

PhD Thesis Booklet

Photoalignment at Liquid Crystal–Polymer Interface

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Budapest

2024

Overview and objectives

The proper alignment of the molecules at the boundaries is a key factor for correct operation of all devices based on liquid crystals (LCs). Standard methods have been developed to ensure the required orientation of LCs. One of the most prevalent alignment method is mechanical rubbing of a polymer layer spin-coated on the solid substrate. However, this method has drawbacks, such as, it may produce and accumulate static charges and dust particles, can damage the alignment layer, can not align LCs in enclosed areas, or in microfluidic channels, etc. Therefore, the need for alternative techniques without these drawbacks has arisen.

One of the most promising alternative method is the so called photoalignment of nematic liquid crystals, discovered more than three decades ago. The control of the surface alignment of liquid crystals by light has attracted a considerable attention since its discovery, partly because of the absence of the above mentioned drawbacks, and partly because of its contactless and reversible nature.

Most of the experiments related to photoalignment exploit trans-cis (E/Z) isomerization of azobenzene derivatives. The widespread use of azobenzenes as photochromic units is due to their remarkable photo- and chemical stability, relative ease of synthesis, good solubility in liquid crystals, and due to the reversibility of their polarization dependent photoisomerization.

The motivation for this doctoral work follows from an earlier experimental observation on the photoalignment at an LC–polymer interface¹. Namely, when a polymer containing an azobenzene derivative was interfacing various nematic LCs having biphenyls in their molecular structure, the photoalignment mechanism turned out to be far more complex than the usually considered two-dimensional photo-reorientation. First, depending on the temperature, both azimuthal and zenithal photo-reorientations have been observed. Second, at high temperatures, close to the nematic-to-isotropic phase transition temperature T_{NI} , a temperature induced reorientation (anchoring transition) has occurred, without any photo-excitation. Finally, when the photo-, or thermal-excitation has been switched off, the system has relaxed back to the initial orientation relatively fast. The authors have proposed different temperature dependence of the azimuthal and zenithal anchoring strengths as an explanation, and suggested that the LC–polymer interface should be regarded as a coupled system, where the two components mutually influence each other¹.

To shed light on the predicted interaction between the interfacing polymer and LC, the aim of my research was to answer the questions such as: Does the molecular structure of LCs influence the photoalignment? Does the type of the LC phase play a role in the photoalignment process? Does the photoalignment mechanism depend on how the

¹T. Tóth-Katona and I. Jánossy, *J. Mol. Liq.*, **285**, 323–329 (2019).

azobenzene derivative is embedded in the polymer layer? What happens with the free polymer surface upon photo-excitation?

Methods

The research on photoalignment was conducted experimentally. For the determination of the azimuthal photoalignment angle, and for the detection of the zenithal photoalignment, a table-top experimental setup has been constructed, which combines the pump-probe optical setup with lock-in technique. Taking into account the absorption spectra of the azobenzene derivatives, blue lasers (of $\lambda = 457$ nm, $\lambda = 444$ nm, or $\lambda = 405$ nm) served as a source of the pump beam, and a He-Ne laser ($\lambda = 632.8$ nm) for the probe beam.

For visual observations polarizing optical microscope equipped with CCD camera and controllable hot stage has been used. For detecting the photo-induced changes at the free polymer surface, atomic force microscope with medium soft silicon cantilevers has been employed.

Theses

1. In order to clarify the role of the molecular structure of the nematic liquid crystal (NLC) in photoalignment, I have systematically varied the rigid core of the NLC from biphenyl, through phenylcyclohexane, to bicyclohexane. I found substantial differences in the photoalignment process depending on the molecular structure of NLCs. In NLCs with biphenyl rigid core, I have confirmed the previous results regarding the existence of both azimuthal and zenithal photoalignment, their temperature dependence, as well as the relatively fast back-relaxation of the system to the initial orientation when the photo-excitation is switched off. In contrast, in NLCs with phenylcyclohexane, or bicyclohexane rigid core only azimuthal photoalignment has occurred, and the back-relaxation of the director was extremely slow upon switching off the irradiation. No zenithal photoalignment has been detected at any temperature in these systems.

The different temperature dependence of the azimuthal and zenithal anchoring strengths can not solely explain the observed differences in photoalignment phenomena. Therefore, in addition to it, the possibility of the offset stacked aromatic π - π interaction has been proposed between the NLC biphenyl rigid core, and the trans isomer of the azobenzene moiety in the polymer layer. [N1]

2. To validate the role of the aromatic π - π interaction between the NLC biphenyl rigid core, and the interfacing azobenzene moiety in the polymer layer, I have chosen for further studies a NLC compound containing biphenyl in the rigid core, with one of the phenyl rings being modified with three fluorene atoms, which invert the molecular electrostatic surface potential (MESP) of the ring. This modification, in principle, prevents the offset stacked π - π aromatic interaction between the biphenyl part of NLC and the azobenzene moiety of the interfacing polymer. Therefore, instead of both azimuthal and zenithal photoalignment, only an azimuthal photoalignment was expected for this particular NLC compound. The experimental results have confirmed this expectation, thus, indirectly verifying the role of the aromatic π - π interaction in photoalignment. [N2]

3. To clarify how the type of the LC phase influences photoalignment, I have chosen a LC compound with biphenyl rigid core, having both nematic (N) and smectic A (SmA) phase. In the N phase, the compound possessed similar photoalignment characteristics as the other nematics with biphenyl rigid core, i.e., zenithal photoalignment occurred in the high temperature range of the N phase, and azimuthal photoalignment in the lower temperature range. With further decrease of the temperature, just

above the nematic-to-smectic A phase transition temperature (still in the N phase), however, both the azimuthal and the zenithal photoalignment vanish. This is attributed to the pretransitional smectic fluctuations, which suppress the photoalignment (both the azimuthal and the zenithal) in the nematic phase, due to the large increase of the bend and twist elastic constants, that are the most important parameters for the azimuthal and zenithal photoalignment, respectively. In the smectic A phase no azimuthal, nor zenithal photoalignment has observed, since the bend and twist deformations would involve changes in the layer spacing that request very high energies. [N2]

4. I have compared photoaligning properties of polymer layers fabricated from the same constituents: polymethyl-methacrylate (PMMA) and azo-dye Disperse Red 1 (DR1), either chemically attached to the PMMA main-chain, or physically mixed with it. The efficiency of the photoalignment decreases drastically in case of the physical mixture compared to that detected in case of polymer functionalized with DR1. Only a slight azimuthal photoalignment and no zenithal photoalignment has been obtained for the polymer layer prepared by physical mixing. The poor photoalignment performance of the polymer layers prepared from mixtures has been attributed to the rigidity of the PMMA matrix. [N3]

5. I have revealed photoinduced changes on the free polymer surface in contact with the air by atomic force microscopy (AFM). The polymer functionalized with DR1 became smoother after the illumination, and the photoinduced changes in surface relief were accompanied with a significant photoinduced mass transfer. In contrast, the polymer layer surface obtained by physical mixing did not change noticeably upon the illumination. [N3]

Publications related to theses points

[N1] A.R.K. Nassrah, I. Jánossy and T. Tóth-Katona, “Photoalignment at the Nematic Liquid Crystal-Polymer Interface: The Importance of the Liquid Crystalline Molecular Structure.” *J. Mol. Liq.*, **312**, 113309/1-7 (2020).

<https://doi.org/10.1016/j.molliq.2020.113309>. Q1, IF.: 6.165

[N2] A.R.K. Nassrah, I. Jánossy, V. Kenderesi, T. Tóth-Katona, “Polymer-Nematic Liquid Crystal Interface: On the Role of the Liquid Crystalline Molecular Structure and the Phase Sequence in Photoalignment.” *Polymers* **13**, 193/1-13 (2021).

<https://doi.org/10.3390/polym13020193>. Q1, IF.: 4.967

[N3] A.R.K. Nassrah, M. Batkova, N. Tomašovičová, T. Tóth-Katona, “Photoaligning Polymeric Command Surfaces: Bind, or Mix?.” *Polymers* **15**, 4271/1-12 (2023).

<https://doi.org/10.3390/polym15214271>. Q1, IF.: 5

Conference presentations related to theses points

[N4] A.R.K. Nassrah, I. Jánossy and T. Tóth-Katona, “Photoalignment at the nematic liquid crystal-polymer interface: the importance of the liquid crystalline molecular structure”. 18th International Conference on Thin Films & 18th Joint Vacuum Conference (ICTF -JVC2020). November 22-26, 2020, Budapest, Hungary. (poster

presentation, [book of abstracts](#), pp. 157-158).

[N5] A.R.K. Nassrah and T. Tóth-Katona, “Nematics interfacing photosensitive substrates”. Oral presentation at Doctoral Student Conference ([DOFFI-2021](#)). September 16-18, 2021, Balatonvilágos, Hungary.

[N6] A.R.K. Nassrah and T. Tóth-Katona, “Nematics interfacing photosensitive substrates: experiments on photoalignment”. 28th International Liquid Crystal Conference ([ILCC2022](#)). July 24-29, 2022, Lisbon, Portugal. (poster presentation, [book of abstracts](#), pp. 79, PC.100).