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Oscillatory dynamic surface structures in patterned liquid crystal network coatings

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ABSTRACT

Controlled formation of surface topographies has led to an interesting set of applications (friction control, cell adhesion and motility, self-cleaning and many more). Utilizing light-sensitive molecules in combination with liquid crystal network (LCN) coatings allows for the creation of surface structures upon irradiation. For these LCN coatings, the alignment determines the shape of the topography and thus the application of the material. An outstanding method to control the alignment of the liquid crystals locally, is utilizing a so-called photo-alignment layer. Here, we present the use of such a layer in combination with azobenzene-doped LCN coatings to create different shapes of topographies that can be used for oscillatory deformations. Azobenzene-doped LCN coatings were made with different planar alignments and defect lines. Upon UV light actuation, we obtained asymmetric or symmetric topographies defined by the symmetry of the defect. In this way we create asymptotic, hills, valleys or continuous sinusoidal topographies. In addition we show that these topographies can be addressed locally. We induced these oscillatory deformations by utilizing polarized UV light in combination with blue light to control the *cis* and *trans* formation of the azobenzene crosslinker. Since the azobenzene has dichroic properties, this illumination method induces a local actuation of the azo-LCN coating. Upon rotation of linear polarized UV light, the actuation becomes oscillatory and the surface structures dynamic.

Keywords: liquid crystal coatings, light-responsive, surface structures, oscillating topographies, photoalignment, actuator

1 INTRODUCTION

Polymeric materials responding to external stimuli with a mechanical deformation have received great interest in recent years. With the ability to control shape-changing properties in a more precise fashion, well-defined patterned nanomaterials have been developed. The use of liquid crystal (LC) is attractive to fabricate such materials.¹ For example, LC polymers can be fine-tuned precisely for the desired response by controlling their molecular alignment. Different mechanical deformation is achieved by modulating the LC's director in space and the so-called order parameter in time. A reduction of the order parameter by an external stimulus leads to a contraction along and an expansion perpendicular to the director.² This specific deformation can be further tuned by patterning the material.

Liquid crystal networks (LCNs) can be designed with responsive mesogens, leading to deformations towards specific stimuli (mainly heat³, light⁴⁻⁷, electricity^{8,9} and humidity^{10,11}). For example, azobenzene-containing LCN (azo-LCN) free-standing films aligned in a splay pattern, gradually changing the alignment from planar to homeotropic though the thickness, bends in the same direction regardless of the direction of UV light with respect to the sample side.¹² If the UV light is switched off, the materials returns to its original shape. The bending deformation can be used to create artificial cilia working in water⁶ or light-induced walking actuators that walk away from or towards the light source.⁵ Three-dimensional alignment has been achieved by photo-patterning LCNs. The resulting actuators show for example accordion-shaped or spiky deformations¹³⁻¹⁴ For surface-attached azo-LCNs (coatings), the only deformation that is possible, is the *z*-direction leading to the generation of surface topographies.¹⁵ By altering the alignment, large topographies can be achieved by local expansion and contraction in the *z*-direction.^{7,16} Work on different point defects revealed the formation of hills and valleys depending on the LCN's change in director¹⁷ and showed the effect of different alignment deformations (namely splay, bend or twist) on the created topographies. The use of these type of alignments only result in two states and the continuous oscillatory deformation has not been reported.

Previously we have reported on the generation of oscillatory deformation, using $0^\circ/90^\circ$ alignment.¹⁸ Here, we focus on the generation of different geometric light-induced oscillating topographies. We present a symmetric line pattern and a polarization grating (PG) pattern in azo-LCN coatings supported on glass. We investigate the shapes produced upon illumination.

2 RESULTS AND DISCUSSION

2.1 Oscillating topographies of random symmetric boundaries with a $-45^\circ/45^\circ$ alignment

Topographical changes are first investigated in an azo-LCN coating having a symmetric alternating line alignment with domains at an angle of -45° and 45° with respect to the lines. It should be noted that the change between alignment (topological defect lines) is randomly defined (Figure 1, splay or bend). The two adjacent domains reach the boundary at the center and the alignment will undergo two different elastic deformations: a bend or a splay elastic deformation. This will lead to different types of stress created in the coating upon UV illumination.

Figure 1. Illustration of the liquid crystal moieties of the $-45^\circ/45^\circ$ aligned azo-LCN. Gray are inert LC mesogens and yellow are azobenzene moieties. The backbone of the polymer is not illustrated for simplification. Bend and splay represent the change in the alignment direction.

The symmetric $-45^\circ/45^\circ$ aligned azo-LCN coatings were made by using a cell having two patterned photo-alignment layers on glass. These cells were made by exposure in two steps to achieve orthogonal aligned lines with different widths. After filling the cell with the LC monomer mixture and curing with light, the patterned azo-LCN coating is obtained by removal of one of the glass plates. Upon investigation with polarized optical microscopy with the patterned lines parallel to one of the polarizers (P and A), we observe the birefringence of the individual domains ($-45^\circ/45^\circ$) with black defect lines. At 45° , we observe the birefringence of the defect lines, indicating the topological changes at the boundary of the orthogonal aligned domains (Figure 2). However, the defect lines contain small and local defects (see insets Figure 2). This is due to the ability of the LC's to undergo a splay or bend alignment, without the preference to one or the other (Figure 1). Upon investigation with solely one polarizer (bottom Figure 2), we observed the alignment of the dichroic azobenzene moieties. The domains with the director parallel to the polarizer show up yellow compared to the domains with the director orthogonal.

Figure 2. Polarized optical micrographs of the $-45^\circ/45^\circ$ azo-LCN coating. Crossed polarizers (top, P and A) and single polarizer (bottom, P) images show the alignment. Pitch of the domains is $50\ \mu\text{m}$. The insert in the crossed polarized micrographs show a $3\times$ zoom-in of the topological defect line with defects.

To analyze the oscillatory deformation of the patterned azo-LCN coatings, we used a UV – blue light intensity ratio of 0.10 and a rotation speed of $2.5^\circ\ \text{s}^{-1}$ for the polarizer for topography formation at room temperature.^{18,19} We monitor the center of the individual domains (zone 1 and 2, $20\ \mu\text{m}$ away from the defect line) and the topological defect line (zone 3 and 4) (Figure 3). For zone 1 & 2, we observe an oscillation out-of-phase near their initial height. We observe that the topographies on the defect line are different depending on the transition (splay or bend) between the adjacent -45° and 45° domains. Here, zone 3 (bend) creates a hill and oscillates, while the topography in zone 4 (splay) becomes a valley upon actuation without any pronounced oscillations. The azo-LCN coating creates either only a hill or a valley, thus a symmetric topography as result of the symmetric alignment. Since the topographies are only pronounced on the defect line without large lateral dimensions, changing the width of the domains led to no further improvement of the height changes or oscillations.

Figure 3. Digital Holographic Microscopy results of the $-45^\circ/45^\circ$ aligned azo-LCN coating upon illumination. Left) An illustration of the monitored $-45^\circ/45^\circ$ coating with monitor zones 1-4. The dashed line represents the topological defect line. Right) Height changes in function of time for zones 1-4. Rotating polarizer ($2.5^\circ\ \text{s}^{-1}$) and LEDs (365 and 455 nm),

200 mW cm⁻² and 20 mW cm⁻², resp.) are turned on at $t = 30$ s. Zone 1 and 2 monitor the bulk of the -45° and 45° domain, respectively. Zone 3 and 4 monitor the defect line at different locations.

To shed more light on the deformation of the defect line, the topography was investigated in more detail (Figure 4). Remarkably, we observe that besides an oscillation in height, a lateral oscillation takes place in x -direction. The clockwise oscillating deformations are 15 nm in height and 4 μ m in width (Figure 4b) and is only observed at the defect lines with the bend alignment. As expected, the clockwise rotation of the linear polarized UV light induces the in-phase deformation of the azobenzene moieties (Figure 1) causing lateral clockwise stress rotations.

Figure 4. Oscillation in the -45°/45° aligned azo-LCN coating. Contour plot of the -45°/45° topography (left) and the profiles at $y = 25 \mu\text{m}$ for different arbitrary angles of linear polarized UV light (right). The defect at $X = 40 \mu\text{m}$ and $Y = 55 \mu\text{m}$ represents a $+1/2$ defect. The black arrows indicate the height and lateral clockwise oscillation upon rotation of linear polarized UV light.

We investigated the thermal influence of the -45°/45° azo-LCN topography by increasing the operating temperature from 30 °C to 90 °C (Figure 5). Without exposure to light, the surface starts deforming at temperatures above the polymerization temperature (37 °C). The thermal deformation arises from a decrease in order leading to the generation of topographies (Figure 5b). Upon illumination, we observe that the amplitude of the oscillation is temperature independent above the glass transition temperature (46 °C) of the coating. However, the absolute height changes above at the glass transition. This behavior is different from the 0°/90° alignment as earlier reported.¹⁸ The -45°/45° alignment shows lateral movement upon irradiation with rotating polarized UV light. Thus inducing a difference in height laterally close to the topography. Moreover, the symmetric defect line also undergoes a symmetric stress from both domains. This induces a larger topography upon increasing temperature. The lateral oscillation is apparently restricted by the width of the bend alignment.

Figure 5. Influence of temperature on the actuation of a $-45^{\circ}/45^{\circ}$ aligned azo-LCN coating. The actual topography height in function of time (a) and the surface profiles (b) of the topography on the $-45^{\circ}/45^{\circ}$ defect line at different temperatures. Solid and dashed lines are in dark and exposed state, respectively. Rotating polarizer ($2.5^{\circ} \text{ s}^{-1}$) and LEDs (365 nm: 200 mW cm^{-2} ; 455 nm: 20 mW cm^{-2}) turned on at $t = 30 \text{ s}$.

2.2 Oscillating topographies of controlled symmetric boundaries with alternating bend and splay alignment

In order to control the bend and splay alignment in the defect lines, we used a polarization grating alignment to create an alternating bend and splay pattern (Figure 6). An azo-LCN with PG alignment was obtained by patterning brilliant yellow (BY) coated glass plates with a holographic polarization interference pattern (pitch $15 \mu\text{m}$). These patterned cells were filled with the LC monomer mixture and cured. A coating was obtained by removal of one the glass plates. Alternatively, coatings were made by spincoating and curing LC mixture directly on a glass plate having a patterned alignment.

Figure 6. Illustration of the liquid crystal moieties of the polarization grating (PG) aligned azo-LCN. Gray are inert LC molecules and yellow are azobenzene moieties. The backbone of the polymer is not illustrated for simplification.

After creation of the azo-LCN coating with the PG alignment, the coating was investigated with polarized optical microscopy to ensure the alignment (Figure 7). Under each given angle, with respect to the polarizers (P and A), continuous blue colored and black lines are observed with a pitch of approx. $15 \mu\text{m}$. This proved the desired alignment was achieved without the loss of order, hence the blue color. We assume that the small differences in the tint of blue arise from a different in height, and thus thickness. We can also clearly observe an initial topography at the two monitored zones, the bend and splay deformation alignment of the PG alignment. This height difference can lead to a different color observed in the micrographs.

Figure 7. Polarized optical microscopy images of the PG azo-LCN coating at different angles with respect to the polarizer (P) and analyzer (A).

Upon illumination, the initial topography is inverted without any oscillations (I in Figure 8). After 720 s (12 min) of illumination, we observe a relative stable oscillation mainly expressed by the bend alignment of the PG azo-LCN (II in Figure 3.8). The topographies reach to nearly 200 nm in height and show oscillations of 20 nm, thus 10% of the total topography (Figure 8a). We speculate that the initial height of ca. 20 nm results from the periodical tension induced by azo-LCN upon cooling from the polymerization temperature (37 °C) to room temperature. The order of the azo-LCN is larger at room temperature leading to the generation of topographies with maxima located at the splay alignment. In Figure 8b, the initial surface topography has its extrema located at the inverse location of the final illuminated state. During illumination, no deformation along the changing LC director is observed while rotating the polarizer. Over the 20 s timespan plotted in the graph, the polarizer moved 50°. If the surface would form topographies solely at the maximal absorption locations (linear polarized UV light parallel to LC director), the topography should travel and a travelling wave on the surface would be observed. This means that the light induced stresses dictate the formation of topographies in these coatings. As seen before and as reported by Babakhanova *et al.*¹⁷, these coatings form maxima and minima at splay and bend alignments, respectively.

Figure 8. Actuation of the PG aligned azo-LCN coating. (a) Actual height of the PG azo-LCN coating under rotating polarized UV light and unpolarized 455 nm light illumination. Surface profile of the PG azo-LCN coating during the first 20 s of illumination. Rotating polarizer (2.5° s^{-1}) and LEDs (365 and 455 nm, 200 mW cm^{-2} and 20 mW cm^{-2} , resp.) are turned on at $t = 60 \text{ s}$. (b) Surface profiles during the first 20 s of illumination with initial topographies of ca. 20 nm. I and II indicate the timespans discussed in more detail in graph Figure 3.8b and Figure 3.9, respectively.

When taking a closer look at the oscillating topography in the graph and the different contour plots at different angles of the polarizer for one single rotation, lateral deformations are observed (Figure 9). The oscillation laterally is limited to approx. 10% of the PG pitch, corresponding to an oscillation of $2 \mu\text{m}$. Here the oscillation is counter clockwise in correspondence with the counter clockwise rotation of the polarizer. Furthermore, we also clearly observed that the adjacent topography maxima oscillate laterally in phase; this is due to the repetitive alignment of the PG azo-LCN.

Figure 9. Oscillations in the PG aligned azo-LCN coating. Surface profile (a) and contour plot (b) of the PG aligned azo-LCN coating during one full rotation of the polarizer. Arrows indicate the trajectory of the topography over time. The black dotted line shows the change in position of the topography maxima at the different polarizer angles. Timespan corresponds to the gray box II in Figure 8a.

Lastly, we tested the influence of a lower UV intensity at 50 mW cm^{-2} and operating temperatures (room temperature and 50°C). As expected, the topography height and the corresponding oscillation of the bend alignment transition are smaller compared to the higher intensity (200 mW cm^{-2}) at room temperature (Figure 10a). At elevated temperatures (50°C) we observe an initial surface topography with the maxima at the bend alignment and minima at the splay alignment (Figure 3.10b). This coincides with the topographies found with previous illumination experiments. Upon illumination, the topographies reach the ‘stable’ state around which oscillation occurs nearly instantly while approximately doubling the oscillation amplitude. Meanwhile the splay aligned area start showing a more pronounced oscillation. These enhanced effects are due to the actuation at temperatures barely above the glass transition temperature (46°C), leading to faster actuation and relaxation kinetics of the azobenzene moieties and higher mobility in the polymer network.

Figure 10. Actuation of the PG aligned azo-LCN coating with lower intensities. (a-b) Oscillations created in a PG azo-LCN with 50 mW cm^{-2} rotating linear polarized UV light and 5 mW cm^{-2} unpolarized blue light at room temperature (a) and at 50°C (b). Polarizer (2.5° s^{-1}) and LEDs are turned on after 30 s.

3 CONCLUSION

Different director patterns were made in azo-LCN coatings by means of photo-alignment layers. These patterned coatings show a specific topographic response to UV and blue light exposure depending on the alignment pattern. For alignments with symmetric boundaries, the topographic geometry is also symmetric. However, depending on the alignment pattern, splay or bend, the forming topography becomes either a hill or a valley. Depending on the alignment pattern, these topographies show lateral oscillations in combination with height oscillations and go up to 200 nm with approx. 40 nm oscillations.

The controlled oscillating patterns are interesting for the variety of applications, such as friction control, cell culturing, or in case of diffractive coatings, even optical applications as topographies can improve the diffraction efficiency. Furthermore, the alignments patterns are not limited to line structures and can be extended to point defects leading to new oscillating surface topographies.

4 EXPERIMENTAL SECTION

4.1 Materials

The azo-LCN coatings are made from a mixture of liquid crystalline acrylates and necessary additives shown in Scheme 1 and was described previously in more detail.^{6,20} Monomer **1** to **3** were obtained from Merck UK. Monomer **4** was custom-synthesized by Syncom (Groningen, the Netherlands). Photoinitiator **5** was obtained from Ciba. A typical azo-LCN composition consists of 42 wt% monomer **1**, 21 wt% monomer **2**, 31 wt% monomer **3**, 5 wt% monomer **4** and 1 wt% photoinitiator **5**. 2-(N-ethylperfluorooctanesulfonamido)ethyl acrylate (surfactant) was bought from BOC Sciences. The constituents were mixed by dissolving in dichloromethane and stirred until a homogeneous solution was obtained. Dichloromethane was removed under reduced atmosphere to achieve a reactive LC monomer mixture. The photoalignment layers, LPP ROP-108/2CP and brilliant yellow (BY), were obtained from Rolic and the group of Philip Bos (Kent State University), respectively. All chemicals were used as received unless stated otherwise.

Scheme 1. Chemicals used to create responsive nematic liquid crystal network coating.

4.2 Fabrication of the patterned azo-LCN coating

Symmetric -45°/45° alignment

Glass substrates (3×3 cm²) were cleaned by sonication using acetone and propanol-2 followed by UV ozone cleaning. Photoalignment material (LPP) was spincoated onto the cleaned substrates. Two substrates were glued together using adhesive containing 6 μm spacers. The LPP surfaces of the thus obtained LC cells are patterned by a 2-step exposure. In the first step the sample was exposed through a line mask with polarized light at 45° to the lines for 15 minutes. In the second step the mask was removed and a shorter flood exposure, 3 minutes, was applied with light with polarization orthogonal to the first exposure (135°). The second exposure aligns the areas that were unaddressed but does not overwrite the alignment achieved by the first exposure step, thus creating orthogonally aligned pattern. The LC cells were filled at 75 °C with the LC monomer mixture by capillary forces and cured at 38 °C with light > 400 nm (EXFO Omnicure S2000) followed by a short post-cure at 125 °C for 5 minutes. Afterwards, one of the glass plates was removed leaving a coating adhering to glass at one side and with a free surface at the other side.

Polarization grating alignment

The PG patterned layers and cells were supplied by the group of Philip Bos (Kent State University). The BY substrates or empty cells (5 μm gap) were patterned using holographic exposure created by two beams with opposite handedness circular polarization ($\lambda_{\text{laser}} = 457 \text{ nm}$, Optotronics VA-I-200-547). Both beams were of the same intensity (4.7 mW). The BY substrates were exposed for 10 minutes. In case of the single substrate, the LC monomer mixture with the addition of

1 wt% surfactant was spincoated at a 33 wt% solution in DCM (2500 rpm, 28 s) and cured at 38 °C with light > 400 nm (EXFO Omnicure S2000) followed by a short post-cure at 125 °C. For the 5 μ m BY cells, the empty cell was loaded at the open edge with crystalline LC monomer mixture at room temperature, heated to 75 °C in a vacuum oven and left overnight under reduced pressure. The molten isotropic LC monomer mixture filled the BY cell by capillary forces and was brought back to atmospheric pressure. The filled BY cell was cured at 38 °C with light > 400 nm (EXFO Omnicure S2000) followed by a short post-cure at 125 °C.

4.3 Characterization and actuation of the patterned azo-LCN coating

The monomeric mixture and coatings are characterized with a crossed polarized microscope (Nikon Ci Eclipse) with a thermocontrolled stage (Linkam). For the monomeric mixture the transition temperature, nematic to isotropic, is determined by cooling from isotropic liquid to nematic LC phase. Both the polymeric and monomeric transitions were confirmed with differential scanning calorimetry (DSC Q1000, TA Instruments). The surface of the coating is monitored with a digital holographic microscope (DHM® R210, Lyncée Tec SA, Switzerland) equipped with a thermocontrolled stage (Linkam) and mounted with UV (λ = 365 nm) and blue light (λ = 455 nm) collimated LEDs (M365L3 and M455L3 respectively, Thorlabs). The UV light originated from the UV LED was redirected with a UV mirror (Thorlabs) and polarized with a polarizer (10LP-UV, Newport) mounted in a rotating stage (Thorlabs). Typical experimental procedure is described in more detail in Chapter 2.

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