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Abstract

We provide experimental evidence that photoalignment at the nematic liquid crystal (NLC) - polymer interface can not be simply considered as a two-dimensional process. Moreover, our experiments clearly indicate that the photoaligning process does not depend on the individual properties of the NLC material and those of the interfacing polymer exclusively. The polymer and the NLC layer interact, i.e., the polymer-liquid crystal interface should be regarded as a coupled system, where the two components mutually influence each other. Furthermore, we show that the temperature induced anchoring transition also has to be taken into account for the complete description of the photoalignment mechanism.

Keywords nematic liquid crystals; photoalignment; nematic–polymer interface

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Corresponding Author Tibor Toth-Katona

Corresponding Author's Institution Wigner Research Centre for Physics

Order of Authors Tibor Toth-Katona, Istvan Janossy

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Data will be made available on request

Please find enclosed our manuscript entitled „Photoalignment at the nematic liquid crystal - polymer interface: experimental evidence of three-dimensional reorientation” by T. Tóth-Katona and I. Jánossy. The manuscript is submitted for J. Mol. Liq. as regular article.

Sincerely yours,

Tibor Tóth-Katona

Hereby we resubmit our manuscript entitled „Photoalignment at the nematic liquid crystal - polymer interface: experimental evidence of three-dimensional reorientation” by T. Tóth-Katona and I. Jánossy. All changes are made according the Reviewers comments, and are indicated by red typesetting in the text of the resubmitted manuscript.

Sincerely yours,

Tibor Tóth-Katona

REMARKS TO THE REFEREES:

First of all, we are grateful to the Reviewers for carefully reviewing the manuscript (MS), as well as for their constructive and useful comments which helped us to improve the quality of the MS. For clarity, we give our response to the Referees comments by red typesetting.

-Reviewer 1

-

This experimental manuscript reports an evidence that photoalignment at the liquid crystal-polymer interface can be considered as a three-dimensional process. Photoalignment is most often realized exploiting trans-cis isomerization of azo dyes. The azo dyes are either coated on the substrate as a molecular monolayer or embedded in a polymer film. In a typical experiment, the trans configuration of the given azo substance induces homeotropic orientation of the LC molecules on the photosensitive plate, while the cis isomer induces planar one. In this case, with one azo substrate, the surface being irradiated by the laser beam provides a homeotropic-to-planar transition. Often, with other azo substances, the liquid crystal molecules remain in the plane of the substrate and the azimuthal angle of the director can be controlled with polarized light, therefore creating a twisted nematic cell.

First of all, by authors there has been shown that the standard two-dimensional description of photoalignment is unsuitable in a number of cases. Second, that the polymer-liquid crystal interface should be regarded as a coupled system, where the two components mutually influence each other.

Specifically, it has been found that at temperatures far from the nematic–isotropic phase transition of the liquid crystals, the photoalignment takes place mostly in the usual way, where the azimuthal reorientation of the surface director occurs. As the temperature is raised, the azimuthal reorientation becomes more and more incomplete; at a critical temperature, it disappears completely and instead, the planar-to-homeotropic transition takes place. It has been shown that this critical temperature for different LC compounds is not the same neither on the absolute scale, nor on the scale of $\Delta T = T_{NI} - T$, relative to the clearing point of the nematics. It was made an assumption that the interactions between the polymer and LC molecules play a crucial role in description of the photoalignment mechanism.

This paper well fits to J. of Molecular Liquids and I recommend publication of this manuscript.

Response:

No addressable comments.

-Reviewer 2

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The manuscript of Tóth-Katona and Jánossy describes experimental investigation of temperature dependence of the liquid crystal (LC) photoalignment mechanism.

It brings an important finding that both azimuthal and zenithal photo-reorientation angles are strongly dependent on relative temperature with respect to the nematic-isotropic phase transition. The authors propose that the entire phenomenon of the photoalignment has to be reconsidered and mutual interaction between the photosensitive polymer layer and the bulk LC medium has to be taken into account. The manuscript is well written, the experiments and the results are clearly presented and the main outcome messages of the work are clearly communicated. The paper will for sure rise the interest of the LC community, as temperature stability of the alignment mechanism is undoubtedly an important issue in any kind of technological application. **I therefore recommend the manuscript for publication in Molecular Liquids.**

My main minor concern is, that the authors provide no information on the temperature dependence of the photoalignment layer itself. I wonder – how does the

isomerization kinetics of the film changes with the temperature. Fig. 1 demonstrates that this kinetics depends on the LC material that is put in contact with the photoalignment layer (azo-doped PMMA) and that there is a strong temperature dependence. But, one would like to see more clearly temperature dependence of photoisomerization kinetics in contact maybe just with air or with some simple liquid. It would be also interesting to see how light-induced orientational order of the photoalignment film itself depends on the temperature, as variation of this order directly affects the LC anchoring energy.

To my opinion, not only properties of the LCs, but also properties of the azo-doped photoalignment film strongly depend on the temperature and the only way to fully understand the mutual effects between them is to know their intrinsic temperature dependencies independently from each other. The orientational anisotropy and trans-cis and cis-trans kinetics can, for instance, be deduced from measurements of absorption anisotropy of the film close to or at the resonant wavelengths. This would definitely provide a more complete picture of the entire problem. The authors probably cannot perform the above described additional measurements in short time – but I suggest that at least a comment on this is given somewhere.

Response:

We agree with the Reviewer that future measurements on the temperature dependence of the photoisomerization kinetics of pDR1 in contact with the air, or other isotropic fluid would significantly contribute to a better understanding of the problem. A comment on this is now given at the end of the 1st paragraph of Section 4 (pages 6 and 7, lines 382-389).

As regards previous research – there were some observations of mutual interaction between the LC and the (photo)alignment layer. i.e so called "gliding of the easy axis" reported already previously. Maybe the authors can add some references. Some examples are:
M. Vilfan et al., PRE 63, 061709 (2001)
M. Vilfan and M. Copic, PRE 68, 031704 (2003)
S. Joly et al., PRE 70, 050701 (2004)
S.V. Pasechnik et al., LCs 33, 175 (2006)
P. Oswald et al., PRE 77, 061703 (2008)

Response:

We thank the Reviewer for drawing our attention to the above papers. The suggested references are now included (pages 1 and 8, lines 52-54 and 566-575).

-Reviewer 3

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Before any criticism, this is a brilliant investigation that obviously deserves publication. A correlation between the azimuthal and zenithal photoalignments is investigated in several NLC compounds. It was found that much below the NI transition temperature the azimuthal photoalignment mainly takes place, while near the NI transition temperature the zenithal photoalignment mainly takes place. The authors conclude that near the NI transition temperature the zenithal anchoring weakens, while the azimuthal anchoring still remains strong, and this could be the reason of the observed phenomenon. A correlation between the bulk properties of LC and the surface effects is mentioned several times, but, frankly speaking, I could not find any details.

First of all, I recommend the authors to avoid (at least in their Abstract) using the words "according to our measurements, the polymer and the NLC sense each other" looking self-evident. Meanwhile, there exist theoretical approaches explicitly explaining a correlation between the surface and the bulk orientational

properties of LC in various geometries [PRE 84, 041701 (2011); Phase Transitions 90, 86 (2017)], and it's worth mentioning them.

Response:

The abstract has been changed according to the comment (3rd and 4th line of the abstract), and the suggested theoretical papers are now included to the list of references with a short remark in the text (pages 1 and 8, lines 54-56 and 576-579).

Minor changes:

1. At the end of Sec. 3.1 I would skip using the words "No systematic dependence of ϕ is observed". There can be some non-trivial dependence.

Response:

The sentence has been reformulated (page 2, lines 148-149).

2. Next sentence – please check the grammar.

Response:

The sentence has been corrected (page 2, lines 149-152).

3. In the name of Sec. 3.2 I would remove the words "Temperature-induced", because the content of the section is wider.

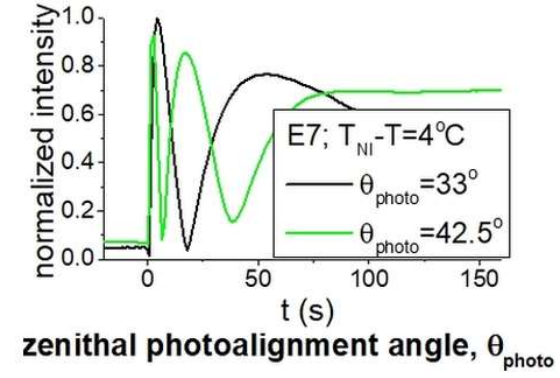
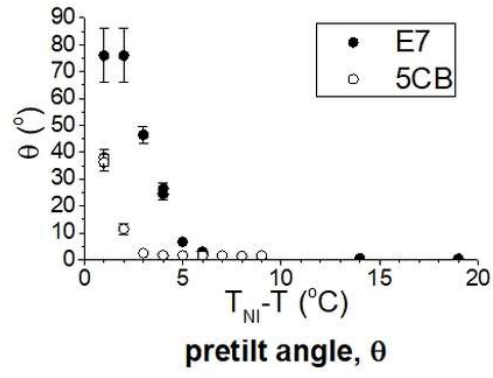
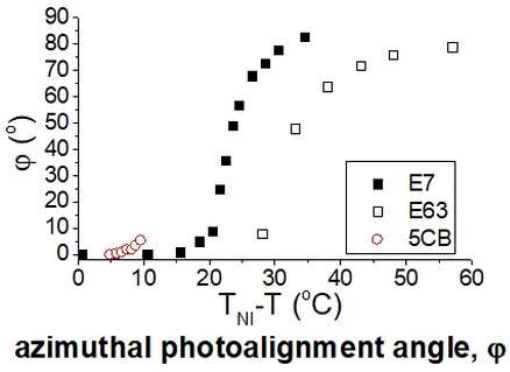
Response:

The title of the subsection has been changed (page 2, line 155).

My comments are in no way of diminishing the importance of the paper. I would recommend this paper for publication in Molecular Liquids after a minor revision.

HIGHLIGHTS:

- The phototalignment process at nematic – photosensitive polymer interfaces has been investigated experimentally.
- Both, the azimuthal and the zenithal photoalignment processes have been found incomplete.
- Experiments indicate that the liquid crystal – polymer interface is a coupled system, mutually influencing each other.
- The zenithal angle of the director at the polymer surface strongly increases near the nematic-isotropic phase transition.
- Measurements strongly suggest the need for a 3-dimensional coupled model, where the pretilt is also taken into account.



Photoalignment at the nematic liquid crystal - polymer interface: experimental evidence of three-dimensional reorientation

Tibor Tóth-Katona*, István Jánossy

Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary.

Abstract

We provide experimental evidence that photoalignment at the nematic liquid crystal (NLC) - polymer interface can not be simply considered as a two-dimensional process. Moreover, our experiments clearly indicate that the photoaligning process does not depend on the individual properties of the NLC material and those of the interfacing polymer exclusively. **The polymer and the NLC layer interact**, i.e., the polymer-liquid crystal interface should be regarded as a coupled system, where the two components mutually influence each other. Furthermore, we show that the temperature induced anchoring transition also has to be taken into account for the complete description of the photoalignment mechanism.

Keywords: Nematic liquid crystals, Photoalignment, Nematic-polymer interface

1. Introduction

The interaction of liquid crystals with solid substrates is a particularly significant research area. The problem is important for both the basic research and for various applications, because the proper alignment of the molecules at the boundary of a liquid crystal cell is the key factor for correct operation of devices based on LCs. Although standard methods have been developed in the last decades to ensure the required orientation of liquid crystals (like mechanical rubbing of polyimide layers spin-coated on the solid substrate), there is a continuous search for new methods of alignment. One of the most stimulating alternative method is the so-called photoalignment of nematic liquid crystals, discovered in the early 1990-s [1, 2, 3]. Moreover, photoalignment can be used not only to ensure the desired orientation in LC devices, but opens up the possibility to reorient the liquid crystal director through light irradiation. The exceptional advantage of the orientation control by light lies in its contactless nature [4].

Photoalignment is most often realized exploiting trans-cis (E/Z) isomerization of azo dyes [5]. The azo dyes are either coated on the substrate as a molecular monolayer [6, 7, 8, 9, 10], or embedded in a polymer film [1, 3, 11, 12, 13, 14, 15, 16]. In a typical experiment, a liquid-crystal (LC) sandwich cell is constructed with one photosensitive substrate and one traditionally prepared reference plate. In one scheme, the trans (E) configuration of the given azo substance induces homeotropic orientation on the photosensitive plate (the liquid crystal molecules are aligned perpendicularly to the substrate), while the cis (Z) isomer induces planar one (the liquid crystal is oriented

in the plane of the substrate). In this case, the light irradiation creates cis isomers, triggering a homeotropic-to-planar transition – often called 'out-of-plane alignment' photocontrol [6, 12, 17]. More often, with other azo substances, the liquid crystal molecules remain in the plane of the substrate and the azimuthal angle of the director can be controlled with polarized light, therefore creating a twisted nematic cell. As a rule, after irradiation the director becomes perpendicular to the light polarization direction, and is referred to as the 'in-plane alignment' photocontrol [1, 3, 12, 13, 16]. The mechanisms of the photocontrol, as well as the most commonly used photosensitive materials are well summarized in a review on photoalignment of liquid crystal systems [18].

Hereby we present observations that have far-reaching consequences regarding the photoalignment process, and can change the concept of its mechanism profoundly. First, we will show that the standard two-dimensional description of photoalignment is unsuitable in a number of cases. Second, we will provide evidence that the nematic liquid crystal does not play a purely passive part in the photoalignment process, in contrast to what is assumed in most papers. Instead, the polymer-liquid crystal interface should be regarded as a coupled system, where the two components mutually influence each other [15]. **Such interactions have been considered previously via the so called "gliding of the easy axis" [19, 20, 21, 22, 23], or via the correlation between the surface and the bulk orientational properties of LCs in various geometries [24, 25].**

2. Experimental details

2.1. Sample preparation

To obtain the photosensitive substrate, the following procedure has been employed. The polymer polymethyl-methacrylate functionalized with the azo-dye Disperse Red 1 (pDR1, for the

*Corresponding author.

Email address: tothkatona.tibor@wigner.mta.hu (Tibor Tóth-Katona)

chemical structure see Fig. 1b of [26]) has been dissolved in toluene (concentration of pDR1: 2wt%) and spin-coated on glass plates (some of them having SnO₂ conducting layer serving as an electrode). Spin-coating has been performed with Polos SPIN150i at 800rpm for 5sec, and then at 3000rpm for 30 seconds (all with spin acceleration of ± 1000 rpm/sec). The spin-coated substrates has been baked in an oven for about 2 hours at 140°C.

Rubbed polyimide coated slides from E.H.C. Co. (Japan) have been used as reference plates. The thickness of the assembled LC cells has been measured by interferometric method and were found in the range of 7 – 50 μ m. The LC cells have been filled either with 4-cyano-4'-penthylbiphenyl (5CB), with LC mixture E7, or with mixture E63 (both from Merck). Before filling in the material, the cell was illuminated with white light, polarized perpendicularly to the rubbing direction on the reference plate. This procedure ensured a good quality planar initial alignment of the nematic liquid crystal. The nematic-to-isotropic phase transition temperature T_{NI} has been determined for all LC cells, and typical values of 34°C, 60°C and 83°C have been found for 5CB, E7 and E63, respectively.

2.2. Experimental setup

Measurements on the photoalignment and photo-reorientation have been performed on an improved version of the pump-probe optical setup developed in our laboratory recently, and described in details in Ref. [26]. The polarized pump beam from a DPSS laser (25mW, $\lambda = 457$ nm) entered the cell from the photosensitive side, defocussed to a spot size of few mm (much larger than the diameter of the probe beam). The polarized probe beam from a He-Ne laser (5mW, $\lambda = 633$ nm) was sent through the cell, entering it at the reference plate. Behind the sample the probe beam was sent through a rotating polarizer and its intensity was detected by a photodiode; the signal was connected to a lock-in amplifier. The setup provides the phase and the amplitude of the probe beam transmitted through the sample. In order to determine the induced twist angle, the probe beam was polarized parallel to the rubbing direction; the twist angle is given by the phase of the signal. To detect the zenithal reorientation, the probe beam was polarized at 45° from the rubbing direction and the amplitude of the signal was measured. For the determination of the initial pretilt angle at the photosensitive substrate an additional electric-field has been subjected to the sample in a standard measurement setup for the electric-field-induced Fréedericksz transition, in which the sample is placed between crossed polarizers (polarization direction of both enclosing 45° with the initial director \mathbf{n}), and the transmitted light intensity from a He-Ne laser is measured during the transition.

3. Results

3.1. Azimuthal (in-plane) photoalignment

We start with the results on the in-plane (azimuthal) photoalignment. In these measurements the polarization of both the pump and the probe beam has been set parallel with the initial \mathbf{n} ,

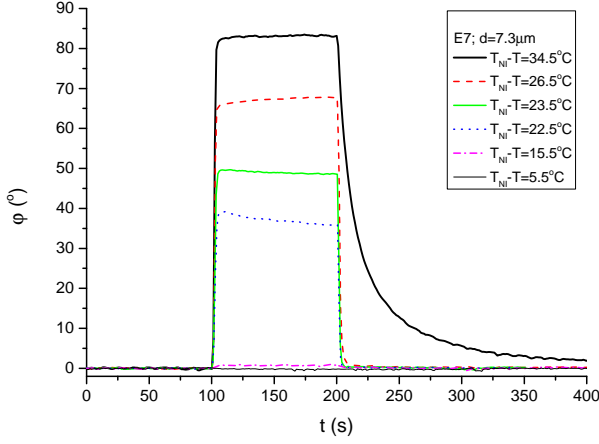
and the phase of the probe beam has been measured. The temperature of the samples has been varied from room temperature up to T_{NI} . Under these conditions the so called 'in-plane alignment' photocontrol is expected, so that the pump beam induces a twist deformation at the photosensitive substrate resulting in a twisted LC cell from the initially planar one. In the case of a perfect azimuthal reorientation the twist angle should be 90°.

Figure 1 shows the temporal evolution of the photoinduced twist angle φ for LC cells filled with E7 (a), E63 (b), and 5CB (c), measured at different temperatures $\Delta T = T_{NI} - T$. The pump-beam has been switched on at $t = 100$ s in all measurements, and switched off somewhere in the range $t = 200 - 1200$ s, depending on the dynamics of the photoalignment. As one sees, for E7 and E63 at low (room) temperature the azimuthal twist deformation saturates at $\varphi \geq 80^\circ$ [see Fig. 1(a) and (b)], which is close to the complete reorientation $\varphi = 90^\circ$. With the increase of the temperature, however, the twist angle gradually decreases, and vanishes far below T_{NI} . Moreover, for 5CB no significant twist deformation has been detected – $\varphi < 4^\circ$ has been measured even at the room temperature (Fig. 1(c)). Besides the decrease of the twist angle with the increase of the temperature, from Fig. 1 – especially from subfigure (b) – one can also see that the photoalignment process slows down, while (after switching off the pump beam) the back relaxation speeds up with the increase of the temperature.

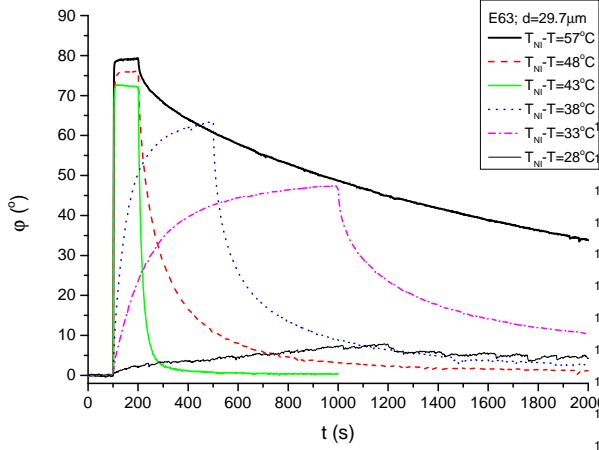
The temperature dependence of the saturated twist angle for 5CB, E7 and E63 is plotted in Fig. 2. For all NLCs a sudden decrease of φ has been observed far below T_{NI} : for E63 in the temperature range $T_{NI} - T = 30 - 35^\circ\text{C}$, for E7 in the range of $T_{NI} - T = 20 - 25^\circ\text{C}$, and for 5CB the range of $T_{NI} - T > 10^\circ\text{C}$ can be deduced from the measurements (the present experimental setup does not allow for measurements below the ambient temperature). In Fig. 2 results for E7 measured in LC cells having different thickness d are also shown. **No straightforward d dependence of φ was observed. It is worth to note, however, that the higher is the T_{NI} of the NLC, the larger is the value of the relative temperature $\Delta T = T_{NI} - T$ at which the sudden decrease of φ occurs.** In summary, in all samples a broad temperature range of the nematic phase is detected in which practically no azimuthal photo-reorientation is observed, i.e., $\varphi \approx 0$.

3.2. Temperature dependence of the pretilt angle

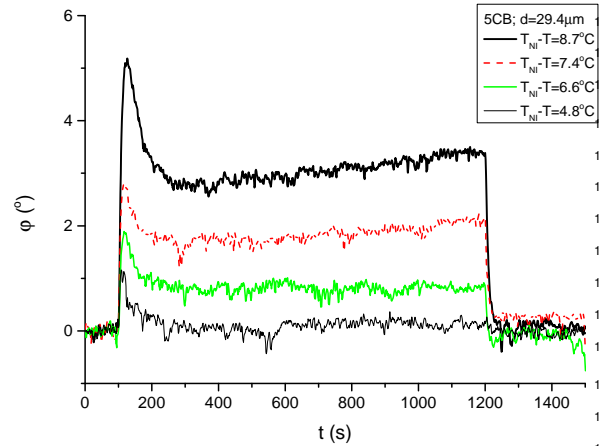
In this section we investigate the temperature dependence of the pretilt angle θ at the photosensitive substrate. We note that the pretilt angle at the reference plate (rubbed polyimide) has been found temperature independent over a wide temperature range for various nematic liquid crystals [27]. In particular, for the type of the polyimide substrate used in our experiments (manufactured by E.H.C. Co., Japan) the pretilt is estimated in the range $0 < \theta < 1^\circ$ [28]. We have used the electric field induced Fréedericksz transition [29] in order to estimate the pretilt angle θ at the photosensitive substrate. Namely, NLCs with positive dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ (ε_{\parallel} and ε_{\perp} are the dielectric permittivities parallel with-, and perpendicular to \mathbf{n} , respectively) and with planar initial alignment, undergo an orientational (Fréedericksz) transition upon application of an electric field at a threshold voltage $U_F = \pi \sqrt{K_{11}/(\varepsilon_0 \Delta\varepsilon)}$, where



(a)



(b)



(c)

Figure 1: Azimuthal photo-reorientation angle φ in time, measured at different temperatures in cells filled with NLCs: (a) E7, (b) E63, and (c) 5CB. The pump beam was switched on at $t = 100$ s, and switched off at a time ranging from 200s to 1200s, depending on the photo-reorientation dynamics.

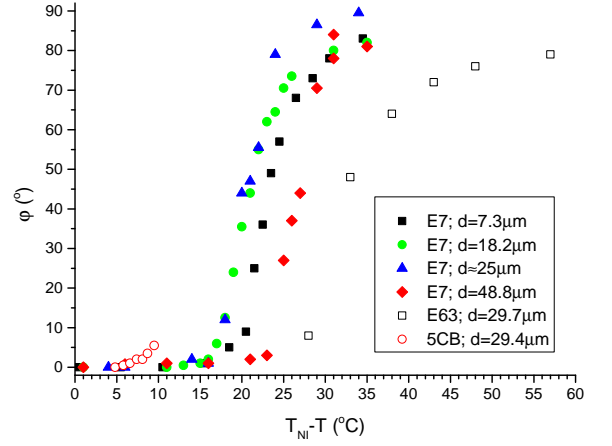


Figure 2: Temperature dependence of the azimuthal photo-reorientation angle φ measured in cells of thickness d as indicated in the legend, and filled with various NLCs (E7, E63 and 5CB).

K_{11} is the splay elastic constant. We note that U_F is a material parameter, which does not depend on geometrical factors. However, the threshold character of the electric-field induced reorientation is connected with the strictly planar alignment. If the director configuration deviates from the perfect planar alignment, i.e., there is a pretilt, the threshold-like behaviour of the reorientation is smoothed out. The birefringence vs. applied voltage curves around the Fréedericksz threshold voltage exhibit an inflexion point. The curves are extremely sensitive to the pretilt angle, especially below and around U_F [28]. Taking this fact into account, we have measured the birefringence change as a function of the applied voltage, and compared the results with numerical calculations in which only the pretilt θ at the photosensitive substrate entered as a free parameter. The measurements were performed from the room temperature to T_{NI} .

As already mentioned, measurements on the Fréedericksz transition have been performed in a standard setup with crossed polarizers for 5CB and E7, for which the temperature dependence of all relevant material parameters is available in the literature. At each temperature the transmitted light intensity is measured with voltage steps of 0.02V in the range from 0.04V to 7V, in an increasing and decreasing voltage cycle, with waiting time of 1s between each step.

Numerical calculations are based on equations given in [30], to which we have included the influence of the pretilt angle at both bounding substrates of the LC cell. The sample thickness d and the phase transition temperature T_{NI} have been measured for each LC cell ($d = 17.6\mu\text{m}$ and $20.2\mu\text{m}$, $T_{NI} = 34^\circ\text{C}$ and 59°C , for 5CB and E7, respectively), while the wavelength of the probe beam ($\lambda = 633\text{nm}$) is known. The temperature dependence of the relevant material parameters has been taken from the literature as follows: splay and bend elastic constants [$K_{11}(T)$ and $K_{33}(T)$, respectively] for E7 from [31], while for

205 5CB from [32] which is in excellent agreement with another
 206 independent measurement [33]; the ordinary and extraordinary
 207 refractive indices [$n_o(T)$ and $n_e(T)$, respectively] from [34] for
 208 E7, and from [35] for 5CB; the dielectric permittivities parallel
 209 with-, and perpendicular to \mathbf{n} [ε_{\parallel} and ε_{\perp} , respectively] from [31]
 210 for E7 and from [32] for 5CB. In the calculations, in agreement
 211 with [28], a temperature independent pretilt angle of 0.3° and
 212 1° has been chosen at the reference plate for E7 and 5CB, re-
 213 spectively. We will see in the followings that such a somewhat
 214 arbitrary choice of the pretilt at the interface with the rubbed
 215 polyimide layer (in the range of $0 < \theta_0 \leq 1^\circ$) is not influenc-
 216 ing the main results on the pretilt angle θ at the photosensitive
 217 substrate.

218 After the choice of parameters as described above, only the
 219 pretilt angle θ at the interface with pDRI remains the free fit
 220 parameter in numerical calculations to compare with the ex-
 221 perimental results. In the calculations, the measured sample
 222 thickness has also been slightly adjusted (within about $\pm 5\%$
 223 compared to the measured one), in order to bring together the
 224 measured and calculated normalized light intensities together at
 225 low voltages, far below U_F . In this sense d can be regarded as
 226 a quasi-fit parameter, however, such a small variation of d may
 227 also originate from the error of the interferometric method, or
 228 from spatial thickness variations within the LC cell.

229 The total phase shift $\Delta\Phi$ can be calculated from the light
 230 intensity variations observed while the sample undergoes the
 231 Fréedericksz transition [32]. In Fig. 3 we give a representative
 232 example of the voltage dependence of $\Delta\Phi$ measured in a 5CB
 233 sample in increasing (U up) and decreasing (U down) voltage
 234 steps, together with the calculated $\Delta\Phi(U)$ curve for a pretilt of
 235 $\theta = 1.5^\circ$. Fig. 3 is representative in the sense that reflects in
 236 general the characteristics observed both for 5CB and E7 LCs
 237 in the whole temperature range of the nematic phase. The mea-
 238 sured $\Delta\Phi(U)$ deviates from the calculated one at higher vol-
 239 ages: in the experiments the Fréedericksz transition ends at a
 240 somewhat lower voltage than it is predicted by the calculations.
 241 This systematic deviation (presumably originating from the val-
 242 ues of material parameter(s) taken from the literature) occurs at
 243 all temperatures, both for 5CB and for E7, and could not be
 244 eliminated by adjusting the fit parameter θ . Below U_F (where
 245 the influence of θ is the most significant), however, an excellent
 246 agreement between the experiments and the calculations could
 247 be reached just by fitting the value of θ – see the inset in Fig. 3.

248 The sensitivity of the onset of the Fréedericksz transition
 249 to the variation of the fit parameter θ is illustrated in Fig. 4,
 250 where the voltage dependence of the normalized light intensity
 251 I is shown below U_F for the measurement with increasing
 252 voltage steps and for calculations with slightly different pretilt
 253 angles (1.4° , 1.6° and 1.8°) in 5CB at $\Delta T = 5^\circ\text{C}$. As one sees,
 254 even such a small variation of θ causes a considerable change:
 255 $\theta = 1.4^\circ$ seems to give an overestimate of the experimental
 256 curve, while $\theta = 1.8^\circ$ underestimates it. The best fit to experi-
 257 mental data is obtained for $\theta = 1.6^\circ$. In general, for both 5CB
 258 and E7 far enough below T_{NI} , the pretilt θ has been estimated
 259 with a precision better than 1° .

260 In Fig. 5 the voltage dependence of the normalized light in-
 261 tensity I is given below U_F , measured in 5CB together with

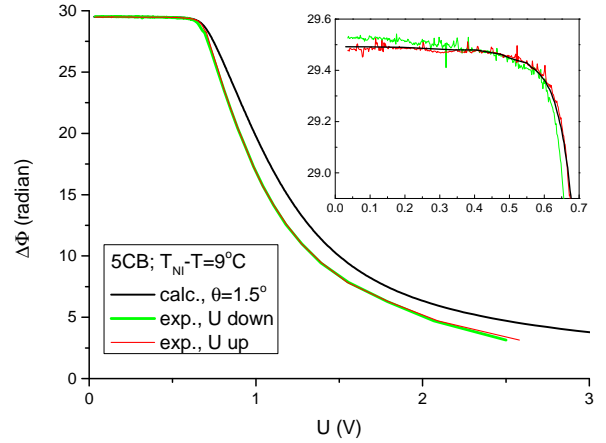


Figure 3: Comparison of the calculated total phase shift with the measured one in an increasing/decreasing voltage cycle (U up/ U down cycle) for a 5CB sample at $\Delta T = T_{NI} - T = 9^\circ\text{C}$. Inset: the blowup of the voltage range below $U_F = 0.72\text{V}$.

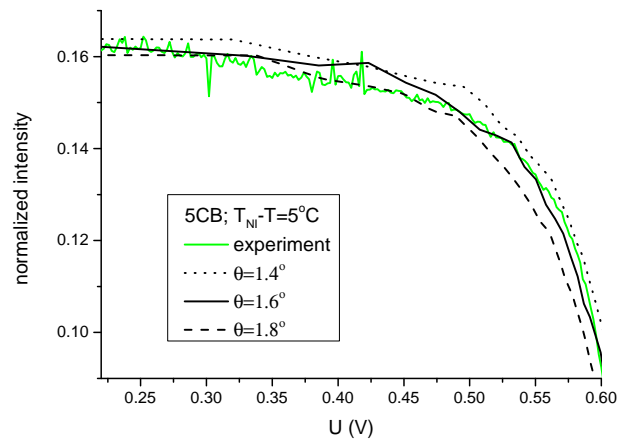


Figure 4: Voltage dependence of the normalized light intensity I below $U_F = 0.68\text{V}$, measured in 5CB at $\Delta T = 5^\circ\text{C}$ and calculated for three slightly different pretilt angles θ .

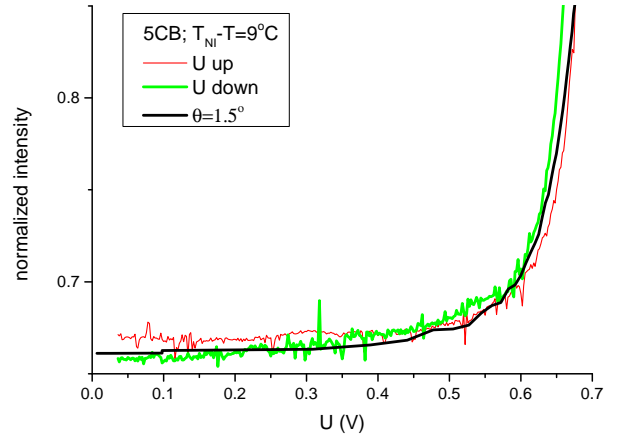
262 the calculated best fits to the experimental data at two differ-
 263 ent temperatures (a) $\Delta T = 9^\circ\text{C}$ and (b) $\Delta T = 1^\circ\text{C}$. The figure
 264 well illustrates the differences at low (far below T_{NI}) and high
 265 temperatures (close to T_{NI}).

266 At low temperatures [Fig. 5(a)] experimental data with in-
 267 creasing and decreasing voltage steps (U up and U down, re-
 268 spectively) agree with each other, and they can be fitted with
 269 a single calculated curve with a well defined $\theta = 1.5^\circ$. At
 270 high temperatures, close to T_{NI} , however, several differences
 271 occur as demonstrated in Fig. 5(b). First, the electric-field in-
 272 duced reorientation becomes completely thresholdless. Second,
 273 the experimental data with increasing and decreasing voltage
 274 steps differ substantially – *cf.* U up and U down curves in
 275 Fig. 5(b), and they can not be fitted with a single calculated
 276 curve with a given value of θ . Third, in this temperature range
 277 only few oscillations have occurred as the result of the director
 278 reorientation, however, with considerably different amplitude.
 279 Consequently, the normalization of the experimental data is not
 280 straightforward [not all of the extremal values reach 0 or 1 af-
 281 ter normalization – see Fig. 5(b)]. These conditions have oc-
 282 curred in the temperature range of $0 < \Delta T \leq 2^\circ\text{C}$ for 5CB, and
 283 $0 < \Delta T < 5^\circ\text{C}$ for E7. In this temperature range the pretilt θ
 284 could not be determined with such a high precision as in the
 285 lower temperature range. Taking into account the total phase
 286 shift $\Delta\Phi$, fitting the calculated $I(U)$ curves to the first experi-
 287 mental extremum, and doing this separately for the increasing
 288 and decreasing voltage steps has led, however, to the determi-
 289 nation of θ with acceptable precision – see e.g., Fig. 5(b).

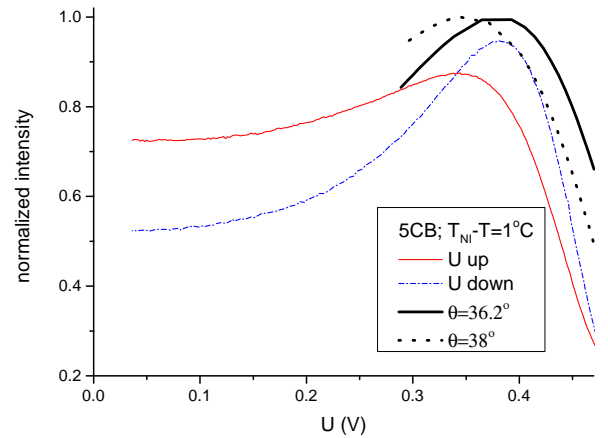
290 The temperature dependence of the pretilt angle θ at the
 291 pDR1 substrate, determined as described above is presented in
 292 Fig. 6. As one sees, at low temperatures θ remains small (be-
 293 low 2°) providing a planar initial alignment of the LC cells. At
 294 higher temperatures ($\Delta T < 3^\circ\text{C}$ for 5CB, and $\Delta T < 6^\circ\text{C}$ for
 295 E7), however, θ starts to increase rapidly, and for E7 almost a
 296 complete temperature induced orientational transition from planar
 297 to homeotropic is observed just below T_{NI} . One has also to
 298 note that the relative temperatures at which θ starts to grow dif-
 299 fer substantially for E7 and 5CB, indicating a subtle interaction
 300 between pDR1 and the interfacing LC.

301 3.3. Zenithal (out-of-plane) photoalignment

302 Next, we turn to the question how the photo-induced reorien-
 303 tation takes place in the high temperature range of the nematic
 304 phase, where no azimuthal photo-reorientation is observed (see
 305 Fig. 2). In accordance with the general rule, stating that af-
 306 ter the irradiation the director becomes perpendicular to the
 307 light polarization direction, one naturally expects that an out-
 308 of-plane photoalignment takes place in that case, instead of
 309 the in-plane photoalignment. To test this expectation, the ex-
 310 perimental setup for measuring the zenithal reorientation was
 311 used. With this setup, if a significant out-of-plane photoalign-
 312 ment occurs, oscillations in the transmitted light intensity of
 313 the probe beam should appear, similarly to the measurements
 314 on the electric-, or magnetic-field induced Fréedericksz transi-
 315 tion – see e.g., Ref. [36]. Measurements have been performed
 316 both with the polarization of the pump beam parallel with-, and
 317 perpendicular to the initial \mathbf{n} . In the latter case no azimuthal



(a)



(b)

Figure 5: Voltage dependence of the normalized light intensity I below U_F measured in 5CB and the calculated best fits to the experimental data at two different temperatures $\Delta T = 9^\circ\text{C}$ ($U_F = 0.72\text{V}$) (a) and $\Delta T = 1^\circ\text{C}$ ($U_F = 0.61\text{V}$) (b).

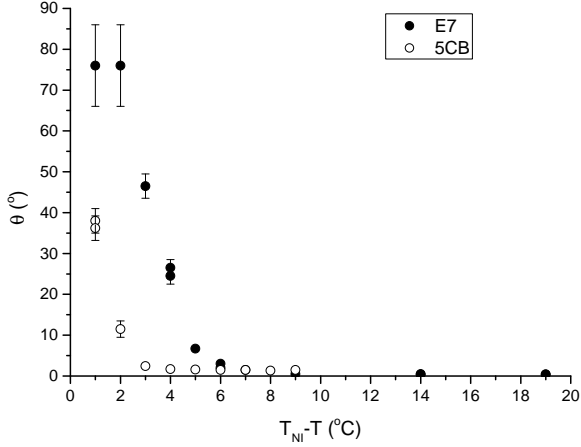


Figure 6: Temperature dependence of the pretilt angle θ at the pDR1 substrate for 5CB and E7.

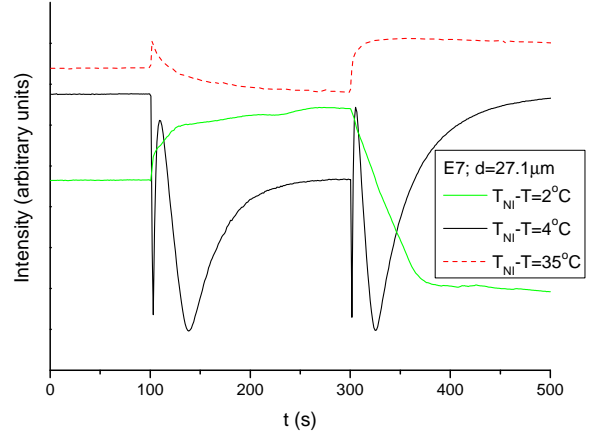


Figure 7: Temporal variation of the transmitted light intensity of the probe beam measured in an E7 cell at different temperatures in the setup for detection of zenithal photo-reorientation (pump beam polarization perpendicular to \mathbf{n} , probe beam polarization encloses 45° with \mathbf{n}).

318 photoalignment should occur. In the high temperature range of
 319 the nematic phase, where $\varphi \approx 0$, we have obtained identical,
 320 temporal response of the transmitted light intensity for both po-
 321 larization settings of the pump beam. In the low temperature,
 322 range, where $\varphi \gg 0$, the contribution of the azimuthal (twist)
 323 deformation has slightly modified the detected response for the
 324 light polarization parallel with \mathbf{n} compared to the case of the
 325 perpendicular light polarization.

326 In Fig. 7 we give the temporal variation of the light inten-
 327 sity in a $d = 27.1\mu\text{m}$ thick cell filled with E7 for three tem-
 328 peratures $\Delta T = T_{NI} - T = 35^\circ\text{C}$, 4°C , and 2°C , for simplicity
 329 all measured with the pump beam polarization perpendicular to
 330 \mathbf{n} , when no azimuthal photoalignment takes place. The pump
 331 beam has been switched on at $t = 100\text{s}$, and switched off at
 332 $t = 300\text{s}$. At low temperature ($\Delta T = 35^\circ\text{C}$) a slight change in
 333 the intensity has only been observed, which may originate ei-
 334 ther from a small misalignment of the director at the two bound-
 335 ing surfaces, or from a small misalignment of the polarization
 336 direction of the pump beam and \mathbf{n} , or from a slight zenithal pho-
 337 toalignment. At high temperature ($\Delta T = 4^\circ\text{C}$), the switching on,
 338 and off the pump beam is immediately followed by oscillations
 339 in the light intensity indicating a significant zenithal (out-of-
 340 plane) photoalignment. Interestingly, at even higher tempera-
 341 ture, close to T_{NI} ($\Delta T = 2^\circ\text{C}$), oscillations in the light intensity
 342 disappear and only a moderate intensity change is detected in-
 343 dicating that the zenithal photoalignment is much smaller than
 344 that at $\Delta T = 4^\circ\text{C}$. The reason for this can be understood by con-
 345 sidering the temperature dependence of the pretilt angle θ at the
 346 photosensitive substrate shown in Fig. 6: at $\Delta T = 2^\circ\text{C}$ the tem-
 347 perature induced anchoring transition has resulted in an almost
 348 homeotropic alignment $\theta \approx 75^\circ$, and therefore, no significant
 349 zenithal photoalignment can take place.

350 Though, no systematic thickness dependence of the az-
 351 imuthal photo-reorientation angle φ has been found, the tem-
 352 perature dependence $\varphi(T)$ varied from sample to sample con-

353 siderably, as illustrated in Fig. 2 for E7. It is reasonable to as-
 354 sume a similar variation of the pretilt angle θ , and of the zenithal
 355 photo-reorientation angle θ_{photo} . Therefore, for a more quantita-
 356 tive estimation of the zenithal photoalignment angle θ_{photo} one
 357 has to use the sample for which the temperature dependence of
 358 the pretilt angle θ is determined. In Fig. 8 we present the tempo-
 359 ral evolution of the probe beam normalized intensity measured
 360 in the cell filled with E7 at $T_{NI} - T = 4^\circ\text{C}$ (where a pretilt of
 361 $\theta \approx 25.5^\circ$ has been determined – see Fig. 6), with the pump
 362 beam of polarization $\mathbf{P} \perp \mathbf{n}$ and $\mathbf{P} \parallel \mathbf{n}$ switched on at $t = 0$.
 363 From the intensity variations zenithal photoalignment angles of
 364 $\theta_{photo} = 33^\circ$ and $\theta_{photo} = 42.5^\circ$ have been calculated for $\mathbf{P} \perp \mathbf{n}$
 365 and $\mathbf{P} \parallel \mathbf{n}$, respectively. These values provide an estimate for
 366 the total zenithal deformation angle $\theta + \theta_{photo}$ in the range from
 367 56° to 81° at this particular temperature.

4. Discussion

The temperature dependence of the dynamics of azimuthal
 photoalignment and relaxation processes [the best illustrated in
 Fig. 1(b)] can be explained with the temperature dependence
 of the trans-cis (E/Z) isomerization. At lower temperatures,
 the equilibrium concentration of the trans-conformers is much
 higher than that of the cis-conformers, and the trans-to-cis iso-
 merization (upon excitation) is much faster than the cis-to-trans
 relaxation process (when the excitation is off). With the in-
 crease of the temperature, the equilibrium ratio of the two con-
 formers slightly change in favor of the cis isomer, the trans-to-
 cis isomerization somewhat slows down, while the cis-to-trans
 relaxation speeds up. These processes result in the observed
 slower photoalignment and faster relaxation at higher tempera-
 tures. Besides the temperature dependence of the isomerization
 kinetics, Fig. 1 also demonstrates that this kinetics depends on
 the LC material that is put in contact with pDR1 (E7 or E63).

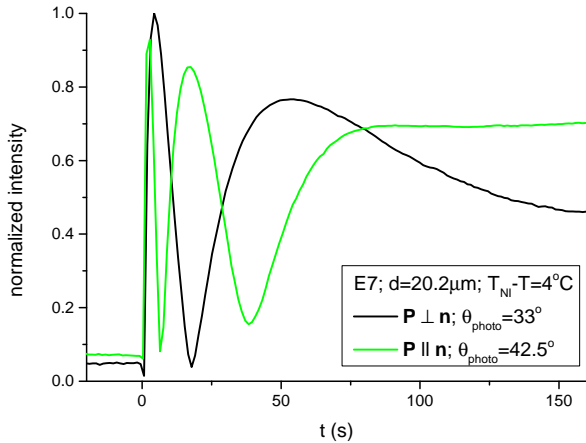


Figure 8: Temporal variation of the normalized light intensity indicating
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385 Therefore, it is desirable in a future work to measure the tem-
 386 perature dependence of the photoisomerization kinetics for the
 387 pDR1 layer itself (e.g., in contact with air). Namely, the varia-
 388 tion in the photoinduced orientational order of the pDR1 film
 389 directly affects the LC anchoring energy.

390 It is much more difficult to understand, however, the obser-
 391 ved decrease of the saturation value of the azimuthal reorien-
 392 tation angle presented in Figs. 1 and 2. First, even in samples
 393 with E7 and E63, in which a significant azimuthal photoalign-
 394 ment is detected at low temperatures, the photoinduced twist
 395 angle φ has remained slightly below the expected value of 90° .
 396 In principle, this result can be interpreted by a small misalign-
 397 ment in the experimental setup (that of the \mathbf{n} at the two bound-
 398 ing surfaces, and/or that between the pump beam polarization
 399 and \mathbf{n}). However, it is very unlikely that all investigated sam-
 400 ples were misaligned in a similar way, which always resulted in
 401 $\varphi < 90^\circ$. A more probable cause of the incomplete azimuthal
 402 photoalignment could be the finite zenithal anchoring strength
 403 at the pDR1 nematic LC interface as it was proposed in our re-
 404 cent work [26], allowing a slight zenithal tilt that prevents the
 405 complete azimuthal photo-reorientation.

406 Second, the drastic decrease of the azimuthal photoalignment
 407 occurring at quite different temperatures (both on the absolute
 408 scale and on the one relative to T_{NI}) for different nematic LCs
 409 can not be explained by the temperature dependence of individ-
 410 ual properties of pDR1 and LCs separately. Namely, most of
 411 the decrease in φ occurs in the temperature range of $48 - 53^\circ\text{C}$,
 412 $35 - 40^\circ\text{C}$, and $\leq 24^\circ\text{C}$ for E63, E7, and 5CB, respectively,
 413 while the glass transition temperature T_g for pDR1 has been
 414 found by DSC measurements in the much higher temperature
 415 range of $110 - 130^\circ\text{C}$. On the other hand, LCs investigated
 416 in this work are all cyano-biphenyl based compounds/mixtures
 417 differing only in the length of their alkyl-chain, thus their physi-
 418 cal properties are not expected to differ significantly on the tem-

419 perature scale relative to T_{NI} . This expectation can be easily
 420 confirmed for example, by comparing the temperature dependen-
 421 cies of the refraction indices, the elastic constants, and the
 422 dielectric permittivities on the scale relative to T_{NI} for 5CB and
 423 E7 from the literature data that we have used in our numeri-
 424 cal calculations [31, 32, 33, 34, 35]. In contrast to these simi-
 425 larities, the decrease of φ occurs at quite different values of
 426 $\Delta T = T_{NI} - T$ as shown in Fig. 2.

427 Third, our measurements on the estimation of the pretilt angle
 428 θ at the interface between pDR1 and the nematic LCs E7 and
 429 5CB have clearly indicated a temperature induced anchoring
 430 transition from planar towards the homeotropic alignment at the
 431 interface just below T_{NI} which has further implications. Tak-
 432 ing into account the temperature dependence of the pretilt angle
 433 shown in Fig. 6, it becomes clear why no sign of a significant
 434 zenithal photoalignment has been observed for E7 at $\Delta T = 2^\circ\text{C}$
 435 in Fig. 7: at that temperature the initial orientation \mathbf{n} is already
 436 almost homeotropic at the interface with pDR1, thus no signifi-
 437 cant zenithal photoalignment can occur. Next, if comparing
 438 the temperatures ΔT , where the azimuthal photoalignment an-
 439 gle φ starts to decrease (Fig. 2), and where the pretilt angle θ ,
 440 i.e., the initial zenithal tilt starts to increase (Fig. 6), a signifi-
 441 cant mismatch is found. Namely, the temperature induced anchoring
 442 transition starts to occur at much higher temperatures
 443 ($\Delta T < 3^\circ\text{C}$ for 5CB, and $\Delta T \leq 6^\circ\text{C}$ for E7) from the tempera-
 444 tures where the azimuthal photoalignment efficiency decreases
 445 by about 90% ($\Delta T > 10^\circ\text{C}$ for 5CB, and $\Delta T \geq 20^\circ\text{C}$ for E7).
 446 Consequently, the temperature dependence of the pretilt angle
 447 (the temperature induced anchoring transition) can not be re-
 448 lated directly to the disappearance of azimuthal photoalignment
 449 at high temperatures.

450 However, according to our interpretation, the two phenom-
 451 ena (the anchoring transition, and the disappearance of the az-
 452 imuthal photoalignment) are closely related, and have com-
 453 mon origin. Namely, we interpret our observations with the
 454 temperature dependence of the zenithal anchoring strength at
 455 the interface of pDR1 with the nematic LCs. We propose
 456 that the zenithal anchoring strength weakens with the increase
 457 of the temperature much faster than the azimuthal anchoring
 458 strength. Therefore, at certain temperature the zenithal anchoring
 459 strength becomes weaker than the azimuthal one, and the
 460 out-of-plane photoalignment gets energetically favorable upon
 461 irradiation. With further increase of the temperature, just be-
 462 low T_{NI} the zenithal anchoring strength becomes so weak that
 463 thermal fluctuations trigger an anchoring transition from ini-
 464 tially planar alignment towards the homeotropic one, even in
 465 the absence of the irradiation. Most remarkably, the tempera-
 466 tures where these phenomena occur do not depend alone on the
 467 individual properties of pDR1, nor on those of the interfacing
 468 LCs exclusively. According to the presented results, the pDR1
 469 layer senses the interfacing LC, and vice versa, i.e., the interac-
 470 tions between the two media have to be taken into account for
 471 the full description of the photoalignment process.

5. Conclusions and outlook

We found that at temperatures far from the nematic–isotropic phase transition of the liquid crystals, the photoalignment takes place mostly in the usual way (i.e., azimuthal reorientation of the surface director occurs). As the temperature is raised, the behaviour of photoalignment becomes anomalous, i.e., at elevated temperatures, the azimuthal reorientation becomes more and more incomplete; at a critical temperature, it disappears completely and instead, the planar-to-homeotropic transition takes place. Experiments have shown that this critical temperature for different LCs is not the same neither on the absolute scale, nor on the scale of $\Delta T = T_{NI} - T$, relative to the clearing point of the nematics. It seems to be determined rather by the interactions between the polymer and LC, i.e., by the temperature dependence of the azimuthal and zenithal anchoring strengths, the determination of which is one of the future tasks. Other, for pDR1 – LC system relevant future works could include, e.g., (i.) to replace the interfacing cyano-biphenyl based LC with other type of nematic(s); (ii.) to systematically vary the thickness of the pDR1 layer, (iii.) to change the surface density of the azo-moieties in the pDR1 layer.

Nonetheless, the experiments presented here have evidently shown that photoalignment at the photosensitive pDR1 interfacing a nematic LC can not be considered as a two-dimensional process. For the full description of the mechanism a more complex, three-dimensional model is needed that includes both the azimuthal and the zenithal photoalignment, takes into the account the coupling between the polymer layer and the LC (anchoring strengths), as well as the role of the pretilt angle θ_0 (which can also be temperature dependent as in our case).

To our opinion, the observed photoalignment effects are more general, they are not restricted to the pDR1 – LC interface only. In principle, these effects can take place at numerous other photosensitive polymer – LC interfaces. The photoalignment process in such systems needs to be revisited, and its description needs to be extended to three-dimensions.

Moreover, the role of the coupling between the polymer and the interfacing LC (determining the azimuthal and zenithal anchoring strengths) is not restricted to photosensitive polymers. There are numerous polymer – LC interfaces at which the anchoring transition is triggered by other means. A representative example of such systems is the perfluoropolymer CYTOP (Asahi Glass Co. Ltd.) interfacing with the LC 4'-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47, Merck), which exhibits thermally induced homeotropic-to-planar anchoring transition around the temperature 50°C [37, 38]. According to recent investigations, when CYTOP interfaces other type of nematic LC, the temperature of the anchoring transition is substantially different [39]. This observation also supports our idea about the importance of the coupling between the polymer and the LC layer.

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