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Cholesteric Polymer Scaffolds Filled with Azobenzene-Containing Nematic Mixture with Phototunable Optical Properties

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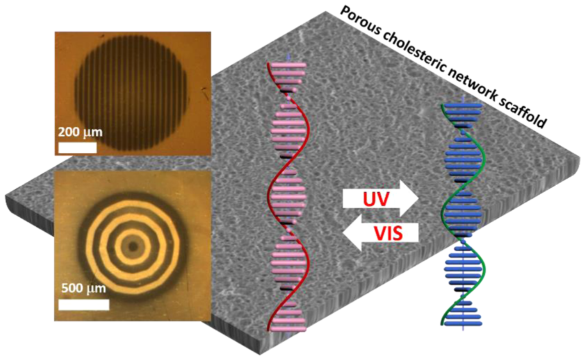
Supporting Information



ABSTRACT: The past two decades witnessed tremendous progress in the field of creation of different types of responsive materials. Cholesteric polymer networks present a very promising class of smart materials due to the combination of the unique optical properties of cholesteric mesophase and high mechanical properties of polymer networks. In the present work we demonstrate the possibility of fast and reversible photocontrol of the optical properties of cholesteric polymer networks. Several cholesteric photopolymerizable mixtures are prepared, and porous cholesteric network films with different helix pitches are produced by polymerization of these mixtures. An effective and simple method of the introduction of photochromic azobenzene-containing nematic mixture capable of isothermal photoinducing the nematic–isotropic phase transition into the porous polymer matrix is developed. It is found that cross-linking density and degree of polymer network filling with a photochromic nematic mixture strongly influence the photo-optical behavior of the obtained composite films. In particular, the densely cross-linked films are characterized by a decrease in selective light reflection bandwidth, whereas weakly cross-linked systems display two processes: the shift of selective light reflection peak and decrease of its width. It is noteworthy that the obtained cholesteric materials are shown to be very promising for the variety applications in optoelectronics and photonics.

KEYWORDS: *liquid crystalline polymer, azobenzene, cholesteric phase, phototunable optical properties, selective light reflection, LC composites*

1. INTRODUCTION

Cholesteric mesophase possesses a number of marvelous optical properties predetermining worldwide scientific and technological interest to low-molar-mass and polymer systems forming this type of liquid crystalline (LC) state.[1,2] Among different optical properties, selective light reflection is the most remarkable feature of the cholesteric mesophase. The reflection wavelength is determined by the simple eq 1:

$$\lambda_{\max} = nP \tag{1}$$

where n is the average refractive index and P is the helix pitch. The specific values of helix pitch depend on the chemical structure of the substances forming cholesteric phase and the concentration of chiral moieties. The width of the selective light reflection $\Delta\lambda_{\max}$ depends on the birefringence Δn:

$$\Delta\lambda_{\max} = \Delta nP \tag{2}$$

where $\Delta n = n_e - n_o$ (n_e and n_o, extraordinary and ordinary refractive indices respectively).

Thus, according to these relations, the variation of the helix pitch simultaneously changes the wavelength of selective light reflection, whereas the gradient of the helix pitch or changes in refractive indices enable control of the selective light reflection bandwidth. A possible effective solution for the regulation of supramolecular helical structure and consequently optical properties is the use of so-called photoactive switchers contained in the nematic LC hosts.[3−5]

One of the most promising types of cholesteric materials is that of cross-linked polymer networks having helical supramolecular organization.[6−21] Introduction of various functional fragments into the cholesteric network allows one to obtain films and coatings capable of changing their optical properties (position of photonic band as well as its intensity and bandwidth) under different external stimuli. Presence of the cross-linked polymer structure provides stability of the

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responsive films, good mechanical properties, and reversibility of the structural changes. In a number of works, the concept of exploiting of cholesteric networks as supports, templates, or scaffolds for a variety of low-molar-mass and polymeric materials is demonstrated.[14−18] It was also reported on different optical sensors based on functionalized cholesteric polymers networks.[19−21] All aspects relating to LC cross-linked polymer networks are described in detail in two comprehensive books published in 2011[6] and 2016.[7]

Another class of responsive cholesteric materials is that of photochromic systems based on azobenzene derivatives[22−33] or other types of photochromes[34−41] introduced into the low-molar-mass or polymer LC matrices. This approach is fruitful for obtaining photosensitive films with photovariable helix pitch,[24−28,34−41] the possibility of holography recording,[29−33] and a variety of other applications and effects.[22,35,37]

The combination of above-mentioned responsive materials and cross-linked polymer structures with photosensitive moieties opens up new perspectives for materials design and allows one to form mechanically stable films with fast photo-optical[6] and photomechanical responses,[7] photocontrollable adhesion and wettability,[8] and other properties.

The main goal of this paper is the preparation of porous cholesteric cross-linked polymer films which could be used as some sort of scaffolds or “macromolecular containers” for the incorporation of photosensitive nematic mixture with the aim of creating photocontrollable cholesteric films. By changing the cross-linking density of these materials, one can obtain the densely and weakly cross-linked polymer composites which can exhibit some unusual optical properties under light illumination. In this article we will compare the photo-optical behavior of these two types of cholesteric films and demonstrate some features of the photopatterning process.

For this purpose, cholesteric photopolymerizable mixtures consisting of the substances listed in Figure 1 were prepared. These mixtures contain mesogenic diacrylate **RM257** and monoacrylate **A6PhCN** as polymerizable substances forming 3D polymer network under UV irradiation in the presence of photoinitiator **Irgacure 651**. These monomers were dissolved in cholesteric mixtures based on nematic mixture **E48** doped with chiral dopants **CB15** or **HexSorb** (Figure 1). Compositions and the wavelengths of selective light reflection of four prepared mixtures are presented in Table 1. Figure S1a shows transmittance spectra of planar-oriented films of the mixtures after polymerization with selective reflection of light in the visible and the near-IR spectral ranges.

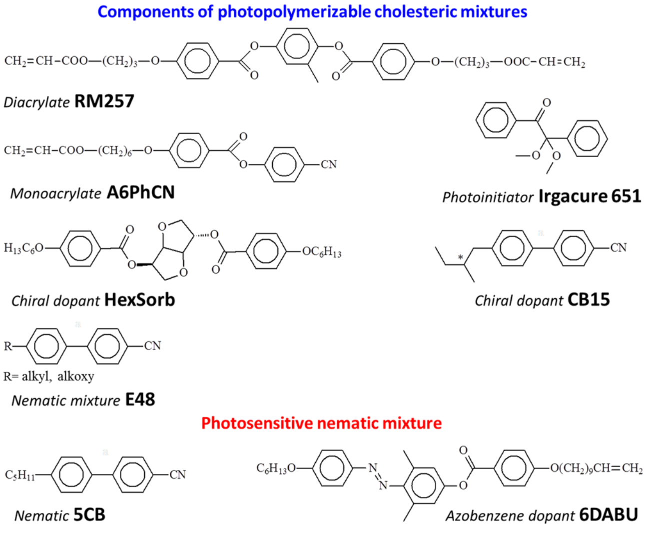


Figure 1. Chemical structures of the compounds used for the preparation of photopolymerizable cholesteric mixtures and photosensitive cross-linked polymer composites.

Table 1. Compositions (wt %) of the Photopolymerizable Cholesteric Mixtures[a]

	E48	CB15	HexSorb	A6PhCN	RM257	λ_{max} (nm)[b]
Mix1	65	11	2	13	8	595
Mix2	25	25			49	650
Mix3	72		2.3	15	9.7	>1000
Mix4	42	18			39	980

[a]All mixtures contain 1 wt % of photoinitiator **Irgacure 651**. [b]Selective light reflection peak (λ_{max}) of the cholesteric mixture after photopolymerization.

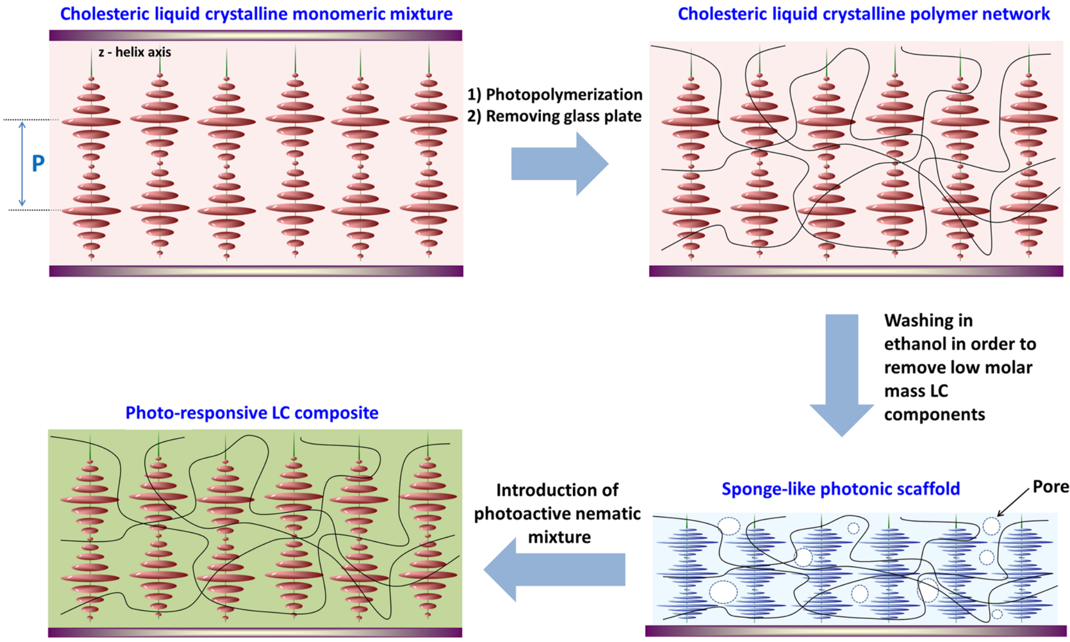
Scheme 1 demonstrates several steps of photoresponsive cholesteric film preparation. The first step includes the photopolymerization of planar-aligned cholesteric mixture between two glass plates under UV irradiation. Then, one glass plate is removed, and the cholesteric gel is washed by ethanol in order to get rid of low-molar-mass compounds. As result, a porous polymer cholesteric network (scaffold) is formed. Finally, a photosensitive nematic mixture containing nematic substance **5CB** mixed with 30 wt % azobenzene-containing substance **6DABU** is incorporated into the pores of the cholesteric scaffold by capillary forces.

Azobenzene-containing substance **6DABU** is capable of *E*−*Z* photoisomerization accompanied by an extreme change in molecular anisometry (Scheme 2a; see also Figure S2). This process causes an isothermal transition from nematic to isotropic state of the prepared mixture (Scheme 2b). Two lateral methyl substituents in **6DABU** molecules increase the photosensitivity of this substance and provide high thermal stability of the photoinduced *Z*-isomer. Experiments have shown that thermal back-conversion from the photoinduced isotropic state into the nematic one is time-consuming at more than 18 days (Figure S3).

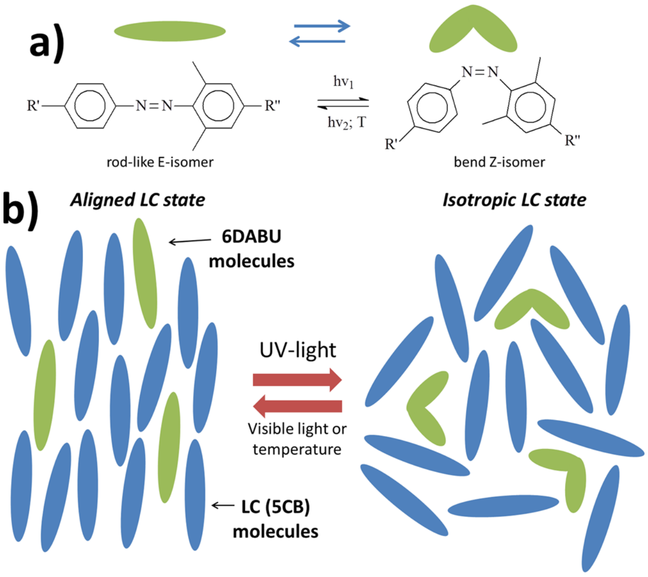
Isothermal phase transition of the photosensitive mixture **5CB+6DABU** incorporated into the cholesteric polymer network could induce two main photo-optical changes. The decrease in birefringence associated with isotropization should decrease the bandwidth of selective light reflection peak. However, isotropic liquid **5CB+Z-6DABU** formed after UV irradiation can be considered a bad solvent for the LC network leading to shrinkage of the LC network. Thus, we may assume that in our case UV irradiation and shrinking of the cholesteric polymer network should result in a decrease of helix pitch values and a shift of selective light reflection to the shorter wavelengths.

Herein, we report the investigations of photo-optical properties of cholesteric polymer-stabilized films in order to demonstrate their great potential for use as “smart” photopatternable media. The influence of diacrylate and chiral dopant concentrations and the degree of filling of cholesteric polymer scaffold by low-molar-mass photosensitive mixture on the photo-optical properties of the polymer composite films is studied.

The method proposed in this paper has important advantage: any LC mixture having low solubility in polymer network, Scheme 1. Schematic Representation of Cholesteric Composite Films Preparation



Scheme 2. (a) *E*/*Z* Photo-Isomerization of Dopant 6DABU (b) and Photo-Induced Reversible Phase Transition from LC to Isotropic State



substances inhibiting photopolymerization, or having strong absorbance could be introduced into such porous matrices. Moreover, the developed method enables fine-tuning of their photo-optical properties by changing the amount of low-molar-mass photochromic mixture absorbed by polymer network.

2. EXPERIMENTAL SECTION

2.1. Materials. Chiral dopant **HexSorb** and acrylic LC monomer **A6PhCN** were obtained as previously described in refs 42 and 43, correspondingly. Nematic diacrylate **RM257**, chiral dopant **CB15**, and low-molar-mass nematic liquid crystals **5CB** and **E48** were purchased from Merck. Azobenzene-containing dopant **6DABU** was synthesized according to the previously reported procedure.[44]

The cholesteric photopolymerizable mixtures **Mix1−4** of different compositions were prepared by dissolving appropriate amounts of components (see Table 1) in chloroform. Then, the solvent was slowly evaporated, and the residue was dried in vacuum at 50 °C for several hours. The mixtures remain homogeneous over 1 week; therefore, they were used for sample preparation within this time.

The photoresponsive mixture containing the commercial nematic liquid crystal **5CB** and the azobenzene based compound **6DABU** in a ratio 70:30 (by weight) was specially designed in order to obtain the capability of isothermal phase transition under the action of UV light. The mixture was prepared by dissolving the components in chloroform, followed by slow evaporation of the solvent and drying in vacuum. Phase separation did not take place during the preparation of the mixture; finally, it was completely homogeneous. Clearing temperature of the mixture was 60−62 °C.

2.2. Sample Preparation. Glass sandwich like cells with thickness of 10 μm were used for cholesteric polymer films preparation. In order to improve adhesion of polymer network, one of the glass substrates was preliminary functionalized by 3-(trimethoxysilyl)propyl methacrylate,[11] whereas the other was treated with triethoxy(octyl)silane in order to decrease adhesion. Freshly prepared cholesteric monomer mixtures **Mix1−4** were introduced to the cells at room temperature. Mixtures were planar-aligned by shear forces followed by photopolymerization under the action of UV light for 10 min (345−355 nm, 12 mW/cm^2). After polymerization and removing one glass plate (hydrophobized one), the cholesteric polymer film was thoroughly washed in ethanol in order to remove all low-molar-mass components and then dried at room temperature for several hours.

At the final stage, photoresponsive mixture **5CB+6DABU** was introduced into the cholesteric polymer network at 70 °C with subsequent slow cooling down to the room temperature; the excess of material was removed from the surface with paper tissue.

2.3. Light Source. The samples were irradiated at room temperature with the collimated light of a high-pressure mercury lamp (100 W, Osram) equipped with an interference filters at 365 nm, $I \approx 0.92$ mW/cm^2, and at 436 nm, $I \approx 0.78$ mW/cm^2. The intensity of light was measured by a PM-100D power meter (Thorlabs).

2.4. Measurements. The absorbance and transmittance spectra were measured for nonpolarized light (unless otherwise stated) using a TIDAS spectrometer (J&M). The polarized optical microscopic investigations were performed using a microscope (AxioPlan2, Carl Zeiss). Observations were performed in both transmittance and reflection modes. As light source for the reflection optical investigations and local sample exposure, a high-pressure mercury lamp aligned with optical microscope was used. The surface relief

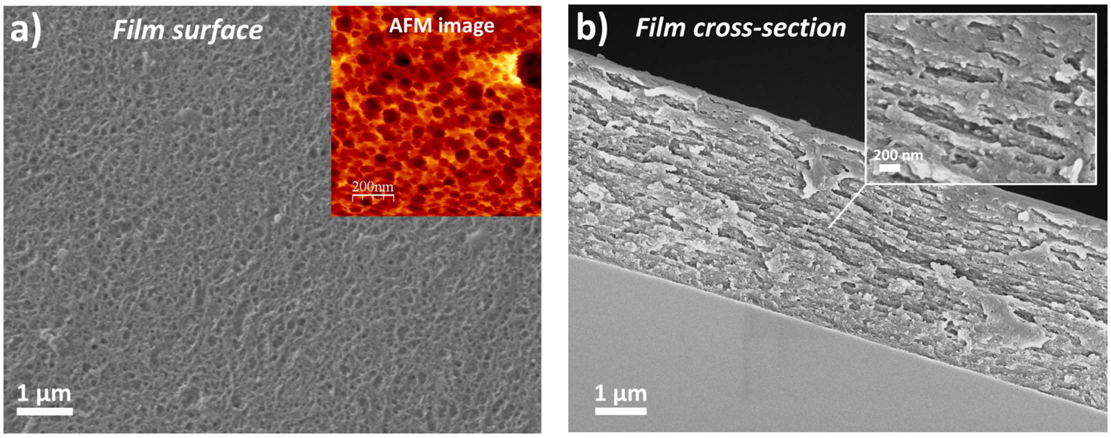


Figure 2. SEM images of the surface (a) and cross section (b) of the cholesteric polymer scaffold based on **Mix2**. Inset in a is AFM image of the surface.

topography of the films was studied by atomic force microscopy (AFM, SPM Smena, NT-MDT) performed in the tapping mode. Film thickness was measured with the help of a profilometer Dektak 150 (Veeco). Scanning electron microscopy (SEM) measurements were carried out with a Neon 40 microscope (Carl Zeiss); samples were covered with gold (30 nm) and imaged with following parameters: ETH, 3.00 kV; aperture size, 30 μm; signal, SE2.

3. RESULTS AND DISCUSSION

First, let us consider how the cross-linked polymer films look after polymerization of the cholesteric mixtures. Figure 2a shows SEM and AFM images of the surface of cholesteric scaffold based on **Mix2** (after polymerization and removing of low-molar-mass substances). Corresponding SEM images of a scaffold cross-section are provided in Figure 2b. As seen in the Figure 2, the polymer film possesses a highly porous structure. Typical pore size lies between 20 and 100 nm. SEM image of cross section (when the cut is directed parallel to the helix axis) of the network displays layer like structure with periodicity of 100−110 nm corresponding to $P/2$ (see eq 1). Cholesteric polymer scaffold based on **Mix1** has lower density and higher porosity due to the reduced content of acrylates (Figure S4). High porosity allows us to consider all these polymer networks as very convenient "containers" for the incorporation of different liquids, including the studied photosensitive nematic mixture. The optical properties of "empty" cholesteric scaffolds used in this work are gathered in Figure S1b. Reasonably, they have selective light reflection in UV region with respect to a considerable shrinkage of cholesteric networks after the removing low-molar-mass components, which is also accompanied by a 2−6 fold reduction of the film thickness. The bandwidth found equals ~50 nm that is much smaller than that of one before washing out. It might be dictated by a lower average birefringence of empty scaffolds.

Since the chiral dopants we used are right-handed, all cholesteric networks prepared and studied in the present work possess right-handed helical structure and selectively reflect right-handed circularly polarized light. Interestingly, the supramolecular chirality is conserved in polymer LC network even after removing all chiral molecular components. Therefore, the empty cholesteric scaffolds as well as ones filled with isotropic liquid also reflect right-handed circularly polarized light (Figure S1c,d).

We have prepared a number of different porous cholesteric scaffolds and filled them with photochromic nematic mixtures **5CB+6DABU**. The thickness of prepared composite films was measured as 9.2, 9.8, 9.3, and 9.4 μm for **Mix1−4**, respectively. For all composite films, UV irradiation results in noticeable changes in their optical properties (Figure 3). These photo-optical changes, as discussed above, are associated with E−Z photoisomerization of azobenzene derivative **6DABU** and an isothermal phase transition of mixture **5CB+6DABU** from nematic to isotropic state (Scheme 2). The E−Z isomerization process was confirmed by investigation of the spectral changes under UV irradiation (Figure S2), whereas the photoinduced transition from nematic to isotropic state is clearly observed by the polarized optical microscopy (Figures S3a, b).

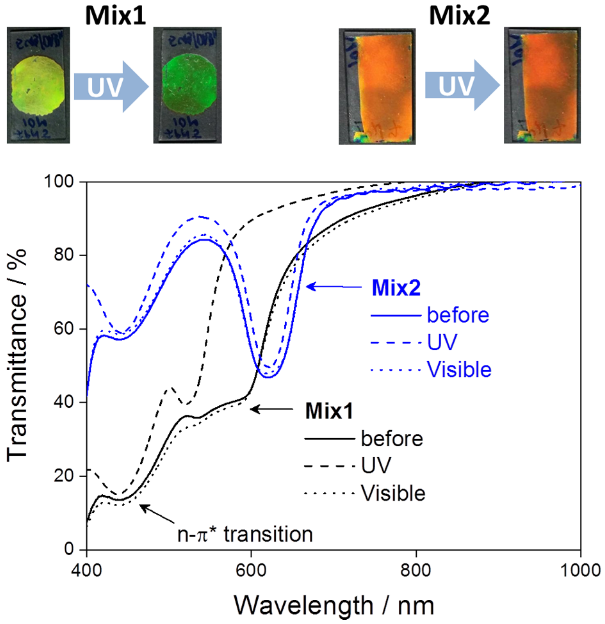


Figure 3. Transmittance spectra of polymer composites based on **Mix1** and **Mix2** before and after irradiation with UV and visible light. Photographs of the samples before and after UV exposure are shown at the top. Irradiation time = 20 min.

It is well-known that the process of E−Z isomerization is thermally and photo-optically reversible. An irradiation of the samples by visible light leads to fast and almost complete recovery of the initial concentration of E-isomer and the nematic phase reappearance. However, at room temperature

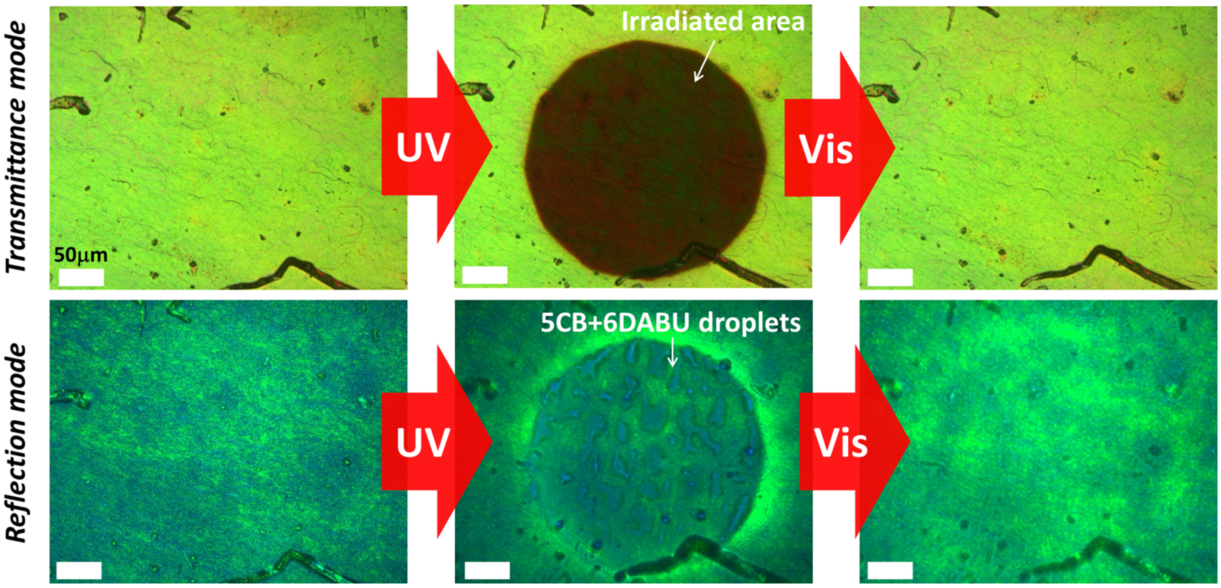


Figure 4. POM images in transmission (top row) and reflection (bottom row) modes of cholesteric composite based on **Mix1** before and after local UV irradiation (365 nm, ∼0.5 W/cm^2, 30 s) followed by visible light exposure (polychromatic light, 1.3 W/cm^2, 40 s).

thermal back-conversion from *Z*- to *E*-isomer is very slow. Formation of first nematic droplets in the UV-irradiated mixture **5CB+6DABU** was detected only after 18 days (Figure S3c), and then the continuous nematic texture filled a wide field of vision. Such high thermostability of the *Z*-isomer offers new perspective of using photochromic mixtures based on **6DABU** for the creation of different materials and devices for photonics.

We have studied the influence of different structural features of prepared cholesteric composite films on their photo-optical properties. **Mix1** and **Mix2** have completely different concentrations of diacrylate **RM257**; in addition, **Mix2** does not contain monoacrylate **A6PhCN**. Such differences lead to the formation of polymer networks with different cross-linking densities. Weakly cross-linked photochromic cholesteric film based on **Mix1** under UV irradiation demonstrates significant shift of the selective light reflection peak to the shorter wavelength accompanied by a decrease of its bandwidth (Figure 3). (Note that for **Mix1** peaks of selective light reflection are highly overlapped with peak associated with $n-\pi^*$ electronic transition of azobenzene chromophore.) For the photochromic film prepared from **Mix2** with six times higher concentration of **RM257**, after UV irradiation the position of selective reflection peak remains unchanged, but a noticeable decrease in peak bandwidth is revealed (Figure 3). Optical changes in selective light reflection wavelength for **Mix1** composite are clearly seen with the naked eye as shown in the inset in Figure 3. A greenish-yellow color of selective light reflection changes to the dark-green one. UV irradiation of **Mix2** film only decreases its relative brightness. An observed decrease in peak bandwidth in both cases is associated with photoinduced reduction in birefringence of the composite films due to the nematic−isotropic phase transition. Notwithstanding the isotropization, the composite film does reflect light with right-handed circular polarization which is confirmed in Figure S1d.

The shift of the selective light reflection peak for cholesteric composite films with low cross-linking density is explained by shrinking of polymer network under UV irradiation. This effect is caused by changes in solvent quality of mixture **5CB+6DABU** due to *E*−*Z* photoisomerization. In the nematic state this mixture can be considered a "good" solvent and it is compatible with scaffold. The mixture containing large concentration of *Z*-form of **6DABU** is isotropic and could be considered a "bad" solvent for the anisotropic cholesteric scaffold. In the latter case, shrinkage of the polymer network with low cross-linking density is observed, resulting in a decrease of its helix pitch value, and a shift of selective light reflection to shorter wavelength is induced. Film thickness measurements of **Mix1** before and after UV exposure have revealed the decrease in thickness by ∼0.7 μm (Figure S5a), which is ∼7%. The measurements of exposed film were carried out after removing of LC droplets from the film surface. Interestingly, the obtained shift of selective light reflection of composite film is about 45 nm (from 565 to 520 nm), in agreement with the value of physical shrinkage of cholesteric network.

The proposed explanation is supported also by several papers[45−47] describing two-component systems comprising nematic polymer network and nematic solvent. It was shown that the thermoinduced transition from the LC to the isotropic state of solvent leads to shrinkage of the LC network.

An interesting phenomenon confirming the shrinkage of the polymer network **Mix1** under UV irradiation is clearly seen in the polarizing optical microscope in reflection mode (Figure 4). Droplets of **5CB+6DABU** mixture in isotropic state appeared on the surface of the mixture after UV irradiation. Subsequent visible light irradiation leads to absorption of the droplets back into the network, yielding its swelling and reappearance of the initial colors in both images taken in transmittance and reflection modes. It should be mentioned that the UV-exposed area looks dark due to very high contrast; nevertheless, this area still reflects light but with shorter wavelength (Figure 3).

The time evolution of the **5CB+6DABU** droplets during their absorption by cholesteric network based on **Mix1** upon visible light exposure is shown in Figure S6. It is noteworthy that for the cholesteric composite based on **Mix2** having high cross-linking density appearance of droplets on the surface has not been observed (Figure S7). This is in accordance with the absence of polymer network shrinking and any changes in

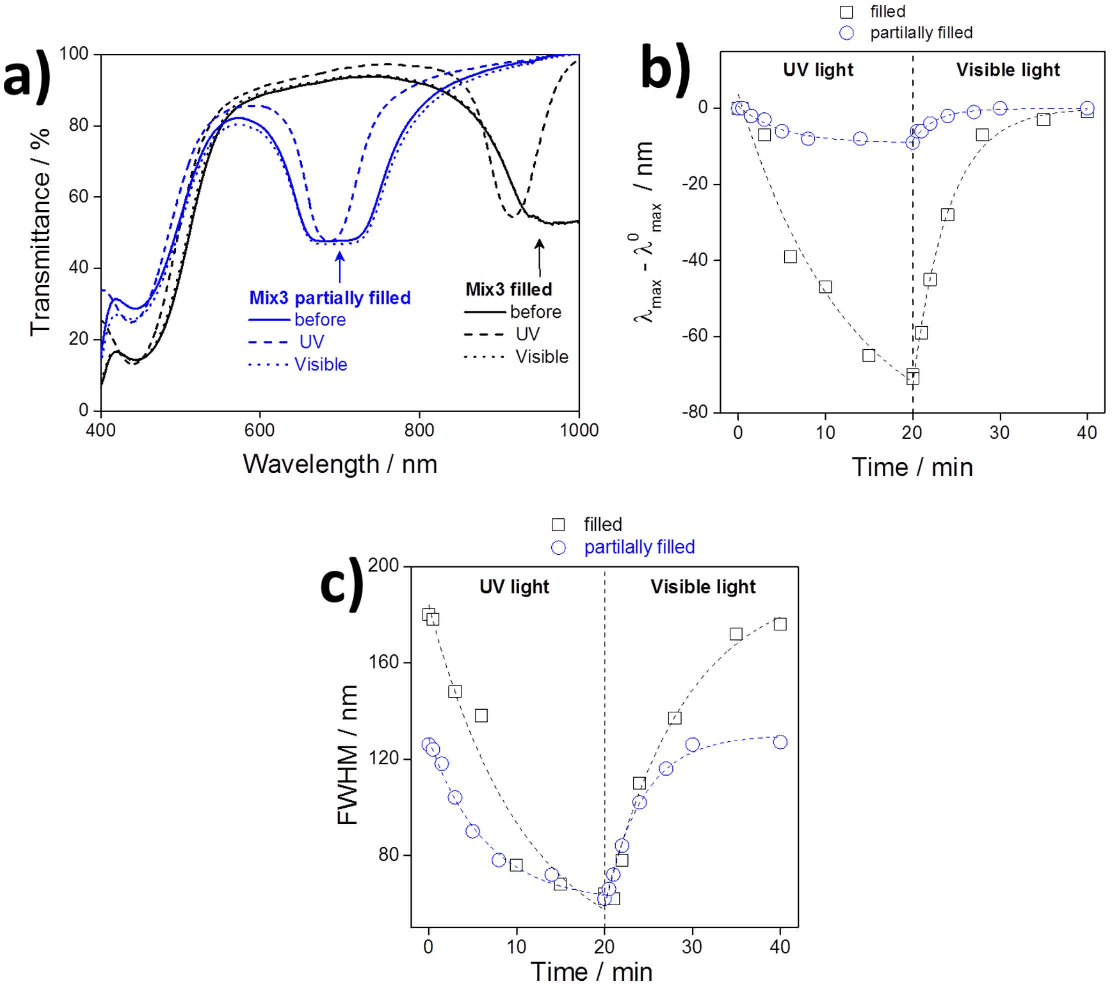


Figure 5. Transmittance spectra of **Mix3 filled** and **Mix3 partially filled** composites during irradiation with UV and visible light (a); dependences of shift of selective light reflection peak (b) and its bandwidth (c) on the UV and visible light irradiation time.

selective light reflection peak position (Figure 3), which was also confirmed by film thickness measurements.

The developed method of the photochromic composite preparation enables fine-tuning of photo-optical properties by changing the amount of low-molar-mass photochromic mixture absorbed by polymer network. For this purpose, cholesteric composite films with different amount of photochromic mixture **5CB+6DABU** have been prepared. One type of the films is completely saturated by the excess of this mixture, denoted as **Mix3 filled**. Another type is partially filled composites (**Mix3 partially filled**). Partially filled composite film was prepared as follows. The drop of **5CB+6DABU** solution in chloroform (20 μL, concentration 1 mg/mL) was spread over the surface (area 2 cm^2) of **Mix3** empty scaffold. After evaporation of solvent, the film was heated up to 70 °C and slowly cooled down to room temperature. This rather simple method allows one to obtain partially filled composite films with homogeneous distribution of mixture **5CB+6DABU** inside the porous cholesteric network.

Due to the different degrees of swelling, these two films have selective light reflection in different spectral regions. Complete saturation of cholesteric polymer network shifts the peak of selective light reflection into the near IR spectral region (>1000 nm), whereas **Mix3 partially filled** has selective light reflection covering the red side of the visible range with maximum at ~700 nm (Figure 5a). The reflection peak position of **Mix3 partially filled** is in agreement with its reduced thickness (6.7 μm in comparison with 9.3 μm for **Mix3 filled**). Moreover, the bandwidth or full width at half-maximum (FWHM) of the reflection peak of **Mix3 partially filled** composite is about 130 nm, which is lower than that for **Mix3 filled** (~180 nm) but is sufficiently larger than that for the empty scaffold (~50 nm, see Figure S1b). The effect of bandwidth variation is associated with amount of LC material having higher birefringent introduced to the cholesteric scaffold.

Different degrees of cholesteric scaffold filling affect the photo-optical behavior of the prepared composite films. UV irradiation of **Mix3 filled** films induces both a strong shift of selective light reflection peak to shorter wavelengths (Figures 5a,b) and a decrease in its bandwidth (Figures 5a,c). The corresponding film thickness reduction is found to be ca. 8% (see Figure S5b). In the case of **Mix3 partially filled** films, only a 2 fold decrease in peak width has been found (Figures 5a, c), and a shift of selective light reflection virtually does not occur. Such difference is explained by the absence of polymer network shrinkage in the case of incomplete filling by the photochromic nematic mixture.

The resulting data have permitted us to demonstrate the possibility of the photopatterning of the cholesteric films. For this purpose, the densely cross-linked composite film based on **Mix4** with selective light reflection in near-IR spectral range has been prepared. UV irradiation of this composite film results in a noticeable decrease in width of the selective light reflection peak (Figure S8). In order to realize photopatterning, the composite films were irradiated by UV light directly through the polarizing optical microscope.

The obtained photorecorded images of different types are shown in Figure 6. Figure 6a presents the circular pattern obtained by stepwise alternation of irradiation by UV and visible light and simultaneous decrease of diaphragm diameter (i.e., decrease of exposure spot). This technique enables us to realize also grating like patterns as illustrated in Figure 6b,c. A multispot grating structure was recorded by UV irradiation through the amplitude mask with the period 90 μm (Figure 6b). Figure 6c shows the locally inscribed grating with the much smaller period (30 μm). In Figure 6d, circular patterns (as in Figure 6a) and a grating like pattern (as in Figure 6b) were combined in order to fabricate more complex optical structures. It should be stressed that such patterns are fully photo- or thermo-erasable; this could be useful for applications. Obviously, the lateral resolution of such patterning is dictated both by cross-linking density of cholesteric network and stability of *Z*-form of azobenzene dopant. Moreover elaborated in this paper approach could be extended, and other photochromic compounds with thermally stable photoinduced forms could be used for photosensitive nematic mixture preparation, e.g. stilbenes, cinnamates, fulgides, and very recently reported fluorinated azobenzenes.[32,33]

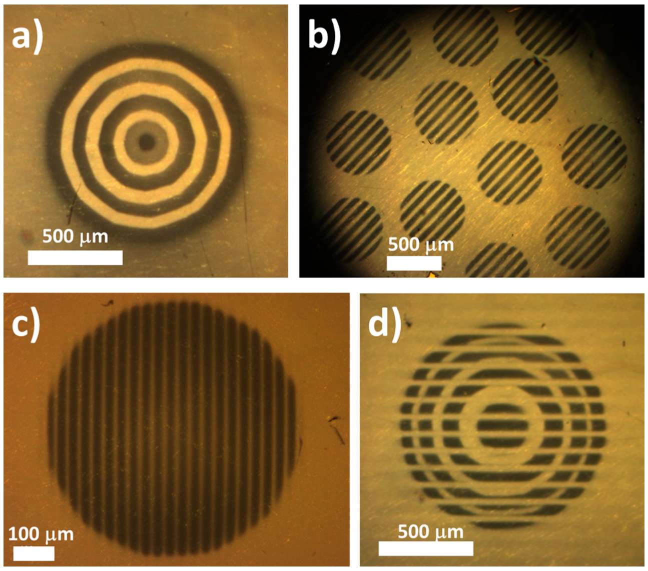


Figure 6. (a–d) POM mages of the patterned structures formed in **Mix4** composite film by UV/visible light exposure.

Thus, the developed cholesteric polymers networks could be potentially exploited in advanced optics and photonics for fine photopatterning, creation of complex diffraction structures, tunable cholesteric lasers, and so on.

4. CONCLUSIONS

The possibility of fast and reversible photocontrol of the optical properties of cholesteric polymer networks is demonstrated. An effective and simple method of introduction of photochromic nematic mixture capable of isothermal photoinduced phase transition nematic−isotropic state is developed. It is shown that cross-linking density and degree of polymer network filling by photochromic nematic mixture play a crucial role in photo-optical behavior of the obtained composite films. In particular, for highly cross-linked films, only a decrease in selective light reflection bandwidth is found, whereas for weakly cross-linked systems two effects, i.e., shift of selective light reflection peak and decrease of its width, are observed. Selective light reflection peak shifts of about 70 nm are achieved. The possibility of fully reversible local phototuning of optical properties of cholesteric polymer networks and, as a result, ability of complex photopatterning are demonstrated. Experimental results obtained in this work show that the developed cholesteric materials are very promising for a variety of photonic applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b09642.

> Absorbance and transmittance spectra of studied composite films, their polarized optical and SEM images as well as surface profiles (PDF)

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Notes

The authors declare no competing financial interest.

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