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Published online: 24 Aug 2016.

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Photo- and thermo-induced variation of photonic properties of cholesteric liquid crystal containing azobenzene-based chiral dopant

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ABSTRACT

Photooptical properties of a new cholesteric mixture containing azobenzene-based chiral dopant were investigated. Presence of a photosensitive dopant in the investigated liquid crystal enabled to effectively manipulate optical characteristics of the photonic band upon temperature change and illumination. Temperature dependence of the optical anisotropy and the orientational order parameter of the liquid crystal were determined. The obtained results are compared with existing theories. Discrete multistable change of the spectral position of the photonic band on illumination is realized.

Introduction

Liquid crystals are generally formed by elongated molecules. The long axes of rigid molecules are orientationally ordered along a direction denoted as the director n of the liquid crystal. Orientational ordering of these molecules is characterized by the order parameter $S = 1/2 <3\cos^2\vartheta - 1>$, where ϑ is the angle of orientation of long molecular axes with respect to director. The order parameter S is among the most important characteristics of liquid crystal. It describes its orientational structure [1–3] and allows one to choose a model, which adequately reflects characteristics of the liquid crystal. Nonchiral molecules whose long axes are orientationally ordered form an optically anisotropic nematic. Anisotropic characteristics of nematic, including the difference of refractive indices $\Delta n = n_{||} - n_{\perp}$ along $n_{||}$ and perpendicular $n_{\perp}$ to the director, are determined by the degree of orientational ordering. The values of S and Δn are temperature dependent and characterize transformation of the structure upon temperature change. Orientationally ordered molecules can form more complex structures. The simplest one is the cholesteric liquid crystal [1], formed by chiral molecules or by nematic with a chiral additive. In cholesteric liquid crystals, the long molecular axes rotate with respect to each other in the direction perpendicular to the director. The chiral nematic phase has a twist along one axis and is described by a helix with a pitch p_0. Spatial periodicity is equal to $p_0/2$, since directions n and $-n$ are equivalent. Pitch of the cholesteric helix is usually temperature dependent [1–4] and can be close to wavelength of visible light. Helical structure of cholesteric manifests itself in nontrivial optical properties. Selective reflection

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band is observed for light with circular polarization whose sign coincides with the direction of helix twisting. For backward reflection, the center of the band corresponds to wavelength $\lambda_0 = \bar{n}\,p_0$, where $\bar{n}$ is a certain average index of refraction [1]. Cholesteric liquid crystal is a one-dimensional photonic crystal. Structure and spectral properties of cholesteric photonic crystal can be modified upon changing temperature, and in the case of employing photosensitive compounds, with illumination by light which transforms molecules between *cis-* and *trans-* configurations [5–10]. Significant progress has been made in the past decade in investigation of photosensitive compounds. Lee *et al.* [11] observed interesting phenomena in cholesteric liquid crystals with two chiral opposite-handed dopants. Upon UV irradiation the reflection band shifts toward longer wavelengths and then returns towards shorter wavelengths. The handedness of the sample becomes opposite. White *et al.* [12] demonstrated extremely large phototuning of more than 2000 nm from visible to infrared spectral region. Lee et al. [13] investigated influence of both irradiation and DC voltage on optical spectra. They found that tuning range increases with irradiation. Broadening of the reflection bandwidth was observed by Relaix, Bourgerette, and Mitov [14, 15] after photopolymerization. The broadening is related to asymmetrical conditions for the irradiation connected with the gradient of the light intensity.

For nematic liquid crystals different optical methods were developed aimed to determine the characteristics of orientational ordering of molecules [2,16]. The most common optical methods used to determine the parameter of orientational ordering of molecules $S(T)$ in nematic liquid crystals are based on measurement of absorption dichroism of dopant molecules and on measurement of refractive indices $n_\parallel$ and $n_\perp$ [16,17]. In the cholesteric phase, the director of the liquid crystal changes its direction in the sample, which does not allow measuring directly the dichroic ratio and refractive indices by methods used in nematic liquid crystal. Determination of the orientational order parameter and its variation with temperature in chiral photonic crystals constitutes a much more complex task [18,19]. In this work, temperature dependence of spectra of selective reflection and transmission in photosensitive cholesteric photonic crystal was measured. For rigid boundary conditions on cell surfaces temperature-induced change of the wavelength of selective reflection occurs in a stepwise manner [20–24] and is accompanied by a change of the number of helix half-turns in the sample by one. In present work a stepwise shift of the wavelength of selective reflection both with decrease and increase of number of helix half-turns in the sample was observed at illumination of a photosensitive photonic crystal. Comparing the experimental selective reflection spectra with the theoretical expression, following from an analytical solution of Maxwell equations for the periodic medium [25–27] we determined the temperature dependence of the anisotropy of refractive index $\delta = \Delta n/n$. Using the relation of the order parameter S with the anisotropy of refractive index, following from the microscopic theory [28–31] and the phenomenological dependence of S on temperature [30-35], temperature dependence of the order parameter was determined. Temperature dependence $S(T)$ differs from the dependence following from Maier-Saupe theory [1]. This can be related with proximity of the system to the tricritical point, where the forth order term of the free energy expansion in Landau theory of phase transitions is close to zero [36]. Employing a cholesteric liquid crystal with a photosensitive chiral component and an optical cell with rigid boundary conditions for orientation of molecules allows realizing switching between discrete states of the photonic crystal at illumination both into states with larger and smaller wavelength of selective reflection.

Table 1. Chemical structures of components used for cholesteric mixture preparation.

Chiral-photochromic dopant

MeAzoSorb

Nonphotochromic chiral dopant
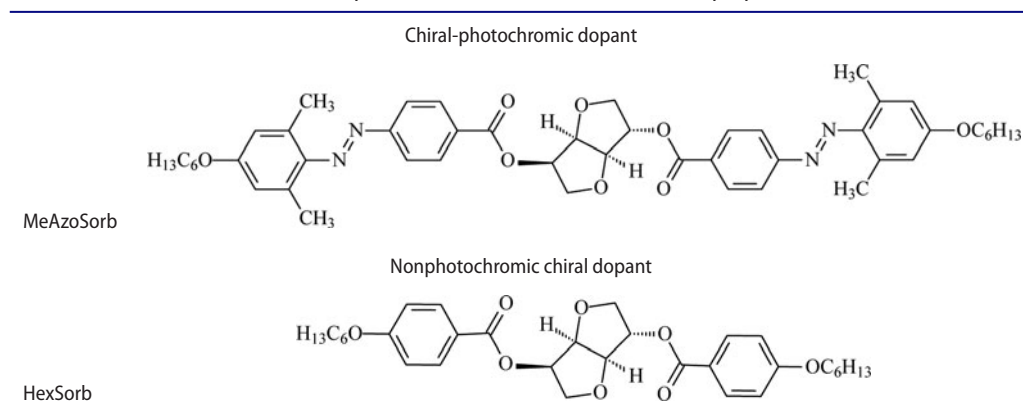
HexSorb

Experiment

The measurements were performed on cholesteric liquid crystal formed by a mixture of nematic liquid crystal MLC6816 (Merck), chiral dopant HexSorb (3.7%), and chiral-photochromic dopant MeAzoSorb (2%) (Table 1) [10].

Synthetic procedures for MeAzoSorb and HexSorb were reported previously [5,10]. The investigated mixture forms a cholesteric phase with selective reflection band in the visible spectral range. The compound was placed in an optical cell, whose inner surfaces were coated by a polymer film which imposed planar orientation of molecules near the surface of the cell. Rubbing direction of the polymer film, which determined the orientation of director, coincided on the two surfaces. The axis of cholesteric helix orients perpendicular to the surfaces of the cell (planar texture). Samples were placed in a thermostatic stage, which allowed regulation of temperature with precision of $\pm 0.05°C$. Transmission and diffraction spectra of the sample were measured. Measurements of diffraction spectra were carried for backward reflection using a CCD-spectrometer AvaSpec-2048L (Avantes). Refractive index in the isotropic phase n_I was determined from interference spectra of the empty cell and the cell filled by the liquid crystal. Photoinduced shift of the wavelength of selective reflection, related to *cis-trans* transitions in MeAzoSorb, was carried with the aid of laser diodes with emission wavelengths 367 and 455 nm.

Results and discussion

In Fig. 1 the solid curve reproduces the experimental reflection spectrum of cholesteric photonic crystal. The spectrum consists of an intensive selective reflection band and additional maxima (Pendellösung oscillations), related to finite thickness of the sample. Presence of additional maxima in the spectrum indicates high quality of the sample. The intensity of reflection from the cholesteric sample in the direction along the helical axis is given by the expression [24–26]

$$I = I_0 \frac{\delta^2 \sin^2 k^- L}{4(k^-/k)^2 + \delta^2 \sin^2 k^- L}, \tag{1}$$

where $k^- = \kappa \sqrt{1 + (\nu_0/\nu)^2 - [(2\nu_0/\nu)^2 + \delta^2]^{1/2}}$, $\delta = (n_{||}^2 - n_{\perp}^2)/(n_{||}^2 + n_{\perp}^2)$, $\kappa = 2\pi n\nu$, $\nu = 1/\lambda$, $\nu_0 = 1/\lambda_0$, L is the sample thickness. The experimental diffraction spectrum was compared with theory (1), values ν_0, δ, and n served as fitting parameters. The dotted line in
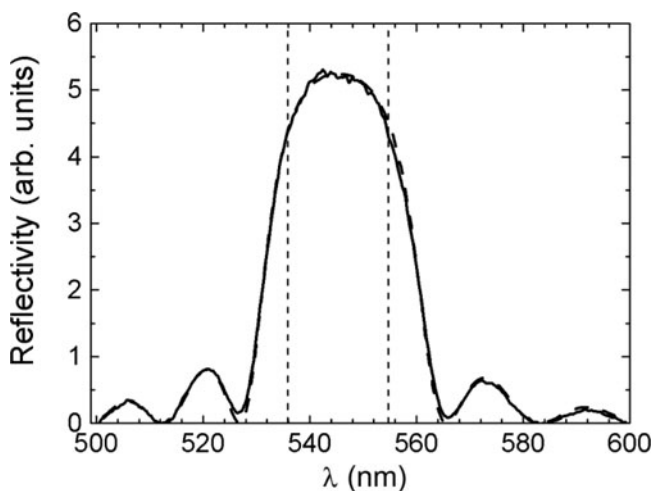
Figure 1. Selective reflection spectrum of the cholesteric photonic crystal (solid line). The spectrum was measured in nonpolarized light. The dotted curve – spectrum calculated according to (1) with parameters $\lambda_0 = 545.8$ nm, $\delta = 0.03453$. Sample thickness is 5.8 μm. $T = 46.0°$C. Vertical lines show the boundaries of the photonic stop band.

Fig. 1 shows the reflection spectrum calculated according to Eq. (1). As can be seen, the agreement of experimental and calculated spectra is very good. An important characteristic of the photonic crystal is the spectral position of the photonic band, i.e., spectral region where the density of states for one circular polarization (in our case right circular polarization) is zero in an infinite sample, and light is totally reflected. Vertical lines in Fig. 1 show the boundaries of the photonic stop band determined by relation $\lambda_{1,2} = \lambda_0 (1 \pm \delta)^{1/2}$. With precision of up to $(\Delta n/2n)^2$ the value $\delta = \Delta n/n$.

At increasing temperature, a change of the intensity of the diffraction band and decrease of its halfwidth occur. Both effects arise from change of the anisotropy of refractive index, and eventually from change of the orientational order parameter, leading to change in Δn. In the investigated sample at a temperature slightly above $T_C = 68°$C, transition to the isotropic phase occurred with disappearance of the diffraction band of cholesteric.

Anisotropy of the refractive index δ is linked with the width of photonic stop band $\Delta\lambda = \lambda_1 - \lambda_2$. For thin samples (in our case the number of helix half-turns $N \sim 32$), width of the diffraction band is larger than photonic stop band width (Fig. 1), which is related to widening of diffraction in samples of small size (in the case of photonic crystal to the finite thickness of the sample). In Fig. 2(a), the temperature dependence of δ is shown, determined from diffraction spectra with the aid of Eq. (1). Increase in δ with decreasing temperature is related to increase of Δn and ordering of molecules [1]. Figure 3 shows the dependence of the halfwidth of reflection band $\Delta\lambda_B$ on temperature (diamonds). $\Delta\lambda_B$ is the width of the reflection band at half of its maximal intensity. Decrease of $\Delta\lambda_B$ on heating is related to decrease of the anisotropy and width of photonic stop band. From the relation $\lambda_{1,2} = \lambda_0 (1 \pm \delta)^{1/2}$ it follows that the width of photonic stop band $\Delta\lambda \approx \lambda_0 \delta$. On heating $\Delta\lambda$ decreases from approximately 21 nm at low temperature (Fig. 3) to approximately 11 nm near the clearing temperature. For the investigated sample ($L \approx 5.8$ μm) $\Delta\lambda_B$ approximately in one and a half times exceeds the photonic stop band width. Whereas the halfwidth of the reflection band depends on sample thickness, the width of the stop band is a function of characteristics of the compound.
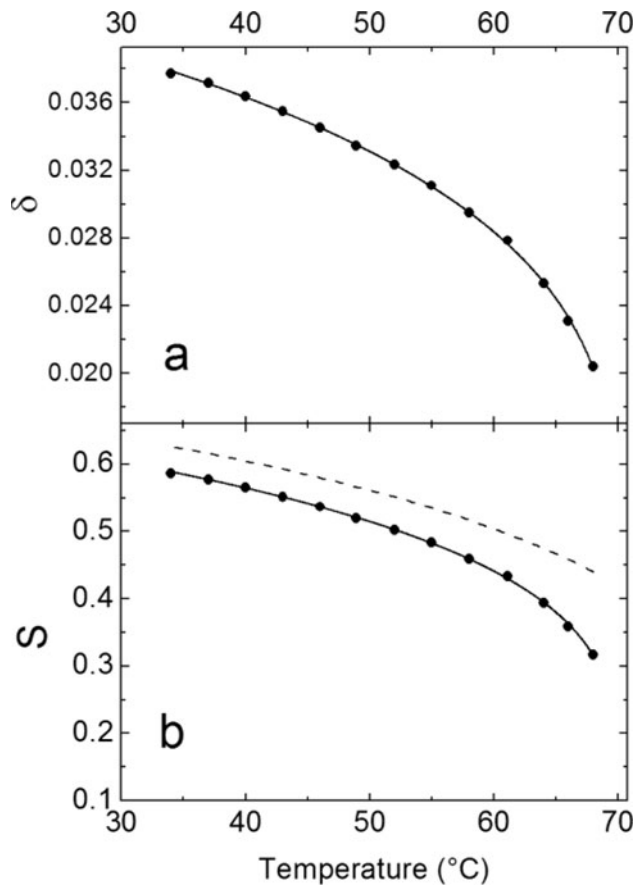
Figure 2. (a) Temperature dependence of the relative anisotropy of refractive index δ in cholesteric photonic crystal, determined from selective reflection spectra. (b) Temperature dependence of the orientational order parameter of photonic crystal, calculated from the data on optical anisotropy (dots). The theoretical dependence (solid line) is drawn according to Eq. (3). The dashed curve is the dependence following from Maier-Saupe theory [1,37] for nematic liquid crystal.
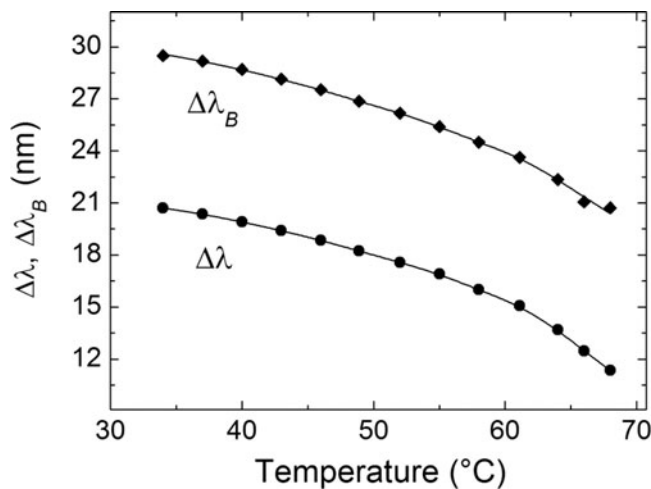

Figure 3. Temperature dependence of diffraction band halfwidth $\Delta\lambda_B$ (diamonds) and the effective width of the photonic stop band $\Delta\lambda$ (dots). Both $\Delta\lambda_B$ and $\Delta\lambda$ decrease on heating.

For a cholesteric photonic crystal, a nontrivial task is determination of its orientational order parameter. For nematic liquid crystals in the model of Vuks, Chandrasekhar, and Madhusudana [28,29] macroscopic properties of liquid crystals, in particular anisotropy of the refractive index, are determined via molecular characteristics, namely polarizability α. Scalar order parameter links macroscopic and molecular characteristics [28–31]:

$$\frac{\Delta\alpha}{\langle\alpha\rangle}S(T) = \frac{2n_I\Delta n}{n_I^2 - 1}, \tag{2}$$

where $\Delta\alpha = \alpha_1-\alpha_t$ is the anisotropy of molecular polarizability, α_1 и α_t – longitudinal and transverse polarizability with respect to the long molecular axis. Analytical expression for the temperature dependence $S(T)$, in agreement with the mean field theory, can be presented in the form [30–35]

$$S(T) = S^{**} + (1 - S^{**})|\tau|^{\beta}, \tag{3}$$

where $\tau = (T-T^{**})/T^{**}$, T^{**} is the spinodal temperature [31,32], i.e., temperature of maximum possible overheating of the liquid-crystalline phase, S^{**} — value of the order parameter at T^{**}. The exponent β is close to the value $\beta = 0.25$ [30–32]. Since with good accuracy, $\delta = \Delta n/n$, and $n = n_I$ [32] from (2,3) a relation between δ and $S(T)$ follows, which allows to determine the temperature dependence of the order parameter

$$\delta = \frac{n^2 - 1}{2n^2}\frac{\Delta\alpha}{\langle\alpha\rangle}\left[S^{**} + (1 - S^{**})|\tau|^{\beta}\right]. \tag{4}$$

Equation (4) contains fitting parameters S^{**}, T^{**}, and $\Delta\alpha/\alpha$. Relation (4) has been used to determine orientational order parameter in nematic liquid crystals [30–32]. We have for the first time applied relation (4) for determination of temperature dependence of the order parameter in a cholesteric photonic crystal. Figure 2(b) shows the temperature dependence of the order parameter $S(T)$, determined by fitting of the data $\delta(T)$, presented in Fig. 2(a), by dependence (4). The solid line $S(T)$ in Fig. 2(b) corresponds to $T^{**} = 70.27°C$. The obtained value of the scalar order parameter is smaller than in Maier-Saupe theory (the dashed line in Fig. 2(b) [1,37], which is also observed in nematic liquid crystals [32]. A sharper temperature dependence of $S(T)$ near the phase transition temperature with respect to the dependence following from Maier-Saupe theory [1,37], seems to be related with proximity to tricritical point. The value of S at the temperature of the transition into the high-temperature phase approximately corresponds to results of measurements in nematic structures [38–42]. T^{**} is higher than the clearing temperature of the liquid crystal, because, as we said earlier, T^{**} is the maximum temperature to which the liquid crystal phase can be overheated.

Figure 4 shows the wavelength of selective reflection λ_0 at illumination of the liquid crystal by UV light ($\lambda\approx367$ nm) as a function of illumination time t. Light-induced *cis-trans* transitions in MeAzoSorb molecules lead to decrease of net chirality and to the long-wavelength shift of selective reflection band. Stepwise dependence of λ_0 is related to rigid planar boundary conditions on the surfaces of the optical cell, which require that sample thickness L is equal to an integer number k of helix half-turns $L = pk/2$. Illumination by light with wavelength $\lambda\approx455$ nm leads to a reverse transition from *trans-* to *cis-* configuration and to the short-wavelength shift of the spectrum of selective reflection (Fig. 5). Step-by-step transitions in Figs. 4 and 5 occurred for low intensity of illumination. At intensive illumination transitions occur in a time scale of the order of several seconds. The state into which the transitions will take place (steps in Figs. 4 and 5), is determined by the product of illumination power W and illumination time Wt.
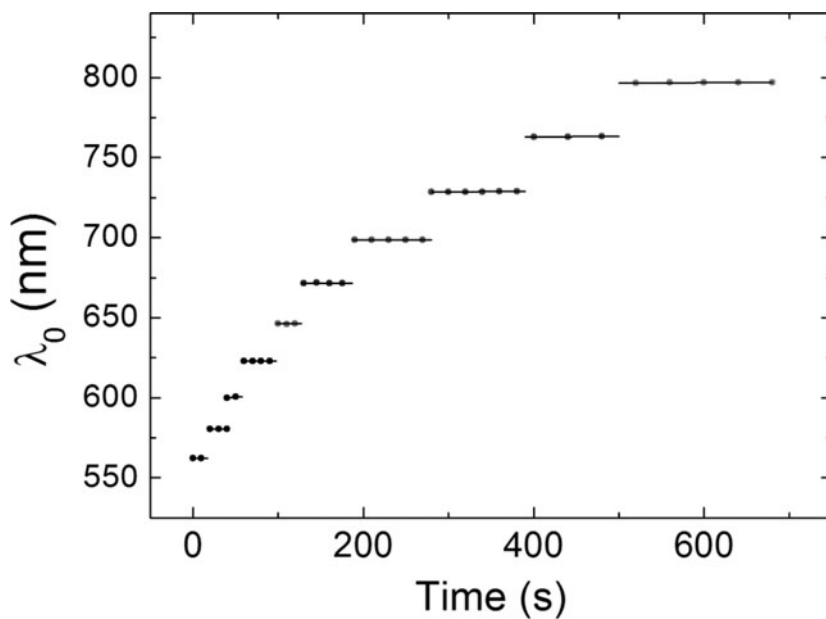
Figure 4. Stepwise shift of selective reflection band as a function of illumination time t for light with wavelength 367 nm ($\sim$0.8 mW/cm^2). Wavelength of selective reflection increases in a stepwise manner at illumination with UV light.
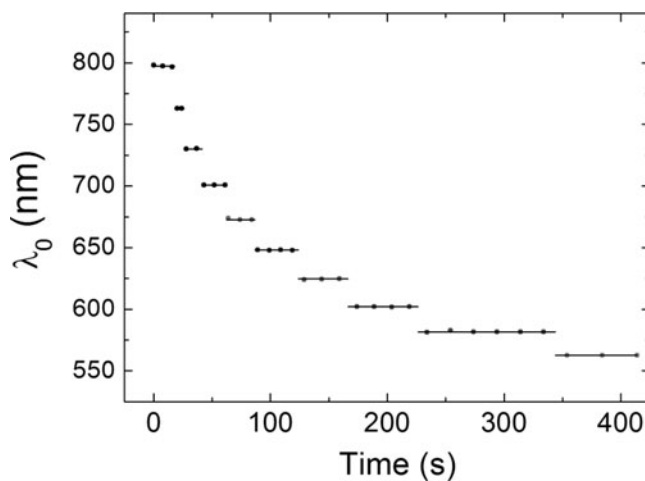

Figure 5. Stepwise change of the wavelength of selective reflection as a function of illumination time t for light with wavelength 455 nm ($\sim$4.5 mW/cm^2).

Conclusion

In this work, temperature dependence of spectra of selective reflection of a photosensitive cholesteric photonic crystal was measured. From the experimental data we determined the temperature dependence of optical anisotropy, orientational order parameter of cholesteric, and spinodal temperature T^{**}. Illumination of the photonic crystal sample with rigid boundary conditions by light of different wavelengths leads to a stepwise modification of spectral characteristics in a wide range of wavelengths.

Acknowledgments

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