Three-Dimensional Ordering of Nematic Liquid Crystals with Azimuth and Tilt Controlled by Patterned Photoalignment and Selective Polymer Stabilization

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Article

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Abstract: In this paper, we present a novel approach for advanced, three-dimensional patterned ordering of nematic liquid crystals. Our method allows for simultaneous control of azimuth and tilt of molecules by using a two-step process based on patterned photoalignment (used to define azimuth) followed by selective polymer stabilization of molecules reorientated with an electric field (used to define tilt). We demonstrate that those two subsequent processes, realized with high-resolution patterned illumination with UV light, allow us to obtain multiple microdomains with independently controlled tilt and azimuth. It opens possibilities to create complex three-dimensional distributions of director within a single liquid crystal cell, not possible with any other technique so far. Moreover, although the polymer-stabilization process is used, it is still possible to retune tilt of the molecules, however, the electric field intensity needed for tuning is slightly higher than in the non-polymerized areas of the sample.

Keywords: liquid crystal; photoalignment; polymer stabilization; polymer-stabilized liquid crystal

1. Introduction

Liquid crystal-based composite materials have been widely studied over the last few decades [1–3]. Materials consisting of a liquid crystal (LC) base and polymer dopant in low concentration (<10%), also known as polymer-stabilized LCs, are of particular interest due to combination of unique electro-optical properties of LCs with added stabilization of LC orientation [4–6] and improved thermal stability [7,8] of the material thanks to the presence polymer network. Polymer stabilization of LCs has been demonstrated to allow for control of LC ordering by stabilization of any desired tilt of LC molecules [9,10], which in the case of planarly oriented nematics results in increased threshold voltage [4]. Selective photopolymerization technique has been successfully implemented for fabrication of optical elements such as LC lenses [6,11,12], diffraction gratings [10,13] as well as waveguides [14–17].

Enforcing a specific LC orientation is often achieved via photoalignment [18–24]. This technique utilizes photosensitive alignment layers to control LC azimuth in the LC cell. Similarly to selective polymer-stabilization, patterned photoalignment has been used to obtain structures with complex arrangement of LC molecules [25–28]. Some groups demonstrated quasi-3D control of LC ordering by using patterned photoalignment either to achieve anchoring on the surface of LC cell filled with chiral LCs [29,30] or through irradiation of orthogonal patterns on top and bottom of the LC cell [31,32].

The presented research was aimed at development of a method allowing for real three-dimensional control of nematic LC's ordering. To achieve this, the LC cell with azo dye layer was utilized to perform patterned photoalignment to control LC azimuth and infiltrated with nematic LC-based composite, which was then photopolymerized in external electric field to stabilize the tilt of LC

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molecules. The obtained results prove that it is possible to achieve LC arrangement that is a superposition of the azimuth enforced by the azo dye alignment layer and tilt stabilized with polymer network. The proposed LC ordering technique can be used for fabrication of complex LC-based structures for various photonic applications.

2. Materials and Methods

2.1. Composite and LC Cells

The composite LC material was based on a nematic LC mixture E7 doped with 5wt% of a 9:1 mixture consisting of RM257monomer (97%, SYNTHON Chemicals, CAS:174063-87-7) and 2,2-dimethoxy-2-phenylacetophenone photoinitiator (99%, Sigma Aldrich, CAS: 24650-42-8) respectively. The material was fabricated by mixing monomer and photoinitiator in desired proportions and adding the LC afterwards. Uniform distribution of the compounds was obtained by mixing the material in ultrasonic bath in temperature above LC's clearing point.

Two types of empty LC cells have been used at various stages of this research. Tests of photoalignment and experiments with two-step illumination (photoalignment and photopolymerization) have been performed in 12μm thick LC cells based on ITO-coated glass spin coated with SD1 azo dye used as a photo aligning material. In the case of tests aimed at optimization of photopolymerization in external electric field, LC cells with 'classic' planar alignment layers (alignment obtained via unidirectional rubbing) have been used (also 12μm thick and ITO-coated) .

2.2. Two-Step Process Based on Patterned Photoalignment Followed by Selective Polymer Stabilization

The sample fabrication procedure was divided into two stages: photoalignment and photopolymerization. In both stages illumination with micro-patterned UV light was required, and it was realized in the setup which is schematically presented in Figure 1. The main part of the setup is a projection system based on DLP LightCrafter 4500 (Texas Instruments), in which a digital micromirror device (DMD) chip was illuminated with 365nm UV LED (modified light engine has been supplied by EKB Technologies). The DMD chip consists of more than 1 million micro-mirrors (7.6x7.6μm), arranged in 912 columns by 1140 rows with diamond pixel array geometry. To control the resolution of illumination, an optical imaging lens has been used to rescale the size of the pixel – it was possible to scale the pixel size in range from about 3x3μm to 10x10μm. LC cells have been positioned precisely to ensure that image plane is exactly in the center of the cell. In the photoalignment step, polarized light was used and azimuth of the polarizer was controlled with dedicated software (it was synchronized with subsequent image pattern displayed by DLP device). Similar setup has been used recently for patterned alignment of LC molecules in microcapillaries [33] and selective polymer stabilization of LC-based composite in LC cells [10]. In the photopolymerization step, LC tilt was steered with waveform generator also controlled with custom software and synchronized with displayed images. The whole process was visually controlled with a digital microscope placed at the back of the LC cell.

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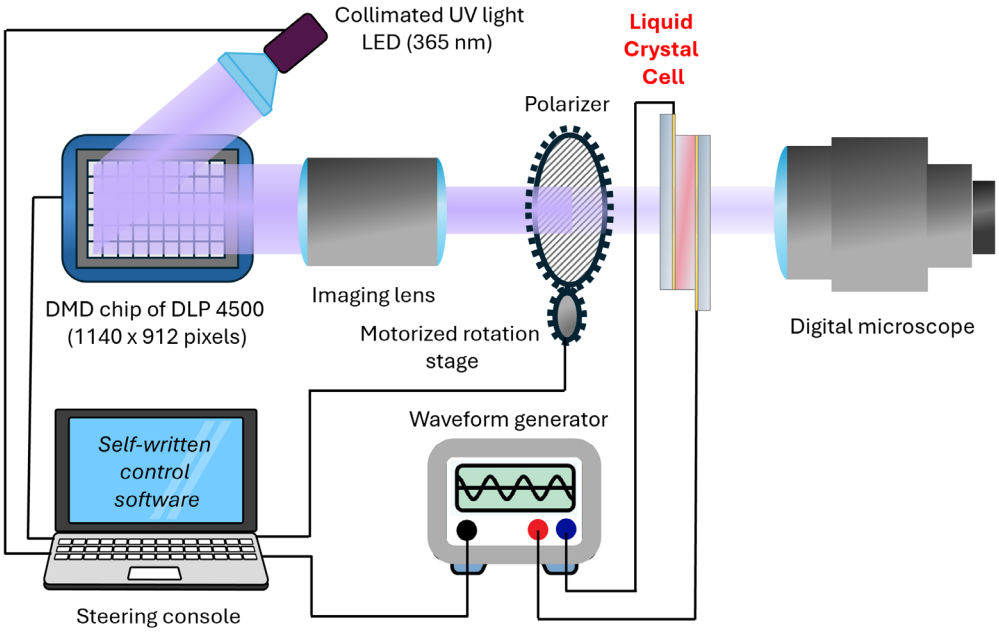

Figure 1. Scheme of the setup used for both photoalignment and photopolymerization. The polarizer is removed from the setup for photopolymerization.

During photoalignment, an empty LC cell was positioned in the image plane of the setup and irradiated with ~2mW/cm^2 intensity for 10 minutes per polarization. This stage of the irradiation procedure required the use of a polarizer in the setup as linearly polarized light with controlled azimuth was needed to irradiate the alignment layer properly. The SD1 azo dye used for photoalignment provides planar orientation of LC with azimuth corresponding to polarization direction of UV light.

After irradiation of the alignment layer, the LC-based composite was introduced into the LC cell using capillary forces. The irradiation intensity was reduced to ~0.7mW/cm^2 to avoid heating of the LC due to absorption of radiation. For this irradiation stage, the polarizer was removed from the setup as polarization of light has no influence on photopolymerization process but further use of polarized light could possibly disrupt the previously obtained alignment. The sample was repositioned to account for the change in optical path resulting from removal of the polarizer. For the purpose of LC control during polymerization, the LC cell was connected to a function generator to set a desired tilt of LC molecules with external AC electric field (1kHz square waveform). The irradiation time per LC orientation was dependent on the LC cell used in the experiment – for the preliminary tests it was 10 minutes, however, the final samples fabricated in the self-made cells required 30 minutes of irradiation due to the use of thicker glass and UV absorption by the azo dye.

Figure 2 shows the general idea of LC control with photoalignment (Figure 2a), photopolymerization (Figure 2b) and combination of both techniques for 3D control (azimuth and tilt) of the molecules (Figure 2c).

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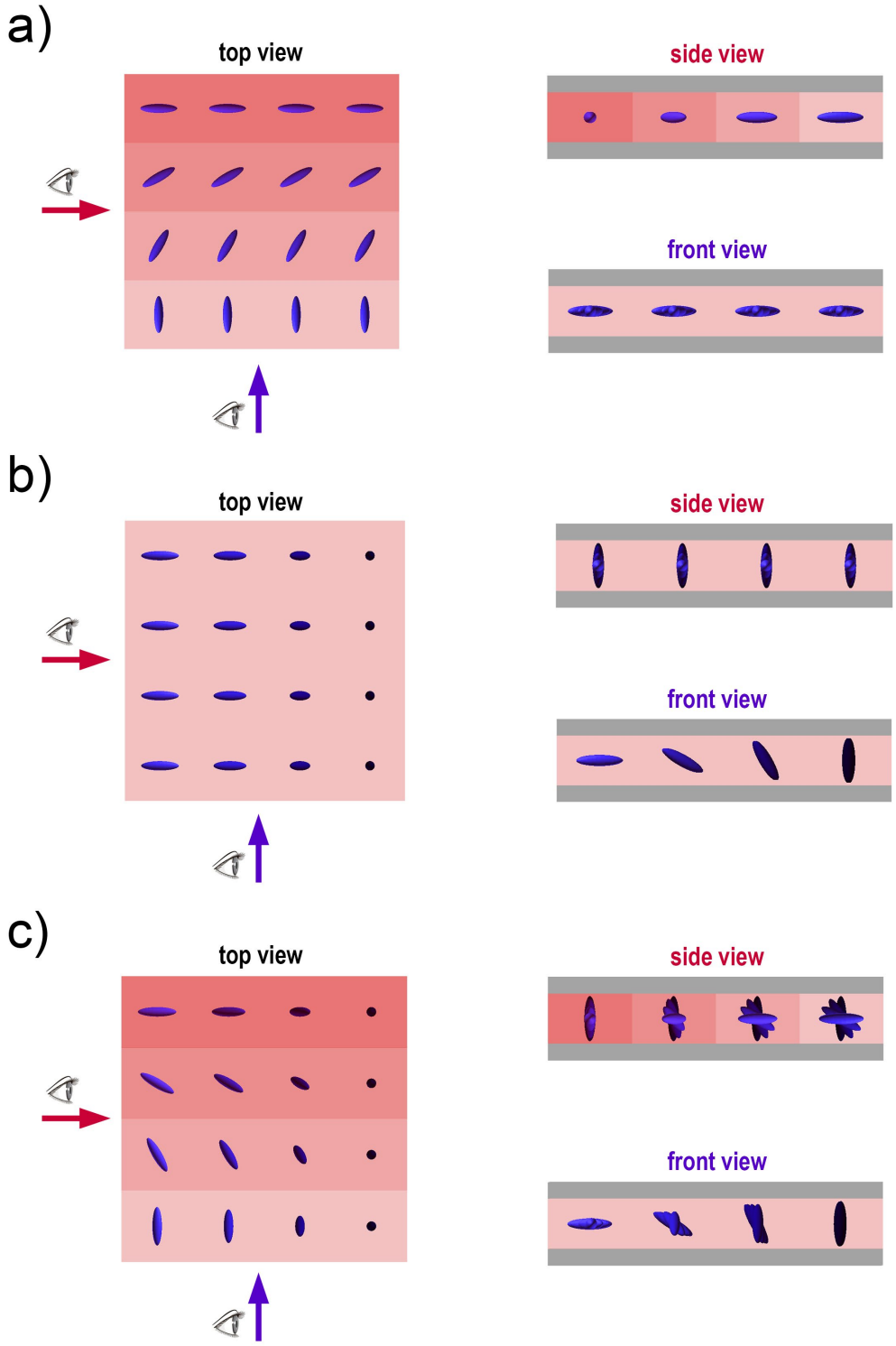

Figure 2. Schematic representation of LC ordering obtainable via: a) patterned photoalignment with linearly polarized light to obtain planar alignment with variable azimuth; b) selective photopolymerization of LC molecules reoriented with external electric field to control tilt of the molecules; c) combination of azimuth control with photoalignment and tilt control with polymer stabilization for 3D control of LC arrangement.

2.3. Sample Analysis

The samples were analyzed under a digital microscope (Keyence VHX-5000) by placing each sample between crossed polarizers to observe differences in phase delay introduced by the LC and thus determine the molecular arrangement. The photoaligned samples were examined via rotation

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between the polarizers as the change in LC orientation was in the plane of the LC cell. In the case of photopolymerization, the LC orientation was changing in the plane perpendicular to the LC cell's surface. For this reason, stabilization of desired LC tilt was verified by applying AC electric field to the sample and comparing the appearance of polymerized and non-polymerized LC for the voltage values used during polymerization.

3. Results

The preliminary tests were aimed at establishing the optimal irradiation parameters for photoalignment and photopolymerization before the two techniques were combined to obtain 3D control of LC arrangement.

3.1. Photoalignment

The first stage of preliminary research was focused on determining both the necessary intensity and time of simultaneous irradiation of the top and bottom alignment layers to obtain a pattern with variable LC azimuth and sharp borders between areas with different LC arrangement as well as optimal method of infiltrating the LC cell after irradiation. In each test the LC cell was irradiated for 4 different polarization directions in the range from 0 to 45 degrees with respect to the cell's edge. Optimization of the irradiation procedure was performed for undoped E7 to eliminate possible influence of the dopant on LC orientation. The infiltration of a photoaligned cell was done with LC in isotropic phase to ensure the most uniform LC orientation possible. Next, the fabrication procedure with optimal irradiation parameters was repeated, but this time the cell was filled with E7-based composite. It turned out that infiltration with the composite in isotropic phase was problematic as the monomer separated from the LC and agglomerated in random spots, which was most likely due to temperature difference between the LC material and the cell. Consequently, the cell was filled with the composite in nematic phase and the results can be seen in Figure 3.

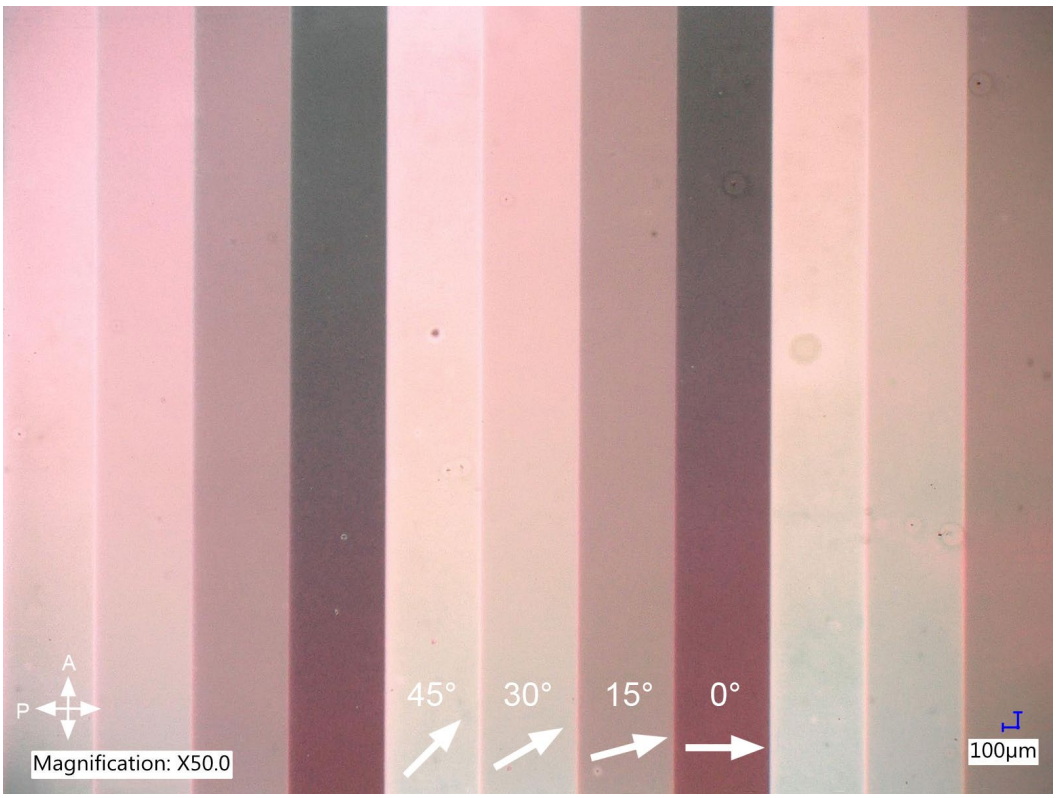

Figure 3. Control of azimuth of planarly oriented LC obtained for 10 minutes of selective UV irradiation per polarization direction. The sample was prepared in a self-made, 12µm LC cell and filled with LC composite after

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irradiation. The LC director in each stripe in the periodic stripe pattern is marked with an arrow and its angle with respect to the polarizer is given above it.

It can be seen that introducing the composite in nematic phase did not cause any visible defects in LC arrangement. As it was expected, photoalignment allowed to obtain domains with planar molecular alignment and various azimuth. The difference in LC azimuth results in different brightness of each stripe observed under a polarizing microscope. The dark region is observed when azimuth of planar orientation is parallel (or perpendicular) to the transmitting axis of a polarizer. On the contrary, the brightest stripe is observed when angle between azimuth and polarizer axis is equal to 45 degrees, as it result in largest phase shift between two orthogonal polarization components. Of course, if the sample would be axially rotated, the brightness of each stripe would be gradually changing. By using this simple method we are able to verify that LC molecules in each subdomain have planar alignment whit expected azimuth.

3.2. Photopolymerization

The focus of further preliminary research was on obtaining stabilization of LC tilt set in external electric field. To eliminate any possible influence of the azo dye on photopolymerization efficacy and quality, the tests were performed in commercially available LC cells with planar alignment layers. The irradiation intensity for this part of the research was lowered compared to photoalignment to avoid heating of the LC composite due to absorption of radiation. The sample obtained for optimized process parameters is presented in Figure 4.

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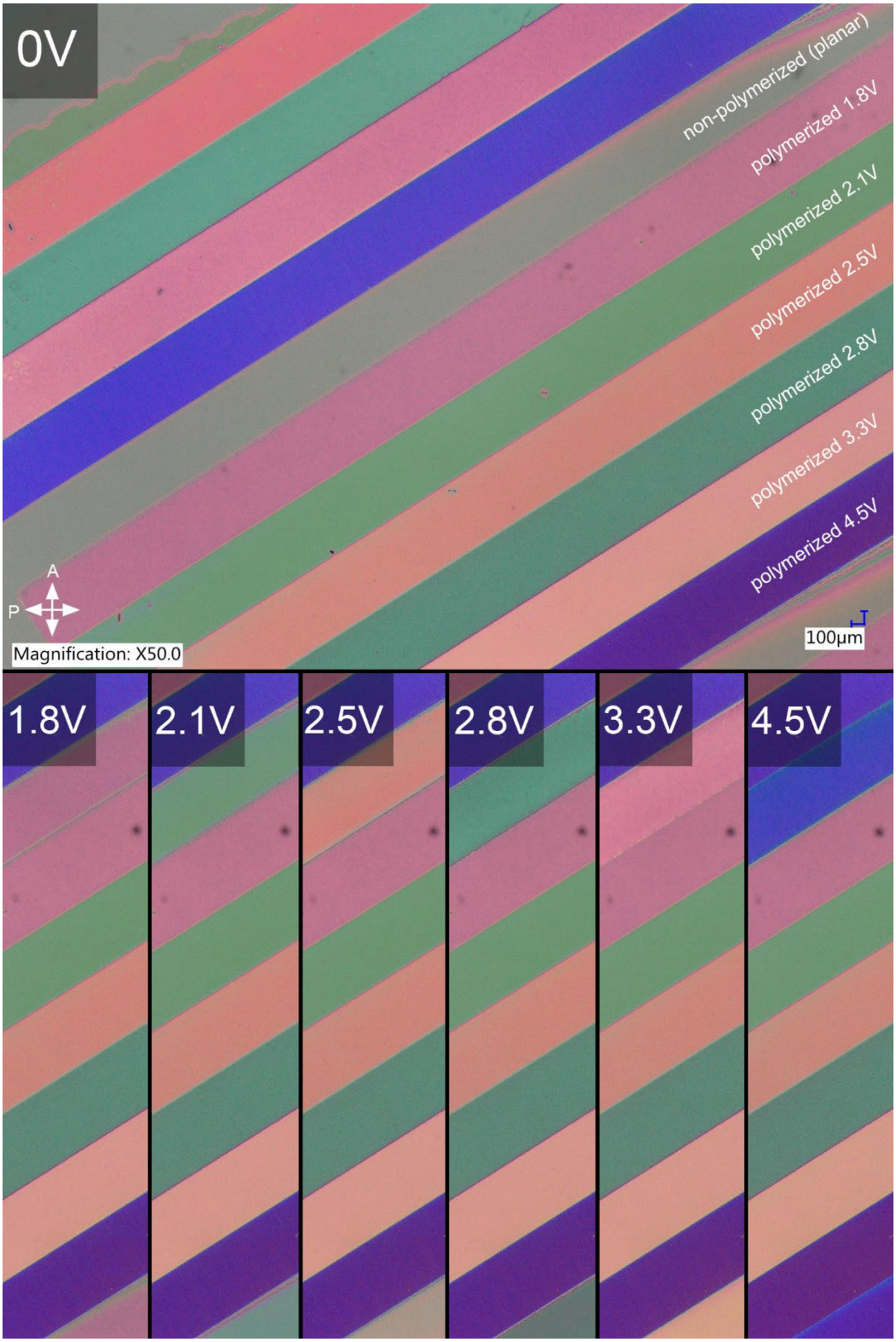

Figure 4. Polymer stabilization of LC tilt obtained via application of external electric field and selective UV irradiation for 10 minutes per voltage value. The sample was prepared in a commercially available, 12µm LC cell with planar alignment layers. Top image shows the polymerized sample with no external electric field applied to it and the AC voltage values used during photopolymerization (one stripe in the periodic stripe pattern was left non-polymerized to be used as a reference). Bottom images show comparison of LC orientation between the reference stripe and the polymerized ones for each of the voltage values used during polymerization. Slight color variation between the sets of stripes is caused by minor tilt of the LC cell under the microscope.

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Polymer stabilization of LC tilt was not only successful in the sense that the molecular arrangement obtained in external AC electric field was preserved after photopolymerization. Figure 4 clearly shows that the effective birefringence of the composite remained identical after irradiation, which is evident in images presented in the bottom row – the color of polymerized stripes (for a specific voltage amplitude) is identical as for the non-polymerized one for each of the voltages used during polymerization. Moreover, no visible light scattering on the polymer network was introduced.

3.3. Photoalignment and Photopolymerization

The first attempt at obtaining 3D control of LC orientation utilized the process parameters determined in the preliminary research: 10 minutes of irradiation per azimuth/tilt with ~2mW/cm^2 and ~0.7mW/cm^2 irradiation intensity for photoalignment and photopolymerization respectively. The results of said procedure can be seen in Figure 5.

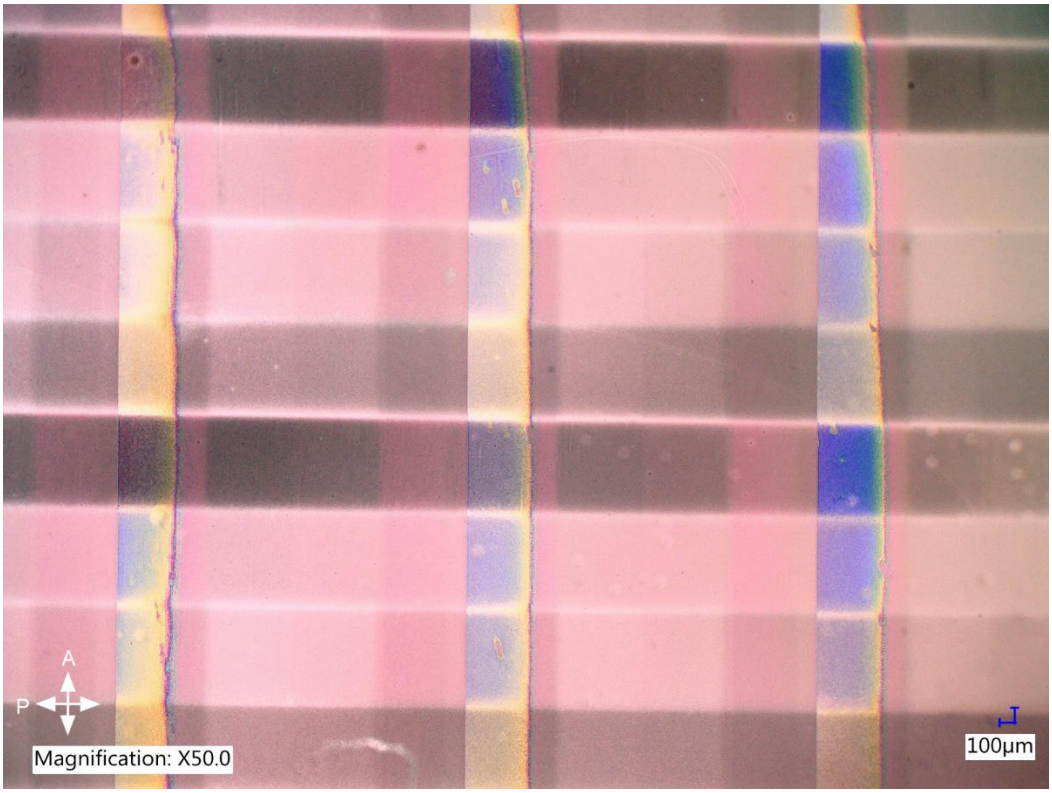

Figure 5. Control of azimuth (horizontal stripes) and tilt (vertical stripes) of LC molecules obtained by photoalignment and subsequent photopolymerization. The sample was prepared in a self-made, 12µm LC cell by UV irradiation of the alignment layer, filling the cell with LC composite after irradiation and photopolymerization of the composite. In each process the irradiation time per polarization direction/voltage value was 10 minutes. It can be seen that polymer stabilization of LC tilt was not successful.

It is clear that photoalignment with the parameters established during the preliminary research was successful, however, polymer stabilization was not despite multiple attempts. The stripes with different LC tilts were somewhat visible but it appeared that the tilt was not stabilized properly due to incomplete formation of polymer chains. It was concluded that a result so vastly different from Figure 4 was most probably due to a change of the LC cell in which polymerization was conducted – the cell used for preliminary tests was made of significantly thinner glass and did not have an azo dye layer. Increase in glass thickness along with introduction of azo dye, which also absorbs UV, must have caused a decrease in the intensity of UV light reaching the LC composite due to absorption of radiation. To counteract this effect, the irradiation time for photopolymerization was gradually increased until the proper value was determined. Successful fabrication of a sample required 30

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minutes of irradiation per LC tilt with the same intensity as in preliminary tests. The final sample, shown in Figure 6, was created by photoalignment (10 minutes of irradiation per azimuth with ~2mW/cm^2), filling the cell with the composite in nematic phase, and consequent polymer stabilization of LC tilt by 30 minutes of irradiation with ~0.7mW/cm^2 per voltage value.

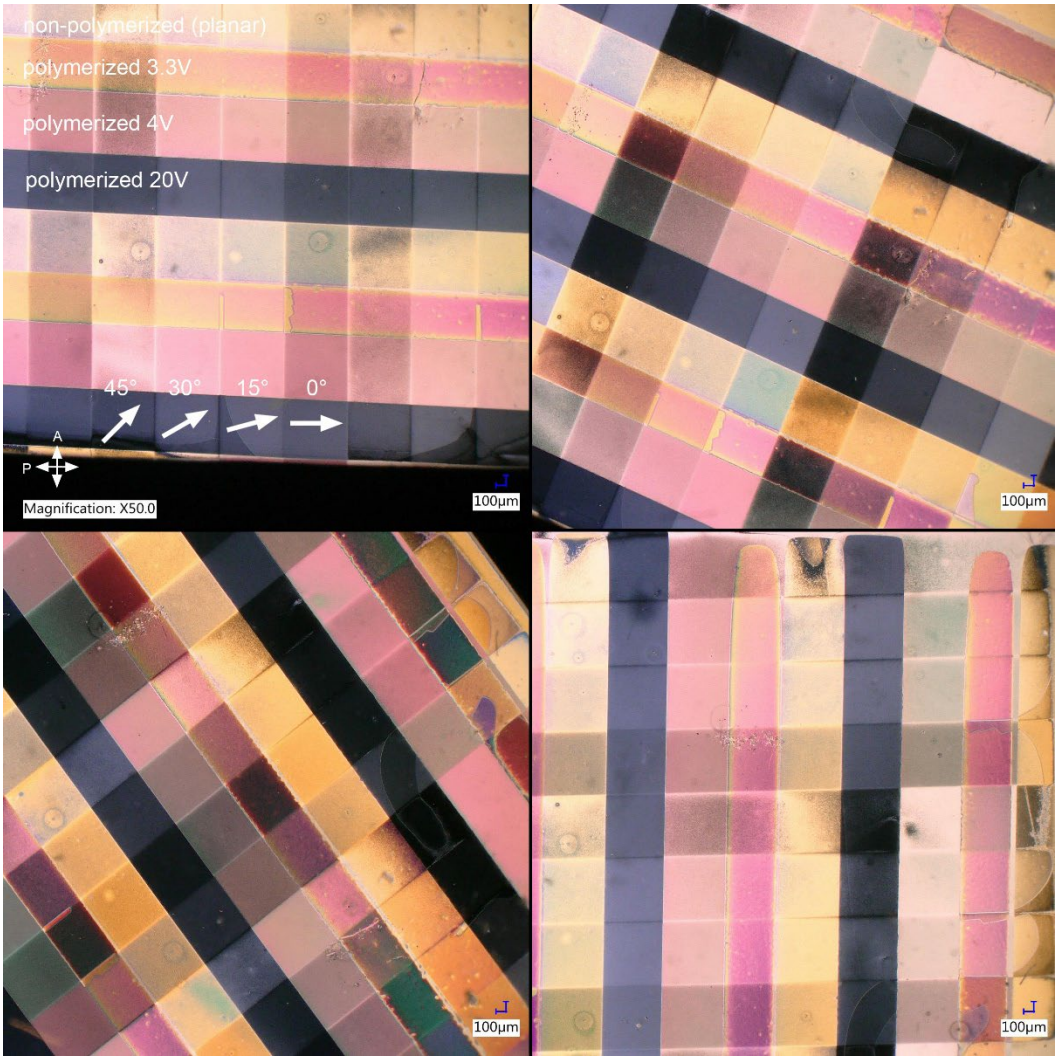

Figure 6. Control of azimuth (vertical stripes in top left picture) and tilt (horizontal stripes in top left picture) of LC molecules obtained by photoalignment and subsequent photopolymerization. The sample was prepared in a self-made, 12µm LC cell by UV irradiation of the alignment layer, filling the cell with LC composite after irradiation and photopolymerization of the composite. The irradiation time per polarization direction was 10 minutes and per voltage value it was extended to 30 minutes to account for increased thickness of LC cell compared to Figure 4. The sample is observed without electric field applied to the LC cell and is rotated between crossed polarizers to demonstrate 3D control of LC ordering. Top left picture shows the LC director in each stripe in the periodic stripe pattern marked with an arrow and its angle with respect to the polarizer as well as the voltage values used during photopolymerization.

It is evident that modification of polymerization parameters allowed to stabilize the LC tilt properly for each voltage value. Analysis of the sample under a polarizing microscope clearly demonstrates that full 3D control of LC orientation was achieved. The color and brightness of each region, being a superposition of orthogonal stripes with different azimuth and tilt, changes differently when the sample is rotated between crossed polarizers. When it comes to the quality of the polymerized structure, some minor imperfections appear at the borders between different stripes,

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which are thought to be either a manufacturing defect in the azo dye layer or, less likely, a result of interaction between the polymer and azo dye.

4. Discussion and Conclusions

The presented research demonstrates an experimental method for obtaining full 3D control of nematic LC's ordering through combination of photoalignment and polymer stabilization to control both azimuth and tilt of LC molecules. To our best knowledge, it is a first practical demonstration of truly three-dimensional patterned alignment of nematic LCs . Other types of liquid crystals (like cholesterics or blue phases) have a 'natural' ability to create three-dimensional local changes of the director, however, it mainly results from intrinsic properties of the LC, thus usually resulting with some periodicity or defects. With such materials it is practically impossible to arbitrarily control three-dimensional ordering of molecules, not to mention the lack of possibility to create patterned alignment with micron-sized pixels. Our approach allows for fabrication of structures with precise local control of tilt and azimuth of the molecules with high resolution, as our setup is based on a high-resolution DMD chip. Of course, this technique could be improved by using DLP-based illumination with even higher resolution or other techniques of patterned illumination (i.e., interferometric, holographic, based on SLMs etc.).

It is worth emphasizing that although the polymer-stabilization process is used, it is still possible to retune tilt of the molecules. It simply requires higher tuning voltages, or more specifically higher intensity of the electric field, than in the case of non-polymerized areas of the sample. This property also opens up the possibility for creating new devices with non-uniform response to the steering voltage, where some areas would be tuned in 'low-voltage' regime, whereas others could be activated in a 'higher-voltage' mode.

We believe that this research can form a foundation for fabrication of complex LC-based optical elements and photonic devices with improved performance.

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Conflicts of Interest: The authors declare no conflicts of interest.

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