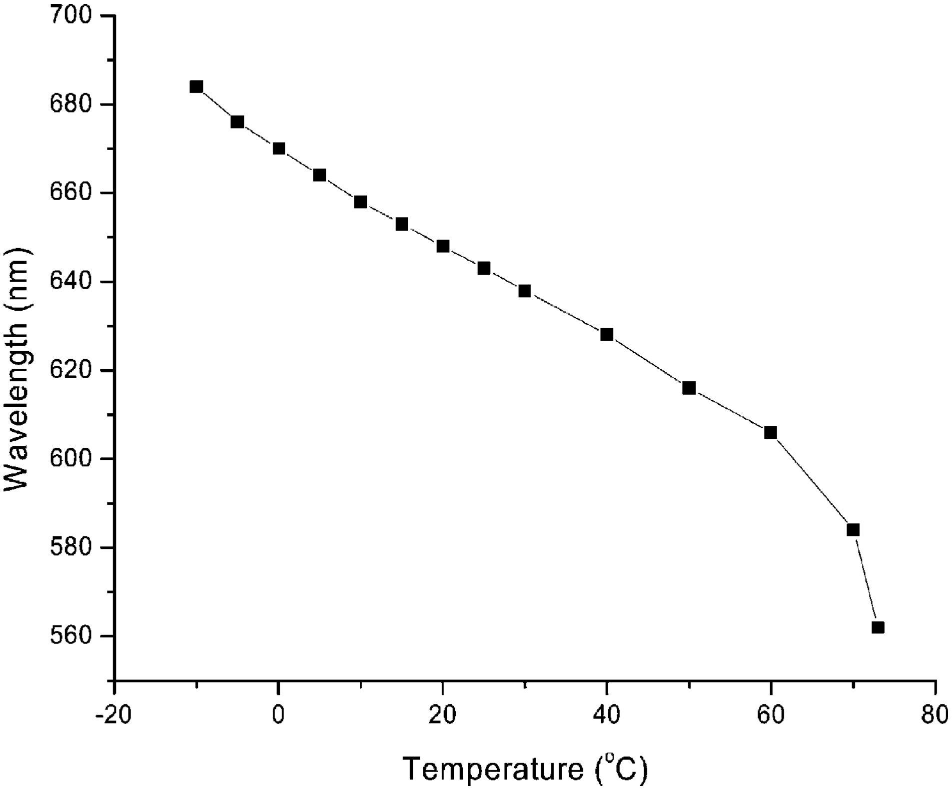


FIGURE 4 Temperature dependence of λ_o for a mixture of 75% ZhK-440 and 25% ZLI-2011.

in these CLCs, mixtures of Zhk-440 with another nematic compound were irradiated with light covering both the UV and visible ranges. The results are shown in Figures 7–10. In the case of the broad filters and the 100% ZhK-440 sample, the blue shift was 140 nm after 10 minutes of irradiation. As is clear from the figures, the shift of λ_o decreased as the concentration of ZhK-440 decreased. Figure 8 shows some examples of the transmission spectrum changes under irradiation.

The last compound investigated was ZhK-999, which represents a mixture of ZhK-440 with two non-azoxycompounds developed as a nematic liquid crystal with a small dielectric relaxation. TC and ChC were added to ZhK-999 and these mixtures were irradiated using different interference filters. The temperature dependence of λ_o for these mixtures was also investigated. The results are shown in Figures 11 and 12. Although $d\lambda_o/dT$ is negative when TC is used as the dopant and positive when the dopant is ChC, in both cases λ_o decreases when irradiated with UV light.

As a first step in understanding these results, the cholesteric structure must be considered. It is known that the pitch in induced

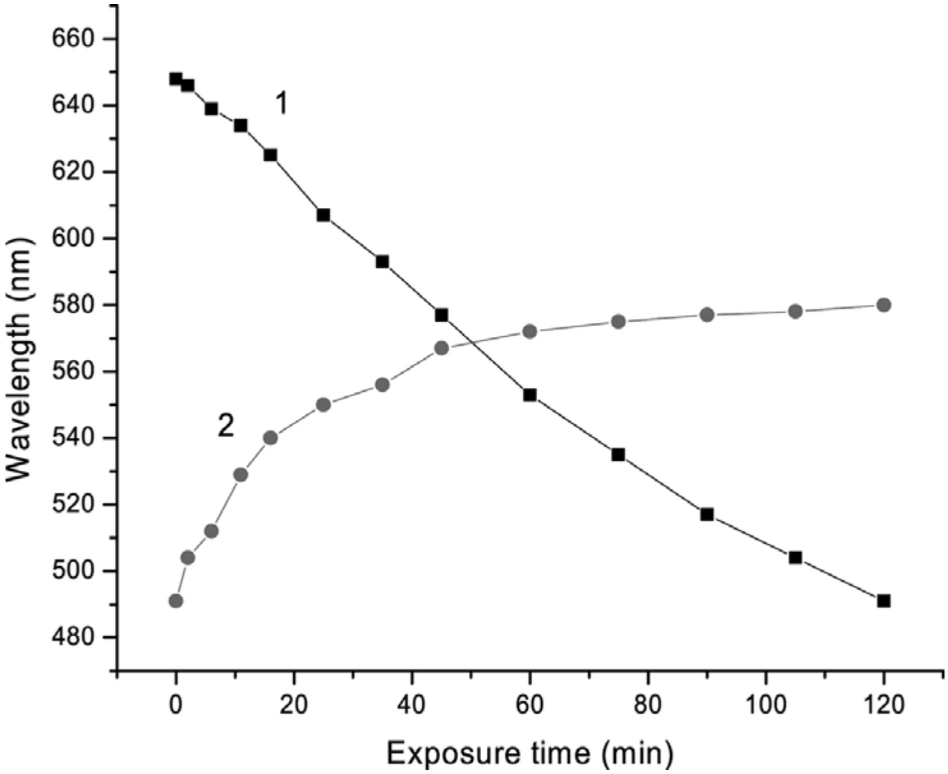


FIGURE 5 Dependence of λ_o for a mixture of 75% ZhK-440 and 25% ZLI-2011 on exposure time using filters F_1 (1) and F_2 (2).

cholesteric systems (nematic-chiral mixtures) depends on the structure of both the nematic host and the chiral dopant [35–38]. Usually the pitch decreases with an increase of the chiral dopant concentration. The ability of the chiral dopant to torque a nematic phase into a twisted structure is called its helical twisting power, β, and is defined by the relation $\beta = (\mathrm{Pc})^{-1}$, where c is the dopant concentration.

Figure 13 shows two neighbouring nematic layers in the helical arrangement of the cholesteric structure [39], where $\mathrm{P} = 2\pi\mathrm{r}/\theta$ (r is the distance between the two layers and θ is the angle between the preferred orientation of molecules or director in the two layers). Reference [39] considers the influence of the stereochemistry of the optically active dopant on the pitch, i.e., on its β. It is evident that to change the pitch either r, θ, or both must change. Clearly the stereochemistry of the molecules plays an important role. The same influence of the molecular stereochemistry on the pitch applies to photo-isomerizable molecules.

Several factors are responsible for the influence of external fields on the pitch, among them are the variation of the orientational order parameter and the conformation of the molecules. A comprehensive

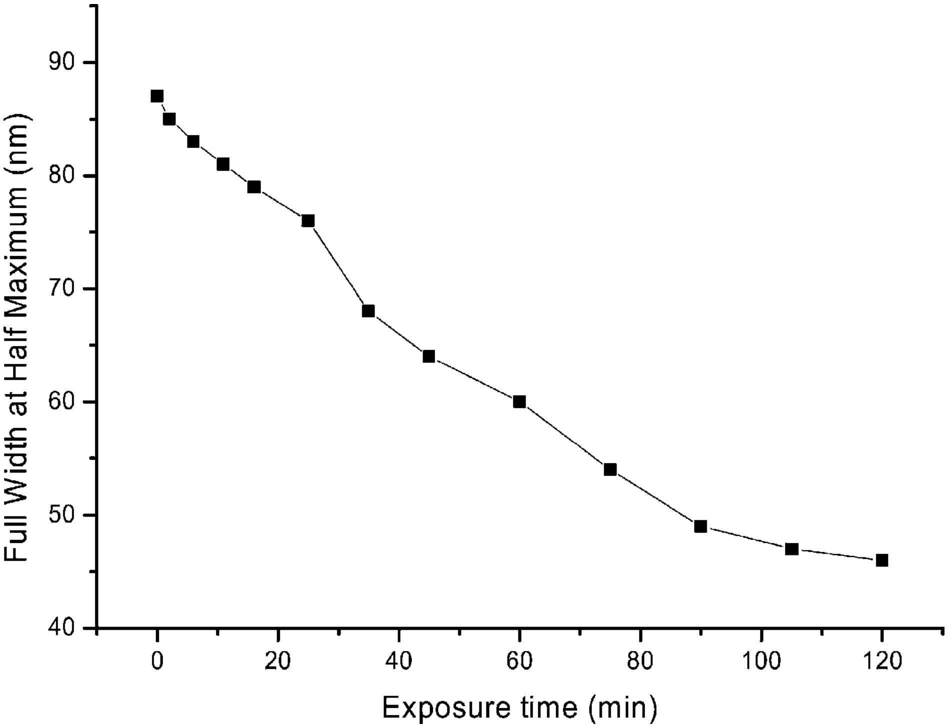


FIGURE 6 Dependence of the full-width-at-half-maximum of the selective reflection for a mixture of 75% ZhK-440 and 25% ZLI-2011 on exposure time during UV radiation (365 nm).

theory explaining the behaviour of CLCs at the molecular level has yet to be developed [40–43].

Regarding the control of the pitch with light illumination, in the early work of Sackmann [4], *trans* and *cis* azobenzene were added to a CLC and it was shown that λ_0 decreases linearly with an increase in the concentration of *trans* azobenzene and increases with an increase in the concentration of *cis* azobenzene. It should be noted that the CLC used by Sackman represents a compensated mixture of two cholesteryl derivatives, and the concentration dependence of various parameters for this mixture is quite complex [38].

Later it was shown that the addition of *trans*-azobenzene shifts the selective reflection band toward longer wavelengths, while the addition of *cis*-azobenzene produces the opposite change [20–30]. The shift also depends on the length of the alkyl chain of the azobenzene. In careful experiments, Ruslim and Ichimura [22] found that adding unsubstituted azobenzenes to CLCs produced the opposite effect observed by Sackmann. This discrepancy was explained by noting that the temperature dependence of the pitch in the CLC needed to be taken into account. In Ref. [25], a schematic picture of

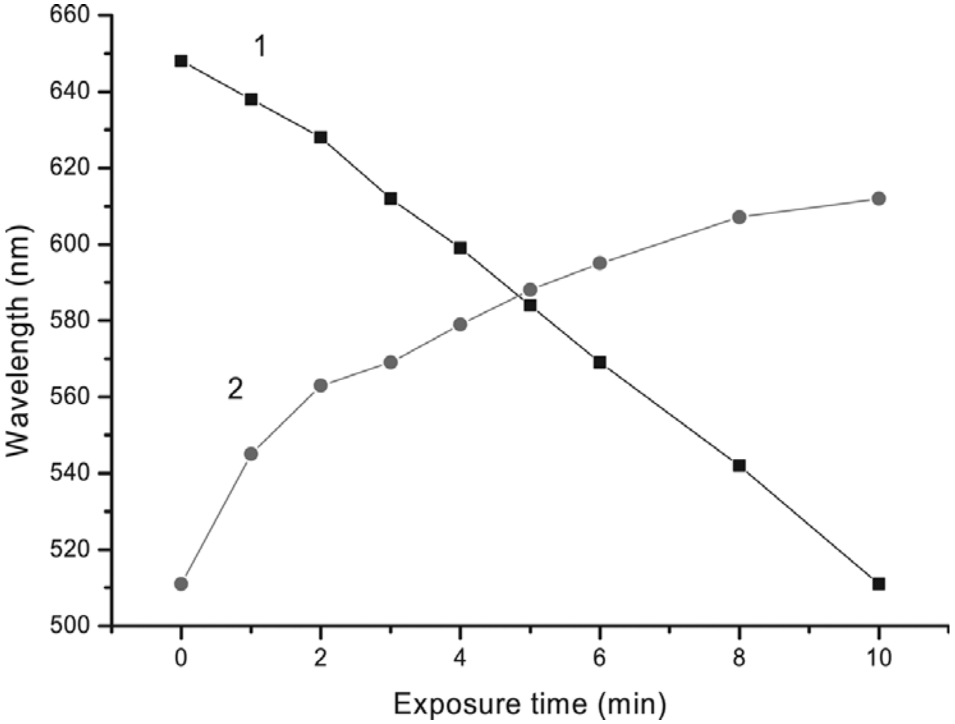


FIGURE 7 Dependence of λ_o for a 100% ZhK-440 sample on exposure time using filters F_3 (1) and F_4 (2).

the alignment of azobenzene derivatives in a CLC is included. The authors hypothesize that the *trans*-azobenzenes align parallel to the local director of the cholesteric molecules and therefore change the cholesteric pitch, while the *cis*-azobenzenes cannot align parallel to the local director due to their bent structure. It is also suggested that rod-like *trans*-azobenzene molecules promote the stabilization of the cholesteric phase, while the bent *cis*-azobenzene molecules lead to the disorganization of the orientationally ordered structure.

It must be taken into account that many substances based on azobenzene possess a nematic phase with *trans* isomers but only an isotropic phase with *cis* isomers [44,45]. Therefore, upon irradiation with UV light, liquid crystal forming molecules are being transformed into non-liquid crystal forming molecules. Thus, *cis* molecules do not “participate” in the organization of the liquid crystal, and in the case of CLCs these molecules are “outside” of the molecular arrangement forming the supramolecular helical structure (as shown in the schematic picture in Ref. [25]). These *cis* molecules, therefore, can be considered as an “isotropic liquid dopant”. Usually any isotropic achiral dopant causes an increase in the pitch. On the other hand, in induced cholesteric systems the *trans-cis* transformation of the isomerizable nematic host molecules leads to a lowering of the concentration of the nematic component of the mixture, resulting in a decrease of the pitch. The results reported here along with previous investigations demonstrate that the loss of some of the liquid crystal forming molecules dominates and a decrease in the pitch is observed. Moreover, the photo-transformation simultaneously produces a change in both the polarizability and orientational order parameter of the liquid crystal molecules [46,47]. The decrease of the order parameter produces a change of the refractive indices and a lowering of the phase transition temperature. Actually, the change of refractive indices is due to both a change in the order parameter and a change in the anisotropy of the polarizability of the molecules. The ordinary index increases and the

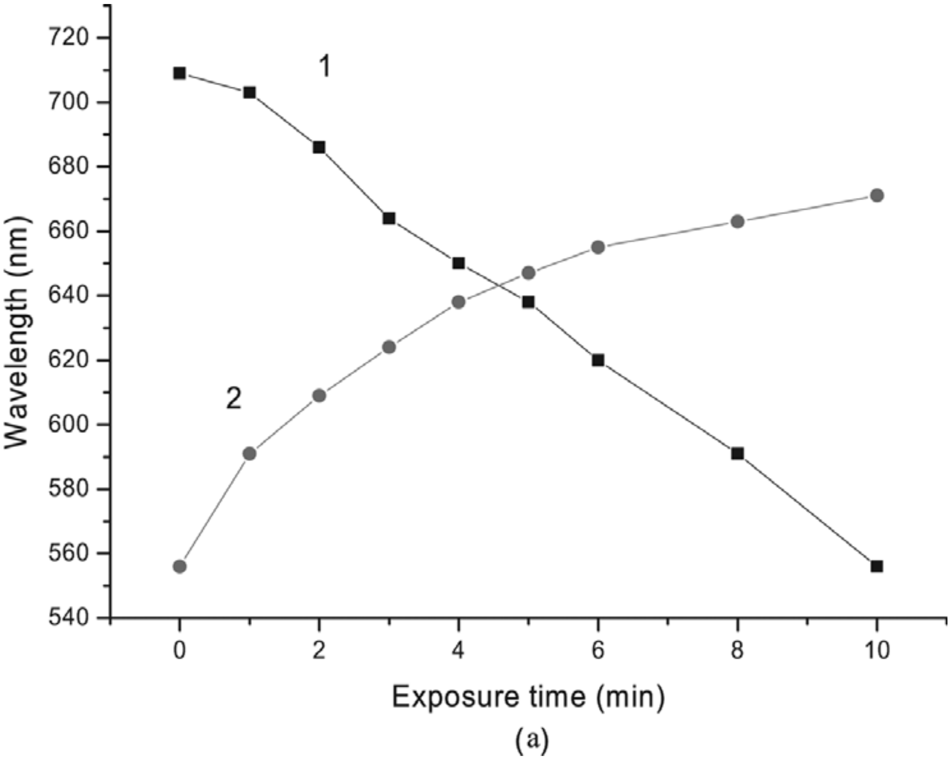
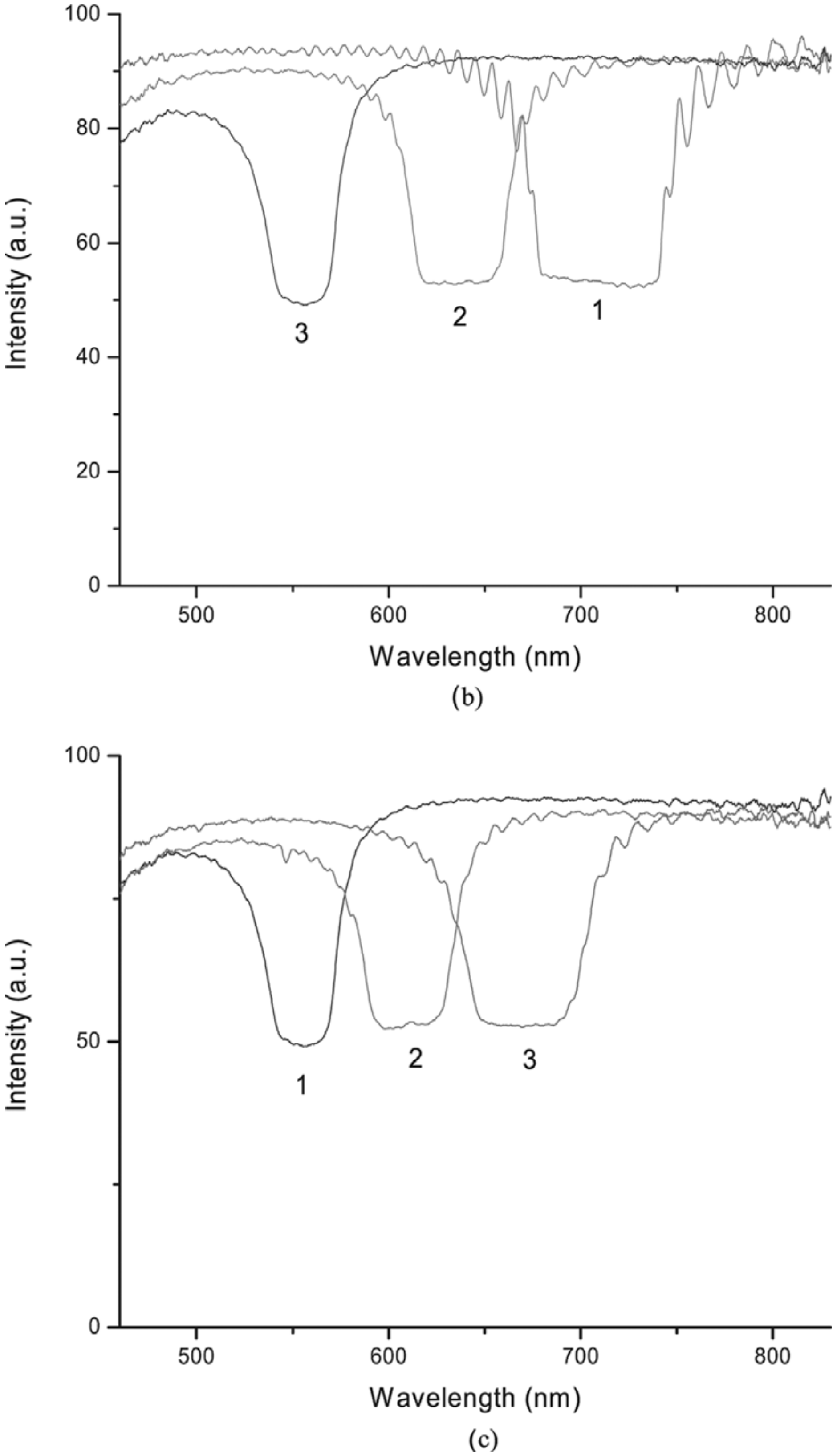


FIGURE 8 (a) Dependence of λ_o for a mixture of 75% (75% ZhK-440 and 25% MLC-6815) and 25% ZLI-2011 on exposure time using filters F_3 (1) and F_4 (2); (b) Transmission spectra for the same mixture after different exposure times using filter F_3: 1 – before irradiation; 2 – after 5 minutes of irradiation; 3 – after 10 minutes of irradiation; (c) Transmission spectra for the same mixture subsequent to UV irradiation (showing the shift of the selective reflection band in the other direction) at different exposure times using filter F_4: 1 – before irradiation; 2 – after 2 minutes of irradiation; 3 – after 10 minutes of irradiation.



(b)

(c)

FIGURE 8 Continued.

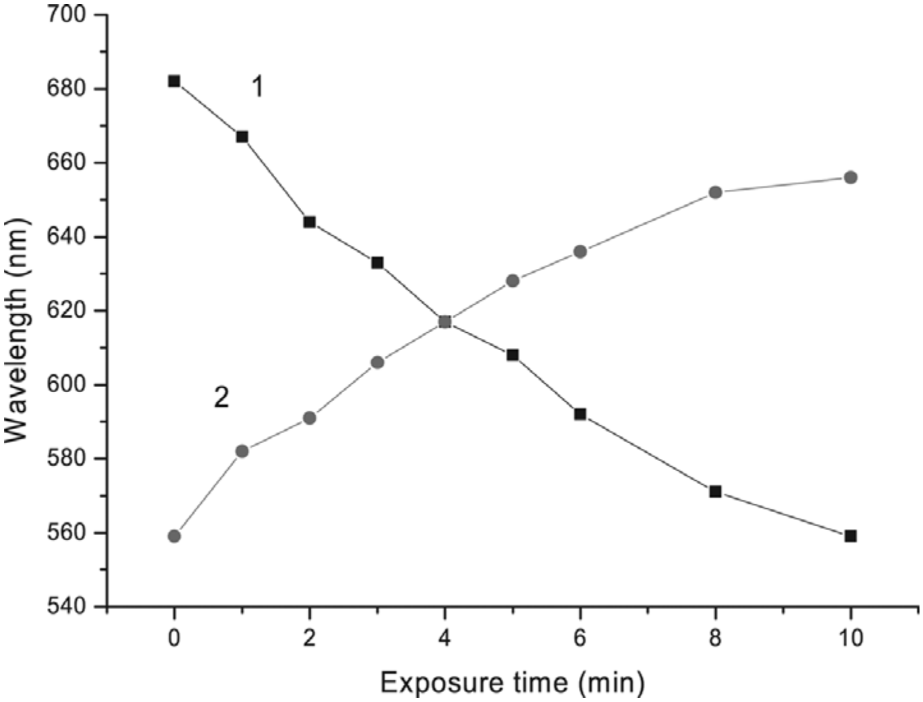


FIGURE 9 Dependence of λ_o for a mixture of 75% (50% ZhK-440 and 50% MLC-6815) and 25% ZLI-2011 on exposure time using filters F_3 (1) and F_4 (2).

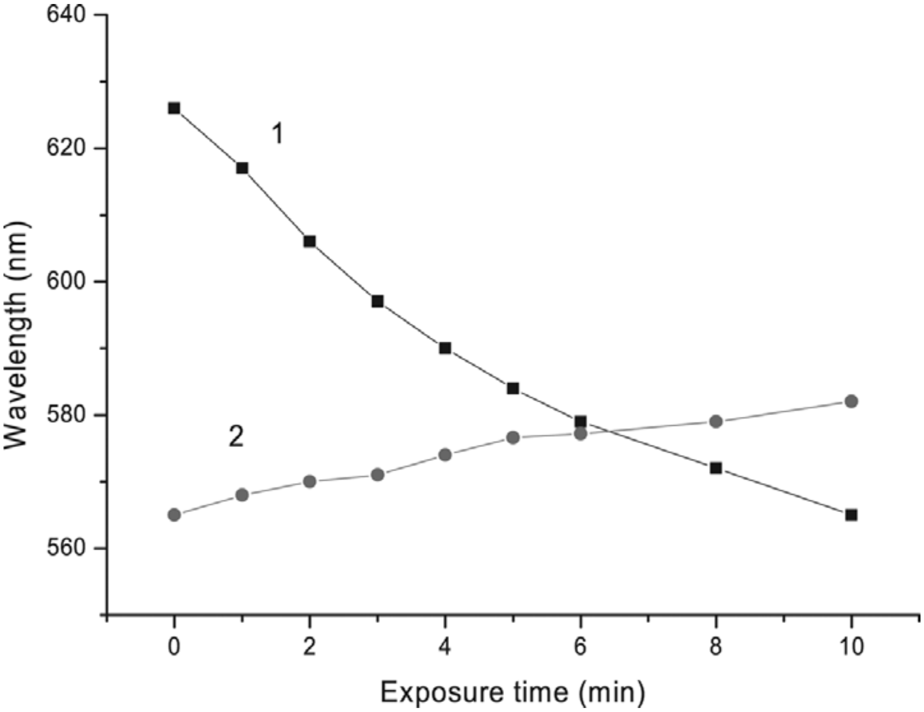


FIGURE 10 Dependence of λ_o for a mixture of 75%(25% ZhK440 and 75% MLC-6815) and 25% ZLI-2011 on exposure time using filters F_3 (1) and F_4 (2).

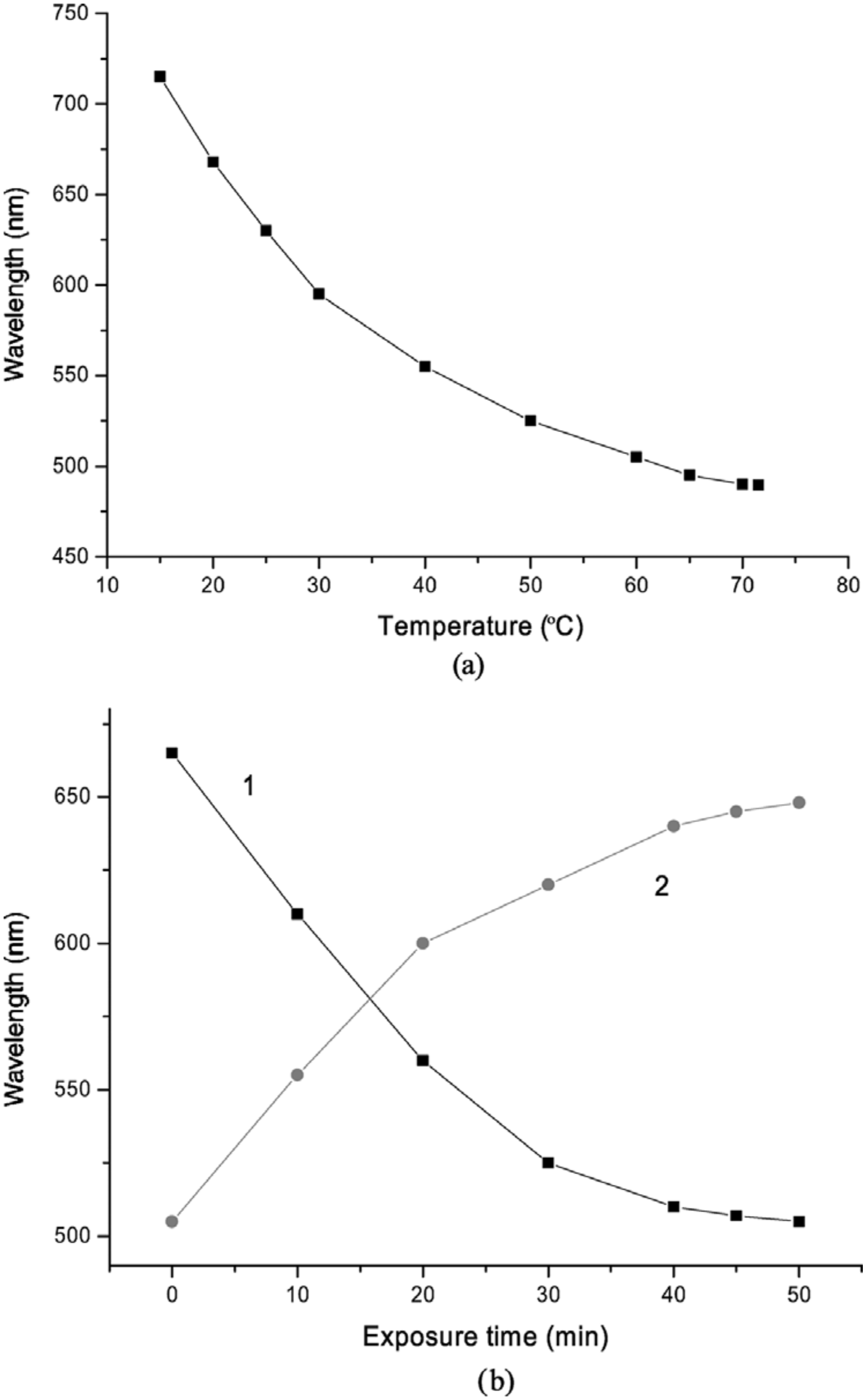


FIGURE 11 (a) Temperature dependence of λ_o for a mixture of 86.7% ZhK-999 and 13.3% TC; (b) Dependence of λ_o for the same mixture on exposure time using filters F_1 (1) and F_2 (2).

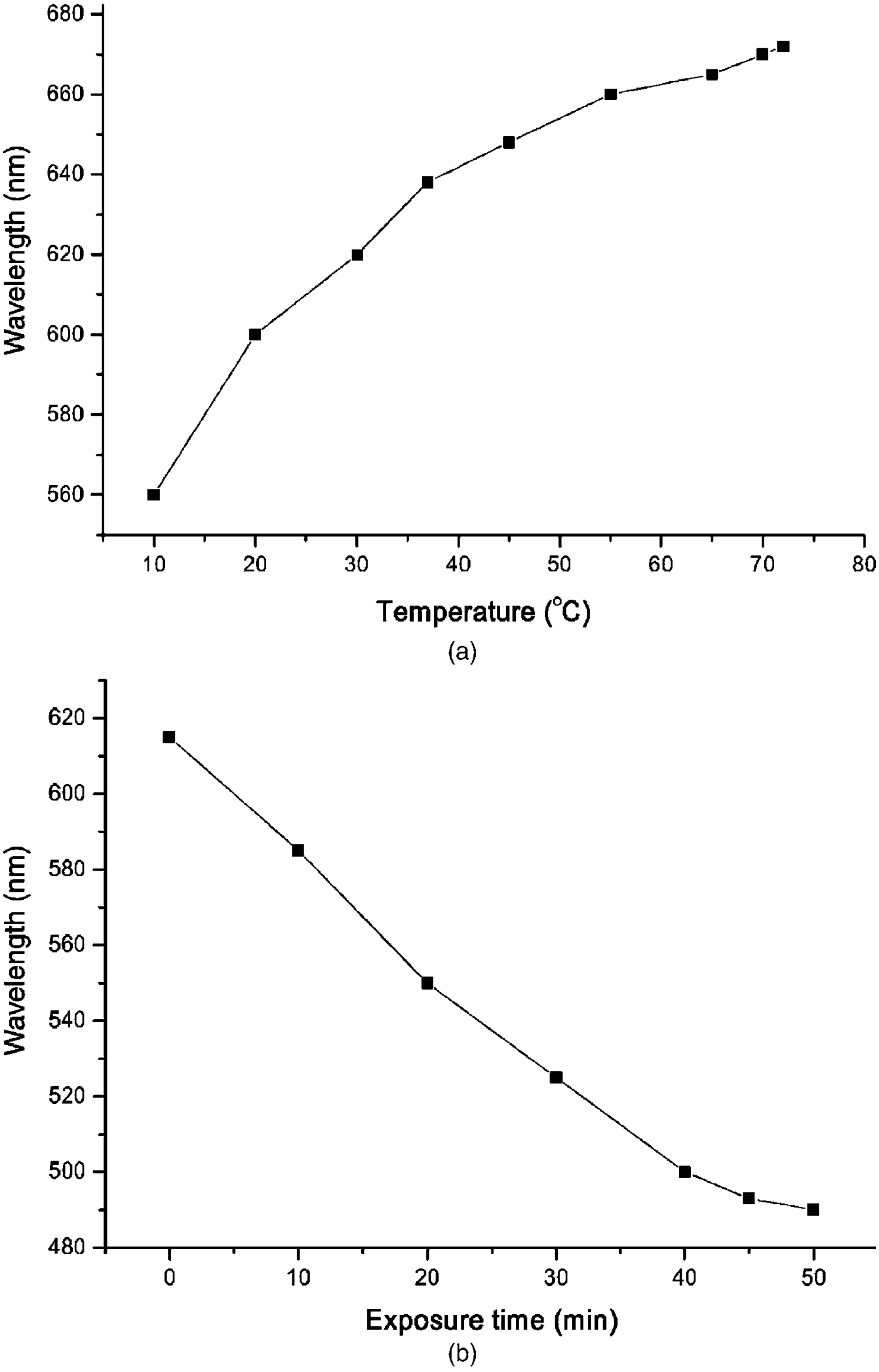


FIGURE 12 (a) Temperature dependence of λ_o for a mixture of 72% ZhK-999 and 28% ChC; (b) Dependence of λ_o for the same mixture on exposure time using filter F_1.

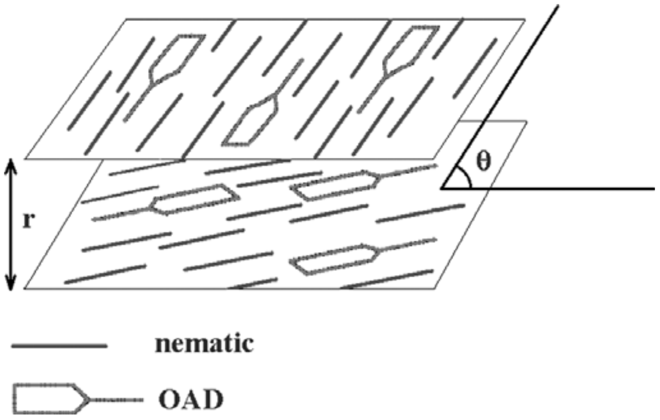


FIGURE 13 Schematic diagram showing the arrangement of nematic and chiral dopant molecules in neighbouring nematic layers of the cholesteric superstructure. The nematic and optically active dopant (OAD) molecules are depicted differently. The distance between layers is r and the angle between the directors of the two layers is θ.

extraordinary index decreases, leading to a decrease in the width of the selective reflection band in CLCs. In the case of *p*-azoxyanizole, the decrease in the amount of orientational order causes the ordinary refractive index to increase slightly while the extraordinary refractive index decreases more [48]. So in CLCs the shift in the selective reflection band and the change of its width are due to changes in both the polarizability and the order parameter.

The behaviour of such systems depends on the concentration of *cis* molecules: increasing their concentration destabilizes the nematic order and in many cases the liquid crystal transforms to the isotropic phase when the concentration of *cis* molecules reaches a certain value. In the experiments reported here, irradiation was stopped as soon as the transition to the isotropic phase started. Irradiation was also stopped when the selective reflection band started to shift into the absorption region of the azoxy-compounds.

In conclusion, it is demonstrated that CLC mixtures based on azoxybenzene nematic components show reversible light control of the selective reflection band with shifts as large as 210 nm. The results reported here show that *trans-cis* isomerization causes several competing and interdependent effects in CLCs, including on one hand, a change of the orientational order parameter, the isotropic phase transition temperature, and refractive indices, and on the other hand, a change in the concentration and shape of the molecules involved in the organization of the liquid crystal state with its helical superstructure. So although a full theoretical treatment is lacking, experiments demonstrate that the reversible control of the pitch in CLCs is a robust phenomenon and could very well be useful in a wide range of practical applications.

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