# Stable Selective Gratings in LC Polymer by Photoinduced Helix Pitch Modulation

Alexander Ryabchun,*[†,‡] Alexey Bobrovsky,[‡] Yuri Gritsai,[§] Oksana Sakhno,[†] Valery Shibaev,[‡] and Joachim Stumpe[†]

[†]Fraunhofer Institute for Applied Polymer Research, Geiselbergstr. 69, Potsdam/Golm, 14476 Germany
[‡]Chemistry Department, Moscow State University, Lenin Hills 1, Moscow, 119991 Russia
[§]Institute of Thin Film Technology and Microsensorics, Kantstr. 55, Teltow, 14513 Germany

**S** *Supporting Information*
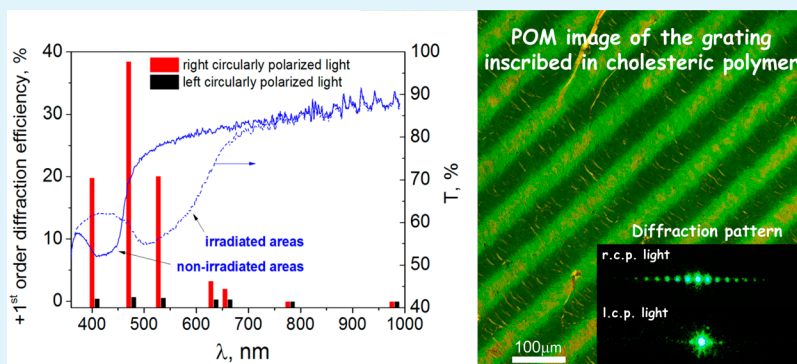
**ABSTRACT:** A cholesteric mixture based on the nematic liquid crystalline side-chain polymer doped with a chiral-photochromic compound was prepared and used as an active medium for creation of stable polarization selective gratings by phototunable modulation of the helix pitch. Such modulation was fabricated in the polymer mixture by a nonpolarized UV-irradiation with spatially modulated intensity that causes E−Z isomerization of a chiral-photochromic dopant, decreasing its helical twisting power. It was shown that the gratings recorded by UV-exposure through a mask are strongly selective to the handedness of circular polarized light. The studied polymer film forms a right-handed helical structure and, correspondingly, the diffraction of only the right-circularly polarized light was found in the transmittance mode. The maximum diffraction efficiencies were found for the wavelength values between the maxima of selective light reflection. The films obtained open very interesting possibilities for further development of materials with stable gratings operating in the entire visible spectral range. Both the position and the width of the spectral range of an efficient diffraction can be easily controlled by the UV exposure and concentration of the dopant. The materials obtained and methods developed can be used for creation of specific diffraction elements for optics and photonics.

**KEYWORDS:** liquid crystalline polymer, cholesteric phase, polarization grating, phototunable helix pitch, selective light reflection

## 1. INTRODUCTION

At the present time the photoresponsive liquid crystalline materials attract considerable attention due to their high potential application in the specific fields of optics, electronics, and photonics as polarization optical elements, modulators, or diffraction gratings for displays, laser devices, sensors, etc.[1−7] One of the most promising types of such materials is cholesteric liquid crystals (LCs), which are characterized by a periodic helical supramolecular structure and high sensitivity to the external fields' actions. The most valuable property of cholesteric mesophase is the selective light reflection. The maximum of the reflection wavelength ($\lambda_{max}$) 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. According to this relation, the variation of the helix pitch simultaneously changes the wavelength of selective light reflection. The important point is that the helical structure of particular handedness induces the Bragg reflection of circularly polarized light of the same handedness. A spectral width of selective light reflection (SLR) depends on the quality of the sample planar orientation (helix axis in the whole sample is directed along normal to substrate) and refractive index anisotropy, $\Delta n$:
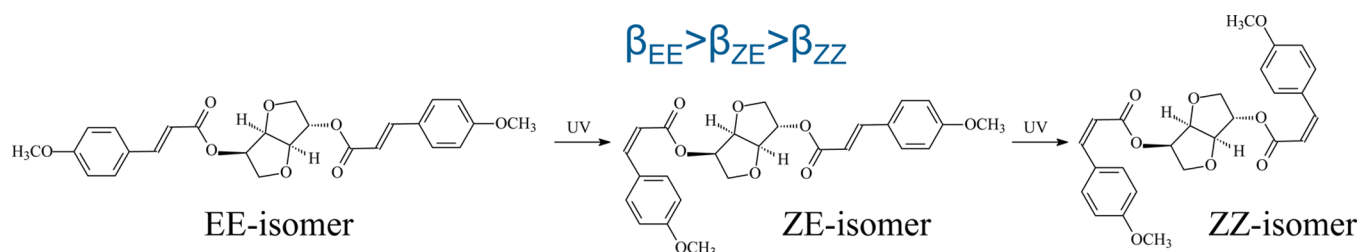
$$\Delta\lambda = \Delta nP \tag{2}$$

**Figure 1.** Scheme of the successive E−Z isomerization of the chiral-photochromic dopant **CinSorb** upon exposure with UV light.
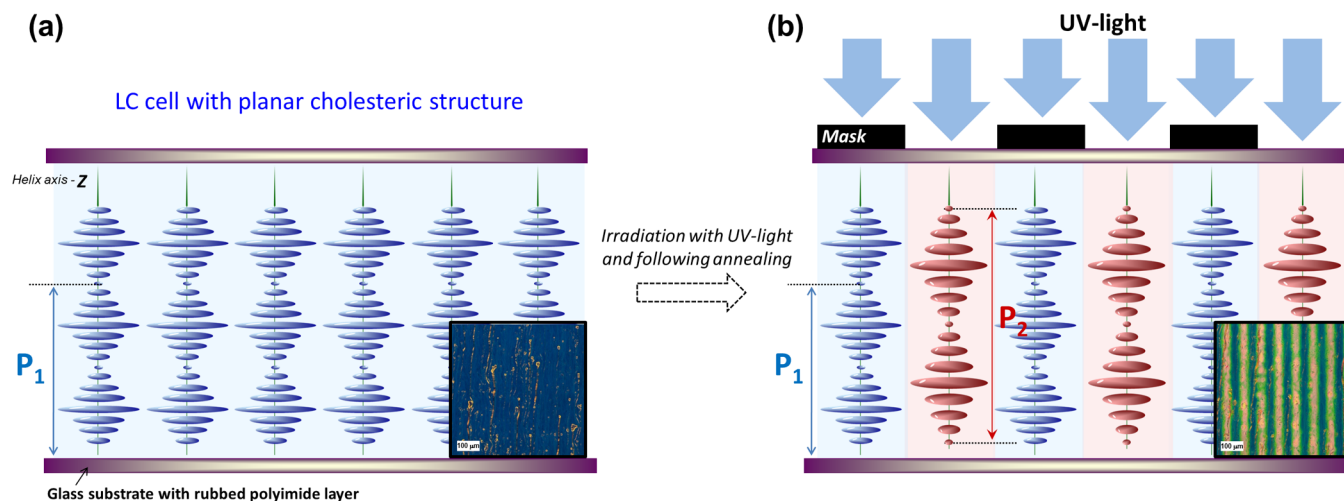


**Figure 2.** Schematic representation of the diffraction grating recorded in the cholesteric polymer **CholPol** with a phototunable helical pitch (a, b). (insets) Polarized optical microphotographs of the observed textures.

The specific values of helix pitch depend on the chemical structure of the substances forming the cholesteric phase. In the most cases the cholesteric mesophase is formed by doping of nematic (LCs) with a chiral additive (dopant) possessing a proper helical twisting power, $\beta$. This phenomenological parameter characterizes the ability of the dopant to twist the nematic structure according to eq 3:

$$\beta = P^{-1}/X \qquad (3)$$

where $X$ is the concentration of the chiral dopant.

One of the most interesting aspects of the application of cholesteric LC materials is the creation of polarization and phase gratings. A number of publications are devoted to the phase gratings that are based on periodically modulated textures ("fingerprint" texture) in aligned cells of the low molar mass cholesteric LCs.[8,9] These modulations are induced and controlled by external electric fields, and they are widely used in optics for beam splitting and steering. Usually these systems can operate in both Raman−Nath and Bragg regimes of diffraction.[10] It was previously shown that periodic fingerprint structures can be effectively stabilized by polymer networks.[11] Two-dimensional gratings based on the undulation of cholesteric layers were previously described as well.[10,12,13] There are also examples of the use of photochromic (often azobenzene-containing) cholesteric polymer systems for holographic applications.[14−17] In the examples, azobenzene moieties are mainly used for the generation of orientation and surface relief gratings (SRG). However, in these cases the cholesteric phase plays only a passive role, which leads to a complete loss of the specific optical properties of this unique material. Nevertheless, in our recent paper[18,19] we described the unusual

dual photorecording based on the combination of photo-induced orientation (with the grating formation) and the selective light reflection typical for cholesteric structures.

However, the number of papers devoted to the grating formation by the modulation of the helix pitch is still limited.[12,20,21] It was shown that for the dye-doped cholesteric mixtures even a small modulation in the helical pitch, with the magnitude ($\Delta P$) of ∼4 nm, is sufficient to observe a diffraction. Such diffraction strongly depends on the polarization of a probe beam.[21] There is also an example of exploitation of dye-doped cholesteric systems for biphotonic gratings using two lasers of different wavelengths (usually an Ar$^+$ ion and a He−Ne laser), when one of them generates an intensity-modulated interference field.[21] In this case turning on/off of the gratings is possible by switching on/off the Ar$^+$ laser beam. Since the gratings in the dye-doped systems are formed by the modulated alteration (and/or disturbance) of the helical order due to the generated Z-isomer of azobenzene nonchiral components, the change of the helical pitch is usually small in comparison with the systems containing chiral-photochromic additives.[22−29] Another feature of the gratings based on all low molar mass LC materials is determined by their instability in the absence of light or electric field. Switching light or electric field off always results in the erasure of the gratings due to diffusion and reverse isomerization of the azobenzene dopants.

To avoid the above-mentioned disadvantages of low molar mass LC compounds used for the gratings preparation and to demonstrate the possibility to fabricate stable selective gratings based on the modulation of helix pitch, in the present work we used a photoresponsive cholesteric mixture (hereinafter

**CholPol**) containing LC nematic polymer (**PAA**) and chiral-photochromic dopant (**CinSorb**), which are shown below:



*Nematic comb-shaped polymer* (**PAA**)



*Chiral-photochromic dopant* (**CinSorb**)
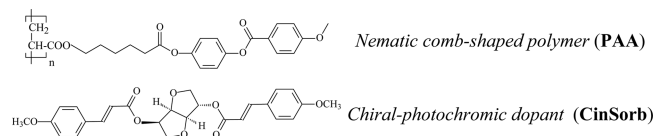
It is well-known that comb-shaped LC polymers combine the sensitivity inherent to LC phase to be oriented under an action of the light, electric, or magnetic fields and the capability for the easy processing. All this allows one to obtain materials in the form of films or thin coatings with desirable structure and optical properties, which could be fixed for a long time period ("frozen") in the glassy state of the polymer materials.[4,5,30−33]

In our work we used **PAA** polymer as a nematic matrix for incorporation of small amounts of the chiral-photochromic dopant **CinSorb**, stimulating formation of a cholesteric phase possessing phototunable optical properties. The dopant **CinSorb** simultaneously contains the molecular fragments of the chiral isosorbitol and the photosensitive derivative of cinnamic acid. The latter undergoes E−Z photoisomerization under UV-light illumination, which significantly changes its molecular configuration. As seen in Figure 1, the rigid rod shape of the initial EE isomer is successively transformed into the bent ZZ isomer, having essentially lower helical twisting power $\beta$ as compared with the initial EE isomer.

The changing $\beta$ values and, as a consequence, a fine phototuning of the helix pitch provides the foundation of this work. The main focus of the present paper is directed to the development and creation of a novel type of cholesteric material with stable selective gratings formed by photoinduced helix pitch modulation.

The developed principle of preparation of cholesteric films based on the aforementioned mixture of polymer **PAA** containing chiral-photochromic dopant **CinSorb** is schematically shown in Figure 2. The chiral photochromic mixture containing 3.6 wt % **CinSorb** and having rather wide temperature interval of cholesteric phase (G 30 Chol 116 I) was placed in the form of a film into the LC cell between two glass plates.

To obtain a diffraction grating, the LC cell with planar cholesteric texture and having a pitch $P_1$ (Figure 2 a) was exposed through the mask with nonpolarized UV light (365 nm) followed by an annealing process at a temperature above the glass transition of the LC polymer mixture. The E−Z photoisomerization of chiral photochromic dopant occurs in the irradiated zones causing a decrease in its twisting power (see eq 3), which in turns results in the untwisting of the cholesteric helix and its pitch ($P_2$) increases (Figure 2 b). Such gratings are adjustable in the wide spectral range and can be visible in the form of alternate color strips on the optical microphotographs in polarized light as shown in the insets of Figure 2.

This paper considers the features of the gratings recording by UV-photoinduced modulation of the helix pitch. For the first time, the results obtained demonstrate the creation of two types of gratings of different disposition—normal and parallel to the film plane. This sophisticated method of the gratings fabrication with high diffraction efficiency (DE) opens new possibilities for their application in nanophotonics and optoelectronics.

## 2. EXPERIMENTAL SECTION

**2.1. Synthesis and Characterization of Materials.** The polymer PAA was prepared by free-radical polymerization of nematogenic 4-phenyl-4′-methoxybenzoate monomer[34] in dry benzene solution with 2 wt % AIBN at 65 °C as an initiator. The obtained homopolymer was purified by the repeated precipitation with methanol and dried in vacuum at 80 °C for 24 h. Molecular masses of **PAA** $M_w \approx 12.6$ kDa, $M_w/M_n \approx 1.96$ were determined by gel permeation chromatography using a Knauer chromatograph (UV detector; columns "LC-100" with the sorbent 1000 Å; solvent = tetrahydrofuran, 1 mL/min, 25 °C, polystyrene standard).

Chiral-photochromic dopant **CinSorb** was synthesized according to procedure described in ref 35. Absorbance spectrum of **CinSorb** is shown in Figure S1 (Supporting Information). The cholesteric mixture **CholPol** was prepared by mixing of nematic polymer **PAA** with chiral-photochromic dopant **CinSorb** (3.6 wt %) in chloroform. The solvent was then slowly evaporated, and residue was dried in vacuum at 90 °C for 24 h. Phase transitions **CholPol**: G30Chol(N*)116I.

The phase transitions of the **PAA** and the mixture were studied by differential scanning calorimetry (DSC) with a Perkin−Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min). The polarizing microscope investigations were performed using a polarizing optical microscope LOMO P-112 (Lomo) and AxioPlan2 (Carl Zeiss) equipped with Mettler FP-86 hot stage.

**2.2. Sample Preparation.** For optical investigations the planar-oriented samples of cholesteric mixture **CholPol** were prepared using the glass cells with polyimide aligning layers (Nissan Chem). The thickness of the cells was 10 $\mu$m. The cells obtained were then filled by polymer cholesteric mixture **CholPol** using the capillary effect at 120 °C, which is above the isotropization temperature (116 °C). After that the samples were slowly cooled to room temperature. The selective light-reflection band was controlled by pre-irradiation with UV light and annealing. Three samples I, II, and III with selective reflection peak at 550, 410, and 650 nm, correspondingly, were prepared. The values of pre-exposure time are gathered in Table 1.

**Table 1. Description of the Studied Samples of Polymer Cholesteric Mixture CholPol**

| name | preirradiation time, s | initial peak of SLR, nm | grating recording time, s | $\Delta$SLR[a], nm |
|---|---|---|---|---|
| sample I | 100 | 550 | 180 | 300 |
| sample II | 0 | 410 | 90 | 120 |
| sample III | 160 | 650 | 90 | 120 |

[a]Spectral difference between SLR peaks of the irradiated and nonirradiated areas after the grating fabrication (i.e., the amplitude of helix pitch modulation).

**2.3. Spectral Investigations.** Electronic transmittance spectra of the **CholPol** samples were recorded using Lambda 2S (PerkinElmer) spectrometer. The optical microscope with reflective objectives (Olympus BX51) combined with spectrometer (Resultec 2200; Xe lamp as a light source) was used for the measuring of local transmittance spectra. The scanning area was $6 \times 6$ $\mu$m.

The samples were irradiated at room temperature with collimated UV light from a high-pressure Hg lamp (HBO lamp, 100 W, Osram equipped with interference light filter at 365 nm; light intensity ≈ 2.13 mW/cm$^2$).

For the monitoring of the grating formation process and determination of the diffraction efficiency of the recorded gratings, the He−Ne laser ($\lambda = 633$ nm, 4.7 mW) and a number of laser diodes were used: 405 nm (1.4 mW), 475 nm (5.3 mW), 532 nm (2.8 mW), 660 nm (3.5 mW), 780 nm (3.3 mW), 980 nm (5.4 mW). Left- and right-circularly polarized laser light was obtained using the polarizer and achromatic quarter-wave plate (optical axis of $\lambda/4$ plane was rotated to $\pm45°$ with respect to the polarizer axis). The intensity of light was measured by LaserMate-Q (Coherent) intensity meter.
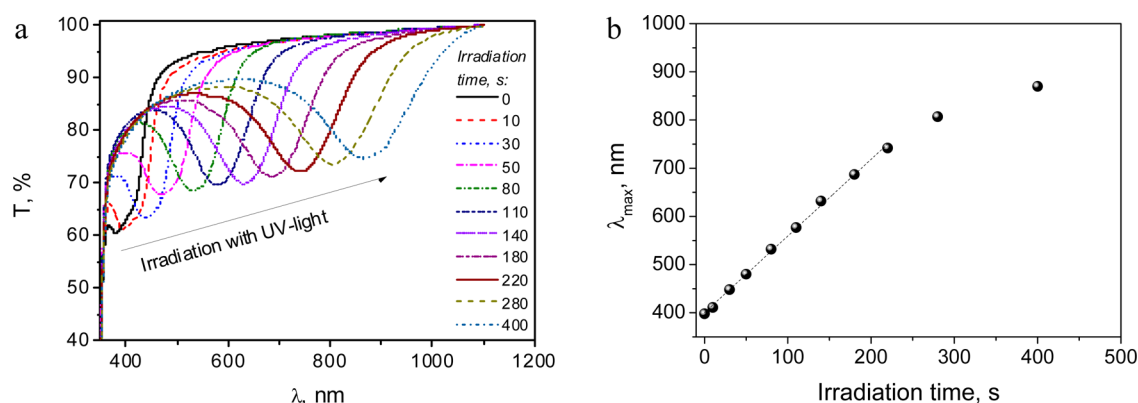
**Figure 3.** Shift of the SLR peak during UV-light irradiation of the planar oriented **CholPol** film (a); kinetics of SLR wavelength shift during the same process (b).

## 3. RESULTS AND DISCUSSION

**3.1. Phase Behavior and Optical Properties of Polymer Cholesteric Mixture CholPol.** According to the polarizing optical microscopy and DSC measurements, the prepared mixture **CholPol** displays a cholesteric (chiral nematic) mesophase with the right-handed helical structure and the isotropization temperature 116 °C, which is ~20 °C lower than that for the initial homopolymer (**PAA**). Such lowering of the mesophase temperature range is explained by the low anisometry of nonmesogenic **CinSorb** molecules, which leads to a partial disruption of the liquid crystalline phase. The glass transition temperature of homopolymer was found to be equal to 30 °C. Planar oriented layer of the **CholPol** with thickness of 10 $\mu$m demonstrated SLR in the UV spectral range, close to the visible one ($\lambda_{max} \approx 410$ nm). It should be pointed out that the sample coloration is not caused by the absorption of light but Bragg by reflection from the periodic supramolecular helical structure (Supporting Information, Figure S2).

**3.2. Photooptical Properties of Polymer Cholesteric Mixture CholPol.** Let us consider the optical properties of the system under study. Figure 3a shows the change in the transmittance spectrum of the sample during irradiation with nonpolarized UV light. The transmittance peak in the spectra corresponds to the SLR by periodical helical structure (Supporting Information, Figure S3). After each irradiation step the cell was annealed at 70 °C for 30 min to stabilize the supramolecular helical polymer structure in accordance with the change of a twisting power of dopant **CinSorb** upon irradiation. Figure 3a clearly shows that the SLR peak is shifted toward red spectral region due to the unwinding of the cholesteric helix. Position of the reflection peak almost linearly depends on the irradiation time (Figure 3b). Additionally a very large shift (by more than 500 nm) of the reflection maximum was observed. Thus, UV irradiation of the **CholPol** film allows modifying its optical properties in the wide spectral fields covering the whole visible and near-IR range.

**3.3. Diffraction Gratings Recording in Planar-Aligned CholPol Films.** For the formation of the diffraction gratings in **CholPol** a striped patterned photomask consisting of transparent and opaque areas with the width of 45 $\mu$m was used. The planar oriented samples were irradiated with UV light through the mask for a certain time followed by an annealing. Thus, the non-irradiated areas keep their initial helical structure with the helix pitch equal to $P_1$ (see Figure 2). The illuminated

zones experience a photoinduced helix deformation, and they are characterized by partially untwisted helical structure. As a result the grating formed consists of the areas of alternating nonchanged and modified supramolecular helical structure.

To study the influence of initial SLR position and the photoinduced shift of SLR on the optical properties of the recorded diffraction gratings, three different planar-oriented samples of cholesteric mixture were prepared (Table 1). The first one possessed a selective reflection in the visible range and high amplitude of helix modulation and, as a consequence, a wide operating range of the grating. Samples II and III had smaller pitch modulation and narrower operation ranges of the inscribed gratings in the UV–vis and vis–near-IR spectral regions, correspondingly.

Sample I was pre-illuminated with UV light during 100 s to shift the initial SLR peak to longer wavelengths. Then the diffraction grating was recorded for three consecutive minutes. The transmittance spectra of the non-irradiated (curve 1) and the irradiated (curve 2) areas are shown in Figure 4. Clearly, the modulation of helix pitch is quite high (the spectral difference between the SLR peaks is of ~300 nm).

The DE was calculated as the ratio of the intensity of ± first-order diffraction beam to the total intensity of all diffraction beams. The values of grating DEs at the emission wavelength of
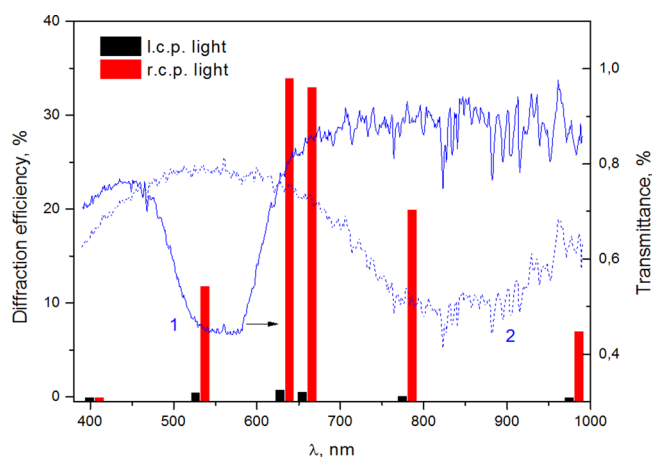


**Figure 4.** Transmittance spectra of the non-irradiated (1) and irradiated (2) areas of sample I. Bars indicate the corresponding diffraction efficiencies for left- and right-handed circularly polarized light.
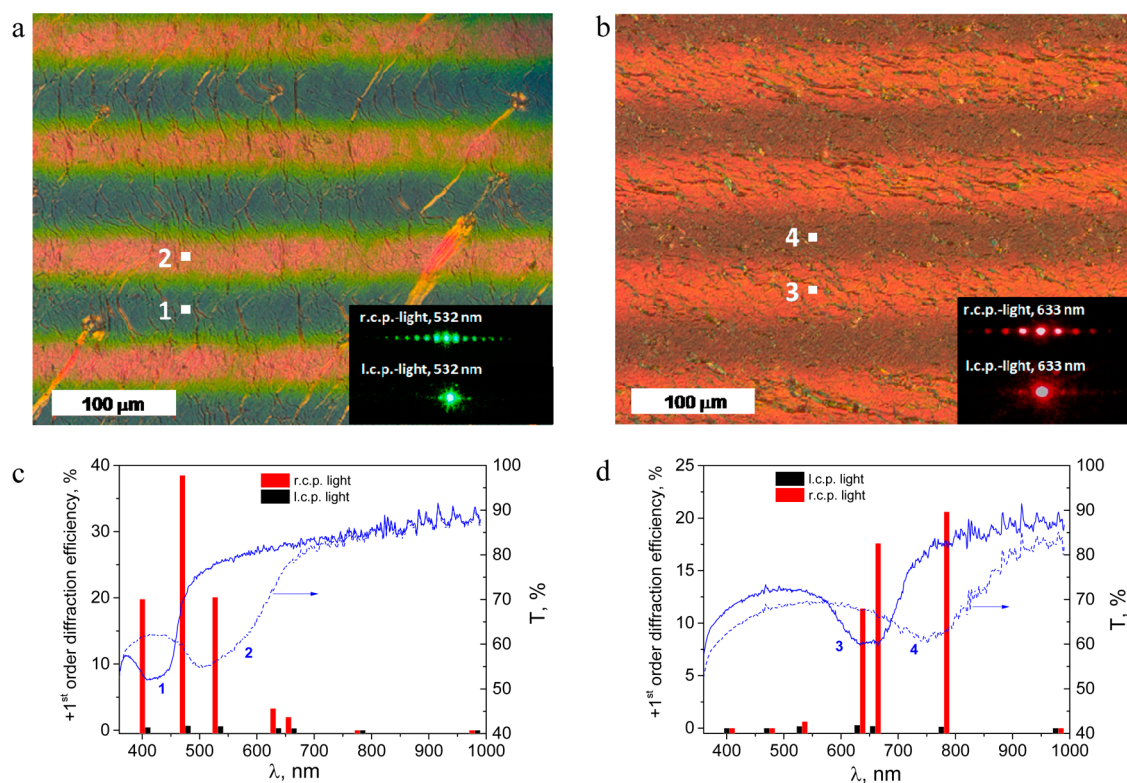
**Figure 5.** Polarized optical microphotographs (between crossed polarizers) of cholesteric textures after the grating formation in sample II (a) and sample III (b) (detailed description see in the text). (insets) The diffraction pattern of the laser beams with right- and left-circular polarization. Transmittance spectra of the non-irradiated (points 1 and 3) and irradiated (points 2 and 4) zones of the sample II (c) and the sample III (d). Bars indicate the corresponding diffraction efficiencies. The spectra 1, 2, 3, and 4 were measured in the same points shown in (a, b).

the laser used are presented in Figure 4 (bars). It is noteworthy that the DE reaches its highest value (~34%) for the wavelengths between two SLR maxima and close to the maximal theoretical DE for thin phase quasi-rectangular grating (of ~40%).[36]

It should be stressed that the DE dramatically depends on light polarization. Right-circularly polarized (r.c.p.) light efficiently diffracts by the grating, while the light of the left-circular polarization (l.c.p.) passes through the sample almost unchanged (DE < 0.4%, which is close to the measurement error). Since the cholesteric helix is right handed, only r.c.p. light experiences the modulation of transmittance. However, the major cause of the diffraction observed is not the modulations of transmittance. First, maximal DE for amplitude grating is rather smaller and does not exceed several percent.[36] Second, maximal DE was observed at wavelength where transmittance in both exposed and nonexposed areas is almost equal. Evidently, the periodical modulation of the refractive index for r.c.p. light in the irradiated and non-irradiated zones ($|n_i-n_n|$) is responsible for the formation of a phase grating in this case. Refractive index for r.c.p. light apparently depends on the values of helix pitch, but detailed description of this complex phenomenon is out of the scope of the current paper.[37]

It was possible to obtain circular-polarization selective grating, which operates in a rather broad spectral range from ~500 to 1000 nm. To create the diffraction gratings operating in a narrower spectral region, sample II and sample III having the initial SLR peaks at 410 and 650 nm, correspondingly, were prepared. In both cases the gratings were recorded for 1.5 min, which is twice shorter than that for sample I. The polarized

optical images of the gratings inscribed in samples II and III are presented in Figure 5a,b, correspondingly. The zones of the different colors are clearly seen. Figure 5c,d shows the SLR bands of the both samples in the irradiated and non-irradiated regions (points 2 and 4, 1 and 3, correspondingly). In both cases the peak shifts of the SLR between the irradiated and non-irradiated zones as large as 120 nm were measured.

The grating DEs at different wavelengths are collected in Figures 5c,d (bars). The DE for the wavelengths corresponding to the reflection peaks reaches ~20%. At the same time the values of DE between those peaks are much higher and run up to 38.5% (Figure 5c; maximal theoretical efficiency = 40%[36]). This finding is in accordance with the phase nature of the recorded grating as discussed above. Another observation is that the inscribed gratings are selective to r.c.p. light. This fact is clearly demonstrated by the diffraction patterns shown in insets at the bottom right corner of Figure 5a,b for both circular polarizations.

Thus, applying nonpolarized UV-light illumination of the cholesteric polymer materials **CholPol** one can create stable gratings, which are selective to a proper circular polarization of light in the desirable spectral range. It should be emphasized that by using the left-handed cholesteric materials one can obtain the diffraction gratings selective to l.c.p. light. Furthermore, the utilization of the spatial designed cholesteric systems with reversible optical tuning and inversion of helix handedness[24−26,38,39] can give the possibility to carry out switchable polarization selectivity of the diffraction gratings.

**3.4. Thermal Behavior and Stability of the Recorded Diffraction Gratings.** Note that the gratings do not appear immediately after irradiation with UV light (this excludes the

formation of a phase grating due to the modulation of the refractive index due to photoinduced E−Z isomerization of dopant) but only during the subsequent annealing. When the temperature rises above the glass transition temperature of polymer, the structural changes lead to the emergence and growth of the DE (Figure 6). The kinetic dependency indicates
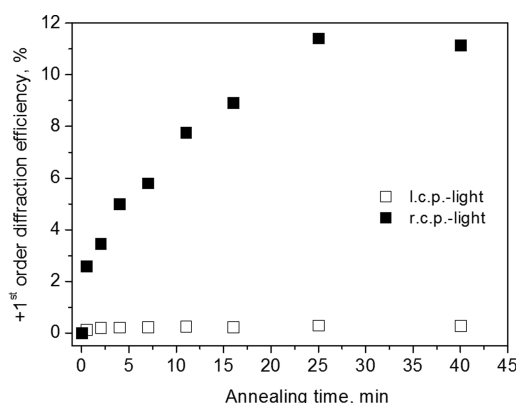


**Figure 6.** Kinetic growth of DE (monitoring with a He−Ne laser, 633 nm) of sample III for both right- and left-circular polarizations during the annealing at 70 °C.

that only the DE of r.c.p. light grows, and 25 min of annealing at 70 °C is sufficient to achieve the maximum value of DE. Further annealing process results in slow reduction of DE due to diffusion of chiral dopant and, as a consequence, spreading of the boundary regions having different helicity. The kinetic curve of DE, which decreases at a prolonged annealing, together with the corresponding polarized optical images, is shown in Supporting Information, Figure S4. During the storage of the sample at room temperature and in daylight no changes in diffraction properties were observed even after eight months of observation. Since the used polymer system **CholPol** is in the glassy state, the recorded polarized selective gratings are stable in time, which is important from the practical point of view.

Thus, the gratings created and studied in this work consist of two subgratings: the first one is the Bragg grating with a periodicity corresponding to a half pitch of the helix and oriented perpendicularly to the film plane. The second grating is the "helix pitch" grating oriented in the film plane. The period of the first grating can be controlled by the UV irradiation conditions. Note that one can reach the fully reversible control by using azobenzene-based chiral-photochromic dopants in the mixture with LC polymers.[24,39] The bandwidth of SLR is dictated by birefringence of the used LC material. The period of the second grating depends on the geometry of the masks used or on the geometry of the holographic experiment (i.e., the period of the UV interference pattern, which can be easily varied), and the value of pitch modulation is dictated by the recording conditions. The presence of two gratings with different natures in the same material gives an elegant and flexible tool for varying and tuning optical properties of cholesteric materials that can be useful for advanced photonics, organic optics, lasing, etc.

## 4. CONCLUSION

For the first time the possibility of creating a stable polarization-selective grating based on polymer cholesteric material was demonstrated. The grating formation is based on

the helix pitch modulation by virtue of the local photoadjustment of supramolecular cholesteric structure. The studied system forms the right helix structure. Only the right circularly polarized light diffraction by the grating was found. The recorded gratings are stable due to the glassy state of the polymer used. The inscribed gratings were a phase type. It was found that the efficient diffraction occurs within the range of SLR peaks, which can be easily controlled. The increase of the exposure dose during gratings recording leads to the broadening of spectral operation range. Pre-illumination of the cholesteric films results in the bathochromic shift of the DE maximum. The theoretical limit of DE of rectangular phase gratings was achieved. Thus, the proposed materials allow to simply create selective diffraction gratings by just using the nonpolarized UV light as well as to adjust flexibly the spectral properties that may be useful in optics and photonics.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Absorbance spectrum of **CinSorb** dopant, photograph of **CholPol** film, circularly polarized light transmittance spectra of polymer cholesteric, and the evolution of DE of sample I during the annealing. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author
*E-mail: ryabchunmsu@gmail.com. Phone: (+49) 15787782958.

### Notes
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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