

# Features of Double-Spiral "Valley-Hills" Surface Topography Formation in Photochromic Cholesteric Oligomer-Based Films and Their Changes Under Polarized Light Action

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Using a novel experimental method combining of polarizing optical microscopy (POM) and atomic force microscopy (AFM), the surface topography and optical properties of chiral-photochromic LC systems were studied. For this purpose, a mixture of cholesteric cyclosi-loxanes with azobenzene-containing dopant was prepared. Correlations between the features of surface topography of mixture films and POM images of planarly oriented texture were found. Polarized light action (532 nm) leads to the formation of partially aligned surface

structure features. The observed photooptical effects are associated with E-Z, Z-E isomerization cycles of azobenzene groups, anisotropic cooperative photoinduced rotational diffusion and directional mass-transport of chromophores and mesogens in the films.



# 1. Introduction

Study of the interfacial phenomena, surface topography, and interactions between different phases is very interesting and important topic of liquid crystals research.<sup>[1-6]</sup> It is noteworthy that polymer materials provide a unique

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possibility to "freeze" bulk and surface structure in rigid glassy state. The latter is very convenient for the investigations by microscopic methods including atomic force microscopy (AFM).<sup>[7–10]</sup> A competition between bulk and surface free energies results in appearance of surface deformation in nematic, smectic, and cholesteric liquid crystals. In particular, cholesteric mesophase demonstrates the very unusual topography at the free surface, which is determined by competition of homeotropic boundary condition at interface air–liquid crystal and planar orientation in the bulk of the films. Focal conics domains appear as micronssized "hills" having double-spiral superstructure.<sup>[7,8,10]</sup>

Moreover, as was shown by Mitov et al.,<sup>[11–13]</sup> the surface topography and defects in cholesteric materials containing nanoparticles can be successfully used for

nanoparticles ordering. It was also demonstrated that the nanoparticle patterns depend strongly on the film thickness. And, moreover, the nanoparticles influence on the optical properties (selective light reflection) of the composites.

All above-mentioned papers have been clearly showing the scientific and technological importance of the investigations of interfacial phenomena and surface topography of liquid crystals.

On the other hand, an introduction of photochromic moieties capable of photochemical transformations allows one to create materials with photocontrollable structure and optical properties.<sup>[14–22]</sup> There are a lot of papers devoted to the investigation of so-called photoinduced surface relief grating phenomena in azobenzene-containing polymers or low-molar-mass materials

induced by interference pattern produced by two coherent laser beams.<sup>[23-30]</sup> Molecular motion over distances much larger than the molecule size is photoinduced upon irradiation within the absorption band of the chromophores that in its turn induces the formation of surface relief gratings.

In several papers,<sup>[31–34]</sup> authors have described spontaneous submicrometer hexagonal pattern formation in azobenzene-containing polymers under uniform polarized laser irradiation. Such self-patterning was explained by interference of incident light with scattered one.<sup>[34]</sup>

For our knowledge up to now, there is no publication concerning the study of photoinduced topography changes in materials forming cholesteric phase. There are several papers concerning photoorientation processes and holography recording on cholesteric polymers<sup>[35–38]</sup> but authors of these publications did not study surface transformations during photoirradiation.

In the present paper, we used combined polarizing optical and atomic force microscopies to study a correlation between mesophase structure in the bulk of the cholesteric films and surface topography. Similar method was described recently by Mitov and co-workers<sup>[10]</sup> and allows one to scan the same region of the film selected from the wider area observed by polarizing optical microscopy (POM). In our case, we for the first time combine this method with the possibility of irradiation of selected part of the film by highly focused laser beam (see "Section 2" and Scheme S2, Supporting Information).

As object for investigations, we have prepared the mixture containing cholesteric cyclosiloxane (**SilGreen**) and 10 wt% of chiral-photochromic dopant **AzoEtLact**, synthesized by us.



The mixture forms cholesteric phase with clearing temperature at 172–172 °C; glass transition temperature is about 50 °C.

Surface topography of pure LC cyclosiloxanes was studied by AFM and described before;<sup>[7–9]</sup> that is why we have focused our attention on this type of oligomer "matrix" for introduction of photochromic dopant.

Chiral-photochromic substance **AzoEtLact** was successfully used as a dopant for creation of phototunable cholesteric mixtures possessing lasing properties.<sup>[39]</sup>

The main goal of this work is to find the correlation between the structure of the cholesteric photosensitive films in the bulk and their surface topography. A special attention is paid to study of the structural and topography changes induced by irradiation with polarized light.

# 2. Experimental Part

### 2.1. Materials

As cholesteric matrix material we have chosen a glass-forming cholesteric cyclosiloxane **SilGreen** manufactured by Wacker Company. It displays a selective light reflection of left-handed circularly polarized light in the green region of the spectrum ( $\lambda_{max} \approx 550$  nm).

Chiral photochromic dopant **AzoEtLact** was synthesized according to the scheme presented in Scheme S1 (Supporting Information). The mixture was prepared by dissolving the components in chlorophorm followed by slow evaporation and drying in vacuum at  $\approx$ 120 °C.

### 2.2. Sample Preparation

For the investigations planarly oriented films of cholesteric mixture having free surface and different thermal prehistory were







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*Figure 1.* POM (a) and AFM (b, c) images of the slowly cooled film before irradiation. Black square in (a) shows region scanned by AFM (b). Defined for POM and AFM "valleys" are indicated by circles and numbers (a, b). The dashed line in (c) shows the projections of cross-sections presented in (d).

prepared as follows. Small amount of the mixture was placed between two glass plates, heated up to 130 °C and subjected to shear deformation to obtain a good planar orientation. After 5 min of annealing at the same temperature, two glass substrates were separated by shearing. As a result, two glass plates covered by cholesteric film were obtained and annealed additionally during  $\approx$ 30 min. In our experiments, we have used two main types of samples:

- (i) First ones are the films annealed at 130 °C followed by slowly cooling down to room temperature with the rate of 0.5°/min using Mettler hot-stage.
- (ii) Second type of samples (quenched films) was obtained by fast cooling down of the films from 130 °C to room temperature (20–30 s).

These two types of the cholesteric films have different wavelength of selective light reflection with maximum at 463 nm for quenched films, and 483 nm for slowly cooled films (Figure S1, Supporting information). These values of selective light reflection correspond to the helix pitches equal to  $\approx$ 290 and  $\approx$ 310 nm, respectively. Such a difference in pitch of helix values can be explained by helix untwisting taking place under slow cooling down that is explained by the formation of smectic order fluctuations.<sup>[40]</sup>

AFM scans of these two types of films are demonstrated a significant difference in topography (Figure 1 and 2).



The polarizing optical microscope investigations were performed using LOMO P-112 polarizing microscope equipped by Mettler TA-400 heating stage.

For selective light reflection study transmittance spectra were recorded by spectrometer (J&M) equipped with rotating polarizer (Glan-Taylor prism controlled by computer program). Combination of polarizer with broad-band (achromatic) quarter waveplate was used for circular polarization of probe light.

### 2.4. Experimental Setup for Simultaneous AFM and POM Investigations

The main idea of our new type of experimental setup (see Scheme S2, Supporting Information) is a combination of the AFM scanning system, upright optical microscope, optical table for inverted optical microscopy, and cross-polarized illumination system.

The samples (1) prepared as described above were placed directly on the top of scanning XY-piezostage (SmartSPM<sup>TM</sup>, AIST-NT) mounted into the XY-positioned table for inverted optical microscopy (2) with open optical axis. The AFM-head (3,

SmartAFM<sup>TM</sup>, AIST-NT) was mounted onto the same optical table in the manner that allows the placement of tip of AFM-probe in few micrometers vicinity to the optical axis. The spot



Figure 2. AFM 3D images of the same region of quenched film before (a) and after irradiation (b) (1 min, 532 nm,  $\approx$ 300 W cm<sup>-2</sup>). The irradiated zone is clearly seen as area with highest relief amplitude.



of the green laser (4, LCM-S-111, LASER-EXPORT Co. Ltd) using for sample irradiation was adjusted to the same spatial area through the deflectometer mirror of the AFM-head as it is shown on the Scheme S2 (Supporting Information)–dashed box.

All optical images were obtained with Optem Zoom 125C upright microscope (5) adjusted to the overall optical axis passed through the same point as the AFM-probe tip.

The cross-polarized illumination system consists of the ACE<sup>®</sup> Light Source (6), the homemade condenser lens system (7), polymer linear polarizing film (as a polarizer) (8) placed directly on condenser at arbitrary and fixed angle and similar film as analyzer (9) placed into rotatable CCD/microscope coupler (10).

Angle of the analyzer film was adjusted with rotation of CCD/ microscope coupler up to achieving of darkest field as microscopic image.

### 3. Results and Discussion

# 3.1. An influence of Thermal Prehistory on Surface Topography of the Mixture Films

As described in experimental part, we have used two types of the samples with different prehistory, namely, slowly cooled and quenched films.

Figure 1 shows POM and AFM images of the slowly cooled cholesteric mixture film. First of all, it is noteworthy, that our developed technique allows one to find exact correlation between POM and AFM images. Typical focal-conics domains in POM are clearly visible as "valleys" in AFM scan (Figure 1a,b). More detailed scans of "valleys" with depth of ca.  $\approx$ 25 nm are revealed the double spiral structure with a period of ca. 200 nm (Figure 1c,d).

POM images of the quenched samples demonstrated the same domains, whereas "hills" are appeared instead "valleys" in AFM images (Figure 2a). Each "hill" has the similar double spiral structure with the same period. Formation of such surface structures, as shown in a number of papers<sup>[7–12]</sup> is related to competition between the boundary conditions at the free surface, homeotropic mesogens orientation, and planar orientation of mesogens in the bulk.

Scheme 1 shows schematic representation of possible structure (cross-section) of one focal conics domain explaining formation of "valleys" in slowly cooled films. For the quenched films, the surface of the each domain has convex shape. As discussed above, slowly cooling of the mixture results in helix untwisting that is manifested by the shift of peak in CD spectra (Figures S1, Supporting Information). It is important to note, that viscosity of liquid crystals and, in our particular case, cholesteric mixture is highly anisotropic.<sup>[41]</sup> Changing of helix pitch value could be accompanied by defect formation.<sup>[41]</sup> or, like in our case, directional flow of mixtures molecules preferably along "cholesteric layers," that is, in direction perpendicular to the helix axes (green bold arrows in Scheme 1).



Scheme 1. Schematic representation of possible structure of one focal conics domain explaining formation of "valleys" in slowly cooled films. The bold arrows indicate material flow during helix untwisting under slow cooling of the film. (Note that the curvature of surface is much smaller than schematically presented in figure.)

From the other hand, molecular flow along helix axes is much slower. Thus, mass transfer along "cholesteric layers" during helix untwisting could be the reason of transformation of convex surface of focal-conics domains to concave one and "valleys" formation in slowly cooled films (Scheme 1).

It should be pointed out that focal conics "hills" were repeatedly observed in papers<sup>[7,8]</sup> for quenched cyclosiloxane materials but "valleys" were found for the first time in our present work. AFM study of undoped cyclosiloxanes matrix SilGreen films showed that independently on the thermal prehistory they form "hills". Moreover, an introduction of nonmesogenic chiralphotochromic dopant 2,5-bis(4-methoxycinnamoyl)-1,4;3,6-dianhydro-D-sorbitol at concentration less than 5% does not change this tendency.<sup>[42]</sup> Probably, the extreme difference in the surface topography (namely, "valleys" formation) can be explained by the introduction of mesogenic rod-like dopant that modifies elastic constants, viscosity, and other physical parameters of materials providing better conditions for helix untwisting and molecular flow.

### 3.2. Photoinduced Changes of Surface Topography of Slowly Cooled Mixture Films: Polarized Light With Low Intensity

Irradiation of slowly cooled mixture films by polarized light of green laser (532 nm) with relatively low intensity

![](_page_3_Picture_18.jpeg)

![](_page_3_Picture_19.jpeg)

![](_page_3_Picture_21.jpeg)

![](_page_4_Figure_3.jpeg)

Figure 3. POM (a) and AFM (b, c) images of the slowly cooled film after irradiation (1 h, 532 nm,  $\approx$ 1 W cm<sup>-2</sup>). The square in (a) shows region scanned by AFM (b). Defined for POM and AFM "hills" are indicated by circles and numbers (a, b). (c) Detailed AFM-scan of the slowly cooled film after irradiation showing spiral superstructure of "hills." Arrows (b, c) show the direction of polarization of green laser light.

 $(\approx 1 \text{ W cm}^{-2})$  during 1 h induces noticeable changes in optical texture and in surface topography (Figure 3). Multidomain texture is similar to that before irradiation (Figure 1a), but green color of planarly oriented parts of the texture changed into the dark and image has the higher contrast (Figure 3a). More significant changes are found for AFM scans showing that the surface topography is extremely different in this case (Figure 3b,c). All "valleys" after the irradiation are transformed to the "hills". In addition, uniaxial deformation of "hills" takes place in direction perpendicular to the polarization plane of the incident light.

Deformation of structural features in direction perpendicular to the polarization plane most probable is related to the photoorientation process well known for azobenzene-containing systems.<sup>[14–16]</sup> This process results in cooperative orientation of photochromic moieties and mesogenic groups perpendicular to the electric field vector of exciting light.

It is noteworthy that "hills" appeared after the irradiation also have doublespiral superstructure with the same period as before irradiation (compare Figure 1c and Figure 3c).

Photoinduced phenomena observed in cholesteric mixture films are related to a number of processes, such as cycles of E-Z, Z-E isomerization of azobenzene groups, rotation diffusion of chromophores and quite possible to the local heating of the films. (However, note that local temperature does not exceed clearing temperature because the "map" of surface features remains the same after irradiation.) These processes might induce anisotropic molecular diffusion in mixture film in direction opposite to green bold arrows in Scheme 1 and perpendicular to the plane of the excitation light polarization. From one hand, the local light-induced heating slightly decreases the helix pitch that is enough to transform "valleys" into "hills", as described above. From the other hand, polarized light initiates the cooperative rotational diffusion of azobenzene chromophores and mesogens resulting in their uniaxial orientation perpendicular to the polarization plane.<sup>[17,18]</sup> As the viscosity of the material along the photoinduced axis

is significantly lower,<sup>[41]</sup> the molecules diffusion along this axis is faster and leads to an anisotropic deformation of "hills."

The observed photoinduced changes are thermally reversible: an annealing at 140 °C followed by slow cooling recovers the initial surface topography and CD spectra (Figure S1, Supporting Information). This allows one to conclude that any side photoreactions in azobenzene moiety or cyclosiloxanes matrix do not occur.

![](_page_4_Picture_12.jpeg)

![](_page_4_Picture_14.jpeg)

Laser treated area AFM-probe 35 µm b я 25 С d 100 300 250 80 200 60 m E 150 Ń 40 Ń 100 20 50 0 25 25 10 20 20 15 10 15 30 **Χ**, μm **X**, μm

*Figure 4.* "Valleys" to "hills" transformation under local irradiation with high intensity light (1 min, 532 nm,  $\approx$ 300 W cm<sup>-2</sup>). POM image of slowly cooled film before (a) and after (b) local irradiation respectively. The squares show the region of film before and after irradiation scanned by AFM (c, d, respectively). Arrows (d) show the direction of polarization of green laser light. Defined for POM and AFM "valleys" ("hills") are indicated by circles and numbers (a–d). The irradiated zone is clearly seen as area with highest relief amplitude. The dashed lines in (c, d) show the projections of cross-sections presented in (e, f), respectively. Arrows with numbers in (e, f) marks the centers of reference "valleys" ("hills") and show the "valleys" to "hills" transformation in case of numbers 3 and 4.

### 3.3. Photoinduced Changes of Surface Topography of Slowly Cooled Mixture Films: Polarized Light With High Intensity

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Irradiation of slowly cooled mixture films by localized beam of polarized light of green laser (532 nm) with very high intensity ( $\approx$ 300 W cm<sup>-2</sup>) during 1 min induces much more considerable changes in the optical texture (Figure 4a,b) and transformations of the surface topography (Figure 4c–f, Figure S2, Supporting Information). Our equipment (Scheme S2, Supporting Information) allowed one to localize spot of laser and perform comparative analysis of

![](_page_5_Picture_6.jpeg)

POM and AFM images as seen in Figure 4.

Polarized light with high intensity induces a strong uniaxial orientation of chromophores and mesogens as become apparent by the appearance of very bright spot in POM image (Figure 4b). Uniaxial orientation is verified by a rotation of the irradiated sample by 45° with respect to crossed polarizer and analyzer leading to the decrease of brightness of this spot (Figure S3, Supporting Information).

Figure 4 shows AFM scans of the same area before (c) and after irradiation (d). Comparison with POM image (Figure 4a,b) clearly demonstrates the textural and surface changes, that is, photoinduced transformation of "valleys" into the "hills" with more pronounced relief amplitude. We have selected four "valleys" clearly visible also in POM image and marked them by numbers (1-4). Light spot activated "valleys" 3 and 4, whereas the "valleys" 1 and 2 are remained in the nonirradiated area. As clearly seen from Figure 4d-f transformation into "hills" was taken place only for "valleys" 3 and 4.

Uniaxial deformation of "hills" perpendicular to the light polarization is also clearly seen in Figure 4d.

### 3.4. Photoinduced Changes of Surface Topography of Quenched Mixture Films

As was discussed above, the topography of quenched films of the mixture is quite different from slowly cooled samples and consists of "hill" having similar double helical superstructure (Figure 5a and

Figure 2a). The irradiation of the quenched films by polarized green light causes a significant growth of the "hills" (Figure 5b, c, Figure 2b) and an uniaxial orientation of chromophores and mesogens (Figure S4, Supporting Information). Cross-section presented in Figure 5c has showed that amplitude of the surface relief increases by one order of magnitude. As described above, the deformation of structural features in direction perpendicular to the light polarization was observed (Figure 5b). Probably, increasing of surface relief amplitude has the similar origin as discussed above for slowly cooled films: local heating and photoinduced orientation causes anisotropic molecular

![](_page_5_Picture_16.jpeg)

![](_page_6_Figure_3.jpeg)

Figure 5. AFM images of the quenched film before (a) and after irradiation (b). (1 min, 532 nm,  $\approx$ 300 W cm<sup>-2</sup>). The irradiated zone is clearly seen as area with highest relief amplitude. The white arrow in (b) shows the direction of light polarization. The dashed lines in (a, b) show the projections of cross-sections (c) of the same areas demonstrating significant changes in topography.

diffusion and mass-transport along "cholesteric layers" (Scheme 1) and perpendicular to the plane of the excitation light polarization.

### 4. Conclusions

In summary, it should be pointed out that the novel method implying combination of POM and AFM was for the first time applied for the investigation chiral-photochromic LC systems. Correlations between surface topography and POM images were found and discussed. Principal difference in surface relief was observed for the quenched and slowly cooled films. For the slowly cooled samples, a huge number of "valleys" having spiral superstructure were observed for the first time. For the quenched samples obtained by fast cooling, the spiral "hills" were found. Polarized light action on the cholesteric mixture films leads to the azobenzene and mesogenic groups uniaxial orientation in direction perpendicular to the polarized light and formation of partially aligned surface features ("hills" instead "valleys" for slowly cooled films). For the guenched samples, the irradiation results in the extreme (one order of magnitude) increase in topography amplitude. The observed effects are associated with cycles of E-Z, Z-E isomerization, photoinduced rotation diffusion of chromophores and local heating of the films. This combination of processes induces anisotropic molecular diffusion and flow along "cholesteric layers" and perpendicular to the plane of the excitation light polarization.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: This research was supported by the Russian Foundation of Fundamental Research (11-03-01046a, 12-03-00553-a and 11-03-12054-OFI-M) and the Ministry of Higher Education and Science of the Russian Federation (grants no. 11.G34.31.0050 and no. 11.519.11.2005). The authors thank Prof. Oleg Lavrentovitch for the fruitful discussion.

Received: August 6, 2012; Revised: September 14, 2012; Published online: November 8, 2012; DOI: 10.1002/macp.201200462

Keywords: photochromic cholesteric mixture; E-Z isomerization; azobenzene; AFM; polarizing optical microscopy

![](_page_6_Picture_14.jpeg)

![](_page_6_Picture_16.jpeg)

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