



Photo-orientation of nematic liquid crystal without preliminary cell surface treatment

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Abstract: We propose a simple and effective method of liquid crystal photoalignment that does not require any preliminary treatment of the cell substrates. To this aim, a small amount (0.1 wt %) of azobenzene carboxylic acid is added into the nematic liquid crystal. After filling the liquid crystal cell, a part of the dopant molecules is spontaneously adsorbed and attached to the glass surface by hydrogen bonds. This allows one to switch the boundary conditions of liquid crystal between homeotropic and planar due to the reversible trans-cis photoisomerization.

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1. Introduction

Numerous studies in the field of soft matter physics and chemistry are focused on the developing of light controllable liquid-crystalline (LC) materials [1–4]. Nowadays, a wide variety of light-induced phenomena in this field were investigated. Recent advances in this field show fascinating possibilities for developing of adoptive diffractive and polarizing elements, photodisplays, nano- and micro-structured materials, light-driven micro- and nano-objects, etc.

One of the possible realizations of light sensitive LC systems is based on the photoalignment effect [5–7]. This effect is usually obtained, when the LC cell substrates are coated by a photosensitive compound. Light irradiation modulates the orientational distribution of molecules deposited on the surface. The anisotropic interaction of photosensitive molecules with LC leads to the homogeneous alignment of LC film in the bulk. This method was first realized by Ichimura et al., in which the monolayer of azobenzene molecules was used as a command surface for the LC film orientation [8]. The switching between the trans- and cis-configurations of azobenzene compound allows one to modulate the boundary conditions from homeotropic to planar or vice versa by ultraviolet (UV) or blue light illumination. Since then many photoalignment methods were proposed in response to the evident demands in display and photonics technologies [9,10].

A part of these studies is related to the photoalignment effect which takes place without any special treatment of LC cell substrates by photosensitive materials. The principle of the so called bulk mediated photoalignment was described in [11]. This effect was found in nematic liquid crystal (NLC) doped with a small amount of Methyl Red dye and filled into the LC cell with substrates coated by polyvinilcinnamate. The dye molecules are partially adsorbed onto the polymer surface. Under the linearly polarized laser light irradiation, their orientational distribution is modulated by photoinduced exchange between the NLC bulk and the surface [12]. This rearrangement of the adsorbed dye molecules causes an efficient drift of NLC easy axis on the surface. Another study demonstrated more complex processes involving the dye molecule photoisomerization, reorientation, and diffusion [13]. An alternative explanation of this effect is based on the effect of the photo-induced space charges [14,15].

A number of studies focus on the LC systems containing dendrimer compounds [16–18]. It was found that dendrimer molecules are adsorbed from the NLC bulk onto the surface and initiate homeotropic alignment. If the dendrimer compound contains azobenzene terminal fragments, it is possible to modify the boundary conditions of the NLC cell from homeotropic to planar by UV light illumination. It was recently shown that the high-molar-mass azobenzene additives, such as carbosilane dendrimers and side-chain polymers, can cause the photo-orientation processes at NLC-liquid interface [19,20].

There are other examples of photoalignment, which do not require the surface treatment by orienting materials. Specific azobenzene dopants can form nanosized crystalline aggregates on the cell substrates under UV irradiation, modifying the boundary conditions [21]. If NLC consists of the photoisomerizable molecules, the anchoring transition under UV illumination takes place at the solid [22] and liquid [23] surfaces. The photoalignment is induced by the UV irradiation of typical cyanobiphenyl NLC (5CB) on a fused quartz [24,25], but the origin of this effect still remains unclear. The effect can be also achieved in the NLC doped with sophisticated azobenzene surfactants [26].

Here we propose and investigate the photoalignment processes in the NLC doped with azobenzene carboxylic acid. The main idea of our method consists of the possible monolayer formation of dopant molecules containing carboxyl group onto the NLC cell substrates due to hydrogen bonding [27].

2. Experimental

We used a commercially available nematic E7 liquid crystal (Merck) with the large thermal range of nematic phase. The NLC was doped with hexyloxyazobenzene carboxylic acid (HOAC) (Fig. 1(a)). The value of HOAC dopant was varied from 0.01 to 0.1 wt %. To elucidate the role of the hydrogen bonding, the mixture of E7 with 0.1 wt % of similar azobenzene derivative, hexyloxyazobenzene (HOA), which has no carboxylic group (Fig. 1(b)), was also under the study. The HOAC and HOA compounds were synthesized at Chemistry Department of MSU.

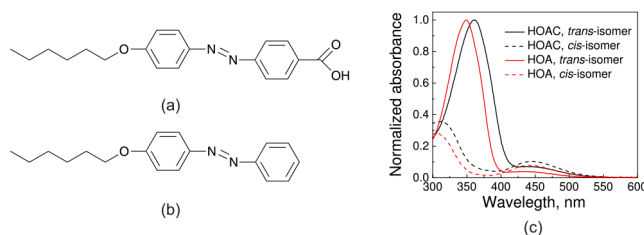


Fig. 1. Structural formulas of HOAC (a) and HOA (b). Normalized spectral absorbance of HOAC and HOA solution in tetrahydrofuran (c) corresponding to trans- (solid lines) and cis-forms (dashed lines).

The spectral absorbance of the HOAC and HOA in tetrahydrofuran was measured using TIDAS (J&M) spectrophotometer. The spectra of stable trans-isomer measured in dark is shown by solid lines in Fig. 1(c), whereas the spectra of cis-isomer was obtained at UV illumination by the light emitting diode (LED) with the 370 nm wavelength and 10 mW/cm² intensity during 10 s (dashed lines in Fig. 1(c)). Thus, UV illumination can be used for the effective isomer conversion into the cis-form.

For each NLC mixture, the two kinds of NLC cells were prepared for investigation of photoalignment effect. Each cell consisted of the two glass plates made of soda-lime glass (Thermo Scientific) treated by a piranha solution (the mixture of concentrated sulfuric acid and hydrogen peroxide in the 3:1 ratio, v/v) during 4 hours. This procedure not only cleans the glass plates, but also increases the number of OH groups on the surface. The glass plates were

separated by the 30- μm -thick Teflon stripes. One of the cells was made of two glass plates, each one without any additional treatment. Another LC cell was assembled from one clear glass plate and another one coated by polyimide with subsequent rubbing by tissue in a certain direction to provide a strong planar anchoring of NLC. The NLC mixtures were filled into the cells by capillarity forces at room temperature.

To initiate the trans \rightarrow cis isomerization process, the UV emitting diode (LED-1) with the luminescence maxima at $\lambda_{max} = 365$ nm and FWHM = 10 nm was used. To obtain the linearly polarized light the Glan-Taylor prism was used. For the reversible cis-trans isomerization, the light emitting diode (LED-2) with the luminescence maxima at $\lambda_{max} = 466$ nm and FWHM = 20 nm was employed. The light intensities $I = 1.2$ mW/cm² and 15 mW/cm² for LED-1 and LED-2, respectively, were measured by a Hioki 3664 power meter. The LED's light beam fell down onto the sample placed on the microscope table at 45° oblique incidence. In the case of linearly polarized UV light by LED-1, the polarization plane was parallel to the NLC cell substrates, which corresponds to s-polarization. The photoinduced orientational processes were studied with the help of Carl Zeiss Axio-Pol polarizing microscope with registration by CMOS sensor and photodiode.

3. Results and discussion

The first sample consisting of E7+0.1% HOAC was investigated. The NLC cell with two glass plates without orienting layers was used. Before LED irradiation, the sample does not transmit the light in crossed polarizers at any sample orientation (Figs. 2(a) and 2(b)). In conoscopic image, the dark cross appears (see the insertion in Fig. 2(a)). This indicates that the NLC film has vertical (homeotropic) alignment, i.e. the NLC director is oriented normally to the substrates.

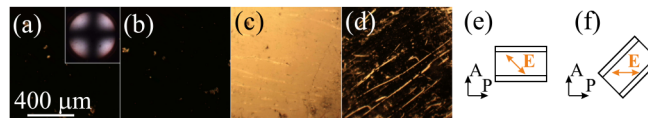


Fig. 2. Microscope images of NLC (E7+0.1% HOAC) cell in crossed polarizers before (a, b) and after (c, d) the UV illumination ($\lambda_{max} = 365$ nm, $I = 1.2$ mW/cm²) at two sample orientations (e, f). P and A are the directions of polarizer and analyzer, E is the UV light polarization direction. Insertion in (a) is the conoscopic image of the NLC cell.

Under the action of LED-1 UV light, when the light polarization direction **E** is at the 45° angle with respect to the directions of polarizer **P** and analyzer **A** (Fig. 2(e)), the sample becomes bright (Figs. 3(a)–3(f)). After the UV light illumination during the exposure time $\tau_{exp} = 100$ s, the rotation of microscope table with the sample at the angle 45° leads to the darkening of the sample image (Figs. 2(c)–2(f)). From this, we can conclude that the optical axis of the NLC after the UV illumination is either perpendicular or parallel to the light polarization direction. If the UV light is unpolarized, the NLC film orientation becomes degenerated planar. Note that the increase of UV light intensity leads to the proportional reduction of the switching time.

To reverse the process, the sample was illuminated by the LED-2 unpolarized light (Figs. 3(g)–3(l)). During this process, the image of the sample in crossed polarizers gradually becomes dark. This corresponds to the reverse cis \rightarrow trans photoisomerization at which the boundary conditions become homeotropic again. The same process occurs due to the thermal cis \rightarrow trans relaxation during about 10 min. Practically, it is possible to use the ortho-substituted azobenzene compounds, which have the long-living cis-form [28].

The described photoalignment processes are well repeatable without any degradation of the sample within several hours. The quality of homogeneous orientation of the sample decreases

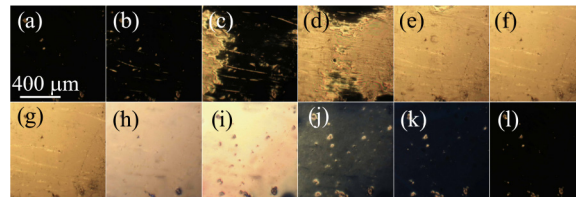


Fig. 3. Microscope images of NLC (E7+0.1% HOAC) cell in crossed polarizers during the illumination at $\lambda_{max} = 365$ nm ($I = 1.2$ mW/cm², linearly polarized light, experimental geometry is shown in Fig. 2(e)) at the exposure time τ_{exp} : 0 s (a), 30 s (b), 40 s (c), 50 s (d), 60 s (e), 100 s (f); and during the consequent illumination at $\lambda_{max} = 466$ nm ($I = 15$ mW/cm², unpolarized light) at the exposure time: 0 s (g), 7 s (h), 9 s (i), 10 s (j), 11 s (k), 14 s (l).

with time (during several days), possibly, due to forming and subsequent adsorption of dimers consisting of two hydrogen-bonded HOAC molecules or their degradation under UV irradiation.

The similar experiments were performed with the NLC containing 0.1 wt % of HOA compound. After filling the E7+0.1% HOA mixture into the cell consisting of two glass plates without the orienting layers, the NLC has the homeotropic alignment: the microscope images are analogues to those for the E7+0.1% HOAC mixture (see Figs. 2(a) and 2(b)). Note that the homeotropic alignment is also observed in the case of the undoped E7. No orientational changes in E7+0.1% HOA layer were detected during the LED-1 UV illumination with intensity up to 10 mW/cm² and exposure time about several minutes. This indicates that HOA compound is mostly dissolved in the bulk of NLC and does not affect its alignment. In addition, the photoalignment processes for E7+0.1% HOAC mixture were not observed on the surfaces, which do not contain hydroxyl groups, for instance, on the polyimide coated substrates. Thus, one can conclude that the photoalignment is induced by HOAC molecules incorporated into the NLC matrix and adsorbed onto the glass surface due to the hydrogen bonds. In trans-form, the HOAC molecules are oriented normally to the substrate because of their hydrophobic tails and set homeotropic boundary conditions. The isomerization of the elongated trans-isomer into the bent cis-isomer gives rise to changing the surface anchoring from homeotropic to planar.

Now let us clarify, whether the director orientation of E7+0.1% HOAC on the glass substrates is induced parallel or perpendicular to the UV light polarization. For this purpose, let us consider the photoalignment effect in the NLC cell consisting of one untreated glass plate and one plate with the rubbed polyimide layer. Initially, the sample is dark in crossed polarizers and bright in parallel ones, when the rubbing direction \mathbf{r} is perpendicular to the analyzer A (Figs. 4(a), 4(b), 4(g), and 4(h)). In this case, the NLC film has initially hybrid alignment (Fig. 4(c)). After the UV light exposure during 100 s, when the polarization direction is parallel to director orientation \mathbf{r} on the bottom substrate, the light transmittance of the sample changes to the opposite one (Figs. 4(d)–4(h)). This corresponds to the formation of twisted structure in the NLC film (Fig. 4(f)). When the light comes through the sample, its polarization direction “follows” the NLC director due to Marguin regime and rotates by the angle of 90°. The described easy axis alignment perpendicularly to the UV light illumination is typical for azobenzene-based orienting layers [6].

The variation of NLC film orientation from hybrid to twist occurs gradually that gives us a convenient way to investigate the effect of the HOAC concentration. For this aim, the mixtures of E7 with different concentrations (0.1, 0.08, 0.05, 0.02, and 0.01 wt %) of HOAC were prepared. NLC was filled in the glass cell with one polyimide-coated substrate and illuminated by the polarized UV light ($I = 1.5$ mW/cm²) in the previously described geometry (Fig. 4(g)). The transmittance of microscope white backlight passed through the sample in crossed polarizers was

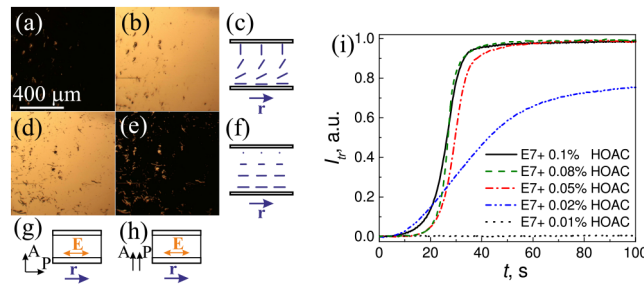


Fig. 4. Microscope images in crossed (a, d) and parallel (b, e) polarizers of the NLC (E7+0.1% HOAC) cell with one polyimide-treated substrate possessing planar alignment along vector \mathbf{r} before (a, b) and after (d, e) the illumination at $\lambda_{max} = 365$ nm ($I = 1.2$ mW/cm², $\tau_{exp} = 100$ s, linearly polarized light, the experimental geometries for (a, d) and (b, e) are shown in (g) and (h)). Before the UV illumination the NLC film has a hybrid orientation (c), while after the illumination it has a twisted planar orientation (f). Blue dashes in (c, f) show schematically the NLC director projection on the image plane. Time dependences of the transmitted light intensity I_{tr} for NLC cells with one polyimide-treated substrate at different HOAC dopant concentrations (i). The sample was placed between crossed polarizers and illuminated by LED-1 with $\lambda_{max} = 365$ nm, $I = 1.2$ mW/cm², polarized light, the experimental geometry is shown in (g).

registered by a photodiode. The signal from photodiode was passing through the analog-digital converter and recording on PC. For the samples with 0.1, 0.08, 0.05 %, the corresponding time dependences of the transmitted intensity I_{tr} are almost identical (Fig. 4(i)). At further decrease of the HOAC concentration to 0.02 % transmittance varies more slowly. Finally, at 0.01 %, the transmittance almost does not change with time.

It is reasonable to assume that the photoalignment effect is mainly obliged to the existence of the adsorbed monolayer of HOAC molecules and does not depend on the HOAC concentration in the bulk of NLC. When the HOAC concentration is not sufficient to form a monolayer, the photoalignment process is suppressed. Using the critical dopant concentration $n_{cr} \approx 0.05\%$, one can easily evaluate the relation of adsorbed HOAC molecules to those in the bulk of NLC $X = l/Ln_{cr} \approx 10$ %, where l and L are the dopant molecule length and cell thickness. This indicates that a relatively small fraction of HOAC molecules is adsorbed onto the glass substrate because of the dimer formation and environment of polar NLC molecules possessing C≡N group.

4. Conclusion

To summarize, the light-induced anchoring transition was observed in the dye-doped NLC filled into the glass cell without any special treatment of the substrates. The NLC was doped with carboxylic azobenzene compound, which is spontaneously adsorbed and attached to the glass surface by hydrogen bonds, providing homeotropic boundary conditions. The linearly polarized UV light illumination causes the trans→cis photoisomerization process, and the boundary conditions changed from homeotropic to planar. The easy axis orientation is found to be perpendicular to the UV light polarization. The reverse transition can be caused by the blue light illumination or occur spontaneously during the thermal cis→trans relaxation.

This approach can be useful for realization of a particular LC alignment in confined geometries, for instance, in capillaries and microcavities, where the direct surface treatment is hindered.

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