

Polarization Holographic Grating Recording in the Cholesteric Azobenzene-Containing Films with the Phototunable Helix Pitch

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Abstract: The recording of polarization gratings in films of a cholesteric liquid crystalline polymer with different helix pitch was studied in detail. For this purpose, the cholesteric mixture of the nematic azobenzene-containing copolymer with a chiral-photochromic dopant was prepared. The utilization of such mixture has made possible to realize dual optical photorecording in one system, first due to the phototuning of the helix pitch by UV light and second the polarization grating recording process by exposure with polarized visible light. The diffraction efficiency strongly depends on the cholesteric helix pitch and films thickness: the increase of the confinement ratio d/p (where d , film thickness; p , helix pitch) results in growth of the diffraction efficiency. Comparison of the induction of polarization gratings in cholesteric, nematic (copolymer without chiral dopant), and amorphous (nonannealed) cholesteric films revealed that only the cholesteric films were characterized by significant oscillations in the diffraction efficiency signal as

well as by the presence of the maximum in the first-order diffraction efficiency in the initial stage of the grating recording process. It was found that in addition to the polarization grating surface relief gratings (SRGs) were also formed in the studied systems, however, the amplitude of the SRG inscribed in the cholesteric films was lower (~ 20 nm) compared to the grating amplitude obtained in nematic films (~ 60 nm). Moreover, increasing helix pitch resulted in a decrease of the SRG amplitude. The obtained experimental data demonstrate the great potential of cholesteric LC mixtures of such type for different applications as photoactive materials for photonics. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 773–781

KEYWORDS: azo polymers; cholesteric mesophase; liquid-crystalline polymers (LCP); polarization grating; tunable helix pitch; supramolecular structures

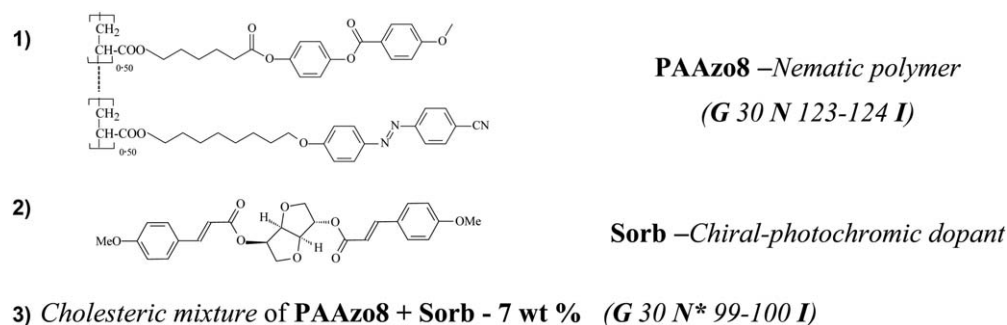
INTRODUCTION Nowadays liquid crystalline (LC) polymers containing azobenzene fragments are a topic of intensive studies. An interest in these compounds is dictated by the presence of azobenzene groups capable of E–Z photoisomerization allowing effective changes of the optical properties of material by different light induced processes. The high optical anisotropy (birefringence, dichroism) typical for LC states makes it possible to use such polymers as materials for optical information recording and storage,^{1,2} phase and amplitude holography,^{2–4} optoelectronics and photonics.^{5–7}

It is well known that under the action of linearly polarized light with wavelengths corresponding to π – π^* or n – π^* electron transitions of the azobenzene fragments a cyclic reversible process of E–Z–E isomerization takes place establishing a

photo-stationary state with a certain ratio of Z and E isomers. Due to the angular selective character of light absorption after numerous repetitive cycles of isomerization, the azobenzene groups become uniaxially oriented in a plane perpendicular to the electric field vector of the incident light. As a rule, the nonphotochromic mesogenic groups included in the azo-containing copolymers become also oriented along with the azobenzene moieties. Thus, owing to the cooperative character of the orientation process very high values of photoinduced optical anisotropy can be reached. This phenomenon underlies the use of these polymers for holographic recording and can result in the formation of polarization gratings in the bulk. Alongside with the modulation of the refractive index in the bulk surface relief gratings (SRGs) are often observed in films of azobenzene-containing

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SCHEME 1 Chemical structures and phase behavior of the nematic copolymer **PAAzo8** (1), the chiral-photochromic dopant **Sorb** (2) and cholesteric mixture (3).

polymers illuminated by two interfering polarized laser beams. Appearance of such SRGs is usually attributed to the photoinduced polymer mass transport.^{8–11}

A very large number of studies on holographic recording have been carried out on azobenzene-containing LC polymers of the nematic and smectic types.^{12–18} However, there are only a few works devoted to the grating recording in photochromic LC polymer systems of cholesteric type.^{19–22a} In these studies, the ability to record polarization gratings (with diffraction efficiency up to ~40%) in relatively thick (>10 μm) films of cholesteric systems as well as combined with the ability to be quick erasing by heating above the glass transition temperature was demonstrated. The general stream of the research in the field of holography is trying to avoid LC systems of the cholesteric type due to the complexity of the study and interpretation of the results, having in mind the creation of the physical models explaining the recording process.

In comparison with the classical amplitude and phase gratings, the polarization grating is notable for the high diffraction efficiency (~100%) in thin material layers and polarization-dependent diffraction, which makes it an effective tool for variety of applications.^{22b}

In this article, the polarization grating recording (PGR) in thin films (<5 μm) of LC polymers with the azobenzene groups is reported. The special attention was paid to the PGR in the cholesteric LC polymers films. The results were compared with those obtained for the nematic films (both, the uniaxially oriented and nonoriented ones). Revealing of the features of the polarization-grating recording in cholesteric azobenzene-containing polymer systems and the attempt to explain their origin is a major and important goal of this work.

Investigation of the PGR in cholesteric systems seems to be very important since such systems revealed a new remarkable feature, which is the possibility of performing dual photorecording. In our previous article, we have shown that it has become possible to realize such dual photorecording in cholesteric system based on two different photoprocesses (i) the helix pitch phototuning by UV light and (ii) the holographic diffraction grating recording by polarized visible light, which might be very interesting for a number of applications.²³

In order to perform the reliable comparison of the holographic grating recording process in the cholesteric and nematic polymer systems the special selection of the polymers with close chemical structure, molecular mass characteristics and glass transition temperature is required. For this reason, we have chosen the following azobenzene-containing LC polymer systems: the nematic copolymer **PAAzo8** (1) and its mixture (3) with the chiral-photochromic dopant **Sorb** (2) (based on isosorbital and cinnamic acid) forming the cholesteric phase (Scheme 1).

Synthesized copolymer **PAAzo8** contains the azobenzene-based side group in the one of the monomers. **PAAzo8** forms a nematic phase with the clearing temperature 123–124 °C. The azobenzene groups are known to exist in two isomeric states, the thermodynamically stable *trans* (or E) and a meta-stable *cis* (Z) form. Therefore, when they are irradiated by light of appropriate wavelength they undergo a multiple reversible *trans* to *cis* photoisomerization processes.²⁴ Upon exposure with linearly polarized light, photoinduced optical anisotropy is generated as result of photoalignment of the azobenzene molecules perpendicular to the electric field vector of the actinic light.²⁵ Additionally, when the polymers functionalized with the azobenzene derivatives are illuminated by two interfering beams the cyclic photoisomerization of azobenzene groups can lead to a large-scale mass transport of the polymer which results in the formation of surface relief gratings.^{9,26}

It is well known that planarly oriented films of cholesteric materials possess a unique optical property associated with the selective light reflection.²⁷ The wavelength of selective light reflection (λ_{\max}) is determined by the pitch of the supramolecular helix (p) according to the eq 1:

$$\lambda_{\max} \sim np \quad (1)$$

where n is the average refractive index of the material (it is of about 1.6 for azobenzene-containing polyacrylates).

Values of a helix pitch depend on the helical twisting power of chiral fragments, in other words, on their ability of cholesteric helix induction. The helical twisting power is predetermined by the geometry of chiral moieties that allow one to explore approaches for the creation of materials with a

phototunable helix pitch and selective light reflection wavelength. These approaches in most cases deal with the introduction in LC-system chiral dopants capable to E-Z photoisomerizing under light action.²⁸ Moreover, there is another new approach of the helix pitch phototuning based on nano-localized heating.²⁹

In order to realize phototunability of a helix pitch in the present work, we have introduced in the nematic polymer the low-molar-mass chiral-photochromic dopant **Sorb** (Scheme 1). The main feature of the dopant **Sorb** is the consecutive isomerization of two double C=C bonds taking place under the action of UV light.³⁰ This photoinduced isomerization leads to a decrease in the dopant's twisting power, which in turns causes the untwisting of the cholesteric helix. Thus, the irradiation of the film of the studied cholesteric mixture with UV light causes the untwisting of the supramolecular helix and results in large changes in the optical properties of the film.

The prepared mixture (3) of **PAAzo8** and **Sorb** (7 wt %) displays a cholesteric (chiral nematic) mesophase with the right-handed helical structure and the isotropization temperature 99–100 °C, which is of about 25 °C lower than for the initial copolymer (Scheme 1). Such lowering of the mesophase temperature range is explained by the low anisotropy of nonmesogenic **Sorb** molecules which, in a consequence, leads to partially disruption of the LC phase. The glass transition temperature for both polymeric systems was about 30 °C.

It is noteworthy that the prepared cholesteric mixture is very complex since it contains (i) the LC groups responsible for the formation of the nematic phase, (ii) the photoisomerizable azobenzene-based groups responsible for the creation of the photoinduced optical anisotropy and the formation of surface relief gratings, and (iii) the chiral dopant responsible for formation of the cholesteric phase possessing the additional feature which is the photoinduced isomerization, caused by the UV light, leading to untwisting of the cholesteric helix. Because of this complexity, using of such cholesteric mixture makes possible to (i) realize the variable helical pitch within the same material and also (ii) realize and distinguish two different processes the process of phototuning of the helix pitch and the polarization holographic grating recording.

EXPERIMENTAL

Synthesis and Characterization of Copolymer and Mixture

Nematic photochromic LC polymer was synthesized by a copolymerization of cyanoazobenzene-containing monomer with the nematogenic phenylmethoxybenzoate monomer. 4-Cyanoazobenzene and 4-phenyl-4'-methoxybenzoate monomers were obtained according to the previously described procedures.^{31,32} Chiral-photochromic dopant **Sorb** was synthesized as stated before.²⁷ The copolymer **PAAzo8** was prepared by radical polymerization of equimolar mixture of

monomers in dry benzene solution at 65 °C; 2 wt % of AIBN was used as an initiator. The obtained copolymer was purified by the repeated precipitation with methanol and dried in vacuum at 80 °C for 24 h. **PAAzo8** possesses the following molecular mass characteristics: $M_w \sim 11.8$ kDa, $M_w/M_n \sim 1.8$. Molecular mass was determined by GPC using a "Knauer" chromatograph (UV-detector; columns "LC-100" with the sorbent 1000 Å; solvent – THF, 1 mL/min, 25 °C, PS-standard). The cholesteric mixture was prepared by mixing of nematic copolymer **PAAzo8** with chiral-photochromic dopant **Sorb** (7 wt %) in chloroform. Then the solvent was slowly evaporated and residue was dried in vacuum at 90 °C for 24 h.

The phase transitions of the polymer and mixture were studied by the 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 microscopes LOMO P-112 (Lomo) and AxioPlan2 (Carl Zeiss) equipped with "Mettler FP-86" hot stage.

Film Preparation

Cholesteric films were prepared by the spin-coating (2000 rpm, 1 min) of the chloroform solution of the cholesteric mixture (**PAAzo8** and 7 wt % of **Sorb**) on glass substrates with the rubbed polyimide layer. After preparation, films were annealed at 85 °C for 5 h and slowly (1 K/min) cooled down to room temperature. In order to change the helical pitch, films were irradiated by UV light (HBO lamp, 100 W, "Osram" equipped with an interference light filter at 313 nm; light intensity ~ 1.2 mW/cm²) and then they were annealed as described previously. Film thickness was measured with the help of profilometer "Dektak 150" (Veeco). In all cases of the cholesteric films (except amorphous cholesteric film) the helix axes were perpendicular to the film plane and all films have a selective light reflection property.

Nematic films were prepared by spin-coating of the chloroform solution of the **PAAzo8** polymer on a glass substrate with and without rubbed polyimide layer, and then they were annealed. Amorphous film of the cholesteric mixture **PAAzo8+Sorb** was obtained as describe above but without following annealing, because the rate of solvent evaporation is very high that is preserve films from LC order formation.






Spectral Investigation

Absorbance spectra of the spin-coated polymers films were recorded using "Lambda 2S" (Perkin Elmer) spectrometer. Circular polarized light absorbance spectra were measured by "Lambda 19" (Perkin Elmer) spectrometer equipped with polarizer and achromatic quarter-wave plate (optical axis of $\lambda/4$ plane was rotated to +45°/–45° with respect to the polarizer axis).

Holographic Grating Recording

The polarization grating was recorded using Ar⁺ laser light at wavelength $\lambda = 488$ nm (Innova 90, Coherent). The intensities of the interfering beams were the same and equal to about 250 mW/cm² and the exposure time lasted 1 h. Films

TABLE 1 The Resulting Polarization Pattern of the Light Interference Used for the Grating Recording for $\pm 45^\circ$ Polarization Geometry

Position (x)	0	$\Lambda/4$	$\Lambda/2$	$3\Lambda/4$	Λ	Light Intensity in the Film Plane (x,y)
$\pm 45^\circ$						I

I is a sum of light intensities of the interfering beams.

were illuminated by the interference pattern of two orthogonally polarized beams. Polarization planes of laser beams were $+45^\circ/-45^\circ$ with respect to the incidence plane. The resulted polarization distribution in the interference pattern is presented in Table 1. The angle between the beams was set to 10.4° , which corresponds to a grating period $\Lambda \sim 2.7 \mu\text{m}$ (according to $\Lambda = \lambda/2\sin(\theta/2)$). The grating formation process was monitored *in situ* by the weak power He-Ne laser ($\lambda = 632.8 \text{ nm}$, 2.8 mW , s-polarization). The first-/second-order diffraction efficiency values were calculated as the ratio of the intensity of the first-/second-order diffraction beam to the initial probe beam intensity. All experiments were made at room temperature. In the case of aligned samples the rubbing direction of polyimide coating was vertical.

AFM Measurements

The surface relief topography of films was studied by atomic force microscope (MultiMode Scanning Probe Microscopy, Digital Instruments, Veeco Metrology Group) performed in the tapping mode.

RESULTS AND DISCUSSION

Polarization Grating Recording in Cholesteric Films with Different Helix Pitch

The polarization grating recording was performed in the cholesteric films with different helix pitch using a holographic setup previously described in ref. 33. The film was irradiated by the polarization interference pattern formed by two linearly orthogonally polarized beams with polarization planes at $\pm 45^\circ$ to the incidence plane. Such polarization configuration characterizes the constant intensity along the grating wave-vector and spatially variation of the resultant polarization state between linear, elliptical and circular ones (more details in Experimental part, Table 1). The angle between the beams was fixed to 10.4° resulting in a grating period $\Lambda \sim 2.7 \mu\text{m}$. Intensities of the interfering beams were the same and equal to about 250 mW/cm^2 . The exposure time was 1 h. The grating formation process was monitored *in situ* by s-polarized low power probe beam at 633 nm by measuring the intensity of both first- and both second-orders diffraction signals, that is, $\pm 1\text{th}$ and $\pm 2\text{th}$, respectively. The first-order (second-order) diffraction efficiency (DE), defined as a ratio between the intensities of the first-order (second-order) diffracted beam and the incident beam, was measured as function of irradiation time. The films after the grating inscription were exam-

ined by atomic force microscope (AFM) in order to evaluate the amplitude of the surface relief grating.

The diffracted signal observed during the holographic grating recording usually results from the light diffraction on the phase grating, due to the refractive index changes and/or film thickness changes, and on the amplitude grating, resulting from the changes of absorption coefficient.^{34,35} In the case of amorphous polymers containing azobenzene derivatives, the mechanism of the grating formation process is well understood.^{34,35} It has been established that three coupling phase gratings are formed simultaneously during the holographic grating recording: the reorientation grating, the bulk density grating and the surface relief grating. The reorientation grating is related to the geometrical changes of azobenzene groups arising from the E-Z-E photoisomerization cycles an light-induced orientation, whereas the bulk density and the surface relief gratings result from the spatial reorganization of the polymer (initiated by the photoisomerization of the azo-groups as well) caused by mass transport in the bulk of the polymer material (bulk density grating) and expressed as the surface corrugation (surface relief grating). The absorption grating results from the molecular reorientation process due to the angular hole burning and dichroism caused by photoalignment of azobenzene derivatives. This model can be used to explain the process of the grating recording in the systems reported in the present study keeping in mind the differences. Very important is the LC nature of the samples. Thereby the volume grating and the surface relief grating originate not only from the reorganization of the main polymer chain, but also from the aligning of the mesogenic side groups. The mesogens, through the cooperative motion, have a tendency to align along with the azobenzene derivatives. Moreover, the presence of the chiral dopant that leads to the helical supramolecular organization inside the system can hinder the process of the light-induced reorientation of the azobenzene moieties, the mesogens reorientation; thus, the process of the grating formation. The influence of the helical organization was revealed in studies on the dichroism and photoreorientation processes in the cholesteric azobenzene-containing polymer mixture a very similar to the mixture investigated here.³¹ Thus, it seems to be clear that during the holographic grating recording process there is a competition between the existing helical organization and just emerging the periodical organization resulting from the process of the grating creation.

The presence of chiral-photochromic dopant in the prepared cholesteric mixtures provides the easiest way to manipulate

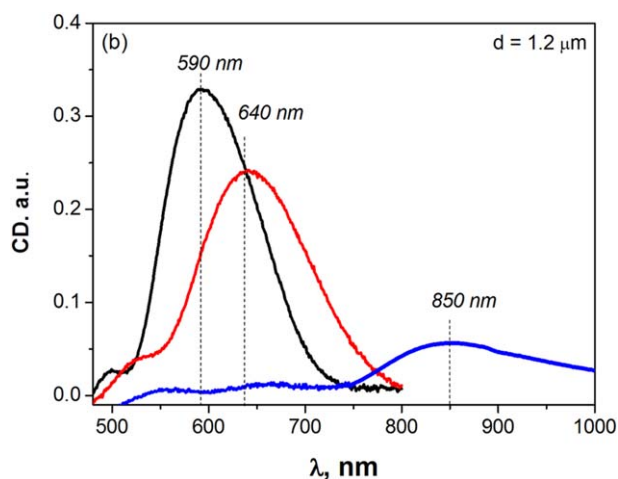


FIGURE 1 Circular dichroism spectra of films of the cholesteric mixture **PAAzo8+Sorb** with different helix pitch (at fixed thickness, $d \sim 1.2 \mu\text{m}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the cholesteric helix pitch and examine its influence on the holographic recording. Thus, three films of the cholesteric mixture with the same film thickness ($d \sim 1.2 \mu\text{m}$), but with different helix pitch were prepared. In order to change the helical pitch of the films UV light with $\lambda = 313 \text{ nm}$ (corresponding to the maximum absorption of the chiral-photochromic dopant **Sorb**) was applied with different irradiation times. It is worth noting that the UV wavelength and the maximum absorption of the azobenzene fragments are widely separated (cf. Supporting Information Fig. S1a). The influence of the irradiation time on the selective light reflection wavelength is shown in Supporting Information Figure S1b where it can be seen that longer UV exposure time causes the shift of the λ_{max} to longer wavelength. Due to the difference in the absorption maxima of the chiral-photochromic dopant and the azobenzene moieties it becomes possible to control the helical pitch by irradiation with UV light at 313 nm and to record the diffraction grating using an Ar^+ laser with 488 nm line.

Using aforementioned procedure, we have obtained cholesteric films of the mixture **PAAzo8+Sorb** possessing a maximum of the selective light reflection at ~ 590 , ~ 640 , and $\sim 850 \text{ nm}$, or expressed in the values of the helix pitch p : ~ 370 , ~ 400 , and $\sim 530 \text{ nm}$, respectively, which corresponds to the UV irradiation (313 nm, at 85°C with the following annealing for 5 h) for 0, 15, and 180 s, respectively (Fig. 1). The films thickness corresponding approximately to two or three values of the helix pitch is sufficient for the effective light reflection, and, as a consequence, for high values of the circular dichroism (CD). Figure 1 shows the spectra of the circular dichroism of the three prepared films (the principles of CD spectrum measurements are briefly discussed in the Supporting information Fig. S2). It is understandable, that increase of the helical pitch p (or λ_{max}) leads to reduced number of the helix turns placed within the film thickness and thus causes a decrease of the intensity of the peaks in the spectra of the circular dichroism, (in another words, the efficiency of the right-circular polarized light reflection is reduced (cf. Fig. 1).

Figure 2 shows the first-order (+1st) DE dynamic curves of the cholesteric films with different helix pitches. Corresponding curves of -1st and $\pm 2\text{nd}$ orders of the diffraction efficiency are collected in Supporting Information Figure S3. The values of the $+1\text{st}$ order DE and the amplitudes of the surface relief grating are compared in Table 2 (corresponding data for -1st and $\pm 2\text{nd}$ orders DE are gathered in Supporting information Table S1).

The gratings had started to be formed right after turning on the writing laser. Very fast increase in the diffraction efficiency was observed at the beginning of the grating recording reaching the maximum. Subsequently, DE started to decrease and again slowly increase reaching the saturation level within the first few hundred of seconds. The saturation was characterized by considerable oscillations. When discussing about oscillations one fact should be recalled. The curves of the diffraction efficiency reported in the present studies come from the diffraction of the monitoring beam coming of the He-Ne laser. If it would be a case of self-diffraction, that is, the measured diffraction efficiency comes from the diffraction of one of the writing beams, for which oscillations can be

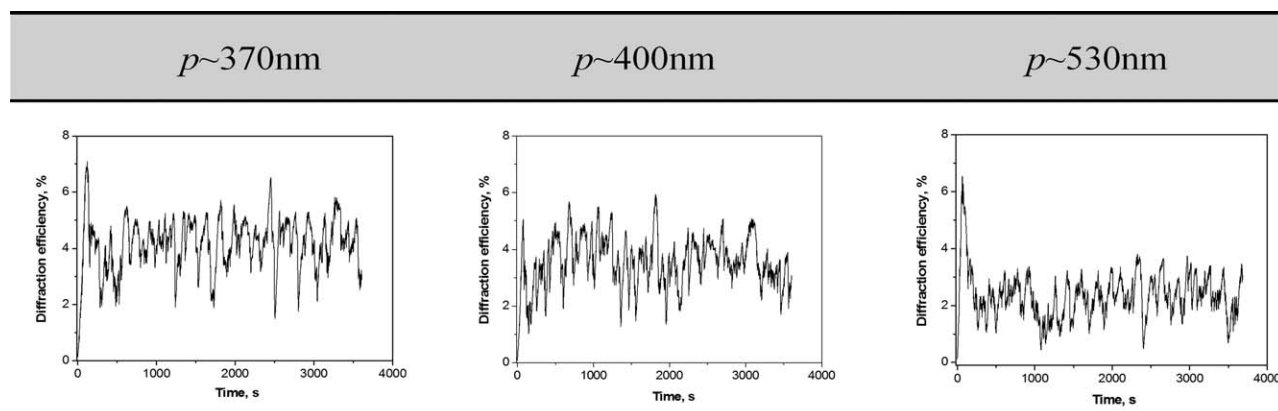


FIGURE 2 First-order (+1st) diffraction efficiency dynamics for films of the cholesteric mixture **PAAzo8+Sorb** with the same film thickness ($d \sim 1.2 \mu\text{m}$), but with different helix pitch p .

TABLE 2 First-Order (+1) Diffraction Efficiency (DE) and the Amplitude of the SRG (Δd) for the Cholesteric, Nematic and Amorphous Films of Azobenzene-Containing Polymer Systems

	Film Thickness, d (μm)	Helix Pitch, p (nm)	(+1st) Order DE (%)	SRG Amplitude, Δd (nm)
Cholesteric films of mixture PAAzo8+Sorb	1.2	370	4.2	21
	1.2	400	3.7	13
	1.2	530	2.4	7
Nematic film of copolymer PAAzo8	1.2 ^a	–	5.7	58
	1.2 ^b	–	5.2	54
Amorphous films of mixture PAAzo8+Sorb	1.5	–	6.6	10

^a Uniaxially oriented nematic film.^b Nonoriented nematic film.

very often observed,^{35–37} they could have been easily explained by the energy exchange between the beams.³⁴ In our case, the origin of the oscillations is different. They can be explained by the mentioned above competition between the helical organization and the growing grating, which, in order to be created, requires the orientational reorganization of the system. The proof of this explanation is given later. After the comparison of these results with those obtained for nematic films, it becomes clear that the presence of the cholesteric mesophase in the system is the reason why the oscillations are observed in the diffraction signal.

It can also be seen on Figure 2 that the increase of the helix pitch has led to the noticeable decrease in the DE values (cf. Table 2). This feature can be resulted by the decrease of SRG amplitude and as consequence diminishing the contribution of the surface grating to the total diffraction efficiency. We also have studied the cholesteric film with different thickness at constant pitch (diffraction efficiency curves and spectra of circular dichroism are gathered in Supporting Information Figs. S4 and S5). It is noteworthy that not only the helix pitch is important for hologram recording efficiency, but DE values also depend on the confinement ratio³⁸ d/p (where d , film thickness; p , helix pitch). It was found the diffraction efficiency of both orders grows linearly with the increasing of confinement ratio (Fig. 3).

Therefore, it can be concluded that in the systems having more full turns of a helix within the film thickness, and, therefore, having the stronger helical organization inside, the process of formation of the diffraction grating is more effective. The confirmation of this fact is given in the part devoted to comparison the nematic, cholesteric, and amorphous films.

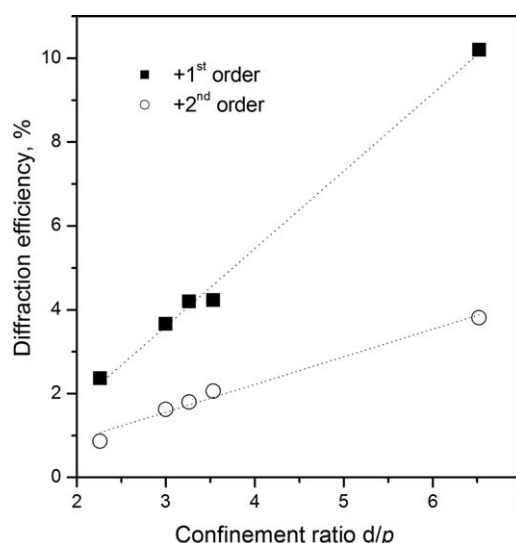
Effect of Holographic Grating Recording on the Selective Light Reflection of Cholesteric Films

It is noteworthy that in all discussed cases so far after the holographic grating recording performed for about 1 h a complete destruction of the cholesteric helical structure had occurred. This was confirmed by the absence of the selective light reflection after such a relatively long process of writing

which is shown in Figure 4. Although after annealing of the films at temperatures above T_g , the diffraction grating was erased, and the cholesteric supramolecular helix was re-established and the ability of the selective light reflection was recovered (cf. Fig. 4). On the other hand, when the process of the grating inscription will be stopped in the right time such the system will possess both the ability of the selective light reflection and the light diffraction. This feature was already explored and possibility of such dual photorecording was reported in detail in ref. 23.

Peculiarities of the Surface Relief Grating Formation in Cholesteric Films

Let us consider the peculiarities of photoinduced surface relief grating formation in cholesteric films. Figure 5 shows the microphotographs of the polarizing optical microscopy (POM) and the surface relief scans measured by the atomic force microscopy (AFM) of the cholesteric film before and after the

**FIGURE 3** Diffraction efficiency versus confinement ratio d/p of the cholesteric polymer films PAAzo8+Sorb.

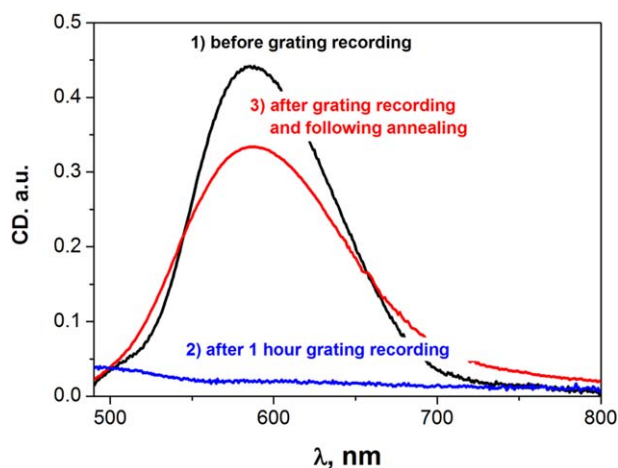


FIGURE 4 Spectra of circular dichroism (CD) of the cholesteric films (**PAAzo8 + Sorb**) before (1) and after the grating recording performed for 1 h (2) and after annealing for around 3 h at 85 °C (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grating recording process. The original film made from the mixture had an oily streaks texture typical for the cholesteric mesophase. The surface topography studied by AFM revealed many “hills” and “valleys,” which is also typical for cholesteric materials.³⁹ Such an unusual topography at the free surface is determined by the competition of homeotropic boundary condition at the interface air-liquid crystal and the planar orientation in the bulk of the films. After 1 h of grating recording, the bulk diffraction grating was formed which was clearly observed in POM microphotographs. The neighboring bright (or dark) grating lines correspond to the regions with the mutual orthogonal orientation of the side groups of the copolymer. It should be mentioned the illumination of the sample with the interference pattern of two orthogonal laser beams brings to either areas with linear and circular birefringence.^{40,41} The periodicity of the grating lines observed in POM images (the distance between two bright or black lines corresponds to the half of grating period, i.e., $\Lambda/2$) and the grating period measured with the help of AFM was approximately the same and equals to periodicity of the polarization pattern defined by geometry of the experiment ($\Lambda \sim 2.7 \mu\text{m}$).

It can be seen that the increase of the helix pitch has led to reducing the amplitude of the SRG (cf. Table 2). The surface relief gratings were formed with a very low amplitude despite applying $+45^\circ/-45^\circ$ polarization combination which is recognized as the one of the most effective one for obtaining very high amplitude surface relief gratings in the case of amorphous polymers containing azobenzene derivatives.⁴² At the moment it is hard to give an explanation of such behavior.

Influence of Phase Behavior on Polarization Grating Recording: A Comparison of Nematic, Cholesteric and Amorphous Films

In order to study the differences in the polarization grating recording process in cholesteric and nematic systems, we

prepared two films of nematic copolymer **PAAzo8** and used them as comparison systems. One of the films was casted on the glass plate with the rubbed polyimide layer whereas the second one was prepared on the glass substrate with no rubbing layer. It means that, respectively, uniaxially oriented and a non-oriented nematic films were obtained. Beside these systems, the amorphous film of the cholesteric mixture was also investigated (details of the films preparation procedure are presented in the Experimental part).

Figure 6 depicts the first-order (+1st) DE dynamic curves obtained for the uniaxially oriented, nonoriented nematic films of copolymer **PAAzo8** and for the amorphous film of the cholesteric mixture **PAAzo8 + Sorb** (corresponding dynamics for -1st and $\pm 2\text{nd}$ orders are shown in Supporting Information Fig. S6). The diffraction efficiency and the surface relief grating amplitudes are collected in Table 2 (data for -1st and $\pm 2\text{nd}$ orders are gathered in Supporting Information Table S1).

Investigations of the PGR in the nematic azobenzene-containing copolymer **PAAzo8** have allowed one to explain the features of the grating recording observed in cholesteric systems. It can be clearly seen in Figure 6 that, for both oriented and nonoriented nematic films, there were no such oscillations in the diffraction efficiency as observed for films made from the cholesteric mixture. The lack of oscillations in the nematic systems has confirmed the explanation based on the competition between the helical organization and the process of the grating formation during PGR in the cholesteric systems. It can be concluded that the oscillations are

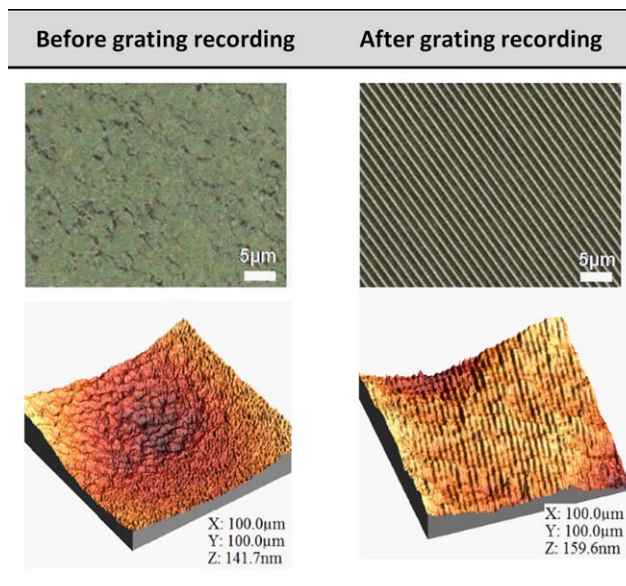


FIGURE 5 Polarized optical microscopy images (the top row) and AFM surface relief scans (the bottom row) of the cholesteric polymer film ($d \sim 1.2 \mu\text{m}$, $p \sim 530 \text{ nm}$) before and after grating recording performed for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

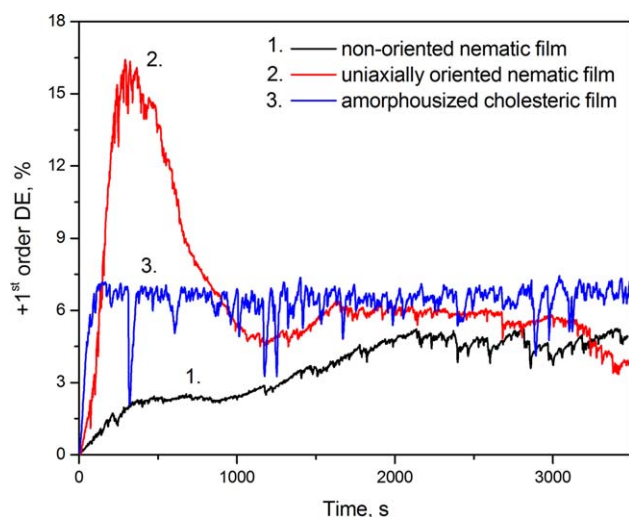


FIGURE 6 First-order (+1st) diffraction efficiency dynamics for the nonoriented (polydomain) (1), uniaxially oriented nematic films ($d \sim 1.2 \mu\text{m}$) of the copolymer **PAAzo8** (2), and amorphous film ($d \sim 1.5 \mu\text{m}$) of the cholesteric mixture **PAAzo8+SorB** (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristic for the presence of the cholesteric mesophase in the system.

Comparing the DE dynamics curves for oriented and nonoriented nematic films one can notice a clear maximum in the diffracted signal at the beginning of the recording process in the case of the first film which is evidently caused by the uniaxial orientation of side groups (cf. Fig. 6). The maximum in DE was also observed for the cholesteric films at the initial stage of the grating recording. Apparently, it has the same origin: as far as the cholesteric films were prepared on the glass substrates coated with a rubbed polyimide, which means that there was a thin uniaxial oriented layer of cholesteric mixture next to the substrate as it was shown in ref. 43. This assumption seems to be confirmed by the absence of the maximum in the DE for amorphous film of the cholesteric mixture without any orientation of the side groups (Fig. 6 and Supporting Information Fig. S6).

Furthermore, the amplitude of the SRG for the nematic films is larger than for the cholesteric system (Table 2). It indicates that the process of the formation of the surface relief grating is much less effective for cholesteric films. This effect can also be explained by the presence of the helical organization of the bulk, which hinders the process of the mass transport and thus the formation of the grating.

The presence of the rubbed polyimide layer influenced significantly the behavior of the diffraction efficiency in the nematic film when compared to the nematic film without such layer, in other words, the preorientation of the mesogenic groups has its impact on the grating formation process. However, similar DE values were found for these two films at the end of recording, as well as, the amplitude of the SRG is almost the same.

The obtained results have revealed that the process of polarization grating recording in cholesteric azobenzene-containing LC polymer systems is complicated and differs significantly from the process of the grating formation in the nematic azobenzene-containing LC polymer system. Due to the performed comparison with the isotropic and aligned nematic films, we were able to explain some of the features of the PGR process in the cholesteric films. The main conclusion that can be drawn is the fact that the presence of the chiral mesophase in the nematic system hinders the process of the grating formation that is clearly reflected in particular in the behavior of the diffraction efficiency, but also in the efficiency of formation of the surface relief grating. Additionally, it was shown that the presence of a rubbed polyimide layer influence the diffraction efficiency dynamics which was clearly observed especially in the case of the nematic azobenzene-containing LC polymers.

We are sure that presented investigations here shed a light on the process of the polarization-grating recording in cholesteric azobenzene-containing LC polymers, but it still undoubtedly awaits further study. We also believe that will be very helpful in the understanding of the PGR process in other cholesteric systems.

CONCLUSIONS

Cholesteric films of mixture of azobenzene-containing copolymer and chiral-photochromic dopant with different helix pitch and thickness were studied in the context of polarization holographic grating recording. The comparison of the cholesteric, nematic, and amorphous polymer films was made revealing the differences in the process of the grating formation. The differences were observed mainly in the behavior in the diffraction efficiency, but also in the efficiency of the formation process of the SRG. It was shown that significant oscillations in the DE are typical only for the films forming the cholesteric mesophase and reflect the competition between the helical organization in the system and the process of the formation of the grating or complicated optical phenomena due to chiral periodical structure of cholesteric mesophase. The significant difference in the DE growth was revealed for the uniaxially oriented and nonoriented nematic films. Based on this observation, it was concluded that the sharp peak in the DE at the initial stage of the grating recording process in all cholesteric films can be explained by the presence of thin uniaxially oriented layer next to polyimide aligning coating.

Thus, in the considered polymer system, there is a competition of order principles: the cholesteric order suppresses the photoorientation process and the mass transport, which determines resulted properties and its behavior during hologram recording processes. Taking into account, the fact that the chemical composition of the studied systems allows controlling to some amount the mentioned above order principles, such polymer materials represent an undeniable interest in terms of their possible practical use in optics and photonics.

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