Polymerization-Induced Modification of the Switching Process of a Nematic Liquid Crystal

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In this paper, we demonstrate a method for modifying the switching process of a liquid crystal by utilizing selective photopolymerization of a nematic liquid crystal-based composite. The proposed method is based on point-by-point irradiation of a uniformly oriented nematic with a high-intensity blue laser to create unusual polymer chains. Instead of a typical polymer network consisting of long chains, shorter chains are obtained that are unanchored to the aligning surface of the liquid crystal cell. This is possible due to the irradiation of the composite only at one small point at a time and the heating of the material resulting from the absorption of radiation. Consequently, the polymerized pattern is visible only during the reorientation of the liquid crystal.

topics: liquid crystal (LC), photopolymerization, polymer-stabilized liquid crystal, switching times

1. Introduction

Liquid crystals (LCs) are anisotropic materials characterized by high birefringence and sensitivity to external electric field [1–4]. These properties enable control over the light transmitted through the LC, which was the basis for the creation of the first commercial LCDs in the 1960s, which were based on nematic LCs (NLCs) [5]. Since then, the properties of LCs, such as switching times, molecular arrangement, or thermal properties, have been significantly improved by introducing new types of LCs or modifying existing materials with various types of dopants. Consequently, new LC-based devices have been introduced, such as lasers [6, 7], temperature sensors [8–11], spatial light modulators [12, 13], biosensors, and muscle-like actuators [14, 15].

Currently, extensive research on the introduction of various types of dopants into LC hosts is being conducted [16–21]. The main focus is on modifying the electro–optical properties of LCs either to improve their performance in already existing applications or to make them suitable for some new ones. Various groups study the effects of doping LCs with polymers [16, 22–33]. Photopolymerization of monomer-doped LCs is typically done by continuous irradiation with relatively low-intensity light to avoid heating of the material. It was observed that the behavior of liquid crystal is strongly dependent on the polymer concentration, resulting in the categorization of LC + polymer composites as either polymer-stabilized LCs (PSLCs) or polymer-dispersed LCs (PDLCs). PSLCs are created for low dopant percentages ($> 10\%$) and the molecular arrangement after polymerization remains typical for a specific liquid crystal [34], whereas PDLCs are formed for high polymer concentrations (~ 20–80%) and the polymerization process results in the separation of the LC and polymer [35]. When it comes to PSLCs, it was demonstrated that the polymer network can stabilize a desired LC arrangement (which enables the fabrication of structures with variable LC orientation [24]), as well as improve the thermal stability of the LC phase [28, 32, 33] and increase the threshold voltage [31]. In the case of NLCs, polymer stabilization is often used for fabrication of both refractive [25] and diffractive [22] micro lenses and other diffractive optical elements [24], as well as to improve display performance [36, 37]. However, the use of PSLCs for planar waveguides is rarely observed [30]. Moreover, the waveguides demonstrated so far have been obtained by selective polymer stabilization of a variable molecular arrangement and can be either switched off by applying an external electric field or permanently switched on by an external electric field due to the difference in the threshold voltage between the polymer-stabilized areas and the rest of the sample.

In this paper, we demonstrate a new photopolymerization method, which results in the modification of the switching process of a nematic liquid crystal without introducing a difference in the effective birefringence of the sample before and after polymerization in both ON and OFF voltage states.

We suspect that point-by-point irradiation with high-intensity laser pulses can cause quite significant heating of the material during polymerization and result in the formation of short polymer chains that merge LC molecules into small groups instead of forming a uniform polymer network through the entire volume of the sample. Consequently, the proposed photopolymerization technique allows us to obtain a pattern visible only during the switching of the LC. We think that this method can be used to fabricate waveguiding structures that appear only for a very short time, which is of great importance for applications such as liquid crystal-based optical switches.

2. Materials and methods

2.1. Sample preparation

2.1.1. Composite preparation

The NLC-based composite consisted of:

- 90 wt% of 5CB (i.e., 4-Cyano4'-pentylbiphenyl, purity > 99.5%)

doped with

- 8 wt% of RM257 monomer (i.e., 1,4-Bis[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene, 97%, SYNTHON Chemicals, CAS: 174063-87-7)

and

- 2 wt% of 2,2-Dimethoxy-2-phenylacetophenone photoinitiator (99%, Sigma-Aldrich, CAS: 24650-42-8).

The material was prepared by mixing the dopant components in the desired proportions and adding the LC to the mixed powders. The correct amount of the components was controlled using an analytical balance (RADWAG, AS 62.R2 PLUS). Next, a uniform distribution of the components was achieved by 30 min of vortex mixing of the material. The finished composite was introduced into an empty sandwich-type planar LC cell (HG12.0 with unidirectional rubbing and indium tin oxide (ITO) coating; purchased from the Military University of Technology) using capillary forces. To ensure a uniform distribution of the material components during polymerization, each sample was prepared just before the infiltration process and ultraviolet (UV)-light irradiation. The entire procedure was conducted at room temperature. It should be noted that doping the 5CB LC with RM257 monomer at different concentrations can increase the phase transition temperature of the mixture. However, the polymerization process can lead to a decrease in this temperature to values close to the pristine 5CB LC [38]. Based on our previous research and observations, the RM257 dopant did not have a significant influence on the nematic–isotropic phase transition temperature of 5CB in this experiment.

2.1.2. Photopolymerization

The samples were irradiated point-by-point with short laser pulses (pulse length 60 ms per point using a NEJE DK-8-FKZ laser plotter with a power of 1500 mW, $\lambda = 405$ nm, optical power 100 mW). The irradiation intensity was controlled with a polarizer positioned above the sample. It should be noted that the stability of the laser beam has a significant impact on the results. For this reason, we performed tests on the laser source to investigate the stability of the light beam using an optical power meter (Newport 2936-R) with a dedicated detector head. Our tests indicated that the optical power of the laser remained stable in time. In the case of the samples used to demonstrate the differences in the switching process, the laser was used to create a specific pattern. For the switching time measurements, we have prepared a second set of samples in which the entire surface of the LC cell was irradiated point-by-point to create a uniform structure, since it allowed us to avoid some of the critical problems with the switching time measurements. We suspect that point-by-point polymerization of the composite with short high-intensity pulses, instead of longer simultaneous irradiation of the entire sample with a low-intensity UV source, resulted in the formation of shorter polymer chains. Moreover, the high intensity of irradiation caused heating of the material due to radiation absorption, which most likely resulted in the formation of even shorter polymer chains (compared to point-by-point irradiation with a low-intensity light source), as the kinetic energy of the LC molecules increased and the chaotic molecular movements disrupted the formation of the polymer network.

2.2. Sample examination

2.2.1. Polarizing optical microscopy

The samples were analyzed optically under a digital microscope (KEYENCE VHX-5000) with a white light source. The LC cell was positioned between crossed polarizers and connected to a function generator (RIGOL DG4062) to observe the phase delay introduced by the LC in both the ON and OFF state as well as during switching. The switching of the LC was achieved by applying a square waveform signal with a frequency of 1 kHz and a modulation period longer than LC's relaxation time. The observation of differences in the reorientation process between polymerized and

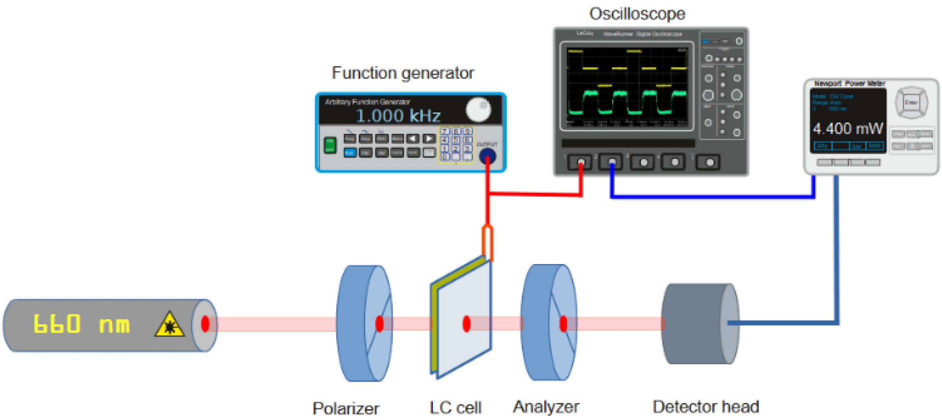

Fig. 1. Scheme of the switching time measurement setup.

non-polymerized LC is possible since the effective birefringence of the LC depends on the relative orientation of the molecules with respect to the polarization direction of incident light. The change in LC's effective birefringence, and thus the introduced phase delay, is observed as a change in the color of the sample when observed in white light.

2.2.2. Switching time measurements

The electro–optical behavior of the samples — specifically the switching time measurements — was analyzed in a setup consisting of a 660 nm laser, two polarizers, an optical power meter (Newport 2936-R), a function generator (RIGOL DG4062), and an oscilloscope (Velleman PCSU1000). The sample was connected to the function generator and positioned between the crossed polarizers in a way that provided the maximum phase difference. Both the function generator and the optical power meter were connected to the oscilloscope to observe sample's reaction to a square waveform signal. The entire setup is presented in Fig. 1.

The material was examined at room temperature before and after polymerization. For these measurements, the entire area of the LC cell was polymerized to simplify the positioning of the sample in the measurement setup. Switching times were determined by applying a modulated (7 s interval) square-shaped 1 kHz signal to the sample and observing its response on an oscilloscope. The phase delay introduced by the liquid crystal was calculated using the Stokes–Müeller method [29] based on the normalized light intensity described by

$$I_{\mathrm{norm}} = \frac{1-\cos\left(\Delta\varphi\right)}{2}, \tag{1}$$

where $\Delta\varphi$ is the phase delay introduced by the liquid crystal, and $I_{\mathrm{norm}} = I/I_{\mathrm{max}}$ is the measured intensity of light transmitted through the sample after normalization.

Rise and fall times were calculated as the time needed for the phase of transmitted signal to change between 10% and 90% of the total phase change.

3. Results

Initial tests were aimed at determining the optimal irradiation intensity and duration of a single laser pulse. This was done experimentally by irradiating the sample with pulses of different intensity and duration and analyzing the results under a polarizing microscope. The goal was to obtain a uniformly oriented sample, in which the polymerized and non-polymerized regions would differ only in the switching time. In case of too intense and/or too long pulses, a large volume of the LC underwent a phase transition to the isotropic phase during polymerization due to the absorption of radiation. Consequently, the increased vibration of the LC molecules caused a random formation of the polymer network and a chaotic arrangement of the liquid crystal. Consequently, the material introduced significant light scattering after polymerization. On the other hand, too short or low-intensity pulses were not sufficient to initialize the photopolymerization process, and the irradiated pattern was not visible at all. The results of polymerization after optimization of these parameters, as well as the electro–optical behavior of the sample, are shown in Fig. 2.

It was observed that the sample before and after reorientation appeared uniform in color under a polarizing microscope, which suggests that the phase delay introduced by the polymerized parts and the rest of the sample was identical. The only difference between polymerized and non-polymerized regions could be observed as a difference in color during reorientation of the liquid crystal. This means that during the switching, the effective birefringence of the sample in the irradiated regions, and consequently the introduced phase delay, was

Fig. 2. Polymerized NLC-based sample observed under a polarizing microscope. The sample is examined during switching on with 20 V (a) and then during relaxation after the voltage is switched off (b). The ON and OFF states are marked with 20 V and 0 V, respectively. In each row, the images between the ON and OFF states show the sample during the switching process, which is further demonstrated in Fig. 3.

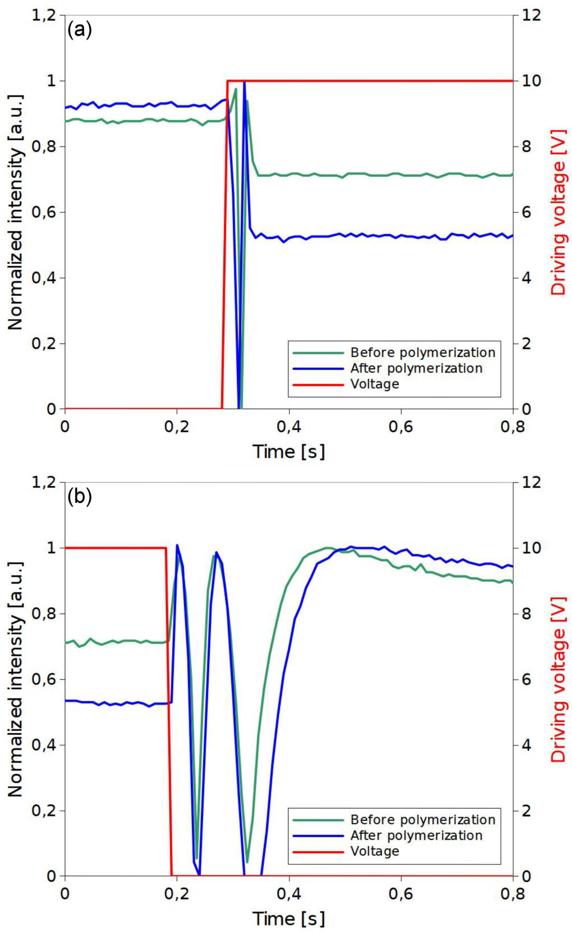

Fig. 3. Comparison of switching (ON — panel (a), OFF — panel (b)) of NLC-based composite before and after polymer stabilization. The plots show both the sample's electro–optical response in the form of normalized light intensity transmitted through the sample (main vertical axis) and the driving signal in the form of a square waveform (supporting vertical axis). The normalized light intensity is used for further calculations of the phase delay introduced by the LC using the Stokes–Müeller method to enable the determination of switching times.

TABLE I

Comparison of switching time values before and after polymerization of NLC-based composite.

Polymerization	Rise time [s]	Fall time [s]
before	0.03	0.15
after	0.03	0.19

different than elsewhere. Such behavior can only be explained by a different tilt of LC molecules at a certain point in time during reorientation. Additionally, the lack of observable light scattering on the polymerized parts of the sample strongly suggests that the overall density of the polymer network was low. Moreover, a significant difference in the fall time between polymer-stabilized and non-polymerized parts of the sample was observed — relaxation in the polymerized regions was noticeably longer (Fig. 2b). This result may be due to the fact that groups of LC molecules connected by short polymer chains need more time to reorient than a single molecule in the absence of an electric field. In the case of the rise time, the observed difference between the two types of regions was far less significant, which resulted in poor visibility of the irradiated pattern (Fig. 2a).

Further measurements were aimed at determining the difference in the switching process before and after polymer stabilization of the liquid crystal. The obtained results are presented in Fig. 3 and Table I.

The electro–optical measurements seem to be consistent with the observations under the polarizing microscope. A minor phase difference between polymerized and non-polymerized LC in ON and OFF states is most likely due to a slight misalignment of the LC cell during measurements, as this phase difference is not visible in Fig. 2. According to these, the rise time remained identical after polymer stabilization. The minor difference in reorientation that was observed under the microscope was also observed on the oscilloscope (Fig. 3a). The pattern's visibility under the microscope, despite no change in rise time, was most likely due to slightly different reorientation rates in different stages of reorientation, which can be seen in Fig. 3. When it comes to fall time, quite a significant difference was observed after polymerization. It is believed that the extended relaxation time resulting from polymerization was caused by the need for reorientation of groups of LC molecules instead of single molecules bound only by intermolecular interactions and anchoring on the LC cell's surface. An increase in fall time strongly suggests that the angular velocity of grouped LC structures decreased compared to non-polymerized LC molecules, which means that their inertia increased. In the case of the rise time, such a significant difference was not observed, as the switching process is mostly determined by voltage amplitude and anchoring conditions. In conclusion, the observed LC behavior is highly unexpected, considering that typical planarly-oriented PSLCs would have faster relaxation than non-polymerized LC caused by the polymer network enforcing planar molecular arrangement.

4. Conclusions

The presented results clearly demonstrate the possibility of modifying the switching process of a nematic liquid crystal without introducing light scattering on the polymer network and any visible changes in the LC's birefringence. The only observable difference between the polymer-stabilized and non-polymerized LC can be observed during the switching process. This new polymerization method can be used for the fabrication of liquid crystal-based optical switches.

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