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## Molecular Crystals and Liquid Crystals

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# Liquid Crystal Aligning Ability of Photosensitive Polymer Material

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*In the present work the usefulness of photoalignment as a nematic liquid crystal aligning technique has been evaluated. A photocrosslinking mechanism of photosensitive polymer material has been used to cause anisotropy in the layer. The influence of the UV dose on the LC alignment of liquid crystal material in the TN-type cell has been examined.*

**Keywords** photoalignment; photocrosslinking; polyimide; electrooptical characteristic

## 1. Introduction

In order to obtain good quality and homogeneity of liquid crystal alignment in liquid crystal devices many different technological routes are used. A typical liquid crystal, LC, cell is clearly depicted in [1]. The aligning materials, both the organic and inorganic ones, cover the substrates and ensure an orienting process in the LC material thanks to their anisotropic properties. Anisotropy in layers may be generated in such physicochemical processes as: laser writing [2], silica oxide deposition [3, 4], microrubbing [5], plasma beam irradiation [6], ion-beam irradiation [7], photoalignment, PA, Langmuir-Blodgett layer deposition [8], usage of dendrimer-like structures with azo-moieties attached [9], or with an ordinarily used technique—rubbing. Each of the processes mentioned above has its advantages and disadvantages in preparation of liquid crystal devices, dependent on their further utilisation. For example the rubbing technique gives good and strong anchoring of LC molecules, but it has some limitations for manufacturing certain structures in which different parts of one cell are to be arranged in different directions and, for instance, to prepare ferroelectric LC cells which require very low cell thickness and high purity of aligning medium [10]. As for preparing layers that are suitable to providing diversified optical axes in one LC cell the photoalignment technique seems to be the appropriate one. Moreover, the PA technique opens the route to providing an appropriate molecular tilt and controlled anchoring energy.

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Photoalignment of selected polyimide material will be the main focus of the present paper.

### 1.1. Photoalignment Techniques

Polyimide materials are widely used in semiconductor technology due to their thermal, chemical and physical durability and high electrical resistivity [11]. The introduction of some photosensitisers to the polyimide precursor mixture [12] or some photoreactive groups to the polyimide structure opened the path to easy chemical etching processes in manufacturing elements for the needs of the optoelectronic industry. These chemical agents, which have incorporated groups like cinnamates [13, 14, 15], coumarins [16, 17] and chalcones [18], may also be used in the process of liquid crystal device preparation. Thus photoalignment techniques are those in which light is the factor that induces anisotropy of the aligning layer [19].

Not only is the change occurring during (or after) irradiation able to display chemical, irreversible nature, but can also be achieved by some physical changes, such as *cis-trans* isomerisation which is present in azo-compounds. Photosensitive agents can be divided into two main groups: positive-tone and negative-tone materials depending on the type of chemical reaction—decomposition, dimerisation or topochemical photocrosslinking [20].

The present contribution had two main goals. The first one was to obtain homogeneous and very thin layers of photodefinable material. The other one was to induce the anisotropy in layers using polarised light and then use those layers to prepare liquid crystal cells and measure electrooptical characteristics of these cells.

## 2. Experimental Methods

In the present work photoalignment polyimide agent (manufactured by HD Microsystems) was investigated. This was negative-tone PI named as HD-4110 (esterified polyamic acid ester), routinely used as photoresist in semiconductor technology.

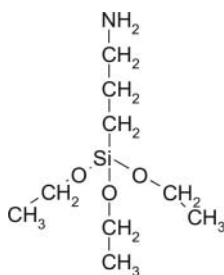
The procedure of polyimide layers preparation involves several steps, which are: (1) cleaning and drying the substrates, (2) preparation of adhesion promoter solution (3) preparation of the polyimide solutions, (4) deposition of the adhesion promoter, (5) baking of substrate covered with adhesion promoter, (6) deposition of polyimide, (7) soft bake process—evaporation of diluent, and (8) UV exposure (usually linearly polarised ultraviolet light, LPUV).

Layers prepared in such a manner should be ready to use to build LC cells.

### 2.1. Preparation of Polyimide Layers, Thickness Measurements

In our work 0,5% to 5% solution of polyimide precursor HD-4100 in *N*-methylpyrrolidone, NMP, were used. Such solutions show insufficient adhesion to the substrates (glass plate covered with indium-tin oxide, ITO), which means that they do not yield homogenous layers and roll up at the edge of the substrates. The first technological step was then to prepare the solution of adhesion promoter. The adhesion promoter used is named U-13 (made by Unisil), the chemical structure of which is shown in Fig. 1.

The substrates were dipped in 0,1% water solution of U-13 for 30 minutes and after that each of them was treated with compressed air followed by 15-minute baking at 115°C.



**Figure 1.** Chemical structure of adhesion promoter U-13, 3-aminopropyltriethoxysilane [21].

After this procedure the solution of polyimide precursor was deposited on substrates covered with adhesion-promoter layer and soft-baked in a convector for 10 minutes at 80°C. The adhesion of HD-4110 solution was fairly good. Thickness measurement was carried out with use of SPM 9001 spectrophotometer (Prema). Thickness of obtained layers varied from 80nm up to 145nm, which was dependent on the polyimide precursor concentration.

## 2.2. Anisotropy Generation in PI Layers, LC Cell Assembling

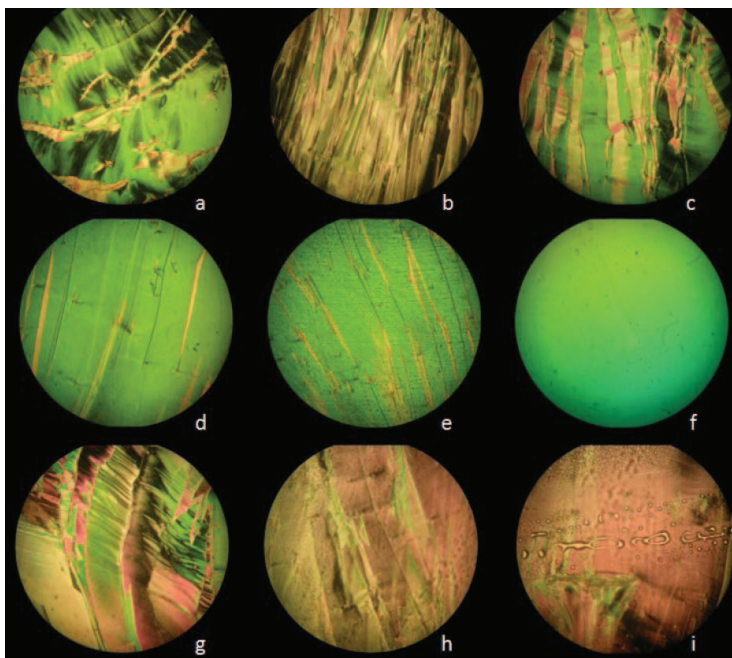
When HD-4110 layers are irradiated with UV irradiation the chemical reactions (topochemical photocrosslinking) take place. It forces the emergence of anisotropy in the structure, especially when linearly polarised ultraviolet irradiation is used. As a source of UV-light matrix of nine diodes (APG2C1 UV-LED, 365 nm, Roithner Lasertechnik) was used. To polarise the UV irradiation Glan-Taylor polariser PGT6320 (Dayoptics) was employed. Three types of layers were prepared, which means three different doses of LPUV were used. The layers were irradiated with 67,5 mJ/cm<sup>2</sup>, 135 mJ/cm<sup>2</sup> and 202,5 mJ/cm<sup>2</sup> so as to examine the influence of the UV dose on layer anisotropy generation.

Liquid crystal cells were assembled in such a manner that two layers irradiated with the same UV dose were pulled together to form a twisted structure using NOA-91 (Norland Optical Adhesive) photosensitive glue and 10 micrometer spacers. The term 'twist' means that on both substrates the irradiation with LPUV was carried out in the perpendicular direction of polarisation. The reference 10 micrometer cells were assembled in twisted nematic, *TN* mode using identical substrates covered by rubbed SE-130 (Nissan) aligning agent. All the cells were filled with nematic liquid crystal 1223A (Military University of Technology) in the isotropic phase.

## 2.3. Qualitative Investigations of Prepared Cells

Figure 2 shows microscopic photographs of TN LC cells obtained using crossed polarisers. The diagonal of the visible field is 2,5 mm.

As it can be clearly seen, the best uniformity of liquid crystal layer was obtained using the layers which were irradiated with 135 mJ/cm<sup>2</sup> (Fig. 2: d and e). The dose of 67,5 mJ/cm<sup>2</sup> is insufficient to cause proper degree of anisotropy in the layer (Fig. 2: a, b and c). The dose of 202,5 mJ/cm<sup>2</sup> probably caused competitive photochemical reactions due to the other (residual, perpendicular) polarisation direction of the LPUV which is unfortunately present in polarised UV light. These reactions may efficiently exacerbate the anisotropy of the orienting layer (Fig. 2: g, h and i). The bright pink strips which can be observed in the Figs. 2: d and e are clefts in the aligning layers. It was proved by the conductivity



**Figure 2.** Photographs of liquid crystal cells: a, b and c are cells prepared using the layers irradiated with  $67,5 \text{ mJ/cm}^2$ , d and e are cells prepared using the layers irradiated with  $135 \text{ mJ/cm}^2$ , f represents the reference cell prepared using rubbed layer of SE-130, g, h and i are cells prepared using the layers irradiated with  $202,5 \text{ mJ/cm}^2$ .

measurements carried out with an AFM device. It should be stressed that these strips are located along the polarisation direction of the LPUV.

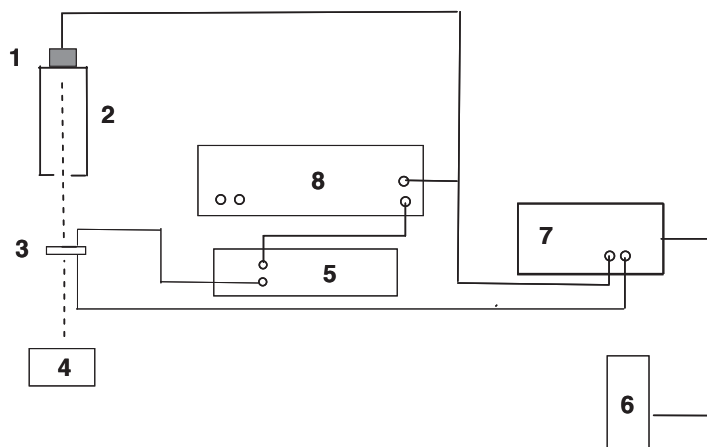
#### 2.4. Static and Dynamic Electrooptical Measurements

In order to verify the alignment existence in liquid crystal layer caused by the photoalignment layers dynamic electrooptic characteristics of obtained LC cells were measured. It was assumed that obtained cells were TN cells in which photoalignment technology was used instead of the classic rubbing method.

To measure the dynamic electrooptic characteristics the equipment showed in Fig. 3 was used. The presented equipment is characterised in detail in [22–24].

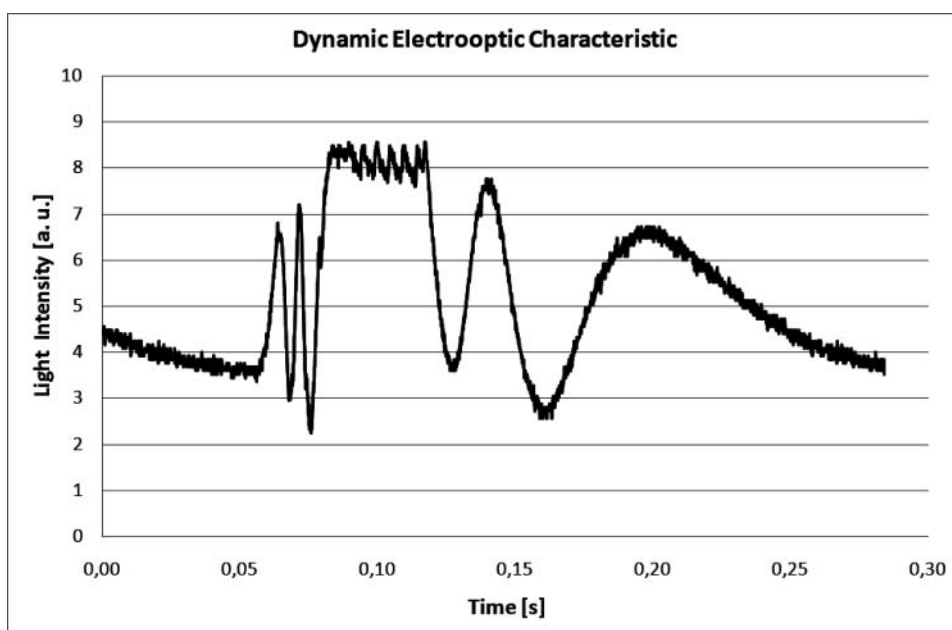
The sample cell was placed between polarisers with parallel direction of polarisation vector (negative mode). The liquid crystal mixture 1223A (Institute of Chemistry, Military University of Technology, birefringence:  $\Delta n = 0,17$  for  $25^\circ\text{C}$ ) was used to fill prepared cells. Cell thickness was approximately:  $d = 10 \mu\text{m}$ , which gives:  $\Delta n d = 1,7$  (third transmission maximum). Figure 4 shows the exemplary dynamic characteristic.

To confirm that the twisted orientation of a liquid crystal layer was obtained within a LC cell, numerical calculations of dynamic characteristics of the TN cell with thickness equaling  $d = 10 \mu\text{m}$ , containing liquid crystal with a birefringence of  $\Delta n = 0,17$  were performed. A computer program called *Computer Support of Optimisation Process* used in the Institute of Applied Physics (Department of New Technologies and Chemistry, Military University of Technology, Warsaw) was used. This program enables calculation

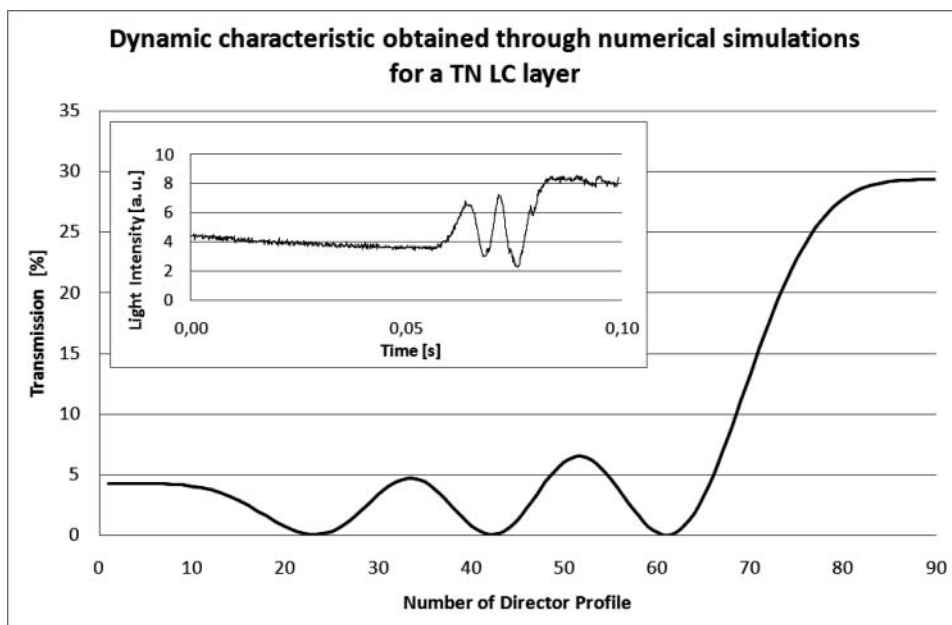


**Figure 3.** The electrooptic measuring system used in our work: 1-photodetector, 2-polarizing microscope, 3-sample, 4-the source of light, 5-voltage amplifier, 6-driving PC, 7-oscilloscope, 8-signal generator.

transmission and reflection coefficients for any observation angle and for all required properties of a particular layer of a display. This software is based on Jones matrix method. It was modified by the authors in order to reduce the simplifications and was described in detail in previous papers [25, 26]. This program takes into account multi-interference phenomena occurring in the system, absorption, real directions of ordinary and extraordinary waves as



**Figure 4.** Dynamic electrooptic characteristic for TN-type LC cell. Characteristic switching times:  $t_{\text{on}} = 21\text{ms}$ ,  $t_{\text{off}} = 139\text{ms}$ .



**Figure 5.** Dynamic characteristics obtained through numerical simulations for a TN LC layer (thickness  $d = 10 \mu\text{m}$ , birefringence  $\Delta n = 0.17$ ). The polarisers had a polarisation coefficient of  $PC = 0.999$  and were oriented parallel (negative mode). The results were obtained for monochromatic light with a wavelength of  $\lambda = 550 \text{ nm}$ . In the top left corner of Fig. 5 the dynamic electrooptical characteristics for TN-type LC cell is depicted (the repetition of Fig. 4 is purposeful—it facilitates the comparison of the two curves).

well as their polarisation. For this reason the results obtained with the use of this program are highly accurate. It also provides possibility to calculate the optical parameters of a LC display for any function of a director profile in liquid crystal layer and this option was used in the calculations carried out.

The obtained results—the dynamic characteristics of a twisted nematic display with the layer properties accorded to these used in experimental measurements (Fig. 4) are depicted in Fig. 5.

As it has been mentioned above, the characteristics were calculated to confirm the existence of twisted structure in a liquid crystal layer placed between the surfaces with photoalignment layers. Those layers were assembled in such a way that their orientation axes (obtained through irradiation process) were perpendicular on the first layer to the other one. It was vital to check whether the results (both theoretical and experimental) would be similar to each other. In this case it would be another proof that the present photoalignment method is effective. It should be pointed out, that the theoretical results in the numerical simulations were obtained in universal way, independent on such parameters of a display as: anchoring energy, elastic constants, viscosity, driving voltage, temperature etc. It was obtained (as it was clearly described in [27]) using a set of functions of a director profile in LC layer that describe the reorientation process. In the other words, the switching process is represented by set of the functions of a director profile. This function set has very important properties: in switching process these profiles are achieved in a required, precisely established sequence and each profile is obtained only once. Therefore in the

$x$ -axis description in Fig. 5 the variable is the “number of director profile” (the number of a director profile function in LC layer from used function set), and not time.

The comparison of the two characteristics given in Fig. 5 clearly shows that the switching process features are almost identical for both of them—there are three subsequent minima and two maxima up to the saturation state (*plateau*). The differences between the transmission values are due to the design of theoretical simulation computable model and its simplifications, which are: using a monochromatic wave instead of the light source used in actual measurements, omission of absorption and scattering phenomena and limiting the computations to two first beams reflected in layers.

### 3. Conclusions and Perspectives

The present paper is dedicated to technological process for photosensitive polyimide HD-4110. The influence of linearly polarised UV light doses on the anisotropy generation in obtained polyimide layers was investigated. A series of liquid crystal cells were made in which the TN structure was confirmed by the comparison of the collected dynamic characteristic with the theoretical plot.

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